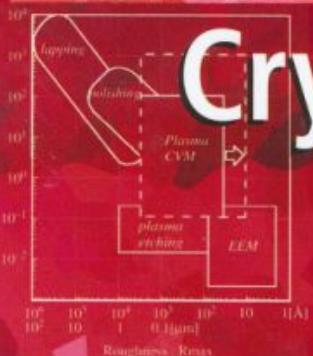
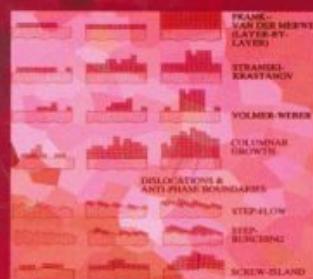


# Crystal Growth Technology

 **WILEY**

Editors  
Hans J. Scheel  
Tsuguo Fukuda



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**Tsuguo Fukuda**

K. Byrappa T. Ohachi (Eds.)

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# **DEDICATION**

This book has been dedicated to:

Professor C.N.R. Rao, FRS  
President, JNCASR  
Bangalore, India

# FOREWORD

Approximately fourteen years ago I was privileged to attend a conference in Japan whose title now escapes me, but whose scope covered a broad spectrum of modern technology. One lecturer has stood out in my memory over the years. He was Dr. Sekimoto, a Japanese businessman and eminent scientist whose specialty was in the field of communications. In his career at NEC he became President and finally Chairman of the Board. At the Conference I was particularly impressed by the content of one of his slides on which the following prophetic handwritten phrase occurred, "Who dominates materials dominates technology." The message was true and unambiguous then and history has simply emphasized its significance.

The ability to dominate materials requires an in-depth knowledge of the science and technology of crystal growth since crystals, especially single crystals have increasingly become a vital necessity in modern technology. How this domination is achieved is what this book is about. Crystal Growth is a universal phenomenon in the field of materials. It has a long history but a significant impetus, which accelerated its evolution from "a substance potting art" to a science in its own right, was the invention of the transistor in 1948, and the subsequent need for high purity semiconductor single crystals. As a result crystal growth has developed into a core discipline in materials science.

The evolution of our knowledge of crystal growth requires not only scientific understanding, but the driving force of applied technology which so often provides a significant influence in highlighting our lack of scientific knowledge and the need for a more refined science and indeed the development of new concepts. It is the knowledge of this balanced scientific evolution which Professor Byrappa and Professor Ohachi, the editors have achieved in the selection of critically important materials and technologies.

Both editors have international reputations in crystal growth. Professor Byrappa is an expert in the field of hydrothermal growth and is well-known for his work on the growth of complex coordination compounds especially in the field of phosphates, silicates, germinates and vanadates. He has carried out extensive pioneering work in the scientific application of physical chemistry and thermodynamics to the role of solution media, and the elucidation of the mechanisms of crystal growth in this difficult field. Such work has been at the forefront of knowledge, which has transformed the growth of many very difficult crystals from an empirical art to a controlled engineering science.

Professor Ohachi has extensive experience in the study of crystal growth mechanisms especially in the field of semiconductors and has been a leading fig-

ure in unraveling the mechanisms involved in the growth of GaAs by MBE. He is an expert in the field of ionic conduction in solids and has pioneered many fundamental studies in this more exotic field of crystal growth including the crystal growth of silver from silver chalcogenides using solid-state ionics. His work for the crystal growth community is also extensive. He has just been appointed President of the Japanese Association of Crystal Growth and held a pivotal position as Secretary of the recent combined International Conferences on Crystal Growth and Vapor Growth and Epitaxy (ICCG-13/ICVGE-11) held at Doshisha University, his Alma Mater. In this connection one must mention the role of Professor Nishinaga, one of the authors, who was Co-Chair of the ICCG-13/ICVGE-11 Conference. He was President of the International Organization of Crystal growth for the last six years and has just been appointed President of Toyohashi University of Technology.

Crystal growth now embraces an immense field of materials and technologies, which could not be covered in-depth by any one book. Nevertheless the present selection of chapters does provide a comprehensive coverage, which has succeeded in advancing our knowledge of the latest developments in crystal growth. For this purpose the editors have commissioned a fine selection of authors who are leading authorities in their respective fields of crystal growth. In broad terms the coverage deals with electronic materials and optical materials.

The basic science involved in vapor and solution growth provides an excellent initial introduction for advancing the role of fundamental science in our understanding of crystal growth. Also fundamental to our scientific understanding of hydrothermal growth is the need for detailed modeling with intelligent engineering. This is now possible thanks to advances in our knowledge of solution chemistry, phase equilibria and applied thermodynamics.

One must not miss the significance of the morphology of crystals, which is well reviewed in connection with mineral crystals. The observation of growth spirals on the surface of crystals was important evidence used by the late Professor Sir Charles Frank in his discovery the role dislocations can play in crystal growth.

The electronic materials discussed involve the III-Vs, the Zn chalcogenides, diamond and SiC as well as essential thermal modeling that is needed for achieving the effective growth of this difficult material. The oxides include families of materials related to lead zirconate titanate (PZT), the perovskites, the vanadates, bismuth germanate, and lithium niobate. Also, quartz and a range of high temperature non-linear optical materials including the borates as well as BiSrCaCu and related superconducting compounds are discussed in depth. A very welcome addition is that of the hydroxyapatite materials involved in biocrystallisation, which are important in bone development. Also, recent ideas on the growth of nano crystals are highlighted. A chapter on gemstones enhances the variety of materials and their compelling interest.

In order to achieve the successful crystal growth of these materials a whole range of different technologies are needed, they include vertical crystal pulling, CVD, sublimation and epitaxial growth for MOCVD and MBE. The oxides illustrate the full extent of the difficulties that can be encountered in crystal growth and the wide range of technologies needed to overcome them. In addition to the

growth technologies mentioned above laser assisted vapor deposition, hydrothermal growth solution, as well as flux and Verneuil growth are discussed.

The value of this interesting book lies not just in the increased scientific understanding of crystal growth, which one gains but in the extensive knowledge which is presented on the wide variety of technologies required to achieve application-quality crystal properties of an ever increasing range of crystals for modern technology. The reader is cordially invited to explore and assess the crucial role and significance of crystal growth in the various technologies for him or herself.

J.B. Mullin  
U.K.

## PREFACE

Crystals are the unacknowledged pillars of modern technology. Crystal growth can be regarded as an ancient subject, owing to the fact that the crystallization of salt and sugar was known to the ancient Indian and Chinese civilizations. The subject of crystal growth was treated as part of crystallography and never had an independent identity until the last century. The fundamentals of crystal growth were entirely bestowed upon the morphological studies of the naturally occurring crystals. Thus began the scientific approach for this subject during the 17th century by Kepler, followed by quite a few others like Nicolous Steno, Descartes, Bartholinus, etc. This type of morphological study slowly led to the understanding of the atomistic process of crystal growth. Recent bursting research on nanostructured materials depends on the crystal growth theory and technology.

In the early 20th century, crystal growth evolved as a separate branch of science and several theories from Kossel, Donnay-Harker, Volmer and Burton, Cabrera and Frank (BCF), etc., were proposed. Although the science of crystal growth originated through the explanations of Nicolous Steno in 1669, the actual impetus to this field began after the BCF theory was formulated and also when there was a great demand for crystals during World War II. Professor H. Scheel has dealt with the subject of historical development of crystal growth remarkably in the first volume of Hydrothermal Crystal Growth, edited by D.T.J. Hurle. Since there are other books dealing with similar topics, the present book omits the historical aspects and basic techniques of crystal growth and focuses extensively on the techniques of current importance.

The editors conceived the idea of publishing a volume that covers both theory and practice together, containing all the latest developments in the area of crystal growth. The book deals mainly with the crystals of commercial value with an emphasis on the science of their growth.

There are 17 chapters in this book, beginning with a chapter by Professor Ichiro Sunagawa dealing with the growth history of mineral crystals as seen from their morphological features as a key to the understanding of essential points of fundamental growth. The editors are lucky to have contributions from the most eminent crystal growers like Professors T. Nishinaga, S. Naritsuka, T. Inoue, H. Komatsu, I. Sunagawa, M. Hosaka, V. Lantto, and a host of others in spite of their busy schedules. The topics have been selected based on their current significance in this frontier area of technology and thus there is a wide range of topics including modeling of crystal growth and thermochemical calculations which in turn lead to the intelligent engineering of the crystal growth processes. We have a perfect blend of

senior crystal growers with the upcoming talents of the recent generation. The range of crystals included in this book varies from electronic, electro-optic, piezoelectric, ferroelectric, jewelry, to bioelectric fields. Furthermore, techniques like MOCVD, hydrothermal, laser assisted, CVD, flux, melt, etc., dealing with the actual process of crystal growth are discussed.

We hope that this book will be highly valuable to the entire crystal growth community and remain as an important source for crystal growers, beginners and specialists alike. The editors greatly acknowledge the help and cooperation extended by each and every author in this book. Our special thanks go to Professor Brian Mullin for penning the foreword for this book. Also, thanks to our esteemed friends like Prof. Masahiro Yoshimura of Tokyo Institute of Technology, Japan; Prof. Richard E. Riman of Rutgers University, NJ, USA; Prof. Jan Bart of DSM, The Netherlands; Prof. H. Klapper, Germany; Prof. J.N. Sherwood, UK; Prof. D.T.J. Hurle, UK; Prof. H. Scheel, Switzerland; Prof. T. Nishinaga, Japan; Prof. H. Komatsu, Japan; Dr. R. Fornari, Italy; Prof. M. Dudley, USA; Dr. David Bliss, USA; Prof. K. Sato, Japan; Prof. T. Duffar, France; Prof. Derek Palmer, UK; Prof. Keshra Sangwal, Poland; Prof. Rafael Rodriguez Clemente, Spain; Prof. Salvador Gali, Spain, and many others who have helped us directly or indirectly for the successful completion of this useful volume. Also, our indebted thanks to our family members Dr. K.T. Sunitha Byrappa, Mr. Shayan M. Byrappa, Mr. Nayan M. Byrappa, Mrs. Michiko Ohachi, Mr. Shinobu Ohachi, and daughters Kyoko and Keiko for their patience and cooperation.

Lastly, our thanks to all those from William Andrew and Springer publications associated with the production of this book, especially to Kathy Breed, Keith Stein, Brent Beckley, Jim Willis, and Nanette Anderson.

June 2002

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K. Byrappa

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# Crystal Growth Technology

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This volume deals with the technologies of crystal fabrication, of crystal machining, and of epilayer production and is the first book on industrial and scientific aspects of crystal and layer production. Highest-quality crystals and epitaxial layers form the base for many of industries technological advances, including telecommunication, computer and electric energy technology, and those technologies based on lasers and nonlinear-optic crystals. Furthermore, automobile electronics, audiovisual equipment and infrared night-vision all depend on high-quality crystals and epilayers, as do novel technologies currently in development and planned for the future.

This book contains 29 contributions from leading crystal technologists covering the following topics:

- General aspects of crystal growth technology
- Silicon
- Compound semiconductors
- Oxides and halides
- Crystal machining
- Epitaxy and layer deposition

Scientific and technological problems of production and machining of industrial crystals are discussed by top experts, most of them from the major crystal growth industries and research centres.

It is anticipated that this volume will serve all scientists and engineers involved in crystal and epilayer fabrication. In addition, it will be useful for the users of crystals, for teachers and graduate students in materials sciences, in electronic and other functional materials, chemical and metallurgical engineering, micro-and optoelectronics including nanotechnology, mechanical engineering and precision-machining, microtechnology, and in solid-state sciences. Also consultants and specialists will profit from this book, as will those interested in crystals, epilayers, and their production for saving energy (GaN- and SiC-based high-power electronics and light-emitting diodes for illumination) and for renewable energy sources (economic high-efficiency solar cells and forthcoming laser-fusion energy).

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# Contents

## 1 Growth Histories of Mineral Crystals as Seen from Their Morphological Features

Ichiro Sunagawa .....	1
1.1 Introduction.....	1
1.2 Morphology of Crystals.....	3
1.3 Diamond .....	7
1.4 Beryl .....	13
1.5 Trapiche Ruby.....	18
1.6 Summary .....	22
References .....	22

## 2 Theory of Crystal Growth from Vapor and Solution

Toshiharu Irisawa .....	25
2.1 Various Crystal Growth Processes.....	25
2.1.1 Driving force .....	25
2.1.2 Rate-determining process .....	27
2.2 Vapor Growth .....	28
2.2.1 Step velocity .....	31
2.2.2 Mechanism of two-dimensional nucleation growth .....	35
2.2.3 Mechanism of spiral growth .....	39
2.3 Growth of a Crystal in a Solution.....	42
2.3.1 Solvation effects and growth rates .....	42
2.3.2 Handling of polyhedral finite crystals.....	49
References .....	54

## 3 Epitaxial Growth of III-V Compounds

T. Nishinaga and S. Naritsuka.....	55
3.1 Introduction .....	55
3.2 MBE of III-V Compounds.....	56
3.2.1 MBE system .....	56
3.2.2 RHEED intensity oscillation.....	57
3.2.3 Surface diffusion and stepped surface.....	59
3.2.4 2D-nucleation and step flow modes .....	61

3.2.5 Critical temperature and growth conditions.....	64
3.2.6 Incorporation diffusion length.....	66
3.2.7 Intersurface diffusion.....	68
3.2.8 Elementary growth processes.....	70
3.3 MOCVD of III-V Compounds .....	71
3.3.1 Growth of high-purity materials by MOCVD .....	71
3.3.2 <i>In situ</i> monitoring and study of growth kinetics in MOCVD .....	75
3.3.3 Nanostructure fabrication by MOCVD.....	80
3.3.4 Highly-mismatched heteroepitaxy and microchannel epitaxy with MOCVD.....	84
3.4 Summary .....	89
References .....	90

## 4 CVD Diamond Growth

C. Chang, Y. Liao, G.Z. Wang, Y.R. Ma, and R.C. Fang .....	93
4.1 Introduction.....	93
4.2 Preparation and Application of CVD Diamond Film.....	94
4.2.1 Preparation methods .....	94
4.2.2 Applications of diamond film.....	98
4.3 Nucleation and Growth of Diamond Films .....	102
4.3.1 Homoepitaxy of diamond film .....	102
4.3.2 Heteroepitaxy of diamond film .....	103
4.4 Phase Diagram and Gas-Phase Species in CVD Diamond Growth Processes .....	111
4.4.1 Phase diagram .....	112
4.4.2 Gas phase species.....	113
4.5 <i>In Situ</i> Diagnostic Techniques for Diamond Growth.....	116
4.5.1 Molecular beam mass spectroscopy .....	117
4.5.2 Laser-induced fluorescence .....	120
4.5.3 Optical emission spectroscopy .....	123
4.6 Summary .....	131
References .....	132

## 5 Laser-Assisted Growth and Characterization of Multicomponent Lead-Zirconate-Titanate Films

Jyrki Lappalainen, Johannes Frantti, and Vilho Lantto .....	143
5.1 Introduction .....	143
5.1.1 Laser-assisted growth of thin films .....	143
5.1.2 Ferroelectric PZT thin films .....	144
5.2 Film Deposition Process.....	145
5.2.1 Principles of pulsed-laser-deposition technique .....	145
5.2.2 Growth and structure of thin films .....	147
5.3 Case Study: Nd-Modified PZT Films .....	149
5.4 Results from XRD and EDS Measurements.....	151
5.5 Compositional and Structural Changes in the Target.....	154

---

5.6 Raman Spectroscopy Studies of PZT Films .....	158
5.6.1 Basic concepts of the Raman effect .....	158
5.6.2 Raman active modes .....	160
5.6.3 Raman spectra of ceramics .....	160
5.6.4 Raman active phonons of PZT ceramics.....	161
5.6.5 Characteristic features of the Raman scattering from the structural point of view .....	162
5.6.6 Raman spectra of PZT thin films.....	163
5.7 Electrical Properties of PNZT Films.....	166
5.7.1 Permittivity and spontaneous polarization .....	166
5.7.2 Electronic conduction .....	168
5.7.3 Role of macroscopic residual stresses.....	171
5.8 Summary .....	174
References .....	176

## 6 Silicon Carbide Crystals — Part I: Growth and Characterization

G. Dhanaraj, X.R. Huang, M. Dudley, V. Prasad, and R.-H. Ma.....	181
6.1 Introduction.....	181
6.1.1 Applications of SiC.....	183
6.1.2 Historical development of SiC crystal growth.....	185
6.2 Vapor Growth .....	186
6.2.1 Acheson method.....	186
6.2.2 Lely method.....	187
6.2.3 Modified Lely method .....	189
6.2.4 Sublimation sandwich method.....	190
6.2.5 Chemical vapor deposition .....	191
6.3 High Temperature Solution Growth.....	193
6.3.1 Bulk growth.....	193
6.3.2 Liquid phase epitaxy .....	193
6.4 Bulk Growth by Seeded Sublimation: The Industrial Process.....	194
6.4.1 Growth system .....	195
6.4.2 Seeding and growth process .....	197
6.5 Doping in Bulk and Epitaxial Growth .....	200
6.5.1 Doping in modified Lely method .....	200
6.5.2 Doping in epitaxial films .....	200
6.6 Growth Defects .....	201
6.6.1 Growth spirals and micropipes .....	201
6.6.2 Polytypism.....	202
6.6.3 Graphitization.....	203
6.7 Defect Analysis .....	204
6.7.1 Micropipes and closed core screw dislocations .....	204
6.7.2 Basal plane dislocations.....	221
6.7.3 Small angle boundaries.....	221
6.7.4 Hexagonal voids.....	222
6.8 Summary .....	223

References .....	225
<b>7 Silicon Carbide Crystals — Part II: Process Physics and Modeling</b>	
Q.-S. Chen, V. Prasad, H. Zhang, and M. Dudley .....	233
7.1 Introduction.....	235
7.2 Modeling of Heat and Mass Transfer and Growth Rate .....	236
7.2.1 Growth process .....	236
7.2.2 Flow and heat transfer parameters .....	237
7.2.3 One-dimensional network model .....	240
7.2.4 Thermal transport model .....	241
7.2.5 Mass transport model.....	244
7.2.6 Numerical method.....	249
7.3 Growth Simulation.....	251
7.3.1 Electromagnetic field and heat generation.....	251
7.3.2 Temperature field.....	253
7.3.3 Growth rate calculations.....	257
7.3.4 Thermally induced stress.....	263
7.4 Summary .....	265
References .....	266
<b>8 Thermodynamics of Multicomponent Perovskite Synthesis in Hydrothermal Solution</b>	
Malgorzata M. Lencka and Richard E. Riman .....	271
8.1 Introduction.....	271
8.2 Thermodynamic Model .....	272
8.2.1 Computational method .....	274
8.2.2 Standard-state properties .....	276
8.2.3 Stability and yield diagrams .....	277
8.2.4 Stability and yield diagrams for the stoichiometric ratio of precursors ( $A/B = 1$ ).....	279
8.2.5 Stability and yield diagrams for the nonstoichiometric ratio of precursors ( $A/B > 1$ ) .....	286
8.2.6 Carbon dioxide contamination .....	289
8.3 Validation and Applications of Thermodynamic Modeling .....	292
8.4 Summary .....	294
References .....	294
<b>9 Growth of Multicomponent Perovskite Oxide Crystals: Synthesis Conditions for the Hydrothermal Growth of Ferroelectric Powders</b>	
Bonnie L. Gersten .....	299
9.1 Introduction .....	299
9.2 General Overview .....	299
9.2.1 Description .....	299
9.2.2 Perovskite ferroelectrics .....	300

---

9.2.3 History .....	301
9.3 Synthesis Conditions for Controlled Chemical and Phase Purity .....	305
9.3.1 Thermodynamic conditions .....	305
9.3.2 Mineralizers and additives.....	309
9.3.3 Homogeneity .....	310
9.3.4 Reaction time and temperature.....	311
9.3.5 Hydroxyl groups .....	311
9.3.6 Summary .....	312
9.4 Kinetics and Rate Controlling Mechanisms .....	312
9.4.1 Rate determining step in the mechanisms.....	312
9.4.2 Precipitation .....	314
9.4.3 Reaction rate.....	314
9.4.4 Variables affecting the reaction rate.....	318
9.5 Synthesis Conditions for Controlled Morphology .....	319
9.5.1 Precursor.....	319
9.5.2 Temperature .....	321
9.5.3 Reagent concentration.....	322
9.5.4 Additives .....	322
9.5.5 Mineralizer type and concentration.....	322
9.5.6 Summary .....	324
9.6 Synthesis Conditions for Controlled Particle Size.....	324
9.6.1 Precursor.....	324
9.6.2 Concentration and molar ratio .....	325
9.6.3 Mineralizer type and concentration.....	325
9.6.4 Reaction time .....	326
9.6.5 Temperature .....	326
9.6.6 Summary .....	326
9.7 Summary .....	327
References .....	327

## 10 Crystal Growth, Size, and Morphology Control of Nd:RVO<sub>4</sub> Under Hydrothermal Conditions

K. Byrappa, B. Nirmala, K.M. Lokanatha Rai, and M. Yoshimura .....	335
10.1 Introduction .....	335
10.2 Technologically Important Vanadates .....	336
10.3 Phase Equilibria .....	336
10.4 Structure of Nd:RVO <sub>4</sub> .....	338
10.5 Synthesis and Growth of Rare Earth Vanadates.....	339
10.5.1 Zone melting .....	339
10.5.2 Czochralski technique.....	340
10.5.3 Flux growth .....	341
10.5.4 Top seeded solution growth (TSSG).....	342
10.6 Solubility Study .....	343
10.7 Crystal Growth.....	347
10.8 Morphology.....	351

---

10.8.1 Surface morphology.....	355
10.9 Characterization.....	358
10.9.1 XRD and IR studies .....	358
10.9.2 Laser spectroscopy.....	358
10.9.3 Absorption measurements .....	361
10.10 Summary .....	362
References .....	363
 <b>11 Hydrothermal Growth of Quartz Under Specific Conditions and the Raman Spectra of Ion Species in a Hydrothermal Growth Solution</b>	
M. Hosaka .....	365
11.1 Introduction.....	365
11.1.1 Growth of quartz with small content of Al <sup>3+</sup> .....	367
11.1.2 Synthesis of micro $\alpha$ -quartz crystals by hydrothermal hot-pressing method.....	368
11.1.3 Growth of quartz crystals above transition temperature and morphology of synthetic crystals .....	368
11.1.4 Raman spectral studies of SiO <sub>2</sub> -NaOH-H <sub>2</sub> O and SiO <sub>2</sub> -Na <sub>2</sub> CO <sub>3</sub> -H <sub>2</sub> O system solutions under hydrothermal conditions .....	369
11.2 Growth of Quartz with Poor Al <sup>3+</sup> Content.....	370
11.2.1 Experimental method.....	370
11.2.2 Experimental results .....	371
11.3 Synthesis of Micro $\alpha$ -Quartz Crystals by Hydrothermal Hot-Press Method .....	372
11.3.1 Experimental method.....	372
11.3.2 Experimental results .....	373
11.4 Growth and Morphology of Quartz Crystals Synthesized Above Transition Temperature.....	374
11.4.1 Experimental method.....	374
11.4.2 Experimental results .....	376
11.5 Raman Spectral Studies of the Solution Chemistry of SiO <sub>2</sub> -NaOH-H <sub>2</sub> O and SiO <sub>2</sub> -Na <sub>2</sub> CO <sub>3</sub> -H <sub>2</sub> O Systems Under Hydrothermal Conditions .....	379
11.5.1 Experimental method.....	379
11.5.2 Experimental results .....	381
11.5.3 Discussion .....	383
11.5.4 Summary .....	384
References .....	384
 <b>12 Growth and Characterization of Technologically Important Oxide Single Crystals</b>	
Krishan Lal, R.V. Anantha Murthy, Ashutosh Choubey, and Niranjana Goswami .....	387
12.1 Introduction.....	387

---

12.2 Crystallographic Structure .....	388
12.3 Growth of Lithium Niobate Crystals: Earlier Work.....	389
12.4 Growth of Bismuth Germanate Crystals: Earlier Work .....	390
12.5 A Crystal Growth System for Cz Growth of Nearly Perfect Crystals .....	392
12.5.1 A crystal growth system for low thermal gradient Czochralski (LTG Cz) technique.....	393
12.6 High Resolution X-ray Diffractometers.....	395
12.6.1 Double crystal X-ray diffractometer .....	395
12.6.2 Five crystal X-ray diffractometer .....	397
12.7 Synthesis of Lithium Niobate and Bismuth Germanate Powders.....	398
12.8 Growth of Nearly perfect Crystals of $\text{LiNbO}_3$ and BGO .....	400
12.8.1 $\text{LiNbO}_3$ single crystals .....	400
12.8.2 Bismuth germanate single crystals .....	402
12.9 Evaluation of Perfection of Lithium Niobate and Bismuth Germanate Single Crystals by High Resolution X-ray Diffractometry and Topography .....	404
12.9.1 Characterization of lithium niobate crystals .....	405
12.9.2 Characterization of bismuth germanate single crystals .....	407
12.10 Summary .....	412
References .....	413

## **13 Growth and Development of Nonlinear Optical Borate Crystals for Generation of Visible and UV Light**

Takatomo Sasaki, Yusuke Mori, Masahi Yoshimura,  
and Yoke Khin Yap ..... 419

13.1 Introduction .....	419
13.1.1 Coherent solid-state light source in the visible and UV regions by nonlinear optical crystals .....	419
13.1.2 NLO borate crystals .....	420
13.2 CLBO Crystals for High-Power Generation of Deep-UV Light .....	422
13.2.1 The search for $\text{CsLiB}_6\text{O}_{10}$ (CLBO) .....	422
13.2.2 Growth of CLBO .....	425
13.2.3 Structural and optical properties of CLBO .....	426
13.2.4 Degradation of CLBO crystallinity and solution .....	427
13.2.5 Performance of CLBO for generation of deep-UV light .....	432
13.2.6 Relation between crystal quality and resistance to bulk laser-induced damage .....	433
13.3 GdYCOB Crystal for Noncritical Phase-Matching (NCPM) of Visible and UV Light .....	434
13.3.1 The search for $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ (GdYCOB) .....	434
13.3.2 Noncritically phase-matched THG for Nd:YAG lasers by GdYCOB .....	436
13.3.3 Noncritically phase-matched SHG for Nd:YAG lasers by GdYCOB .....	438

13.3.4 Noncritically phase-matched SHG for Ti:sapphire lasers by GdYCOB .....	439
13.3.5 Optical damage of GdYCOB and its solution .....	440
13.4 KAB Crystal: Difficulty of Growing Borate Crystal with Layered Structure .....	443
13.4.1 The search for $K_2Al_2B_2O_7$ (KAB) .....	443
13.4.2 Growth of KAB .....	445
13.4.3 Optical properties of KAB .....	447
13.5 Summary and Perspective .....	447
References .....	448
<b>14 Growth of High <math>T_c</math> Crystals</b>	
T. Inoue, S. Miyashita, Y. Nishimura, J. Takemoto, Y. Suzuki, S. Hayashi, and H. Komatsu .....	453
14.1 Introduction .....	453
14.2 Growth of the High $T_c$ Phase of BSCCO .....	453
14.2.1 Synthesis of the high $T_c$ phase by sintering the powder of Bi-Sr-Ca-Cu .....	454
14.2.2 Preparation of single crystals containing the high $T_c$ phase of a Bi-Sr-Ca-Cu-O superconductor .....	458
14.2.3 Conversion of superconducting Bi-system single crystals from 2212 to 2223 by the annealing method .....	462
14.3 Liquid Phase Epitaxial Growth of Low $T_c$ Phase of BSCCO .....	467
14.3.1 $SrTiO_3$ (100) substrate .....	469
14.3.2 $LaAlO_3$ (100) substrate .....	471
14.3.3 $NdGaO_3$ (001) substrate .....	472
14.4 Construction of Phase Diagrams by <i>In Situ</i> Observation and Their Application to Crystal Growth of Oxide Superconductors .....	474
14.4.1 Apparatus .....	475
14.4.2 Phase diagram of $SmBa_2Cu_3O_{7-\delta}$ and its application .....	478
14.4.3 Phase diagram of Bi-based oxide superconductors .....	483
14.4.4 Primary crystallization field of Bi-based oxide superconductors and its application .....	491
References .....	493
<b>15 Growth of Zinc Chalcogenides</b>	
Robert Triboulet .....	497
15.1 Introduction .....	497
15.2 Zn Chalcogenide Growth .....	498
15.2.1 ZnTe .....	498
15.2.2 ZnSe .....	502
15.2.3 ZnS .....	509
15.2.4 ZnO .....	510
15.3 Properties and Defects of the Crystals .....	512

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15.4 Purity, Contamination and Doping.....	513
15.5 Applications and Perspectives.....	513
References .....	514
<b>16 Growth of Hydroxyapatite Crystals</b>	
Atsuo Ito and Kazuo Onuma.....	525
16.1 Introduction.....	525
16.2 Calcium Orthophosphates.....	526
16.3 <i>In Vivo</i> Calcification of Biomaterials.....	528
16.3.1 Calcification of biomaterials used in contact with bone.....	528
16.3.2 Calcification of biomaterials used in contact with blood .....	529
16.4 Apatite Deposition on Biomaterials as Surface Modification.....	532
16.5 Calcium Phosphate Cements .....	536
16.6 Hydroxyapatite Ceramics .....	537
16.7 Hydrothermal Growth of Hydroxyapatite.....	538
16.8 Factors Influencing Apatite Formation in Hard Tissues .....	540
16.9 Ectopic Calcifications.....	542
16.10 Kinetics of Hydroxyapatite Crystal Growth in Solution.....	544
References .....	548
<b>17 Crystal Growth of Gemstones</b>	
Shuji Oishi.....	561
17.1 Introduction.....	561
17.2 Growth Methods of Gemstones.....	563
17.2.1 Verneuil method.....	564
17.2.2 Czochralski method .....	566
17.2.3 Hydrothermal method.....	567
17.2.4 Flux method.....	567
17.3 Emerald .....	569
17.3.1 Growth of emerald crystals.....	569
17.3.2 A simple method of growing emerald crystals .....	570
17.4 Summary .....	578
References .....	579
<b>Index .....</b>	<b>581</b>

# 1 Growth Histories of Mineral Crystals as Seen from Their Morphological Features

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## 1.1 Introduction

The late Sir Charles Frank once said, “If one could understand enough about the morphology of crystals, he understood essential points of the fundamentals of crystal growth.” This sentence captures the importance of morphology of crystals in understanding how crystals nucleate and grow. He also answered in the following haiku to a haiku by Ukichiro Nakaya “A snow flake is a letter to us from the sky.”

“Diamonds are letters  
Still better worth the reading;  
We can reach the sky.”

Interest in the morphology of crystals started in the 17th century when Kepler observed elaborately varied dendritic snow crystals in 1611, and Steno was fascinated by the variety of polyhedral forms that rock crystals from Alpine mineral fissures exhibited. Kepler considered that the building unit of snow crystals, in spite of their varied forms, was spheres of equal size. Steno gave an explanation in terms of growth rate anisotropy for his observations that the same mineral, rock crystal, could take a variety of polyhedral forms in his treatise published in 1669. Kepler’s idea was the origin of structural crystallography, and Steno’s explanation was the starting point of the science of crystal growth.

Interest and understanding of the morphology of crystals which started in the 17th century, independently one of dendritic forms and the other of polyhedral forms bounded by flat faces, have now advanced to a state to be understood from a unique viewpoint, the atomistic process of crystal growth. This is due to the development of the science of crystal growth in the 20th century, particularly after the 1950s. For simple and pure model systems, it is now possible to explain at the atomistic level why and how the same crystal can take a variety of forms, from dendritic, hopper, to polyhedral forms, and why different crystal species exhibit different characteristic forms or Habitus. How our understanding of morphology

and growth mechanism of crystals has developed since the time of Kepler and Steno has recently been summarized by Sunagawa [1].

Both snow crystals and rock crystals are naturally formed crystals under uncontrolled, fluctuating, and often sharply changing growth conditions. Any mineral crystals constituting the solid earth and planetary bodies were formed under such conditions and in impure, complicated, and complex systems. Also inorganic and organic crystals are formed in various organs and cells of animate bodies, through biological processes necessary to sustain life or to eliminate unnecessary waste compounds. How crystals nucleate and grow, and how their forms are controlled in such complicated and complex systems are problems still waiting for proper answers at the atomistic level.

The temperature and pressure conditions of mineral formation have been estimated based on equilibrium thermodynamics and phase relations. Information about conditions of mineral formation may be obtainable assuming that any geological systems have already reached the equilibrium state. However, crystals can neither nucleate nor grow under equilibrium condition. Driving forces, namely conditions deviating from the equilibrium state, are necessary to realize nucleation and growth of crystals. In natural crystallization, growth rates may fluctuate or abruptly change during their growth processes, and morphology and element partitioning are influenced accordingly. Crystals may be partially dissolved during the process of formation, or experience transformation in their post growth histories.

We are unable to observe *in situ* the growth or post growth process of mineral formation, but we can investigate samples that experienced these processes, provided that these processes are recorded in the samples in some form and can be visualized by appropriate methods. In nearly perfect single crystals, these are recorded in the form of various physical imperfections and chemical heterogeneities, preserving the records of morphological evolution during the growth or post growth processes. Information obtainable from such samples is equally important and informative in understanding the formation of solid earth and planetary materials, provided that such information can be evaluated properly.

Since the morphology of a crystal appears through growth or dissolution processes, and is controlled by both internal (structural) and external (growth or dissolution parameters) factors, morphological features of crystals are the most useful information in deciding the growth or post growth history that a crystal experienced, since both growth and dissolution uniquely take place on the solid-liquid interface, that is, crystal surfaces and surface microtopographs of crystal faces offer useful information on how the crystal grew or partially dissolved at an atomistic level. Various optical microscopy and interferometry techniques, such as phase contrast microscopy (PCM), differential interference contrast microscopy (DISM) and interferometries, atomic force microscopy (AFM), and scanning tunneling microscopy (STM) can visualize and measure growth steps of nanometer height. External morphology (crystal habit or Habitus and Tracht) is a result and reflection of crystal growth. Depending on growth conditions, the same crystal species may show different external forms. Morphological changes and accompanied variation in element partitioning are recorded in single crystals in the form of

growth banding, growth sectors, and sector boundaries. Generation and spatial distribution of dislocations and other lattice defects in single crystals are also records of what happened during the growth process. Inclusions serve as informative indicators of growth and environmental conditions. At present we have various sophisticated methods to visualize and analyze these physical imperfections and chemical inhomogeneities, such as X-ray topography, laser-beam tomography, cathodoluminescence tomography, electron-probe microanalyzer, micro-focused X-ray fluorescence, and so forth.

It is the purpose of this chapter to demonstrate how one can decode letters sent from the deep interior of the earth, based on the analyses of morphological features recorded in mineral crystals. For this purpose, the author has selected diamond crystals as a representative example of crystal growth taking place in deep-seated magma and in the subduction zone, beryl crystals occurring in pegmatites which represent crystallization in super-critical liquid phase at the latest stage of magmatic solidification, and trapiche ruby formed by contact metasomatism due to intrusion of a granitic magma into carbonate rocks. The author has deliberately selected gem minerals in this chapter, since they occur as nearly perfect single crystals, and information obtained on such crystals serves as very useful diagnostic features in distinguishing natural from synthetic gemstones.

Following this introduction, the present understanding of morphological aspects of crystals will be briefly summarized in Section 1.2. Then discussions on diamond, beryl, and trapiche ruby will be presented in their respective sections. In this chapter, descriptions and discussions on mineral crystals formed by regional metamorphism and sedimentogenesis are excluded, since these were treated in [2,3].

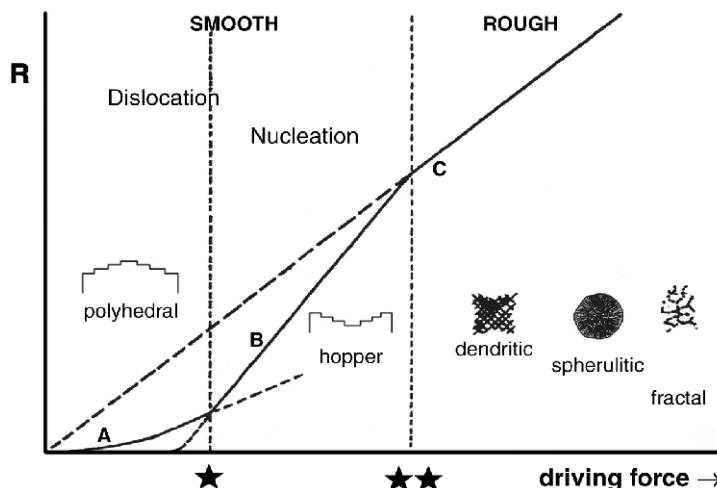
## 1.2 Morphology of Crystals

Growth and dissolution of crystals uniquely take place on the surfaces of a crystal, that is on the solid-liquid (ambient phase) interface. Depending on the structure of an interface (rough or smooth), the growth mechanism, and thus the relations between the driving force and growth rate are different. The growth mechanisms can be classified into three types depending on interface roughness: adhesive type for rough interface, two-dimensional nucleation growth, and spiral growth for smooth interface. The interface roughness (smooth or how rough) is different depending on crystallographic directions, which are related to the crystal structure. The interface structure transforms from smooth to rough with increasing growth temperature (thermodynamic roughening transition) and driving force (kinetic roughening transition). Under the conditions where a smooth interface is assumed, growth proceeds tangentially parallel to the interface, and the crystal will take a polyhedral or hopper (skeletal) morphology bounded by crystallographic flat faces. Under conditions where a rough interface is assumed, the crystal is bounded by rounded noncrystallographic interfaces. If morphological instability occurs on such a rough interface, the crystal takes dendritic form. By further increasing the

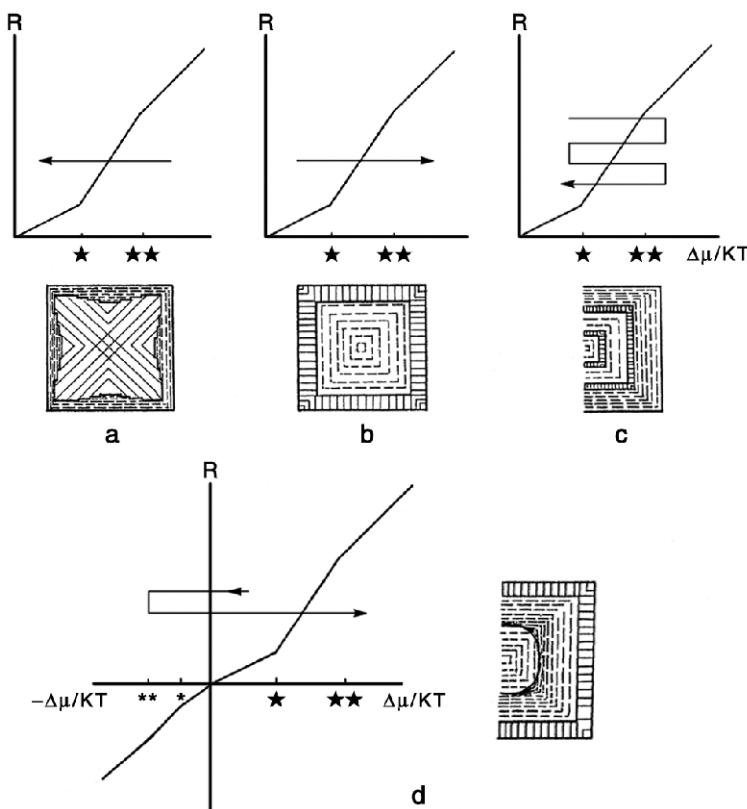
driving force, spherulitic and fractal patterns will appear through aggregation of polycrystals. Summarizing these, the relations among polyhedral, hopper, dendritic, spherulitic, and fractal morphologies may be represented as schematically shown in Fig. 1.1, which represents only one section of events. Positions of \* and \*\* indicate where growth mechanism and morphology changes are different depending on crystallographic directions, ambient phases, solute-solvent interaction energies, and other factors. The analysis and discussion of these problems are given in [1–4].

In mineral formation, crystals nucleate and grow in impure, complicated, and complex systems, and the growth conditions are not controlled, but variable. There may be abrupt changes or gentle fluctuations in growth parameters during the growth or post growth process. External forms, perfections, and element partitioning change accordingly, and the changes are recorded in various forms of physical imperfection and chemical inhomogeneity in single crystals.

When a crystal grows in a closed system, the driving force diminishes monotonously as growth proceeds. As a result, starting from dendritic morphology appearing at the earlier stage and under higher driving force conditions, the morphology transforms to a polyhedral one. Within a polyhedral single crystal, record of dendritic growth may be discernible surrounded by straight growth banding (Fig. 1.2a), if a bisected sample is investigated by appropriate methods to reveal



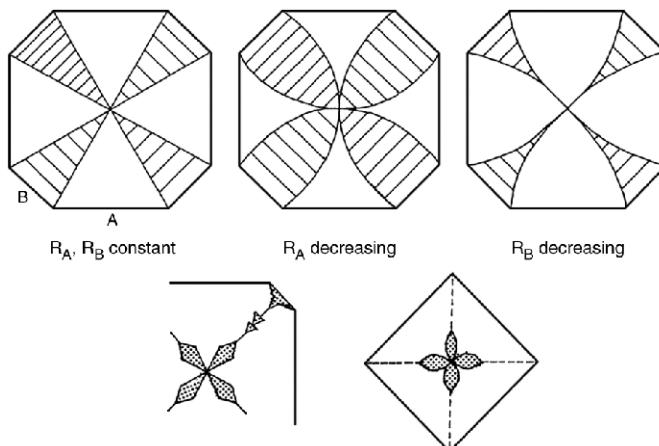
**Fig. 1.1.** Morphologies of single crystals (polyhedral, hopper, dendritic) and polycrystalline aggregates (spherulitic and fractal) in relation to growth rate  $R$ , driving force, interface roughness (smooth and rough) and growth mechanisms. Curve *a* represents the spiral growth, curve *b* the two-dimensional nucleation growth, and curve *c* adhesive-type growth mechanisms. The critical points \* and \*\* are the points where the predominant growth mechanism changes [4]



**Fig. 1.2.** Expected internal morphologies in single crystals due to the change of growth parameters during the formation of a single crystal. Arrows in respective  $R$  vs.  $\Delta\mu/kT$  diagrams indicate the route of change of driving force conditions during the growth process. Broken lines represent growth banding formed by smooth interface growth, and solid lines dendritic or fibrous textures which appeared by rough interface growth [4]

faint heterogeneity and imperfection. If a magma containing polyhedral crystal is uplifted, the growth condition changes abruptly to another condition under which dendritic growth or partial dissolution will take place. Surrounding a clear single crystalline core, a mantle portion with fibrous texture will be formed (Fig. 1.2b), or a rounded discontinuous outline will be recorded in a single crystal (Fig. 1.2d). Various internal morphologies may be expected to be seen depending on the changes of parameters. Figure 1.2 schematically illustrates some of these internal morphologies.

Similarly, since interface roughness and growth kinetics are different in different crystallographic directions, growth sectors appear in a single crystal. Depending on relative growth rates in neighboring sectors, various forms of growth sector boundaries appear, some examples of which are schematically shown in Fig. 1.3.



**Fig. 1.3.** Various growth sector boundaries: Upper three figures show expected growth sector boundaries in relation to relative growth rates  $R_A$  and  $R_B$ . Lower two figures show actually observed growth sector boundaries [4]

Growth rates within one growth sector, and also among crystallographically equivalent growth sectors are neither constant nor uniform, which results in the formation of growth banding. Since both thermodynamic and kinetic parameters contribute to growth banding, growth sectors which control element partitioning may be visualized by various techniques, including X-ray topography, cathodoluminescence tomography, element mapping techniques using EPMA, XFA, and other spectroscopies.

Polyhedral crystals appear principally by a spiral growth mechanism under conditions shown below \* in Fig. 1.1. Spiral step patterns of molecular height are observable on as-grown low index crystal faces. The morphology of growth spirals varies depending on different crystallographic faces, and on growth parameters. They offer useful information to evaluate how and under what condition the crystal grew. Similarly, surface microtopographs of crystal faces, such as dissolution steps and etch figures, tell us information relating to the dissolution process.

In terms of morphological features of crystals, the following are included in this chapter, which demonstrate how growth, dissolution, or transformation of natural crystals proceeded:

1. External morphology (polyhedral, hopper, and dendritic forms of single crystals, or spherulitic and fractal forms of polycrystalline aggregates)
2. Morphology of polyhedral crystals (crystal habit, Habitus and Tracht [4])
3. Surface microtopography of crystal faces (spiral step patterns, dissolution steps, etch figures [4])
4. Growth sectors, sector boundaries
5. Growth banding
6. Element partitioning associated with the above

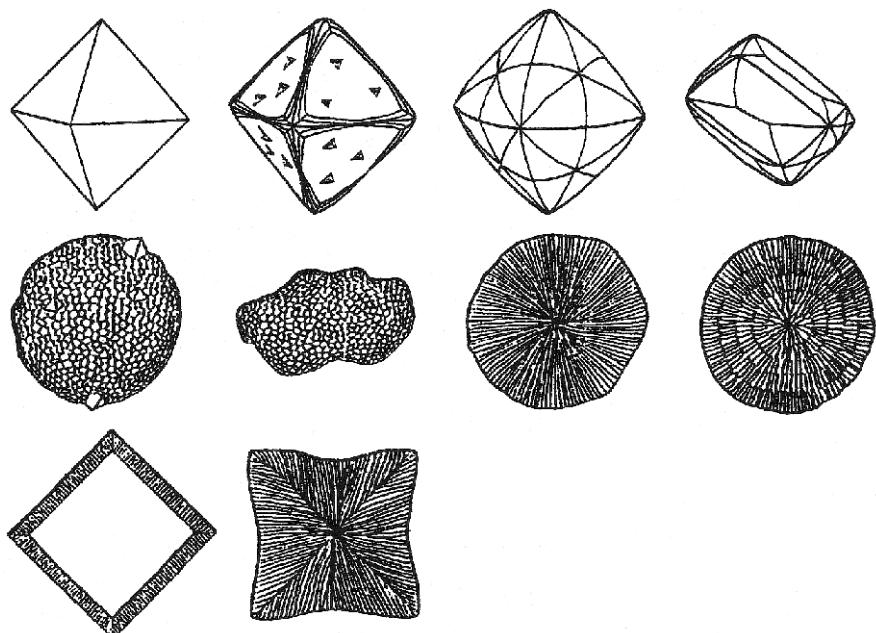
## 1.3 Diamond

The origin of natural diamonds has been an enduring subject of interest and controversy. Some believe that they were formed in magmas in the mantle, others argue mantle metasomatic origin. There are also some who argue that carbonados (polycrystalline aggregate of diamonds) were formed near the earth's surface by radiogenetic energy, and some even assume cosmic dust origin for carbonados. Some believe the mantle originated inorganic carbon as the carbon source for diamond formation, and others suggest organic carbon origin derived from subducted oceanic sediments.

Natural diamonds occur in a variety of forms, to which different variety names have been given. The names include, in addition to single crystalline diamond, ballas, coated stone, bort, shot bort, hailstone bort, framesite, stewartite, and carbonado. Only single crystalline stones and coated stones have been used for gem purpose, others have been used for industrial purposes. Orlov [5] classified natural diamonds into ten types on the morphological basis, whereas Sunagawa [6] classified them into three major types, based on the relation between morphology and driving force as shown in Fig. 1.1. According to Sunagawa's classification, diamonds of single crystalline type are formed under small driving force conditions, below \*\* in Fig. 1.1, polycrystalline type are formed under much higher driving force conditions, above \*\*, and coated stone and cuboid are those that experienced two different driving force conditions. The three types are schematically illustrated in Fig. 1.4.

Extensive X-ray topographic and cathodoluminescence tomographic investigations have been made principally on gem quality single crystalline diamonds, and secondarily on cuboid and polycrystalline diamonds [7,8]. Commonly observed dislocation distributions in single crystalline diamonds are those originating from the center of a crystal, and radiating nearly perpendicular to {111}, with dislocation direction <110>. Growth banding in such crystals is in most cases straight and parallel to {111}. These suggest that natural diamond crystals of single crystalline type grew freely in a fluid phase, that is in magma, by the spiral growth mechanism. In fact, the spiral growth was proved on an octahedral crystal from Siberia, by correlating the growth step pattern on as-grown {111} faces and outcrops of dislocations which were identified as screw type [8].

In contrast to single crystalline type, most polycrystalline type diamonds except for carbonado show a spherulitic radiating texture consisting of fibrous thin diamond needles and other interstitial minerals. Such textural characteristics represent formation under high driving force conditions. The mantle portion of coated stones and cuboids show basically the same texture as those of polycrystalline aggregate, surrounding a clear central single crystalline core. Thus, it is considered that the central clear single crystalline core portion and fibrous mantle portion were formed under different driving force conditions. Namely, the core portion grew in magma under small driving force conditions, then the magma containing the diamond crystals was uplifted, and on the core fibrous growth of diamond took



**Fig. 1.4.** Three types of morphologies encountered among natural diamonds. Top four figures show morphologies of single crystalline type, middle four those of polycrystalline type, and the bottom two those of diamond crystals which experienced two different growth parameters

place under higher driving force conditions. Similar textures are commonly observed on phenocrysts of various rock-forming minerals in volcanic rocks, which experienced similar magmatic solidification history, and diamond of this type is no exception. For the origin of carbonado, a randomly oriented polycrystalline type, arguments are still not settled.

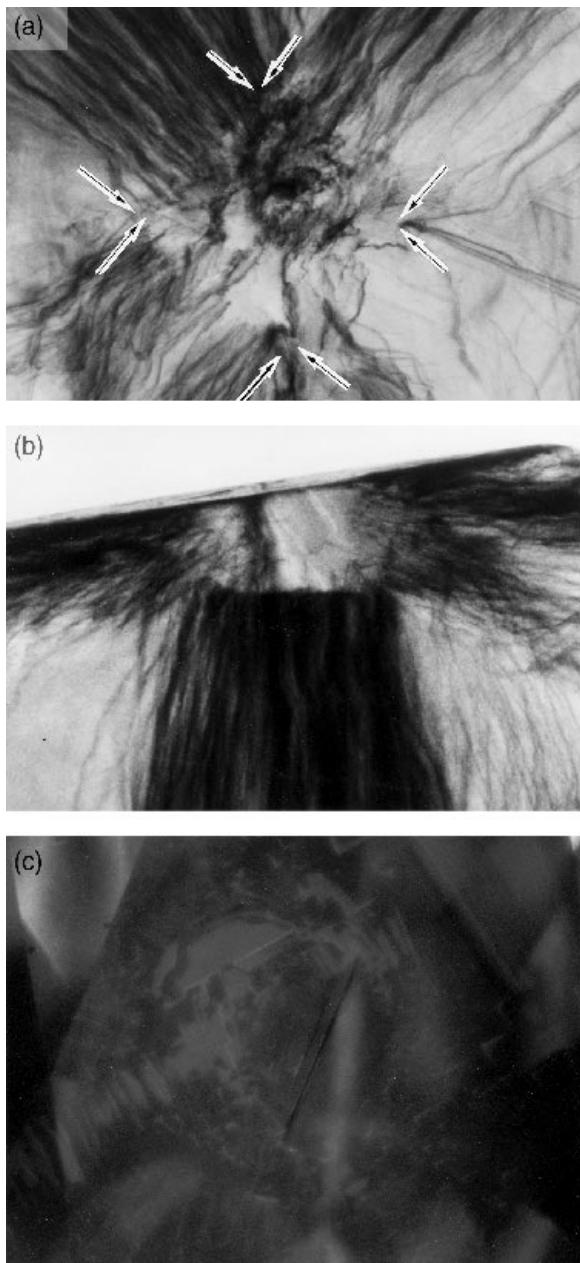
Tiny diamond crystals, less than a few tens of microns across, were reported to occur in crystals of garnet and zircon in ultra-high-pressure metamorphic rocks formed in a subduction zone [9]. Similar occurrences of micro-diamonds have been reported at many localities. Ultra-high-pressure metamorphic rocks are the third type of environment where diamonds were formed, in addition to the previously known two types, ultramafic suite (kimberlite and lamproite) and eclogitic suite.

These micro-diamonds occur sporadically in the grains of silicate minerals formed by metamorphism, and in very high content (much higher than in kimberlite or lamproite). Although simple octahedral crystals are found among these micro-diamonds, many of them take cuboid form or forms of polycrystalline aggregates. Their cuboid faces are rugged and not crystallographic {100} faces, unlike {111} faces, which are smooth. Thus a term ‘cuboid’ and not cubic is given here.

When diamond crystals grow in nature, only the {111} faces behave as a smooth interface on which spiral growth can take place, and the {100} faces behave as rough interfaces [6]. Namely, under the conditions of natural diamond formation, the position of \*\* in Fig. 1.1 for {100} is much closer to the origin than for {111}. This implies that under high driving force conditions, rough cuboid faces appear first, followed by the appearance of smooth {111} faces on which spiral growth takes place. It is reasonable to expect a higher proportion of cuboid or spherulites, and higher concentration of diamond in ultra-high-pressure metamorphic rocks due to subduction as judged from the following. The original source for ultra-high-pressure metamorphic rocks are subducted slabs, consisting of oceanic crust and sediments, which contain organic carbon. Since the melting temperature of silicate-carbon eutectic is lowered, liquid droplets are formed sporadically in solid silicate mineral grains. If diamond crystallization takes place within such liquid droplets, a higher content of source carbon and higher driving force conditions can be assumed for diamond formation than in a larger scale magma. It is natural to expect a higher content of diamond and higher proportion of cuboid or spherulitic forms than simple octahedral crystals in ultra-high-pressure metamorphic rocks than in ultramafic magmas.

When solvent components are different, the morphology of crystals can be different, since the difference in solute-solvent interaction energies modifies the morphology. In the case of synthetic diamond under high pressure and temperature conditions using metals or alloys as solvent, both {111} and {100} behave as smooth interfaces. Growth spirals have been observed on both faces. In the case of natural diamond, only the {111} faces behave as smooth interfaces on which growth spirals are expected, whereas {100} faces behave as rough interfaces. The difference in growth mechanism and morphological characteristics between natural and synthetic diamonds serve as diagnostic features, since their morphologies are recorded in the form of internal morphologies, which remain unchanged by later cutting and polishing processes and can be visualized by cathodoluminescence (CL) tomography [10].

Recently, evidence to prove the presence of seed crystal in gem quality single crystalline diamond has been reported [11]. The presence of seed crystal was proven on the basis of X-ray topographic and cathodoluminescence tomographic investigations of three brilliant cut stones. One round brilliant stone shows the ordinary spatial distribution of dislocations, which originate from a point center and radiate in bundles perpendicular to the {111} surface. The dislocation directions are parallel to  $\langle 110 \rangle$ . A pair of round and pear-shaped brilliants, which proved to have been cut from the same rough, show entirely different dislocation distributions. The core portion with cuboid form is detected in the two brilliants as a square discontinuity line on X-ray topographs. Dislocations mostly generate from the boundary between the core and major portion, and radiate in bundles in  $\langle 100 \rangle$  directions in the major portion of the brilliants. The concentration of CL emitting centers is high and uniformly surrounds the core-major portion boundary. Figure 1.5a,b show X-ray topographs and Fig. 1.5c shows a CL tomograph around the core portion. This type of dislocation generation and element partitioning is universally observed when a seed crystal is used in growing larger single crystals.



**Fig. 1.5.** X-ray topographs (a and b) and cathodoluminescence tomograph (c) of core portion of a round (a) and pear-shaped (b and c) brilliant cut diamonds. (a) and (b) are plan and profile views, respectively, (c) is a plan view. White arrows in (a) indicate the boundary of the core portion [10]

The observations described above indicate that the core portion was formed elsewhere and later transported into a new growth environment where the core acted as a seed for further growth under lower driving force conditions. This was the first evidence to verify the presence of seed crystal in the formation of natural diamond crystals.

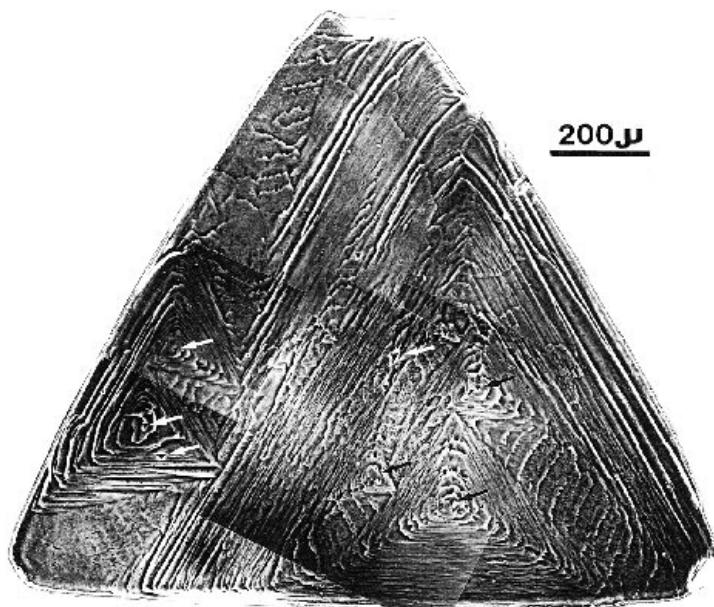
The most likely place where the core portion was formed is in subducted ultra-high-pressure metamorphic rocks. Assuming that ultra-high-pressure metamorphic rock containing micro-diamond crystals of cuboid form was subducted further and eventually trapped into a magma, where further growth of diamond took place, the presence of a seed crystal in the natural diamond formation can be understood reasonably. It is impressive to see the whole circulation history taking place in plate, subduction, and mantle convection, within a small cut stone of diamond.

Natural diamond crystals were formed at a depth greater than 100–120 km, then rapidly uplifted to the Earth's surface by kimberlite or lamproite magma, and quenched metastably by adiabatic expansion due to volcanic eruption of the magma. During uplifting, they passed through the thermodynamic conditions unfavorable for diamond; also they received severe stress. All these processes are recorded in the form of surface microtopographs, external forms of crystals, dislocation nature, precipitation textures, and so forth. Most natural diamond crystals

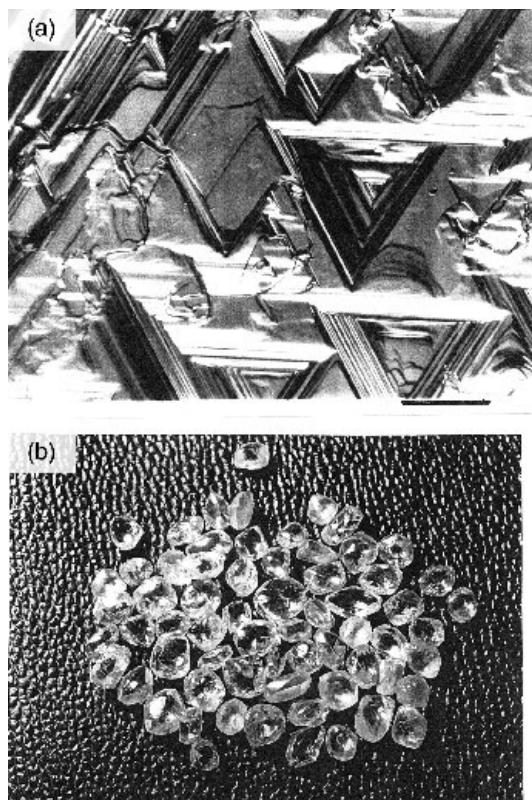
**Table 1.1.** Morphological Features Observed on Natural Diamond Crystals Indicating Dissolution Process

(I) External Forms	(II) {111} Surfaces	(III) Dodecahedroidal Surfaces
Rounded corners and edges	Trigons (mostly negatively oriented to the triangle of {111} face) are universally observed on {111} surface.	Scaly surface
Curved surfaces		Network ditches
Curved hexaoctahedral forms		Superimposed ring or circular patterns
Curved dodecahedroidal forms	Both point bottomed (P type) and flat bottomed (F type) are seen corresponding to etch pits at surface outcrops of dislocations and point defect, respectively. Deep and shallow trigons are present in both P and F types; respectively name PD, PS, FD and FS types. Depending on etching condition, trigons may show change their orientations and forms from truncated negative trigons, hexagons, truncated positive trigons to positive trigons.	

show morphological characteristics as summarized in Table 1.1, which are due to partial dissolution during the uplifting process. However, there are rare cases in which crystals received only a very little dissolution, preserving their as-grown surfaces. On such crystals, triangular growth hillocks can be observed, as the example shown in Fig. 1.6. The summits of these hillocks correspond to the outcrops of dislocations, where we see tiny trigons (triangular etch pits with opposite orientation to the triangle of the {111} face). Dissolution proceeded very weakly, attacking only the outcrops of dislocations. In this particular case, dissolution features are observed together with growth features. But, on most natural diamond crystals, dissolution proceeded more severely, and as-grown surface microtopographs are entirely erased out. Figure 1.7 shows an example of such surface microtopographs.



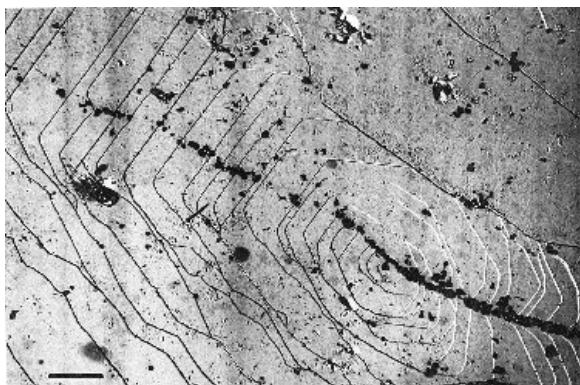
**Fig. 1.6.** Mosaic phase contrast photomicrograph of a (111) face of an octahedral diamond crystal from Siberia, which received only a slight dissolution. Note triangular growth hillocks with the same orientation as the triangle of the (111) face, and a tiny triangular pit (opposite orientation; trigon) at the respective summit of the former growth hillocks. The thinnest growth layers, which consist of growth hillocks, have a step height of less than 0.5 nm. Bar = 200  $\mu$ m



**Fig. 1.7.** DICM photomicrograph of triangular etch pits (trigons) on a (111) face (a). Bar = 0.1 mm. (b) Rounded morphology of natural diamond crystals. Both features are due to dissolution

## 1.4 Beryl

Pegmatite is a lenticular or vein form of discordant igneous rock mass or cutting in the surrounding strata, and produces much larger and more perfect crystals than those in mother rocks. It is also a treasure box of unusual mineral species containing large cations. Crystals grow in a void in solidifying magma due to the concentration of volatile components and large cations, which cannot find the sites in the structure of rock-forming minerals. Various gem quality crystals and radioactive or rare earth minerals occur in pegmatite. As a representative example to investigate how crystals grow in pegmatites, the author has selected beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ) crystals from several pegmatite localities, and investigated their surface microtopographs, spatial distribution of dislocations, inclusions, and growth banding [12]. Beryl is the most persistent mineral among 8 beryllium-



**Fig. 1.8.** DICM photomicrograph of elemental growth spirals on (0001) face of a beryl crystal from Minas Gerais, Brazil. Bar = 500  $\mu\text{m}$ . Small dots are etch pits selectively formed at dislocation outcrops [12]

containing minerals of 18 minerals belonging to the BeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (BASH) system [13], and its stability field ranges from about 320° to 680°C in temperature and up to 10 kbar in pressure. It is therefore assumed that beryl represents the conditions covering the major range of pegmatite formation.

Many beryl crystals show partially dissolved morphological features, rounded corners and edges or pencil-like tapered prismatic forms, but some crystals preserve their as-grown crystal faces. On such as-grown {0001} and {10̄10} faces, one observes elemental growth spirals with unit cell height, originating either from an isolated or group of dislocations. These growth spirals are essentially polygonal in form following the symmetry of respective faces, and the values of step separation versus step height are in the range of  $10^4$  to  $10^6$ . This means that the spirals have profiles of 10,000 m to 1,000,000 m flat terrace and 1 m cliff. This also indicates conditions of very small driving force, and diluted ambient phase, probably a supercritical vapor phase [14].

Figure 1.8 is a representative growth spiral on a {0001} face. Small dots are etch pits formed selectively at the outcrops of dislocations, both active and inactive for the spiral growth.

Figure 1.9 shows an X-ray topograph (a), a photomicrograph under crossed polarizers before (b) and after etching (c) of a section cut parallel to the (0001) face of a beryl crystal from Arasuai, Minas Gerais, Brazil. From this set of photographs, we obtain information relevant to the growth process of the beryl crystal, which is summarized below.

1. There are three types of dislocations: one parallel to (labeled A), the second perpendicular to (labeled B), and the third inclined to (labeled C) the (0001) face. Dislocations A originate from inclusions trapped at the discontinuity boundary in contrast on the X-ray topograph. Dislocations B give strain birefringence under crossed polarizers (Fig. 1.9b), and dislocations C form etched

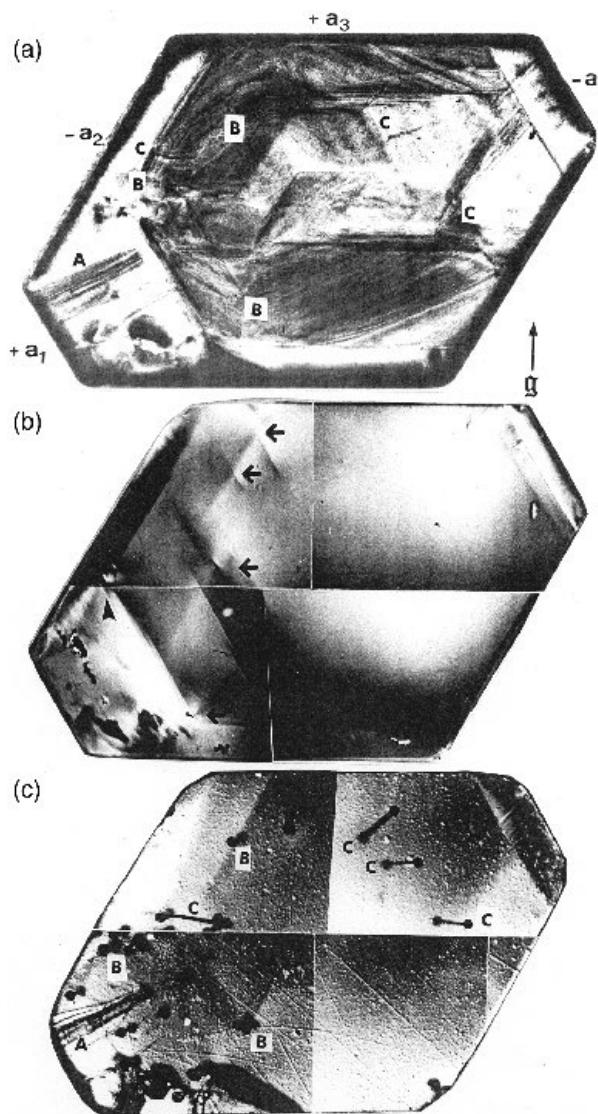
tunnels with pits on the terminations. Most of these dislocations are considered to have acted as growth centers to produce elemental growth spirals on the {0001} (B and less probably C) and {1010} faces (A).

2. At least three stages of intermission and associated changes of morphology are discernible during the growth process of this particular crystal. Two discontinuities in contrast are discernible on the X-ray topograph of Fig. 1.9a, the outlines, that is the morphology of this beryl crystal change at these discontinuities. Partial dissolution is also discerned from the rounded outline of the second discontinuity line, where inclusion entrapment is seen, and from which dislocations A generates.
3. Growth rates are markedly different among crystallographically equivalent directions, as judged from the width between the successive discontinuity lines. For example, the growth rates in +al and -a2 directions are nearly twice those in -al and +a2 directions, respectively. This indicates that there was a directional flow of the fluid phase, and the direction changed during the growth process.

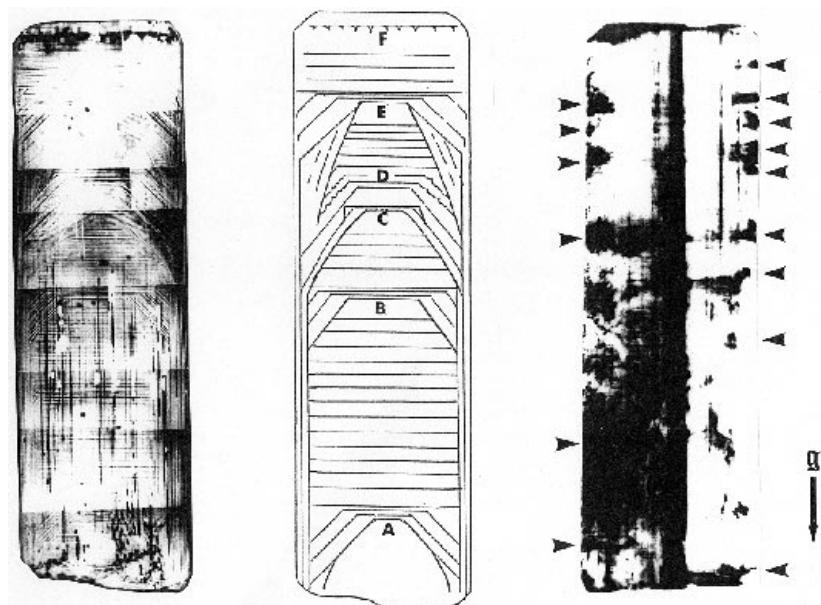
Figure 1.10 shows a mosaic photograph (a) of a prismatic crystal immersed in n-methylaniline solution with RI = 1.5702, taken under crossed polarizers, and the corresponding sketch (b), as well as an X-ray topograph of another similar prismatic crystal (c). From Fig. 1.10, one can see the following growth history for beryl crystals.

4. There were at least five stages of partial dissolution followed by regrowth during the growth process of the crystal shown in Fig. 10a and b, indicated by labels A to E. Rounded corners of hexagonal prismatic outline, truncating the straight growth banding, show the presence of a partial dissolution period. The subsequent regrowth period is witnessed by transformation from the rounded outline to the straight banding parallel to the hexagonal dipyramidal faces, which eventually disappear from the crystal. The crystal takes on a hexagonal prismatic habit bounded by the {0001} and {1010} faces alone, when the condition is stabilized.
5. From Fig. 1.10c, it is seen that many bundles of dislocations generate on the surface of prismatic crystal where discontinuities are seen in the contrast image of the X-ray topograph. The dislocations run nearly perpendicular to the prism faces. The outcrops of these dislocations on the {1010} faces are considered to have acted as sources for growth spirals on the prism faces.
6. In Fig. 1.10a, tube-like inclusions and dislocations are seen running parallel to the *c*-axis. They originate from solid inclusions present on the boundary surface between partial dissolution and regrowth periods.

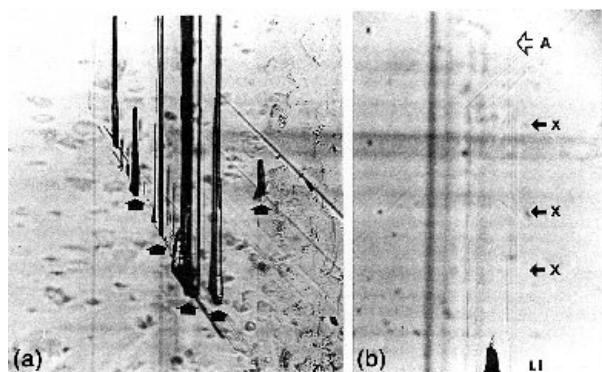
Figure 1.11a and b are the polarization photomicrographs of the tube-like two-phase inclusions and negative crystals running parallel to the *c*-axis. It is seen that the two-phase inclusions are formed behind solid inclusions of platy form, probably mica flakes, adhered on the surface when regrowth started after partial dissolution. The negative crystal in Fig. 1.11b appeared by growth on the wall of an inclusion from the entrapped mother liquid. An interesting point is that dislocations parallel to the *c*-axis are generated at the tip of tube-like inclusions, when enclosure failed.



**Fig. 1.9.** X-ray topograph (a) and photomicrographs taken under crossed polarizers before (b) and after (c) etching of a section parallel to the (0001) face of a beryl crystal from Ara-suai, Minas Gerais, Brazil. Bar = 1 mm. Arrow with label of  $g$  indicates  $g$ -vector [12]



**Fig. 1.10.** (a) Mosaic photomicrograph under crossed polarizers, (left) and the corresponding sketch (middle) showing the internal texture of a hexagonal prismatic beryl crystal from Hefferman's mine, Australia. Labels A to F indicate the stages where partial dissolution or change of conditions took place. (Right) X-ray topograph of another prismatic beryl crystal from the same locality. Arrows indicate the positions of generation of dislocations running perpendicular to the prism faces. Arrow  $g$  indicates  $g$  vector. Bar = 1 mm [12]



**Fig. 1.11.** (a) Photomicrograph of tube-like two-phase inclusions formed behind solid inclusions indicated by arrows. (b) Strain field (arrow A) around a dislocation generated from a misfit in the incorporation of the inclusion and negative growth banding (arrows X). LI is a two-phase inclusion [12]

From the preceding explanation, we may consider the growth process of beryl crystals in pegmatitic conditions in the following manner. Crystallization of minerals in pegmatite does not take place in a closed system under static conditions. Directional inflows of nutrients into a void formed in a solidifying magma took place many times, resulting in partial dissolution and regrowth of crystals. At the onset of regrowth, solid inclusions were trapped on the surface, which formed tube-like two-phase inclusions and generated dislocations. Dislocations thus generated acted as self-perpetuating step sources of spiral growth on both the {0001} and {1010} faces. Hexagonal dipyramidal faces appeared only during the regrowth period, and are taken as transient faces.

## 1.5 Trapiche Ruby

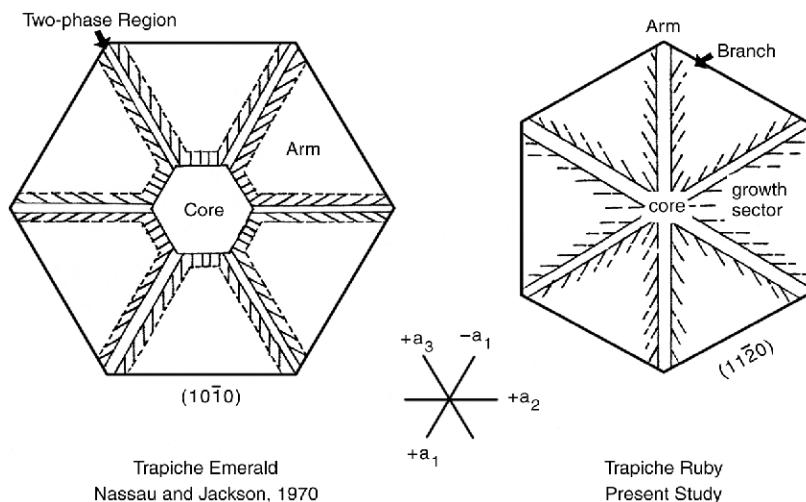
When a magma intrudes into pre-existing strata, contact metamorphism takes place and mineral crystals are newly formed, which are stable phases for the new pressure and temperature conditions. Since magma intrusions supply higher temperature and additional compositions, such processes are customarily called *contact metasomatism*. How nucleation and growth of newly formed crystals take place in the pre-existing solid rocks under such conditions has not been thoroughly understood. It has been a subject of controversy whether the crystallization should be regarded as solid-state crystallization or a solution growth dissolution-precipitation process.

Trapiche ruby is an unusual type of ruby crystal showing unique textures, which resemble a sugar cane crushing gear. *Trapiche* is a Spanish word for such gears, and was originally applied to emerald crystals from Chivor and Muzo, Colombia showing similar texture. Trapiche emerald occurs in hydrothermally metasomatized country slates around calcite-emerald veins cutting into the slate strata [15]. Trapiche ruby occurs in contact metasomatized carbonate strata in the Mong Hsu mining area, Myanmar [16].

In Fig. 1.12, schematic diagrams of textures seen in both trapiche emerald and ruby are compared [17]. Different terms have been used to describe the textures seen in Fig. 1.12, but we adopt the terminology given for trapiche ruby in this figure.

Trapiche ruby occurs in the form of barrel-shaped prisms, with internal texture characterized by a core, six arms extending along the <1010> direction, and branches there from running parallel to the z axes, with six clear ruby growth sectors. The barrel-shaped crystal is bounded by basal {0001} and tapered prism {11 $\bar{2}$ 0} faces, although for the latter faces very high indexed scalenohedral faces, like {14 14 28 3} were assigned in [16].

The arms and branches are yellow, white, or black in color and translucent to opaque. Through EPMA analysis, it was confirmed that these portions consist of several mineral phases, corundum, carbonate, and tiny unidentified K-Al-Fe-Ti



**Fig. 1.12.** Schematic illustration of textures and terms used to denote respective portions in trapiche emerald (a) [15] and trapiche ruby [16]. From [17]

silicate mineral grains [16]. The pattern shown by the arms and branches is typical for dendritic growth, such as snow dendrites. The six growth sectors are triangular or trapezohedral in form, and transparent to translucent red in color, and consist of pure ruby single phase. The growth sectors appear filling the interstices of arms and branches. The core portion is in most cases black and opaque and mineralogically and texturally the same as the arms and branches, but in rare cases a hexagonal prismatic clear ruby core portion is present.

The problems we intend to understand here are how such textures were formed, how element partitioning was governed, and how long it took to form the present size in the contact metasomatic condition.

The arms run from a central point or from six corners of a central hexagonal core to the six corners of a hexagonal prism, nearly parallel to the  $\{0001\}$  face, with about  $5^\circ$  bending toward the center. The arms and branches extend from the core with similar texture as the arms in most samples, but the arms start from the corners of the core hexagon and branches from the core-growth sector boundaries when a clear ruby core is present. The boundary of the hexagonal core and the six growth sectors are thus rugged and splintered. The branches show similar appearance in color, transparency, and mineral compositions as the arms. Six growth sectors consist of corundum single phase, but color-zoning parallel to tapered prism faces is also observed.

It has been well established that a dendritic pattern appears due to morphological instability [18] of the growing rough interface, where an adhesive type growth mechanism operates. The arms and branches can be taken as representing such rough interface growth. In contrast to this, a layer-by-layer growth mechanism on the  $\{0001\}$  and  $\{11\bar{2}0\}$  faces form growth sectors. Namely these two faces be-

haved as smooth interfaces during their formation. Therefore, it can be assumed that both interfacial roughness and growth mechanisms were different in the formation of portions of arms and branches and of growth sectors.

By means of X-ray microfluorescence analysis (XRMF) and electron microprobe analysis (EPMA), elemental mapping was performed on slices cut perpendicular to the *c*-axis. The results clearly indicated a marked difference in chemistry and mineralogy between arms and branches, and growth sectors. Important differences between the two portions noticed in the element mappings are:

1. The arms and branches are composed of polyphases; corundum, carbonate, and silicate. But the corundum in these parts is chemically homogeneous, showing no chemical zoning from the root to the tip of an arm or a branch. The Chromium (Cr) content in corundum in these parts is constant and much lower than in the corundum in the growth sectors. The Cr content in corundum is nearly the same or at the most two times higher than that in carbonate or silicate grains coexisting in the arms and branches.
2. The growth sectors consist of single phase ruby, but distinct chemical zoning in Cr content, and less distinct Ti content are seen parallel to the tapered prism faces. The Cr content in the growth sectors is much higher than in the arms and branches, and ranges from 0.60 to 1.70%. The Cr content in the growth sectors sharply increases more than 8 times at the boundary between the central core and growth sectors. It gradually decreases going outward, namely as growth proceeded and increases slightly again followed by sharp decrease at latest stage.
3. The black and opaque core portion shows the same character as that of the arms and branches, whereas the clear hexagonal core resembles that of the growth sectors except for Cr zoning.

Figure 1.13 shows plots of EPMA point analyses along the A-A, B-B lines and section 2 in Fig. 1.13a. All analyses were performed with beam diameter 1  $\mu\text{m}$ ; A and B, point separation, 20  $\mu\text{m}$ , 1.5–1.6 mm extension; section 2, point separation 3  $\mu\text{m}$ , extension 300  $\mu\text{m}$ . Figure 1.13 clearly indicates the above summaries.

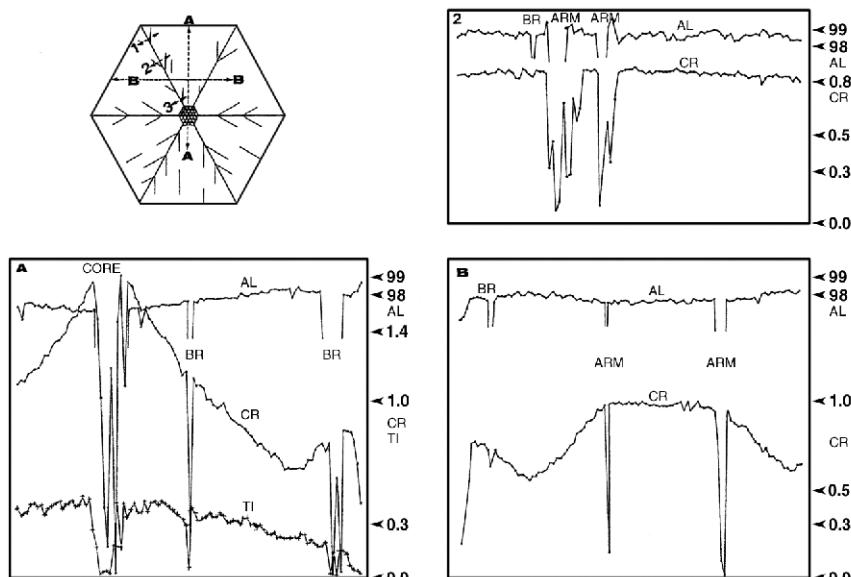
From the textural and chemical characteristics described above, the author concludes the following:

- a. The arms and branches are formed by dendritic growth by an adhesive-type growth mechanism on the rough interface, during which eutectic-type multi-phase precipitation took place.
- b. The growth sectors are formed by a layer-by-layer growth mechanism on the smooth interface, principally the {0001} and {11 $\bar{2}$ 0} faces, and a later or concurrent filling-in process of interstices of earlier formed dendrite arms and branches.
- c. Elemental partitioning was governed by thermodynamic parameters during the dendritic growth stage on rough interfaces, and by kinetics (growth rates) during the formation of growth sectors.
- d. Dendritic growth took place under higher driving force conditions, followed by a filling-in process of the interstices of arms and branches through a layer-by-

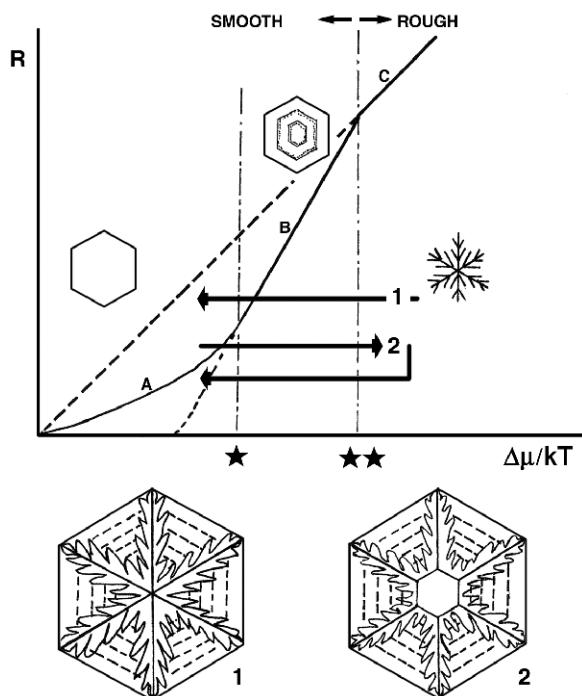
layer growth mechanism. The filling-in process took place either concurrently with dendritic growth or slightly later, since the concentration at the root of the dendrites is depleted.

- e. Depending on the conditions, layer-by-layer growth may sometimes precede dendritic growth, forming a hexagonal core of single phase ruby, on which dendritic growth followed by layer-by-layer growth takes place.
- f. The present size of the trapezoidal ruby was formed during the dendritic growth stage, and thus in a very short time.

In Fig. 1.14, superimposing the routes and textural changes of trapezoidal rubies on Fig. 1.1 illustrates the above discussions.



**Fig. 1.13.** Positions of scans A, B, and 1–3 (a), and corresponding plots of microprobe analyses of  $\text{Al}_2\text{O}_3$  (AL),  $\text{Cr}_2\text{O}_3$  (CR) and  $\text{TiO}_2$  (TI). Core indicates opaque core portion, arm and br indicate, respectively, arms and branches [17]



**Fig. 1.14.** Schematic diagram showing two routes 1 and 2 for trapiche ruby without (route 1) and with clear ruby core (route 2), superimposed on Fig. 1.1 [17]

## 1.6 Summary

Diamond, beryl, and trapiche ruby are used to demonstrate how the present understanding of growth, morphology, and perfection of crystals can be used to decode the letters sent from the depths of the earth. The same concept is applicable to other earth and planetary processes, as well as to organic and inorganic crystal formation in animate bodies.

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# 2 Theory of Crystal Growth from Vapor and Solution

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## 2.1 Various Crystal Growth Processes

For a crystal to grow, a seed crystal capable of maintaining a stable condition in a melt, solution, or vapor phase must first be produced. In vapor deposition, the substrate serves as the seed crystal. The process by which a seed crystal is born and grows into a nucleus is called the nucleation process, which plays an important role in the process of crystal growth. The seed requires the formation of a three-dimensional nucleus, but because the workings of three-dimensional nucleation are analogous to those for two-dimensional nucleation, only the latter is treated here. In this part of the book, we will discuss what happens after a nucleus has formed and the crystal has grown in size, specifically, how crystals grow and at what speeds [1,2,5].

### 2.1.1 Driving force

For crystals to grow, some driving force is required. We first define this driving force. The conditions in any given system change according to the laws of thermodynamics in such a manner that the free energy in the whole of the system decreases. This means that any decrease in free energy associated with the crystallization process works to promote the growth of crystals. Namely, the difference  $\Delta\mu = \mu_m - \mu_c$  between the chemical potential  $\mu_m$  of a melt, solution, or vapor phase (*the growth medium*) and the chemical potential  $\mu_c$  of the crystalline phase becomes a driving force towards crystal growth. In the nucleation process, the number of atoms that form a surface or interface is as important as the number of atoms that form crystals because those forming a surface supply the energy needed to grow the crystals. After a nucleus forms and the crystal grows to a sufficient extent, the contribution of the interface energies can be ignored and the difference in bulk free energy in each phase becomes the difference in chemical potential. Therefore, a difference in chemical potential in various growth environments can be associated with measurable, physical quantities as shown below.

When the growth medium is a melt, the molten and crystalline phases coexist in a stable state if the system is at the melting point  $T_m$ . If the temperature falls below  $T_m$ , crystals grow. That is, the level of supercooling  $\Delta T = T_m - T$  becomes the driving force for crystal growth. The relationship between the level of supercooling  $\Delta T$  and  $\Delta\mu$  can be expressed as follows:

$$\Delta\mu = L\Delta T/T_m \quad (2.1)$$

Here,  $L$  is the latent heat of melting.

In the case where the growth medium is a vapor, crystals will grow when the vapor pressure  $p$  is higher than the equilibrium or saturated vapor pressure  $p_e$ , and then the level of supersaturation  $\sigma = (p - p_e)/p_e$  becomes the driving force. A difference in chemical potential between the vapor phase and the crystal phase based on vapor pressure can be expressed as follows:

$$\Delta\mu = k_B T \log(p/p_e) \quad (2.2)$$

Therefore, the relationship between  $\Delta\mu$  and the level of supersaturation  $\sigma$  can be expressed as follows:

$$\Delta\mu = k_B T \log(1 + \sigma) \approx k_B T \sigma \quad (2.3)$$

Here,  $k_B$  is Boltzmann's constant.

If the growth medium is a solution, the threshold concentration of solutes that can be dissolved into the liquid (i.e., the concentration  $C_e$  of a saturated solution) is used as the criterion. The level of supersaturation  $\sigma = (C - C_e)/C_e$ , which can be calculated from  $C_e$  and the actual solute concentration  $C$ , can be defined as the driving force. The relationships of the chemical potential differences between the solution phase and the crystal phase can be expressed as follows:

$$\Delta\mu = k_B T \log(C/C_e) \quad (2.4)$$

$$\Delta\mu = k_B T \log(1 + \sigma) \approx k_B T \sigma \quad (2.5)$$

In a typical crystal growth experiment, the supersaturation  $\sigma$  becomes positive by lowering the system temperature to decrease the concentration  $C_e$  of the saturated solution instead of increasing the concentration  $C$ .

There is also a mechanism for solid-phase growth that occurs when a polycrystal that formed through the agglomeration of small crystal grains is then subjected to heat and pressure, and then grows into a large single crystal. In this case, the growth driving force can be expressed as the distortion or intergranular energy in crystal grains. However, this chapter focuses on the growth of crystals that are surrounded by vapor or other fluid growth media: we do not deal with solid-phase growth.

Although a growth unit can be an atom, molecule, or a larger cluster, we will routinely use an atom as the unit of growth in this book.

### 2.1.2 Rate-determining process

The next question to address is the actual growth mechanism, or how crystals grow when put under certain driving forces. In general, crystals grow in three different processes as shown below:

1. Atoms and molecules are introduced into the crystal phase through an interface between the crystals and the growth medium. This is called the interface, or surface, kinetic process.
2. Atoms and molecules in the growth medium are supplied to the growth interface, or crystal surface. This stage is called the volume diffusion process.
3. Latent heat generated at the growth interface during crystallization is removed.

The growth rate is determined by the rate at which the crystals pass through each of these processes. The process that has the largest impact on the overall rate of growth is clearly the process in which the rate of growth is the slowest. This particular process is therefore known as the *rate-determining process*. Exactly which of the processes becomes the rate-determining process depends on the growth environment and the growth conditions. To accurately identify the rate-determining process, the points described below must be considered.

If the environment is a melt, the number density of atoms in the melt and the analogous density of atoms in the crystal are considered to be approximately the same (known as a *dense environment phase*). Therefore, process (2) is not the rate-determining process. Also, because the growth interfaces of almost all substances grown in a melt are not flat if viewed on an atomic scale, the orientation time during which the atoms are contained in the crystals is not a factor that affects the rate. Thus, process (1) can be ignored and process (3) is the rate-determining process.

If the growth medium is vapor or solution, many of the crystals in it will grow as polyhedrons. Although this will be described later in greater detail, in this case the growth interface is flat on an atomic scale. Therefore, the rate-determining step is the interface kinetic process (1) because the orientation time for this particular process is sufficiently long compared with both the atom-supply process (2) and the heat removal process (3). Process (2) can be ignored if a crystal grows in vapor because the concentration in the growth medium is sufficiently low, and thus volume diffusion can take place easily. If the crystals grow in a solution, the concentration of solute atoms in the growth medium is lower than that in the crystals, but the density of the solution itself is almost equal to that of the crystal. Therefore, the volume diffusion coefficient is estimated to be smaller by two orders of magnitude than that of the mixed gas phase, so it is not necessarily appropriate in this case to ignore process (2). This point will be discussed in greater detail in the section that describes growth in a solution.

Because the density of solute atoms in a vapor or solution phase is sufficiently low compared to that in crystals, vapor and solution phases are called *thin growth media*. However, the density of atoms in the environment surrounding the crystals is significantly different from that of the atoms in the crystals, so one phase can be clearly distinguished from the other at a boundary (surface). In this chapter, we

will restrict our discussion to the mechanism of crystal growth seen in relation to a thin growth medium.

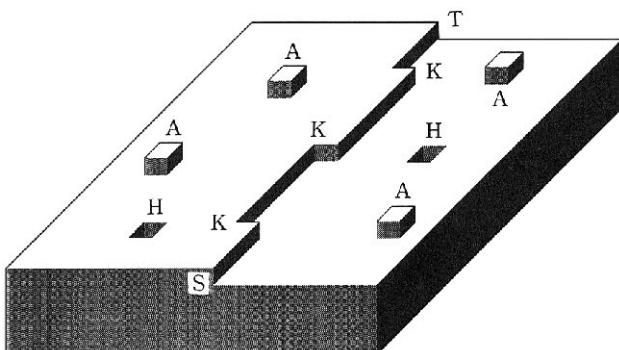
## 2.2 Vapor Growth

Atoms that leave the vapor phase and enter the surfaces of crystals give up almost all of their energy to the crystals in the form of kinetic energy. Therefore, they are captured on the surface as adatoms. There are also some atoms that jump back into the vapor phase. This raises the question of how we can identify the atoms that have been included within the crystal phase from those that have not. It is presumed that a sufficiently large number of atoms, which is defined as  $N$ , coalesce to form a bulky crystal. The decrease in  $\Delta E$  per atom in potential energy resulting from interatomic binding can be calculated using the following formula:

$$\frac{\Delta E}{N} = \frac{1}{2} \sum n_i \phi_i = \phi_{1/2} \quad (2.6)$$

Here,  $\phi_i$  is the binding energy of the nearest neighbor atoms with position labeled by  $i$ .  $n_i$  is the number of nearest neighbor atoms for the atom at position  $i$ . The factor  $1/2$  means that two atoms bound to each other share the energy gain produced by their interatomic bond. Therefore, if there is an energy gain larger than  $\phi_{1/2}$  when the atoms enter the surfaces of the crystals, we can consider that these atoms have been included within the crystals. If we observe the actual surfaces of the crystals, an energy gain of  $\phi_{1/2}$  is seen when an atom enters the bent portion K, a kink site, which has a size of one atom and exists along the step S-T. This has a thickness of one atomic layer on the surface, as shown in Fig. 2.1. Figure 2.1 shows the (001) plane of a simple cubic lattice. This energy gain principle also applies to a plane that has a different orientation or any plane in the other crystal lattices. Table 2.1 shows a list of some values of  $\phi_{1/2}$  for various crystal lattices with particular consideration given to the second nearest neighbor. The kink does not disappear when atoms are added to it; it only slides along a step [3, 4]. This point is important because we cannot observe the same phenomenon at other surface positions. For example, consider the lattice point H (surface vacancy) shown in Fig. 2.1. If atoms enter this point H, they can have an energy gain greater than when they enter at a kink position. The point H (surface vacancy) disappears the instant they enter it. Therefore, their chance to contribute to the growth of the crystal is lost. The kink position is also called the half-crystal position, which means that the binding energy of atoms at the kink position is half that of the internal atoms in the bulk crystal. Supposing that the surface shown in Fig. 2.1 is made by cutting a bulk crystal into two parts, then the surface of one cut crystal has the same number of steps and kinks as that of the other cut crystal surface.

The number of atoms that leave the vapor phase and enter the surface of a crystal per unit time per unit area is  $p/\sqrt{2\pi mk_B T}$ . Here,  $p$  is the vapor pressure,  $m$



**Fig. 2.1.** Surface structure of Kossel model

**Table 2.1.** Binding Energies for Various Crystal Lattices

Lattice	$\phi_{1/2}$
Simple cubic	$3\phi_1 + 6\phi_2$
Face center cubic	$6\phi_1 + 3\phi_2$
Body center cubic	$4\phi_1 + 3\phi_2$
Diamond lattice	$2\phi_1 + 6\phi_2$
Hexagonal	$6\phi_1 + 3\phi_2$

is the mass of an atom,  $k_B$  is Boltzmann's constant, and  $T$  is temperature. The greatest growth rate occurs if all of the incident atoms condense into the crystal. It must be kept in mind, however, that atoms on the surfaces of crystals can jump out into the vapor phase if heat fluctuations cause them to acquire energy larger than the adsorption energy. Therefore, the growth rate can be estimated based on the difference between the number of atoms entering the surfaces of the crystals and that of atoms jumping back out into the vapor phase. Because the growth rate is zero in an equilibrium, or saturated, state, the number of atoms jumping out of the surfaces is equal to that of the atoms entering the surfaces. Therefore, the number of atoms jumping out of the surfaces of the crystals is  $p_e / \sqrt{2\pi m k_B T}$  per unit time per unit area under the equilibrium vapor pressure  $p_e$ .

Because the number of atoms that jump out is not dependent on vapor pressure, the maximum growth rate at any given vapor pressure  $p$  can be calculated using the following formula:

$$R_{\max} = \frac{\Omega(p - p_e)}{\sqrt{2\pi m k_B T}} = C\sigma \quad ; \quad C = \frac{\Omega p_e}{\sqrt{2\pi m k_B T}} \quad (2.7)$$

Here,  $\Omega$  is the atomic volume. This formula is called the Hertz-Knudsen formula. It must be noted that the maximum growth rate calculated with this formula is proportional to the supersaturation,  $\sigma = (p - p_e)/p_e$ , which is the growth driving force in the vapor phase.

The maximum growth rate quoted above is obtained under the condition where all atoms leaving the vapor phase and entering the surfaces of the crystals are then included within the crystalline phase. This total containment can occur if the surfaces of the crystals are uneven and rough, or if all of the lattice points are at kink positions (or at positions where an even greater energy gain can be obtained through crystallization). This growth pattern is called *adhesive growth*. The different types of roughness relating to crystal surfaces can be classified into *geometrical roughness* and the roughness caused by a roughening transition. The geometrical roughness is the type seen on the (111) plane of a simple cubic lattice or other high-index plane. Specifically, a lattice plane exposed after a crystal is cut in half is rough and uneven if viewed from the point of view of geometry. The roughness caused by a roughening transition is the sort of unevenness seen on a plane that initially had a smooth surface at low temperature, but which developed a rough surface after it was exposed to its critical temperature  $T_c$  or higher, and then transformed into a different phase.

Rough, uneven planes grow at the maximum growth rate  $R_{\max}$ , but they disappear as the crystals grow large. As they disappear, the crystals retain only flat, smooth surfaces, and their external form becomes a polyhedron enclosed by such smooth planes. These planes are called *singular surfaces*; the interatomic binding in these planes is strong, and they have a high roughening temperature. They are usually low-index planes, such as those of simple cubic lattices (001). Considering the observations above, a key factor in the growth of crystals in the vapor phase is whether flat, smooth singular surfaces can develop or not. (See Fig. 2.2.)

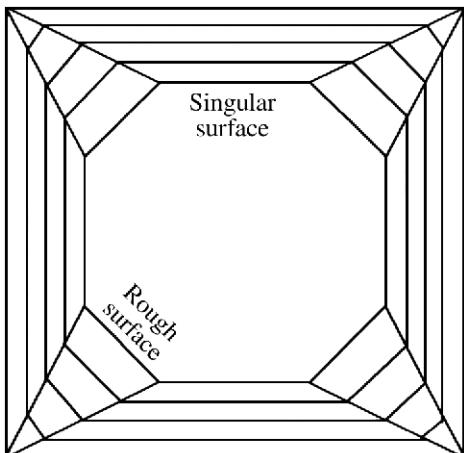
A singular surface does not have kinks where atoms are contained in a crystalline phase. Hence, for a singular surface to grow, steps that contain kinks must appear. The two-dimensional nucleus formation and screw dislocation methods are both used as a means of providing a singular surface with steps. These will be described in more detail later in this book.

Once a step is provided on a singular surface, atoms enter the kinks and crystallization begins. Atoms that enter a flat plane (terrace) are first adsorbed onto the surface of the plane as explained earlier. These adatoms reside on the surface until they acquire the required adsorption energy  $E_a$ , which is created through heat fluctuations. The average residence time  $\tau_s$  can be expressed using  $E_a$  as follows:

$$\tau_s = v^{-1} \exp(E_a / k_B T) \quad (2.8)$$

Here,  $v$  is a frequency term of the adatoms. During the residence time  $\tau_s$ , the adatoms do not stay fixed in the same position; they diffuse over the surface. If these adatoms on the terrace diffuse sufficiently and reach a kink before they desorb into the vapor phase, they can then be acquired by the crystal phase. Assuming that the activation energy for the adatoms diffusing on the surface is  $E_{sd}$ , which is the energy needed to move adatoms to an adjacent lattice point, the surface diffusion coefficient  $D_s$  can be defined as follows:

$$D_s = a^2 v \exp(-E_{sd} / k_B T) \quad (2.9)$$



**Fig. 2.2.** Disappearance of rough surface

Here,  $a$  is the lattice constant. The average distance  $\lambda_s$  that the adatoms diffuse during the residence time  $\tau_s$  can be calculated using Einstein's expression  $D_s \tau_s = \lambda_s^2$  as follows:

$$\lambda_s = a \exp[(E_a - E_{sd}) / 2k_B T] \quad (2.10)$$

$E_{sd}$  is smaller than  $E_a$  and has a typical magnitude such that  $\lambda_s \sim 10^2 a$  if the crystals are growing in the vapor phase. This means that atoms entering a position at a distance of  $\lambda_s$  or less from a kink can contribute to the growth, indicating that surface diffusion plays an important role in growth in the vapor phase.

As described above, atoms entering a terrace near to a step provided on a singular surface can diffuse across the surface, reach a kink and become included in the crystal. This growth mechanism is called the Kossel mechanism [3].

Once the adatoms attach at a kink, the kink moves forward a step. As this movement of the kink takes place repeatedly, the step moves forward across the surface and this is the way that the crystal growth process proceeds. This growth pattern is called *lateral growth* and differs from the adhesive growth mentioned previously. To determine the growth rate of this growth mechanism, it is necessary to identify the forward speed of a step, also called the step velocity.

## 2.2.1 Step velocity

### Velocity of advance of a single step

A straight step that does not contain a kink has an advantage in terms of energy; however, this is a disadvantage in terms of entropy. Therefore, a step will contain a certain number of kinks at finite temperatures. We find that the average distance

between neighboring kinks is far smaller than the average surface diffusion distance  $\lambda_s$  of the adatoms. Thus, if the kink density is sufficiently high, a step functions as a sort of hole through which adatoms can be drawn in an unbroken flow.

To determine the step velocity, the quantity of atoms drawn onto the growth front must be calculated. Interactions between the vapor phase and the surface should first be examined. Based on the difference between the number of atoms entering kink sites after leaving the vapor and the number of atoms leaving the surface, the net flow  $j_v$  per unit time per unit area crossing from the vapor phase to the surface can be expressed as follows (Fig. 2.3):

$$j_v = \frac{p}{\sqrt{2\pi m k_B T}} = \frac{n_s}{\tau_s} \quad (2.11)$$

Here,  $n_s$  is the density of adatoms adsorbed onto the surface. On the other hand, the surface diffusion flow of adatoms per unit time per unit area  $j_s$  can be calculated based on the two-dimensional gradient of density  $n_s$  as follows:

$$j_s = -D_s \text{grad } n_s \quad (2.12)$$

Using the above equation, the following continuity equation can be calculated regarding the density of atoms adsorbed onto the surface:

$$\frac{\partial n_s}{\partial t} = -\text{div } j_s + j_v \quad (2.13)$$

Here, divergence is two-dimensional. Because the step velocity calculated in this way is much slower than the surface diffusion speed of adatoms, the movement of a step can be ignored.

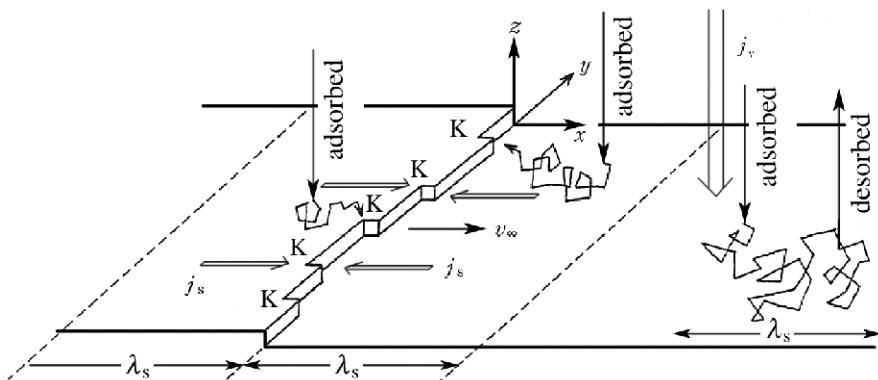
If we can obtain a solution for the steady state ( $\partial n_s / \partial t = 0$ ) of this continuity equation, the density distribution  $n_s$  of the adatoms can be determined. Because a step is effectively a hole through which atoms are drawn in one unbroken flow,  $n_s$  is uniform in the direction parallel to the step and is dependent only on its distance  $x$  from the step.

In an equilibrium state, there is no surface diffusion flow and the number of atoms arriving and the number of atoms leaving are balanced; thus  $j_v = 0$ . Therefore, from Eq. (2.11), the equilibrium density of adatoms  $n_{se}$  is

$$n_{se} = \frac{p_e}{\sqrt{2\pi m k_B T}} \tau_s \quad (2.14)$$

At a point far from the step ( $x = \infty \gg \lambda_s$ ), the quantity of atoms entering and the number that are leaving is also balanced, even in a state of supersaturation, which results in  $j_v = 0$ . If we define the level of supersaturation of the adatoms as  $\sigma_s(x) = (n_s(x) - n_{se})/n_{se}$ , then  $\sigma_s(\infty)$  is equal to the level of supersaturation of the vapor phase  $\sigma = (p - p_e)/p_e$ . On the other hand, the density of adatoms  $n_s(0)$  at the step position ( $x = 0$ ) can be considered to be equal to the equilibrium density  $n_{se}$ . This is because there are no energy barriers when the atoms are contained in the kink position, and the atoms in the crystal can interact fully with the adatoms.

In summary, assuming that the density of adatoms is  $\phi(x) = \sigma - \sigma_s(x)$ , we should calculate the following equation using the boundary conditions in (2.16) below.



**Fig. 2.3.** Motion of a step and adatoms

$$\lambda_s^2 d^2 \phi / dx^2 = \phi \quad (2.15)$$

The boundary conditions are:

$$\begin{aligned} \phi(0) &= \sigma \\ \phi(\infty) &= 0 \end{aligned} \quad (2.16)$$

The solution that we derive is  $\phi(x) = \sigma \exp(-x / \lambda_s)$ . Therefore, the density of adatoms can be calculated as follows:

$$n_s(x) = n_{se} + (n_s - n_{se})[1 - \exp(-x / \lambda_s)] \quad (2.17)$$

Here,  $n_s$  is the density of adatoms that matches the vapor pressure  $p$ . The step velocity  $v_\infty$  can be obtained from the gradient at that step position as follows:

$$v_\infty = \frac{2D_s}{n_0} \left| \frac{dn_s}{dx} \right|_{x=0} = \frac{2\lambda_s}{n_0} \frac{p_e}{\sqrt{2\pi n k_B T}} \sigma \quad (2.18)$$

Here,  $n_0 (= 1/a^2)$  is the density of lattice points on the surfaces of the crystals. The factor of 2 appears here because we assume there are flows running from both sides of a step. We should also note here that the step velocity  $v_\infty$  is proportional to both supersaturation  $\sigma$ , which is the driving force for growth, and is proportional to  $2\lambda_s$ . The step velocity can then be obtained from the simple assumption that all atoms entering at a point which is a distance of  $\lambda_s$  or less away from a step (i.e., an area  $2\lambda_s$  wide) diffuse over the surface, reach a step and are included in the crystal, but atoms entering at a point farther away than  $\lambda_s$  cannot reach a step and hence do not contribute to the growth. The step velocity obtained based on this simple assumption is consistent with the results described above. Therefore, we can refer to areas of  $\lambda_s$  in width on both sides of a step as the capture areas.

### **Velocity of advance of parallel steps at regular intervals**

We can observe that many steps caused by screw-dislocations (to be explained later in this book) are formed nearly parallel to each other at regular intervals on the actual surfaces of the crystals. By applying the above assumption, we can estimate that the forward speed of these steps is slower than that of a single step because the capture areas of each step will overlap if the interval  $\lambda$  between neighboring steps is smaller than  $2\lambda_s$ . Assuming that  $n_s(x)$  equals the equilibrium density  $n_{se}$  at  $x = 0, \lambda$ , we can obtain  $n_s$  using the following equation:

$$n_s(x) = n_s + (n_{se} - n_s) \frac{\cosh[(x - \lambda/2)/\lambda_s]}{\cosh[\lambda/2/\lambda_s]} \quad (2.19)$$

Therefore, the step velocity can be expressed based on the above equation as follows:

$$v(\lambda) = v_\infty \tanh\left(\frac{\lambda}{2\lambda_s}\right) \quad (2.20)$$

If  $\lambda \gg 2\lambda_s$ , the step velocity  $v(\lambda)$  of parallel steps at regular intervals  $\lambda$  are equal to that of a single step  $v_\infty$ . On the contrary, if  $\lambda \ll 2\lambda_s$ , we obtain  $v(\lambda) = v_\infty \lambda / 2\lambda_s$  and we can assume that the capture area of each step has become equal to the interval  $\lambda$  between steps.

Parallel steps at regular intervals can move forward by a specified step interval  $\lambda$  during a set time period  $\tau$ , which can be calculated using  $\tau = \lambda/v(\lambda)$ . Because the surface of the crystal grows by one layer during this time period, the growth rate  $R$  can be calculated as follows, providing that the thickness of one layer is  $d$ :

$$R(\lambda) = \frac{d}{\tau} = \frac{(p - p_e)\Omega}{\sqrt{2\pi m k_B T}} \frac{2\lambda_s}{\lambda} \tanh\left(\frac{\lambda}{2\lambda_s}\right) \quad (2.21)$$

Here,  $\Omega = d/n_0$  is the atomic volume. This growth rate  $R(\lambda)$  increases in proportion as the step interval  $\lambda$  decreases. At the point where  $\lambda \ll 2\lambda_s$ ,  $R(\lambda)$  becomes equal to the maximum growth rate  $R_{max}$ , which can be calculated using the Hertz-Knudsen formula (2.7). If the capture area spreads all over the surface, the growth rate becomes a maximum, even if the surface is not uneven or does not have many kinks.

### **Velocity of a curved step**

So far we have assumed that a step is straight (the width is partly uneven since a step contains many kinks). An actual step, however, is curved. In the case of a step on the surface of a crystal, a loss in the step energy per unit length  $\gamma$  can occur because a chain of atomic binding is terminated on the edges of a step.

If a step curves or bends, the step energy per unit length becomes large compared to that of a straight step. As a result, the equilibrium vapor pressure  $p_e(\rho)$  for a step with a curvature of radius  $\rho$  becomes larger than the equilibrium vapor pressure  $p_e$  of a straight step. Providing that the level of supersaturation is  $\sigma_e(\rho) = (p_e(\rho) - p_e)/p_e$  [5]:

$$\sigma_e(\rho) = \exp\left(\frac{\gamma}{\rho n_0 k_B T}\right) - 1 \quad (2.22)$$

The equilibrium density of adatoms at the step position is consistent with the result obtained using the above equation. To obtain the forward speed  $v(\rho)$  of a step with a curvature of radius  $\rho$ , Eq. (2.15) is converted to a polar form to calculate the density distribution of adatoms under the above boundary condition, and the result is substituted into Eq. (2.18):

$$v(\rho) = \frac{\lambda_s [1 - \sigma(\rho)/\sigma]}{2\rho I_0(\rho/\lambda_s) K_0(\rho/\lambda_s)} \quad (2.23)$$

Here,  $I_0$  and  $K_0$  are class-1 and class-2 deformation Bessel functions, respectively. In the range where the conditions  $\rho \ll \lambda_s$  and  $\sigma \gg 1$  can be satisfied,  $v(\rho)$  can be approximated as follows:

$$v(\rho) = v_\infty \left(1 - \frac{\rho_c}{\rho}\right) \quad (2.24)$$

Here,  $\rho_c$  is the radius of curvature of a step that neither advances nor retracts when exposed to a supersaturation of level  $\sigma$ .  $\rho_c$  is called the critical radius of curvature.

$$\rho_c = \frac{\gamma}{n_0 k_B T \log(1 + \sigma)} \quad (2.25)$$

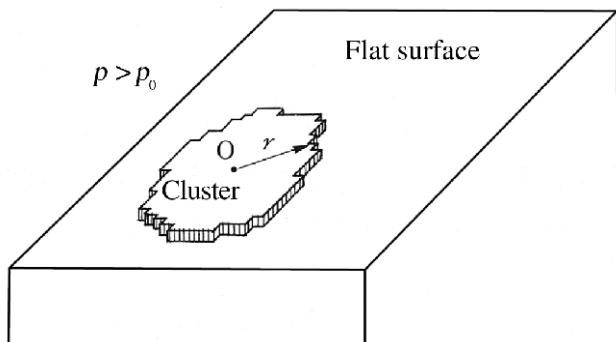
If the density of kinks on a step is low and the step cannot then be regarded as a hole through which atoms are drawn in one continuous flow, or if a resistance exists when adatoms are contained in kinks, thereby making it difficult to consider the density of adatoms to be an equilibrium value, it then becomes necessary to make some modifications to this derivation [5].

As described previously, the formation of a two-dimensional nucleus or of a screw dislocation are two mechanisms that can provide the surface of a crystal with a step. In the following section, we explain how a crystal grows after it has acquired a step.

## 2.2.2 Mechanism of two-dimensional nucleation growth

### *Frequency of two-dimensional nucleus formation*

As explained in the section that describes how the step velocity can be calculated, atoms that enter the surface and those that leave the surface are in equilibrium; adatoms exist in a certain density and they are moving about on the surface. Therefore, they can collide and attach to each other. As these collisions and attachments take place repeatedly, many adatoms congregate and form a two-dimensional cluster. A small cluster might lose atoms and disappear, but if a cluster is exposed to fluctuations and increases in size, the probability that it will survive becomes higher. If the probability that a certain nucleus could increase in size



**Fig. 2.4.** Cluster on the flat surface (two-dimensional nucleus)

is equal to the probability that it could decrease, then such a nucleus is called a critical nucleus. To understand the size of such a cluster more clearly, we will attempt to estimate its size by assuming that the shape of a two-dimensional cluster is circular (Fig. 2.4).

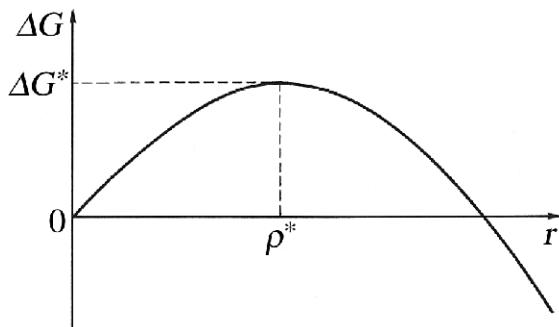
We must keep a watch on the whole system, including the crystal and the growth medium. When a cluster forms on a flat crystal face, all of the atoms can be considered to be in crystalline form except those along the fringe of the cluster. The free energy decreases by the difference between the chemical potential of the growth medium and that of the crystal phase,  $-\Delta\mu$  per atom. Atoms along the fringe of a cluster are exposed to external turbulence, and they behave in such a manner that they disturb the process of cluster formation. The loss in the step energy per unit length needed to form this edge is defined as  $\gamma$ , and the radius of the cluster is defined as  $r$ . The number of atoms that comprise a cluster is approximately  $\pi r^2 n_0$ , and the circumference is  $2\pi r$ . Therefore, the increase of  $\Delta G(r)$  in free energy in the whole system can be expressed as follows:

$$\Delta G(r) = -\pi r^2 n_0 \Delta\mu + 2\pi r\gamma \quad (2.26)$$

Here, the Boltzmann factor  $\exp[-\Delta G(r)/k_B T]$  is proportional to the probability of survival of a cluster with a radius of  $r$ . When a cluster has a radius of  $\rho^*$  or larger, which will serve to maximize  $\Delta G(r)$ , the probability of its survival increases. A cluster having a radius of  $\rho^*$  or smaller will decrease in size. This radius  $\rho^*$  is known as the two-dimensional radius of a critical nucleus. The two-dimensional radius of a critical nucleus  $\rho^*$ , and the maximum value  $\Delta G^*$  of the free energy can be expressed based on maximum value conditions as follows (Fig. 2.5):

$$\rho^* = \frac{\gamma}{n_0 \Delta\mu} = \frac{\gamma}{n_0 k_B T \log(1+\sigma)} \quad (2.27)$$

$$\Delta G^* = \frac{\pi\gamma^2}{n_0 k_B T \log(1+\sigma)} \quad (2.28)$$



**Fig. 2.5.** Change of the free energy with cleaving the disk cluster

Although the system is in a nonequilibrium state, nucleus formation seldom occurs. Assuming that the process proceeds according to the theory of equilibrium distribution, the density  $N^*$  of a critical nucleus can be calculated as follows, where the density of a single atom is defined as  $n_s$ :

$$N^* = n_s \exp(-\Delta G^*/k_B T) \quad (2.29)$$

Assuming that a nucleus becomes stable when one extra atom is added to it, as assumed by Volmer and Weber [6], one adatom moves to an adjacent lattice point with a frequency of  $D_s/a^2$ . Taking this into consideration, the frequency  $v^+$  can be calculated using the following equation:

$$v^+ = 2\pi\rho^* D_s / an_0 \quad (2.30)$$

Therefore  $J$ , the frequency of nucleus formation, can be calculated as follows:

$$J = v^+ N^* = 2\pi\rho^* (D_s/a) n_0^2 \exp(-\Delta G^*/k_B T) \quad (2.31)$$

This approach assumes that the process proceeds according to the theory of equilibrium distribution. Becker, Doring [7] and Zeldovich [8] demonstrated that the density of a critical nucleus in a stable state is lower than that in a state of equilibrium distribution. The value presented by them is smaller by  $Z$  (the Zeldovich factor, shown below) than  $J$  in the above equation. The Zeldovich factor  $Z$  can be calculated as follows:

$$Z = \{\Delta G(i^*) / 4\pi k_B T \cdot i^*\}^{1/2}$$

Here,  $i^*$  is the number of atoms that comprise a critical nucleus. Therefore,

$$J(\sigma) = D_s n_s^2 \{\log(1+\sigma)\}^{1/2} \exp\left[-\pi\left(\frac{\gamma}{k_B T}\right)^2 / \log(1+\sigma)\right] \quad (2.32)$$

As is apparent from Eq. (2.32), the frequency of two-dimensional nucleus formation  $J$  is extremely low if the level of supersaturation is low, but it quickly increases as the level of supersaturation rises. The formation of two-dimensional nu-

clei and the frequency of nucleus formation is observable if the level of supersaturation is over 10% [5].

### **Two-dimensional nucleus formation and growth rate**

As a two-dimensional nucleus that forms with a frequency  $J$  spreads with a step velocity  $v$ , layers are formed and a plane is completed. Therefore,  $J$  and  $v$  are factors that determine the growth pattern of crystals [1].

Providing that the area of the surface of a crystal is  $S$ , the waiting time  $t_w$  during which a two-dimensional nucleus forms on the surface is  $t_w = 1/JS$ . On the other hand, the approximate time  $t_s$  during which the fringe of an already formed two-dimensional nucleus spreads with a step velocity  $v$  and covers the whole surface of a crystal can be estimated as  $t_s = \sqrt{S}/v$ . Growth patterns of two-dimensional nuclei can be classified into two different mechanisms as follows, depending on the relationship between  $t_w$  and  $t_s$ .

If  $t_w \gg t_s$ :

Because a nucleus that has been formed after a long waiting time quickly spreads over the whole surface, one two-dimensional nucleus alone contributes to the growth of one layer. This growth pattern is known as single nucleation growth. The growth rate  $R_{sn}$  [6] is:

$$R_{sn} = dJS \quad (2.33)$$

In this growth mechanism, it should be noted that the growth rate is proportional to the area of the surface of the crystal  $S$ .

If  $t_w \ll t_s$ , many two-dimensional nuclei form one after another, all over the surface. They spread and couple with each other and develop layers. This growth pattern is known as multinucleation growth. Two-dimensional nuclei can also form on existing nuclei that are already spreading; this particular growth pattern is called *multinucleation multilayer growth*.

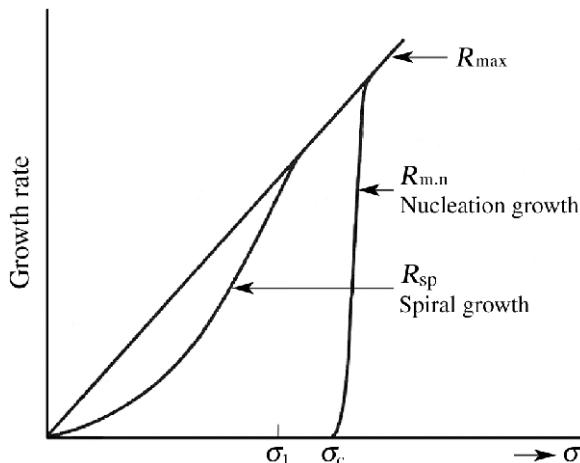
If the average distance that a nucleus travels before it couples with an adjacent nucleus during the multinuclear growth process is  $A$ , the time  $\tau$  that it takes for this nucleus to travel this average distance is  $\tau = \sqrt{A}/v$ . On the other hand, two-dimensional nuclei form in an area  $A$  with the waiting time defined as  $\tau$ , and thus steady, consistent growth can be achieved. Therefore,  $\tau = 1/JA$  becomes true. From this equation, we can obtain the following:

$$\tau = \left( \frac{1}{Jv^2} \right)^{1/3}$$

Because the formation of one layer takes place in time  $\tau$ , the growth rate  $R_{mn}$  can be expressed as follows:

$$R_{mn} = d/\tau = dJ^{1/3} v^{2/3} \quad (2.34)$$

We should note that the growth rate is not dependent on the area  $S$ . Area  $A$  is called the territory of influence per stable nucleus.



**Fig. 2.6.** Supersaturation dependence of the growth rate

In the case of multinuclear multilayer growth, the waiting time  $\tau'$  from when the first nucleus forms to when the next nucleus forms on top of the first one can be estimated using the following equation:

$$\int_0^{\tau'} \pi J(vt)^{1/2} dt = 1 \quad (2.35)$$

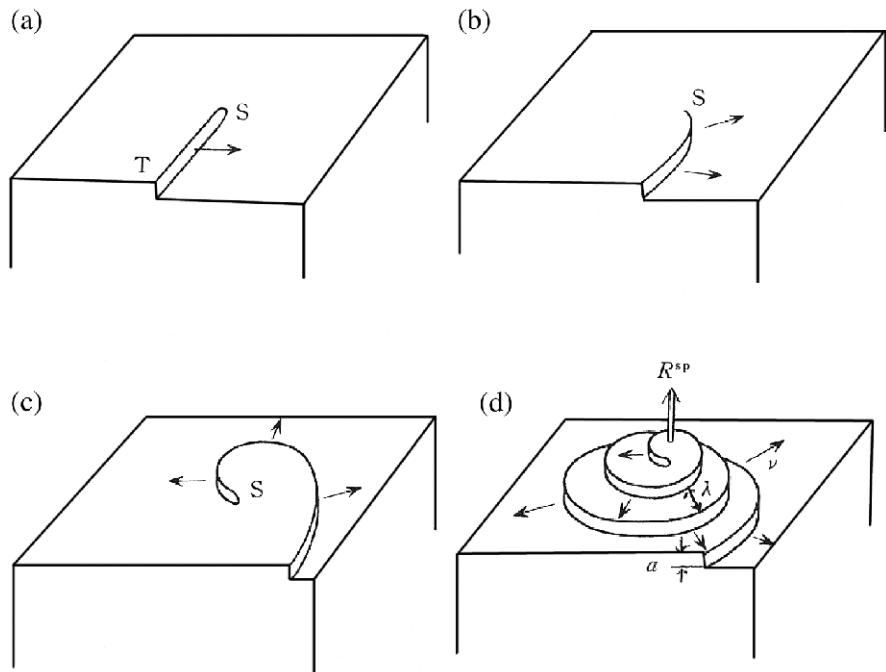
The rate obtained using this equation is the same as that obtained for multinuclear growth [9].

The level of supersaturation is low under the particular condition  $t_w \gg t_s$ , under which single nucleus growth occurs. The growth rate is so slow that it is not observable. Therefore, any two-dimensional growth that is observable is either multinuclear growth or multinuclear multilayer growth. Fig. 2.6 shows how the level of supersaturation affects the growth rate. When the level of supersaturation is low, the rate is almost zero. As it increases, the rate quickly increases. If the level of supersaturation is high, an overestimated value will be obtained. (See section 2.3.1 d.)

### 2.2.3 Mechanism of spiral growth

In the majority of cases however, the growth of two-dimensional nuclei is observable at a low level of supersaturation, even if we hardly expected the growth to happen. This is because many crystals grow according to a spiral growth mechanism, which is closely associated with the screw dislocation.

Real crystals are not perfect crystals, and they contain defects in varying degrees. If the end of screw dislocation, which is a line defect, is exposed on the surface of a crystal, a step extending from this exposed end to the edge of the crystal



**Fig. 2.7.** Spiral growth by screw dislocation

surface is formed, as shown in Fig. 2.7. Although this step continues to move forward, it never disappears. Therefore, steps do not need to be supplied to allow two-dimensional nucleus formation. Growth will continue at a low level of supersaturation without any additional supply of steps. This growth mechanism is called the Frank mechanism, after F. C. Frank who first developed this theory [10].

As the step created by the screw dislocation continues to move forward, it reaches out from the point where it intersects with the surface and soon forms a spiral pattern. This is because the point where it emerges is fixed. Because the forward speed at which a curved step travels in the direction normal to the line can be calculated using Eq. (2.24), the shape of a step can be determined. On a curved coordinate system ( $r, \theta$ ) with the center of the spiral as the origin, an approximate stationary solution can be calculated as follows [5]:

$$\log\left(1 + \frac{r}{\sqrt{3}\rho_c}\right) = 2\left(1 + \frac{1}{\sqrt{3}}\right)\left[\theta + \frac{vt}{2\rho_c\left(1 + \frac{1}{\sqrt{3}}\right)}\right] \quad (2.36)$$

According to this equation, the movement of the step can be represented as being very close to an Archimedean spiral under the condition where  $r \propto \theta$ . Far from the

center of this spiral, the steps are aligned nearly parallel to each other with step interval  $\lambda$ :

$$\lambda = 4\pi(1 + 1/\sqrt{3})\rho_c \approx 20\rho_c \quad (2.37)$$

(The value  $20\rho_c$  was later corrected to  $19\rho_c$  by Cabrera and others [14].) The step interval  $\lambda$  is proportional to the critical radius of curvature,  $\rho_c$ . This is because the spiral movement continues until the radius of curvature  $\rho_c$  of a step in the center becomes  $\rho_c$ . If the step interval  $\lambda$  in a parallel step line is determined, the growth rate can be obtained, as previously explained, and the growth rate  $R_{sp}$  of a step moving according to the spiral growth mechanism can be calculated as follows:

$$R_{sp} = \frac{(p - p_e)\Omega\sigma^2}{\sqrt{2\pi n k_B T}} \tanh\left(\frac{\sigma_1}{\sigma}\right) \quad (2.38)$$

Here, the level of supersaturation  $\sigma_1$  is introduced as a parameter, which can be defined as follows:

$$\sigma_1 = \frac{\lambda}{2\lambda_s} \sigma \cong \frac{10\gamma}{n_0 k_B T \lambda_s} \quad (2.39)$$

If we examine the dependence of growth rates on the level of supersaturation with reference to the results obtained using Eq. (2.38), we note that  $R_{sp}$  is proportional to  $\sigma^2$  if the level of supersaturation is low ( $\sigma \ll \sigma_1$ ), and  $R_{sp}$  is proportional to  $\sigma$  and equal to  $R_{max}$  if the level of supersaturation is high ( $\sigma \gg \sigma_1$ ), as shown in Fig. 2.6. If the level of supersaturation is high, we should note the following point: If the level of supersaturation becomes high, the step interval becomes smaller and many adatoms in the center of the spiral are assimilated into the surrounding steps.

This causes the actual level of supersaturation to decrease below  $\sigma$ , the radius of curvature of a step in the center becomes large, and the step interval  $\lambda$  increases. Therefore, the growth rate drops below the estimated value. Any steps generated by a step itself cause the density to decrease, and eventually the growth rate to increase, which is called the back-force or back-stress effect. This phenomenon was pointed out by Cabrera and others [11], and was analyzed by Van der Erden and others [12] in greater detail.

To obtain a reliable, approximate value, the center radius  $\rho_c$  of a spiral should not be estimated from the level of supersaturation  $\sigma$  in the vapor phase. Instead, we should estimate it from the level of surface supersaturation  $\sigma(\rho_c, 0)$  in the center, assuming that there is a circular step with a radius  $\rho_c$ . We will not discuss this in detail here.

So far we have only dealt with the type of step that is created from one screw dislocation, and which has a height equal to that of a single atom. However, mention must be made of the fact that in the actual crystal formation process, complex steps can be created through a combination of screw dislocations of the same or of different types, and a step which is several atoms in height can be created through screw dislocations with a Burgers vector of one or greater. The points discussed here have already been analyzed in great detail by Burton, Cabrera, and Frank. The theory developed by them is called the BCF theory.

## 2.3 Growth of a Crystal in a Solution

In this section we discuss the mechanism of the growth of a crystal in solution. Although the density of a solution phase is higher than that of a vapor phase, the density of each growth unit (dissolved atom) in a solution phase is low. Therefore, the theory that each individual growth unit is *contained in a crystal phase* still holds true [1]. For a crystal to grow in a solution, the principle that soluble atoms can be easily dissolved into a solvate (solvation) must be used. Therefore, desolvation must take place when dissolved atoms are included into a crystal. This applies to the growth of a crystal in the vapor phase in which a strong interaction with the vapor occurs, as is the case in the chemical vapor deposition (CVD) process. In the case of growth in the vapor phase, the process where atoms are supplied from the growth medium could be ignored. In the case of growth in a solution, the diffusion coefficient of the atoms dissolved in the solution is far smaller than that in the vapor phase. Therefore, the density of atoms varies greatly in solution, so the process by which the dissolved atoms are supplied from the growth medium cannot be ignored, and the process of diffusion of dissolved atoms in a solution must be examined.

### 2.3.1 Solvation effects and growth rates

#### *Diffusion in a solution [2]*

Although the diffusion of dissolved atoms in a solution is taken into consideration, it is almost impossible to apply the BCF theory strictly from the analytical viewpoint. Therefore, two different approaches were taken. First, we conceived the volume diffusion model, which assumes a condition where the surface diffusion is totally ignored and the dissolved atoms are taken out of solution and placed directly onto kink positions. The second model is the surface diffusion model, which assumes that the condition for the BCF theory is applied to the neighborhood of an interface, through simplification of the volume diffusion. There is also the coupled bulk-surface diffusion model of Gilmer, Ghez, and Cabrera [13].

The first approach is based on the assumption that the volume diffusion coefficient  $D$ , is larger than the surface diffusion coefficient  $D_s$  in the case of growth in a solution, whereas the second approach maintains that desolvation should not take place with all atoms simultaneously. Instead, the atoms should first be adsorbed onto the surface of a crystal to allow them to diffuse over the surface, and then they should migrate into kink positions, which is effectively step-by-step desolvation. When designing an experiment to observe the growth of a crystal in a solution, the solution is often stirred and therefore the level of supersaturation  $\sigma$  (namely, density  $C$ ) in an area remote from the surface of the crystal by a distance of  $\delta$  or more, is defined as a constant value that is controlled for the duration of the experiment.

In an attempt to develop a volume diffusion model, Chernov [15] inferred a diffusion field through analysis using the conformal transformation method, on the

assumption that linear steps are formed at a regular interval  $\lambda$  on the surface of the crystal. The boundary condition was defined as follows:

The volume diffusion flow  $D(\partial C / \partial r)_{r=a}$  that arrives into a radius  $r = a$  (approximately equal to the lattice constant) with a step as its origin is equal to the atomic flow  $\beta_{st}[C(a) - C_e]$  entering a crystal phase from any point where there is a step. Namely,

$$D\left(\frac{\partial C}{\partial r}\right)_{r=a} = \beta_{st}[C(a) - C_e] \quad (2.40)$$

Here,  $C_e$  is the equilibrium density and  $\beta_{st}$  is the rate constant. These are termed the kinetic coefficients of a step. Fig. 2.8 shows the diffusion field qualitatively: the dotted line is the isosbestic line. Using Eq. (2.40), the rate of step movement  $v$  can be calculated. Also, using Eq. (2.37), the step interval  $\lambda$  can be calculated. Therefore, the following equation can be established, based on the spiral growth rate  $R_{v,d}^{sp} = av/\lambda$ , which was obtained using the volume diffusion model:

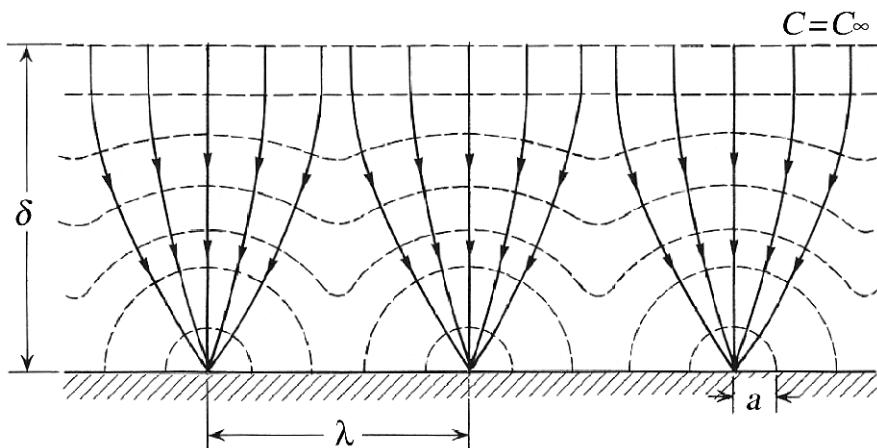
$$R_{v,d}^{sp} = \beta_{st} \frac{a^2 k_B T C_e}{4\gamma} \frac{\sigma_\delta^2}{1 + (\beta_{st} a / D) \log \left[ \frac{\delta\sigma_0}{a} \sigma_\delta \sinh \left( \frac{\sigma_\delta}{\sigma_0} \right) \right]} \quad (2.41)$$

Here,  $\gamma$  is the step energy,  $a$  is the lattice constant, and  $\sigma_\delta$  is the level of supersaturation in the solution. Because there are only a few cases in which this approach can be applied, it is recommended that you refer to the original work for greater detail. Here we should only mention that the square law  $R_{v,d}^{sp} \propto \sigma^2$  applies if  $\sigma \ll \sigma_0$  and the linearity law  $R_{v,d}^{sp} \propto \sigma$  applies if  $\sigma \gg \sigma_0$ , which is characteristic of spiral growth.

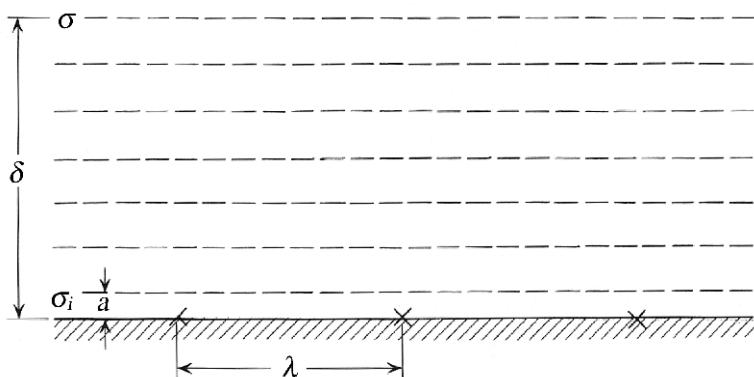
On the other hand, we also have the surface diffusion model, as created by Bennema and others [16,17]. As shown in Fig. 2.9, this model assumes that the isosbestic point in a solution is parallel to an interface, and that the diffusion field is one-dimensional. The reasoning behind this assumption can be explained as follows: For the dissolved atoms to diffuse in a solution towards kink positions and then become included in the crystalline phase, layers of solvates on atoms must be removed. The activation energy  $\Delta G_k^{vd}$  needed for desolvation is far larger than the  $\Delta G_d$  needed for volume diffusion (see Fig. 2.10). Therefore, it is inconceivable to think of a flow running from a solution directly to a step from the standpoint of kinetics. On the other hand, if the dissolved atoms first adsorb onto the surface of the crystal, diffuse over the surface, and then enter kinks, the activation energy needed for desolvation can be divided into the energy for adsorbing onto the surface  $\Delta G_{desolv}$  and the energy for leaving the surface and entering the kinks  $\Delta G_k^{ad}$ .

Therefore, the atoms can move more smoothly by traveling this route rather than taking the route of entering kinks directly. The relaxation time  $\tau_{desolv} = v^{-1} \exp(\Delta G_{desolv}/kT)$  needed for atoms to adsorb onto the surface is sufficiently longer than  $\tau_d = v^{-1} \exp(\Delta G_{desolv}/kT)$ , which is needed for atoms to diffuse in a solution. Therefore, the dissolved atoms become stagnant on the surface of the crystal, and

the solute density becomes uniform along its surface; that is the isosbestic surface is parallel to the surface of the crystal.



**Fig. 2.8.** Distribution of concentration for the volume diffusion model. The dotted line is the isosbestic line.



**Fig. 2.9.** Distribution of supersaturation for the surface diffusion model by Bennema. There are steps at the cross point.

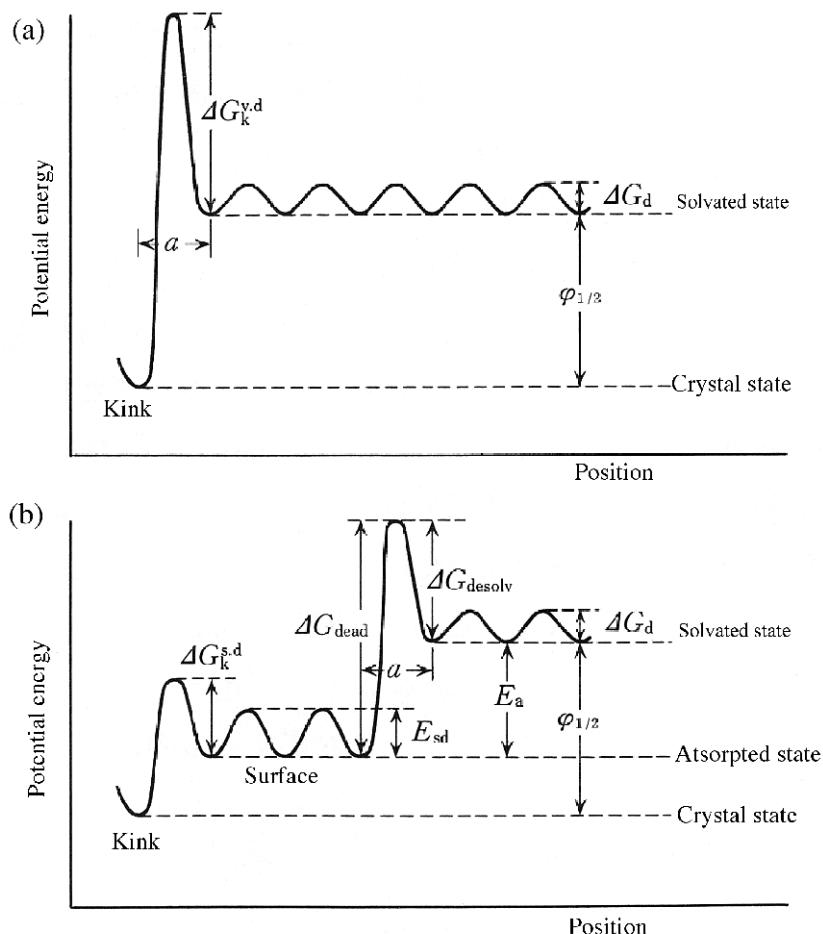


Fig. 2.10. Potential energy of desolvation

### Modifying the BCF theory

The level of supersaturation at a point  $\delta$  away from an interface is defined as  $\sigma$ , and a point which is one lattice constant  $a$  away from an interface is defined by  $\sigma_i$ . The excitation energy needed to allow atoms to enter kinks is  $\Delta G_k^{s,d}$ . Therefore, it can be assumed that a kink position, which can be considered as identical to a step because a step has many kinks, has a supersaturation  $\sigma_k$ . If we use the same approach as that used for growth in the vapor phase, the net flow  $J_v$  from the solution to the surface of the crystal can be calculated as follows. Assuming that the solute density directly above the surface is  $C_i$  and the equilibrium density of the surface is  $C_e$ :

$$J_v = a(C - C_e)v \exp(-\Delta G_{desolv}/k_B T) = aC_e v \exp(-\Delta G_{desolv}/k_B T)(\sigma_i - \sigma_k) \quad (2.42)$$

Therefore, a counterpart equation to Eq. (2.21) for the growth in a vapor phase is

$$R_{BCF} = \frac{a}{\tau_{desolv}} C_e \Omega \left[ \frac{2\lambda_s}{\lambda} \tanh\left(\frac{\lambda}{2\lambda_s}\right) \right] (\sigma_i - \sigma_k) \quad (2.43)$$

However, the surface diffusion distance  $\lambda_s$  is not controlled by the adsorption energy  $E_a$ , but depends on the excitation energy  $\Delta G_{dead}$  needed for desolvation. According to the result obtained from  $\Delta G_{dead} \gg E_a$ , the value of  $\lambda_s$  is nearly as long as the length that we found in the case of growth in the vapor phase.

The growth rate  $R_{diff}$  that is determined from the volume diffusion in a solution can be calculated using the volume diffusion coefficient  $D$ , as follows:

$$R_{diff} = DC_e \Omega \frac{\sigma - \sigma_i}{\delta} \quad (2.44)$$

Lastly, the rate  $R_{kink}$ , which is determined by the speed that atoms enter the kink positions, can be calculated using the flow of atoms into kinks per unit length of step  $J_s$  as follows:

$$R_{kink} = 2\Omega / \lambda J_s = \frac{2an_e \Omega}{\lambda \tau_k} \sigma_k \quad (2.45)$$

Here,  $n_e$  is the equilibrium density at the kink position, and  $\tau_k$  is the relaxation time that atoms require before they enter kinks.

$$\tau_k = V^{-1} \exp(\Delta G_k^{s.d.}/k_B T)$$

Because these three growth rates must be equal in a steady state, we have the following equation:

$$R_{diff}(\sigma - \sigma_i) = R_{BCF}(\sigma_i - \sigma_k) = R_{kink}(\sigma_k) \quad (2.46)$$

The growth rate  $R$  can be calculated using the following equation, which takes the results from  $\sigma = (\sigma - \sigma_i) + (\sigma_i - \sigma_k) + \sigma_k$  into account:

$$R = \frac{C_e \Omega a}{\tau_{desolv}} \sigma \left[ \frac{\delta a}{\tau_{desolv} D} + \frac{\lambda}{2\lambda_s} \coth\left(\frac{\lambda}{2\lambda_s}\right) + \frac{\tau_k}{\tau_{dead}} \frac{\lambda}{2a} \right]^{-1} \quad (2.47)$$

The first term is the resistance resulting from the volume diffusion, the second term is the resistance resulting from the surface diffusion mechanism, and the third term is the kink resistance. Although the second term is always greater than unity, the first and second terms are considered to be  $\ll 1$  in a system in which the solvation effects are significant. Therefore, the assumptions of  $\sigma - \sigma_i \approx \sigma$ ,  $\sigma_k = 0$  are valid, and we can approximate as follows:

$$R \approx \frac{C_e \Omega a}{\tau_{desolv}} \sigma \frac{2\lambda_s}{\lambda} \tanh\left(\frac{\lambda}{2\lambda_s}\right) \quad (2.48)$$

Because the step interval  $\lambda$  in spiral growth is  $20\rho_c$ , which was calculated for growth in the vapor phase, the growth rate can be calculated as follows:

$$\begin{aligned}
 R_s &= C \frac{\sigma^2}{\sigma_1} \tanh\left(\frac{\sigma_1}{\sigma}\right) \\
 \sigma_1 &= 10 \frac{\gamma}{k_B T} \frac{a}{\lambda_s} \\
 C &= C_e \Omega a / \tau_{desolv}
 \end{aligned} \tag{2.49}$$

In the region where the level of supersaturation is low, that is, where  $\sigma \ll \sigma_1$ , the growth rate is proportional to the supersaturation squared. In the region where the level of supersaturation is high, that is, where  $\sigma \gg \sigma_1$ , growth rate is proportional to the supersaturation. If an interface has many steps and the surface is rough, the growth rate can be calculated using the following equation, which is called the *Wilson-Frenkel Formula*:

$$R_{\max} = av \exp(-\Delta G_{desolv}/k_B T) C_e \Omega \sigma \tag{2.50}$$

### **Two-dimensional nucleation growth**

As far as the basic concept of the growth mechanism from a two-dimensional nucleation is concerned, growth in a solution is the same as growth in the vapor phase. However, for growth in a solution, the following equation is used, which contains the solution density  $C$  and the equilibrium density  $C_e$  to obtain the driving force  $\Delta\mu$ :

$$\Delta\mu = k_B T \log(1 + \sigma), \sigma = (C - C_e)/C_e \tag{2.51}$$

Including desolvation effects, the frequency  $v^+$  at which one adatom is included into a critical nucleus can be expressed as follows:

$$v^+ = 2\pi\rho^* \frac{D_s}{a} \exp(-\Delta G_{k_b}^{s,d}/k_B T) \tag{2.52}$$

The growth speed of multinuclear multilayer growth  $(\pi/3)^{1/3} v^{2/3} J^{1/3}$  can be calculated using the above equation in combination with the following:

$$R_n = A \sigma^{5/6} \exp[-\Delta G^*/3k_B T] \tag{2.53}$$

$$A = \left( \frac{2\pi c_0}{3} \right)^{1/3} \frac{2\lambda_s}{a} C$$

Here it is assumed that  $\sigma \ll 1$ , so  $\log(1 + \sigma) \sim \sigma$ , and  $c_0$  results from the desolvation effects [17].

The energy needed to form a critical nucleus  $\Delta G^*$  governs the frequency of two-dimensional nucleus formation, and it is greatly influenced by a reduction in step energy of a two-dimensional nucleus  $\gamma$ . Because atoms in a step can interact with the solutes when growing in a solution, it is expected that the step energy  $\gamma$  is smaller by one order of magnitude than that for growth in the vapor phase. Solvation effects work to inhibit growth if a crystal undergoes the spiral growth process,

whereas they work to promote growth if a crystal undergoes two-dimensional nucleus growth.

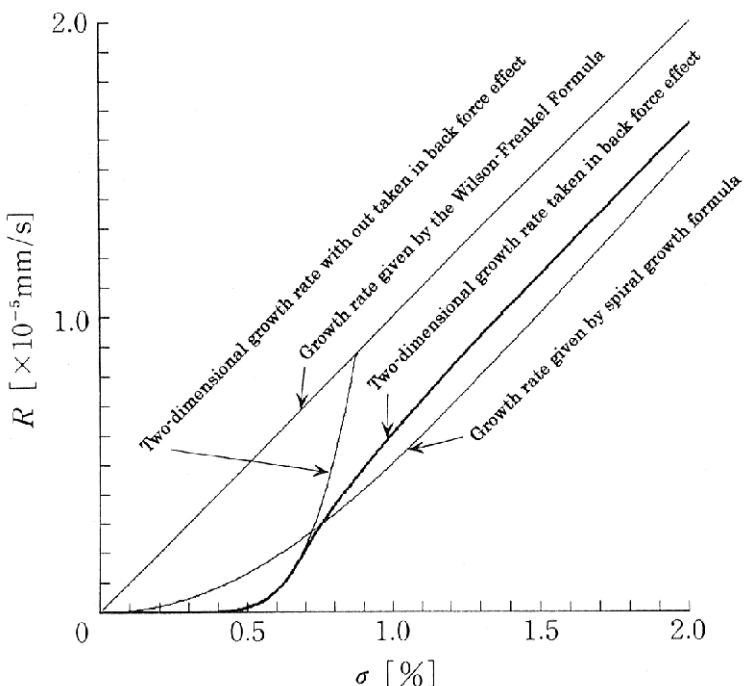
Figure 2.11 illustrates the spiral growth formula (2.49) based on the step energy  $\gamma/(n_0 k_B T) = 0.2$ ,  $\lambda_s = 100a$ , the rate constant  $C = 10^{-3}$  mm/sec,  $c_0 = 10^{-2}$ , and the two-dimensional nucleus growth formula (2.53). The two-dimensional nucleus growth formula does not include the effects of the slowdown of migration speeds that result from a decrease in the level of supersaturation on a terrace when the interval  $\lambda$  between steps becomes smaller than  $\lambda_s$ . Neither does it include the decreased frequency of two-dimensional nucleus formation (back-force effects), which results from a decrease in the level of supersaturation on a two-dimensional nucleus when a two-dimensional nucleus is growing. Therefore, the result given by this formula may exceed the maximum growth rate given by the Wilson-Frenkel formula. However, at a level of supersaturation of 0.7% or lower, it is estimated that the growth rate can be measured correctly. Unlike growth in the vapor phase, realistic growth rates can be obtained at such low supersaturations.

### **Back-force effects**

If the level of supersaturation becomes high and nucleus formation occurs frequently, the intervals between the creation of steps becomes small. If multinuclear multilayer growth is taking place, the crystal should be growing while straight steps are forming at an interval  $\lambda$  if this is taking place at a location remote from where the nucleus forms. For a crystal to grow in a steady state, the growth rate  $R(\lambda)$ , which is determined by  $\lambda$ , must be equal to the rate of nucleus formation,  $R_n$ . In Eq. (2.53),  $R_n$  is the migration speed of steps at the fringe of the nucleus  $v_\infty$ . The migration rate  $v_\infty$  should be slower than the migration rate  $v(\lambda)$  of steps being formed at an interval  $\lambda$ . Therefore, a minor modification must be made by replacing  $v_\infty$  with  $v(\lambda)$ . If this modification is made, the growth rate of two-dimensional nucleus formation does not exceed the maximum growth rate given by the Wilson-Frenkel formula. However, calculations must be done using specific numerical values. Besides this, the presence of steps was ignored in our estimation of the frequency of nucleus formation; therefore, the supersaturation is overestimated. In the case of steps near a nucleus, their speed of movement is slower than  $v(\lambda)$  and the step interval is less than  $\lambda$  because the curvature cannot be ignored, that is after a nucleus forms, the next nucleus will form on a cluster that has a radius smaller than  $\lambda$ . Assuming that the cluster is circular and that its radius is  $\rho$ , the level of supersaturation  $\sigma_s(0)$  in the center of the cluster can be expressed using the level of supersaturation of an interface  $\sigma_i$  as follows:

$$\sigma_s(0, \rho) = \sigma_i - (\sigma - \sigma_{eq}(\rho)) / I_0(\rho/\lambda_s) \quad (2.54)$$

Here,  $\sigma_{eq}(\rho)$  is the equilibrium level of supersaturation of a circular step that has a radius of curvature of  $\rho$  and  $I_0$  is a class-1 Bessel function.



**Fig. 2.11.** Growth rate for a solution growth

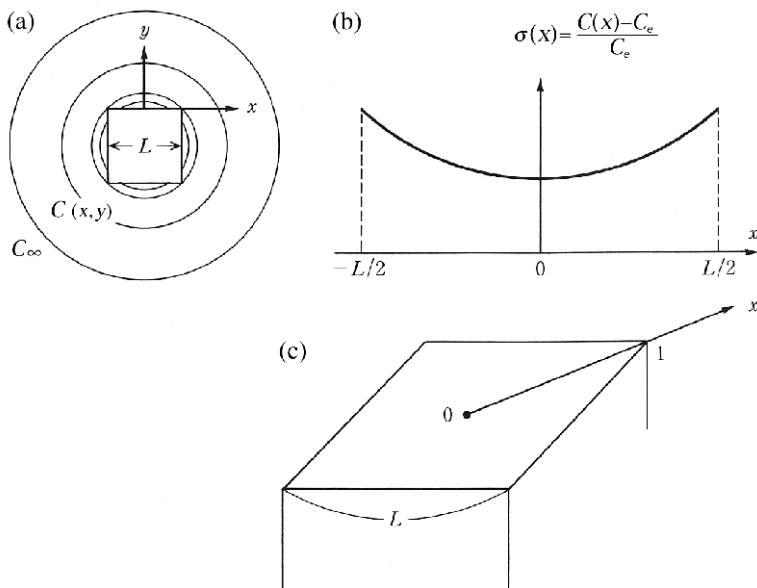
Therefore, to estimate the frequency of nucleus formation, the level of supersaturation  $\sigma(0,\lambda)$  at the center of a disk with a radius of curvature of at least  $\lambda$  must be used. In Fig. 2.11, the thick line shows the growth rates obtained by making these modifications and performing numerical calculations. This indicates that the result obtained using the back-force effects deviates from that obtained using the formula (2.53) if the supersaturation is low. Also, these growth rates exceed the rates of spiral growth. This is because the introduction of the back-force effect was insufficient. For further details, refer to Reference 18.

### 2.3.2 Handling of polyhedral finite crystals [2,19]

When a crystal is still small and growing slowly at a moderate supersaturation in solution or in the vapor phase, its form is a clear-cut polyhedron. If the level of supersaturation is increased as the crystal grows in size, we can observe an osseous crystal or a dendriform crystal, which looks like a snow crystal. Using the conventional approach, where the surface of the crystal is infinitely large, we cannot explain this phenomenon. We should note that there is a limit to the size of a polyhedral crystal, and we will discuss here the stability of such a crystal. Although growth in a solution is taken as an example, the observations presented here can also be applied to growth from a gas mixture in the vapor phase.

### Berg effects

It is well known that a crystal extracted from a lean or rarefied growth medium will be a polyhedral crystal. This means that the crystal is undergoing epitaxial growth, with the growth rate determined at the interfaces. Berg [20] examined a crystal undergoing epitaxial growth to verify the density, or supersaturation, distribution in a solution using the light interference technique. He found that the density distribution is not uniform at the interface of a crystal, and that the density is high at the edges and smallest in the center, as shown in Fig. 2.12. This is called the Berg effect. If the migration speed of each point at an interface is proportional to the local supersaturation, then the edges grow more than the other regions, and therefore a polyhedron cannot be maintained.



**Fig. 2.12.** Solute density distribution in a solution

### Stable growth

Here we assume that a crystal is a cube with side of length  $L$ . Because the growth rate is very slow, the distribution,  $C$ , of solute density in a solution is considered to be in a quasistationary state (stationary distribution), that is:

$$\Delta C = 0 \quad (2.55)$$

Boundary conditions include the density  $C_\infty$  specified at a sufficiently remote point (the solution is not stirred), as well as the uniform density gradient ( $\partial C / \partial n$ ) in the

direction of a normal line on the surface, which can be calculated with the following equation:

$$\left( \frac{\partial C}{\partial n} \right)_{\text{surface}} = q \quad (2.56)$$

Eq. (2.56) means that the growth rate to be determined by the volume diffusion flow must be uniform at any point on the surface when a polyhedral crystal grows. The growth rate can be expressed as follows:

$$R_D(x) = \Omega D q \quad (2.57)$$

Here,  $\Omega$  is the volume of a dissolved atom and  $D$  is the volume diffusion coefficient. If space is two-dimensional, this equation can be solved holomorphically using the conformal transformation method [21]. If space is three-dimensional, it must be solved numerically. If the solutions of the equation  $f(x, y, z)$  are obtained in advance under each condition of  $L = 1$ ,  $q = 1$ ,  $C_\infty = 0$ , then solutions for  $L$ ,  $q$ , and  $C_\infty$  can be calculated based on the linearity of the Laplace formula by using the following equation:

$$C(x, y, z) = C_\infty + q L f(x/L, y/L, z/L) \quad (2.58)$$

Here, although  $f$  is negative, the  $f$ -coefficient is equal to a value obtained by multiplying the growth speed  $q$  by the crystal size  $L$ . The greater the magnitude of  $qL$ , the larger the difference between the density in the center and that at the edges.

Focusing on the surface kinetics, the growth rate at each point of an interface is

$$R(x) = a v(x) / \lambda(x) = p(x) \cdot v(x) \quad (2.59)$$

Here,  $v$  is the migration rate of a step,  $\lambda$  is the interval between steps,  $a$  is the lattice constant, and  $p(x) = a/\lambda(x)$  is the tilt of an interface from the low-index plane. Hereafter, the center of the plane is defined as  $x = 0$  and an edge is defined as  $x = 1$ .  $v(x)$ ,  $\lambda(x)$ , and  $p(x)$  are not uniform on an interface. According to Eq. (2.59), a polyhedron cannot be maintained unless these parameters are uniform across each face. If fluctuations in the migration rate  $v(x)$  of a step can be compensated by the local tilt  $p(x)$  of an interface, it becomes possible to maintain a polyhedron [22]. Because  $v(x)$  actually becomes higher at the edges and slower in the center due to the nonuniformity in the supersaturation (Fig. 2.13), an interface should be tilted more toward the center of the plane.

A step-source that produces a step must then be determined. To create a step source, two mechanisms are conceivable: the formation of a two-dimensional nucleus and the activation of a screw dislocation. If a step source is created by a screw dislocation, the crystal seed is exposed around the center of an interface in the majority of cases. In this case, the growth rate near the step source is governed by the level of supersaturation  $\sigma(0)$  in the center of the plane, and Eq. (2.49) is used with  $\sigma$  replaced by  $\sigma(0)$ . If the formation of a two-dimensional nucleus is the step source, the growth rate is governed by the level of supersaturation at the edges  $\sigma(1)$ , where the level of supersaturation is highest. To obtain the growth rate at the edges, Eq. (2.53) is used, with  $\sigma$  replaced by  $\sigma(1)$ .

$R_s$  and  $R_n$  are generally not equal. Therefore, a plane must be covered by steps that are generated by higher-value step sources. That is,

$$R_k = \max \{R_s, R_n\} \quad (2.60)$$

In this equation,  $R_k$  must be equal to the growth rate  $R_D$ , which is determined by the diffusion flow. It is evident that  $R_D(\sigma_\infty, L, q)$  is a function of the supersaturation at a remote point  $\sigma_\infty$ , the size of the crystal  $L$ , and the density gradient  $q$ . Additionally,  $R_k(\sigma_\infty, L, q)$  is a function of  $\sigma_\infty$ ,  $L$ , and  $q$  in terms of the supersaturation

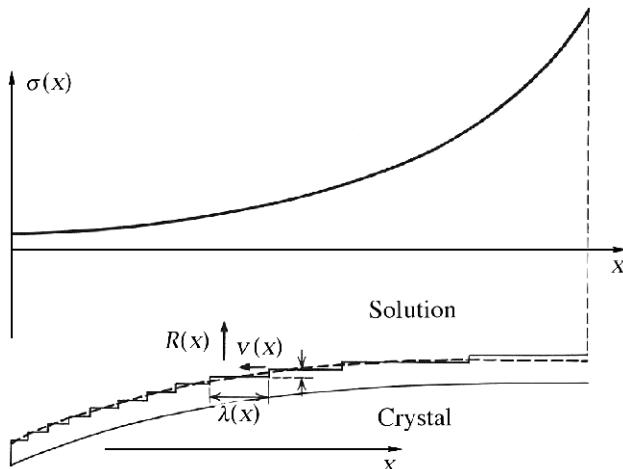


Fig. 2.13. Distribution of supersaturation and a surface morphology

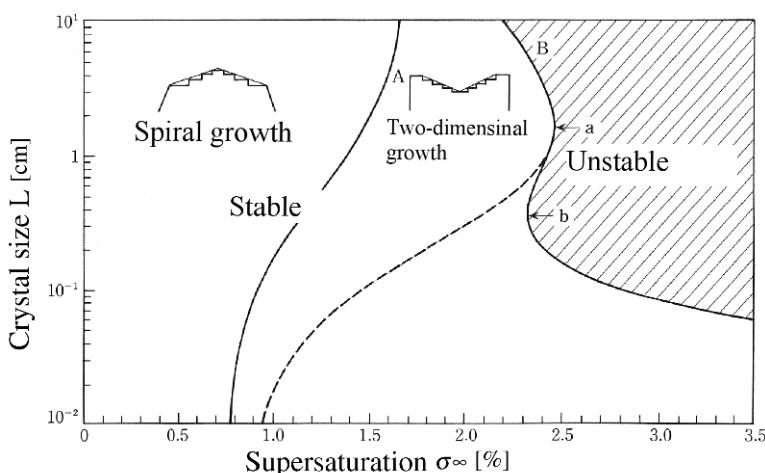


Fig. 2.14. Critical line for stable growth condition

at the interface. Therefore, if the values of  $\sigma_\infty$  and  $L$  are known, the growth rate  $q$  can be determined. At the same time, the step source can be identified as well as its external form.

Therefore, the criticality condition that determines the step source can be expressed as follows:

$$R_s \{ \sigma(0; \sigma_\infty^*, L^*) \} = R_n \{ \sigma(1; \sigma_\infty^*, L^*) \} \quad (2.61)$$

Figure 2.14 shows the supersaturation at remote points  $\sigma^\infty$  along the abscissa and the crystal size along the ordinate. The base values in the diffusion field are approximately  $f(0) = -0.9$  and  $f(1) = -0.7$ . The curved line A shows the critical levels of supersaturation that may transform step sources in the stable growth region. Because it is difficult for the formation of a two-dimensional nucleus to take place where the supersaturation is low, the screw dislocation governed by the supersaturation  $\sigma(0)$  on the surface center becomes the step source, and the external form of the crystal becomes convex. A screw dislocation can produce a concave surface too (see Fig. 2.9a of Nelson and Knight). On the other hand, if the level of supersaturation at a remote point is increased, the level of supersaturation at the edges becomes high, and the formation of a two-dimensional nucleus governed by  $\sigma(1)$  becomes the step source. In this case, the external form of the crystal surfaces becomes concave.

### ***Occurrence of unstable conditions***

As Eq. (2.58) suggests, the nonuniformity in the supersaturation increases if the size of a crystal becomes large, or if the growth rate  $q$  becomes too high.

$$R(x) = p(x) \cdot v(x) = R_D = \text{constant} \quad (2.62)$$

At the point where the above conditional expression holds true, the crystal is unable to maintain its polyhedral form and consequently cannot grow with uniform flux across the face. This is because, technically, this is *not* a growth instability; it is a uniform-flux impossibility. The cause of this is that the migration rate of a step becomes dependent on not only the supersaturation  $\sigma$ , but also the step interval  $\lambda$ ; thus, the growth rates of local interfaces reach a maximum, even if the tilt of the plane around the center is increased. Therefore, the criticality condition for stable (or “uniform”) growth can be expressed as follows:

$$R_{\max}(0) \equiv C \sigma(0; \sigma_\infty^{**}, L^{**}) = R_n [\sigma(1; \sigma_\infty^{**}, L^{**})] \quad (2.63)$$

The dotted line of the criticality curve B in Fig. 2.14 shows stable growth without including the back-force effects (Eq. 2.53), whereas the thick solid line includes the back-force effects. As is apparent from this figure, we could postulate that the back-force effects are a key factor responsible for allowing a small crystal to grow in a stable way while still maintaining a polyhedral form. At point **a** of the criticality curve, the supersaturation at the edge of the crystal surface is about 0.64% and at point **b** it is around 0.84%. This level of supersaturation at the interface is much lower than the value of 2.3% at a remote point. Although  $\lambda_s$  was de-

fined as being equal to  $100a$  in this calculation, the growth rate becomes slow if the surface diffusion distance becomes short. Therefore, the stable region moves off to the side, where the level of supersaturation is high.

In the course of studying growth in an unstable region, an equation was introduced for verifying how the external form of a crystal develops over time. This is a new topic that has many applications to the formation of crystal forms [24–26].

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# 3 Epitaxial Growth of III-V Compounds

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## 3.1 Introduction

The first event that showed the importance of III-V epitaxy was the success of Al-ferov in 1969 in fabricating a cw laser diode that operated at room temperature by liquid phase epitaxy (LPE). For this, he received the Nobel Prize in physics in 2000 with two other scientists. LPE, which was proposed by Nelson [1], makes high quality, thin-film semiconductors. In III-V LPE, the compounds are grown from group-III metal solution on a substrate, which gives highly stoichiometric, thin, pure, and perfect films.

The next important event in the history of III-V epitaxy is the invention of a high electron mobility transistor (HEMT) by Mimura et al. [2], which was made by molecular beam epitaxy (MBE). They used the idea of modulation doping, which was originally proposed by Dingle et al. [3].

The growth technology of high quality and ultra-thin III-V films of about 10 nm thickness was required for the fabrication of HEMT. At that time, such films could be grown only by MBE. Almost at the same time, the technology of metal organic chemical vapor deposition (MOCVD) was developed and employed for growing high quality thin films. Without MBE and MOCVD, neither HEMT nor high performance laser diodes such as quantum well (QW) and multi-quantum well (MQW) lasers could be made.

Recent success in growing high quality GaN and related compounds was made by Amano et al. [4] by using a low temperature buffer layer on sapphire in MOCVD. The huge improvement in crystal quality thus realized made it possible to get p-type GaN. The success of p-GaN was a real breakthrough for making blue-ultraviolet lasers and light emitting diodes.

In this chapter, we focus on MBE and MOCVD as examples of epitaxy because they are the major technologies in III-V epitaxy.

## 3.2 MBE of III-V Compounds

In molecular beam epitaxy (MBE), the growth is conducted under an ultra-high vacuum of up to  $10^{-8} \sim 10^{-9}$  Pa. Under such a high vacuum, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> contamination on the growing surface can be negligible. This makes it possible to reduce the growth rate down to nm/sec, so that precise control of the growth thickness is possible.

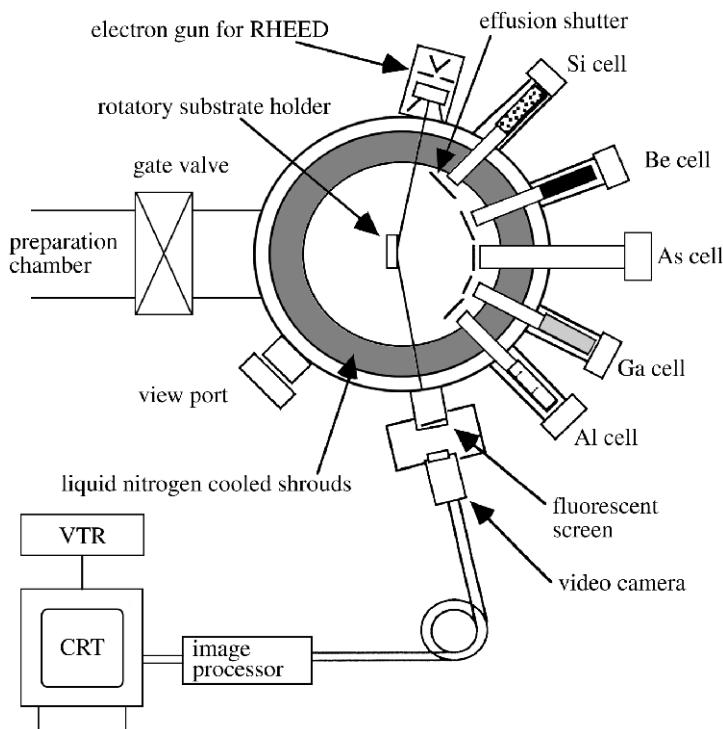
As described in the next section, MBE uses a Knudsen cell (or effusion cell) from which growth elements are evaporated. By opening and closing the shutter in front of the Knudsen cell, the operator can abruptly switch on or off the fluxes; hence, sharp interfaces between successively grown layers are possible.

Another important advantage of MBE is that *in situ* monitoring of the growing surface is possible. Reflection high-energy electron diffraction (RHEED) is one of the most powerful tools used to see the flatness and atomic structure of the surface during growth. Furthermore, intensity oscillation of the RHEED signal accurately measures the growth rate in Å/sec.

### 3.2.1 MBE system

Figure 3.1 shows a schematic of a conventional MBE machine. An ion-sputtering pump evacuates the growth chamber to a high vacuum, typically. To keep the chamber at high vacuum during the growth, a liquid N<sub>2</sub> shroud like that shown in the figure is employed. An electron beam is aimed at the substrate, then the diffracted beam strikes a fluorescent screen. In the case of GaAs MBE, at first the substrate is heated at high temperature under arsenic pressure to remove the oxide layer. Because the oxide evaporation happens at around 580°C and this event can be monitored by RHEED, the oxide removal can be used to calibrate the temperature of the substrate. Then, after setting the substrate temperature at the required value, the Ga shutter is opened to start the growth. To grow (Ga, Al)As, one opens the shutters of both Ga and Al cells. Choosing Ga and Al cell temperatures varies the composition of the alloy. An n-type and p-type GaAs layer can be grown by opening the shutter of the Si cell and Be cell, respectively.

Sample exchange should be carried out keeping the growth chamber at high vacuum. This can be done employing either a two-chamber or a three-chamber system. Figure 3.1 shows a two-chamber system, which is composed of a growth chamber and a preparation chamber. The preparation chamber is also evacuated at high vacuum and the second sample is already installed inside. After the experiment, without breaking the vacuum, the grown sample is transferred through the gate valve to the preparation chamber, and the next sample is transferred to the growth chamber by a transfer rod. Thus, a high vacuum is kept for a long time until a problem occurs in the chamber. In such a case, the chamber should be opened to the air during the repair. When source materials such as Ga, As, Al are finished, the growth chamber should be opened and new sources recharged.



**Fig. 3.1.** Schematic illustration of the conventional two-chamber MBE

### 3.2.2 RHEED intensity oscillation

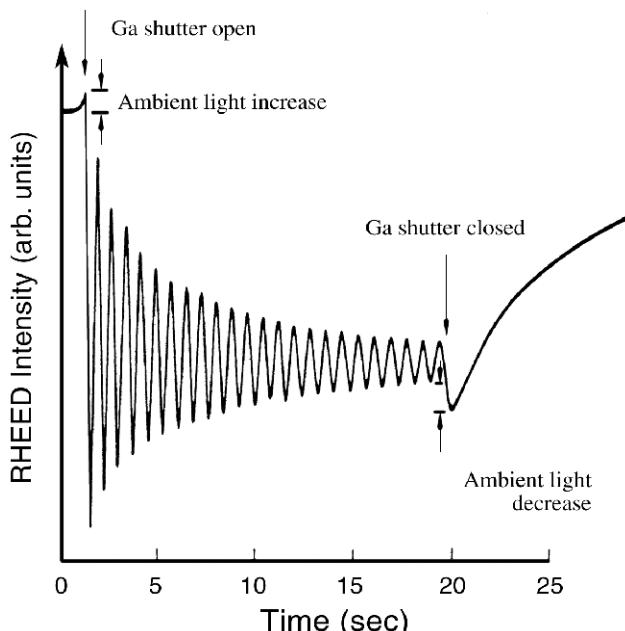
RHEED intensity oscillations (hereafter, RHEED oscillations) provide extremely important information about the growth in real time. Already in 1980, it was reported that an AES (Auger Electron Spectroscopy) signal shows oscillation as the growth thickness of a thin film is increased [5]. Just after this work, Harris et al. reported that the RHEED intensity oscillates as the film thickness is increased in GaAs MBE, and they showed that the period coincides with the time for monolayer growth [6]. One year later, Gronwald and Henzlan observed intensity oscillations of the low energy electron diffraction (LEED) signal during the MBE of Si on a (111) substrate, and confirmed that the period coincides with the growth time of (111) double layers [7].

In 1983, Neave et al. studied RHEED oscillations of GaAs in more detail, and concluded that this oscillation is caused by the birth and spread of 2D-nuclei that happen repeatedly during growth [8].

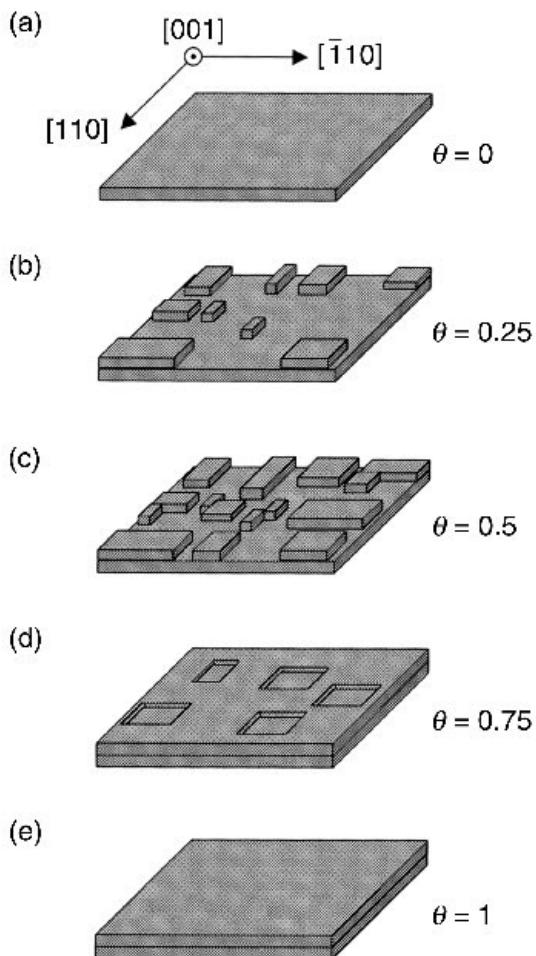
Schematics of this process from Neave et al. are given in Fig. 3.2 and 3.3. As shown in Fig. 3.2, just after the shutter of a Ga cell is opened, the intensity drops sharply while it recovers to a value slightly below the previous peak. Figure 3.3

shows what happens during one period of the oscillation. Here,  $\theta$  is the coverage of the surface. Before growth, the surface of the substrate, in this case (001), is very flat as shown in (a). This can be realized by preparing the surface of the substrate exactly ( $< 0.01^\circ$ ) oriented to (001). Then, the steps supplied from misoriented substrate can be nearly eliminated. As the growth starts, 2D-nuclei are generated on the substrate as shown in (b). The electron beam is partly scattered by the 2D nuclei and lost resulting in the decrease of the RHEED intensity. As growth proceeds, many 2D nuclei are generated (c), and the intensity is further decreased. However, those 2D nuclei start to coalesce to form a continuous layer (d) and as the flatness is recovered the intensity begins to increase. When the coalescence is completed the intensity increases to the initial value. In the experiment, as we see in Fig. 3.2, the recovery of the intensity is not complete. This happens because 2D-nucleation of the second layer starts on the surface like that in Fig. 3.3 (d). Due to this, this growing surface becomes rough as growth proceeds. However, the surface flatness is recovered when the Ga shutter is closed and the growth is stopped as shown in Fig. 3.2.

RHEED oscillations can be used to control the growth thickness on the order of a monolayer and actually is a very powerful tool used to fabricate sophisticated electronic and optical devices with complicated structures. RHEED oscillations are also a very powerful tool for studying the elementary growth process of MBE because it can detect the birth and spread of 2D-nuclei under various growth conditions.



**Fig. 3.2.** RHEED intensity oscillation observed in MBE of GaAs [8]



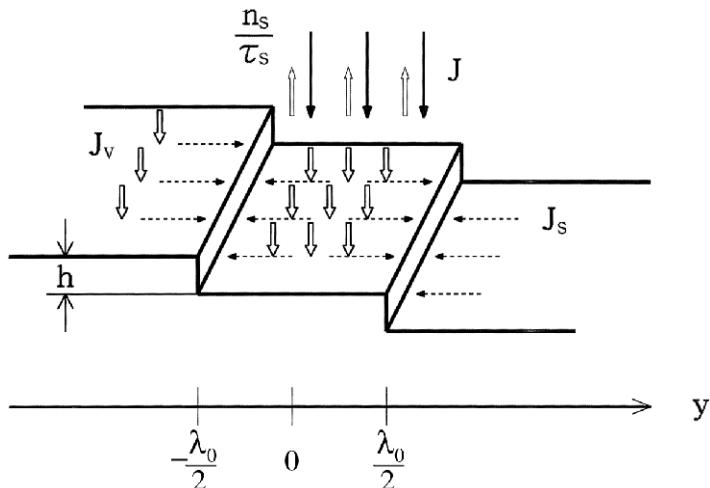
**Fig. 3.3.** Illustrations of the surface during MBE in 2D-nucleation growth mode.  $\theta$  denotes the surface coverage [8].

### 3.2.3 Surface diffusion and stepped surface

According to BCF theory [9], the adatom concentration  $n_s(y)$  on a vicinal (stepped) surface shown in Fig. 3.4 is given by

$$n_s(y) = J\tau_s + (n_{\text{step}} - J\tau_s)\cosh(y/\lambda_o)/\cosh(\lambda_o/2\lambda_s) \quad (3.1)$$

where  $J$ ,  $\tau_s$ ,  $n_{\text{step}}$  and  $\lambda_o$  are respectively the incident flux of growing atoms, the re-evaporation time, the diffusion length for re-evaporation, the adatom concentration near the step edge, and the interstep distance.

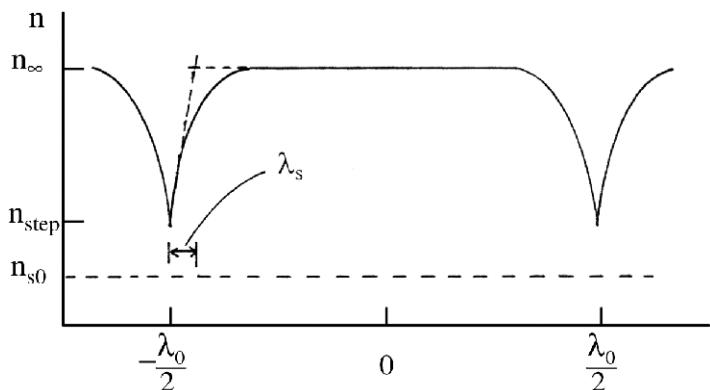


**Fig. 3.4.** Vicinal (stepped) surface

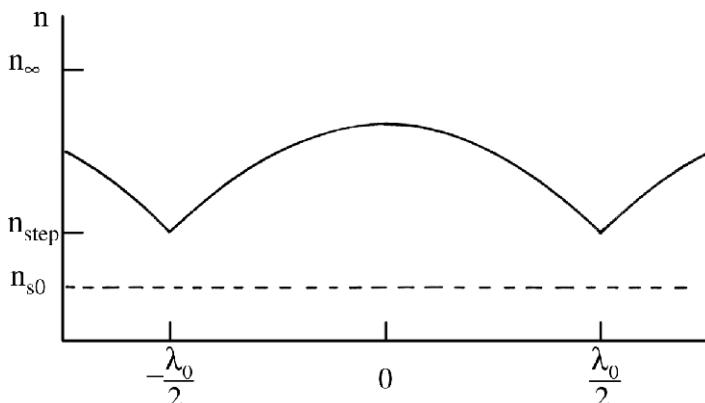
$n_s(y)$  is schematically shown in Figs. 3.5 and 3.6 respectively for  $\lambda_o \gg \lambda_s$  and  $\lambda_o \ll \lambda_s$ . If  $\lambda_o$  is much larger than  $\lambda_s$ ,  $n_s(y)$  increases as a function of distance from a step edge and saturates at a constant value after a certain distance, as shown in Fig. 3.5. On the other hand if  $\lambda_o \ll \lambda_s$ , one can neglect the evaporation of adatoms from the surface and  $n_s(y)$  is given by

$$n_s(y) = n_{\text{step}} + (J \lambda_o^2 / 8D_s) [1 - (2y/\lambda_o)^2] \quad (3.2)$$

In this case,  $n_s(y)$  is parabolic as shown in Fig. 3.6. In III-V MBE, the vapor pressure of a group III element is very low at the growth temperature and  $\lambda_o \ll \lambda_s$  is usually established.



**Fig. 3.5.**  $n_s(y)$  as a function of the position between steps for  $\lambda_o \gg \lambda_s$



**Fig. 3.6.**  $n_s(y)$  for  $\lambda_o \ll \lambda_s$

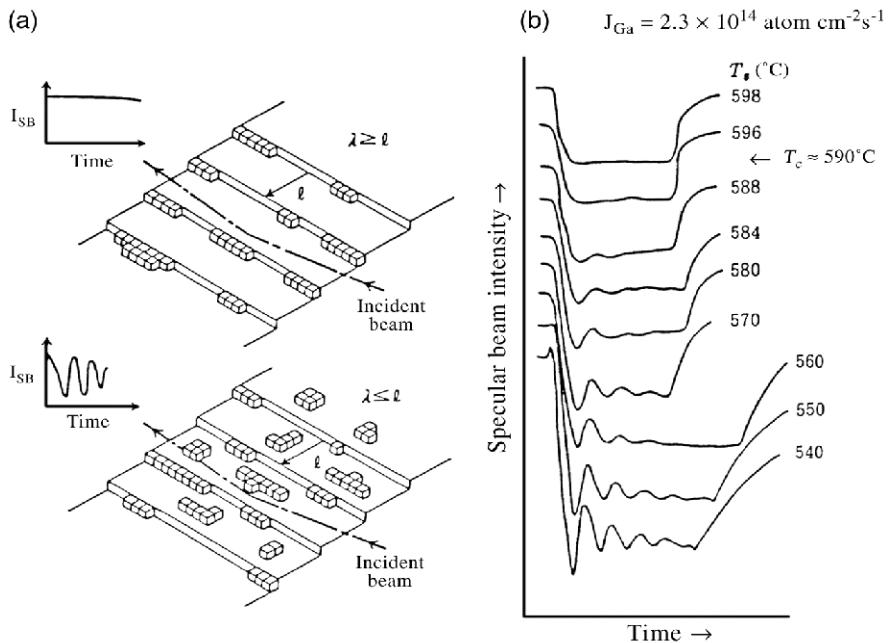
### 3.2.4 2D-nucleation and step flow modes

In 1985, Neave et al. did an important experiment [10]. They used a slightly misoriented (001) GaAs as a substrate and observed the surface by RHEED during MBE growth of GaAs. The result is shown in Fig. 3.7. They found that as the growth temperature increased, RHEED oscillations vanished at a certain temperature. They explained the reason for the vanishing oscillations as follows. When the temperature is low and the adatom migration velocity is slow, it takes time for the adatom to reach the step edge and thus the adatoms can instead cluster to form 2D-nuclei. This causes the RHEED oscillation as shown in the bottom figure of Fig. 3.7 (a). On the other hand, when the growth temperature is high, adatoms can move very fast to easily reach the step edge before contacting other adatoms. In this case, all adatoms go to the step edges without forming the 2D-nuclei as shown in the top figure of Fig. 3.7 (a). Under their growth condition, the critical temperature for the mode transition  $T_c$  is 590°C. Above this temperature, all steps advance in one direction and this mode of the growth is called step flow. On the other hand, below this temperature, 2D-nuclei are generated between steps and as growth proceeds, they coalesce to each other to form a new layer. This growth mode is called the 2D-nucleation growth mode.

From this experiment, Neave et al. calculated the surface diffusion length as a function of temperature as follows. They assumed at the critical temperature for the mode transition the diffusion length becomes equal to the step distance,  $\lambda_o$ . This assumption gives

$$\lambda_o = \sqrt{D_s \tau}, \quad (3.3)$$

where  $\tau$  is some kind of relaxation time and  $D_s$  is the surface diffusion coefficient. For the numerical value of  $\tau$ , they used the monolayer growth time.



**Fig. 3.7.** Change of growth modes between 2D-nucleation and step flow. (a) Illustrations of the surface for the two modes, (b) RHEED oscillations and growth temperature [10]

With Eq. 3.3, they calculated  $D_s$  as a function of growth temperature. However, there is no physical meaning of the diffusion length for monolayer growth. Instead,  $\tau$  should be used as an average nucleation time. Namely, if adatoms can diffuse in a longer distance than  $\lambda_o$ , the adatoms can reach the step edge before generating nuclei and the growth occurs in step flow mode. Hence, the critical condition for the mode transition should be

$$\lambda_o = \sqrt{D_s \tau_{nuc}} \quad (3.4)$$

where  $\tau_{nuc}$  is an average time for one adatom to form a nucleus. If the size of the critical nucleus is two atoms,  $\tau_{nuc}$  becomes identical with a collision time  $\tau_{coll}$ . However, this assumption may not be true for all cases so we have to derive a more reliable equation.

Before doing this, we will estimate  $D_s$ . If we employ the equation given by Neave et al., we get  $D_s \sim 10^{-12} \text{ cm}^2/\text{sec}$  with  $\lambda_o = 10 \text{ nm}$  and  $\tau = 1 \text{ s}$ . On the other hand, a typical value of  $\tau_{nuc}$  is 1 msec, which gives  $D_s \sim 10^{-9} \text{ cm}^2/\text{sec}$ . This value is  $10^3$  larger than Neave's value. Hence, we have to study this problem more carefully.

Figure 3.8 shows the distribution of interface supersaturation between two steps. In this figure, we assumed that a thermal equilibrium is established at the step edges and we defined supersaturation ratio as

$$\alpha = n_s/n_{so}, \quad (3.5)$$

where  $n_{so}$  means the equilibrium surface concentration of adatoms. This ratio is unity at the step edges. However, once 2D-nuclei are generated the supersaturation drops around them so that profile of supersaturation given in Fig. 3.8 no longer exists.

At the critical temperature, the top of the parabola touches the line of critical supersaturation ratio  $\alpha_c$  shown in Fig. 3.8. The critical supersaturation for 2D nucleation is given by [11]

$$\alpha_c = \exp\left\{\Omega\pi h\sigma^2\left[\left(65 - \ln 10^{12}\right)K^2 T^2\right]^{-1}\right\} \quad (3.6)$$

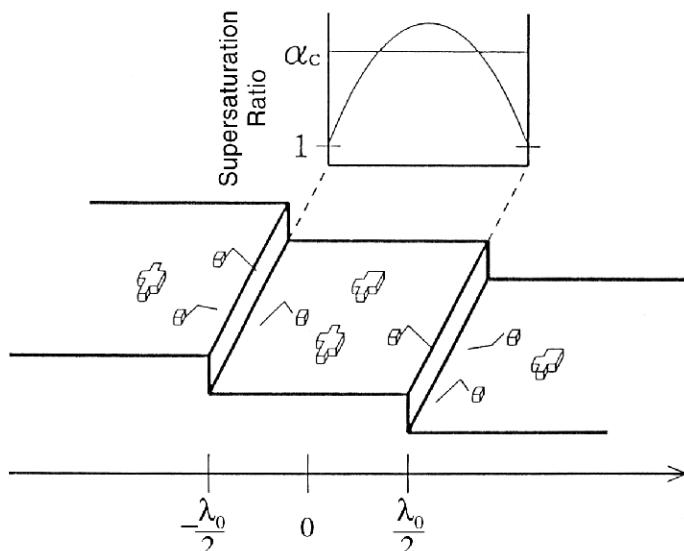
where  $\Omega$ ,  $h$ , and  $\sigma$  are, respectively, the solid atomic volume, the step height, and the free energy of the side surface surrounding a 2D-nucleus. Because the supersaturation is maximum in the center of the step terrace, one can calculate the value with Eq. (3.1) as

$$\alpha_{\max} = 1 + J\lambda_0^2 / 8D_s n_{so} \quad (3.7)$$

At the critical temperature,

$$\alpha_c = \alpha_{\max} \quad (3.8)$$

should hold. The values for  $T$ ,  $J$ , and  $\lambda_0$  can be obtained if the growth conditions are known.  $\sigma$  can be given if an approximation such as a bond breaking model is employed. However,  $n_{so}$  includes the unknown re-evaporation time of the group III element. If we can know this value, we can determine  $D_s$  from the experiment, but so far this has not been possible.

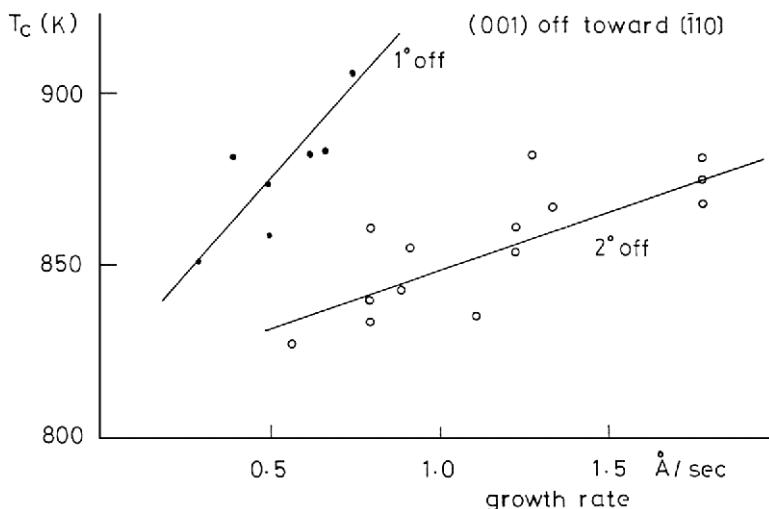


**Fig. 3.8.** Distribution of supersaturation between two steps

### 3.2.5 Critical temperature and growth conditions

Figure 3.9 shows  $T_c$  as a function of growth rate for two different misorientations. As seen in the figure,  $T_c$  increases as the growth rate increases. This means that as the growth rate increases, 2D nucleation occurs more easily. The schematic for the Ga adatom distribution between steps is given in Fig. 3.10, where  $\alpha_{\text{step}}$  denotes  $\alpha$  at the step edge. If the re-evaporation rate of Ga is negligibly small, as in the case of GaAs MBE,  $n_s$  follows a parabolic curve [12] and takes the maximum and the minimum, respectively, at the center between steps and at their edges. Now, at low growth rates, the number of Ga atoms arriving on the terrace is small so that the maximum supersaturation cannot reach  $\alpha_c$  and the growth occurs in step flow mode. However, if the growth velocity is increased, the maximum increases and above a critical growth velocity  $\alpha$  exceeds  $\alpha_c$  and the mode change occurs from the step flow to the 2D nucleation.

Figure 3.11 shows  $T_c$  as a function of the interstep distance under a constant growth rate. As seen in the figure,  $T_c$  increases with increasing step distance. This means that a larger step distance makes 2D nucleation easier. Schematics of the Ga adatom distributions for two different interstep distances are given in Fig. 3.12. When the step distance is short, the total number of Ga atoms arriving on the step terrace becomes small so that the gradient of  $n_s$  at the step edge becomes small. This makes the maximum at the center also small, leading to step flow growth.



**Fig. 3.9.** Critical growth temperature for the mode transition vs. growth rate

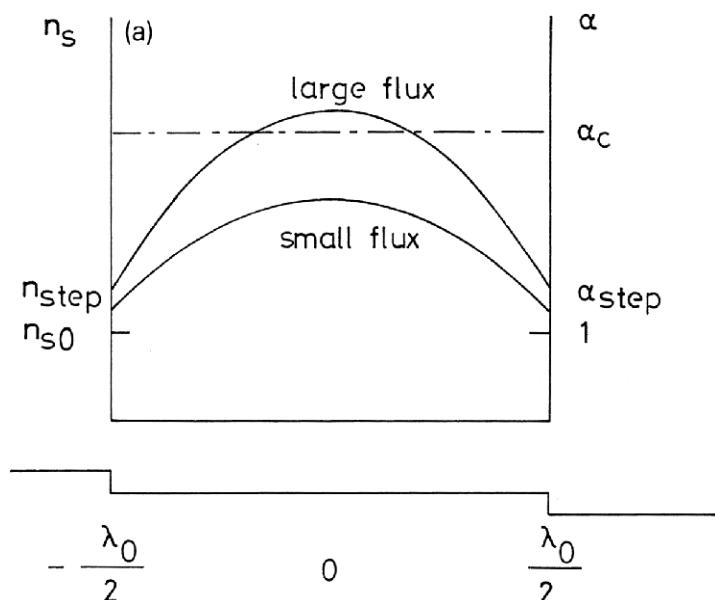


Fig. 3.10. Distribution of the adatom concentration between steps for different Ga fluxes

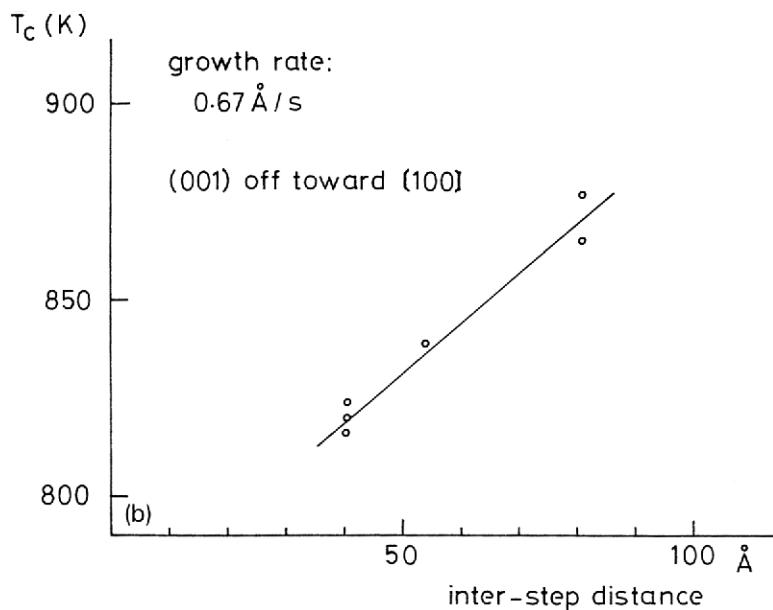
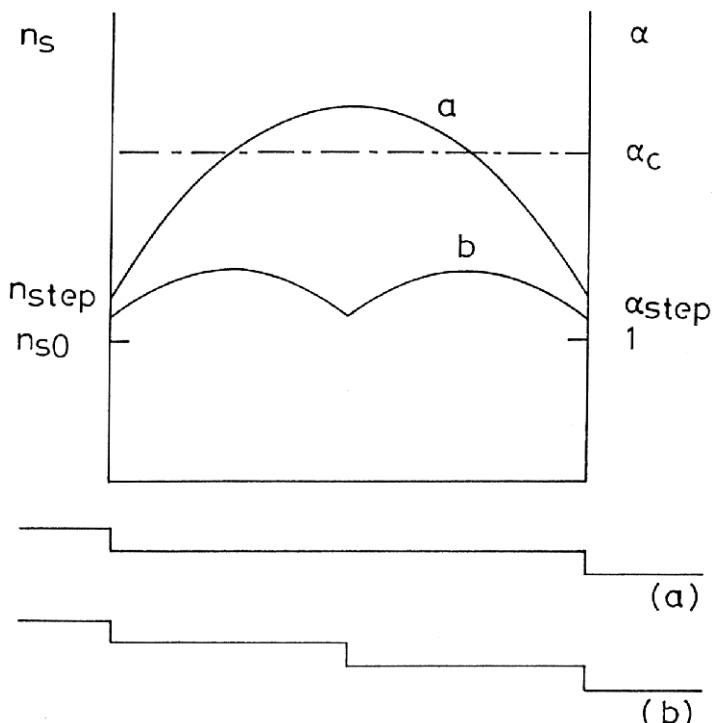


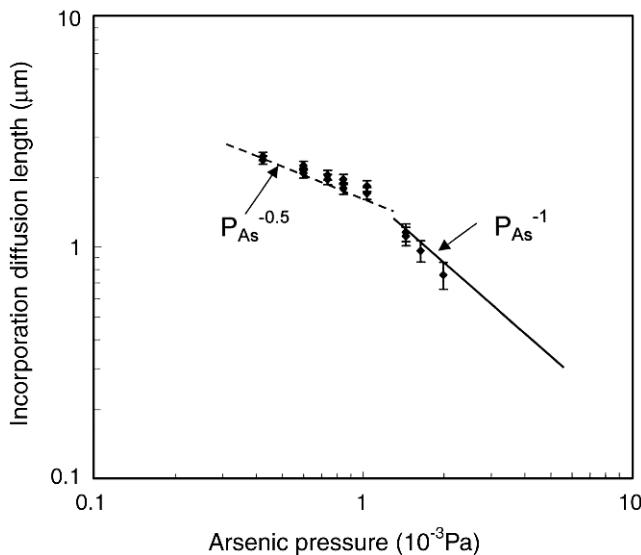
Fig. 3.11. Critical growth temperatures for the mode transition vs. step distance



**Fig. 3.12.** Distribution of the adatom concentration between steps for different step distances

### 3.2.6 Incorporation diffusion length

There are two kinds of diffusion lengths employed in the theory of crystal growth. One is the average distance of an adatom between arrival and evaporating points. However, in MBE of GaAs, Ga atoms are difficult to evaporate at typical growth temperatures and stay until they are incorporated into the crystal. The other is the incorporation diffusion length  $\lambda_{inc}$  that is defined as the distance between arrival and incorporating points. The concept of the incorporation diffusion length is not clear compared with the evaporation diffusion length because the former depends on the step density and the arsenic pressure in the case of GaAs MBE, whereas the latter is defined on an ideal surface where no step exists and hence is a simple function of the temperature, and also depends on the adsorption and desorption energies. However, the incorporation diffusion length is a key parameter that characterizes the growth in nanostructure fabrication.



**Fig. 3.13.** Arsenic pressure dependence of the incorporation diffusion length of Ga on the (001) surface. The growth temperature and the side surface were respectively 580°C and (110).

The incorporation diffusion length can be determined experimentally by measuring the distribution of growth rate on a facet where the growth atoms diffuse laterally from or to the next facet. During MBE of GaAs, Ga adatoms can diffuse about 1–10 μm before incorporation. It has been shown that on (001) surfaces, the incorporation diffusion length of Ga depends on the arsenic pressure [13,14]. In our previous report, we showed the diffusion length is inversely proportional to the As<sub>4</sub> pressure. However, we found that when the arsenic pressure is low, the diffusion length is inversely proportional to the square root of the As<sub>4</sub> pressure. The dependence of  $\lambda_{\text{inc}}$  on arsenic pressure on (001) surface is given in Fig. 3.13. For this figure, the arsenic pressure has been recalculated so that the arsenic flux impinges normal to the (001) surface.

$\lambda_{\text{inc}}$  is given by the well-known formula

$$\lambda_{\text{inc}} = \sqrt{D_s \tau_{\text{inc}}} \quad (3.9)$$

where  $D_s$  and  $\tau_{\text{inc}}$  denote the diffusion coefficient and the incorporation lifetime of Ga adatoms, respectively. Because the GaAs growth rate  $R_{\text{GaAs}}$  is proportional to the inverse of  $\tau_{\text{inc}}$ ,

$$R_{\text{GaAs}} = A_1 / \tau_{\text{inc}} \quad (3.10)$$

where  $A_1$  is a constant. From Fig. 3.13,

$$\lambda_{\text{inc}} = A_2 P_{\text{As}_4}^{-n} \quad (3.11)$$

where  $A_2$  is a constant and  $n$  takes the values of 0.5 and 1 when  $P_{\text{As}_4}$  is lower than  $8 \times 10^{-4}$  Pa and higher than this value, respectively. With the Eqs. from (3.9) to (3.11) we get,

$$R_{\text{GaAs}} = A_3 P_{\text{As}_4} \quad (P_{\text{As}_4} \leq 8 \times 10^{-4} \text{ Pa}) \quad (3.12)$$

$$= A_3 P_{\text{As}_4}^2 \quad (P_{\text{As}_4} \geq 8 \times 10^{-4} \text{ Pa}) \quad (3.13)$$

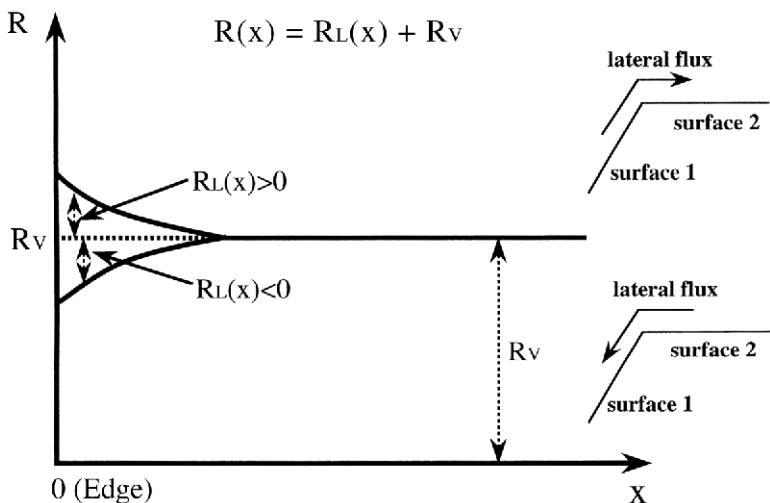
respectively, for lower and higher  $\text{As}_4$  pressures. Eq. (3.12) shows that at lower  $\text{As}_4$  pressure  $R_{\text{GaAs}}$  is proportional to  $P_{\text{As}_4}$ , which means one  $\text{As}_4$  molecule decomposes and gives active arsenic atoms or molecules for the growth. On the other hand, at high arsenic pressure, Eq. (3.13) shows that two  $\text{As}_4$  molecules react to give the active arsenic atoms or molecules. There is no information to determine the kind of the active arsenic atoms or molecules, but  $\text{As}_2$  is the most probable candidate [15–17].

### 3.2.7 Intersurface diffusion

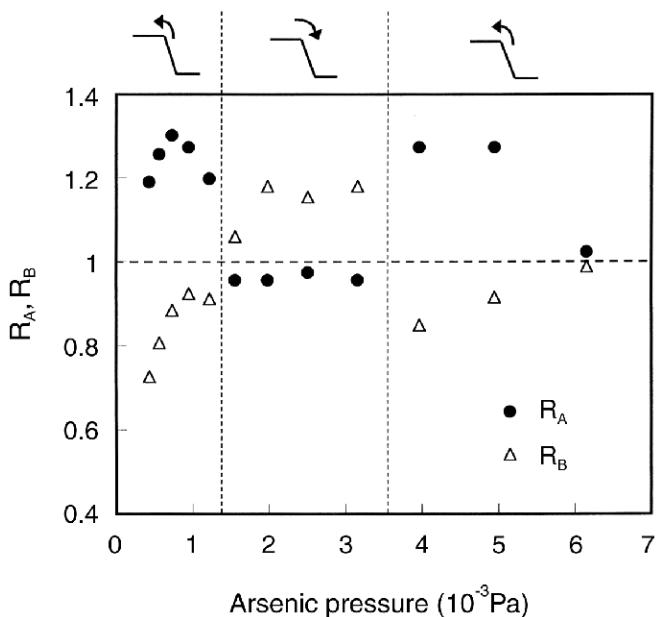
When two facets are generated side by side during the growth, Ga atoms diffuse from one facet to the other depending on the growth conditions. We call this intersurface diffusion. If there is a difference in adatom concentration, surface diffusion occurs assuming there is no potential difference and no barrier exists between the facets. Once intersurface diffusion occurs, one facet grows faster than the other, and the facet growing fast will disappear quickly [18,19]. Thus, during growth many facets appear and disappear and only a few facets remain in the final stage of growth. For the fabrication of nanostructures, the relative growth rate among various facets during the growth is important. However, the growth rate of facets depends on the growth conditions, and hence one should understand what the factor is that determines the growth rate.

By measuring the growth rate distribution on one facet near the boundary, one can know the direction of the intersurface diffusion [20,21]. Figure 3.14 shows the principle. In this figure,  $x = 0$  is the position of the boundary between two facets. The growth rate distribution can be obtained by microprobe-RHEED by measuring the intensity oscillation. As shown in the figure, if the growth rate decreases as the distance is increased, one knows the lateral flux occurs from the adjacent facet ( $x < 0$ ) to the facet ( $x > 0$ ) on which the growth rate distribution is measured. Whereas, if the growth rate increases as the distance is increased, the intersurface diffusion is in the opposite direction.

We measured the distribution of the growth velocity on the (001) surface of GaAs. As the side facet, we have chosen the (111)B surface. Instead of measuring the whole distribution, we measured the growth rate at two points. One is on the facet and close to the boundary and the other is the point on the facet very far from the boundary. We define each growth rate as  $R_{\text{corner}}$  and  $R_{\text{planar}}$ , respectively. Figure 3.15 shows the results for a combination of (111)B–(001) facets. In the figure,



**Fig. 3.14.** Schematic of the growth rate  $R(x)$  as a function of position  $x$  from the boundary between two facets.  $R_V$  is the growth rate caused by lateral flux, and  $R_L$  is the growth rate caused by the direct flux.  $R_V$  equals the growth rate far from the boundary.



**Fig. 3.15.** Normalized growth rate on (001) near the boundary and that on (111)B vs. arsenic pressure.  $R_A = R_{\text{corner}}^{(001)} / R_{\text{corner}}^{(001)}$  and  $R_B = R_{\text{corner}}^{(111)B} / R_{\text{planar}}^{(111)B}$

closed circles and open triangles denote  $R_{\text{corner}}^{(001)} / R_{\text{planar}}^{(001)}$  and  $R_{\text{corner}}^{(111)\text{B}} / R_{\text{planar}}^{(111)\text{B}}$ , respectively. Here, we define these normalized growth rates as  $R_A$  and  $R_B$ , respectively. When the arsenic pressure is low,  $R_A$  is larger than unity. As easily understood with Fig. 3.14, this indicates that Ga adatoms diffuse from (111)B to (001). On the other hand,  $R_B$  is lower than unity which indicates that Ga adatoms diffuse from (111)B to (001); this is consistent with the direction given by  $R_A$ . As the arsenic pressure increases,  $R_A$  decreases and crosses the line of unity at the arsenic pressure of  $1.4 \times 10^{-3}$  Pa, which means the direction of the lateral flow is reversed, namely, from (001) to (111)B. At the same arsenic pressure,  $R_B$  also crosses the line of unity from the lower side to the higher side. This is very important because if this does not happen, one cannot assume a pure two-face inter-surface diffusion [20]. As the arsenic pressure is increased, both  $R_A$  and  $R_B$  keep almost constant values, but as the arsenic pressure is further increased, they again cross the line of unity which means the direction of the diffusion has reversed again. The direction of the diffusion for each arsenic pressure range is given at the top of the figure.

### 3.2.8 Elementary growth processes

Based on the above experimental results, we discuss the elementary growth processes involved in the MBE growth of GaAs.

#### **Growth mode**

In section 3.2.7, we showed that Ga adatoms diffuse from one facet to the other. With the measured growth rate distribution on a facet, such as that drawn in Fig. 3.14, one can deduce the diffusion length of incorporation. This is how we obtained the arsenic pressure dependence of the incorporation diffusion length in Fig. 3.13. Here, the experimental growth rate was measured by RHEED intensity oscillations so that the growth can be understood as being conducted in 2D nucleation mode. This means that the birth and spread of 2D nuclei are continually happening during growth and Ga adatoms diffuse between and over the 2D nuclei. The incorporation lifetime of Ga,  $\tau_{\text{inc}}$  that was defined in section 3.2.6, should be the function of the available number of incorporation sites. Hence, in this situation, the number changes periodically with the same periodicity but in opposite phase of RHEED intensity oscillations. Nevertheless, we can define the time average of  $\tau_{\text{inc}}$  and  $\lambda_{\text{inc}}$  that was described in section 3.2.6.

The average distance of the adatom incorporation is about 1  $\mu\text{m}$ ; therefore, under arsenic pressure, Ga adatoms can cross over many steps formed by 2D nucleation. Hence, the sticking coefficient of Ga adatoms at the step edges is much less than unity.

### **Change in the direction of intersurface diffusion**

Intersurface diffusion occurs if there is a difference in Ga adatom concentrations between two facets. Here, we assume there is no potential difference and no barrier between these faces. But, there is no evidence for these assumptions.

The adatom concentration of Ga,  $n_{\text{Ga}}$ , is proportional to the incident flux of Ga,  $J_{\text{Ga}}$ , and  $\tau_{\text{inc}}$  as

$$n_{\text{Ga}} = J_{\text{Ga}} \tau_{\text{inc}} \quad (3.14)$$

As we have discussed,  $\tau_{\text{inc}}$  is inversely proportional to the available number of Ga sites, in other words, to the step density. The step density depends on the number of 2D nuclei and their sizes. Hence,  $\tau_{\text{inc}}$  depends on the nucleation rate and the energy barrier for Ga adatoms to enter and to leave the kink site on a step. There is almost no information on their energies, so that we should be satisfied at this moment with qualitative discussions.

In section 3.2.7, we showed the experimental observation for the change in the diffusion direction. These experimental findings also give us information of elementary growth processes. Figure 3.15 showed that the direction of the intersurface diffusion changes twice as the arsenic pressure increases. At the reversal with the highest arsenic pressure, the reconstruction of (111)B changes from  $(\sqrt{19} \times \sqrt{19})$  to  $(2 \times 2)$  as arsenic pressure increases, while the reconstruction of (001) remains at  $(2 \times 4)$ . It is known that the  $(2 \times 2)$  reconstruction consists of an arsenic trimer that is difficult to decompose. Hence, once the  $(2 \times 2)$  reconstruction is formed, 2D nucleation might be more difficult, and this causes the increase of  $\tau_{\text{inc}}$  and hence increases the Ga adatom concentration.

The direction reversal with the lower As pressure of  $1.4 \times 10^{-3}$  Pa was explained in terms of the difference in arsenic pressure dependence of  $\tau_{\text{inc}}$  on (001) and (111)B facets. In our previous paper, we extrapolated the  $P_{\text{As}_4}^{-4}$  dependency of  $\tau_{\text{inc}}$  on (111)B, but as described in section 3.3, we recently found that there is a region in the lower arsenic pressure side where  $\tau_{\text{inc}}$  depends on  $P_{\text{As}_4}^{-2}$ . So that up to now, our previous conclusion for the  $P_{\text{As}_4}^{-4}$  dependency of  $\tau_{\text{inc}}$  that is responsible for the direction reversal probably should be changed to a  $P_{\text{As}_4}^{-2}$  dependency. If this is the case, we should assume a  $P_{\text{As}_4}^{-1}$  dependency for the (001) surface and a  $P_{\text{As}_4}^{-2}$  dependency for the (111)B surface that allows the crossing of  $\tau_{\text{inc}}$  on (111)B and  $\tau_{\text{inc}}$  on (001) at the arsenic pressure of around  $1.4 \times 10^{-3}$  Pa.

## **3.3 MOCVD of III-V Compounds**

### **3.3.1 Growth of high-purity materials by MOCVD**

It has been said that the materials grown by MOCVD have inferior purity compared to those grown by other growth techniques such as MBE and LPE. But it is time to correct this inaccurate description about MOCVD. State-of-the-art data

shows that the purity of materials grown by MOCVD already have become a strong competitor to MBE-grown materials. In this section, we describe the present status and the origins of the residual impurities in GaAs and AlGaAs grown by MOCVD.

Hata et al. reported on an extensive study of the origin of residual impurities in GaAs and AlGaAs grown by MOCVD [23]. In their experiments, epitaxial layers of GaAs and AlGaAs were grown using two lots of TMG, two lots of TMA, and six lots of AsH<sub>3</sub> to examine the effects of source materials on their properties. The analytical data for TMG and TMA are listed in Table 3.1, and the electrical properties of undoped GaAs obtained from Hall measurement at 77 K are summarized in Table 3.2. Though the analytical data of TMG #1 and TMG #2 show a noticeable difference, the electrical properties of GaAs layers are nearly identical. The properties of the layers seem to depend more on the choice of the AsH<sub>3</sub> cylinder. Germanium (S8, S9, S10, and S15) and silicon (S11) were detected as main donors in each layer. From these results, they concluded that most of the residual impurities of donors, Ge or Si, were carried into the system by AsH<sub>3</sub> because the same TMG were used throughout the series of experiments.

On the other hand, carbon acceptors were detected by the photoluminescence measurement in all samples [23]. The residual C, probably coming from TMG, decreases as the AsH<sub>3</sub>/TMG ratio increases. The highest mobility at 77 K of 153,000 cm<sup>2</sup>/V s with an electron concentration of  $3.4 \times 10^{13}$  cm<sup>-3</sup> was obtained by optimizing the conditions. This value is nearly comparable to those from MBE-grown GaAs layers. In addition to this measurement, Hanna et al. also reported a high purity GaAs layer with an excellent mobility of 162,000 at 77 K with an electron concentration of  $8.7 \times 10^{13}$  cm<sup>-3</sup> [23].

The electrical properties of undoped AlGaAs were reported to largely depend on the purity of the source materials [22]. Figure 3.16 shows the electrical properties of undoped Al<sub>0.2</sub>Ga<sub>0.8</sub>As obtained from Hall measurements at RT. When AsH<sub>3</sub> was used without purification, the layers grown at 700°C showed a p-n conversion depending on the AsH<sub>3</sub>/(TMG+TMA) ratio, which is similar to the case of GaAs. However, the layers grown at 650°C had a high resistance for a wide range of AsH<sub>3</sub>/(TMG+TMA) ratios, and had no near-band emission in the PL measurement. This indicates that a large amount of deep centers associated with oxygen in AsH<sub>3</sub> are included in these layers. When AsH<sub>3</sub> was passed through a ternary (Al:In:Ga = 1:10:100) melt, the quality of the AlGaAs layers grown at 650°C was

**Table 3.1.** Analytical Data for TMG and TMA by Atomic Absorption [22]

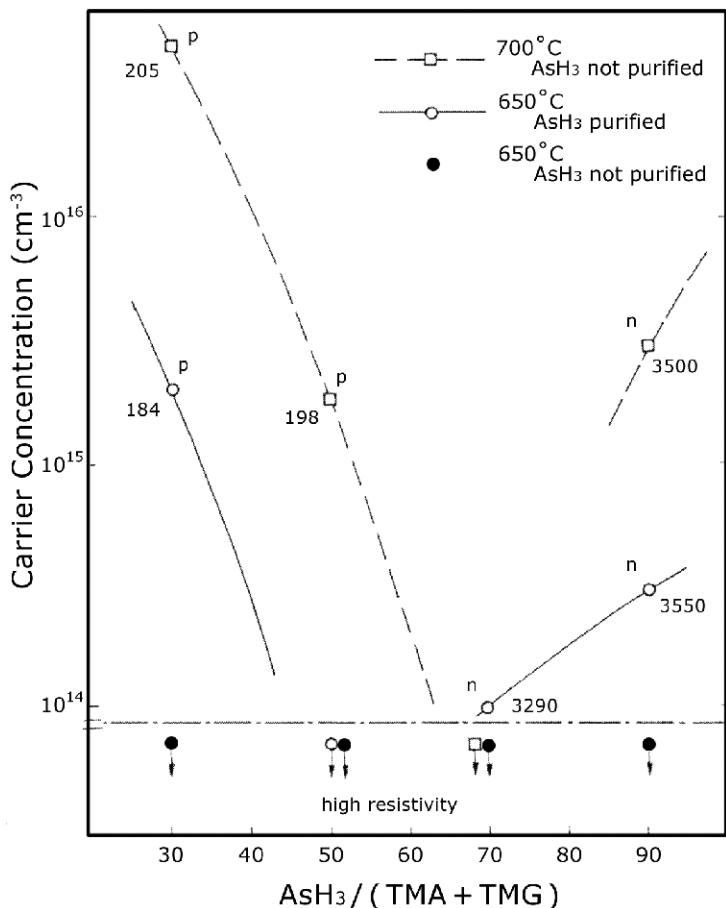
Lot No.	Si [ppm]	Fe [ppm]	Zn [ppm]	Cu [ppm]	Sn [ppm]
TMG #1	0.3	< 0.2	0.6	0.2	0.2
TMG #2	0.2	< 0.1	0.1	< 0.1	< 0.1
TMA #1	0.1	< 0.1	< 0.1	0.3	< 0.1
TMA #2	< 0.1	0.1	< 0.1	< 0.1	< 0.1

**Table 3.2.** Electrical Properties of GaAs that were Obtained from Hall Measurements [22]

Sample No.	Source lot		Growth conditions		Electronic properties	
	TMG	AsH <sub>3</sub>	AsH <sub>3</sub> /TMG	Temp. [°C]	n at 77 K [cm <sup>-3</sup> ]	μ at 77 K [cm <sup>2</sup> /V • s]
S1	# 1	# A	50	650	$2.2 \times 10^{14}$	80,200
S2	# 1	# D	50	650	High resistivity	
S3	# 1	# D	70	650	$3.6 \times 10^{13}$	152,000
S4	# 2	# D	30	650	High resistivity	
S5	# 2	# D	40	650	High resistivity	
S6	# 2	# D	50	650	High resistivity	
S7	# 2	# D	60	650	High resistivity	
S8	# 2	# D	70	650	$3.4 \times 10^{13}$	153,000
S9	# 2	# D	80	650	$4.2 \times 10^{13}$	139,000
S10	# 2	# A	50	650	$3.2 \times 10^{14}$	89,000
S11	# 2	# B	50	650	$6.1 \times 10^{13}$	135,000
S12	# 2	# C	50	650	$8.1 \times 10^{14}$	63,300
S13	# 2	# E	50	650	$1.3 \times 10^{15}$	57,400
S14	# 2	# F	50	650	$3.8 \times 10^{15}$	32,000
S15	# 2	# F	200	700	$5.1 \times 10^{16}$	9,280

improved to equal that of layers grown at 700°C. The purity of TMA is also very important to obtain high-quality AlGaAs layers. The oxygen impurities in TMA, such as methoxcide (-OMe), was reported to be the origin of oxygen impurities in AlGaAs layers [24]. The oxygen concentration increases when the AlAs mole fraction increases, but decreases when either the AsH<sub>3</sub>/(TMG + TMA) ratio or the growth temperature increases [24]. Oxygen is thought to form deep electron traps that compensate carriers and act as nonradiative centers. Similarly, Yamanaka et al. reported that oxygen-related deep levels also exist in MBE-grown AlGaAs layers. The concentration of these levels increases with increasing AlAs mole fraction and decreases with increasing growth temperature. But, on the contrary to the former report, these levels increase with increasing As/Ga flux ratio [25,26]. The incorporation behavior is similar, and these oxygen-related deep levels were known to act both as electron traps and nonradiative centers [26]. Naritsuka et al. reported that the deep levels originate from arsenic oxide, usually from a surface oxide of arsenic source in the MBE [27]. They also reported that oxygen becomes a deep donor in InAlAs grown by MOCVD and that the oxygen incorporation dependence on the growth conditions is quite similar to that of AlGaAs [28,29], which strongly suggests that the origin of the oxygen impurities is almost the same.

As described above, O, Si, Ge, and C are major impurities in MOCVD. Numerous studies have found ways to decrease these residual impurities and, as a result, the quality of epitaxial layers has significantly improved. Various kinds of



**Fig. 3.16.** Electrical properties of AlGaAs ( $X_{\text{Al}} = 0.2$ ) obtained from Hall measurements at RT: (Y) AsH<sub>3</sub> was purified ( $T_g = 650^\circ\text{C}$ ), (λ) AsH<sub>3</sub> was not purified ( $T_g = 650^\circ\text{C}$ ), (♦) AsH<sub>3</sub> was not purified ( $T_g = 700^\circ\text{C}$ ). The same AsH<sub>3</sub> cylinder and TMA (#1) were used throughout [22].

devices are commercially available, including ones made from materials that contain phosphorous, made using MOCVD. In addition, by fabricating a low-threshold current MQW laser, Naritsuka et al. found that epitaxial layers grown at high growth temperature of about 800°C by MOCVD had superior optical properties to those grown by MBE. Finally, submilliamperes lasing of AlGaAs/GaAs MQW laser at 77 K has been achieved for the first time using the wafers [30].

The incorporation of residual impurity is usually a difficulty in MOCVD, but it sometimes has a wonderful outcome. Carbon, which comes from the methyl groups of TMG and TMA or actively from halomethanes, such as  $\text{CH}_y\text{X}_{4-y}$ , where X = Cl, Br, or I, is a very promising dopant for p-type because C has a very low

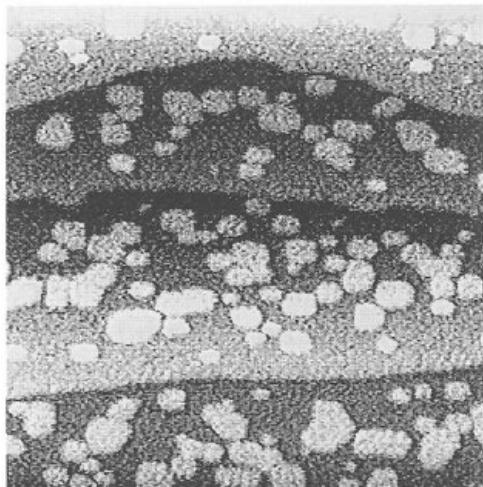
acceptor binding energy and a low diffusion constant even at a very high doping level [31]. Therefore, C doping by MOCVD is widely and commercially used, and a variety of kinds of devices including HBT or lasers are produced.

It is appropriate to add the hydrogen passivation of dopants in MOCVD, here. Hydrogen, which comes from ambient  $H_2$  or the products of decomposing reaction of source materials, is easily incorporated into a growing crystal at interstitial sites and makes complexes with the dopant that can passivate either type of doping. These hydrogen atoms are very mobile and are easily annealed out from the crystals for activating dopants.

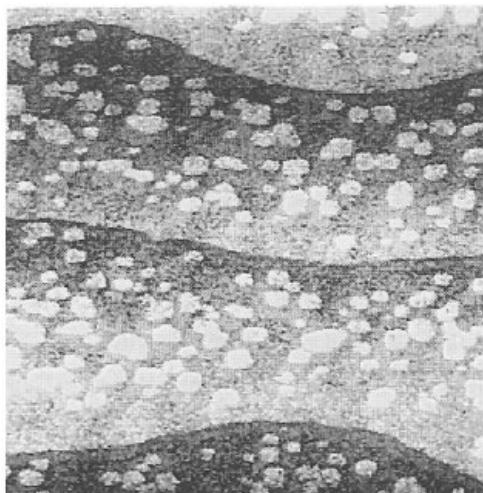
Low toxicity in MOCVD is another important issue. This has been attained by the development of new precursors, for example, TBAs, TMAs, or TBP, as alternatives to the toxic hydride of  $AsH_3$  or  $PH_3$ . Further study of new precursors is also useful to decrease unintentional doping. TMAA is a promising substitute for TMA to decrease the oxygen incorporation. Besides this, TBAs are useful not only to decrease toxicity, but also to decrease the oxygen incorporation. For example, Leu et al. reported that  $Al_{0.3}Ga_{0.7}As$  with an excellent low O-concentration of  $2.5 \times 10^{16} \text{ cm}^{-3}$  was able to be grown using TBAs [32]. The value is much less than the critical O-concentration of  $1.0 \times 10^{17} \text{ cm}^{-3}$  as required for low threshold current density ( $AlGa$ )As/GaAs MQW lasers [33].

### **3.3.2 *In situ* monitoring and study of growth kinetics in MOCVD**

*In situ* monitoring is essential for the study of growth mechanisms. A considerable part of the MOCVD growth mechanism has been understood using newly developed *in situ* monitors. For example, using high-vacuum scanning tunneling microscopy (STM), Kasu et al. observed 2D nuclei on the surface of a GaAs layer grown by MOCVD [34,35]. They also studied surface diffusion kinetics of GaAs and AlAs in MOCVD [36]. Figure 3.17 shows STM images of 2D nuclei and denuded zones of GaAs (a) and AlAs (b) formed at 630°C. From the figure, the following was found. 2D nucleation occurs on each terrace during growth, which is similar to that with MBE. The AlAs 2D nucleus density is about two times larger than that of GaAs. The 2D nucleus sizes in the <110> direction are about twice as large as those in the <-110> direction. They attributed the anisotropy to the difference in the lateral sticking probability (Ps). The lateral sticking probability at steps along <110> directions (B steps) is more than three times greater than that at <-110> (A steps). The elongation direction on 2D nuclei in MOCVD is different to that in MBE. They thought that this is due to the difference in reconstructions: c(4 × 4) in MOCVD and (2 × 4) in MBE. The denuded zone widths on the upper terraces are about two times wider than those of lower terraces and they ascribed this to the difference in Ps. The Ps at descending steps was 10 to 300 times larger than that at ascending steps. Using Monte Carlo simulations, they also estimated the surface diffusion coefficient of GaAs and AlAs to be  $2 \times 10^{-6}$  and  $1.5 \times 10^{-7} \text{ cm}^2/\text{s}$  at 530°C, and the energy barriers for migration to be 0.62 and 0.8 eV, respectively.

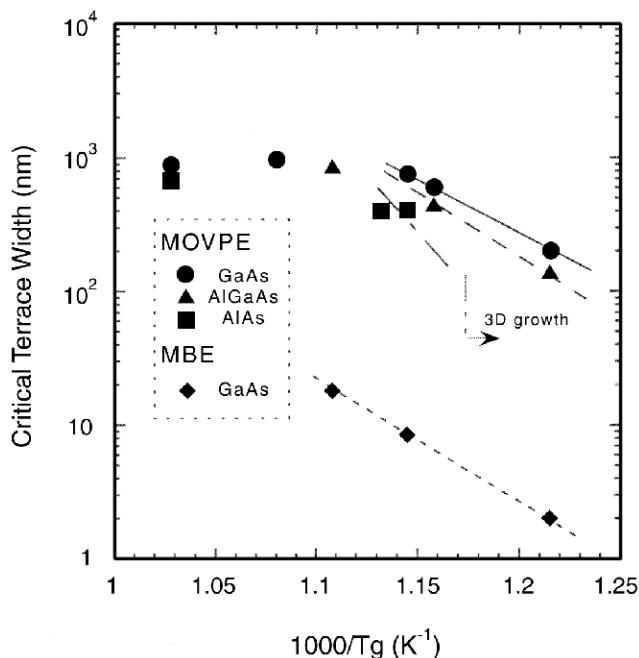


(a)  $\downarrow [1\bar{1}0]$  200 nm Down



(b)  $\downarrow [1\bar{1}0]$  200 nm Down

**Fig. 3.17.** STM images showing the denuded zones near steps and the 2D nuclei of (a) GaAs and (b) AlAs. About a 1/6 ML of GaAs or AlAs was deposited on a very flat (001) GaAs surface at 630°C [36].



**Fig. 3.18.** Dependence of the critical terrace width for 2D nuclei generation on the growth temperature [37]

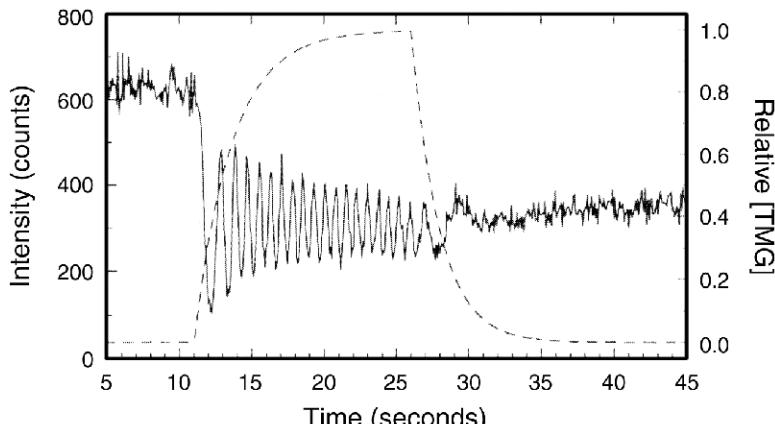
On the other hand, Shinohara et al. studied the enhancement of surface diffusion of column-III species in MOCVD. From AFM observations of GaAs surfaces after growth, they found that the critical terrace width for MOCVD was much larger than that of MBE, as shown in Fig. 3.18 [37]. They attributed this to the enhancement of surface diffusion of column-III species on H-terminated As atoms. Hydrogen radicals are produced by the decomposition of arsine and terminate on the top layer of As atoms during growth. The H-terminated As surface enhances the surface diffusion and, consequently, the critical terrace width increases.

*In situ* monitoring is effective not only for the study of growth mechanisms but also for process control. Though electron-based analytical tools under UHV cannot be used in H<sub>2</sub> ambient MOCVD, X-ray or light-based tools can be used in MOCVD. *In situ* and real-time monitoring of growth using grazing incidence scattering of X-ray (GIXS) was reported [38]. Synchrotron-based X-ray sources were used in GIXS because the source of X-rays must be bright for real-time measurements. First, surface reconstructions of (001) GaAs surfaces were studied. After heating in ambient hydrogen for 10 min at 580°C, a (4 × 2) reconstruction was observed, but it was not consistent with the typical (4 × 2) reconstruction in MBE that is modeled with missing rows. On the other hand, after annealing in TBAs, the GIXS indicated that the surface had the c(4 × 4) reconstruction, which was very similar to that in MBE. After a dose of TMG ( $2 \times 10^{-3}$  Torr) for 2 s, this

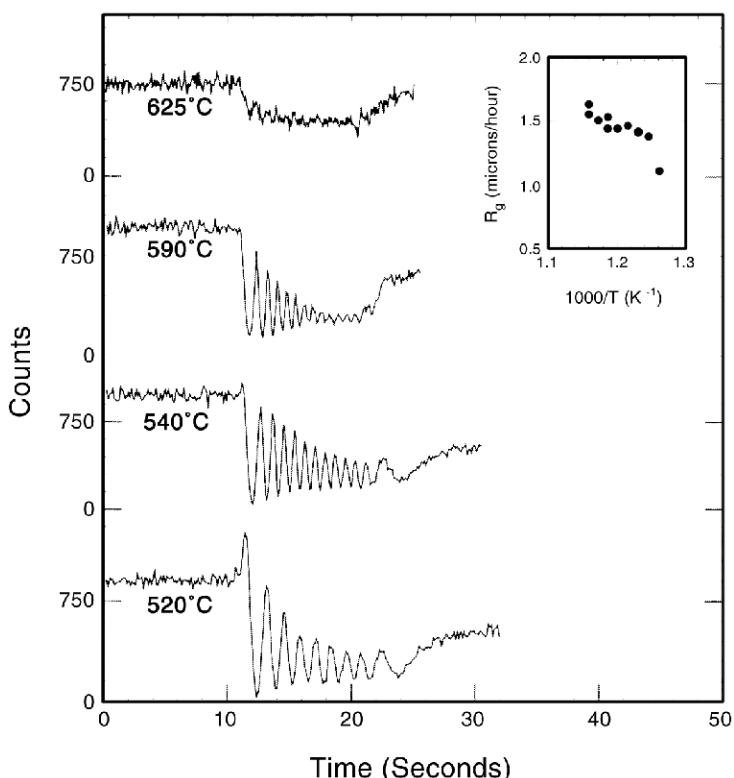
changed to the  $(4 \times 2)$  Ga-based reconstruction, which is the same as the former  $(4 \times 2)$  reconstruction. In a typical growth condition of MOCVD, the  $c(4 \times 4)$  reconstruction is maintained during growth. Therefore, the  $c(4 \times 4)$  reconstruction should be destroyed for continuing growth. Monte Carlo simulation indicates that the existence of Ga dimers on the surface increases the exchange of surface As atoms for Ga atoms, which helps Ga atoms to come into the correct crystal sites by preserving the  $c(4 \times 4)$  reconstruction during growth [39]. This phenomena is called the self-surfactant effect [40].

As the crystal truncation rod (CTR) is extremely sensitive to surface roughness, its intensity oscillates when GaAs nuclei form, grow, and finally coalesce. The cyclic behavior is the evidence of layer-by-layer growth and can be used as a direct, *in situ* monitor of growth. Figure 3.19 shows the GaAs growth performed for 15 s at 40 Torr and 540°C. The dashed line in the figure shows the calculated TMG concentration in the reactor. From the figure, it is found that the oscillation shows very good correlation to the flow of TMG. Figure 3.20 shows the results at several temperatures from 520 to 625°C. The inset in the figure shows the growth rate change. It can be seen that the growth rate is reduced at the lowest temperatures because of the limited decomposition of the sources. At higher temperature, the growth rate becomes constant, as expected for the mass transport limited regime. Moreover, the oscillation is gone at 625°C, which indicates the presence of the step-flow mode in MOCVD as it does in MBE. This is expected because the column III species are very mobile on the H-terminated As surface, and thus they can reach the step sites.

Using reflectance difference spectroscopy (RDS), the layer-by-layer growth can also be monitored in real time in MOCVD [41]. Figure 3.21 shows the RDS response of a (110) GaAs surface when TEG is supplied to an  $\text{AsH}_3$ -stabilized



**Fig. 3.19.** CTR intensity during growth. Solid line: intensity of 110 CTR as layer-by-layer growth occurs. Dashed line: Calculated TMG concentration [38]



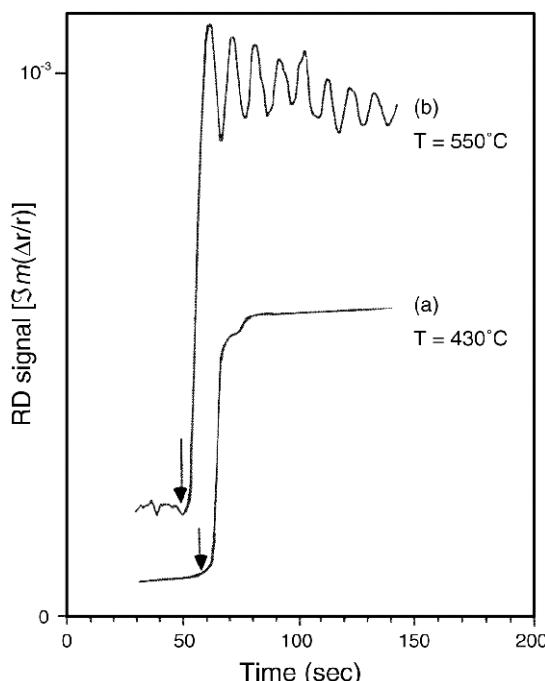
**Fig. 3.20.** Effect of temperature on layer-by-layer growth. Inset: Arrhenius plot of the temperature-dependent growth rate [38]

surface at (a) 430°C and (b) 550°C. The arrows indicate the event when TEG starts to be supplied. Each period of the oscillation corresponds to the growth of a monolayer of GaAs in MOCVD. The oscillation, and hence, layer-by-layer growth was maintained a long time at 550°C, whereas the oscillation immediately disappeared at 430°C. This means that the surface became rough immediately at 430°C because the migration length of surface species is very short at such a low temperature. RDS is also sensitive to the chemical nature of the surface dimers. Therefore, it can be useful to control precisely the formation of heterointerfaces, which will likely be necessary to fabricate novel, sophisticated devices. Other useful techniques to monitor growth in real time are ellipsometry and photoreflectance (PR). Although *in situ* monitoring in MOCVD began only recently, such techniques have revealed a lot about the elemental processes in MOCVD.

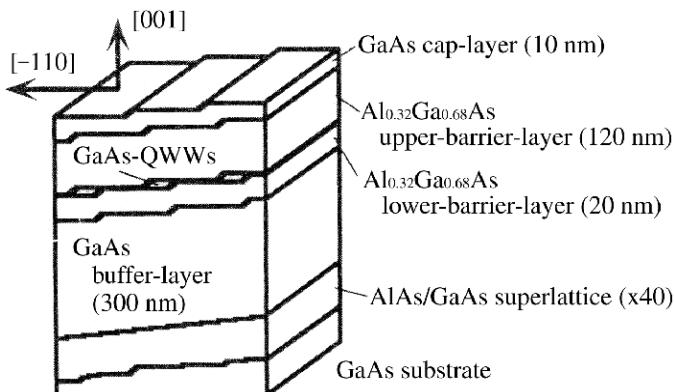
### 3.3.3 Nanostructure fabrication by MOCVD

MOCVD, similar to MBE, is very good for fabricating nanostructures. Some kinds of growth mechanisms are effectively used to fabricate nanostructures. These types of fabrication methods are very promising because they require no damage-introducing processes such as lithography and dry etching, and nanostructure sizes can be controlled simply by changing the crystal growth conditions. The typical example is quantum well wires (QWWs), which uses the step bunching mechanism. Another example is the “self-assembled” quantum dot, which requires the Stranski-Krastanow (S-K) growth mode.

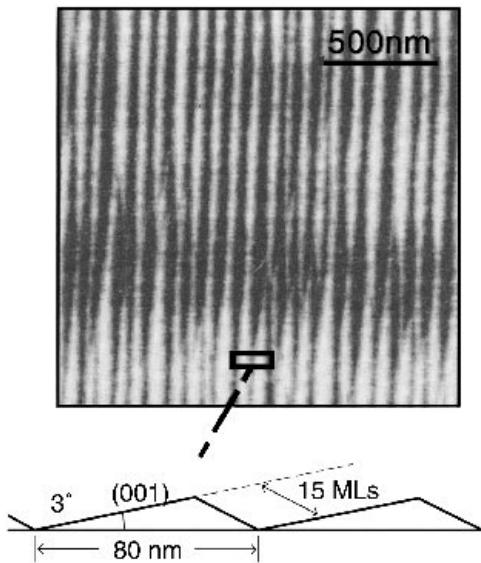
The QWWs technique was first proposed by Fukui et al. [42]. At first, a GaAs buffer layer is grown. Then, the wafer is annealed under an  $\text{AsH}_3$  atmosphere to obtain straight multiatomic steps. Then, the GaAs/AlGaAs QWW structure is grown on the multiatomic steps. The GaAs active layer becomes thicker at the corners of the multiatomic steps and, consequently, quantum wire structures are formed as shown in Fig. 3.22. In QWWs, (001) vicinal GaAs substrates misoriented by a few degrees towards the  $<-110>$  direction are usually used to supply the surface steps. Because the bunched steps are very straight, as seen in the AFM image in



**Fig. 3.21.** RDS response of a (001) GaAs surface when TEG is supplied to an  $\text{AsH}_3$ -stabilized surface at (a)  $430^\circ\text{C}$  and (b)  $550^\circ\text{C}$ . The arrows indicate the event when TEG was injected into the growth chamber [41].



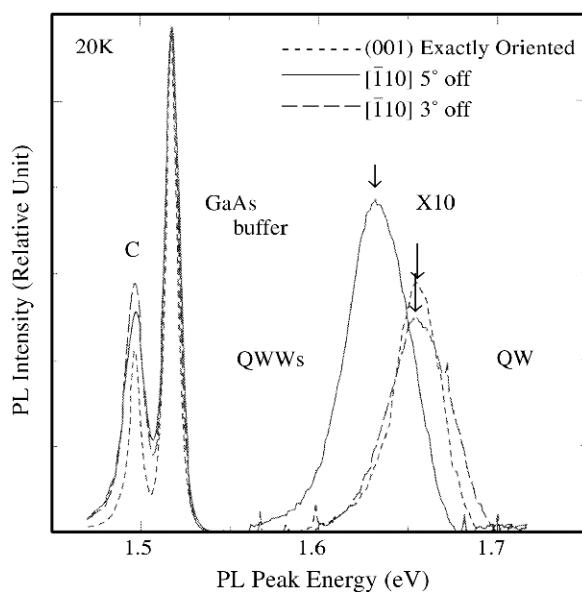
**Fig. 3.22.** Schematic illustration of a QWW structure on a GaAs vicinal substrate [43]



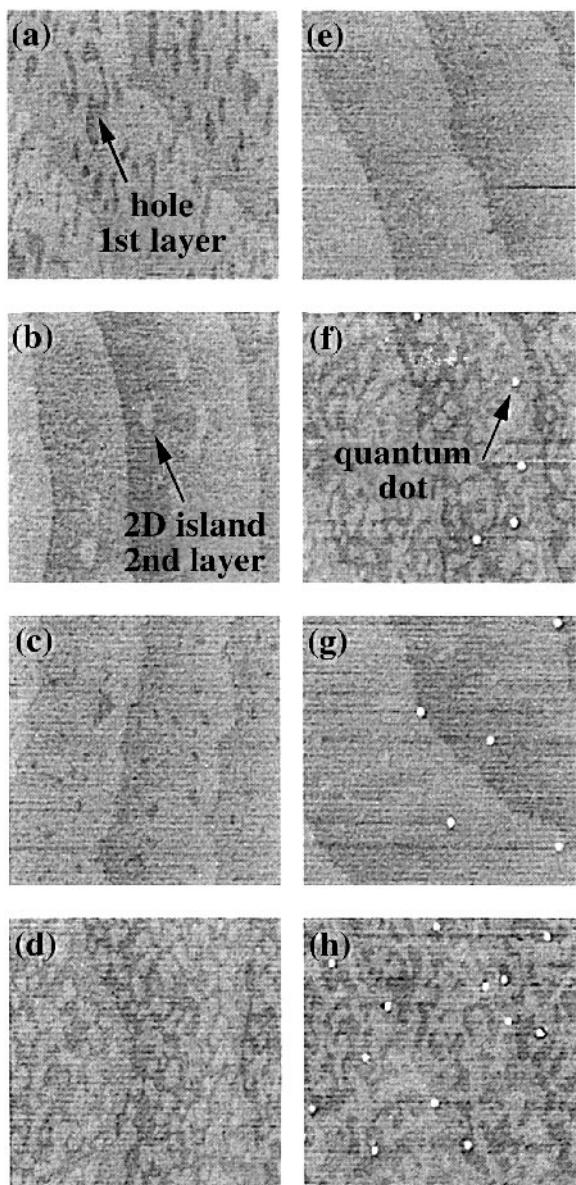
**Fig. 3.23.** AFM images and cross-section of a thick GaAs buffer layer surface on a vicinal substrate. Observed area is 1700 nm × 1700 nm [43]

Fig. 3.23 [43], the fabricated QWWs have superior optical characteristics. Figure 3.24 shows the photoluminescence spectra of QWW structures on 5° misoriented substrates and on 3° misoriented substrates and single quantum well on exactly oriented substrates. The PL peak energy of the QWW structures grown on 5° misoriented substrate was 23 meV smaller than that of QW on the exactly oriented substrate. This indicates that the quantum well wire structures were successfully formed at the corners of multiaatomic steps, as schematically shown in Fig. 3.22.

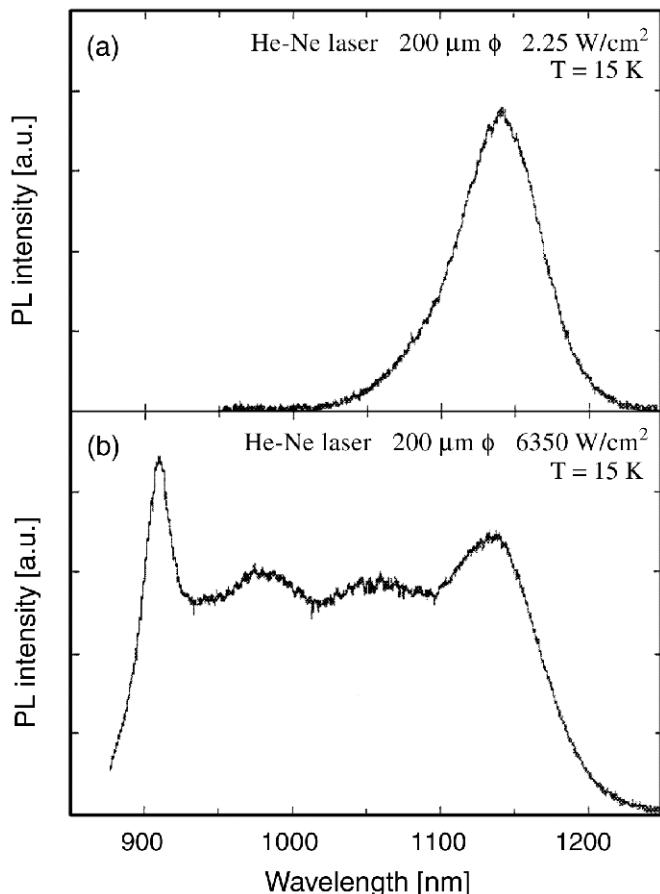
In SK mode, 2D layer-by-layer growth changes to 3D island growth at a certain critical thickness [44]. No dislocations are introduced as long as the island sizes are small. Moreover, the residual stress will limit their size, which is quite useful for the fabrication of quantum dots (QDs). The high uniformity of QDs leads to a narrow luminescence linewidth, which increases the gain in optical devices. Therefore, a lot of reports have been published about QD fabrication that used the SK mode. Here, we show one example of the early stage of the research. Figure 3.25 shows AFM images of InGaAs surfaces grown on GaAs [45]. The deposition times were (a) 0.5 s, (b) 1.0 s, (c) 1.5 s, (d) 2.0 s, (e) 2.5 s, (f) 3.0 s, (g) 3.5 s, and (h) 3.7 s. The scan size of the images was  $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ . Below 2.5 s of InGaAs deposition time, the growth mode was 2D. On the other hand, once the thickness reached the critical thickness of 3 ML, which required a deposition time of 3 s (Fig. 3.25 (f)), the QDs started to form on terraces. As seen from the figure, the increase in the deposition time above 3 s only leads to an increase in the density of the QDs. Figure 3.26 shows the PL spectrum from the sample grown for 3.7 s. The excitation intensities were 2.25 and  $6350\text{ W/cm}^2$ . The PL spectrum of 1136 nm at low excitation intensity in Fig. 3.26 (a) is thought to originate from the QDs. On the other hand, the PL spectrum at high excitation intensity in Fig. 3.26 (b) has another three peaks that are caused by higher energy subbands at 980 nm and 1060 nm and from a 2D InGaAs layer of 4 ML at 915 nm. In this way, nanostructures can be fabricated in MOCVD using special growth modes. Furthermore, intersurface diffusion of column III species or material transport in the gas phase is also important in the fabrication of nanostructures.



**Fig. 3.24.** Photoluminescence spectra of QWW structures [43]



**Fig. 3.25.** AFM images of InGaAs surface grown on GaAs. The deposition times were (a) 0.5 s, (b) 1.0 s, (c) 1.5 s, (d) 2.0 s, (e) 2.5 s, (f) 3.0 s, (g) 3.5 s, and (h) 3.7 s. The scan size of the images was  $1 \mu\text{m} \times 1 \mu\text{m}$  [45].

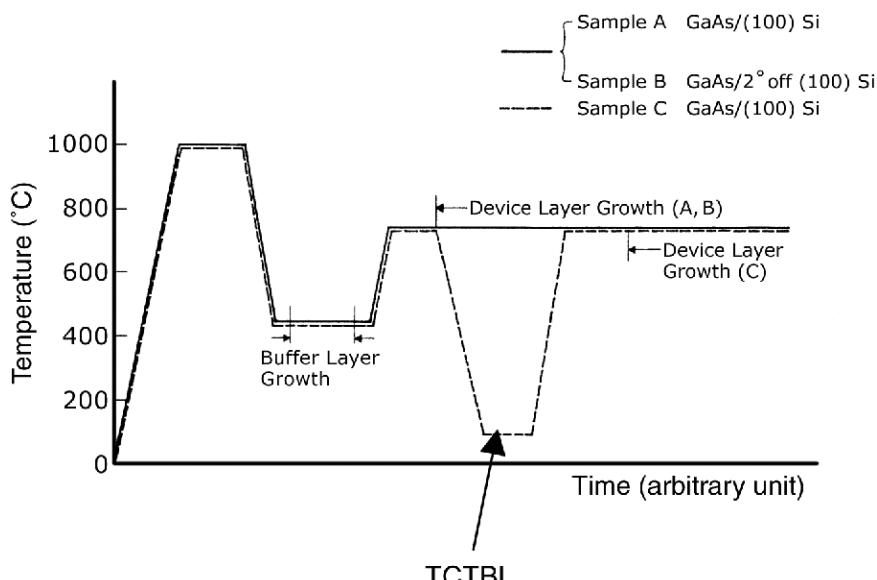


**Fig. 3.26.** PL spectrum from a dot sample that was grown with a deposition time of 3.7 s. The excitation intensities are (a)  $2.25\text{ W/cm}^2$ , (b)  $6350\text{ W/cm}^2$  [45]

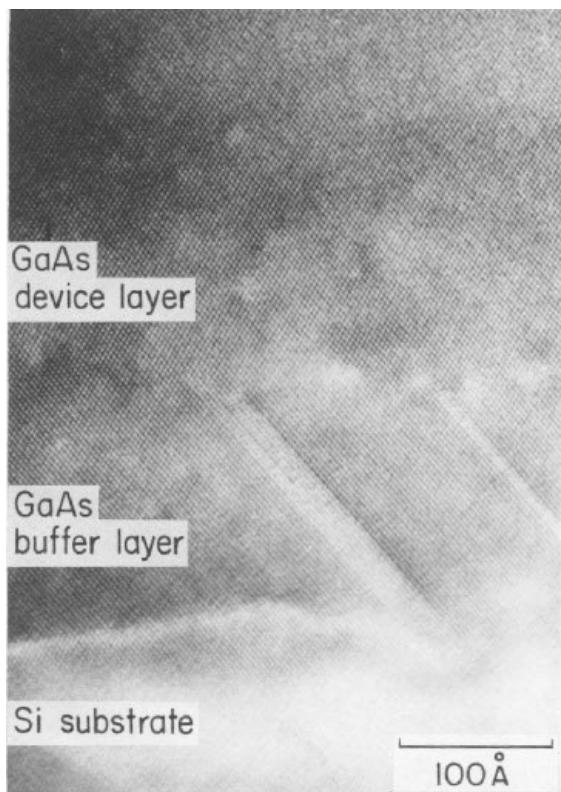
### 3.3.4 Highly-mismatched heteroepitaxy and microchannel epitaxy with MOCVD

Highly-mismatched ( $\text{HM}^2$ ) heteroepitaxy is another important issue in the growth of III-V compounds. Using low temperature buffer layers [46–48], Akiyama et al. succeeded in growing antiphase domain-free (APD-free) GaAs layers on Si substrates [49,50]. Subsequent studies achieved a decrease in the dislocation density to about  $1 \times 10^6\text{ cm}^{-2}$  by using superlattice buffer layers or thermal cyclic annealing or both. But it is not sufficient for the fabrication of devices with excellent characteristics. The subject of dislocation reduction is extensive; in this subsection, we add only some special issues concerning the elimination of defects.

The residual stress in HM<sup>2</sup> heteroepitaxial layers is one of the most important properties; it can even produce dislocations in the cooling stage after growth. Narituska et al. reported a particular example of a good use for the residual stress to eliminate twins in a GaAs layer on (001) Si [51]. They used nominally just (001) Si, within 0.5° misorientation, as a substrate. Usually, use of just (001) Si substrates only leads to the formation of APDs. On the contrary, they obtained an extremely smooth surface of GaAs layers without APDs using a particular thermal treatment on a low temperature GaAs buffer layer. As shown in Fig. 3.27, this included the crystal growth of a buffer layer at low temperature, annealing for 10 min at 700°C, cooling to room temperature, and second annealing at 700°C. The process was named the thermal cycle treatment to buffer layer (TCTBL). The TCTBL brought not only APD-free smooth GaAs surfaces, but also the truncation of twins in the buffer layer. The detailed process was investigated using TEM and SEM observations [52]. Figure 3.28 shows the (001) lattice image of GaAs layer grown on (001) Si substrate with TCTBL. The figure shows that twins generate at the Si substrate surface, and propagate into the buffer layer. However, they disappear at the interface between the buffer and overgrown GaAs layer. The strain on the surface of the buffer layer induced by TCBL might introduce dislocations for destroying the twins. As a result, the upper layer became twin-free. This is an example of stress-assisted epitaxy, which might open up a new field of epitaxy in the near future.

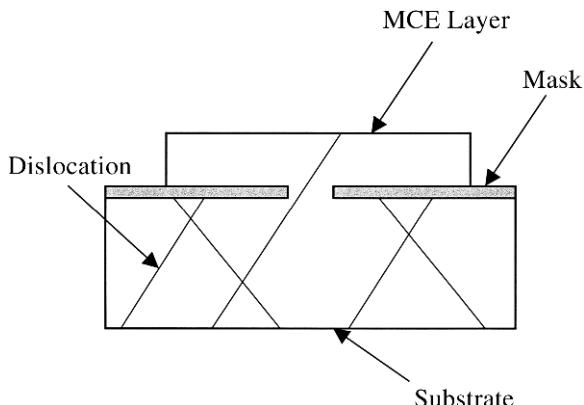


**Fig. 3.27.** Temperature diagrams [52]

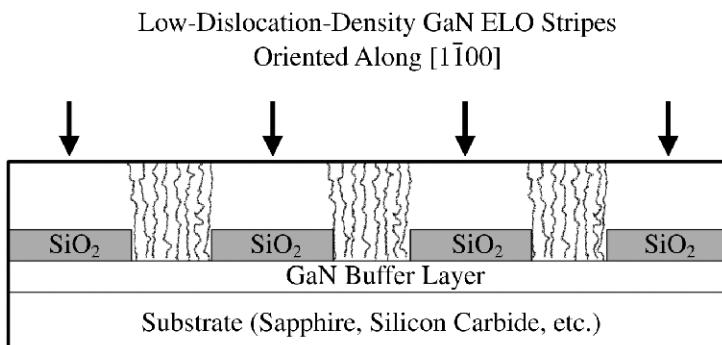


**Fig. 3.28.** The (011) lattice image of GaAs layer grown on a (001) Si substrate using TCTBL [52]

As shown above, the generation of a high dislocation density and large residual stress are the main problems in HM<sup>2</sup> heteroepitaxy. To reduce both dislocations and residual stress, a successful method was proposed by Nishinaga et al. called microchannel epitaxy (MCE) [53,54]. In MCE, a narrow channel is used to transfer only crystal information but not defect information from the substrate. Figure 3.29 shows an illustration of MCE. An opening in a mask acts as a microchannel that transfers crystal information to the overgrown layer, whereas the mask prevents dislocations from transferring to the overgrown layer. Hence, the overgrown layer becomes dislocation free. The 3D structure of MCE also gives it another advantage in stress release. The residual stress can be released effectively because the overgrown layer easily deforms. We have demonstrated these advantages in various kinds of materials including homoepitaxies of Si [55,56], GaP [57], GaAs [53,58], InP [59,60], and heteroepitaxies of GaAs on Si [61–63], and InP on Si [64–67] by employing the MCE technique. These advantages are definitely important for device fabrication because devices with superior characteristics cannot be produced unless the number of dislocations is reduced.

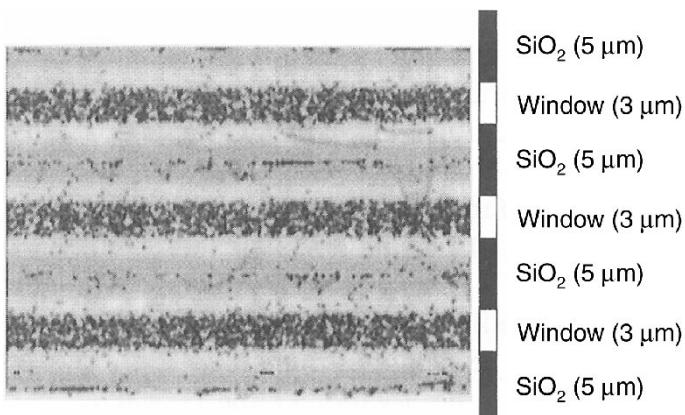


**Fig. 3.29.** Schematic illustration of MCE

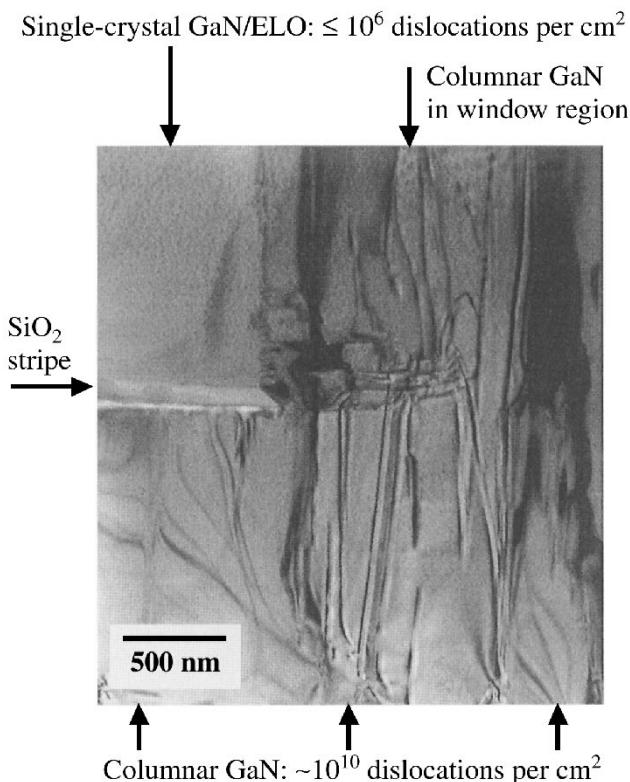


**Fig. 3.30.** Schematic illustration of the MCE process for GaN. The GaN emerging from the window regions has a high density of threading dislocations, whereas the GaN overgrowth on the SiO<sub>2</sub> masks has a drastic reduction in dislocation density [68].

The MCE technique was also applied to GaN growth in MOCVD. Figure 3.30 shows an MCE structure of a GaN layer on an Al<sub>2</sub>O<sub>3</sub> substrate, in which a GaN buffer layer is used to improve the crystallinity. Each stripe of overgrown layer coalesces together, thus forming a flat and uniform surface of MCE [68]. A CL image of the MCE layer is shown in Fig. 3.31 that indicates dislocation-free regions in the overgrown areas [68]. The vertical cross-sectional TEM image in Fig. 3.32 shows that single crystal GaN with low dislocation density ( $<10^6 \text{ cm}^{-2}$ ) was obtained in the region above the SiO<sub>2</sub> mask, whereas columnar, high-dislocation-density ( $\sim 10^{10} \text{ cm}^{-2}$ ) GaN existed in the window region. These GaN layers with low dislocation are quite beneficial for making devices with excellent characteristics. Using MCE, Nakamura et al. has produced laser diodes having very long CW



**Fig. 3.31.** CL image of a GaN MCE layer for which coalescence at the centers of the SiO<sub>2</sub> masks is completed [68]



**Fig. 3.32.** Vertical-cross-section TEM image ( $g = (0001)$ ) [68]

lifetime of more than 10,000 hours [69]. Furthermore, MCE has another advantage for selective growth: devices can be fabricated at any point one wants. For this reason, MCE is very suitable to fabricate future 3D ICs including opto-electronic integrated circuits (OEIC).

If the size of the microchannel is decreased to the nanoscale, a completely new phenomenon will occur where no dislocation is produced at a heterointerface. That is to say, when the width of the MCE is narrower than a certain value, the stress in the layer does not exceed the critical one, above which dislocations start to form. The MCE can be grown heteroepitaxially without the formation of misfit dislocations even when the lattice mismatch is fairly large; this includes pseudomorphic epitaxial growth. Naritsuka estimated the critical width ( $L_c$ ) of the MCE layer in  $\text{HM}^2$  heteroepitaxy [70]. From his estimation,  $L_c$  for GaAs on Si was found to be 440 Å. Namely, we can grow  $\text{HM}^2$  heteroepitaxial material systems as if they have no lattice mismatches.

### 3.4 Summary

Epitaxial growth of III-V compounds was described using molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) as examples. MBE was described first. Elementary growth processes involved in MBE were described using GaAs as a model material. The origin of the mode transition that is observed experimentally in MBE on a vicinal substrate was discussed. This model assumes that 2D nucleation occurs on the terrace between steps at supersaturations above a critical value. With this model, the growth rate and the inter-step distance dependencies of the mode transition temperature were explained.

The elementary growth processes were discussed based on measurements of the incorporation diffusion length. The experiments show that the arsenic pressure dependence of the incorporation diffusion length is different in different ranges of the arsenic pressure. From the dependencies, it was concluded that on (001) surfaces  $\text{As}_4$  molecules decompose to give active arsenic elements for the growth at lower arsenic pressure, while at high arsenic pressure two  $\text{As}_4$  molecules react to give active arsenic elements, which agrees with the model given by Foxon and Joyce. Intersurface diffusion was studied and it was concluded that the factor governing the direction of the intersurface diffusion is the incorporation lifetime of Ga, which depends on the available number of growth sites and the arsenic pressure. The former depends on the step density and hence on the nucleation rate, which is influenced by the type of surface reconstruction.

In the second part, a short review of up-to-date MOCVD technologies was described. For the growth of high-purity materials by MOCVD, understanding the incorporation mechanism of impurities is extremely important. For this purpose, *in situ* monitoring becomes very useful. The elementary growth process of MOCVD was discussed, and we pointed out some similarities between elementary processes in MOCVD and MBE. Understanding of the growth mechanism often gives rise to new growth technologies. As examples of such newly-born technologies in

epitaxial growth, nanostructure fabrication and highly-mismatched (HM<sup>2</sup>) heteroepitaxy were described. By understanding basic growth phenomena such as step-bunching or nucleation in SK mode, fabrication of nanodot and wire structures became possible. MCE in HM<sup>2</sup> heteroepitaxy is a very promising technique for both decreasing the dislocation density and reducing the residual stress. MCE will open new fields of epitaxy, which should enable the growth of novel materials that have not yet been studied in detail. We conclude that thin-film growth technologies such as MBE and MOCVD will open a new era that will realize the potential of devices such as OEICs.

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# 4 CVD Diamond Growth

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## 4.1 Introduction

Diamond is becoming an increasingly important material in the recent decades. The unique predominance of diamond that brings together both excellent physical and chemical properties shows its promise for applications in many areas. However, the rarity and the high cost of natural diamond have severely limited its applications and thus has stimulated scientists to search for methods to synthesize diamonds.

The first successful synthesis of diamond was reported by Bundy and co-workers (1962) [1]. They used the high pressure and high temperature (HPHT) technique in which diamond was prepared at 8 GPa pressure and 1500 °K, and graphite was the source of carbon and Fe, Ni, and Co were used as catalysts. After that the HPHT technique was developed by many researchers. Until now diamond for industrial consumption has been produced mainly from the HPHT synthesis method.

Other synthesis methods of diamond were also found. It's known that the hydrothermal process may be responsible for most natural diamonds. Using this idea, diamond from metal-carbon solution was reported in 1990 and there is now a revival of interest in synthesizing diamonds hydrothermally in the laboratory [2].

Owing to the cost of production and the small size, applications of diamond prepared by the above techniques were always limited, unlike those of natural diamond. Diamond film formation under relatively low pressure and temperature has always been a dream of researchers. Fortunately, Russian researchers reported the successful growth of diamond from a gas phase under metastable conditions in the 1960s. The major breakthrough in diamond growth using the chemical vapor deposition (CVD) method was reported by Spitsyn et al. [3], and after that the hydrocarbon and hydrogen gas mixture has been widely used as a basic gas source in diamond growth systems.

Many CVD techniques have been used to prepare diamond. The growth rates of polycrystalline diamond from different methods vary from several microns to several hundreds of microns per hour. Although the techniques are different, the growth conditions are very similar, that is 10 to 100 Torr pressure, 700 to 1100°C

substrate temperature, and about 1% C/H ratio. The results show that the properties of polycrystalline diamond films are close to that of single crystal diamond. With the development of CVD techniques diamond films have the commercial potential to surpass the HPHT diamond technique.

Although diamond can be routinely produced using a myriad of techniques, our understanding of the deposition mechanism of metastable diamond is far from complete. It is known that the saturated atomic hydrogen must be present in the growth process of diamond film, but there is no satisfactory model available to explain it until now. Therefore, scientific interest in diamond CVD processes stems not only from the potential applications, but also from the need to understand the formation processes of diamond under apparently metastable conditions.

## 4.2 Preparation and Application of CVD Diamond Film

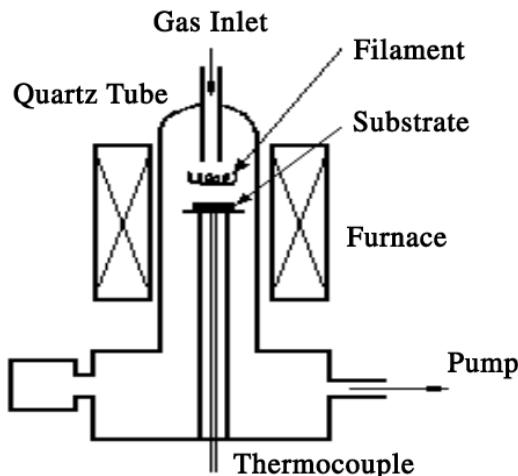
### 4.2.1 Preparation methods

Numerous chemical vapor deposition techniques are used to produce diamond films, since diamond can be successfully synthesized from the gas-phase activation condition. These techniques are grouped into four categories: thermal activation, plasma activation, laser ablation, and combustion flames. Beside CVD, most of the physical vapor deposition (PVD) techniques have also attempted to synthesize diamond at low temperature recently. Here, the authors will introduce three kinds of CVD technique for diamond film preparation.

#### ***Hot-filament CVD (HFCVD)***

The schematic diagram of a hot-filament CVD apparatus is shown in Fig. 4.1. This technique was first reported by Matsumoto et al. (1982) [4]. One or multiple filaments, such as W, Ta, and Re, are mounted near the substrate and electrically heated to over 2000°C, where the simultaneous production of atomic hydrogen during the hydrocarbon pyrolysis will promote the growth of diamond film. Therefore, the filament temperature plays an important role in the diamond deposition process in HFCVD. The substrate temperature is measured by a thermocouple placed under the substrate and controlled to between 700 and 1100°C. The gas source usually is the mixture of 99% hydrogen and 1% methane. Diamond films are formed at chamber pressures between 10 and 100 Torr. Depending on the deposition conditions, such as the properties of the substrate surface, methane concentration, filament or substrate temperature, the growth rate of diamond films is from 0.5  $\mu\text{m}/\text{hr}$  to several  $\mu\text{m}/\text{hr}$  and the surface morphology and the quality of diamond films also vary.

In the case of HFCVD design, a modification has been developed. A moderately positive voltage and negative voltage are put to the substrate and to the filament, respectively. This is the so-called electron-enhanced HFCVD technique.



**Fig. 4.1.** Schematic diagram of the hot-filament CVD apparatus

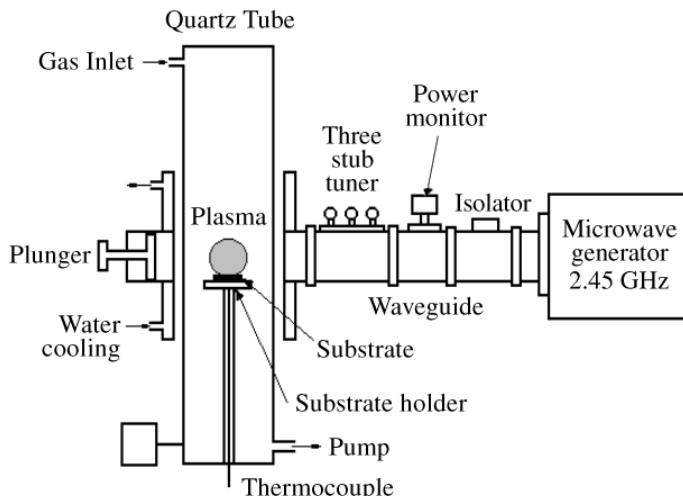
The application of DC bias results in electron or ion bombardment to gas species that promote the decomposing reaction of the gas species. In addition, electron or ion bombardment to the substrate also enhances the desorption of the surface hydrogen and the diffusion of carbon-containing species on the substrate surface.

HFCVD technique is a simple method compared to others used in the growth of diamond film under low pressures. Large areas of deposition of diamond films ( $\sim 30$  cm in diameter) and highly-oriented diamond films have been realized by this technique. Therefore, it is also the most popular method for the growth of CVD diamond film. However, a series of problems including carbonization and distortion of the filament at high temperature and contamination of the metal filament onto the deposited diamond film were discovered. Hence, the carbide-forming pretreatment of refractory metal filaments is necessary for the deposition of diamond film.

### ***Microwave plasma-assisted CVD***

A schematic diagram of microwave plasma-assisted CVD (MPCVD) is shown in Fig. 4.2. It was first applied to the diamond film area by Kamo and colleagues at NIRIM in 1983 [5]. Like hot-filament CVD technique, microwave plasma-assisted CVD technique is also thought to be potentially applied in the industrial production of diamond films.

First, a gas mixture of hydrogen and methane or hydrocarbon is provided into a reaction chamber that contains the substrate to be coated. Then microwave power with a typical excitation frequency of 2.45 GHz is coupled into the chamber in order to create a discharge. High ionization fractions are generated as oscillating electrons collide with gas molecules and form the so-called microwave plasma.



**Fig. 4.2.** Schematic diagram of the microwave plasma-assisted CVD apparatus

The ions formed do not destroy the substrate surface and the deposited diamond film due to their low kinetic energy. Generally, the growth rate of diamond film with the MPCVD technique is in the range of several micrometers per hour.

The technique has found a lot of success because of its simplicity, flexibility, and the early commercial availability of reactors from New Japan Radio Corporation based on the work at NIRIM. The first successful deposition of highly-oriented diamond film was reported using this technique in 1993 [6,7]. The quality of diamond films produced with this apparatus is outstanding as judged by their optical transparency and thermal conductivity [8].

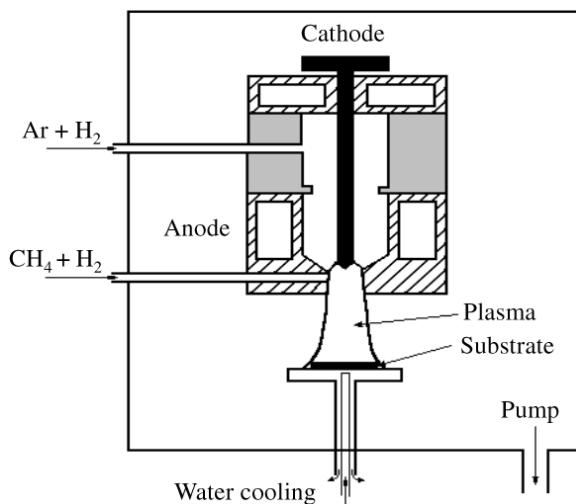
However, it is very difficult to prepare a large area of diamond film due to the size limitation of the standing wave cavity. In addition, the plasma stability and shape during the process of creating diamond film is another problem to be improved upon. These problems can be partially overcome by using a larger plasma with higher microwave power. A new reactor with 915 MHz has been designed to produce the diamond film. At this frequency magnetron tubes are available at power levels of up to 100 kW continuous power. A manufacturer, AsteX, has finished such a prototype, and with this apparatus diamond films 20 cm in diameter having uniformity of 15% have already been obtained [9]. The deposition rate of diamond film is also increased from 0.5 mg/h to 1 g/h. Recently, Füner et al. (1998) have used a rotational ellipsoid as a reactor cavity instead of the conventional cylindrical shape [10]. The position of this new design is very stable and independent of gas pressure and microwave power. With these ellipsoid reactors, diamond films of 15 cm diameter have been produced.

### **DC arc plasma jet CVD**

DC arc plasma jet CVD is a modified DC plasma-assisted CVD. DC plasma CVD is another effective technique used to activate a gas source (a mixture of hydrogen and hydrocarbon) for diamond film deposition. Under conditions of high voltage ( $\sim 1$  kV) and current density ( $\sim 4$  A/cm $^2$ ) the substrate temperature is controlled at about 1100 °K by a water-cooling adjusting system. DC plasma-assisted CVD possesses have the ability to produce large areas of diamond films, but are limited by the electrodes and DC power supply.

A schematic diagram of DC arc plasma jet CVD is shown in Fig. 4.3 and is being applied popularly in the deposition of diamond film by researchers in Japan [11]. The advantage of DC arc plasma jet CVD is the significant increase in the growth rate of diamond film. The typical growth rate is several tens of micrometers per hour. Recently, diamond films with a high growth rate of 930  $\mu\text{m}/\text{h}$  and higher quality have been obtained using DC arc plasma jet CVD and supply the need for a tool-cutting coat and heat sink in electronic devices. However, the thickness uniformity of diamond films is expected to be enhanced.

In addition, other methods, including electron cyclotron resonance (ECR) microwave plasma-assisted CVD [12,13,14], combustion flame CVD [15,16,17], and laser ablation CVD [18] were reported in the recent decade. Among these, the most popular method is the combination of DC-plasma or MW-plasma with HFCVD [19,20,21]. Therefore, the success of CVD diamond films enables the wider application of diamond films to be likely. Similarly, the study of preparation methods of diamond films also promotes the development of CVD techniques.



**Fig. 4.3.** Schematic diagram of the DC arc plasma jet CVD apparatus

## 4.2.2 Applications of diamond film

Interest in CVD diamond film, which is deposited from the gas phase, is replacing natural or HPHT diamond in the market. CVD diamond film inherits part of the outstanding properties of single crystalline diamond and is finding applications where bulk diamond is usually used. With the development of CVD diamond film, one can see a tremendous range of possibilities, the most exciting of which seem to be in active electronics, and the most immediate as abrasive or cutting tool coatings and heat sinks or other passive substrates for electronic circuitry.

### ***Properties and general applications***

In the diamond structure, each carbon atom is covalently bonded to four other atoms with  $sp^3$  tetragonal bonds. The stable  $sp^3$  structure enables diamond to possess many excellent properties as shown in Table 4.1 [22,23].

**Table 4.1.** Some of the Outstanding Properties of Diamond [22,23]

	Properties	Diamond
Mechanical properties	Density	3.51 g/cm <sup>3</sup>
	Hardness	10 <sup>3</sup> kg/mm <sup>2</sup>
	Young's modulus	1200 Gpa
	Bulk modulus	1040 Gpa
	Compressibility	4.0 Gpa
	Friction coefficient	0.05–0.1
	Poisson's ratio	0.2
Thermal properties	Thermal impact coefficient	10 <sup>7</sup> W/m
	Thermal conductivity	20 W/cm·K
Optical properties	Thermal expansion coefficient	2.3 × 10 <sup>-6</sup> /K
	Light transmission	225 nm – far IR
	Light absorption	5 μm
Electronic properties	Refractive index	2.41 (590 nm)
	Band gap	5.5 eV
	Dielectric constant	5.5
	Breakdown voltage	3.5 × 10 <sup>6</sup> V/cm
	Electrical resistivity	10 <sup>16</sup> Ω.cm
	Electron mobility	2200 cm <sup>2</sup> /V.s
	Hole mobility	1800 cm <sup>2</sup> /V.s
Acoustic property	Saturated electron drift velocity	2.5 × 10 <sup>7</sup> cm/s
	Longitudinal sound velocity	18.2 km/s
Chemical property		Inertness

It is known that diamond is the hardest material in the world, and obviously diamond has a great application as a coating on abrasive and cutting tools to prolong their application life. In addition, diamond has the highest bulk modulus ( $\sim 1.2 \times 10^{12} \text{ Nm}^{-2}$ ) and the lowest compressibility ( $\sim 8.3 \times 10^{-13} \text{ m}^2\text{N}^{-1}$ ) compared with other known materials. Diamond is known as the most suitable material for acoustic products, such as speaker diaphragms, due to its large longitudinal sound velocity (18.2 km/s). At room temperature, the dynamic friction coefficient of diamond is only 0.05, as low as that of teflon and the lowest among the materials of interest.

Diamond also has the highest thermal conductivity, which is about 20 W/cm·K at room temperature, roughly four times higher than that of copper. Thermally conducting substrates or “heat sinks” are one of the most imminent of the potential applications of CVD diamond films whose thermal conductivity is close to that of bulk diamond [24]. In fact diamond heat sinks have already been sold in the market now. In general, the diamond films with thickness of about 250  $\mu\text{m}$  are needed. Compared with that of bulk diamond, diamond film heat sinks are likely to make an impact on much larger substrates, such as semiconductor laser repeater assemblies, and subsequently on smaller devices through the advantages of CVD technology.

Diamond is an ideal candidate for optical windows or lenses, especially in extreme conditions since it is optically transparent from the ultraviolet (UV) to the far infrared (IR). The use of polycrystalline CVD diamond film in optics depends mainly on the surface morphology, grain size, impurities, and quality of the film, which determine the transparency and the spectral range of transparency of optical components. At present, the best CVD diamond films with a transparency in the visible spectrum were prepared in the MWCVD chamber [25]. Generally, CVD diamond films are transparent in the range of infrared at least, which seems to be an imminent application of this window material. At the other end of the spectral range CVD diamond film supports are in use for X-ray lithography.

As to its chemical resistance, diamond will oxidize at high temperatures, and dissolve in carbide forming metals, but it is not attacked by other reactions. Diamond coatings could replace platinum in many laboratory applications having an extreme environment.

**Application in electronics.** The electronic properties of diamond, such as wide band gap, high dielectric constant, and electron and hole mobility are prominent in semiconductor materials. Coupled with its excellent thermal properties, diamond would be a promising material for high-power and high-temperature electronic devices. In addition to its other useful electrical properties, diamond has a stable, intrinsic negative electron affinity.

**Doping of diamond.** The realization of *n*-type and *p*-type doping is the key step for diamond application in electronics. The ideal doping is expected to form the substitution solid solution and no other defects are electrically active. This type of doping will not influence the energetic characteristics of the host diamond lattice. To date, boron has been successfully demonstrated to be the only dopant which

exists with the substitution incorporation in the diamond lattice. It makes diamond *p*-type with an activation energy of 0.37 eV [26].

The boron incorporation in CVD diamond film can be achieved by *in situ* doping during the growth process. Toxic diborane, which is the only gaseous form of boron, was widely used during the growth process of CVD diamond film [27,28,29]. Nontoxic and more easy to handle sources in solid form, like boron powder [30] and boron trioxide [31], or liquid form, such as trimethylborate [32], have been successfully introduced. The nongaseous boron sources are usually heated or dissolved in a high-pressure liquid in order to enhance their vapor pressure sufficiently. It was also found that the addition of boron can act as a catalyst to promote the diamond film growth and control the surface morphology of diamond film [33].

The other doping technique for diamond is ion implantation. During the ion implantation process, the temperature is maintained either at room temperature or at 1200°C, but the subsequent annealing is performed at 1400°C. The graphitization of the damaged diamond is its main problem and limits the amount of dopant in the diamond [34]. Using the low diffusivity of point defects created in the implantation, doping of diamond with boron was successfully obtained by combining low-temperature (at 77 °K) ion implantation into the samples that were predamaged by carbon implantation [35].

Recently, it was noted that the *p*-type diamond layer has been produced in polycrystalline diamond by means of rapid thermal diffusion of boron where the deposited boron on thin film is the source and the temperature is near 1600°C [36]. The average sheet resistance of the conducting layer formed is about 356 Ω.cm and the diffused-layer thickness is about 0.6 μm. The advantages of this approach are that a low contact resistance can be obtained and only one high-temperature step is involved.

Unfortunately, the *n*-type doping of diamond has not been completely achieved until now. The potential dopants are nitrogen, phosphorus, lithium, and sodium. However, the low thermal diffusivity of these in diamond matrix does not fit the need of *n*-type semiconductor enough. Most of the attempts on *n*-type diamond have been focused on nitrogen that was introduced into the gas phase with N<sub>2</sub> or NH<sub>3</sub> during the preparation process of diamond film. It was shown that nitrogen couldn't form the ideal substitution doping. Theoretical calculation also shows that nitrogen forms a deep energy level of 1.2 eV below the bottom of the conduction band [37]. Like in the case of boron, the growth rate of diamond film in the nitrogen-containing environment can be increased and smooth diamond films are obtained.

The attempt of phosphorus doping into diamond film has also been reported [38]. Okano et al. (1990) have used phosphorus doping to fabricate a *p-n* junction in CVD diamond film [39]. However, it was dubious whether the *n*-type conductivity was due to phosphorus incorporation into the diamond lattice or to lattice damage due to its extremely low electron mobility. Recently, Koizumi et al. (1997) produced *n*-type diamond films with activation energy of 0.43 eV when phosphorous was introduced during the CVD process [40]. Further studies are required to confirm the success of this work.

**Field-electron emission of diamond.** Diamond has been considered as a cold cathode material due to its negative electron affinity (NEA). Electrons from the conduction band can easily escape from a diamond surface into a vacuum, provided that as they leave they are replaced from another source. Expelling electrons from most materials requires temperatures between 1000 and 3000°C, or electric fields greater than 10 MV per centimeter. Semiconductors such as silicon and gallium arsenide can be given a negative electron affinity by coating them with a thin layer of cesium, but extremely small amounts of water or oxygen can react with the coating and destroy its effect. Once free of the diamond surface, these electrons can be accelerated by an electric field, formed into a beam to strike a target (perhaps a phosphor, which will glow in proportion to the current impinging on it) or modulated by an external signal. Due to the electrons that can easily emit from diamond, vacuum tubes fabricated with diamond cathodes should not be subjected to the factors that limit the life of conventional cathodes. Hence, the cold diamond cathodes could be used in small gas discharge lamps, panel computer and television displays, and perhaps even submicron triodes that would out-perform conventional semiconductors.

The early work on field-electron emission from diamond was done in the beginning of 1990. Geis et al. (1991) fabricated such cathodes of *p*-type single crystalline diamond where a current density of about  $10 \text{ A/cm}^2$  was observed [41]. Givargizov et al. (1995) also obtained a high current density from microcrystalline diamond particles on the tips of silicon [42]. Although single crystalline diamond is not applied widely in flat-panel displays due to its high preparation cost, such studies are beneficial to our understanding of the diamond electron emission process.

The field-electron emission of diamond film has been currently of much interest in the development of CVD diamond [43,44]. As far as such field emission applications of diamond film are concerned, considerable technological progress has been achieved recently with emission thresholds as low as  $1 \text{ V}/\mu\text{m}$  [45]. In fact, CVD diamond films are polycrystalline and contain nondiamond components. Besides the negative electron affinity of diamond, these factors also determine the electron emission from CVD diamond films. Emission results for carbon-based emitters strongly depend upon the materials phase purity, dopants, and surface treatment.

By comparison of the different doped diamond samples, Geis et al. (1995) found that the best emission was obtained from nitrogen-doped diamond samples, followed by carbonized polymer, the lithium-doped, polycrystalline phosphorus-doped diamond films, and boron-doped diamonds [46]. All samples had enhanced emissions compared with undoped diamond, except for boron-doped samples. This was proven by Sowers and colleagues (1999) [47]. Sub-bands or defects formed by N and Li impurities are believed to be responsible for this enhanced emission. Although *p*-type semiconducting diamond is readily available by doping with boron, it is not helpful for achieving low-field electron emission due to the Fermi level of 5.0 eV below the vacuum level. Therefore, a reliable shallow *n*-type dopant for diamond is needed for the low-field and efficient electron emission of CVD diamond films.

The effect of defects on electron emission of diamond films was studied by Zhu et al. (1995) [48]. They have found that the threshold electric field required to generate sufficient emission current densities for panel display applications ( $>10$  mA/cm $^2$ ) can be reduced when the diamond is grown so as to contain a substantial number of structural defects. The succeeding works of these authors have further confirmed the role of defects by reporting the effects of ion bombardment on the field emission characteristics of CVD diamond films [49]. They believed that the defects create additional energy bands within the band gap of diamond and thus contribute electrons for emission at low electric fields.

Surface states below the conduction band of 1 eV are supposed to be attributed to the electron emission of diamond [50]. In fact, surface states do exist in the band gap on reconstructed diamond surfaces [51]. However, this viewpoint does not explain that the non-surface-reconstructed or H-terminated diamond films, where there exist no surface states, also can emit electrons. In addition, it is also not known how the electrons are transported to these surface states to sustain the emission from the undoped or *p*-type-doped diamonds.

As mentioned above, the carbon phase also influences the electron emission. Recently, a few other carbon materials, such as nanodiamond [52], diamond-like carbon [53], carbon nanotubes [54] and nanostructured carbon films [55] can also emit electrons. However, the emission mechanism of these materials is not completely understood but seems to be related to a substantial geometric enhancement factor or perhaps an electrical field enhancement created by highly nonuniform electronic properties over short (nanometer) distances.

Indeed, the electron emission of diamond cathode is limited for practical purposes by three factors, which include the large area heteroepitaxy of diamond film, the resistance of the conducting substrate that supplies it with electrons, and the mechanism of electron emission of CVD diamond films. However, with the development of CVD diamond film the application of field electron emission has never been seen as uncertain. Recently, the success of the 1"  $\times$  1" diode display of diamond was reported by American Si-Diamond Company. It reveals the application potentials of CVD diamond films.

## 4.3 Nucleation and Growth of Diamond Films

### 4.3.1 Homoeptaxy of diamond film

For electronic applications of diamond films there is great interest in the growth of high-quality single-crystal diamond film. Early in 1990s the diamond deposition on natural or high-pressure-synthesized diamond substrate was successfully achieved by many research groups [56,57,58]. This kind of diamond growth mode is called homoeptaxy. Although the diamond application with the homoepitaxial method is greatly limited by the cost of natural diamond and the small size ( $<0.5$  mm) of high-pressure-synthesized diamond crystals, homoepitaxial growth studies

promise to be extremely useful in advancing our understanding of the growth mechanism.

An understanding of the growth mechanism of diamond film is necessary to explain the variation in growth rate and surface morphology observed for deposition on the low-index faces of diamond. Investigation of homoepitaxial growth shows that the diamond growth rate decreased in the order (110), (111), and (100) [59,60]. Doping with boron during deposition can change the growth rates of diamond crystalline faces. Growth rates of (110) and (100) faces were significantly increased to 14 and 6.6  $\mu\text{m}/\text{hr}$ , respectively, whereas a decreasing growth rate was observed on the (111) face [61].

Flat films were observed only on the (100) face, while (110)- and (111)-oriented diamond film surfaces have been rough on the  $\mu\text{m}$  scale. Sutcu et al. (1992) have studied the surface morphology on the nanometer to micrometer scale of homoepitaxy diamond films using atomic force microscopy [62]. Their observations showed that (100) epitaxial films displayed a growth-condition-dependent morphology: rough on the  $\mu\text{m}$  scale with pyramidal features and penetration twin at a low substrate temperature and  $\text{CH}_4$  flow; and nearly atomically smooth at higher temperature and hydrocarbon flow rate. The facts imply that the growth predominantly at steps, ledges, or kinks occurs much faster than nucleation of a new layer when the hydrocarbon mole fraction and the substrate temperature are increased. However, the (110) surface of diamond film is found to be extremely smooth on the nm scale, which suggests that the gross morphology is built up from one- or few-atom-high steps and kinks and that growth occurs preferentially at these low-coordination sites.

The films on (111) face of diamond with a high degree of defects and cracks have been observed by many authors [59,61,63]. It is believed that the cracking is a consequence of tensile stress, which is caused by unequal thermal expansion coefficients of the substrate and diamond film. The cause of the increased thermal expansion coefficient in the (111) film is still unclear, but Raman spectra study shows some incorporation of amorphous carbon into the film. In addition, several authors have also reported that stacking-fault formation and twinning are ubiquitous in (111)-oriented growth, and either of these cracks may be responsible [64,65]. A high degree of defects and twins were also usually found in the boron-doped (111)-oriented diamond films.

### 4.3.2 Heteroepitaxy of diamond film

#### ***Nucleation process***

It is known that the initial nucleation step of thin film is an area of importance that has bearing on adhesion, film properties, and the type of substrates that can be successfully deposited. Unlike homoepitaxy, the biggest problem of diamond film deposited on mirror polished nondiamond substrate is that it is more difficult for diamond nucleation due to its higher surface free energy ( $6\text{--}9 \text{ J/m}^2$  for low-index faces) than for heterosubstrates and also the relatively low sticking probability of

the precursor of diamond nucleation. Without surface pretreatment, the diamond nucleation density only reaches  $10^5/\text{cm}^2$  which isn't high enough for heteroepitaxial growth of diamond film. Therefore, the low diamond nucleation density on nondiamond substrates has been an obstacle for heteroepitaxy and the wide application of diamond film.

In order to enhance the diamond nucleation density on heterosubstrates, many pretreatment methods have been developed. They may be grouped into four major categories: (1) diamond powder scratching of the substrate surface [66,67]; (2) predepositing the buffer layer on the substrate surface [68,69]; (3) electrochemical etching [70,71]; and (4) bias-enhanced nucleation method [72,73]. Of these methods, the bias-enhanced nucleation method is reported to be the best way to increase the diamond nucleation density on nondiamond substrates and to better realize the heteroepitaxial growth of diamond films, followed by diamond powder scratching.

Diamond powder scratching of the substrate surface using mechanical and ultrasonic techniques is usually done before the deposition of diamond films. The common density of diamond nucleation is about  $10^8/\text{cm}^2$ , three orders of magnitude higher than that of the substrate without pretreatment. The nucleation enhancement by diamond powder scratching is first attributed to the presence of defects and sharp edges on the substrate surface. It was known that the large density of defects and sharp edges can provide the high-energy nucleation sites (unsaturated bonds) which can capture carbon atoms rapidly enough to directly form the critical diamond nuclei. It has also been proposed that surface defects or pseudomorphic lattice matching reduce the free energy of diamond, compared with graphite, and thus stabilize the diamond nucleation. This view can also explain the nucleation enhancement by the electrochemical etching method, where it was found that almost all the diamond nuclei grow at the edge of the etched pores on porous silicon substrate [70].

It is thought that the seeding effect also promotes the increase of diamond nucleation density by diamond powder scratching. Iijima et al. (1990) found a diamond residue of  $\sim 100\text{ nm}$  on the diamond-abraded substrate surface [74]. This observation strongly implies that presetting is indeed responsible for nucleation enhancement by promoting diamond-on-diamond growth.

In 1991, Yugo et al. reported that the nucleation density of diamond was greatly increased to over  $10^{10}/\text{cm}^2$  when the negative bias at the substrate was used [75]. Thereafter, the bias-enhanced nucleation is usually applied in the CVD diamond film process. The first successful growth of high textured (100) diamond film was reported by Stoner and Jiang et al. using the MW CVD technique in 1993 [6,7]. It was also reported in the hot-filament CVD system in 1995 [76]. The bias-enhanced nucleation method allows for control of the nucleation density and film morphology and offers a better potential for heteroepitaxial diamond film growth. However, the mechanism remains unclear so far.

It is known that the bombardment of an active gas species to the substrate surface is very important for the deposition of thin film in physical vapor deposition. The bombardment effect not only provides the large active sites on the substrate surface for the precursor, but also promotes the diffusion of adsorptive species on

the substrate surface. The effect also exists in the CVD process. It is out of question that the negative bias application at the substrate enhances the bombardment effect, where the impact of the positive gas species hastens the movement of the diamond precursors on substrate surface and gets them together regularly to form the orientation nuclei of diamond. Tomelini et al. (1991) also found that the ion impact could increase the defect density (such as point defects, steps) on the substrate surface that were like the high-energy sites for diamond nucleation [77]. It was proven by Wang et al. (1997) who directly observed the micro-pit caused by ion impact, with the atomic force microscope technique [78]. In the bias-enhanced nucleation process, Sattel et al. (1996) found that peak values of the nucleation density always correspond to ion energies in the range of 70 to 90 eV, independent of the methane concentration used [79]. Further studies by these authors have shown that the range of ion energy is close to the optimum energy for ion subplantation, responsible for  $sp^3$  bonding in diamond-like carbon. They thought that it was the key process for diamond nucleation. The diamond crystallites only along the  $<001>$  axes in the flow direction of the bombarding ions are usually obtained, but no proper explanation is available.

Although the explanation of ion bombardment for negative bias enhanced nucleation is widely accepted [80], it also encounters a series of problems. It is found that using the positive or AC bias can also enhance the nucleation density of diamond on mirror-polished substrate surface [81,82]. This phenomenon can't be completely explained by the ion bombardment effect. Hence, Chen et al. (1995) suggested that the electron emission from diamond surface is the key to nucleation enhancement [83]. The high electron emission accelerates the dissolution of hydrogen molecules and other gas species and increases the concentrations of atomic hydrogen and hydrocarbon species near the substrate surface, thereby enhancing the nucleation density of diamond. It is deduced that the growth of diamond (111) facet is suppressed or etched due to its low work function compared with the (100) facet and therefore displays the (100) orientation of diamond nuclei. Shigeato et al. (1993) also suggested that the impact of accelerated ions or electrons on gas species changes the chemistry near the substrate surface [84,85]. However, the study of *in situ* optical emission spectra shows that the variety of atomic hydrogen and hydrocarbon species is not as great as the nucleation density of diamond.

Stoner and Glass (1992) found that biasing pretreatment creates a layer of non-crystalline carbon, however, increasing substrate temperature promotes the formation of a sublayer of SiC by reaction with the Si substrate [86]. The formation of a SiC buffer layer was also observed by other researchers [87,88,89]. Hence, the SiC buffer layer possibly plays an important role in promoting diamond nucleation. Also the SiC interface prepared by microwave-assisted growth has been identified as crystalline  $\beta$ -SiC, while an amorphous SiC layer was found in the case of biased hot-filament CVD process. However, the SiC buffer layer may be a competitive carbon reaction channel and not a necessary condition for the diamond growth, because the final formation of the SiC layer is achieved in only ~2 min, long before diamond nucleation occurs. The results of Williams et al. (1990) indicated that a deposited SiC layer on silicon substrate didn't promote diamond

nucleation [64]. Therefore, the formation of a SiC intermediate layer along with seems to be an inadequate explanation for the nucleation enhancement.

Recently, our group used a novel bias method that is applied parallel to the substrate surface [90,91,92]. The typical features of this new method are: (1) the substrate is not biased to avoid the ion or electron bombardment of the silicon surface; and (2) the pretreatment process of the silicon substrate is isolated from the growth process. Using this method a significant increase in diamond nucleation density was also found. The nucleation density on silicon substrates pretreated by the discharge at room temperature is similar to that treated at high temperature. Due to no obvious impact of charged particles, it was suggested that the increase in hydrocarbon concentration leads to the formation of a thin amorphous layer and thus promotes the diamond nucleation on the substrate surface. In the conventional substrate bias process, the formation of amorphous carbon was also found and is obviously beneficial for the nucleation of diamond [93]. The results of Chiang et al. (2000) also showed that surface pretreatment would introduce a substantial amount of carbon species on the substrate surface and that was the primary reason for the enhancement of diamond nucleation [94]. As mentioned above, the diamond nucleation density could be enhanced by amorphous carbon deposited on the silicon surface. The amorphous carbon layer can offer the nucleation sites and saturated carbon for diamond nucleation. On the other hand, amorphous carbon contains  $sp^2$  and  $sp^3$  components and the application of high temperature for normal diamond growth dissolves the  $sp^2$  bonded carbon faster than  $sp^3$  structures, and eventually there are more  $sp^3$  clusters on which the diamond can grow. Additionally, Geyber et al. (1994) observed that diamond crystals 5 nm in size were embedded in the amorphous carbon after bias pretreatment [95]. A similar result was also reported by Zarabian et al. (1997) using the electron cyclotron resonance technique at room temperature [96]. Therefore, another possibility for amorphous carbon enhanced nucleation might be that the diamond nucleates on the nanodiamond particles embedded in the amorphous carbon.

**Growth process.** Single crystal silicon has been used as the most common substrate for diamond film due to its low cost and compatibility in electrical device applications. In addition, it is one of the substrates on which the heteroepitaxial growth of diamond film was first achieved. Therefore, much of the understanding of CVD diamond film, including nucleation and growth process, is based on this kind of substrate. To date, the heteroepitaxial growth of diamond films on silicon have only been observed either in MWCVD chamber or in HFCVD chamber. And as stated above, the application of the negative electrical potential to the substrate plays an important role in the nucleation process.

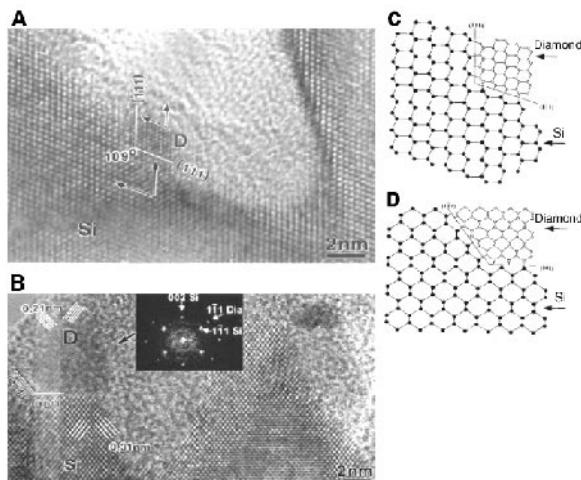
In the initial stage of CVD diamond film deposition an amorphous carbon layer or SiC layer was usually found to form on the silicon surface. The role of the intermediate layer in CVD diamond deposition is still a controversy, because it has also been shown by using cross-sectional transmission electron microscopy that diamond could be grown directly on silicon substrate without any intermediate buffer layer [97]. A recent study by Lee et al. (2000) implied that the diamond nucleation site is important to the epitaxial growth of diamond [98]. Cross-section

HRTEM in Fig. 4.4 shows a grooved Si morphology onto which a predominantly amorphous carbon is deposited and no SiC crystallites were found. Some diamond crystallites have grown directly on Si, and some are embedded in the  $\alpha$ -C matrix. Two nucleation sites in Fig. 4.4 for the diamond crystallite directly grown on Si contribute to the epitaxial growth of diamond. Therefore, a mechanism for the heteroepitaxial growth of diamond is suggested, in which etching of the nondiamond carbon binder exposes and removes nonadherent nanodiamond nuclei, leaving intact only those directly nucleated on the silicon substrate.

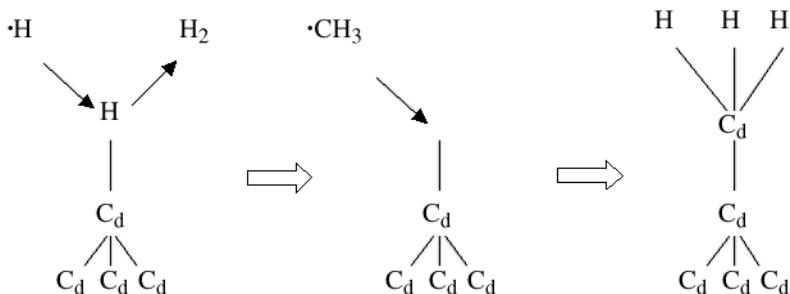
An understanding of diamond film growth under CVD conditions is attributed to the role of atomic hydrogen. Figure 4.5 shows the possible reaction process. Atomic hydrogen and methyl radicals, which come into being by thermal or electronic methods, are the important growth precursors for diamond. Generally, the dangling bonds of carbon atoms on the growing surfaces of diamond film were terminated by atomic hydrogen to prevent the surfaces from reconstructing to the graphite-like surface. Due to the stronger H-H bond in molecular hydrogen than the C-H bond, the surface-bonded atomic hydrogen can be abstracted by a gas-phase atomic hydrogen with the formation of a stable molecular hydrogen and lead to activating a vacant site. This process is called the abstraction effect of atomic hydrogen. Then a methyl radical occupies this vacant site to form a new C-C bond, therefore providing a possible extension of the diamond lattice. In addition, atomic hydrogen can etch both diamond and graphite, and the etching rate of atomic hydrogen to the former exceeds that to the latter. Thus, the diamond film can be synthesized under the CVD conditions. These processes indicate that the abstraction of atomic hydrogen and the etching of atomic hydrogen to diamond and graphite on the diamond growth surface influence the growth, growth rate, and the quality of the diamond film.

The growth modes of diamond films were studied by many researchers. Kreutz et al. (1995) reported that screw dislocations in the middle of spirals serve as continuous sources of steps for layer growth producing (111) facets of high crystal perfection on boron-doping CVD diamond using the scanning tunneling microscopy (STM) technique [99]. Godbole et al. (1997) indicated that the basic mechanisms for growth in the (100) and (111) directions could be of a different kind according to the investigations on the hot filament CVD diamond using STM technique [100,101]. A large number of nanofacets exhibit a layer structure which commensurates with the underlying micron-sized parent (100) crystallites, and this is in contrast to their earlier STM studies on (111) diamond crystallites where they frequently observed the presence of screw dislocations. Zhu et al. (1992) reported the observation of a two-dimensional step growth mechanism on (110) faces of diamond films made by an oxyacetylene combustion flame technique [102]. Furthermore, these are some reports available on the step flow growth on (001) diamond substrates [103,104,105,106].

Recently, Han et al. (1999) reported the presence of terraces on (111) facets, and fairly convincing evidence for two kinds of growth mechanisms on (111) diamond facets of the same crystallite by scanning electron microscopy (SEM) is that shown in Fig. 4.6 [107]. Both left- and right-handed spirals were obtained

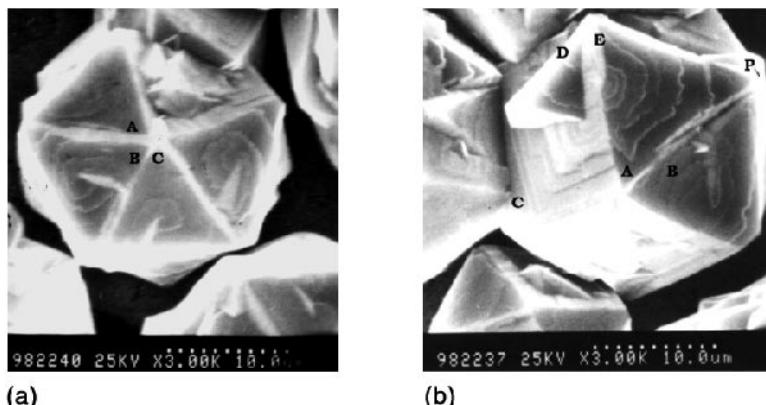


**Fig. 4.4.** (A) HRTEM image of a diamond crystallite (diameter  $\sim 2$  nm) grown directly on a Si step with an epitaxial alignment. (B) HRTEM image of a diamond crystallite (diameter  $\sim 6$  nm) grown directly on a Si (001) surface with an epitaxial alignment. (C) and (D) Ball-and-stick diagrams illustrate the interfaces between the diamond crystallites and the Si substrate in (A) and (B) [98].



**Fig. 4.5.** A possible reaction schemes for the growth of CVD diamond film

on a five-fold multiply twinned particle. According to the classical crystal growth theory of Burton-Cabrera-Frank (BCF), the growth mechanism on singular surfaces can be either a two-dimensional (2D) nucleation or spiral growth. The steps intrinsically connected to a screw dislocation on the original surface, which act as continuous sources of growth steps, winds up to a spiral. Crystals grown that way are of high perfection. On the other hand, 2D nucleation and step flow are used to elucidate those features of facets A and D in Fig. 4.3(b). When the facet is free of screw dislocations, some impurities segregated onto the underlying diamond substrate surface might act as nucleation sites in the initial growth stage, resulting



**Fig. 4.6.** Scanning electron micrographs of diamond film. (a) A five-fold twin particle. Facets B and C show right- and left-handed spirals, respectively. (b) A multiply twinned particle. Facet A shows some terraces by step flow growth mode; facet B shows a spiral growth [107].

in 2D nucleation on the edge or apex of terraces, which have a lower nucleation barrier than the center. Then, those precursors for diamond growth reach the substrates and migrate onto the surfaces, before being incorporated into macrosteps. These steps adsorb carbon atoms with  $sp^3$  hybridization from the gas phase and flow forward continually until they cover the crystal face completely.

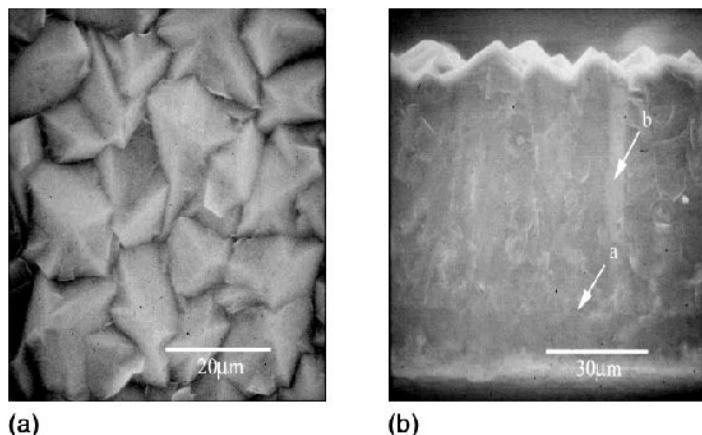
**Substrate materials.** Besides Si, heteroepitaxial or textured growth of diamond has been reported on c-BN [108,109], Ni [110,111], Cu [112],  $\beta$ -SiC [113,114], and BeO [115], in which c-BN showed the most promise as a heteroepitaxial substrate due to its similar structure to diamond, close lattice match ( $\sim 1.3\%$ ) and relatively high surface energy. However, the growth of large single-crystal c-BN is probably as difficult as growing large diamond single crystals. There were some reports on the local epitaxial growth of diamond on Ni or Cu substrate due to their close lattice match with diamond. The large thermal mismatch to diamond makes them unsuitable as substrates for epitaxial growth of diamond film. As mentioned earlier, higher nucleation density and local epitaxial growth on silicon were found through a buffer layer of silicon carbide. It is known that the lattice mismatch between  $\beta$ -SiC and diamond is rather large; the following epitaxial relationship  $(100)_{\text{diamond}}//(100)_{\beta\text{-SiC}}$  and  $[110]_{\text{diamond}}// [110]_{\beta\text{-SiC}}$  found by Stoner et al. (1992) probably indicates such a lattice mismatch couldn't prohibit heteroepitaxy. The theoretical studies of the interfaces between diamond and c-BN or BeO show that BeO is, like c-BN, a potentially suitable substrate for heteroepitaxial growth of diamond film [116,117,118]. The BeO/diamond adhesion energy was estimated to be  $4.6 \text{ J/m}^2$ , slightly smaller than that of c-BN/diamond ( $5.4 \text{ J/m}^2$ ). The success of diamond epitaxial growth on BeO substrate and the easy synthesis of high-quality large BeO crystals seem to bring us the hope of heteroepitaxial growth of CVD diamond film. However, attention must be paid to the fact that BeO is a toxic ma-

terial, which complicates processing. Here, the authors emphasize some other substrates recently reported as having some novel possibilities.

Recently, a new kind of material,  $\text{LaAlO}_3$ , was attempted as a possible substrate for diamond film [119]. It was noticed that at about  $460^\circ\text{C}$ ,  $\text{LaAlO}_3$  single crystal undergoes a phase transition from perovskite-like at room temperature to simple cubic structure. Its crystalline direction of (012) changes into (100), and its lattice constant is about  $3.82 \text{ \AA}$  at temperatures above  $800^\circ\text{C}$ , which is close to that of diamond. The lattice mismatch of 7.2% to diamond at high temperature is much smaller than the lattice mismatch between silicon and diamond ( $\sim 52\%$ ). As an insulating substrate, a nucleation density of more than  $10^8 \text{ cm}^{-2}$  was achieved on ultrasonically cleaned wafers. The epitaxial relationship between them was found to be  $(110)_{\text{diamond}}/(100)_{\text{LaAlO}_3}$  [120]. The high quality and no stains found in diamond films are attributed to the better lattice match. X-ray photoelectron spectroscopy (XPS) analysis shows that the diamond film is formed directly on the  $\text{LaAlO}_3$  substrate without a buffer layer. Hence, it may be a good heteroepitaxial substrate for diamond film.

AlN ceramic, a dielectric and passivation material for compound semiconductors, is routinely used as a heat sink for integrated circuits and photoelectric devices [121]. Godbole et al. (1995) have studied nucleation and growth characterization of diamond film on nickel with an AlN buffer layer. It was found that the AlN layer plays a crucial role in limiting carbon diffusion and inhibiting the formation of graphic carbon, while simultaneously enhancing the nucleation and adhesion of diamond film [122]. The similar results of Chen et al. (1996) have supported this effect [123]. Recently, the (100)- and (110)-textured diamond films directly grown on AlN ceramics were reported by Shang et al. (1998) in a hot-filament CVD system [124,125]. Our group has studied the thermal properties of the diamond film/AlN ceramic composite by the photothermal deflection (PTD) technique [126,127]. We have found that the thermal conductivity of AlN ceramic could be greatly improved when diamond film is deposited on it. The unusual stability and very good adhesion of the diamond film on AlN ceramic substrate are attributed to the formation of carbide, and the small thermal mismatch between them make it satisfactory for the application as a heat sink for high-power integrated circuits and electronic devices. So, considering the cost and realistic aspects, the diamond film/AlN ceramic composite may be a more suitable heat sink material than thick diamond film.

It may prove interesting to deposit the diamond film on polycrystalline diamond substrate. It has been found that using homogeneous material as a buffer layer can markedly improve the quality of GaN films due to the exact lattice and thermal expansion match between them [128,129]. It would seem more logical to use a diamond buffer layer in the growth of diamond film. This approach has been successfully employed to obtain high quality diamond films by Liao et al. (1999) [130]. First, a diamond film grown for 4 hours was cleaned using an *in situ* method (such as hydrogen plasma etching) or *ex situ* method (such as strong oxidants), then the sequential growth of diamond film was carried out on this buffer



**Fig. 4.7.** SEM photographs of diamond film with the two-step growth method. (a) (110)-orientation diamond film and (b) the cross section of diamond film [130]

layer for 6 hours. This is called the two-step growth method. By this method two-layer structure, high-quality diamond film with high growth rate was obtained, and is shown in Fig. 4.7. Significant improvement in surface resistivity was also found. The authors believe that the improvement is attributed to the decreasing activated carbon concentration and increasing second nucleation density of diamond on the first diamond layer [130]. The same lattice and thermal stability of the buffer layer is also beneficial to the deposition of high quality diamond film. The buffer layer approach will perhaps enable the evaluation of electronic devices fabricated with this material to commence in the future.

#### 4.4 Phase Diagram and Gas-Phase Species in CVD Diamond Growth Processes

The growth of diamond films on nondiamond substrate by chemical vapor deposition (CVD) was first reported by Spitsyn et al. in the 1970s [3]. This technique was later implemented by Matsumoto et al. (1982) [4]. They used a CH<sub>4</sub> and H<sub>2</sub> mixture as input gases. These pioneering experiments opened new perspectives in diamond applications and were shortly followed by a large number of researchers. To date, different input gas mixtures, such as CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub>, CO/H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub>, and N<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>, different deposition techniques, such as hot-filament CVD, microwave CVD, and combustion flame CVD, have been successfully utilized for diamond film growth. CVD is now a highly reproducible growth process for synthetic diamond films. Although the diamond quality obtained is comparable to single-crystalline natural diamond to some extent, the possibility of including another carbon phase, the polycrystalline nature of CVD diamond films, and their conse-

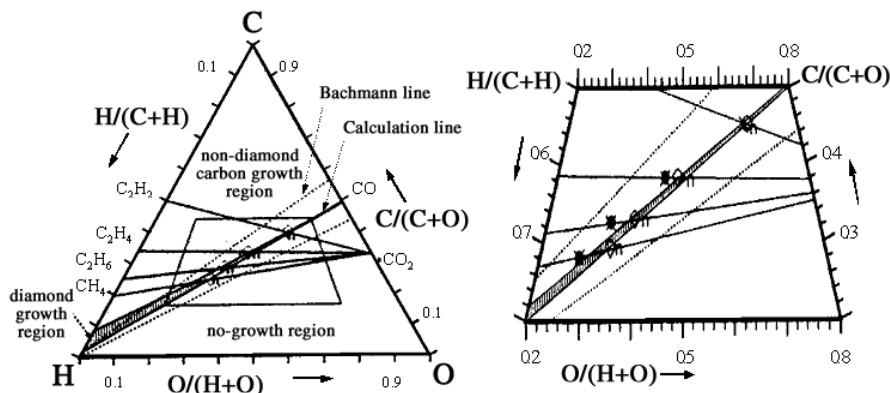
quent high surface roughness still limit its practical application. Many experimental and theoretical works have been produced to better understand the diamond growth mechanism, in the attempt to find the answer to why diamond films can be deposited from these different gas sources by different synthesis techniques.

#### 4.4.1 Phase diagram

Bachmann et al. (1991) have analyzed a number of experiments on diamond growth, and obtained a very important realization regarding understanding the effects of the gas mixtures used in the growth of films [131]. In the ternary C-H-O phase diagram only a restricted region (named the “diamond domain”) leads to the growth of diamond. This diamond domain seems to have the shape of a triangle, nearly centered on the H-CO tie line, with one angle roughly coincident with the H vertex. If the gas composition lies outside this triangle, either no growth occurs (in the region towards the O vertex), or nondiamond carbon phases are obtained (in the region towards the C vertex). Bachmann proposed that if the experimental point is located in the diamond domain, diamond growth should occur irrespective of the gas composition.

From this diagram, we can see that only the overall content of C, H, and O in the gas mixture determines the final outcome of the growth process. By using various kinds of input gases at a given C, H, and O atomic ratio, the same gas-phase environment and diamond precursor should form. Although this scheme is now accepted, there are practical problems in the direct use of this diagram for choosing a gas composition suitable for diamond growth, because careful flow meter calibration is needed, and other experimental parameters, such as substrate temperature and gas pressure, also have strong influences on diamond growth. Even in this region, the growth rate, quality, and morphology of the diamond films grown may be very different. Furthermore, the exact limits of the diamond domain region are still under discussion, so that a new mixture cannot be made to induce diamond growth by just finding the corresponding position in the C-H-O diagram.

Marinelli et al. (1994) have verified this diamond domain by “spanning” the C-H-O ternary phase diagram using several gas mixtures, each consisting of two gases, such as  $\text{CH}_4\text{-CO}_2$ ,  $\text{C}_2\text{H}_6\text{-CO}_2$ ,  $\text{C}_2\text{H}_4\text{-CO}_2$ , and  $\text{C}_2\text{H}_2\text{-CO}_2$  [133]. By varying the relative concentrations of two gases, a line was obtained in the C-H-O diagram for each gas mixture. The lines have been made to cross the diamond domain, and properties of the films obtained by different mixtures also were compared. They found that the borders of the diamond domain deduced from these experiments considerably differ from the ones originally indicated by Bachmann et al. (1991). A very sharp border between the no-growth zone and the diamond domain occurs for higher C concentrations, and coincides with the H-CO tie line. The width of the diamond domain is much narrower, and shrinks while moving away from the H vertex. These results are shown in Fig. 4.8, which compares the triangular C-H-O diagram of the diamond domain proposed by Bachmann et al. (1991) and the



**Fig. 4.8.** Triangular C-H-O diagram for comparison of the diamond domain proposed by Bachmann and the experimental points investigated by Marinelli et al. [132]. The right graph is an enlarged view of the diamond domain region.

experimental points investigated by Marinelli et al. (1994). The right graph is an enlarged view of the diamond domain region. In this figure, the open triangles correspond to the onset of diamond growth; open squares mark the texturing conditions, and filled stars correspond to heavy graphite contamination.

In the C-H-O system, the phase equilibria are dominated by the very stable species  $H_2$  and  $CO$ . As a consequence, only compositions lying above the  $H-CO$  line can produce carbon atoms that are “free” from the  $CO$  ties, and therefore available for the growth of any carbon phase [134]. It should be noted that the substrate temperature and the gas pressure could play an important role, affecting the total extension of the diamond domain. Actually, the Bachmann et al. (1991) phase diagram is a projective diagram in some range of temperature and pressure, which is formed by overlapping of many different phase diagrams, each one having a certain temperature and pressure. So the Bachmann et al. (1991) diamond domain may include nondiamond growth and nongrowth experimental points. Hwang et al. (1993) employed thermodynamics to calculate the theoretical diamond domain [134], and the results are consistent with the experimental points of Marinelli et al. (1994).

#### 4.4.2 Gas phase species

Many ideas have been proposed over the past decade to rationalize the experimental results that diamond can be prepared by chemical vapor deposition. Most of them demand the presence of atomic hydrogen as a primary reactant and assign it to one or more roles, depending on one’s point of view. A popular suggestion was that atomic hydrogen acted as a means of etching graphite rather than diamond and therefore prevented the nucleation and growth of graphite or graphitic

carbons; diamond is kinetically stable relative to graphite in the presence of atomic hydrogen [135]. The vapor phase growth of diamond films can be thought of as the result of two processes. The first one involves reactions in a gas-phase environment to produce the precursor of diamond growth (dissociation); the second one is the process of adding material to the growing solid by the reactions between the precursor and growth surface, and then relaxation of this material to a lower free energy configuration or accommodation to the underlying lattice structure (deposition). These processes have been widely investigated in many experimental and theoretical works. Although the diamond film growth should be a non-equilibrium thermodynamical process, the equilibrium composition calculation can also give general information about the situation in the gas-phase chemical environment.

An established method for evaluating chemical equilibrium is the element-potential method. This is done by assuming that the gas-phase is a mixture of ideal gases and selecting atomic populations by the identity of initial species and their fraction in the mixture, as well as by state parameters [136]. The state parameters can be specified in a number of different ways, including a) temperature and pressure; b) pressure and entropy; c) enthalpy and pressure; and d) volume and entropy.

The basic theory for the element-potential method of determining equilibrium is based on the minimization of Gibbs free energy. The Gibbs function of a system is:

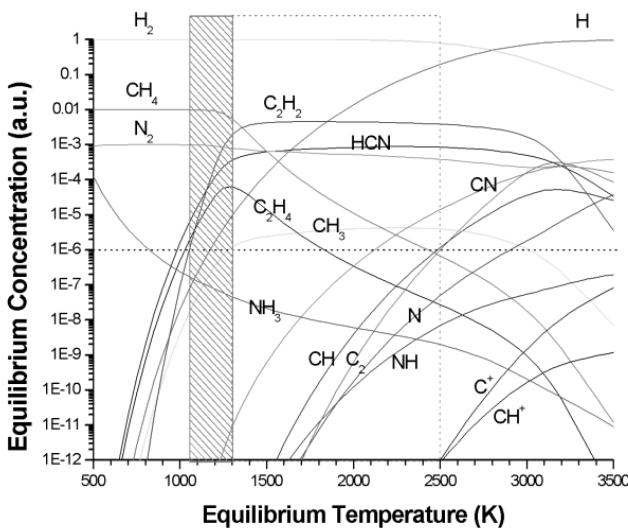
$$G = \sum_{k=1}^K \overline{g_k} N_k, \quad (4.1)$$

Where  $\overline{g_k}$  is the partial molal Gibbs function and  $N_k$  is the number of moles of each species  $k$  in the system.  $K$  is the total number of species. For ideal-gas mixtures or ideal solutions, the partial molal Gibbs functions are given by:

$$\overline{g_k} = g_k(T, P) + RT \ln X_k, \quad (4.2)$$

where  $g_k(T, P)$  is the Gibbs function for the pure species  $k$ , evaluated at the system temperature and pressure;  $R$  is the universal gas constant; and  $X_k$  is the mole fraction of the  $k$ th species. The equilibrium solution at a given temperature and pressure is the distribution of  $N_k$  that minimizes the system Gibbs function.

We have calculated the gas-phase chemical equilibrium with an initial gas mixture of  $\text{N}_2/\text{CH}_4/\text{H}_2$  of 0.1/1/100 mole ratios under constant temperature and pressure. By changing gas temperature in the range of 500 to 3500 K and keeping gas pressure at 10 kPa, we got the equilibrium concentrations of main species versus gas temperature, which include  $\text{H}$ ,  $\text{H}_2$ ,  $\text{C}^+$ ,  $\text{CH}$ ,  $\text{CH}^+$ ,  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{N}$ ,  $\text{NH}$ ,  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{CN}$ , and  $\text{HCN}$ , as shown in Fig. 4.9. The shadow region is the range of substrate temperature for successful diamond growth. The right vertical dot line at 2500 K is the highest temperature that filament can approach in a hot-filament CVD diamond environment. The region between these lines can be taken into account as the virtual gas-phase environment for diamond growth.



**Fig. 4.9.** Equilibrium concentrations of main species in  $\text{N}_2/\text{CH}_4/\text{H}_2$  mixture versus temperature [137]

But the surface chemical reactions and the transportation of gas-phase species were not included in our calculations. In practice, the concentrations of the precursor and active species for diamond growth should decrease in the vicinity of the substrate, and depending on its diffusion coefficient or gas flow velocity, the species created near the filament would still have an opportunity to be diffused or convected to the substrate position. For the homogeneous recombination of atomic hydrogen:  $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ , the characteristic reaction time is of the order 1 s at 20 Torr [138] ( $\text{M}$  is the third body for carrying the excess heat of recombination). The diffusion distance of an atom at time  $t$  is of the order  $\sqrt{Dt}$ , where  $D$  is the diffusion coefficient. For  $\text{H}$  in  $\text{H}_2$  at 20 Torr,  $D = 0.12 \text{ m}^2/\text{s}$ . This implies a diffusion distance of 35 cm in 1 s. When we take into account another reaction path in the presence of hydrocarbon, for example,  $\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2$ , the reaction time is deduced to be about 50 ms for a gas composition of 0.5%  $\text{CH}_4$  in  $\text{H}_2$  [138]. The diffusion distance is shortened to about 8 cm. The typical distance between the filament and substrate is about 1 cm, so  $\text{H}$  atoms in an  $\text{H}_2$  background are able to freely diffuse to the substrate. In the DC arc jet CVD diamond reactor, the high speed reactive gas plume strikes the boundary layer above the substrate, and because the gas speed mostly exceeds the speed of sound, the reactive species haven't enough time to completely recombine in this convection process, and the spatial distribution of the species are influenced by both chemistry and fluid mechanics [139].

Although temperature gradients and finite residence time prevent the gas from attaining chemical equilibrium, the equilibrium composition provides a rough first

approximation to the actual composition [140]. The magnitude of real species concentration should be consistent with the result of the equilibrium calculation.

As shown in Fig. 4.9, the dominant hydrocarbon is methane below about 1500 K, while above this temperature it is acetylene. The reason for this becomes apparent if we consider the reaction:  $2\text{CH}_4 \leftrightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$ . With the equilibrium temperature, the atomic H concentration rapidly increases. Besides  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3$  is also one of the most predominant hydrocarbon species; both these two species have already been proposed as the diamond precursor by many researchers. For the N-containing species, HCN has the highest concentration compared to that of the others because it has the highest chemical stability. Many investigations have suggested that the magical influences on diamond growth observed with the addition of nitrogen to the conventional methane/hydrogen mixture are related to the presence of CN radicals. We can see that the atomic N concentration is very low, and in the high temperature region, the concentration of CN is also high, and it shows a trend to exceed that of HCN.

Species whose concentration is below the 1 ppm horizontal line it hardly have notable influence in the typical thermal environment for diamond growth. But in DC arc jet CVD and microwave CVD diamond reactor, both  $\text{C}^+$  and  $\text{C}_2$  have been proposed as the diamond precursor, and in the electron-enhanced hot-filament CVD diamond reactor,  $\text{CH}^+$  also has been suggested as the active species for diamond growth, because if there are a lot of electrons existing in the gas phase or the gas temperature is very high, both of them strongly change the distribution of gas-phase species.

## 4.5 *In Situ* Diagnostic Techniques for Diamond Growth

Despite the progress made in the past decades, the mechanism of the CVD diamond growth process has remained somewhat a mystery. Considering the two growth techniques just mentioned, the hot-filament system is a thermal system, while the microwave plasma involves processes such as excitation, ionization, dissociation, and ion-neutral reactions. It has always been perplexing that these two techniques, being so different in nature, require nearly identical conditions for diamond growth and produce fairly similar results. When using a microwave source (800 W), with the process pressure at ~20 Torr, a feed gas with methane/hydrogen ~0.5%, and a substrate temperature of 1073°K, high quality polycrystalline diamond films can be produced like in hot-filament (2600°K) operated under the same conditions. The only significant difference being that the growth rate is approximately a factor higher in the microwave plasma [141]. However, that the two techniques would produce nearly identical results appears to suggest that under the conditions necessary for diamond deposition the gas phase kinetics existing in a microwave plasma system are not that dissimilar to those in a hot-filament system. This implies that there must be a uniform dominating mechanism for diamond growth.

The physical properties of diamond films grown using CVD techniques have been shown to be sensitive to the changes in the growth environment. As a result, most studies of diamond CVD attempt to optimize film growth properties by either probing different regions of the reactor parameter space or by changing the identity of the carbon source in the reactor feed. For example, film growth rate and morphology have been shown to be affected by changes in both the surface temperature  $T_s$ , and the carbon mole fraction in the reactor feed  $X_c$  [142]. Although these types of studies identify reaction conditions that promote diamond film formation, they provide relatively little insight into the reaction mechanisms that govern diamond CVD.

In order to understand the relationship between the reactor parameters and the properties of diamond film, and also obtain information about the uniform dominating mechanistic pathways for diamond film growth, many *in situ* diagnostic techniques have been employed for growth environment evaluation. These techniques can provide direct, quantitative or semi-quantitative information for a large number of stable and radical gas species about their energy and spatial distribution. With fast, *in situ* diagnostics, we can efficiently correlate gas phase conditions with film properties such as growth rate, texture, morphology, and uniformity. Experience gained with CVD diamond can hopefully be exploited with similar materials and, ultimately, the results and techniques will be applied during deposition for *in situ* process control.

#### 4.5.1 Molecular beam mass spectroscopy

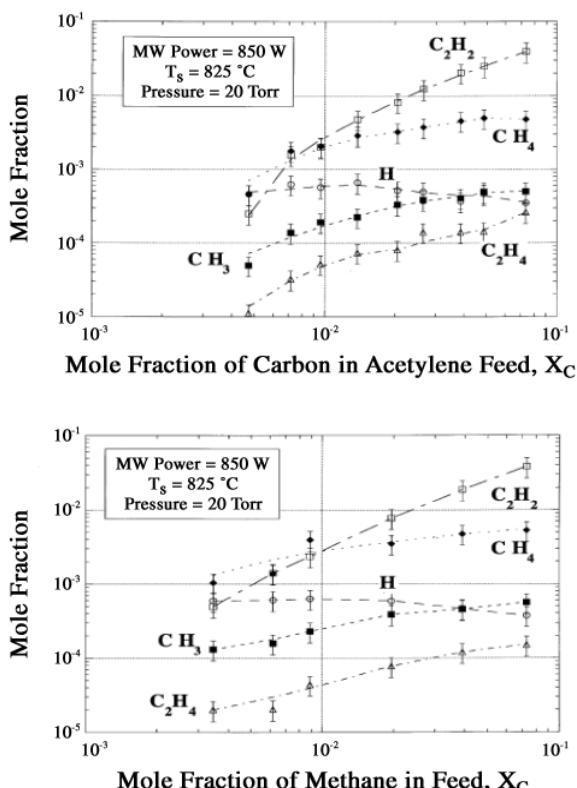
The most useful technique for characterizing the complex diamond CVD gas phase process is molecular beam mass spectroscopy (MBMS), because in the CVD diamond environment (especially for hot-filament system) a large number of neutral species or radicals exist or both neutral and ion forms exist (especially for microwave system). It has the versatility to quantitatively determine the composition of the gas in the immediate vicinity of the growth surface [143], it can detect stable and free radical species, and can be applied to a thermal [144] as well as a plasma environment [145]. The former feature is particularly important since it is the principal species in this region that interact with the surface and directly influence film growth properties.

The molecular beam mass spectroscopy (MBMS) measurements on CVD diamond growth were pioneered by Hsu et al. during the early 1990s [143,144,145,146,147], and then were extended by Rego et al. (1996) and Tsang et al. (1996, 1997) [148,149,150] to cover many important aspects of diamond growth using hydrocarbon, both with and without the presence of chlorine, nitrogen, or phosphorus-containing gases.

Typical mole fractions of species at the substrate under low-pressure diamond CVD conditions in a microwave system are shown in Fig. 4.10, as a function of the carbon content of the feed gas. These results were obtained by McMaster et al. (1995) using molecular beam mass spectrometry, extracting gas through a small

pinhole in the substrate [147]. The microwave power, reactor pressure, and surface temperature were held constant at 850 W, 20 Torr and 825°C, respectively.

We can see that these two figures are very similar, and the species mole fractions are almost independent of whether carbon is introduced into the reactor as methane or acetylene. These results indicate that the identity of the molecular species fed to the MPCVD reactor is lost and the gas phase composition depends only on the C/H ratio of the inlet gas stream. And, in either case, both methane ( $\text{CH}_4$ ) and acetylene ( $\text{C}_2\text{H}_2$ ) are found at the substrate, and these two species account for the majority of the gas-phase carbon. Ethylene ( $\text{C}_2\text{H}_4$ ) is present at much lower levels, and ethane ( $\text{C}_2\text{H}_6$ ) is not detected. Only two radical species, atomic H and methyl radical  $\text{CH}_3$ , are detected under these conditions. The atomic hydrogen mole fraction seems to be nearly independent of the carbon content in the gas, at a level slightly below  $10^{-3}$ . The methyl radical mole fraction rises with increasing carbon content, and is typically about an order of magnitude lower than methane.

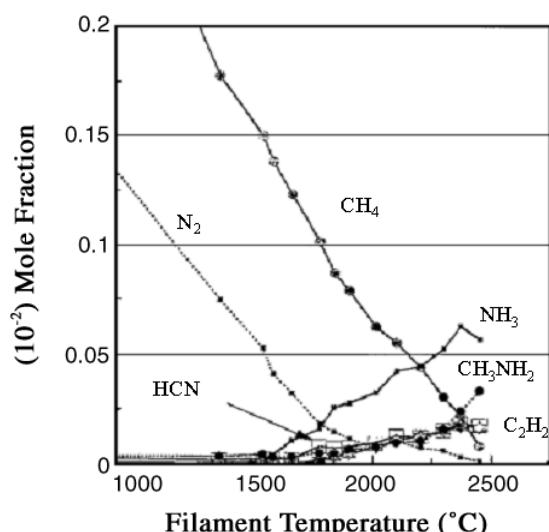


**Fig. 4.10.** Mole fractions measured at the substrate in a microwave plasma reactor as a function of carbon mole fraction in the feed gas  $X_C$ . (a), the carbon is introduced as acetylene, (b) the carbon is introduced as methane [147].

The mole fractions of the microwave system shown in Fig. 4.10 are very similar to those found in the hot-filament system [151,152], the main difference being that there is a sharp decrease in atomic H concentration by about an order of magnitude with the carbon mole fraction increasing in the hot-filament system. Sommer and Smith (1990) attributed this effect to the catalytic poisoning of atomic H production due to hydrocarbon decomposition on the hot-filament surface [153]. And the numerical simulations of the reaction environment predict that the gas-phase reactions will produce only a slight reduction in the atomic H concentration as the hydrocarbon concentration in the feed increases [154]. This prediction is consistent with the results shown in Fig. 4.10.

Nitrogen addition to the conventional hydrocarbon/H<sub>2</sub> mixture has shown significant influences on diamond growth, such as increasing growth rate, inducing (100) texture [155], and decreasing field emission voltage threshold [45]. But the amount of nitrogen incorporation into the diamond films has been found to be very low [155]. Besides N<sub>2</sub> gas, many other nitrogen-containing source gases have been used to investigate the mechanism. To date, the precise reaction kinetics attributed to these observations have not been studied in detail. But these experiments have provided valuable information about the natural processes.

Figure 4.11 shows product distribution of the major stable gas-phase species as a function of filament temperature measured 4 mm from the filament [150], reported by Tsang et al. (1997), and they utilized 0.5% CH<sub>4</sub>/0.5% N<sub>2</sub> in H<sub>2</sub> as the input gas mixture. The methane and nitrogen concentrations decrease steadily with filament temperature, accompanied by a rise in HCN, C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, and NH<sub>3</sub>.



**Fig. 4.11.** Product distribution of major stable gas-phase species as a function of filament temperature measured 4 mm from the filament [150], using 0.5% CH<sub>4</sub>/0.5% N<sub>2</sub> in H<sub>2</sub> as the input gas mixture

concentrations at  $\sim 1700^{\circ}\text{C}$ . Furthermore, in order to investigate the behavior of nitrogen in hot-filament CVD diamond in terms of the changes in the gas-phase chemistry when nitrogen is present, they used different nitrogen-containing sources as input gases, and found the differences in entire gas-phase species concentrations. In these experiments,  $\text{C}_2\text{H}_2$  radicals were detected, which have been proposed by many researchers as precursors for diamond growth [188]. Comparison of the relative concentrations of these major stable species in different nitrogen-containing sources indicates that for a  $\text{CH}_4/\text{N}_2$  gas mixture, HCN concentration decreases to just 1/4 of the original value, with most of the nitrogen-containing species in the gas-phase being  $\text{NH}_3$ , not HCN, but the acetylene concentration is around an order of magnitude greater than that of other nitrogen-containing gases. It is consistent with the film growth result that the  $\text{CH}_4/\text{N}_2$  gas mixture leads to a higher growth rate than that of the others [150]. Atakan et al. (1999) also reported similar results [156]. They investigated diamond CVD in atmospheric acetylene-oxygen flames doped with N-containing species, such as  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{N}(\text{CH}_3)_3$ , and found the growth-effective amount of N-additive decreases by more than an order of magnitude in the sequence  $\text{N}_2 > \text{N}(\text{CH}_3)_3 \approx \text{N}_2\text{O} > \text{NH}_3$ . These results imply that besides the gas-surface reaction, the gas-phase chemistry in the N-doping environment is a more dominant factor for the growth mechanism than the conventional hydrocarbon/ $\text{H}_2$  mixture system.

#### 4.5.2 Laser-induced fluorescence

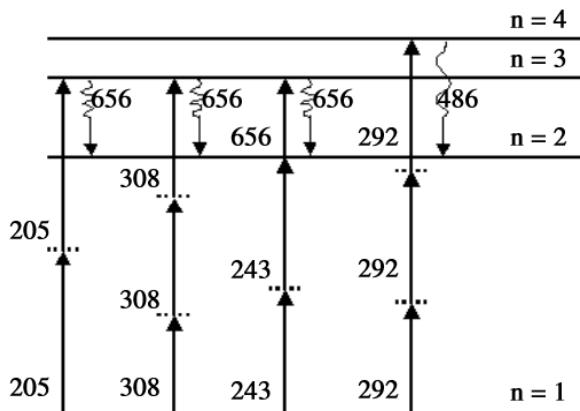
LIF is an optical technique capable of detecting species with good spatial and temporal resolution. Ground-state atoms and molecules can also be observed by laser-induced fluorescence (LIF). In a LIF measurement, the ground-state atoms or species are excited to a selected upper state by absorption of tunable pulsed dye laser energy. This absorption is followed by spontaneous emission of the excited state to lower energy levels. In this situation, emission can also be said to be fluorescence. One of these wavelengths is picked up by an interference filter or spectrometer, then used to record the LIF signal intensity. From measured fluorescence intensities, species or atom concentrations can be determined by calculating the ground-state population.

Several mechanisms have been proposed for the role of hydrogen atoms in CVD diamond film growth. It's generally believed that hydrogen atoms incident on the surface abstract hydrogen to produce vacant sites, where growth species can then stick to the diamond layer, and that atomic hydrogen etches surface graphite [157]. Gas phase hydrogen atoms may also produce condensable carbon radicals by reactions with hydrocarbons [158], and, impinging on the surface, they may create surface radicals and refill vacant sites by absorption [140]. Once absorbed, atomic hydrogen may also stabilize the diamond surface structure [159]. Several multiphoton excitation LIF schemes have been used to measure atomic H concentration in CVD diamond environments. Lucht et al. (1983) measured H-atom concentration in low-pressure flames using 205 nm laser radiation to excite the  $n = 3$  level in a two-photon absorption process [160]. Alden et al. (1984) re-

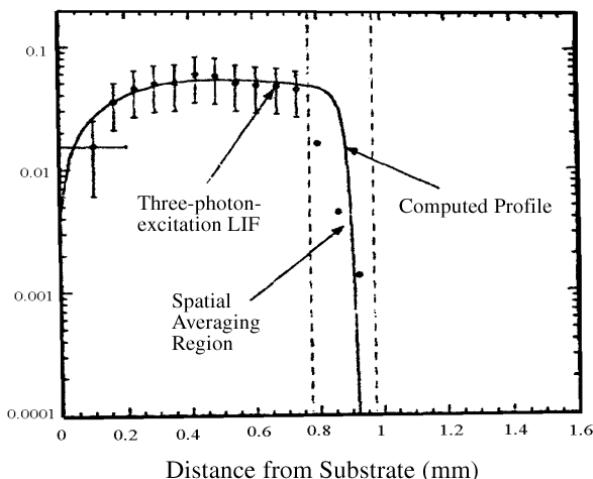
ported using 308 nm light to excite the  $n = 3$  level or using 292 nm light to excite the  $n = 4$  level in three-photon-excitation LIF experiments [161]. Goldsmith (1985) described a multistep process where two photons at 243 nm excite atomic hydrogen from the  $n = 1$  to  $n = 2$  level followed by absorption of a third photon at 656 nm to excite the atom to the  $n = 3$  level [162]. Bertagnolli et al. (1998) recently reviewed the energy level schematic for these multiphoton-excitation LIF techniques for measuring atomic H concentration [163], as shown in Fig. 4.12.

Bertagnolli et al. (1998) have used a three-photon-excitation LIF instrument [163] to measure the atomic hydrogen atom concentration in a stagnation-flow diamond-forming flame apparatus; the results are shown in Fig. 4.13. One can clearly see that the atomic hydrogen concentration decreases sharply near the substrate, because of the heterogeneous recombination of atomic hydrogen with the diamond surface. In thermal plasma and combustion systems, H is nearly in chemical equilibrium outside the boundary layer. In these systems, homogeneous recombination is only of concern within the boundary layer. Numerical simulations have shown that it is usually unimportant in high-speed arc jet or combustion systems [164], although it is predicted to become significant at pressures above about 2 atm [165]. Since homogeneous recombination of H atoms is usually negligible, the loss of H atoms must occur primarily on reactor walls and on the diamond surface itself. Measurements of the H concentration profile near a diamond substrate clearly show that diamond is a sink for H at typical substrate temperatures because of the atomic hydrogen absorption reaction or abstraction reaction ( $H + H \rightarrow H_2$ ). In diamond surface chemistry, the most important aspect is the reaction between atomic hydrogen and the diamond surface. Because of the continual bombardment of the diamond surface with reactive atomic hydrogen during growth, most of the diamond surface is hydrogenated, and is therefore unreactive with incoming hydrocarbon species. In ultra-high vacuum, hydrogen desorbs from diamond as  $H_2$  above about 800°C (ca. 75 kcal/mol activation energy). However, for diamond CVD conditions, this process does not appreciably contribute to creating the vacant site, since the desorption rate only becomes comparable to atomic hydrogen absorption or abstraction reactions at significantly higher temperatures ( $\gg 1100^\circ\text{C}$ ) [166].

In order to determine the mechanism of the magical influences of nitrogen on diamond growth, many experiments have been undertaken to reveal the relationship between gas-phase chemistry and diamond growth [168]. Klein-Douwel et al. (1995) have applied a two-dimensional laser-induced fluorescence (2D-LIF) instrument to the chemical vapor deposition (CVD) of diamond by an oxyacetylene flame to visualize the distribution of CN in the gas phase during the diamond growth process [167]. Clear relations were observed between the distribution of CN and the local variation of the growth rate, the morphology, and the nitrogen incorporation. Figure 4.14 shows horizontal profiles of the CN LIF signal close to the substrate during diamond growth by an oxyacetylene flame (solid and dashed lines, right-hand ordinate) and the deposition rate  $v_d$  of the corresponding diamond layer along the path of the laser beam (diamonds, left-hand ordinate).  $d$  is the distance between the flame front and substrate,  $z$  is the height above the substrate at

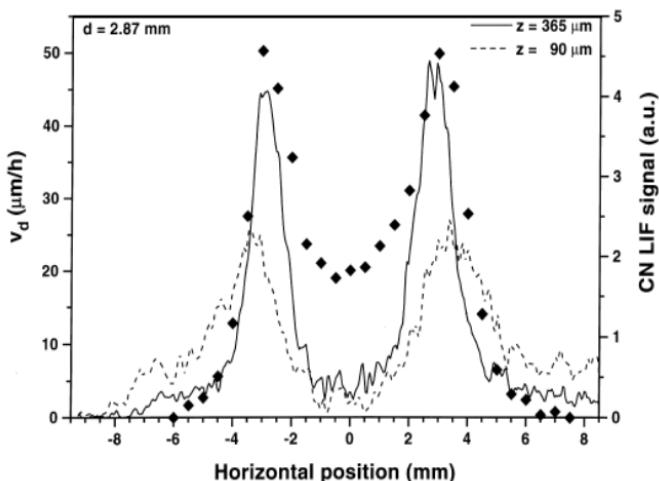


**Fig. 4.12.** Energy level schematic for various multiphoton-excitation LIF techniques for the measurement of atomic hydrogen concentration [163]



**Fig. 4.13.** Atomic hydrogen atom concentration profile measured using three-photon-excitation LIF in stagnation-flow diamond-forming flame apparatus [163]

which the profiles are taken. One can see that the CN LIF signal spatially resolved curves were very similar to that of the diamond growth rate. The fact that the maxima in the horizontal CN profiles coincide with the enhanced growth indicates that CN or a closely related species (only one or two reaction steps away) may be important in determining the local growth rate. In addition, the comparison of CN LIF signal variation with the distance from substrate shows that a low concentration of CN species exist in the vicinity of substrate, which may be due to the CN



**Fig. 4.14.** Horizontal profiles of the CN LIF signal close to the substrate during diamond growth by an oxyacetylene flame (solid and dashed lines, right-hand ordinate) and the deposition rate  $v_d$  of the corresponding diamond layer along the path of the laser beam (diamonds, left-hand ordinate) [167],  $d$  is the distance between the flame front and substrate,  $z$  is the height above the substrate at which the profiles are taken.

species that were consumed in the diamond surface chemical reaction processes. This agrees with the possibility that CN and HCN abstract adsorbed hydrogen from the growing diamond surface [169,170], which creates free growth sites, and with the observed positive effects on the growth rate of nitrogen addition to diamond-growing CVD systems.

### 4.5.3 Optical emission spectroscopy

Optical emission spectroscopy (OES) measurement is another very popular *in situ* diagnostic method, which offers a powerful tool for both monitoring and investigating the process of CVD diamond film growth without disturbing the growth process, and spatially resolved information can be obtained. By comparison with molecular beam mass spectroscopy (MBMS) and laser-induced fluorescence (LIF), optical emission spectroscopy (OES) does not have the potential risk of distorting the gas composition (MBMS) or causing gas composition dissociation or ionization in the photochemical process (LIF). In plasma processing, it has been widely used for real-time monitoring.

The diamond film quality varies with deposition method and conditions, and numerous researches have been undertaken to develop a simple relationship between OES and the quality of deposited diamond film. Klein-Douwel et al. (1998) found a correlation between  $C_2$  emission and the diamond film quality in an oxy-

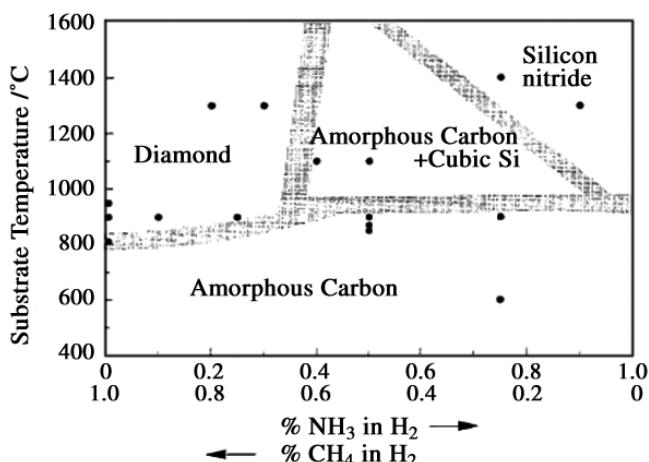
cetylene flame [171]. Lang et al. (1996) found the diamond film quality to correspond to H atom actinometry measurements [172]. Gruen et al. (1995) found OES signals from  $C_2$  emission in a microwave plasma correlate with the growth rate, but not the emission from either H or CH [173]. Cui et al. (1997) observed emission from H and  $CH^+$  relate to high quality diamond, and CH emission indicates the presence of nondiamond carbon [174]. Shang et al. (1998) suggested that the transverse bias-enhanced nucleation of diamond in hot filament chemical vapor deposition is due to the production of many more atomic hydrogen and CH radicals [175]. Luque et al. (1998) reported the quantitative optical emission of H, C,  $C_2$ , and CH, and found all the excited species to be present in concentrations two or more orders of magnitude smaller than the corresponding ground states measured in the same reactor and conditions [176]. Raiche et al. (1993) reported emission from CH,  $C_2$ ,  $C_3$ , in a DC arc jet system [177]. Reeve and Weimer (1995) observed CH(A-X) and  $C_2(d-a)$  emission [178], and found quite different vibrational and rotational temperatures in CH(A) and  $C_2(d)$  by analyzing the spatial distributions of the emission intensities, and it was suggested that the excited  $C_2(d)$  was formed by chemical reactions and CH(A) by electron impact.

Emission lines of various plasma species originate from electrically excited states of these species. The emission intensities are proportional to the densities of electrically excited species and the electron energy distribution function of the plasma. The emission intensity  $I_x$  of species  $x$  is given by [179],

$$I_x = C_x k_x n_e N_x g(\lambda), \quad (4.3)$$

where  $C_x$  is a constant,  $k_x$  the excitation rate constant of species  $x$  by electron collision that is a function of the electron energy and collision cross section,  $n_e$  is the concentration of electrons in the plasma,  $N_x$  is the concentration of the species  $x$ , and  $g(\lambda)$  is the counting ratio of  $\lambda$  photons collected to the total. It can be seen as a constant in a certain experiment, while  $n_e$ ,  $k_{x,j}$ , and  $N_x$  are determined by the reaction conditions. It can be seen that the emission intensity  $I_x$  is proportional to the concentration of species  $x$ , and to the excitation rate constant, that is to the concentration and energy of electrons in the plasma. Therefore, through the OES measurements, one can get information about the species concentration and the electron density and its temperature in the plasma.

Nitrogen is one of the most common impurities encountered both in natural and synthetic diamond. It is either concentrated in small aggregates (type Ia) or incorporated as a single substitutional species (ESP P1-defect) to act as a deep donor. As mentioned above, nitrogen-containing gas addition to conventional methane/hydrogen mixture has many positive effects on diamond film growth. But the mechanism of nitrogen incorporation in chemical vapor deposition diamond is still an open question. This is mainly due to the complexity of the N-incorporation process involved, depending not only on experimental parameters, but also on the diamond crystal orientation and its surface termination. Figure 4.15 shows a diagram of the type of films produced on Si substrates after CVD as a function of different substrate temperatures and methane/ammonia ratios [180]. At substrate temperatures lower than about 800°C only amorphous carbon films were produced,

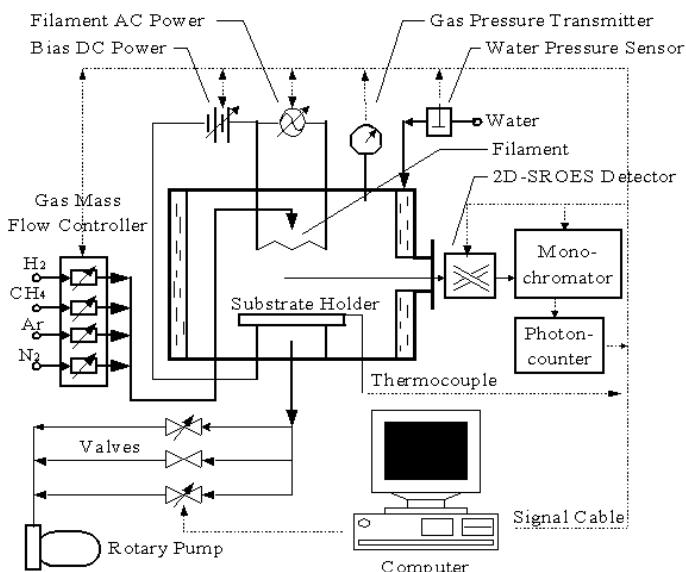


**Fig. 4.15.** Diagram showing the type of films produced on Si substrates after CVD as a function of different substrate temperatures and methane/ammonia ratios. Approximate phase boundaries are included to guide the eye [180]

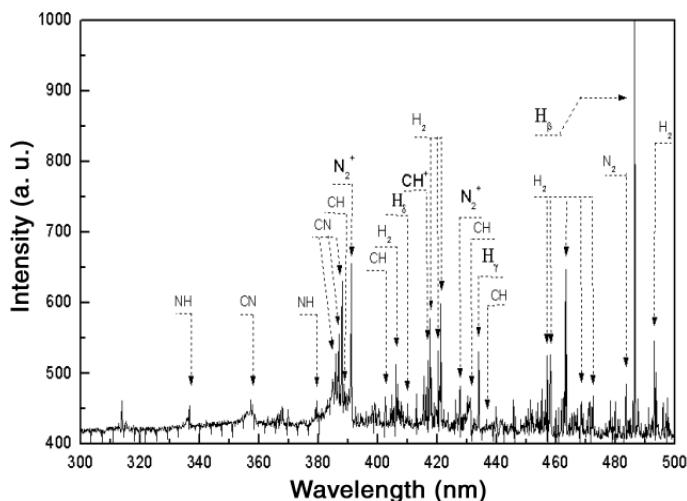
with little or no N content. At higher temperatures, the film composition depended strongly on the ammonia-to-methane ratio. With methane-rich gas mixtures, diamond was grown, the morphology of which was similar to that seen in standard CVD process, although as the fraction of ammonia increased, the films became more nanocrystalline and the growth rate decreased. With ammonia-rich gas mixtures, the Si substrate preferentially reacted with the ammonia to produce a  $\text{Si}_3\text{N}_4$  coating, with no carbon content.

Figure 4.16 shows a schematic diagram of a computerized hot-filament CVD diamond film system for 2-dimentional spatially resolved optical emission spectroscopy measurements [181]. The optical system includes a 2D-SROES detector, a monochromator, and photon counter. The emission light through an optical window is collected at the entrance of the optical system that is driven automatically in two dimensions by a controller connected to the computer. A special design of the optical collection system ensures the spatial resolution of the 2D-SROES system to be better than 0.1 mm. The collection light is decomposed by a monochromator and recorded by a photon counter. The spectral resolution of the monochromator is 0.1 nm. Beside the *in situ* spatially resolved OES, the optical system can be used for wavelength and temporally resolved spectroscopy as well.

In order to understand the mechanism of the diamond growth with nitrogen-containing gas addition to conventional methane/hydrogen mixture, Chang et al. (1999) employed *in situ* OES to do systematical investigating about the influences of system parameters on gas phase species [182]. A typical optical emission spectroscopy during diamond growth within a ( $\text{N}_2+\text{CH}_4+\text{H}_2$ ) mixture in the above hot-filament chemical vapor deposition diamond apparatus is shown in Fig. 4.17.



**Fig. 4.16.** Schematic diagram of experimental apparatus useful for spatially resolved optical emission spectroscopy [181]



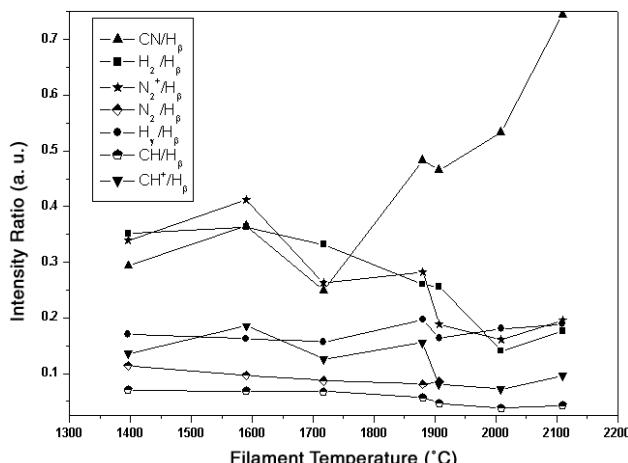
**Fig. 4.17.** Typical optical emission spectroscopy during diamond growth within a (N<sub>2</sub> + CH<sub>4</sub> + H<sub>2</sub>) mixture in the above Hot-Filament Chemical Vapor Deposition diamond apparatus [182]

**Table 4.2.** Observed Optical Emission Lines During Diamond Growth Within a ( $\text{N}_2 + \text{CH}_4 + \text{H}_2$ ) Mixture [183]

Species	Transition	Peak positions [nm]
$\text{H}_\alpha$	$n = 3 \rightarrow n = 2$	656.2
$\text{H}_\beta$	$n = 4 \rightarrow n = 2$	486.2
$\text{H}_\gamma$	$n = 5 \rightarrow n = 2$	434.1
$\text{H}_\delta$	$n = 6 \rightarrow n = 2$	410.1
$\text{H}_2$		406.7, 417.7, 420.5, 421.2, 457.2, 458.2, 463.2, 468.4, 472.3, 493.4
$\text{N}_2$	$A^3\Sigma^+U \rightarrow X^1\Sigma^+G$	483.7
$\text{N}_2^+$	$B^2\Sigma^+U \rightarrow X^2\Sigma^+G$	391.4, 427.8
CH	$A^2\Delta \rightarrow X^2\Pi$	431.4, 438.5
	$B^2\Sigma \rightarrow X^2\Pi$	387.1, 388.9, 402.5
$\text{CH}^+$	$A^1\Pi \rightarrow X^1\Sigma$	417.1, 422.5
CN	$B^2\Sigma \rightarrow X^2\Sigma$	359.0, 385.5, 386.2, 387.1, 388.3
NH	$A^3\Pi \rightarrow X^3\Sigma$	336.0, 379.5

For this example we have chosen a gas mixture of  $0.5\text{N}_2/2\text{CH}_4/100\text{H}_2$  gas flow ratio. In conventional OES measurement of hot-filament CVD, the filament radiation background decreases the signal-to-noise ratio and makes analysis difficult. In Fig. 4.17, it has been avoided by carefully adjusting the optical route and filament fabrication. The negative peaks in the baseline were due to the electromagnetic pulses in the external environment. The emission lines of atomic hydrogen, molecular hydrogen, CH,  $\text{CH}^+$ , CN, NH,  $\text{N}_2$ , and  $\text{N}_2^+$  were observed. The detailed peak positions are listed in Table 4.2.

Figure 4.18 shows the intensity ratios of CN,  $\text{H}_2$ ,  $\text{N}_2^+$ ,  $\text{N}_2$ , H, CH, and  $\text{CH}^+$  to  $\text{H}_\beta$  as a function of the filament temperature. The most remarkable information in this figure is that the CN radical concentration was sharply increased at  $\sim 1700^\circ\text{C}$ , which is close to the conventional filament temperature zone of diamond growth,  $\sim 2000^\circ\text{C}$  to  $2200^\circ\text{C}$ . As shown in Fig. 4.11, the nitrogen containing species HCN,  $\text{NH}_3$ , and  $\text{CH}_3\text{NH}_2$  concentrations started obviously increasing at  $\sim 1700^\circ\text{C}$  by MBMS measurements; this temperature also was pointed out by OES measurements. Below this temperature, because the dissociation of the strong  $\text{N}\equiv\text{N}$  bonds requires much more energy (bond strength:  $\text{N}\equiv\text{N}$ ,  $945.4 \text{ kJmol}^{-1}$ ;  $\text{H}-\text{CH}_3$ ,  $435.0 \text{ kJmol}^{-1}$ ;  $\text{H}-\text{H}$ ,  $435.9 \text{ kJmol}^{-1}$ ), besides CN radicals, few nitrogen-containing radicals are formed. Thus, at lower temperatures,  $\text{N}_2$  is seen as being virtually a spectator to the CVD process. At higher temperatures, CN radicals can be rapidly



**Fig. 4.18.** Effect of filament temperature on the relative emission intensities [182]

converted to HCN by the reaction:  $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$ , which has very low activation energy [184] (only 9.4 kJmol<sup>-1</sup>). And HCN is a very stable species in the typical diamond growth environment. So CN performs the task of transferring N atoms from nitrogen to HCN. Other nitrogen-containing species may be influenced by CN through several reaction steps. The CN radical seems to act as a very important factor in controlling the production of stable species such as HCN,  $\text{CH}_3\text{NH}_2$ , etc. It affects the processes of both gas-phase chemistry and surface reactions.

In Fig. 4.18, decrease of the reactants  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{N}_2^+$  with filament temperature clearly shows that the reaction was accelerated by increasing filament temperature, and that the reactants were consumed in the chemical processes. Accompanying these reactions, CH and  $\text{CH}^+$  species decrease because of the following reaction:  $\text{CH} + \text{N} \rightarrow \text{H} + \text{CN}$ ,  $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$ . Such reactions have been considered in mechanisms occurring within the discharge and in afterglows of microwave plasma [185]. In addition, the ratio of  $\text{H}_\gamma$  to  $\text{H}_\beta$  remains unchanged as the filament temperature increases, that is to say electron temperature was maintained constant.

Nitrogen concentration is a critical parameter for the growth of diamond when nitrogen gas is added to a conventional methane/hydrogen mixture. The growth habit was found to change from (111) to (100) with an increase of nitrogen in the gas phase from N/C = 0.1% to 10%, so also the growth rate of diamond films increases and diamond Raman peak sharpens with the amount of nitrogen [155]. In the microwave system, nitrogen addition even in ppm magnitude has led to significant changes in diamond growth [186]. Figure 4.19 shows the effect of nitrogen concentration on the relative emission intensities. With the concentration of nitrogen,  $\text{CH}^+$  species steadily decrease, accompanied by a rapid increase in the

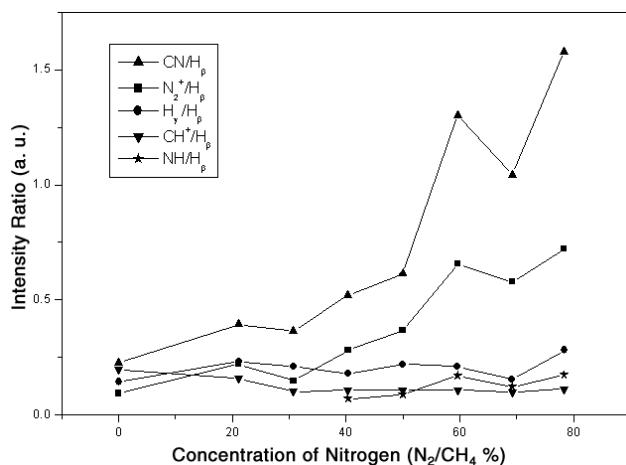
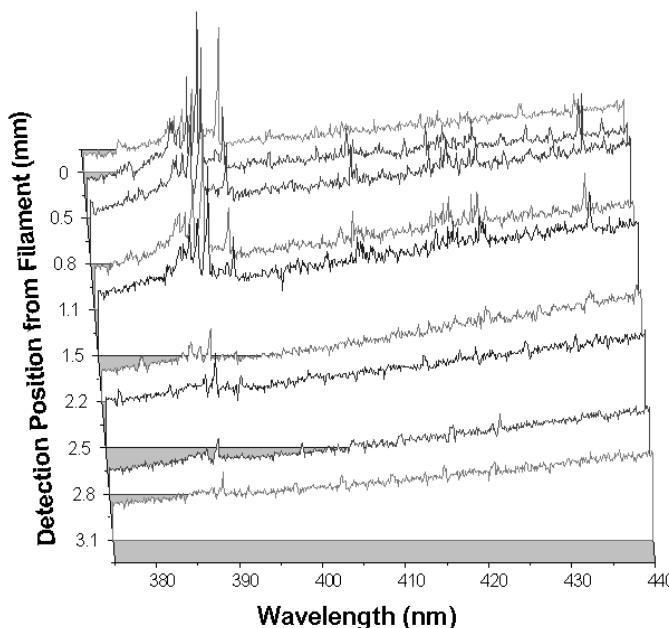


Fig. 4.19. Effect of nitrogen concentration on the relative emission intensities [182]

CN and N<sub>2</sub><sup>+</sup> species and a slight rise in NH species. During these processes, the electron temperature remains unchanged.

Bohr et al. (1996) reported the influence of N<sub>2</sub> admixtures (5% – 40% N<sub>2</sub>/CH<sub>4</sub>) on hot-filament CVD growth [170]. Small N<sub>2</sub> additions (5% – 10% N<sub>2</sub>/CH<sub>4</sub>) improved the diamond phase purity, high concentration (20% – 40% N<sub>2</sub>/CH<sub>4</sub>) revealed a deterioration of the diamond phase purity and low growth rate. As shown in Fig. 4.19, CH<sup>+</sup> falls to a relatively low concentration level when the input nitrogen gas concentration is increased to 30%, accompanied by the rapid rise in CN radicals at this point. The former species, CH<sup>+</sup>, have been attributed to being the active precursor for diamond growth by Cui and Fang (1997) [174]. Lower CH<sup>+</sup> concentration is not favorable for diamond growth. Although CN can abstract adsorbed hydrogen from the diamond surface to create growth sites, and can increase diamond growth rate, with higher nitrogen gas input, too many CN radicals and growth sites are produced. Because CN radicals are not helpful for stabilizing diamond structure, the dangling bonds at growth sites may connect together to produce a graphite structure, and will deteriorate the diamond phase purity.

Figure 4.20 gives the spatial resolved optical emission spectroscopy between filament and substrate; the zero point is the filament position and the whole distance between the filament and the substrate is about 5 mm. For the detection position from filament to substrate, the H<sub>γ</sub> (434.1 nm) line first increased to the peak intensity at a position 0.8 mm from the filament surface and then decreased near the substrate because of the consumption of atomic hydrogen in surface reactions. This is consistent with the LIF measurement results of Bertagnoli et al. (1998), as shown in Fig. 4.13. From this figure, we can clearly see that atomic H was created in the vicinity of the filament surface, and then diffused to the substrate. This process is very important to diamond growth. The heat transfer study gave a

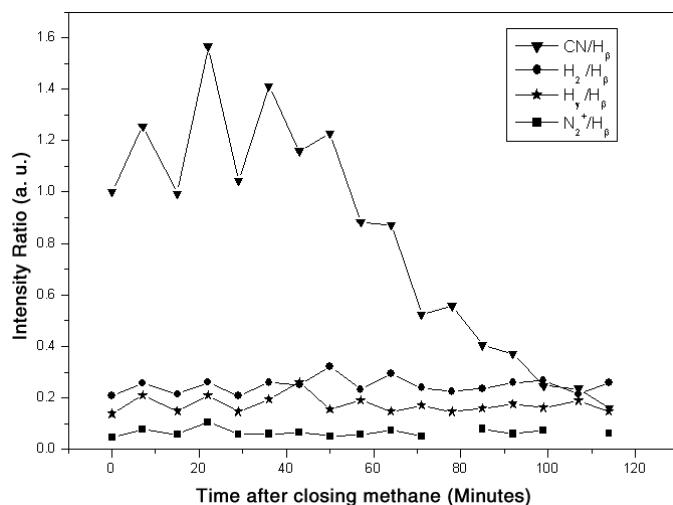


**Fig. 4.20.** Spatial resolved *in situ* emission spectroscopy [182]

complete energy balance for the filament and revealed that hydrogen dissociation accounts for 70% of the total power released from the filament, followed by radiation and conduction/convection at 15% each [187].

At the filament surface, the intensity of the  $\text{N}_2^+$  line was higher than that of CN, but when the detection position was moved to 0.5 mm from the filament, this ratio was reversed. It shows that the  $\text{N}\equiv\text{N}$  bond was broken near the filament surface and N was transferred from nitrogen to N-containing radicals, such as CN. Thus, CN lines still remained obvious near the substrate surface, whereas  $\text{H}_\gamma$  disappeared.

In order to get a better understanding of CN formation, the evolution of CN and other species were examined. For this purpose, after obtaining the steady-state flow of the gas mixture within the reactor, we abruptly stopped the  $\text{CH}_4$  injection at time  $t = 0$ . As shown in Fig. 4.21, the intensities of  $\text{H}_2$  and  $\text{N}_2^+$  lines were kept unchanged, and we can see that the electron temperature remained constant. After closing off the methane, the intensity of the CN line vibrated at a high level, and 40 minutes later, it began to decrease. This result clearly shows that CN is already produced within the pure gaseous phase and its formation is influenced by the amount of methane. However, the concentration of CN was kept high and its OES intensity did not decay rapidly. This means that the solid carbon, graphite, or black carbon that grew on the holders of the filament and substrate in previous experiments act as a carbon source which is sufficiently large to maintain this new



**Fig. 4.21.** Time evolution of the relative emission intensities after closing methane [182]

state of CN production for a very long time, because of the  $\text{C} + \text{N}_2 \rightarrow \text{CN} + \text{N}$  reaction [184]. So the formation of CN can be produced in the gas phase as well as at the surface of the solid phase carbon. It is dissimilar to the formation of gas phase species in the conventional hydrocarbon/hydrogen mixture for diamond growth as shown in Fig. 4.10, in which most gas phase compositions are produced by gas phase reactions.

From these experiments and discussions, we can draw the conclusion that at low nitrogen concentrations, the CN radical behaves much like a growth accelerator, which is responsible for the magical increase in diamond growth rate. But nitrogen is not indispensable for diamond growth. The theoretical situation of a gas phase completely free of nitrogen would produce the lowest film growth rate, but of the best quality. Besides CN radicals, atomic H concentration has already been proposed as a key factor in diamond quality. Atomic H helps to etch surface graphite and stabilize diamond structure. So we can attribute the CN and atomic H lines to different aspects of diamond growth: CN is for diamond growth rate and atomic H is for diamond quality. By detailed controlling of these two emission lines, we can make the best choice between higher growth rate and good quality.

## 4.6 Summary

Diamond films have been successfully prepared using hot-filament CVD, microwave plasma-assisted CVD, DC arc plasma jet CVD, and other methods in recent decades. However, our understanding of the growth mechanism of metastable diamond is still vague. In order to find the answer to why diamond films can be

deposited from different gas sources by different synthesis techniques, scientists have studied the nucleation and growth process of diamond film from the two aspects of surface reaction and gas-phase reaction.

It is found that diamond nucleation density on the heterosubstrates can be greatly increased by the mechanical damage, the predeposited buffer layer, and the bias-enhanced nucleation methods. Of these methods the bias-enhanced method brings the best hope of realizing the heteroepitaxial growth of diamond films. The results of cross-section HRTEM imply that the diamond nucleation site is important to the heteroepitaxial growth of diamond. Under the CVD conditions, two growth modes, i.e., layer growth and spiral growth, were found in the growth process of diamond. In addition, substrate material selections with some novel considerations were attempted to deposit high-quality and epitaxial diamond films.

Many *in situ* diagnostic techniques have been employed for the growth environment evaluation, such as molecular beam mass spectroscopy, laser-induced fluorescence, and optical emission spectroscopy. These techniques can provide direct, quantitative, or semiquantitative information for a large number of stable and radical gas species about their energy and spatial distribution. With *in situ* diagnostics, we can efficiently correlate gas phase conditions with film properties such as growth rate, texture, morphology, and uniformity. It is found that many species, such as H, CH, CH<sup>+</sup>, CN, CH<sub>3</sub>, C<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>, have great influences on diamond growth, and it was generally believed that CH<sub>3</sub> and C<sub>2</sub>H<sub>2</sub> are responsible for diamond growth.

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# **5 Laser-Assisted Growth and Characterization of Multicomponent Lead-Zirconate-Titanate Films**

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## **5.1 Introduction**

Soon after the invention of the ruby laser in 1960, the first theoretical and experimental studies concerning the interaction between laser light and solid material and the evaporation of the material into the form of thin film were published [1,2]. Although the laser facilities were at the prototype level with a low output power of unstable radiation at that time, the fundamental processes of laser-assisted material evaporation and laser-ablation deposition could be performed. Also, the very complex nature of the physical and chemical reactions on the surface of the material being exposed to the intense, highly-oriented coherent and monochromatic beam of photons was revealed. However, due to the modest laser technology and to the fast development and extensive research work in the fields of other thin-film deposition methods, including sputtering technologies as well as molecular beam epitaxy (MBE), little research work on laser-ablation technique as a method for thin-film deposition was made until the technique was utilized successfully in the deposition of high- $T_c$  superconductors by Venkatesan in the late 1980s [3]. During the last ten years, there has been rapid development both in the theory of ablation process and experimental methods as well as in the field of lasers and deposition-equipment technology. Also, a large variety of materials, including single-component materials along with multicomponent semiconductors and dielectrics, have been deposited successfully using the laser-ablation deposition technique.

### **5.1.1 Laser-assisted growth of thin films**

In pulsed-laser deposition, short and intense laser pulses are used to evaporate and ablate the surface of the desired target material. Typically, deposition is done using UV-wavelength lasers due to their high absorption coefficient for a large variety of materials. The most common laser type is the excimer gas laser with a wavelength from 151 to 351 nm depending on the selected gas mixture, or frequency-tripled or -quadrupled Q-switched Nd:YAG lasers with wavelengths of

355 and 266 nm, respectively. In the discussion here, all the laser-ablation deposition was carried out using an XeCl excimer gas laser with a wavelength of 308 nm and pulse duration of around 20 ns. These laser pulses have a peak power on the order of  $10^8$  W and, with appropriate optical manipulation and focusing, are capable of evaporating practically any kind of material. At low-pressure conditions, the evaporation leads to the formation of an adiabatically expanding plasma that is mainly composed of neutral atoms and various ionized and neutral species of the target material that can be collected onto a substrate to form a thin film. The main advantages of the pulsed-laser-deposition technique include experimental simplicity, the capability of evaporating materials with a high melting point and the ease of stoichiometric deposition of multicomponent compounds such as modified lead zirconate titanates (PZTs). However, the formation of large particulates (i.e., splashing) and the non-uniform film-thickness distribution are the main problems involved in this laser-assisted growth of thin films.

### 5.1.2 Ferroelectric PZT thin films

Ferroelectric lead-zirconate-titanate ceramics in the form of thin films have been studied intensively for various applications over the past few years. Their electrical and electromechanical properties, such as a remanent polarization, a high dielectric constant, piezoelectricity, strong electro-optic and acousto-optic effects, and pyroelectricity offer a wide variety of applications in microelectronics and micromechanics.

Lead-zirconate-titanate ceramics,  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ , are a solid solution of  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  with a perovskite  $\text{ABO}_3$  crystal structure with  $\text{Pb}^{2+}$  ions in A sites,  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  ions in B sites, and oxygen octahedra formed by  $\text{O}^{2-}$  ions around the B cations. Between the composition-dependent Curie temperature (about 230°C for  $\text{PbZrO}_3$  and 490°C for  $\text{PbTiO}_3$ ) and room temperature, PZT ceramics actually have five different phases that include antiferroelectric orthorhombic and tetragonal crystal structures in Zr-rich compositions, ferroelectric rhombohedral (trigonal) high- and low-temperature phases in lower Zr compositions, and a tetragonal phase in compositions with a higher Ti content. Above the Curie temperature, PZT ceramics are always in the paraelectric cubic structure [4]. The phase boundary between the ferroelectric rhombohedral (trigonal) and tetragonal phases, with the value of  $x \approx 0.53$  at room temperature, is known as the morphotropic phase boundary (MPB), which is very important for the electrical and mechanical properties utilized in the component applications. At the MPB, both phases are in thermal equilibrium in the ceramics and the phases form a coexistence region in the composition range of  $0.49 \leq x \leq 0.64$  where PZT ceramics possess an increased capability of polarization and thus a high electromechanical coupling coefficient [5]. From the application point of view, the modification of PZT ceramics with rare-earth elements like  $\text{Nd}^{3+}$  (PNZT) and  $\text{La}^{3+}$  (PLZT), substituting  $\text{Pb}^{2+}$  ions in A sites, further improves the properties of the ceramics.

The ferroelectric nonlinear polarization effect with nonzeroremanent polarization and hysteresis is utilized in nonvolatile ferroelectric random-access (FERAM)

memory applications. In the capacitor structure, the direction of the remanent polarization is set by the last polarizing electric field, e.g., 5 V for a film 300 nm thick. In the dielectric material between the electrodes, the polarization state can be deduced from the amount of the charging current directed to the subsequent electric field, e.g., 3 V for the 300 nm film, thus determining the state “1” or “0” for the individual memory cell [6,7]. On the other hand, inverse piezoelectric phenomena causing elongation or shrinkage under an external electric field that depends on the mutual orientation of the field and the remanent polarization of the PZT material can be exploited in various multilayer-stack or mono- and bimorph-type actuator applications to generate accurately-controlled movement from a few nanometers up to several hundreds of micrometers. This is useful, for example, in atomic-force microscopy (AFM), photolithography systems for semiconductor manufacturing, and light-beam deflectors [8–10]. Due to their pyroelectric effect, PZT thin films, especially those with Zr-rich compositions, are sensitive when used in infrared temperature and motion sensors and are, for example, used as detector elements in alarm systems [11,12]. In addition to the group of applications utilizing the piezoelectric effect in PZT ceramics, different kinds of devices based on the surface-acoustic waves (SAW) in film surfaces can be used for RF signal filtering in telecommunication applications, the optical manipulation of light beams, and for gas detection and analyses, just to mention a few applications [13]. Also, the many excellent optical properties of La-modified PZT (PLZT) thin films, such as their high transmittance and low reflectance, together with their strong electro-optic Kerr effect, i.e., the change of the refractive index  $\Delta n$  which is proportional to the square of the applied electric field  $E^2$ , are used in fast optical shutters, modulators, and waveguides [14–16].

## 5.2 Film Deposition Process

In the pulsed-laser deposition with UV lasers, one uses the short and intense laser pulse to both evaporate and ablate the surface of a desired target material. Pulsed-laser ablation (sputtering) without any evaporation can also remove material from the target surface. At low-pressure, laser-ablation forms an adiabatically expanding plasma that mainly consists of neutral atoms and various ionized and neutral species of the target material [17]. This plasma expands in the direction perpendicular to the target surface and can be collected onto a substrate to form a thin film a short distance away from the target.

### 5.2.1 Principles of pulsed-laser-deposition technique

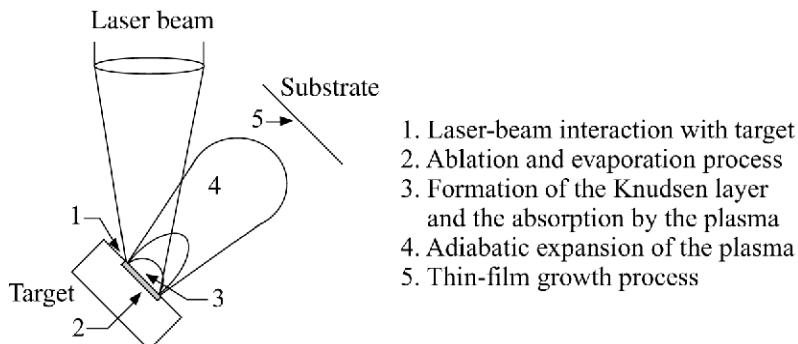
The underlying mechanism in the process of laser-beam interaction with the target material is based on the photoexcitation of electrons. Different possibilities in this excitation process include electronic transitions from valence-band states as well as from the occupied surface and defect states to conduction-band states, leading

to the formation of electron-hole pairs and excitons. Assuming an initially perfect crystal structure, the relaxation of these excitations can occur simply through radiative or nonradiative recombination, thus restoring the system basically to the nondisturbed ground state. On the other hand, the relaxation process can result in a metastable state in the surface layer of the material leaving the original surface structure distorted with a number of defects. Under these metastable conditions, when the optical absorption properties of the material are changed and the surface layer of the target consists of a large number of loosely bound atoms, even a weak photoexcitation can easily create a vacancy and a free atom. When the excitation process is strong enough to cause direct formation of vacancy clusters and consequently multiple-emitted atoms in the form of larger uniform clusters (molecules) and dissociated atoms, the ablation process itself turns on [18]. Different steps of the pulsed-laser-deposition (PLD) process are described in Fig. 5.1.

In addition to the characteristic properties of the ablation process mentioned above, one important feature is the existence of the material-dependent threshold laser-beam fluence  $I_{th}$ . This laser-beam fluence can be determined as a minimum onset fluence to start the ablation process; it is strongly dependent on the target material properties and on the properties of the laser pulse. In the case where laser-beam interaction with the target surface is a thermal ablation process mainly due to the thermal conductivity and the radiation losses of the target, the surface temperature obtains the vaporization temperature  $T_v$  at the time  $t_{th}$  after the beginning of the laser-beam exposure. Because the laser-pulse length  $t_p$  is fixed ( $\approx 10$  ns), a threshold value of the laser-beam fluence  $I_{th}$  is necessary for a sufficient amount of energy to evaporate the target surface [19].

Typically, for the semiconductors and insulators, like the PNZT ceramics, the adiabatic heating-model condition  $2(k_d t_p)^{1/2} < \alpha^{-1}$ , where  $k_d$  is the thermal diffusivity,  $\alpha$  is the absorption coefficient, and  $t_p$  is the length of the laser pulse, is a good assumption [20]. In the adiabatic heating model, the temperature increase inside the target material is due to direct heating by the laser light instead of thermal diffusion from the target surface. Thus, the energy of the laser pulse is mainly absorbed in the thin surface layer of the target.

Under the conditions where the laser-ablation process is possible during the time of laser-beam exposure, a thin plasma layer is formed on the surface of the target as a result of the interaction of the incident laser beam with the ablated and evaporated particles. Initially, the particles emitted from the surface of the target form a thin Knudsen layer where thermal equilibrium among the particles is established through collisions. Initially, the velocity ( $v_x \geq 0$ ) of the particles is perpendicularly pointed out from the target surface and the velocity distribution obeys Maxwellian distribution for the particles emitted through thermal ablation and evaporation, but does not necessarily do so for the emission due to photoexcitation [21]. However, quickly after a few collisions, thermal equilibrium is reached at the outer boundary of the Knudsen layer. A negative velocity component  $-v_x$  is developed and the high temperature  $T_k$  of the plasma is converted into the form of kinetic energy giving the plasma a flow velocity  $u_k$  that always obeys the Maxwell-Boltzmann velocity distribution. At this point, due to the negative



**Fig. 5.1.** Schematic description of different parts of the pulsed-laser-deposition process. In the case of an excimer laser, the pulse duration is around 10 ns and the flight time of the particles from the target to substrate is typically less than 5  $\mu$ s.

velocity component of the plasma, some of the particles are repelled back to the direction of the target and a part of the emitted material recondenses on the target surface.

The plasma layer is typically 100  $\mu$ m, which is thin compared to the dimensions of the plasma in the plane of the target surface that is determined by the spot size of the laser beam (e.g., 1 mm  $\times$  2 mm in the case study in Section 5.3). The pressure gradient inside the plasma is greatest in the direction perpendicular to the target surface [22]. Thus, the adiabatic expansion of the plasma is fastest in this direction leading to a non-uniform thickness distribution of the film on the substrate. A typical thickness distribution of the laser-ablated thin film obeys a cosine-power law that can be used to evaluate the quality factor describing the flatness of the deposited thin film.

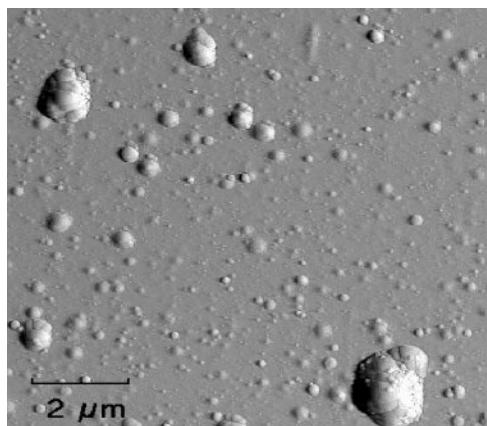
## 5.2.2 Growth and structure of thin films

The growth of the thin film begins as soon as the edge of the ablation plume reaches the substrate and the first species hit its surface. The actual mechanism of the film-growth process depends strongly on the conditions present in the ablation chamber, and also depends on the ablated material characteristics. In addition to the laser-beam fluence at the target surface, also the choice of the substrate material and temperature, as well as, the ambient gas atmosphere have a significant effect on the crystal structure and surface morphology of the growing thin film. Thus, the film deposition with the laser- ablation process is divided into the post-annealing heat-treatment process and *in situ* process according the specific growth parameters.

In the post-annealing process, as is done through the experiments in the case study in Section 5.3, the thin film itself is grown using a simplified process, where the substrate is kept at room temperature, and the chamber is evacuated to the pressure of around  $10^{-5}$  mbar without any background gas. Under such conditions,

the thermal energy on the substrate surface is too low to initiate nucleation and thus the resulting films are generally amorphous, but can contain crystalline particulates originating from the target surface [23]. On the other hand, the most important parameter affecting the composition and the structure of the thin film during the ablation process is the laser-beam fluence. Post-annealing of films gives still another possibility to control the composition and crystal structure of the films. For example, in order to achieve PNZT films with the desired crystal structure, a subsequent annealing process was needed at temperatures between 600 and 900°C [8]. The annealed films are polycrystalline and the grain size is dependent on the annealing temperature and time and, in the case of PZT films discussed here, also on the atomic ratio of titanium and zirconium Ti/Zr [24]. In titanium-rich PZT films, the nucleation of the grains starts more easily, the number of grains is much higher, and the grains are smaller compared to those in zirconium-rich films.

The crystallization of the amorphous PZT film proceeds so that the film first forms a pyrochlore phase at temperatures between 400 and 500°C. Then, at higher temperatures, the upper face of the film starts to crystallize in some ferroelectric phase of perovskite PZTs, and the crystallization emerges deeper into the film during the annealing process [24]. An AFM micrograph of an amorphous PNZT film surface is shown in Fig. 5.2. In the case of the *in situ* deposition process, the substrate is heated up to temperatures from 550 to 750°C and the chamber is partially filled with oxygen gas in order to ensure sufficient nucleation energy for direct crystal growth during the film-deposition process starting from the substrate surface. An appropriate choice of the substrate with the lattice constants close to those of PZT promotes the growth of high-quality epitaxial thin films. Also, by varying the oxygen pressure, substrate temperature, and laser-beam fluence, the crystal structure of the film can be varied [23,25].



**Fig. 5.2.** AFM micrograph of an amorphous PNZT thin film with thickness of 390 nm after deposition at room temperature. The film was deposited at a laser-beam fluence of 1.0 J/cm<sup>2</sup> using 37,500 laser pulses.

### 5.3 Case Study: Nd-Modified PZT Films

The use of the pulsed-laser-deposition technique in the growth of post-annealed Nd-modified PZT thin films, hereafter PNZT, is considered here as a case study. Deposited PNZT films are in the form of single thin films on various substrates and also inside multilayer capacitor structures with platinum thin-film electrodes. Some features and results of the deposition process of films and the characterization of their structural and electrical properties are discussed.

Various  $\text{Pb}_{0.97}\text{Nd}_{0.02}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$  targets with different densities were prepared from a PNZT powder with this composition. Targets were first pressed into the form of pellets under a pressure of 500 kPa at room temperature. In order to adjust the density of the PNZT targets, the sintering was carried out at different temperatures between 900 and 1200°C for 20 minutes at the maximum temperature. The sintering process was carried out under an inverted zirconia crucible together with some extra PNZT powder in order to prevent an excess loss of lead. The quality of the PNZT targets was tested with the X-ray-diffraction method and with the energy-dispersive spectroscopy of X-rays (EDS). For the platinum-electrode deposition, a polished platinum disk was used as a target.

A pulsed XeCl-excimer laser with a wavelength of 308 nm and pulse duration of 20 ns was used for the film deposition processes. The laser-pulse repetition rate was 25 Hz and the laser-ablation process was carried out in a vacuum chamber at a pressure between  $4 \times 10^{-5}$  and  $6 \times 10^{-5}$  mbar at room temperature. The distance between the target surface and the substrate was varied between 20 and 35 mm and the angle between the target surface and incident laser beam was 45°. The laser-beam fluence on the PNZT target surface was varied between 0.2 and 3.0 J/cm<sup>2</sup> by adjusting the spot size of the laser beam on the target surface with a focusing quartz lens. Typically, for the capacitor application experiments, a laser-beam fluence of around 1.0 J/cm<sup>2</sup> was used. The deposition of the films was carried out with the scanning laser-beam condition at a constant scanning speed of 8 mm/s. However, the laser beam was scanned only in one horizontal direction parallel to the target surface so that the spot size of the laser beam and, thus, the laser-beam fluence was kept constant during the ablation process. In some experiments, the local laser-beam condition was also used in order to study the phenomena on the target surface during the ablation process. In the local laser-beam condition, both the target and the position of the laser spot were kept fixed so that the laser pulses hit the target always at the same surface area.

Single-crystal sapphire ( $\text{Al}_2\text{O}_3$ ) substrates with (1̄102) surfaces, MgO(100) and thermally oxidized Si(100) substrates were placed parallel to the target surface after a cleaning treatment. For silicon substrates, an oxide layer was grown by a dry-oxidation method in order to form a buffer layer between the silicon and the Pt/PNZT structure.

After deposition, a part of the PNZT thin-film samples were left amorphous and the rest were post annealed in air at various maximum temperatures between 600 and 900°C for a period of 10 to 20 minutes under an inverted zirconia crucible with some PNZT powder. The thickness of the PNZT thin films varied from 25 to

1200 nm, depending on the experiment. In the post-annealing heat treatment, a heating rate of 400°C/h was found to be appropriate for the single-layer PNZT films on sapphire and MgO substrates. In order to achieve an oriented polycrystalline PNZT thin film with a perovskite-type tetragonal or trigonal lattice structure, maximum annealing temperatures of at least 675 to 900°C had to be used. On silicon substrates, the PNZT films exceeding 300 nm in thickness were annealed at 650°C and the thinner films at 675°C. In order to avoid cracking due to the unequal thermal expansion between the silicon substrate and the PNZT layer, a low cooling and heating rate of 50°C/h had to be used.

For the deposition of the electrode layers in capacitor structures a polished platinum disk was used as a target. The fluence of 2.5 J/cm<sup>2</sup> was found to be appropriate to produce a smooth conductive platinum film. After deposition, platinum bottom electrodes, about 200 nm thick, were annealed in air atmosphere at 700°C. The top electrode was left amorphous. In the fabrication of a Pt/PNZT/Pt capacitor structure, a temperature difference of 25°C or more between the maximum annealing temperatures of the platinum bottom electrode and the PZT film was found necessary to prevent the mixing of the separate layers.

The growth rate of the deposited films as a function of the laser-beam fluence and time was determined with two different methods. The average growth rate was determined from the thickness of the deposited films measured with a Dektak 3030ST profilometer. The growth rate as a function of the number of laser pulses (or time) was measured in the *in situ* ablation process by replacing the substrates with a quartz-crystal sensor connected to the Sycon STM-100 Thickness/Rate monitor.

The structure of the PNZT films was studied with X-ray-diffraction experiments using CuK $\alpha$ -doublet (1.540562 and 1.544390 Å) radiation and a Phillips X-ray diffractometer. The measurements consisted usually of recording the X-ray diffraction intensities at 2θ angles from 10 to 80° with a constant speed of 1°/min. Measurements with greater accuracy were carried out manually, e.g., by measuring an integration time corresponding to 20000 pulses. A commercial curve-fit program (Jandel Scientific PeakFit 4.0) was used to determine the accurate positions of the measured diffraction peaks.

Macroscopic mechanical stresses in PNZT thin films were determined from the diffraction patterns of the CuK $\alpha_1$ -rays. The shifts in the diffraction-peak position from the tetragonal (413) planes at around 2θ = 148° were measured as a function of the tilt angle for the stress analysis [26]. The XRD patterns were measured at the tilt angles of 0°, 30°, 45°, and 60° from both PNZT/Pt/MgO and PNZT/Pt/SiO<sub>2</sub>/Si structures with various PNZT film thicknesses.

The structure and composition of the films were also studied with a scanning electron microscope (SEM) and EDS measurements using the JEOL JSM-6400/LINK AN10-85 facility with a thin-film analysis program. In some compositional analyses, an electron-probe microanalyzer (EPMA) JEOL JCXA-733 was also utilized. For high-resolution SEM micrographs of the ablation-target surfaces, a field-emission microscope (FESEM) JEOL JSM-6300F was used.

In order to study the surface morphology and, especially, the effect of the particulate formation on the quality of the thin-film surface, atomic force microscopy (Digital Instruments Nanoscope II) was used.

Visible laser light (514.532 nm) was used for Raman measurements. The spectrometer used was the Jobin Yvon T64000 model. The resolution of the Raman spectrometer was about  $1\text{ cm}^{-1}$ . The spectra between  $-800\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  were measured using a triple monochromator with a grating of 1800 grooves per mm. The data were collected using output power of 50 mW (laser beam power was a fraction of this in the case of micro-probing) and acquisition time  $3 \times 600\text{ s}$ . All measurements were carried out under the microscope (laser spot diameter 1–2  $\mu\text{m}$ ).

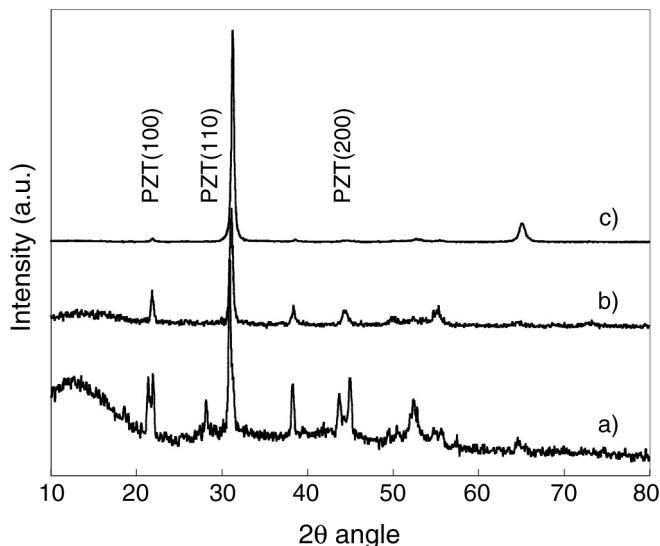
The determination of the dielectric properties of the PNZT thin films was done with an LCR meter (Hewlett Packard 4284A) using a signal amplitude of 1 V and frequencies of 1 and 10 kHz. The measurements of capacitance and loss angle were carried out between 22 and  $500^\circ\text{C}$ . The polarization behavior at room temperature was measured by a modified Sawyer-Tower circuit with a frequency of 165 Hz [27].

The leakage current as a function of the voltage applied across the Pt/PNZT/Pt capacitor structure was measured with a circuit composed of a voltage source (Keithley 263) and a digital current meter (Hewlett Packard 3458A) connected in series with the sample. The value of the current was measured 30 s after each voltage change so that the initial charging current of the capacitor had decayed and the leakage current stabilized. The conductivity measurements were also carried out at several elevated temperatures below the Curie temperature in order to identify the possible thermally activated charge-transport mechanisms.

Raman measurements were carried out at the Microelectronics and Materials Physics Laboratories, University of Oulu, Finland, and at the Materials and Structures Laboratory at the Tokyo Institute of Technology, Japan. The other measurements and preparation of samples were carried out at the Microelectronics and Materials Physics Laboratories, University of Oulu.

## 5.4 Results from XRD and EDS Measurements

The crystal structure of the post-annealed PNZT films was studied with conventional X-ray-diffraction measurements. The films deposited at higher laser-beam fluences above  $1.5\text{ J/cm}^2$  showed a polycrystalline, high-temperature trigonal structure independent of the annealing temperature [see Fig. 5.3(c)]. Deposition at lower laser-beam fluences [Fig. 5.3(a)] gave films with lower Zr contents and tetragonal crystal structure where the axis ratio  $c/a$  increased with increasing annealing temperature. However, from the films annealed at  $600$  and  $650^\circ\text{C}$ , only weak X-ray-diffraction intensities were measured, which showed that the films also contained the pyrochlore phase.



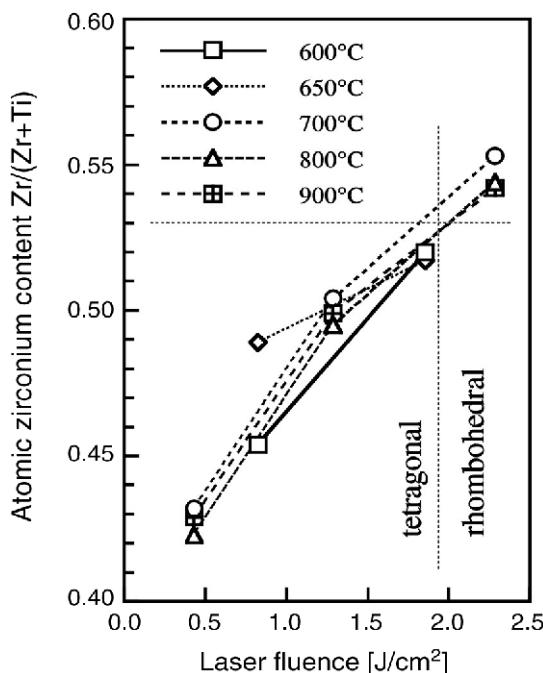
**Fig. 5.3.** XRD patterns from PNZT films deposited on the sapphire substrate at laser-beam fluences of (a) 0.4 (annealed at 850°C), (b) 1.3 (annealed at 850°C) and (c) 2.4 J/cm<sup>2</sup> (annealed at 800°C). The intensity values of the curve (c) were divided by a factor of 10 as compared with the intensity values of other curves (Reprinted from Ref. 30 with permission from Elsevier Science)

The atomic lead content Pb/(Zr+Ti) of amorphous as-deposited PNZT thin films as a function of laser-beam fluence was also studied. At fluences around 0.4 J/cm<sup>2</sup>, the atomic lead content of the films was about 4.0 but decreased with increasing fluence to a value close to 1.0 at the laser-beam fluence of 0.75 J/cm<sup>2</sup>. This behavior can be explained by a two-component model for the ejection of material from the target surface. At low laser-beam fluences (below 0.75 J/cm<sup>2</sup>) the material removal from the target is a thermal evaporation process and thus the composition of the ejected material flux is determined by the characteristic vapor pressures of the elements in the target. The relatively high vapor pressure of the PbO compound from the target leads to film compositions with lead contents exceeding its value in the initial PNZT target [28].

On the other hand, the segregation of lead into separate droplets and the formation of ZrO<sub>2</sub> and TiO<sub>2</sub> phases with high melting temperatures at the PNZT target surface during the ablation process [29] can also increase the amount of lead in the films at low laser-beam fluences. Higher surface temperatures at laser-beam fluences above 0.75 J/cm<sup>2</sup>, on the other hand, ensure a more uniform evaporation of different elements from the target and the process resembles now more of an ablation process [28]. However, the surface temperature of the PNZT target also increases with the increasing laser-beam fluence and the material removal from the target is always a combination of thermal evaporation and ablation processes.

The final chemical composition of the PNZT films also changed during the post-annealing treatment, and the lead content of films annealed at high temperatures was less sensitive to laser-beam fluence. At low fluences, the as-deposited PNZT films contained excess lead and, thus, the ratio Pb/(Zr+Ti) stabilizes close to the stoichiometric value during annealing. However, at high laser-beam fluences, the as-deposited PNZT films suffer from a lead content, which is too low, but at high annealing temperatures, the annealing atmosphere contains more lead evaporated from the extra PNZT powder under the inverted zirconia crucible. In this case, lead is incorporated from the vapor phase into the thin films; therefore, the lead content of the films increases with increasing annealing temperature. For films annealed at low temperatures, the high variation rate of lead content with fluence originates from the re-evaporation of lead (PbO) during the heat treatment; also, due to the low annealing temperature, the compensation from the vapor phase is smaller.

In addition, the enhanced formation of perovskite PZT phases at annealing temperatures above 650°C leaves more lead in the crystal structure of the thin film and leads to compositions closer to that of the original PNZT target [28]. On the other hand, as shown in Fig. 5.4, the zirconium content Zr/(Zr+Ti) of the post-



**Fig. 5.4.** Atomic zirconium content, Zr/(Zr+Ti), of PNZT films as a function of laser-beam fluence used at the deposition. The films were post-annealed at various maximum temperatures between 600 and 900°C (reprinted from Ref. 30 with permission from Elsevier Science)

annealed films increased monotonically from 0.43 up to 0.55 with increasing laser-beam fluences from 0.4 up to 2.4 J/cm<sup>2</sup>, respectively. The zirconium content was also practically independent of the heat-treatment process [30].

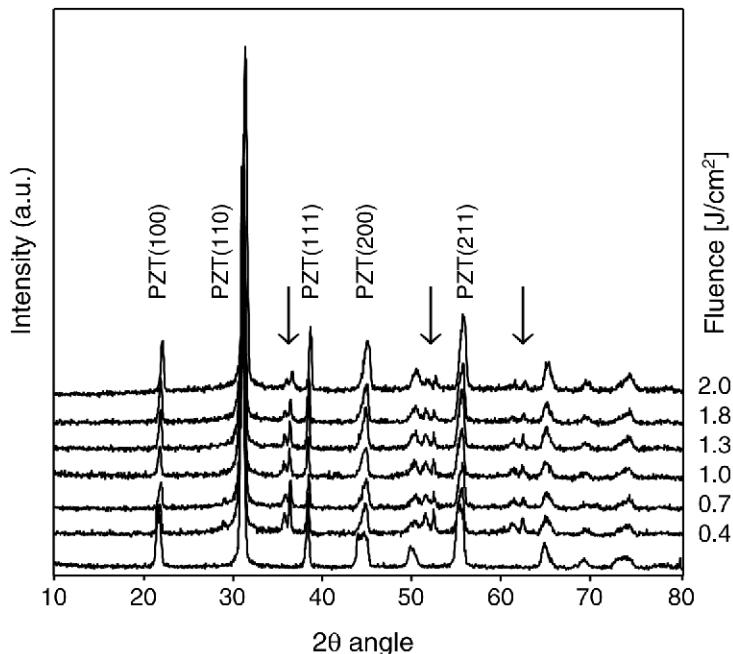
This observation is consistent with the results of the composition measurements of the ablated target surface [29]. At higher laser-beam fluences above 1.0 J/cm<sup>2</sup>, an increased evaporation of Zr and Ti further improves the compositional stability of the post-annealed PNZT thin films.

The dependence of zirconium content on the laser-beam fluence for films near the MPB with  $x \approx 0.53$  also makes it possible to control the crystal structure of the film between the trigonal and tetragonal structures by choosing the correct deposition parameters. As shown in Fig. 5.3, the film deposited at the low fluence of 0.4 J/cm<sup>2</sup> has the tetragonal crystal structure, but the film deposited at the fluence of 2.4 J/cm<sup>2</sup> has the trigonal crystal structure [30].

## 5.5 Compositional and Structural Changes in the Target

Changes in the composition and structure of the PNZT target surface after the ablation process were studied by EDS analyses and XRD measurements. A PNZT target with a density of  $7.4 \times 10^3$  kg/m<sup>3</sup> was ablated with a fluence of 1.0 J/cm<sup>2</sup> for 25 minutes with up to 32700 pulses by using the scanning ablation process. Because of the higher evaporation rate of lead compared to that of zirconium and titanium, a strong lead deficiency was found in the surface layer of the target. Relative values between 0.17 and 0.26 were found for the atomic lead content Pb/(Zr+Ti) in the surface layer after ablation, which are low values when compared with the initial value of around 1.0. The corresponding values of the relative zirconium content Zr/(Zr+Ti) were close to the initial target composition (between 0.52 and 0.58). In this case, the compositional analyses were made on relatively large macroscopic areas at the target surface. The changes in the chemical composition of the PNZT target surface during ablation promote surface segregation and the development of new compounds and phases.

Figure 5.5 shows X-ray diffraction patterns measured with CuK $\alpha$  radiation from a PNZT target surface before and after ablation with various laser-beam fluences. In all patterns measured after the ablation, three additional twin peaks appear at 2 $\theta$  angles of 35.7° and 36.3°, 51.3° and 52.3°, and 61.0° and 62.3°, respectively, indicating a slightly tetragonal new phase (indicated by the arrows in Fig. 5.5). Some changes in the shape and position of the PNZT peaks with increasing fluence are also seen in Fig. 5.5. The spreading of the PNZT peaks, e.g., the reflection from the (200) lattice planes at the 2 $\theta$  angle of around 44° at the bottom of Fig. 5.5, also reveals the presence of both trigonal and tetragonal PZT phases in the clean target surface [31]. In the patterns measured from the target after the ablation with low fluences of 0.4 and 0.66 J/cm<sup>2</sup>, an extra minor peak at the 2 $\theta$  angle of 28.7° is also seen in Fig. 5.5, but it disappeared at higher fluences.



**Fig. 5.5.** X-ray diffraction patterns measured with  $\text{CuK}\alpha$  radiation ( $1.54 \text{ \AA}$ ) from a PNZT-target surface before and after scanning laser ablation with various laser-beam fluences between  $0.4$  and  $2.0 \text{ J/cm}^2$ . The arrows indicate three twin peaks from a new phase (tetragonal  $\text{ZrO}_2$ ) formed in the laser-ablation process.

It is possible to conclude from the EDS results that the topmost target surface after ablation with the scanning process, and the top globules of the laser cones in the local ablation process, contain new Ti- and Zr-oxide compounds such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and possibly  $\text{ZrTiO}_4$  ( $\text{Pb}$  is found only in small droplets on the surface). However, at the high surface temperatures during the ablation process, the  $\text{ZrTiO}_4$  phase should also decompose into the  $\text{TiO}_2$  and  $\text{ZrO}_2$  phases [32,33]. The intensities of the new XRD peaks in Fig. 5.5 are weak which may relate to an amorphous structure of the new surface layer. The three twin peaks in the XRD patterns agree with the (200), (220), and (311) reflections of a cubic structure with the face-centered-cubic (fcc) Bravais lattice after a slight distortion to a tetragonal structure with the body-centered-tetragonal Bravais lattice [29].

The lattice constants of the tetragonal structure are in this case  $a \approx 4.941 \text{ \AA}$  and  $c \approx 5.032 \text{ \AA}$ , which are in close agreement with the values of the tetragonal  $\text{ZrO}_2$  [34,35]. Therefore, the new peaks in the XRD patterns in Fig. 5.5 are related to tetragonal  $\text{ZrO}_2$  because the cooling rate after laser-ablation process is fast. The intensity of the twin peaks also decreases with increasing fluence. An increase in the thickness of the new (amorphous) surface layer after ablation with increasing fluences may be the reason for the intensity decrease. Small amounts of crystalline

$\text{ZrO}_2$  and  $\text{TiO}_2$  phases may be present at the bottom of the surface layer. An average grain size of 32 nm was calculated with the Scherrer equation [36] for this new phase in the surface layer of the ablated target. The EDS measurements from the top globules of the laser cones revealed a significant lead deficiency.

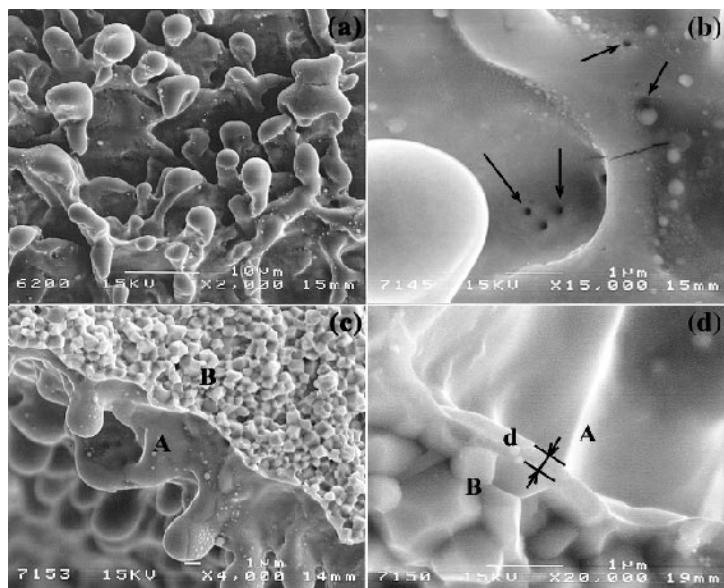
In fact, lead was missing in the top structure of the globules after both the local and scanning ablation processes. Instead, droplets of pure lead were found between the laser cones and on the walls of individual laser cones [see Figs. 5.6(a) and (b)]. On the other hand, the relative zirconium content  $\text{Zr}/(\text{Zr}+\text{Ti})$  was around 0.56 in all cases, which is close to the initial value in the target. These results also support the presence of both  $\text{TiO}_2$  and  $\text{ZrO}_2$  compounds in the top globules of the laser cones.

Raman spectra from a PNZT target surface before and after ablation were also measured [29]. The initial target surface had a typical Raman spectrum from PNZT ceramics with a trigonal structure as the main phase [37]. After ablation with single laser pulse having a fluence of  $1.0 \text{ J/cm}^2$ , a similar Raman spectrum was obtained. However, after ablation with 50 laser pulses, no specific Raman modes were found in the Raman spectrum. On the other hand,  $\text{TiO}_2$  and  $\text{ZrO}_2$  phases have several Raman-active modes in the same Raman-shift region [38]. The penetration depth of the applied argon-ion laser light with the wavelength of 514.532 nm was only a few hundred nanometers, which means that the top layer of the ablated target was either amorphous or possibly metallic. However, surface conductivity measurements from the ablated targets did not show any major conductivity changes with respect to the initial target surface. Thus, the combined information from the XRD and Raman measurements, and also from the EDS analyses, makes it possible to conclude that, because of the high cooling rate after the laser-beam exposure, the topmost surface layer of the ablated target is an amorphous mixture of different oxide compounds such as  $\text{TiO}_2$  and  $\text{ZrO}_2$  with small lead droplets on its surface. At the bottom of this amorphous surface layer, there is also a small amount of crystallized tetragonal  $\text{ZrO}_2$  phase and possibly also a small amount of  $\text{TiO}_2$  phase in the rutile structure in targets ablated with low laser-beam fluences.

In addition to the neutral and ionized atoms, molecular species and electrons, particulates up to micrometer-scale are generated in the laser-ablation process. The formation of these particulates impairs the surface morphology and quality of the growing thin film. The particulates are formed and ejected when the laser beam interacts with the molten surface layer of the target. The existence of the particulates (see Fig. 5.2) impairs the properties of the thin-film structure, especially for optical applications [39]. The explosions of the molten target surface due to the superheating of the subsurface layer and a rapid expansion of gas pores buried below the target surface inside a ceramic polycrystalline target are considered to be the dominant mechanisms responsible for the particulate formation [40,41]. On the other hand, the formation of a laser-cone structure on the target during a pulsed-laser deposition process generates large-scale particulates on the growing thin-film surface. In the case of metal targets, hydrodynamic sputtering has been considered to be a mechanism responsible for the particulate formation [42]. The dependence of the particulate density on the target density is assumed to relate

also to pores inside the sintered ceramic PNZT targets. The concentration of pores decreases with the increasing density of the PNZT ceramics and thus the number of particulates from the explosions of the pores under the target surface decreases.

Changes in the chemical composition of the PNZT target surface during ablation promote surface segregation and the development of new compounds and phases. XRD and EDS studies have revealed that new compounds are formed in a surface layer of the target as a result of changes in the chemical surface composition caused by differences in the evaporation rates of the elements. On the other hand, the surface segregation of certain elements and the fast cooling rate of the molten target surface after laser-beam exposure further promote a formation of amorphous structures and unstoichiometric compounds. These new compounds and phases in the surface layer which have higher melting points than that of the bulk target prevent the etching of the underlying layers of the target in the ablation process [43]. Thus, the etching of the target surface becomes non-uniform and laser-cone structure starts to develop in the target surface. Once the formation of the laser-cone structure is initiated, the laser-beam fluence dilution in the steep walls of the individual laser cones further strengthens the effect. The laser-cone structure in the case of a scanning laser beam is shown in Fig. 5.6. The larger magnifications reveal explosion holes with a diameter between 100 and 200 nm as a result of subsurface heating and a rapid expansion of the gas in the pores below the target surface.



**Fig. 5.6.** SEM micrographs (a) and (b) show surface morphologies with different magnifications and (c) and (d) cross sections of a PNZT target after a scanning laser-ablation process

These explosions at the target surface generate the smaller particulates found on the PNZT thin-film surfaces. The surface of the targets had also numerous microcracks after ablation, which indicates a fast cooling and solidification rate of the molten layer at the target surface. Figures 5.6(c) and 5.6(d) show SEM micrographs of different cross sections of a PNZT target. The figures reveal the porous structure of the PNZT target with a density of  $7.4 \times 10^3$  kg/m<sup>3</sup> and sintered at 1100°C for 20 minutes. According to Fig. 5.6(d), the thickness  $d$  of the molten layer at the PNZT target surface had been less than 300 nm [29].

## 5.6 Raman Spectroscopy Studies of PZT Films

### 5.6.1 Basic concepts of the Raman effect

Despite the fact that most of the light traveling through a medium is either transmitted or absorbed by the medium, a small fraction is scattered, almost in all directions, by inhomogeneities inside the medium. These inhomogeneities may be static (like dislocations or point defects) or dynamic. Fluctuations in the density of the medium that are associated with atomic vibrations is an example of dynamic scattering. We consider the dynamic case and phonons. Inelastic scattering of light by acoustic phonons and optical phonons are called Brillouin and Raman scattering, respectively. The radiation produced in Raman scattering can further be divided to *Stokes* (light scattered with lower energy than the energy of the incoming light) and *anti-Stokes* scattering (light scattered with higher energy).

Raman scattering in crystals can be explained from the classical and from the quantum theoretical point of view. Classically, one determines the dipole moment  $p$  by the equation  $p = \alpha E$ , where  $\alpha$  is the polarizability and the atoms of the sample are subjected to an electric field  $E$ . Polarizability  $\alpha$  is modulated by the thermal excitations (phonons in crystals) present in the sample. The scattered radiation is produced by re-radiation of energy by the oscillating dipole moment  $p$ , the scattered intensity  $I$  being proportional to  $|p|^2$  and inversely proportional to the fourth power of the wavelength of the scattered light [44]. The angular dependence of the intensity  $I$  of the oscillating dipole is given by the relation  $I \propto \sin^2\theta d\omega$ , where  $\theta$  is the angle between the dipole moment axis and the given direction, and  $d\omega$  is a solid angle increment (see, e.g., Ref. 45). Now, considering the modulation of a particular component  $\alpha_{ij}$  as an example, we can see that this component is concerned with an exciting electric field along  $j$  and a resultant dipole along  $i$ . The dipole is modulated in the same way as the component, so that light at the Raman-shifted frequency is emitted as from a dipole of direction  $i$ . The Raman scattered light is polarized in the plane containing  $i$  and the propagation direction [45]. The intensity of the Raman scattered light can be calculated from the time-averaged power radiated by the induced polarizations into unit solid angle. Denoting the polarization of the incident and scattered light as  $e_i$  and  $e_s$ , respectively, the scattered intensity  $I_s \propto |e_i(\partial\alpha/\partial Q)_0 Q(\omega) \cdot e_s|^2$ , where  $Q$  is the vibration amplitude of a vibration of frequency  $\omega$ . The Raman tensor  $R$  is defined by the equation  $R =$

$(\partial\alpha/\partial Q)_0 \hat{Q}(\omega)$ , where  $\hat{Q}(\omega)$  is a unit vector parallel to phonon displacement. By measuring the dependence of the scattered intensity on the incident and scattered polarizations, one can deduce the symmetry of the Raman tensor and hence the symmetry of the corresponding Raman-active phonon. This, however, necessitates single crystals. The case of ceramics is described below.

It is tempting to consider Raman scattering as an interaction involving photons and phonons only. However, this interaction is very weak for visible light. Direct scattering of light by phonons necessitates that phonons and photons have comparable frequencies. Thus, this kind of process could arise at the far-infrared region. A theoretical model for this ionic Raman effect is reported in Ref. 46, but experimental verification seems to be lacking. From the quantum theory point of view, it is usually assumed that the radiation interacts with the lattice vibrations through the intermediary of the electrons in the crystal [44,47]. Loudon [44] has given three different elementary first order Raman scattering processes in terms of the elementary interactions between the radiation, the electrons, and the lattice. The most common of these three processes is the one where a photon with an angular frequency  $\omega_i$  is present in the initial state and a photon with an angular frequency  $\omega_s$  together with a phonon having an angular frequency of  $\omega$  is present in the final state (so that this process is particularly for the Stokes component, but the corresponding process for the anti-Stokes component can be obtained by simple substitutions). The process involves three virtual electronic transitions accompanied by the following photon and phonon transitions: (1) a photon  $\omega_i$  is absorbed, (2) an optical phonon  $\omega$  is created, (3) a photon  $\omega_s$  is emitted. Thus, in a quantum picture the scattering should be viewed as a third-order process. In the first step an electron-hole pair is created and this pair is scattered into another state by emitting a phonon in the second step. The electron-hole pair recombines radiatively in the third step with emission of the scattered photon. The third step involves a spontaneous emission of the scattered photon and thus this process is known as *spontaneous Raman scattering*.

In fact, when electromagnetic waves are propagating in a crystal they propagate only as *polaritons*. However, in the usual Raman scattering setup the wave-vector of the phonons involved is so large that the measured frequency is essentially that of the transverse optical (TO) phonon. Longitudinal optical (LO) phonons do not couple to transverse photons and thus do not participate in the polariton process. Strictly speaking, Raman scattering with phonons is the scattering of *exciton polaritons* under emission or absorption of a *phonon polariton* [48]. An exciton polariton is a coupled state of an exciton with a photon and a phonon polariton is a coupled state of a transverse phonon with a photon. In the weak coupling picture one can say that a photon creates a virtual exciton (electron-hole pair in the treatment given above) and is scattered by emission or absorption of an optical phonon. Polariton dispersion curves can be determined experimentally by forward Raman scattering. The understanding of these experiments necessitates strong-coupling or polariton picture. Since we are not involved in polariton experiments, the weak-coupling picture given above is valid.

### 5.6.2 Raman active modes

The exciting radiation in Raman experiments has a long wavelength; therefore, because of the wave-vector conservation law the wavelength of phonons in the first-order Raman scattering is practically infinite as compared with the dimensions of the unit cell of the crystal. Now, the group theory considerations are restricted to normal modes at the center of the Brillouin zone (in fact, to modes near the zone center, in a region where the polaritons are essentially phonon-like) that are those normal modes transforming as the irreducible representations of the point group of the space group. For general  $k$  directions, the phonons have mixed symmetries. Since optical modes have only nonzero frequencies at  $k = 0$ , these modes may only scatter light in a first-order scattering process. Thus, for  $k$  in any crystal direction, only a maximum of  $3 \times (r-1)$  ( $r$  is the number of atoms in the crystal basis) optical modes may be observable. By changing the crystal orientation with respect to the polarization and propagation directions of the incident light, it is possible to observe another set of modes.

The criterion which determines whether or not a phonon mode is active in *first order* Raman scattering is the condition that it transforms in the same way as the tensor components  $\alpha_{ij}$  under the point group of the lattice. This means that the irreducible representation, according to which the normal modes transform, must be contained in the irreducible representation for which the tensor components  $\alpha_{ij}$  form a basis. The components of the polarizability tensor transform like products of coordinates ( $xx$ ,  $xy$ ,  $xz$ , and so on), whereas the components of the electric dipole moment transform like the coordinates ( $x$ ,  $y$ ,  $z$ ). So, the phonons (normal modes) with even symmetry are Raman active, whereas phonons with odd symmetry are Raman inactive. Similarly, a phonon is IR active if it belongs to an irreducible representation which is contained in the representation for which the components of the electric dipole moment form a basis. In centrosymmetric crystals (like the cubic phase of lead titanate and PZT), IR and Raman activities are complementary, i.e., modes which are Raman active are IR inactive and vice versa. However, also in these crystals some modes may be both Raman and IR inactive and are called silent (like the  $T_{2u}$ -mode in the high temperature phase of lead titanate and PZT). Actually, the high temperature phase of PZT is an extreme example of this complementary property, since all atoms lie at the centers of symmetry (as long as the local distortions are neglected) and thus no first order Raman scattering can occur.

### 5.6.3 Raman spectra of ceramics

In the case of a polycrystalline material, Raman active modes for different directions and polarizations are, in principle, simultaneously observable. Further, Burns and Scott showed [49] how peaks in the Raman spectra of ceramics occur at just those frequencies corresponding to the actual modes propagating along the principal crystal axes. This makes the identification of Raman peaks measured from ceramics possible by directly comparing single crystal spectra and a spectrum measured from ceramics. However, it is not always possible to obtain single crystals, so

another method is needed. In the case of PZTs, this can be done by studying the spectra measured from lead titanate single crystals, and comparing them with the spectra measured from polycrystalline lead titanate. By replacing Ti ions by Zr ions in the structure of  $\text{PbTiO}_3$ , peaks start to shift toward lower frequencies and become broader. However, as long as the symmetry is kept the same ( $P4mm$  in this case), most of the peaks can be identified by this simple method. Particular care must be taken, since there are several other processes which might lead to the formation of peaks in the Raman spectra. For example, second or higher order modes might arise more easily in polycrystalline samples than in single crystals. Also peaks due to the other minor phases, which may not be easily seen by X-ray diffraction techniques, may have such large scattering cross sections that the possible Raman active modes appear in the measurements. Symmetry breaking (such as the breaking of translational symmetry by substitution of titanium by zirconium in lead titanate) may also lead to the cases, where some of the modes become Raman active. Optical transitions can also cause extra peaks. This necessitates a higher order process, and as a result, lower or even higher energy photons can be emitted. In order to study the origin of the peaks, several measurements can be used to find out whether a mode is a true Raman mode or not. Simple ways to verify this are to measure both anti-Stokes and Stokes spectra, to carry out the measurement with several wavelengths; to vary thermodynamic variables such as temperature, pressure, and electric field during the measurement; and plot the mode frequencies and intensities as a function of the selected variable.

#### 5.6.4 Raman active phonons of PZT ceramics

Because the compositions of the thin films considered in this chapter are limited to  $x \leq 0.55$ , we will limit our discussion to the symmetries of these materials. These are cubic  $Pm\bar{3}m$  (high temperature paraelectric phase), tetragonal  $P4mm$ , and trigonal  $R\bar{3}m$  phases. Table 5.1 below summarizes first order Raman active modes in each phase.

In addition, long-range Coulomb forces lift the degeneracy of the  $T_{1u}$  modes in the cubic phase into a doubly degenerate  $T_{1u}(\text{TO})$  mode (polarization transverse to  $k$ ) and a single  $T_{1u}(\text{LO})$  mode (polarization parallel to  $k$ ). Similarly, the degeneracy of the transverse and longitudinal modes in tetragonal and trigonal phases is lifted by the long-range Coulomb forces. The frequencies of long wavelength longitudinal and transverse optical vibrations are related by the Lyddane-Sachs-Teller (LST) relationship provided that the wavenumber is above the polariton region of the dispersion curve. The following labelling scheme in the tetragonal phase was introduced [50] for the optical  $A_1$  and  $E$  modes, originating from the three  $T_{1u}$  representations:

$A_1(3\text{TO})$	$A_1(3\text{LO})$	$E(3\text{TO})$	$E(3\text{LO})$
$A_1(2\text{TO})$	$A_1(2\text{LO})$	$E(2\text{TO})$	$E(2\text{LO})$
$A_1(1\text{TO})$	$A_1(1\text{LO})$	$E(1\text{TO})$	$E(1\text{LO})$

where the numbers in the parentheses increase with the increase of the particular mode frequency. LO and TO refer to longitudinal and transverse modes, respectively. Because the  $E$  and  $B_1$  modes from the splitting of the  $T_{2u}$  modes are essentially degenerate, they are labelled  $E \oplus B_1$  or “silent”.

**Table 5.1.** Classification of normal modes of vibrations for different phases of PZT at  $\Gamma$  ( $k = 0$ ). Each listed phase has one formula unit in the primitive unit cell. The dimensions of the irreducible representations  $T_{1u}$ ,  $T_{2u}$ ,  $E$ ,  $A_1$ ,  $A_2$ , and  $B_1$  are 3, 3, 2, 1, 1, and 1, respectively.

Phase	Normal modes of vibration	Remarks
Pm3m	$4T_{1u} \oplus T_{2u}$	Optical modes in three $T_{1u}$ are IR active, but in $T_{2u}$ they are neither Raman nor IR active (silent). Modes in the fourth $T_{1u}$ correspond to three acoustic modes.
P4mm	$4E \oplus 4A_1 \oplus E \oplus B_1$	Optical modes in $E$ , $A_1$ , and $B_1$ are both Raman and IR active. Modes in a representation $A_1 \oplus E$ correspond to three acoustic modes.
R3m	$4E \oplus 4A_1 \oplus E \oplus A_2$	Optical modes in $E$ and $A_1$ are both Raman and IR active. The mode $A_2$ is neither IR nor Raman active. Modes in a representation $A_1 \oplus E$ correspond to three acoustic modes.

### 5.6.5 Characteristic features of the Raman scattering from the structural point of view

Traditionally, Raman scattering measurements have been used for the studies of first order Raman active modes as a function of various thermodynamic variables, such as temperature, electric field, and pressure. This has offered an experimental way to gain information related to the phase transitions. More recently, it has become possible to study the electronic energy band structure using resonance-Raman spectroscopy techniques. In the case of thin films, Raman imaging has proven to be an efficient way to study polycrystalline films and crystal orientation on a micrometer scale.

Since our studies are related to the structural features of these ceramics, we will discuss the symmetry breaking on a local scale. These local defects or distortions have a very crucial role in the formation of ferroelectric domains, or even in the determination of stable crystal symmetries.

As the name scattering suggests, the information obtainable from Raman scattering is very different in nature from that obtainable from diffraction experiments. Raman scattering can be described as a very local probe, yielding information of a unit cell scale phenomena (such as distortions due to the substitute atoms), whereas the information obtainable from conventional X-ray or neutron diffrac-

tion experiments tells about the average crystal structure. This is clearly demonstrated by observations that show peaks above the Curie temperature  $T_C$  in  $\text{KTaO}_3$  [51] (where no first order Raman scattering should occur, by symmetry). Uwe et al. [51] related the origin of polar nanoregions even far above the bulk  $T_C$  to symmetry-breaking defects which induce randomly-oriented local domains. There were also found broad peaks in the Raman spectra of PZT ceramics above  $T_C$  at roughly the same energies as the first order Raman peaks occur in a ferroelectric phase below  $T_C$  [52]. Thus, these peaks might originate from higher order Raman scattering, or due to the symmetry-breaking defects. This latter explanation is more likely once one takes into consideration the fact that the peak positions were nearly the same below and above  $T_C$ .

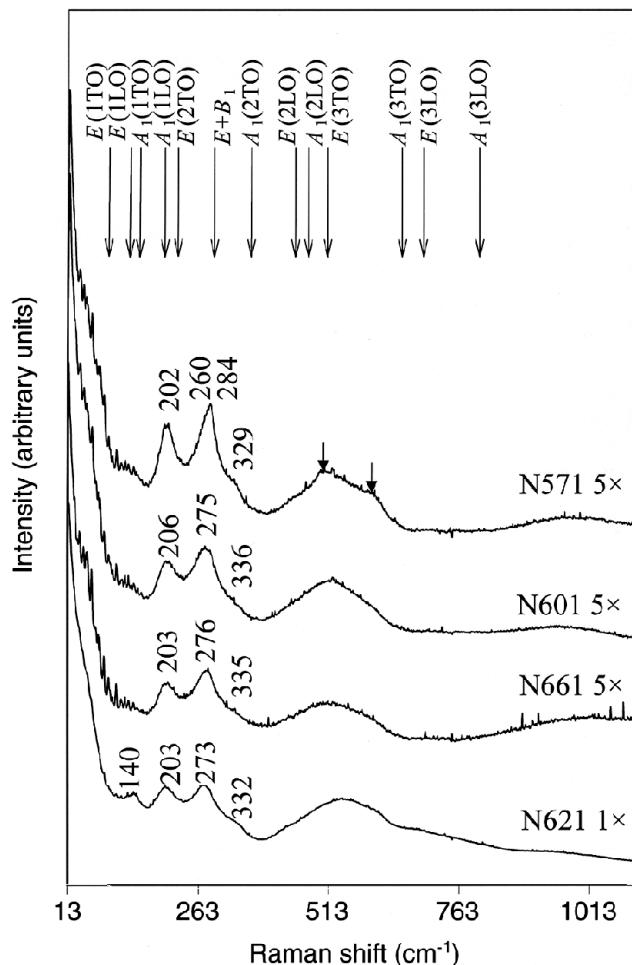
A second example that shows clearly how Raman scattering yields information related to the local defects is the splitting of  $E$ -symmetry modes in tetragonal PZTs [53]. This splitting was observed to increase with increasing Zr concentration and decreasing temperature. Further, a clear frequency jump in the higher frequency peak of the doublet due to the splitting of the  $E \oplus B_1$  mode (which is degenerate in pure lead titanate [50]) occurred when Zr concentration  $x$  changed from 0.40 to 0.50 [54]. This supposes an idea that the increasing amount of symmetry distortions in *ab*-basal planes will finally lead to the phase transition, and so one could consider this kind of symmetry breaking to be an example of precursor effects.

When one is studying the lattice dynamics of crystals, Raman scattering is again a powerful tool. The  $A_1(1\text{TO})$  mode of tetragonal PZT ceramics has a particularly interesting role, since it is the soft mode, which is also related to polarization behavior of PZTs. The strong anharmonicity of this mode was clearly demonstrated by the Raman measurements, which were performed as a function of temperature and Zr concentration [54].

### 5.6.6 Raman spectra of PZT thin films

Figure 5.7 shows the Raman spectra measured from four samples deposited under the experimental conditions mentioned in Table 5.2. All the intensities are comparable to each other except the lowest spectrum, which has to be multiplied by a factor of five. These Nd-doped PZT thin films were deposited by pulsed laser ablation without substrate heating at a pressure of 6 to  $8 \times 10^{-6}$  mbar. Polished  $\text{MgO}$  plates (thickness 500  $\mu\text{m}$ ) with (100) surfaces were used as substrates. The ablation target with the trigonal  $R3m$  structure as the major phase had a composition  $\text{Pb}_{0.97}\text{Nd}_{0.02}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$ , and an  $\text{XeCl}$ -excimer laser with the wavelength 308 nm was used in the ablation process. After ablation, the amorphous films were annealed at 700°C for 20 minutes with Nd-doped PZT powder in order to crystallize the films in a composition with equal amounts of *A*- and *B*-site cations.

We made a curve fit using Gaussians, except for sample A (see Table 5.2), where the peak at around 284  $\text{cm}^{-1}$  was fit with a sum of a Gaussian and Lorentzian line shapes. This peak at around 280  $\text{cm}^{-1}$  was fitted with two peaks, since the



**Fig. 5.7.** Raman spectra measured from four PNZT thin films on the MgO substrate. The positions of different Raman peaks at room temperature in  $\text{PbTiO}_3$  (Ref. 50) are also shown at the top.

fit with one peak was not able to yield a proper fit. Fontana et al. [55] conclude from their computed components of the effective charge of lead ions in  $\text{PbTiO}_3$  that the bonds between lead and oxygen in tetragonal  $\text{PbTiO}_3$  are mainly covalent and ionic, respectively, for directions parallel and normal to the polar  $c$  axis. It was possible to conclude from the high sensitivity of the  $E(1\text{TO})$ -mode frequency on the Zr concentration in PZT that the addition of Zr considerably softens the “ionic” force constant of vibrations with displacement polarization in the direction of the  $a$  axis. For  $A_1(1\text{TO})$ -mode vibrations with polarization in the direction of

**Table 5.2.** Film thickness and laser-beam fluence for four films ablated from a  $\text{Pb}_{0.97}\text{Nd}_{0.02}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3$  target. Also, the sintering temperature of the target used at pulsed-laser deposition is given.

Sample	Films thickness/nm	Laser beam fluence/Jcm <sup>-2</sup>	Sintering temperature of the target/°C	Density of the target/kgm <sup>-3</sup>
A	388	1.0	1100	7400
B	451	0.66	1100	7400
C	328	1.0	1000	6340
D	294	0.4	1100	7400

the  $c$  axis, the force constant, originating primarily from covalent bonding between lead and oxygen, was found to be insensitive to Zr addition [56]. On the other hand, we found that the  $A_1(1\text{TO})$  mode is sensitive to the addition of Nd to replace Pb in Nd-doped  $\text{PbTiO}_3$ .

The low-frequency background is mainly due to the subpeaks of the  $A_1(1\text{TO})$  mode. These subpeaks originate from the anharmonicity and double-well character of the potential energy of this mode, as discussed in more detail in Refs. [52,54,57]. Low-temperature Raman measurements made for the bulk ceramics showed that the anharmonicity model was able to describe qualitatively and even quantitatively the behavior of this low-frequency background [54]. This simple model was capable of describing the intensity behavior of the background as a function of temperature and Zr and Nd concentration.

It is seen that the  $E \oplus B_1$  mode is asymmetrical, which is likely due to the splitting of this mode. This mode is degenerate in  $\text{PbTiO}_3$  single crystals, but this degeneracy is obviously broken. This is the reason why we used two peaks in the fit of the  $E \oplus B_1$  mode of the sample A. In the case of other samples this asymmetry was not so clear, and this peak was fit with one Gaussian peak. Similar observations have also been found from bulk ceramics [52–54], where the peaks were often more clearly split into two parts (particularly the peaks corresponding to the  $E(1\text{TO})$  and the  $E \oplus B_1$  mode at low temperatures). Further, the existence of  $A_1(1\text{TO})$  mode indicates that the films contain both tetragonal and trigonal phases. This mode at around  $135\text{ cm}^{-1}$  does not appear in pure trigonal samples. Also, the shoulder of the  $E \oplus B_1$  mode at around  $330\text{ cm}^{-1}$  disappears from the samples containing only trigonal phase. It is interesting to note, that the peaks at around  $750\text{ cm}^{-1}$  have practically vanished, although their intensity in the bulk ceramics is roughly half of the intensity of the band centered around  $550\text{ cm}^{-1}$ .

Thus, Raman spectroscopy gives information from the two phase coexistence, which is not always easily extractable by X-ray diffraction technique [56,58,59]. This is the case when the tetragonal axis ratio  $c/a$  is close to 1, and the detailed phase analysis by X-ray diffraction necessitates rather tedious calculations. On the contrary, the existence of both phases is seen by inspection from the Raman spectrum.

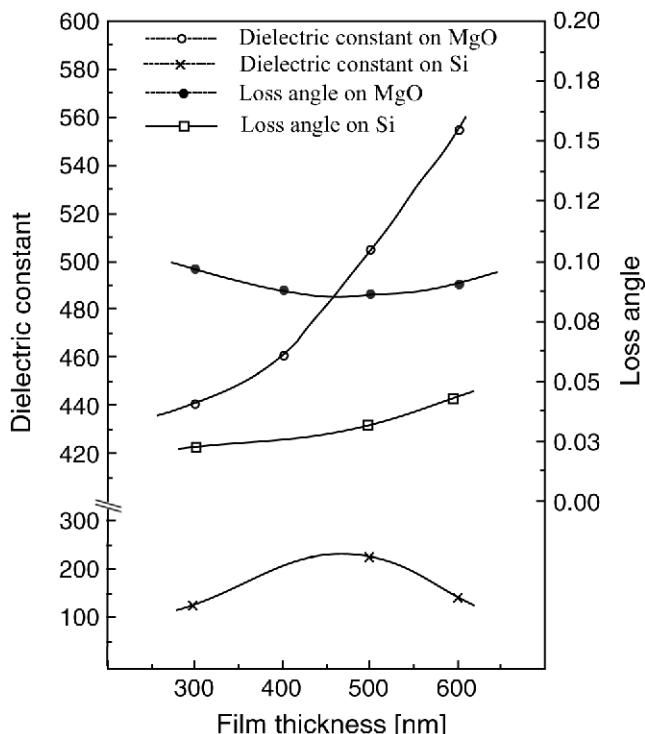
The main differences in the Raman spectra between trigonal and tetragonal phases are in the low- and high-frequency regions. The transverse modes  $A_1(1\text{TO})$  and  $E(1\text{TO})$  from the lowest  $T_{1u}$  representation correspond to the soft modes. However, the soft modes are missing in the Raman spectrum from the trigonal  $R3m$  phase. Soft modes have been found in the low-temperature trigonal  $R3c$  phase [60] and their frequency decreases with increasing temperature, approaching the zero frequency at the transition temperature to the  $R3m$  phase. The splitting of the peak at about  $550 \text{ cm}^{-1}$  in the trigonal phase into the  $E(3\text{TO})$  and  $A_1(3\text{TO})$  peaks at about  $500$  and  $600 \text{ cm}^{-1}$ , respectively, in the tetragonal phase is the other clear difference in the Raman spectra between trigonal and tetragonal phases. This is seen from the Raman spectrum of sample A in Fig. 5.7 and is indicated by small arrows.

## 5.7 Electrical Properties of PNZT Films

### 5.7.1 Permittivity and spontaneous polarization

The dielectric properties of PZT thin films are typically found to be somewhat moderate as compared with the properties of bulk ceramics. Values of the dielectric constant and the remanent polarization of thin films are lower, and dielectric losses are higher. However, high values of the breakdown field have been obtained in thin-film capacitor structures. The dielectric constant and the loss angle of PNZT thin films as a function of the film thickness on both MgO and silicon substrates are shown in Fig. 5.8. In the case of the MgO substrate, the relative dielectric constant increases nearly linearly from 440 to 560 with increasing film thickness. A similar behavior was found also in PZT thin films fabricated with the sol-gel spin-coating and organo-metallic decomposition techniques [61]. Different mechanisms, including the formation of an interfacial layer with a high defect concentration between the electrode and the PZT film, Schottky-barrier formation, differences in the grain size and film density, and the presence of mechanical stresses, have been proposed to be responsible for this behavior [61,62]. As described later in Section 5.7.3, the dielectric constant decreased with increasing compressive stress in PNZT films on the MgO substrate. However, in the films deposited on the silicon substrate, much lower values of the relative dielectric constant between 100 and 200 were obtained, and no clear dependence of the values on the film thickness was found.

According to the results in Fig. 5.8, loss-angle values of about 0.09 and 0.03, with simultaneous impedance values of 2 and  $25 \text{ M}\Omega$ , were measured in the films on the MgO and silicon substrates, respectively. Typical hysteresis loops for the polarization of films in the Pt/PNZT/Pt capacitor structures on both substrate materials are shown in Fig. 5.9. A remanent polarization of  $18 \mu\text{C}/\text{cm}^2$  and a coercive field of about  $100 \text{ kV}/\text{cm}$  were found in the films on the MgO substrate. In addition, it was found that the value of the coercive field depended also on the

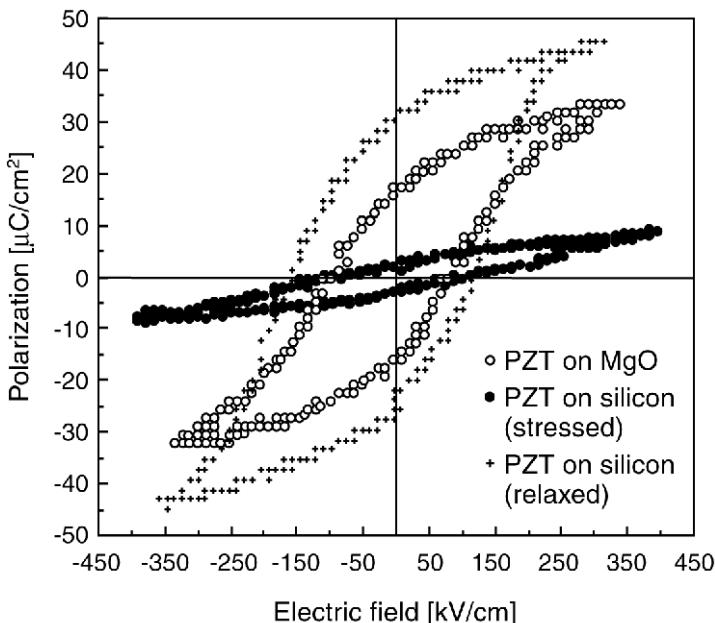


**Fig. 5.8.** Relative dielectric constant and loss angle measured from PNZT thin films on silicon and MgO substrates as a function of the film thickness (reprinted from Ref. 66 with permission from AIP)

compressive stress in the PNZT film. For films on the silicon substrate, a narrow hysteresis loop with a modest remanent polarization of  $3 \mu\text{C}/\text{cm}^2$  and a coercive field of about  $100 \text{ kV}/\text{cm}$  were measured. So far, all the results given to the dielectric properties of PNZT films on the silicon substrate were measured from films with a good morphology and uniform structure.

The dielectric constant of PNZT films was also measured as a function of temperature. A Pt/PNZT/Pt structure with a film thickness of 500 nm was fabricated on the silicon substrate, and measurements were carried out at the frequencies of 1 kHz and 10 kHz. The transition from the ferroelectric tetragonal phase to the paraelectric cubic phase was found to appear in a narrow temperature range, and the Curie temperature was found to be about  $360^\circ\text{C}$ .

Dielectric losses  $\tan\delta$  as a function of frequency were also measured for the Pt/PNZT/Pt capacitor structures on both MgO and silicon substrates with various film thicknesses. At low frequencies, all samples had quite low  $\tan\delta$  values below 0.06. For films on the MgO substrate, the increase of the relative dielectric constant



**Fig. 5.9.** Polarization vs. electric field hysteresis loops of the Pt/PNZT/Pt capacitor structures on MgO and silicon substrates. In the case of the silicon substrate, hysteresis loops measured from both stressed and relaxed PNZT films are shown (reprinted from Ref. 66 with permission from AIP)

$\varepsilon_r$  with increasing film thickness (Fig. 5.8) is also shown in the behavior of  $\tan\delta$  with increasing frequency: the value of  $\tan\delta$  increased from about 0.06 to 0.3 with increasing film thickness at the frequency of  $10^6$  Hz. On the other hand, a typical behavior of  $\tan\delta$  with frequency for stressed PNZT films with a high resistivity on the silicon substrate was similar to that of a 300 nm thick film on the MgO substrate, where the loss angle was almost constant with the frequency up to  $10^6$  Hz.

### 5.7.2 Electronic conduction

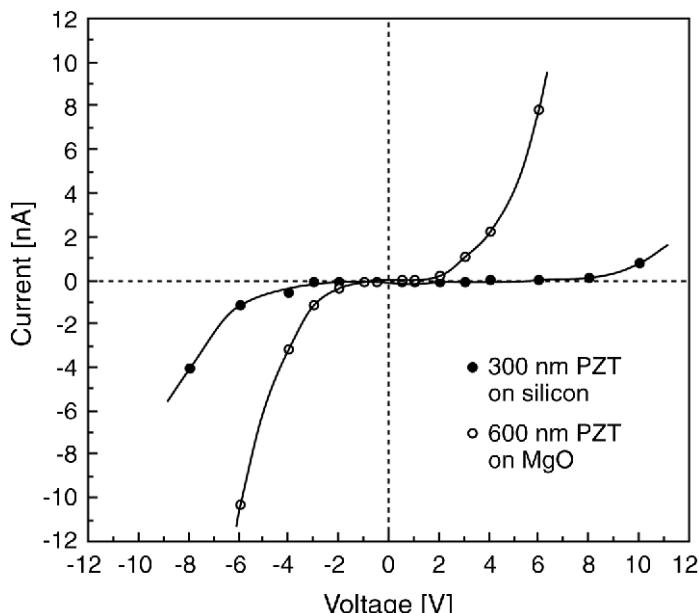
The pure ferroelectric  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  bulk ceramics with compositions near to the MPB ( $x \approx 0.53$ ) show p-type electronic conductivity due to nonstoichiometry. High values of conductivity impair the dielectric and piezoelectric properties of the ceramics. The poling process becomes difficult and PZT samples with high conductivity have rounded sluggish hysteresis loops due to the space-charge response out of phase relative to the alternating external electric field [62]. Also, high dielectric losses and overheating of samples even at low frequencies are typical problems in PZT ceramics with high extrinsic conductivity. However, the substitution of trivalent lanthanide ions like  $\text{La}^{3+}$  and  $\text{Nd}^{3+}$  for  $\text{Pb}^{2+}$  sites tends to de-

crease the p-type conductivity by incorporating excess electrons and thus compensating the effect of holes.

The current response of the Pt/PNZT/Pt structure to the external electric field possesses a typical behavior of a metal-insulator-metal (MIM) capacitor. The time dependence of the current in Pt/PZT/Pt structures can be divided into three different regions. After the introduction of an electric field, a fast-decaying charging current of the capacitor begins to flow. Next, a stabilized long-term leakage current is observed. Finally, after about 100 hours, an electrical degradation of the PZT thin film leads to a strong increase in the leakage current, causing a destructive breakdown [63]. An understanding of the conduction mechanism during the stabilized long-term leakage current gives useful information, not only about the PZT film itself, but also about the properties of the interfaces between the electrodes and the film.

At low electric fields, PZT films exhibit an ohmic (linear) conduction with resistivity values from  $10^8$  to  $10^{13}$   $\Omega\text{cm}$  depending on the structure and defects of the film and also on the substrate and the electrode material and structure. The nonlinear behavior of the leakage current at electric fields exceeding about 50 kV/cm may relate to space-charge-limited current (SCLC), ionic conduction, Poole-Frenkel emission, Schottky-barrier emission or tunneling. In the case of the SCLC process, the carriers injected from the electrode form a quite freely moving space charge due to the reduced conductivity of the insulator. The trap states inside the dielectric decrease the conductivity; thus, the SCLC conduction is bulk controlled and also dependent on temperature. Ionic conduction takes place typically at elevated temperatures only due to a high activation energy ( $\sim 1\text{--}3$  eV) needed for the ions or vacancies to move through the crystal structure. In the case of a high field across a thin insulating film, Schottky emission of electrons may occur from the metal-cathode contact into the conduction band of the insulator (or, in the case of hole injection, from the valence band of the insulator into the metal cathode).

Characteristic leakage currents as a function of voltage for the Pt/PNZT/Pt capacitor structures on both MgO and silicon substrates are shown in Fig. 5.10. From the linear parts of the curves in Fig. 5.10, low-field resistivity values  $\rho$  of  $2.18 \times 10^{11}$  and  $2.97 \times 10^{12}$   $\Omega\text{cm}$  were obtained for the films on the MgO and silicon substrates, respectively. For the film on the MgO substrate, the current-voltage curve in Fig. 5.10 is quite symmetric, but for the film on the silicon substrate, an asymmetric current response is seen. This asymmetry is assumed to relate to differences in the hole emission at the bottom and top interfaces between the Pt electrode and PNZT film [64]. At positive voltages seen in Fig. 5.10 the bottom electrode is the cathode. This electrode interface was annealed during the heat treatment of the PNZT film. On the other hand, the top Pt/PNZT interface had not been annealed after the room temperature processing. This electrode is the cathode at the negative voltage values in Fig. 5.10. As described in Ref. 64, oxygen vacancies  $V_O^{2+}$  become mobile at elevated annealing temperatures and drift to the bottom PNZT/Pt interface to compensate the contact potential and cause a band bending and possible hole accumulation (ohmic contact) at the heat-treated PNZT/Pt contact.



**Fig. 5.10.** Current-voltage characteristics measured at room temperature from a 300 nm thick PNZT film in the Pt/PNZT/Pt structure on the silicon substrate and from a similar structure with a 600 nm thick film on the MgO substrate (reprinted from Ref. 66 with permission from AIP)

Conversely, at the top Pt-electrode contact without any heat treatment there is no band bending because of the lack of positive donors and holes for the compensation of the contact potential. This asymmetric contact structure is assumed to be the reason for the asymmetry in the current response to applied voltage in Fig. 5.10. An ohmic linear current response is seen at low voltages.

It was also found from the leakage-current measurements in the uniformly stressed PNZT thin films on the MgO substrate that the current density at a constant external electric field increased with increasing film thickness. For example, an increase of the current density from 22 to 9820 nA/cm<sup>2</sup> was found with increasing film thickness from 350 to 600 nm at an electric field of 100 kV/cm [65]. This result is an indication of a bulk-limited conduction mechanism, e.g., the Poole-Frenkel conduction. On the other hand, the asymmetry found in the current-voltage characteristics of the Pt/PNZT/Pt capacitor structures, especially on the silicon substrate, should be interpreted as evidence of an electrode-interface-controlled conduction mechanism, such as the Schottky-emission conduction.

The leakage-current density as a function of applied electric field was measured at 295, 323, and 423 K for various PNZT films deposited on both silicon and MgO substrates. From the measurements at elevated temperatures, it was possible to deduce that the Poole-Frenkel conduction is most probably the mechanism responsi-

ble for the leakage currents in the PNZT films at electric fields below 150 kV/cm [65,66]. Assuming the Poole-Frenkel emission mechanism for the long-term leakage conduction, the activation energies of conductivity were calculated to be between 0.15 and 0.18 eV. These values are in agreement with the estimates in Ref. 67 for the binding energies of the Pb<sup>3+</sup> hole traps in PZT ceramics. Two Raman peaks at around 1200 and 1500 cm<sup>-1</sup> (quantum energies about 0.15 and 0.18 eV, respectively) appeared in the Raman spectra from different PNZT samples at exposure with 3.41 eV UV quanta and were related to the trap energies of the Pb<sup>3+</sup> hole traps in Ref. 68. The present conduction results are also in good agreement with the results of Wouters et al. [64].

Both the results for the current-voltage characteristics in Fig. 5.10 and the results from the leakage-current measurements at elevated temperatures support the conclusion that under low-field conditions below 150 kV/cm, the leakage conduction in PNZT thin films occurs through the Poole-Frenkel mechanism due to the hopping of holes between Pb<sup>3+</sup> hole traps with activation energies between 0.15 and 0.18 eV. Although the experimentally obtained results at electric fields above 150 kV/cm suggests Schottky-emission conduction, assuming an abrupt change in the conduction mechanism may be unrealistic. However, external electric fields below 150 kV/cm are the most important from the application point of view.

### 5.7.3 Role of macroscopic residual stresses

In the multilayer capacitor structure, electrical properties of the PNZT thin film are also affected by the substrate material and processing conditions during the fabrication steps. Especially, the thermal stresses originating from unequal thermal expansion coefficients of the substrate and film during a heat treatment above 500°C can lead to a formation of hillocks or cracks, respectively, when high compressive or tensile stresses appear. Stresses in thin films are usually considered to be biaxial, acting only in the plane of the film and being relaxed in the direction perpendicular to the substrate surface. For instance, in the case of the silicon substrate both in sputtered platinum electrodes and in PNZT films deposited by the sol-gel technique, stresses were found to be tensile with values on the order of 1 GPa and 100 MPa, respectively [69]. Typically, the remanent polarization decreases and the Curie temperature increases with increasing stress. Furthermore, some electrical properties like the low-field dielectric constant, loss angle and remanent polarization have been reported to vary with the film thickness [62].

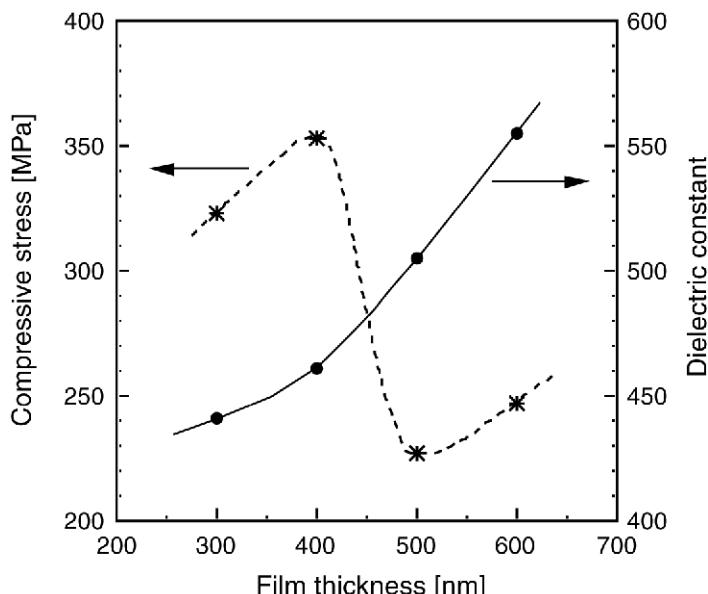
The origin of stresses in a thin film is related, in addition to the thermal expansion, to structural changes in the film during the growth and annealing processes and to the interactions between the film and the substrate or some other underlying layer. The stress can be divided into three different groups according to the phenomena causing the stress. Extrinsic stress is generated during the film-growth process and is strongly dependent on the deposition parameters. Intrinsic stress arises from dimensional changes in the film caused by densification, crystallization, and phase transformations during the heat-treatment procedure. Finally, thermal stresses are produced during a heat-treatment procedure due to unequal

thermal expansions of the film and the substrate [70]. In the case study, the Nd-modified PZT films were deposited at room temperature and were amorphous after deposition. Moreover, the films were post annealed in order to achieve the desired crystal structure. Therefore, the total macroscopic stress in the films can be considered to be a sum of the intrinsic and thermal stresses.

As already discussed, the post-annealed PNZT thin films grown with the pulsed-laser-deposition technique are typically under a macroscopic residual stress due to different thermal processing steps. The (413) lattice planes of the tetragonal crystal structure with a diffraction peak at around  $2\theta = 148^\circ$  in the case of  $\text{CuK}\alpha_1$  radiation were used for the stress analysis of the PNZT films [66]. The XRD patterns were measured at the tilt angles of  $0^\circ$ ,  $30^\circ$ ,  $45^\circ$ , and  $60^\circ$  from both PNZT/Pt/MgO and PNZT/Pt/SiO<sub>2</sub>/Si structures with various PNZT film thicknesses. An increase in the Bragg angle  $2\theta$  with increasing tilt angle, means a decrease in the distance  $d_{413}$  between the (413) planes, and is an indication of a compressive stress in PNZT films on the MgO substrate. An opposite behavior in films on the silicon substrate indicates a tensile stress. By applying Hooke's law, the macroscopic stress in the films was calculated. In the PNZT thin films deposited on the MgO substrate, the compressive stress was found to vary between 352 and 226 MPa with increasing film thickness as shown in Fig. 5.11. Although the dependence is not unambiguous, the stress clearly decreases with increasing film thickness. For PNZT films on the silicon substrate, tensile stresses of 415 and 405 MPa were measured with film thicknesses of 400 and 500 nm, respectively. Thus, the stress is assumed to decrease with increasing film thickness in the PNZT films on the silicon substrate as well [66].

On the other hand, it was found from the X-ray-diffraction results that in the PNZT films on the MgO substrate, the relaxation of the compressive stress favors the formation of ferroelectric tetragonal structure with the *c*-axis perpendicular to the film surface. In the case of the silicon substrate, the PNZT thin film is under a tensile stress, which favors the formation of tetragonal structure with the *c*-axis parallel to the film surface [66]. Then, the external electric field in the capacitor structure is mainly in the *ab*-plane of the tetragonal crystal structure and the polarization by the movement of both *A*- and *B*-site cations in the direction of the ferroelectric polarization (*c*-axis) is prohibited. This leads to moderate values for the permittivity and remanent polarization as shown in Fig. 5.9. Especially, in the PNZT films on the silicon substrate, a relaxation of stress due to cracking of the film or increasing the film thickness seems to release the crystal structure for a more effective polarization under an external electric field. For instance, the relative dielectric constant increased from around 100 to 530 and the remanent polarization, respectively, from 3 to 25  $\mu\text{C}/\text{cm}^2$  after a stress relaxation, as shown in Fig. 5.9.

In the case of compressive macroscopic stress, the directions of the *c*-axis and external electric field are the same, which makes the polarization through movement of *A*- and *B*-site cations easy in the Pt/PNZT/Pt capacitor structures on the MgO substrate. The effects of stress on the polarization and other dielectric properties are much lower in the films on the MgO substrate as compared to the effects



**Fig. 5.11.** Compressive stress and relative dielectric constant as a function of film thickness measured from PNZT films on the MgO substrate (reprinted from Ref. 66 with permission from AIP)

in films on the silicon substrate. However, the relative dielectric constant of films on the MgO substrate increased quite linearly from 440 to 560 with increasing film thickness and with decreasing compressive stress, respectively. It was also found that the value of the coercive field increased from 80 to 150 kV/cm with increasing compressive stress in the Pt/PNZT/Pt capacitor structures on the MgO substrate [66].

Also, the leakage current was found to change drastically with changes in the stress state in PNZT thin films. A strong decrease in the leakage current was found as a result of stress in PNZT films in the Pt/PNZT/Pt capacitors on the silicon substrate. In the case of a PNZT film with a thickness of 300 nm and tensile stress of about 400 MPa, very low values of the leakage current below 50 pA, up to electric fields of 120 kV/cm, were found. The relative dielectric constant  $\epsilon_r$  in these capacitor films with a high tensile stress was typically between 100 and 200 together with a  $\tan\delta$  value of about 0.03 for the dielectric losses and a modest remanent polarization  $P_r < 5 \mu\text{C}/\text{cm}^2$ . The current-voltage characteristics were also measured from a capacitor structure fabricated near a crack in the same PNZT film (the film was annealed with a higher temperature gradient of  $100^\circ\text{C}/\text{h}$ ). In this case, the stress was relaxed in the film due to cracking. The leakage currents in this capacitor were about three orders of magnitude higher. The resistivity  $\rho$  calculated from the linear part of the current-voltage characteristics at low electric fields for this capacitor structure was found to be  $3.6 \times 10^8 \Omega\text{cm}$  [65]. As mentioned before,

stressed PNZT films on the silicon substrate favor an orientation with the *c*-axis parallel to the film surface. As a result, the external electric field in the capacitor structure is mainly in the *ab*-plane of the tetragonal crystal structure; also, the polarization by the movement of both *A*- and *B*-site cations in the direction of the *c*-axis is prohibited causing the moderate values of the dielectric constant. However, the stress relaxation of the PNZT film had such drastic effects on the leakage current that the possibility of a different conduction mechanism was also studied. Other possible conduction mechanisms include the Schottky emission and the SCLC where the existence of space charge originates from the trapping of charge carriers at possible shallow traps in the PNZT film generated by the relaxation process [71]. Dielectric-loss measurements gave some support for the SCLC mechanism [66]. Stress-induced leakage current has been found also in ultra-thin SiO<sub>2</sub> layers in metal-oxide-semiconductor (MOS) capacitor structure on silicon single crystal [72].

## 5.8 Summary

Pulsed-laser deposition was found to be a versatile method for the fabrication of modified PZT thin films for different applications. It makes possible a congruent deposition of complex target materials like modified PZTs on different substrates with good stoichiometry.

Ferroelectric Nd-modified Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> thin films have been used as a case study to consider laser-assisted growth and characterization of multicomponent lead-zirconate-titanate films. The film growth was based on pulsed-laser deposition on various single-crystal substrates including sapphire, MgO, and silicon; the films were grown into the form of single layer PNZT thin films and multilayer capacitor structures with platinum electrodes. The deposition was done from sintered ceramic targets with a nominal composition of Pb<sub>0.97</sub>Nd<sub>0.02</sub>(Zr<sub>0.55</sub>Ti<sub>0.45</sub>)O<sub>3</sub> for the ferroelectric films and from a polished platinum disk for the electrode layers using a pulsed XeCl excimer laser with a wavelength of 308 nm and 20 ns pulse duration. Especially, the discussion concentrated on the properties of post-annealed thin films, which were deposited at room temperature.

EDS analyses revealed that the atomic lead content Pb/(Zr+Ti) in amorphous as-grown PNZT films was about 4.0 after ablation with low laser-beam fluences, but decreased rapidly with increasing laser-beam fluence and reached nearly stoichiometric composition of the target at the laser-beam fluence of 0.7 J/cm<sup>2</sup>. Atomic lead content of the post-annealed PNZT films varied also as a function of the annealing temperature, whereas the atomic zirconium content Zr/(Zr+Ti) was found to be quite insensitive to the annealing temperature, but it increased linearly as a function of laser-beam fluence. Using this dependence of the zirconium content, it was possible to control the crystal structure of the PNZT film between tetragonal and rhombohedral phases by adjusting the laser-beam fluence on the target surface properly.

XRD and EDS studies revealed that new oxide compounds ( $\text{TiO}_2$  and  $\text{ZrO}_2$ ) were formed on the surface layer of the target during the ablation process as a result of changes in the chemical surface composition caused by differences in the evaporation rates of the elements. New compounds and structures cause a shielding effect, which makes it possible to form regular laser-cone structure in the case of the local ablation process. Raman measurements together with XRD results from the ablated targets revealed that the topmost layer of the target surface was amorphous.

The different nature of X-ray diffraction and Raman scattering was discussed. It was found that X-ray diffraction results were inadequate for a proper interpretation of the two-phase (tetragonal and trigonal) coexistence in the films. Measured Raman spectra gave useful information about the two-phase coexistence in the films. For instance, it was found that the  $A_1(\text{ITO})$  mode peak at about  $140 \text{ cm}^{-1}$  in PNZT films was the most sensitive indication of the presence of the tetragonal phase in the film. Also, some common examples of the various sources for light scattering in PNZT samples were given.

Electrical properties of the PNZT thin films were studied by fabricating multi-layer capacitor structures of ferroelectric films with platinum electrodes using pulsed-laser deposition and post-annealing techniques on  $\text{MgO}$  and oxidized silicon substrates. The relative dielectric constant of the PNZT films on the  $\text{MgO}$  substrate was found to increase linearly from 440 to 560 with increasing film thickness. The remanent polarization was around  $18 \mu\text{C}/\text{cm}^2$  and the coercive field between 75 and 150 kV/cm. The smooth, uniform PNZT films on the silicon substrate had dielectric constants between 100 and 200 and remanent polarization around  $3 \mu\text{C}/\text{cm}^2$ . However, when the tensile stress of the film was relaxed by cracking, values of 530 and  $25 \mu\text{C}/\text{cm}^2$  were measured for the relative dielectric constant and the remanent polarization, respectively. In order to determine the corresponding conduction mechanism for the leakage current, the current-voltage characteristics were measured at several temperatures. At higher temperatures, the Poole-Frenkel type conduction mechanism was observed with activation energies between 0.15 and 0.18 eV. The low-field resistivity of these films varied between  $2.2 \times 10^{11}$  and  $2.9 \times 10^{12} \Omega\text{cm}$ .

The state of macroscopic stress in PNZT thin films due to the fabrication process was also discussed on the basis of X-ray-diffraction measurements. In PNZT films deposited on the  $\text{MgO}$  substrate, compressive stresses between 226 and 352 MPa were measured. In films on the silicon substrate, tensile stresses of about 400 MPa were found. The stress in the films decreased with increasing thickness and the leakage current also increased with increasing film thickness. The dielectric constant was found to depend inversely on the mechanical stress in the PNZT films. The coercive field also increased with increasing mechanical stress. Thus, the mechanical stress induced by different fabrication steps was found to have a strong effect on the dielectric properties of the PNZT thin films. Typically, in the uniform stressed films deposited on silicon substrates, the remanent polarization was quite modest. However, in the films on the silicon substrates where the tensile stress was relaxed due to cracking, much higher values for the remanent polariza-

tion and for the dielectric constant were measured. Furthermore, the leakage current in the Pt/PNZT/Pt-capacitor structure was found to be sensitive to the stress in the PNZT film and decreased with increasing stress. In addition, the leakage current in these capacitor structures increased by three orders of magnitude after cracking as compared to values in stressed-film capacitors without cracking, and the low-field resistivity was around  $3.6 \times 10^8 \Omega\text{cm}$ . According to the results of the loss-angle measurements, a possibility for the leakage current in these capacitors is the SCLC conduction mechanism.

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# 6 Silicon Carbide Crystals — Part I: Growth and Characterization

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## 6.1 Introduction

Silicon carbide (SiC), one of the oldest known semiconductor materials, has received special attention in recent years because of its suitability for electronic and optoelectronic devices operating under high temperature, high power, high frequency, and/or strong radiation conditions, where the conventional semiconductor materials like Si, GaAs, and InP are considered to have reached their limits. SiC exists as a family of crystal with more than 200 polytypes and a bandgap range of 2.4 to 3.3 eV. As a wide bandgap material, SiC possesses many superior properties, such as a larger operating temperature range, a high critical breakdown field ( $E_{cr}$ ), high resistance to radiation and the ability to construct visible-range light-emitting devices [1]. It also distinguishes itself by a combination of high thermal conductivity (higher than that of copper), hardness second to diamond, high thermal stability, and chemical inertness. Some of the basic properties of SiC in comparison with many other semiconductor materials are presented in Table 6.1a, and the crystallographic unit cell parameters of the most common polytypes are listed in Table 6.1b. Owing to its outstanding properties, silicon carbide is expected to bring significant breakthroughs in the areas of high temperature applications, power devices, microwave devices, and LEDs. Some of the SiC-based devices and elements that have been developed thus far are listed in Table 6.2. Several review articles devoted to the growth, properties and device applications of SiC have been published in the last five years [2–6].

**Table 6.1a.** The basic parameters of some semiconductors [1,7]

Material	$E_g$ eV	$T_m$ °K	$T_D$ °K	$T_w$ °K	K W/[cm ·°K]	$\epsilon$	$\mu_e$ cm <sup>2</sup> / [V·s]	$\mu_h$ cm <sup>2</sup> / [V·s]	$E_{cr} \times 10^{-5}$ V/cm	$V_s \times 10^{-7}$ cm/s
Ge	0.7	1210	374	280	0.6	16	3800	1800	1.0	0.6
Si	1.1	1690	645	410	1.35	12	1350	480	2.0	1.0
GaAs	1.43	1510	400	570	0.45	12	6000	320	2.6	1.0
BP	2.0	2300	1140	720	2.5	11	1500	300	4.0	2.0
GaP	2.2	1740	520	800	0.7	11	250	150	4.5	1.5
CdS	2.3	2020	290	840	0.2	11	350	15	10.0	1.0
3C-SiC	2.3	3100	1430	840	3–5	9.8	750	40	7	2.5
6H-SiC	3.0	3100	1200	1200	5–7	9.8	370	90	21	2.0
4H-SiC	3.2	3100	1200	—	5–7	9.8	800	115	20	2.0
GaN	3.45	1800	710	1250	1.0	9.5	400	—	14	2.2
ZnS	3.6	2200	340	1300	0.03	10	140	5	—	—
C	5.45	>3300	2230	2100	14	5.7	1800	1500	7.5	2.7
AlN	6.2	3100	1100	2100	2.0	9.1	—	—	—	1.5
BN	10.0	3300	1700	3300	3.0	7.1	—	—	—	1.5

Note:  $E_g$  — band gap;  $T_m$  — melting temperature;  $T_D$  — Debye temperature;  $T_w$  — working temperature;  $K$  — thermal conductivity;  $\epsilon$  — permittivity of the semiconductor;  $\mu_e$  and  $\mu_h$  — electron and hole mobilities, respectively;  $E_{cr}$ : critical electric breakdown field;  $V_s$ : saturated carrier velocity

**Table 6.1b.** Unit cell parameters of the most commonly studied SiC polytypes [8,9]

Polytypes	a[Å]	b[Å]	c[Å]	$\alpha$	$\beta$	$\gamma$
3C	4.439	4.439	4.439	90°	90°	90°
4H	3.073	3.073	10.053	90°	90°	120°
6H	3.073	3.073	15.08	90°	90°	120°
15R	12.69	12.69	12.69	13° 55'	13° 55'	13° 55'

**Table 6.2.** Selected SiC-based devices

Device or element type	Material	Reference
JFET	6H-SiC	(7,12)
UV photo detector	6H-SiC	(7,12)
MOSFET	6H-SiC	(7,12)
p-n-diodes	4H-SiC/6H-SiC	(7)
Vertical MOSFET	4H-SiC	(7)
Operational amplifiers IC	6H-SiC	(7)
Schottky diodes	6H-SiC	(7,10)
Blue/green LEDs	6H-SiC	(13)
MESFET	6H-SiC	(11,12)
BJT		(12)
Thyristor	4H-SiC	(11,12)
SIT		(11)
Schottky rectifier	4H/6H-SiC	(11,12)
MOSFET	15R-SiC	(14)
Sensors	3C	(15)

Note: JFET — Josephson field effect transistor; MOSFET — metal oxide field effect transistor; MESFET — metal field effect transistor; BJT — bipolar field effect transistor; SI — static induction transistor

### 6.1.1 Applications of SiC

#### *High temperature applications*

Current and future applications of electronic components have placed much more critical environmental requirements on semiconductors [7]. For example, high temperature electronic components and systems can play an important role in many areas, such as aircraft, spacecraft, automotive, defense equipment, power systems, and so forth. For reliable functioning of electronic devices under extreme conditions they need to withstand high temperatures. SiC appears to be a desirable candidate because of its high working temperature as well as Debye temperature. As reported by Chelnokov et al. [7], 6H-SiC is superior to Si, GaAs, GaN, and AlN for high temperature applications.

SiC can also find applications in sensors for high temperature, high pressure, and highly corrosive environments (e.g., combustion systems, gas turbines and the oil industry) [10]. For example, pressure sensors based on SiC thin layers deposited on an insulator structure have been successfully used to measure the combustion engine pressure up to 200 bar at temperatures up to 300°C [11].

**High power devices.** Power semiconductor devices are important for regulation and distribution of electricity. Since the efficient use of electricity depends on the performance of power rectifiers and switches, further improvements in efficiency, size, and weight of these devices are quite desirable. SiC has a high breakdown strength and therefore, it is possible to dope it at higher concentration, and still

have thinner layers for a given blocking voltage compared with the corresponding Si devices [11]. Indeed, the power losses can decrease dramatically with the use of SiC-based devices. Another desirable property of SiC for power application is its high thermal conductivity, which can facilitate the heat generated in the component to dissipate quickly. SiC power MOSFETs, diode rectifiers, and thyristors are expected to function over higher voltage and temperature ranges with superior switching characteristics. The size of these devices are expected to become significantly smaller compared to correspondingly rated Si-based devices [12]. This is due to the fact that SiC devices will not require heat dissipating components.

Although GaN and AlN are considered better than SiC in terms of several parameters [1] (see Table 6.1a), substrates of these materials are currently not available. Also, they are grown only heteroepitaxially using substrates of other materials, including SiC [1]. This leads to a very high dislocation density in the films, which limits the application of these materials for high power semiconductor devices. Moreover, high power is often coupled with high temperature where SiC is considered superior to GaN and AlN.

**High frequency devices.** Cellular phones, digital TV, telecommunication systems, and radars have made microwave technology an essential part of everyday life. Although some high power microwave semiconductor components have existed for a long time, such as Gunn, IMPATT, and TRAPATT diodes, these devices can only operate in parametric amplifiers, which are much more difficult to manufacture and tune. SiC-based microwave transistors are predicted to produce more efficient microwave systems and further expand their existing applications [11]. Silicon carbide SITs and MESFETs have already been developed for these applications. Indeed, silicon carbide SITs are challenging devices for high power applications up to 900 MHz. Interestingly, the first microwave MESFETs fabricated on a high resistivity 6H-SiC substrate showed a measured radio frequency gain of 8.5 dB at 10 GHz and  $f_{\max}$  of 25 GHz [12]. Further development of SiC-based microwave devices is underway.

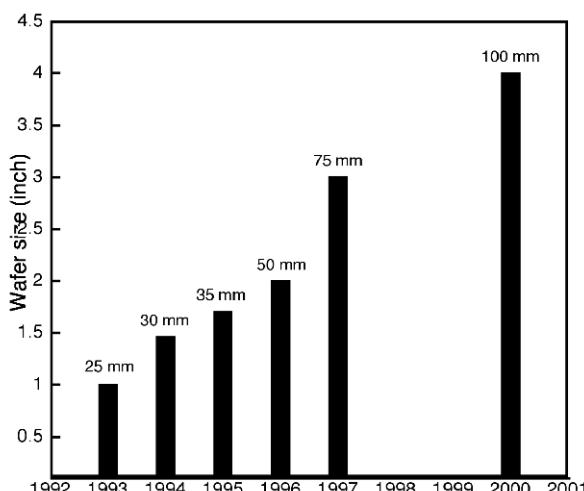
**Optoelectronic applications.** The special physical and optical properties of SiC have been further exploited to fabricate bright blue and green light emitting diodes (LEDs) [13]. From manufacturing considerations there are several advantages in using SiC as a substrate material such as easier handling and cheaper processing. SiC is also being used as a substrate for the growth of GaN, an important material for LEDs. Compared to GaN growth on sapphire substrates, it is possible to obtain structurally more perfect epitaxial GaN layers on SiC due to smaller lattice mismatch and closer match of thermal expansion coefficients.

The primary requirement for SiC-based devices is the production of high quality thin films, which in turn require high quality substrates. Although serious efforts have been made on SiC growth and significant progress has been achieved, the application of SiC-based devices remains limited because of the non-availability of SiC wafers of high quality at a cheaper price.

### 6.1.2 Historical development of SiC crystal growth

Although SiC is considered a new entrant to the electronics industry, it is, in fact, not a newcomer to the materials world. It was first reported in 1824. SiC was recognized as a silicide of carbon in 1895 and could be synthesized successfully by the Acheson process [16] using sand and coke. The SiC-based LEDs were made as early as 1907 using small SiC crystals obtained from the cavities formed in the Acheson system. However, further research on the development of SiC as a semiconductor material was not pursued for several decades because of the difficulty of growing good quality single crystals. In 1955, Lely demonstrated the growth of SiC on a porous SiC cylinder by vapor condensation [17]. This method was further refined by Hamilton et al. [18] and Novikov et al. [19], and is commonly referred to as the Lely method. Based on this method SiC platelets were prepared in the laboratory for several different applications. Halden [20] grew single crystals of SiC using Si melt solutions but this method was not continued because of the difficulty in obtaining bigger crystals. Kendal [21] later proposed a method of cracking gaseous compounds containing C and Si at high temperatures to form SiC crystallites, which is probably the basis for today's SiC CVD technology.

A real breakthrough occurred in 1978 when Tairov and Tsvetkov [22] demonstrated the seeded growth of SiC using the sublimation method. This was the milestone for SiC technology. Since Tairov and Tsvetkov used Lely's concept of vapor condensation, their method is commonly known as the modified Lely method. Further research on bulk growth is only a refinement and improvement of this technology. Commercially, SiC wafers were first made available by Cree Research, Inc., in 1991 [23]. The availability of SiC wafers in recent years has



**Fig. 6.1.** Progress in the increase of diameter of SiC wafers [2]

spurred extensive research on epitaxial growth. Matsunami group's [24] research in establishing step-controlled epitaxy is a notable development in optimizing SiC epitaxial growth morphology.

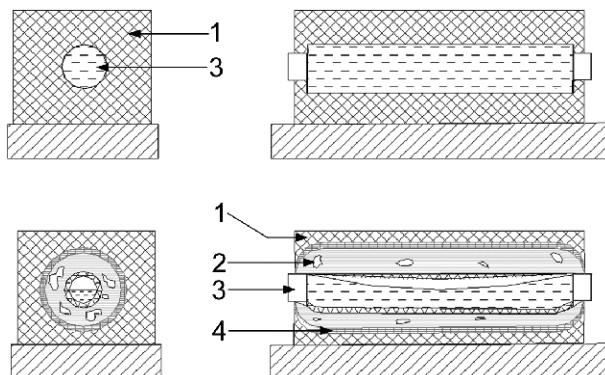
Even though SiC has been used as an abrasive for a long period, specific interest in SiC semiconductors was shown only in the early 1950s by the space and military establishments in the former U.S.S.R. and a little later in the U.S.A. Civil nuclear industries invested substantially in the development of SiC electronics for their use in high radiation areas; Westinghouse in the U.S. and Siemens in Europe being the pioneering companies. Today there is an international consensus that the application of SiC will increase exponentially in a wide variety of applications. As a result, several companies in the U.S., Japan, Europe, and Russia have started producing SiC wafers commercially (Fig. 6.1).

## 6.2 Vapor Growth

Commercially, most of the semiconductor crystals are grown using one of the various melt methods, such as Czochralski, liquid-encapsulated Czochralski, Bridgman, and gradient freeze methods. However, these methods cannot be adopted for the growth of silicon carbide since it is not possible to melt SiC under easily achievable process conditions. The calculated values show that the stoichiometric SiC would melt only at above 100,000 atm and 3200°C [3]. Because of these reasons, single crystals of silicon carbide are grown using the techniques based on vapor growth, high temperature solution growth, and their variants. Since SiC readily sublimes, physical vapor growth can be easily adapted, and has become the primary method for growing large size SiC boules. On the other hand, SiC can also dissolve in certain melts, such as silicon, that makes melt solution growth a possible technique. This method is predominantly used for growing single crystal films. This section will describe the techniques based on vapor transport whereas the melt solution methods are discussed in Section 6.3.

### 6.2.1 Acheson method

The commercial production of SiC was established as early as 1892 [16] using a process known as the Acheson method. This process is primarily used for the synthesis of low purity polycrystalline material. The Acheson method also yields spontaneously nucleated SiC platelets of incomplete habit. In this process, a predetermined mixture of silica, carbon, sawdust, and common salt [25] (e.g., 50% silica, 40% coke, 7% sawdust, and 3% salt) is heated by resistive heating of the core of graphite and coke placed at the center of the furnace. The mixture of reactants is filled around the core (Fig. 6.2). The furnace is heated to 2700°C, maintained at that temperature for a certain amount of time and then the temperature is gradually decreased. The sawdust creates porosity in the mixture through which

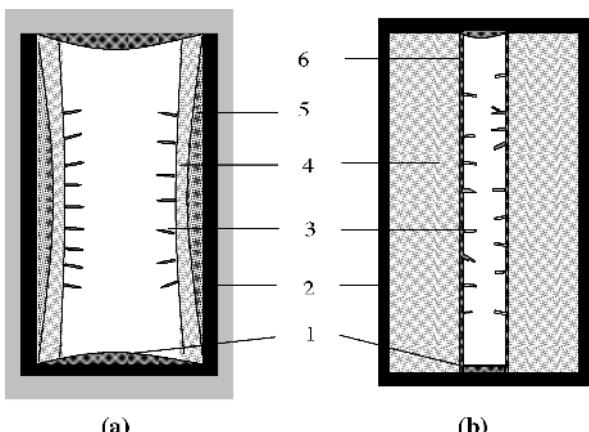


**Fig. 6.2.** Acheson method: (1) unreacted mixture, (2) SiC crystals nucleated in cavities, (3) carbon core with electrodes, and (4) amorphous SiC [25]

carbon monoxide and other gases can escape. The gaseous byproducts, resulting from the reaction in the charge, build up pressure locally, and also form voids and channels. During the thermal cycle, different regions of the reactants are subjected to different temperatures. Because of the lower temperatures in the outermost region, the charge there remains unreacted. In between the outermost and innermost regions the temperature reaches above 1800°C and the mixture transforms to amorphous SiC. In the core region, SiC is formed first but as the temperature increases it decomposes into graphite and silicon. The decomposed graphite remains at the core and the silicon vapor reacts with the carbon in the adjacent cooler regions to form SiC. Crystalline SiC is therefore formed outside the graphite layers. The common salt reacts with the metallic impurities and escapes in the form of chloride vapors improving the overall purity of the charge. The reaction yields predominantly 6H SiC polycrystalline materials. Platelet crystals up to 2–3 cm are formed in some hollow cavities, created by the escape of carbon monoxide. The size of the crystallites decreases with the increasing distance from the core of the furnace. The crystals are carefully extracted and after suitable processing some of these thin platelets are used as substrates. However, this method does not yield reproducible quality and dimensions of single crystals, and hence, is not suitable for commercial production, although one can obtain SiC platelets, suitable for the use as seeds in physical vapor growth.

### 6.2.2 Lely method

In 1955 Lely [17] developed a method that was considered to have a major advantage over the Acheson process. In the Lely method, SiC lumps are filled between two concentric graphite tubes [18] (Fig. 6.3a). After proper packing the inner tube is carefully withdrawn leaving a porous SiC layer inside the outer



**Fig. 6.3.** (a) Original Lely method, (b) Improved Lely method; (1) SiC deposit, (2) graphite crucible, (3) SiC platelets, (4) SiC lump, (5) carbon from decomposed SiC, (6) graphite porous cylinder

graphite tube called the crucible. The crucible with the charge is closed with a graphite or SiC lid and is loaded vertically into a furnace. The furnace is then heated to approximately 2500°C in an Argon environment at atmospheric pressure. The SiC powder near the crucible wall sublimes and decomposes because of a higher temperature in this region. Since the temperature at the inner surface of the charge is slightly lower, SiC crystals start nucleating at the inner surface of the porous SiC cylinder. The nucleation phenomenon, in principle, is similar to that observed in the voids and channels of the Acheson system, except for the difference in the region of formation of SiC crystallites due to a different heating configuration. These thin platelets subsequently grow larger in areas if the heating is prolonged at this temperature. High purity crystals can be obtained using better grade SiC charge and Ar gas. Since crystals are nucleated on the lumps of SiC (at the inner surface) and it is difficult to impose higher supersaturation, there is no control over the nucleation process. The Lely method therefore produces platelets of incomplete hexagonal habit.

The original Lely method was later improved by Hamilton [18], and others [19]. In this improved version, SiC charge is packed in between the two annular graphite cylinders (Fig. 6.3b). The outer cylinder (crucible) is thick and the inner cylinder is thin and porous, and acts as a diaphragm. The sublimed SiC vapor passes through the small holes in the diaphragm and crystals are nucleated at the inner surface. Thick layers of SiC are also deposited on the lids at both ends. This modification offers slightly better control over the number of nucleation sites and yield, and crystals up to  $20 \times 20 \text{ mm}^2$  have been grown using this method. Good quality, larger crystals are obtained when the temperature variation in the cavity is small and the Ar pressure is maintained at about one atmosphere [19]. Similar to the Acheson process, crystals of 6H polytype are predominantly produced by this

method. The amount of crystals of other polytypes such as 15R and 4H, depend on the growth temperature and dopant. The main drawback of this method is still the lack of control over spontaneous nucleation. However, the crystals grow in isothermal conditions and practically at very low growth rates.

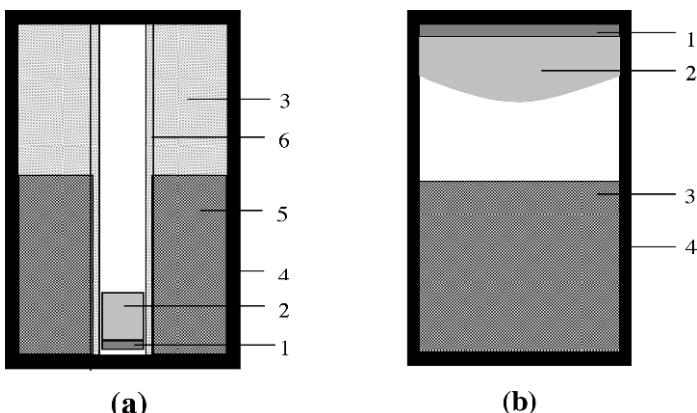
Even though Lely platelets show good structural perfection, they have non-uniform physical and electrical characteristics. Also, since the yield is low (~3%), this method is not suitable for industrial production. The Lely method is, however, ideal for producing platelets of high structural perfection suitable for use as seed crystals in bulk growth using other methods, as discussed later, and high quality substrates for epitaxial growth.

### 6.2.3 Modified Lely method

Even after Lely demonstrated better growth of SiC crystals, the research on bulk growth did not pick up due to the fact that size and yield could not be improved to a desired level. In fact, research on bulk growth of SiC slowed down in the 1970s until Tairov and Tsvetkov [22] developed the seeded sublimation growth technique, commonly known as the modified Lely method. They succeeded in suppressing the widespread spontaneous nucleation occurring on the (inner) graphite cylinder wall and achieved controlled growth on the seed (Fig. 6.4). This method also led to the control of polytypes to some extent. In the modified Lely method, growth occurs in an argon environment at  $10^{-4}$  to 760 Torr in the temperature range of 1800–2600°C and the vapor transport is facilitated by a temperature differential,  $\Delta T = T_2 - T_1$ , between the seed and the source material. The seed temperature,  $T_1$ , is maintained slightly lower than the source temperature. The kinetics of the transport of Si and C containing species are primarily controlled by the diffusion process.

There are two different designs of the seeded sublimation growth system based on the locations of the charge and seed. In earlier research [26–28] on seeded growth, after the pioneering work of Tairov and Tsvetkov [22], the source SiC was placed in the upper half of the graphite crucible in a circular hollow cylindrical configuration between the crucible and a thin walled porous cylinder (Fig. 6.4a). The seed platelet was held on a pedestal in the lower half of the crucible. Using this configuration, Ziegler et al. [26] grew 20 mm diameter and 24 mm long crystals at 20°C/cm temperature gradient and 2 mbar of Ar pressure, at a growth temperature of about 2200°C. Later, Barrett et al. [27] succeeded in growing 6H-SiC of 33 mm in diameter and 18 mm long at a temperature gradient of 20–30°C/cm and pressure of 20 Torr in the temperature range of 2100–2400°C.

In the second configuration [3,29,30–33] (Fig. 6.4b), that is commonly used today, the source material is held at the bottom of the crucible and the seed plate on the top. No graphite diaphragm is used in this configuration. This arrangement has a high yield (90%) [34], and has therefore become the industry standard for the production of SiC boules. Since this is the process that has attracted significant research efforts in recent years and has shown the most promise, it will be discussed in more detail in Section 6.4.

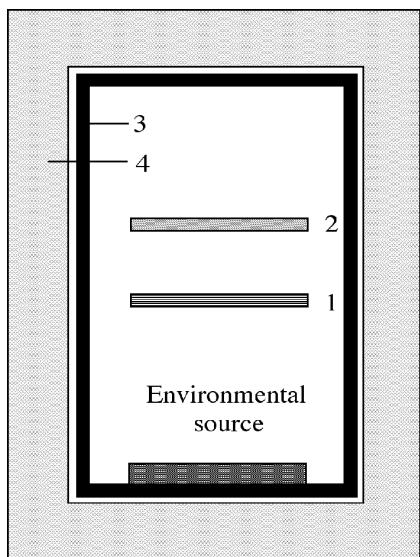


**Fig. 6.4.** Modified Lely method, (a) seed at the bottom, and (b) seed at the top; (1) seed, (2) crystal boule, (3) source material, (4) graphite crucible, (5) graphite powder, (6) porous graphite cylinder

#### 6.2.4 Sublimation sandwich method

The sublimation sandwich method (SSM) is another variant of the physical vapor transport (PVT) growth. It was proposed in 1970 for the growth of thin epitaxial layers of SiC. In this design, the growth cell is partially open and the environment containing Si vapor may be used to control the gas-phase stoichiometry [35–39] (Fig. 6.5). The source material consists of SiC single crystal or polycrystalline plate with a small source to crystal distance (0.02–3 mm). There are several parameters, such as the source to substrate distance, small temperature gradient, and the presence of Ta for gettering of excess carbon that can control the growth process. Even though it has been shown that the process can be used for bulk growth of SiC crystals, growth of large size boules is yet to be realized. The high growth rate is achieved mainly due to the small source-to-seed distance and a large heat flux onto a small amount of source material with a low to slightly moderate temperature differential between the substrate and the source, 0.5–10°C. These facts make the growth of large boules quite difficult. The method is, however, quite promising for better quality epitaxial films with uniform polytype structures. The research on this sandwich sublimation technique includes theoretical models [35,39], and use of Ta as a crucible material for controlling graphitization [37].

Recently, Syvajarvi et al. [40] have reported growth rates as high as 2 mm/h using the so-called sublimation epitaxy method for 4H and 6H SiC. The growth cell construction is similar to the modified Lely technique but retains the feature of low source to seed distance (1 mm) of SSM. This technique is probably easy to implement but does not give much freedom to vary the vapor conditions. Interestingly, using the sublimation epitaxy method, Khlebnikov et al. [41] have



**Fig. 6.5.** Sublimation sandwich method: (1) source wafer, (2) substrate, (3) graphite container, and (4) insulation material

successfully demonstrated the filling of micropipe by depositing a thick film, however, its effect on device performance needs to be tested.

### 6.2.5 Chemical vapor deposition

Chemical vapor deposition (CVD) is a popular method for growing thin crystalline layers directly from the gas phase [24,42–44]. In this process a mixture of gases (source gases for Si and C, and a carrier gas) is injected into the growth chamber with substrate temperatures above 1300°C. Silane is the common Si source and a hydrocarbon is used for C. Propane is quite popular, but methane is of interest because of its availability with very high purity although it has a lower carbon cracking efficiency. The carrier gas is high purity H<sub>2</sub>, which also acts as a coreactant. Conventional Si and C source molecules, called multiple-source precursors have been used successfully and reproducible CVD epitaxial films have been produced. However, the single-source CVD SiC precursor shows several advantages over the multiple-source precursors, including a lower growth temperature (less than 1100°C).

Initially, the available SiC substrates were limited by the size and irregular shapes of the Lely and Acheson plates. SiC epitaxial films were then grown on other substrate materials. The first successful large area, heteroepitaxially grown 3C SiC was obtained by Nishinov et al. [45] on a high quality commercial Si wafer. Growth of 3C SiC was also tried on closely lattice-matched TiC, which

yielded slightly better results. With the availability of 6H SiC wafers grown by the modified Lely method, homoepitaxial growth of 6H SiC and heteroepitaxial growth of 3C SiC have been achieved with good success [24]. SiC epitaxial growth is mainly performed on 4H and 6H substrates. Growth on several crystallographic planes of 6H have also been investigated. However, the growth on the Si face of 6H SiC is preferred because of the superior quality and well understood doping behavior. In general, the quality of films obtained on the (0001) face is poor because of the complex surface morphology resulting from two-dimensional nucleation phenomena on the substrate, which leads to poor device performance. Inclusions of other polytypes like 3C SiC in the grown film has also been observed. This problem can be overcome by adopting a method developed by Matsunami's group [24] in which the wafer misoriented by 3–8° from the basal plane is used to control the morphology of the deposited epilayer. The complex surface morphology is transformed into a smooth stripe pattern and this method is referred to as step controlled epitaxy. True homoepitaxy can be obtained by this process leading to high quality epitaxial films. Doping of the film is obtained *in situ* during the growth of each epilayer by flowing either a p-type or n-type source gas. Nitrogen is commonly used as the n-type dopant. The amount of dopant incorporation and reproducibility can be improved by using a site-competition epitaxy [46]. Further details on doping are presented in Section 6.5.

The growth rates of CVD processes are low, a few tens of microns per hour, making it unsuitable for boule production. It can be increased by increasing the deposition temperature, but that makes the control of the process much more difficult, and also results in many other problems such as homogeneous nucleation in the gas phase. The high temperature CVD (HTCVD) [6,47] is an improved version that can yield thicker films and higher growth rates. In HTCVD the substrate is placed at the top of a vertically held graphite susceptor, similar to the crucible used in the modified Lely method, with holes at the bottom and top. The gaseous reactants are passed from the bottom of the susceptor upwards through the hole at the bottom. To maintain the growth for a long time and obtain the maximum deposition on the substrate, the temperature of the susceptor wall is kept high and the substrate temperature is kept slightly lower. This is basically an inverted stagnant flow reactor operating in the temperature range of 2200–2300°C. In principle, SiC growth by this method can be continued for longer periods and bulk crystals can be obtained. To date, 4H crystals of 35 mm diameter and a few millimeters thickness have been obtained at a growth rate of 0.3 to 0.6 mm/h [6].

The hot-wall CVD reported by Kordina et al. [48] is probably a good method to produce uniform epitaxial films on large diameter wafers. Here the CVD reactor is made of a single graphite block with a protective SiC layer. It has an elliptical outer cross section with a rectangular tapered hole, which runs through the entire length. The substrate wafers are placed appropriately on both sides of the rectangular slit. The mixture of gaseous precursors with a carrier gas is passed through the reactor from the end containing the larger hole. The tapered hole compensates for severe depletion of Si and C content in the reactant. The flow rate of the gas can be sufficiently large. This design provides good temperature homogeneity, and epitaxial films of excellent thickness uniformity can be obtained. The surface

morphology of the film can be controlled by choosing off-C-oriented substrate. Recent technological developments have allowed the growth of uniform epitaxial films on wafers as large as 50 mm in diameter [2,49].

## 6.3 High Temperature Solution Growth

### 6.3.1 Bulk growth

Melt growth is not suitable for SiC because of the fact that realizing its melting temperature and maintaining stoichiometry is beyond the reach of current industrial technologies. However, carbon is soluble in a Si melt that can allow growth of SiC from a high temperature solution. The solubility ranges from 0.01% to 19% in the temperature interval of 1412–2830°C [3]; although at high temperatures the evaporation of silicon makes the growth unstable. The solubility of carbon can be increased by adding certain transition metals to the Si melt [50]. In principle, this can enable the growth of SiC from the saturated solution by seeded solution growth. Unfortunately, there is no crucible material that can remain stable at the required temperatures and with these melts, and also the evaporation of the Si melt poses a serious problem at higher temperatures. It is also speculated that the incorporation of the added metals in the growing crystal is too high to be acceptable in semiconductor applications [3]. These difficulties restrict the application of this method to bulk growth of SiC. Halden [20], however, has grown SiC platelets from Si melt at 1665°C on a graphite tip in a Czochralski configuration. Epelbaum et al. [51] have obtained SiC boules of 20–25 mm diameter and 20 mm long at the pull rate of 5–15 mm/h in the temperature range of 1900–2400°C at Ar pressure of 100–120 bar. Even though solution grown crystals have been produced free of micropipes, they contain a number of flat silicon inclusions and show rather high rocking curve width. Because of the high temperature and high pressure involved in this process the method is not considered economic for large-scale production.

### 6.3.2 Liquid phase epitaxy

Even though the high temperature solution method for SiC poses enormous difficulties and is not popular for bulk growth, it has been successfully adopted for the growth of thin films by liquid phase epitaxy (LPE). Indeed, LPE has been used for the production of several SiC-based optoelectronic devices [26]. In LPE, semiconductor-grade silicon is used as a solvent in a graphite crucible. Carbon from the graphite crucible dissolves in Si melt and is transported to the surface of the SiC substrate, which is placed at the bottom of the crucible at a relatively lower temperature. Bright LEDs have been fabricated using this process. However this method suffers from several setbacks, like cracking of the film due to differential thermal contraction while solidifying, and the cumbersome process of extraction of the substrate containing the epitaxial film by etching off the solidified Si. These

problems can be overcome using a dipping technique [52]. In this improved process a SiC substrate attached to a graphite holder is dipped into the molten Si heated by an induction furnace, and is kept in the lower temperature region of the crucible. The substrate is withdrawn from the melt after obtaining the growth of the epitaxial film of a desired thickness. The growth is performed in Ar environment at 1650–1800°C, and the typical growth rate is 2–7 microns/hour. Doping is obtained by adding Al to the Si melt for p-type layer, and  $\text{Si}_3\text{N}_4$  powder into Si for n-type. It is also possible to obtain n-type film by passing  $\text{N}_2$  gas along with Ar. Epitaxial films obtained on (0001) of 6H SiC substrate have shown degradation in LED performance. This problem can be resolved by using substrates misoriented with respect to the *c* axis by a few degrees (3–10°), which leads to better polytype control and improved surface morphologies [24]. The method is known as step-controlled epitaxy, and has led to improved quality of the film and thereby reliable device performance. A better epitaxial surface morphology is obtained by this process, which has been explained based on the nucleation concept [24].

It is possible to lower the growth temperature range by selecting an alternate melt, which has a higher solubility than Si. Tairov et al. [53] have used Sn and Ga melts in the temperature range of 1100–1400°C and have produced LPE layers by using a sliding boat technique. Dmitriev et al. [54] have grown p-n junctions in the temperature range of 1100–1200°C. In addition they have also demonstrated a container-free epitaxial growth of 6H and 3C SiC films in which the melt is held by the electromagnetic field. It has the advantage of mixing induced by the electromagnetic forces [55]. Recently, Syvajarvi et al. [56] used a special sandwich configuration in LPE and succeeded in obtaining growth rates as high as 300 microns/h. One of the main attractions of LPE of SiC is the potential for filling of micropipes. The substrate after filling of micropipes do not reveal the presence of micropipes by either the optical microscopy or etching [6]. However, a detailed analysis is needed to understand the defect configuration around the filled core of the micropipes.

## 6.4 Bulk Growth by Seeded Sublimation: The Industrial Process

Out of all the methods investigated thus far for bulk growth, the only method that has been implemented by industry is the seeded sublimation growth, commonly known as the modified Lely method. The method has spurred intense worldwide research activity in recent years and has become a standard method for growing SiC crystals [3,22,26–33,57–59]. However, scaling-up of the production has been difficult because of the stringent growth conditions, slow growth rate, and presence of a large number of growth defects in the crystal.

The instrumentation and technology involved in the bulk growth of SiC are complex, and hence, the availability of large size crystals is still limited. This is primarily due to the fact that the operating temperatures are extreme and the monitoring and control are difficult [3]. Even today only a few companies are suc-

cessful in producing SiC boules of reasonable quality and size. The main constraint is the difficulty of finding out the optimum growth conditions for the modified Lely method such as a right combination of pressure, temperature, temperature gradient, charge size, geometric configuration, and so forth. It is not feasible to determine experimentally the exact thermal conditions in the growth zone due to high operating temperatures and the opacity of the graphite crucible. In spite of these limitations, great success has been achieved in the industrial production of SiC crystals in terms of crystal perfection and size [60–63]. Numerical modeling and simulation has been of great help in this endeavor [64]. Figure 6.1 shows the progress made in increasing the boule diameter over the last ten years.

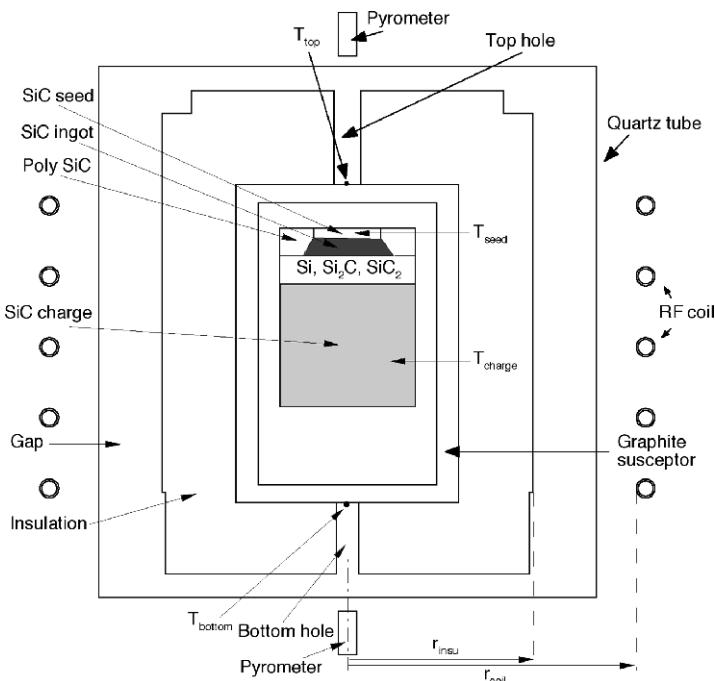
#### 6.4.1 Growth system

As described earlier, there are two main configurations for seeded sublimation growth (Fig. 6.4). The second configuration [3,29,58,62,63], where the source material is held at the bottom of the crucible and the seed plate is fixed onto the crucible lid, is the system commonly used today (Fig. 6.4b). This arrangement yields a higher growth rate compared to the other because of a smaller source to seed distance. Also, since the growing surface is facing downwards there is no danger of the incorporation of charge particles into the growing crystal as in the first case (Fig. 6.4a) where particulates can fall from the top. The main disadvantage of this configuration is that in a system for growing larger diameter boules, maintaining temperature uniformity in the source material becomes difficult. The first configuration is slightly less susceptible to temperature and pressure fluctuations. The operating temperature range of seeded sublimation growth is 1800–2600°C [22], with the actual temperature for growth depending on many different process conditions. Different groups grow SiC crystals at different temperatures by finding narrow windows of process parameters for successful growth.

In spite of some attempts to use a resistively heated furnace, this is not popular because at these high operating temperatures the graphite heating elements are not reliable. As a result, induction furnaces operating at lower frequencies (4 kHz to 300 kHz) [26,65] are commonly used for the modified Lely method. The optimum operating frequency of the induction furnace is 10 kHz, which has a reasonably high skin depth for a graphite crucible. Recently, efficient solid state induction furnaces have become easily available and these low-frequency generators preferentially couple with the susceptor and crucible, with minimum induction on the graphite insulator. Additionally, in an induction furnace it is possible to vary the temperature gradient at the initial stage as well as during the run. Another advantage of the induction furnace over the resistive furnace is the minimal thermal insulation required as the heat is generated directly on the susceptor and crucible. The dimensions and number of turns of the induction coil are selected based on the geometric considerations, temperature, and temperature gradients desired and heat losses. Often, low coil voltage is selected to reduce arcing due to electrical discharge inside the growth chamber at high vacuum used during the degassing and baking of the hot zone. An optimum capacity of the induction furnace and the

number of coil turns and their dimensions are arrived at through experience, along with the simulation results.

The main chamber of the SiC growth system (Fig. 6.6) is a vertically mounted, double walled, water cooled assembly that consists of two concentric quartz tubes sealed with vacuum tight end flanges using double O-ring seals on ground surfaces of the quartz tubes. Cooling water is circulated between the concentric quartz tubes from bottom to the top, although Yakimova et al. [57] have shown that it is also possible to use an air-cooled quartz enclosure. The hot zone consists of a high-density graphite crucible and susceptor surrounded by a rigid graphite insulation. Because of the higher resistivity of the rigid insulation compared to that of the graphite susceptor and crucible, heat is generated primarily on the susceptor by the eddy currents induced by the low frequency magnetic field. The graphite components of the growth chamber, particularly the crucible and susceptor, are treated at high temperatures in fluorine atmosphere to remove metallic impurities. The design of the hot zone is modified based on the requirements of the axial and radial gradient. This is accomplished with the help of computer modeling [64], and prediction of the temperature profile as a function of the growth front, since it is impossible to experimentally find the thermal conditions of the hot zone because of the measurement constraints.



**Fig. 6.6.** Schematic of the SiC growth system

The normally practiced measurement procedure is to monitor temperatures of the top ( $T_1$ ) and bottom ( $T_2$ ) surfaces of the graphite crucible using two color pyrometers (Fig. 6.6). The temperatures are controlled by varying the output power of the induction furnace. Often, the induction coil is mounted on a motorized linear vertical translation stage and the position of the coil is changed during the growth to vary the temperature gradient and the seed temperature. This option is quite useful in achieving the optimized seeding.

The vertical growth chamber is connected to a high vacuum system for obtaining initial degassing (at  $10^{-7}$  Torr) as well as maintaining the required vacuum (e.g., 10 to 100 Torr) conditions during growth. Maintaining vacuum at a predetermined value, as closely as possible, is essential to control the growth rate. This is achieved by using a vacuum throttle valve, a capacitance manometer, and a pressure controller.

#### 6.4.2 Seeding and growth process

After repeated degassing and baking of the growth zone, the chamber is filled with Ar gas. The Ar partial pressure is maintained at about 600 Torr–1 atm while heating up to the maximum required growth temperature (2200–2400°C). The coil position is adjusted such that a desirable temperature gradient of 10 to 20°C/cm can be obtained. The seed temperature,  $T_1$ , and the temperature differential,  $\Delta T$ , can be varied by changing the coil position, however  $T_1$  and  $T_2$  cannot be controlled independently. The Ar pressure is brought down to a lower value between 1 to 40 Torr at a predetermined pumping speed to initiate the growth smoothly. The axial temperature gradient influences the growth rate, whereas the radial temperature gradient changes the diameter of the crystal (see Chen et al. [64], part II of this paper).

The main stages of growth are: (1) dissociative sublimation of SiC source, (2) mass transfer of gaseous species, and (3) crystallization onto the seed. At a high temperature, the SiC source material decomposes into several Si and C containing species such as Si, C, SiC<sub>2</sub>, and Si<sub>2</sub>C. Since the crucible is made of graphite, vapor species will react with the graphite wall and form Si<sub>2</sub>C and SiC<sub>2</sub>, with the graphite crucible acting like a catalyst. Details of the reaction kinetics are described in the companion paper by Chen et al. [64]. The differential temperature between the seed and source,  $\Delta T$ , works as a driving force and facilitates transport of vapor species, mainly Si, Si<sub>2</sub>C, SiC<sub>2</sub>. The presence of a temperature gradient leads to supersaturation of the vapor and controlled growth occurs at the seed.

Initially, a high quality Lely plate is used as the seed crystal, and the diameter of the growing crystal is increased by properly adjusting the thermal conditions. For growing larger boules of approximately uniform diameter, wafers from previously grown boules are used as seed disks.

The seed crystal is attached to the graphite top using a sugar melt [66], which decomposes into carbon and gets bonded with the graphite lid. Optimizing this bonding process is quite important since the differential thermal expansion between the seed and the graphite lid can cause bending of the seed plate, leading to formation of domain-like structure, low angle boundaries, and polygonization

[67]. Micropipes can form at these low angle boundaries. Any non-uniformity in seed attachment, like a void between the seed and the lid, can cause variation in the temperature distribution, and the heat dissipation through the seed may get altered. It can result in uneven surfaces and depressions in the growth front corresponding to the void. Evaporation of the back surface of the seed crystal can create thermally decomposed voids, which can propagate further into the bulk [66]. These voids can then become a source for the generation of micropipes. Protecting the back surface of the seed by a suitable coating eliminates these voids. Seed platelet attachment to the graphite lid is one of the important technical aspects of industrial growth.

If the growth process is not optimized, it can lead to polycrystalline deposition due to uncontrolled nucleation. In addition to optimizing the Ar pressure and temperature gradient to achieve controlled nucleation, removal of a thin layer of the seed surface by thermal etching, obtained by imposing a reverse temperature gradient [68], has been found helpful. Etching is also possible by oscillatory motion of the induction coil. The *in situ* thermal etching helps in cleaning the surface of the seed crystal before starting the growth. In some cases, a small amount of excess silicon is added to the charge in order to maintain the Si vapor concentration and stabilize the growth of certain polytypes. The growth of boules is initiated at a very slow rate and is increased progressively by decreasing the pressure.

The dimensions of available Lely plates are very small (approximately 10 mm size hexagonal platelet with thickness less than 0.5 mm), and hence the boule diameter has to be increased. Depending on the design of the crucible and supersaturation ratio, simultaneous growth of polycrystalline SiC, predominantly 3C, occurs particularly on the graphite lid surrounding the seed crystal. If the growth conditions are not optimal, the polycrystalline SiC can get incorporated into the boule near the periphery, leading to cracking due to high stresses. If the growth rate of the boule is higher than the growth rate of polycrystalline SiC, it favors a smooth growth of the boule dominating over the polycrystalline mass. The design of the crucible for increasing the diameter of the boule is normally accomplished through modeling [64].

Bahng et al. [69] have proposed a method of rapid enlargement of the boule using a cone-shaped platform, where enlargement depends on the taper angle of the cone. It has been reported that in this technique, the broadening of the boule is not affected by the growth of the polycrystalline SiC. After obtaining the required diameter of the boule, the seed disks of larger diameter are prepared from these boules for further growth in a specifically designed hot-zone suitable for promoting predominantly the axial growth. As the growth of the boule progresses, the temperature of the growing surface changes, which can be compensated by moving the induction coil. It is evident that the process parameters must be optimized for a particular crucible design, system geometry, and boule dimension. A detailed discussion of these issues and effects of various process parameters are presented in Reference [64].

Among the numerous SiC polytypes, only 6H, 4H, 15R, and 3C have been studied for different applications. 6H, 4H have been studied extensively in the bulk crystal form as well as epitaxy, whereas 3C has been investigated predomi-

nantly in the epitaxial form. Recently, work on bulk growth of 15R has been initiated for MOSFET applications [14]. Crystals of 4H polytype are grown in a narrow temperature range of 2350–2375°C at 5 mbar using (0001)C face of 4H seed plates [6]. A lower growth rate (0.1 mm/h) is used in the beginning and the growth rate is increased to 0.5 mm/h after growing a 1 mm long boule. Above 2375°C the 4H transforms into 6H; below 2350°C the crystal quality becomes a limiting factor. Among the SiC polytypes 6H is the most extensively studied and the reported growth temperature range varies widely. Perhaps this is due to the difference in the growth cell configuration and temperature measurement conventions. Snyder et al. [61] have reported the growth of 100 mm 6H boules at 2100–2200°C and 5–30 Torr of Ar pressure with 10°C to 30°C/cm temperature gradient. The clearly established result is that (0001)Si face should be used for the growth of 6H whereas (0001)C face is needed for the growth of 4H. It seems that for the bulk growth of 15R seed platelets of the same polytype are required. Schulze et al. [70] have demonstrated the growth of 15R crystals on (0001)Si seed face at 2150–2180°C, 5°C/cm gradient. However, Nishiguchi et al. [65] have shown that 15R polytypes can grow stably on both C and Si of (0001) face at the seed temperature not exceeding 2000°C with the growth rate controlled between 0.1 mm/h to 0.5 mm/h. In addition to temperature there are several other parameters that control the polytypes formation (see Section 6.6.2 for details).

Growth of SiC boule depends on many parameters, such as growth temperature, temperature gradient, Ar pressure, crystal temperature, source to crystal distance, and porosity of the source material [64]. Preparative conditions of the source material alter the vapor species concentrations and vary the growth conditions. The deviation of the stoichiometry can lead to a lower growth rate. The growth rate increases as the seed crystal temperature increases. It also increases with the temperature differential ( $T_2 - T_1$ ) and the temperature gradient, but decreases with the source to seed distance. The growth rate varies almost inversely with the Ar pressure and the trend is consistent with 1/Pa dependence on the molecular diffusion coefficient [58]. There exists a saturation of growth rate at very low pressures and one would tend to select this growth regime but control of the vapor composition becomes more difficult.

The growth rates have been measured by inducing growth bands by instantly introducing N<sub>2</sub> gas along with the Ar flow at different intervals and subsequent postmortem studies. In general, (0001) plate is used as a seed and growth proceeds along the *c* direction. Even though the crystal grows smoothly on (0001) plate, it is also the favorable orientation for the nucleation of micropipes. There have been several attempts [71,72] to grow crystals on non-(0001) orientation. Even though micropipe density reduced in the bulk, the generation of other types of defects such as stacking faults on the basal plane, which hinder electron transport in device application, increased. Presently, the seeding is restricted to (0001) orientation for industrial production of SiC boules.

Monitoring and controlling the growth of SiC is very difficult because of the usage of opaque graphite materials in the hot zone. Recently, radiography has been employed to study the growth interface during the growth process [73]. This imaging technique also revealed the graphitization of SiC source material that

could reduce the growth rate as well as affect the structural perfection of the growing boule. Attempts have also been made to study the defect generation during the growth process by *in situ* X-ray topography [74].

## 6.5 Doping in Bulk and Epitaxial Growth

### 6.5.1 Doping in modified Lely method

Doping in SiC is obtained either by containing the dopant in the source material or by passing it in the gaseous form along with argon. The common dopants are N<sub>2</sub> and Al that give rise to n and p type conductivity. The characteristics of dopant incorporation are in general similar for 6H and 4H polytypes. However, there is a significant variation in N<sub>2</sub> and Al incorporation in sublimation growth for the different crystallographic faces [3]. For example, nitrogen incorporation is greater on (0001)Si face compared to (0001̄)C face, whereas the Al incorporates more on (0001̄)C face. Undoped crystals grown on (0001̄)C face show n-type conductivity while the crystals grown on (0001)Si are p-type. This is due to the preferential incorporation of residual dopants present in the graphite components of the hot zone or in the source material. Nitrogen doping concentration in the grown crystal is approximately a function of the square root of the N<sub>2</sub> partial pressure. Aluminum concentration in the bulk linearly varies with the amount present in the source material. The conductivity of the crystal decreases as the N concentration increases, however beyond 60% of nitrogen there is no considerable increase in the carrier density, and hence growth of low resistive SiC growth can be carried out at this nitrogen partial pressure along with the Ar under stable growth conditions [62]. The incorporation of Al is roughly linear with its concentration in the source up to  $10^{20} \text{ cm}^{-3}$ . Aluminum concentration increases with the increase in growth temperature. However, the nitrogen concentration has exactly the reverse behavior. Low resistive wafers that are required for vertical power devices, are prepared by maximizing the dopant concentration. In the case of microwave devices semi-insulating SiC crystals are required. These are obtained by using a combination of deep level dopants and intrinsic point defects. Wafers of high resistivity  $\sim 10^5 \Omega \text{ cm}$  (measured at 350°C) are made by deep level doping using vanadium. However, recently Mitchel et al. [75] have demonstrated the growth of semi-insulating 4H-SiC without using V doping.

### 6.5.2 Doping in epitaxial films

In LPE growth, Al is added to Si to obtain p-type conductivity, and adding Si<sub>3</sub>N<sub>4</sub> powder into Si or passing N<sub>2</sub> leads to n-type epitaxial films [43,44]. In CVD, doping is obtained by passing gas phase dopant sources. Trimethyl aluminum and diborane (B<sub>2</sub>H) are the common p-type dopant sources. Nitrogen is used as n-type dopant, and phosphorous (PH<sub>3</sub>) is less commonly used. Conventional methods of

varying the dopant concentration by varying the flow rate do not yield reproducible results, and in addition, it is difficult to increase the dopant concentration. It has been reported that using the site-competition epitaxial technique [46] it is possible to achieve both the reproducibility as well as extended doping range. In this technique Si to C ratio is varied within the reactor to control the dopant incorporation during the growth. This technique has been successfully used on SiC (0001) Si-face using either propane or methane, and also in the growth on SiC substrates of different crystallographic orientation. This technique is based on approximately adjusting the Si/C ratio (e.g., 0.1 to 0.5) within the reactor to effectively control the amount of dopant substitutionally incorporated in the SiC lattice. (For nitrogen, varying the Si/C ratio from 0.1 to 0.5 increases the dopant incorporation ( $N_D$ ) from  $1 \times 10^{15} \text{ cm}^{-3}$  to  $1 \times 10^{17} \text{ cm}^{-3}$  [43]). The principle is that there is a competition between the N and C for the C site, and between Al and Si for the Si site during the growth of the epilayer.

## 6.6 Growth Defects

### 6.6.1 Growth spirals and micropipes

The observation of growth spirals on the natural faces of SiC crystals grown from the vapor was reported by Verma [76] and Amelinckx [77] in the early 1950s. These are due to screw dislocations emerging at the growing surface. They play an important role in crystal growth as predicted by Charles Frank through his well-known dislocation theory of crystal growth [78]. More details on this topic are presented in Section 6.7.1. The emergence of screw dislocations on a habit face produces a ledge of height equal to the Burgers vector. Crystal grows by the attachment of molecules to the edge of this ledge. The ledge is self-perpetuating and continues to be present on the surface as long as the dislocation line intersects the surface. The ledge winds itself into a circular or polygonal spiral with the dislocation line at the center, and as the growth proceeds the spiral apparently revolves. The step height of these spirals is equal to an integer times  $c$ . Depending on the sign of the Burgers vector the spiral can revolve in clockwise or anti-clockwise direction, and depending on the magnitude of the Burgers vector the dislocation present at the center of the spiral can have a closed core or hollow core [79]. These hollow core screw dislocations are known as micropipes or pinhole defects. These micropipes propagate into the bulk and the presence of such defects is detrimental to device fabrication. Frank has predicted that for crystals such as SiC, where the Burgers vectors are large, a stable hollow core would form along the dislocation line as a result of the reduction in the local strain energy of the dislocation. Detailed studies on growth spirals in SiC have been made by several investigators including Sunagawa and Bennema [80].

In the modified Lely method, the supersaturation is imposed by the temperature gradient and it is normally higher than that in the Lely method. Formation of a larger number of nucleation sites are expected at higher supersaturations. If the

screw dislocation mechanism is operative, it will lead to more spirals. This is in agreement with the experimental observations reported by Tairov and Tsvetkov [81]. The high resolution HRD study shows that there exists a domain-like structural behavior in the grown crystal. These slightly misoriented domains are surrounded by low angle boundaries containing high dislocation density, perhaps formed by the relaxation process [67]. Etch pits observed in SiC crystals correspond to elementary and large screw dislocations. The etch pits formed on the core of super screw dislocations continue to be present in the bulk, whereas the etch pits formed because of elementary dislocation do not show one to one correspondence after the removal of a certain amount of thickness of the bulk crystal. The origin of micropipes can be classified into three main categories: (a) thermodynamic, (b) kinetic, and (c) technological cause. *In situ* X-ray characterization methods are being attempted to understand the formation of these defects during growth [74]. It has been observed that micropipes are predominantly formed at the seed/boule interface and propagate along the growth direction. Takahashi et al. [71] have demonstrated that with the use of seed plates of orientations perpendicular to [0001], it is possible to suppress the micropipes, however the crystals contained large number of stacking fault defects. Tanaka et al. [82] showed how some micropipes can get terminated at the planar defects, however the details of planar defect formation was not discussed. Recently Khlebnikov et al. [41] demonstrated a new technique for filling up the micropipes by rapidly growing a thick epitaxial film. Even though some work has been carried out [83] on device fabrication using the micropipe filled epitaxy, this method has not gained popularity.

While micropipes are formed during the growth, it is possible that simultaneously occurring processes such as micropipe dissociation, migration, transformation, and coalescence, can progressively reduce the micropipe density. Indeed, by optimizing the growth parameters the micropipe density has been steadily brought down to  $0.5/\text{cm}^2$  [60]. Further discussions on micropipes are presented in Section 6.7.

## 6.6.2 Polytypism

One of the most unique properties of SiC is its ability to exist in over 200 different polytypes. These polytypes possess the same chemical makeup, but the stacking sequence varies along the *c*-axis of the lattice, and hence, they demonstrate different physical properties. Even though the fact that easy formation of different SiC polytypes due to low stacking fault energy makes it possible to obtain a variety of SiC crystals for different applications, the same fact places severe demands on the thermodynamic, kinetic, and thermal conditions of the process and design of the growth cell [3]. If the growth conditions are not optimized, inclusions of different polytypes occur and thereby deteriorate the growing crystal. Among these polytypes, 6H is the most extensively studied, followed by 4H. Other polytypes that are grown are 3C and 15R. Temperature is one of the important parameters that influences the formation of polytypes [84]. It should be noted that more than one polytype can coexist within the same temperature range. Selection of the right

temperature range and proper seed and seed polarity are critical to obtaining the desired polytype. Other growth parameters that influence the stability of polytypes are supersaturation, vapor phase stoichiometry [81], growth pressure, pumping speed, and dopants [5,6,81].

Systematic studies to understand favorable growth conditions for obtaining a specific polytype have been carried out on 6H [58] and 15R [70] by placing two seeds adjacent to each other on the crucible lid. These two seeds are cut from the same wafer, one with a C face and the other with a Si face. Growth results obtained on two seeds of different polarities under identical growth parameters reveal the ideal seed orientation required for obtaining a single polytype. In general, 6H SiC crystals are grown on the (0001)Si face of 6H SiC seed, whereas 4H [58] crystals are grown on the (0001)C face of 6H crystal. When the growth parameters and seed polarity are not optimized, the grown crystals may contain inclusions of other polytypes and these can become the source for the generation of micropipes. Schulze et al. [85] have grown 6H SiC boules on Si face as well as on C face of 6H SiC seed at very low growth rate, which also led to micropipe-free growth in certain regions. The presence of the polytypes can be easily revealed using the differential oxidation, micro-Raman, and X-ray diffraction techniques. Maintaining growth of one polytype is essential to obtain high quality bulk crystals.

### 6.6.3 Graphitization

In PVT growth of SiC, the charge dissociates into different forms of Si- and C-containing molecules and condenses onto the seed. The vapor pressure of Si is higher compared to that of all other species, and therefore if there is any loss of vapors during the growth (due to the leakage), the vapor concentration can become carbon-rich. Similarly, during the thermal etching process, the seed surface becomes carbon-rich due to premature breakdown of the seed surface by the loss of Si from the seed surface [3]. The presence of excess carbon in vapors, seed surface, or source material is known as graphitization. Growth initiated on a carbon-rich seed surface can lead to polycrystalline growth. Carbon-rich vapors can produce inclusions of carbon clusters in the growing boule, which can act as the source for micropipe generation. On the other hand, the graphitization of source material can reduce the growth rate by reducing the sublimation rate of the charge. These problems can be controlled in many different ways. The loss of SiC vapor can be minimized by properly sealing the crucible with the lid, whereas the Si concentration can be maintained by adding excess Si into the charge. However, if the Si concentration is increased beyond a certain limit, the growth rate reduces, and also it favors the formation of 3C SiC polytypes as inclusions in 6H. A recent study [37] shows that the excess carbon concentration can be controlled by using a Ta crucible; the excess carbon atoms are adsorbed by the inner surface of the crucible by the gettering process. Crystals of better structural quality have been obtained using Ta crucibles. However, the growth rate reduces by about 10% due to the reduction in C concentration in the crucible. This method of controlling carbon concentration is successfully used in the sublimation sandwich method.

## 6.7 Defect Analysis

A vital component of the study of crystal growth is an assessment of crystalline imperfections and growth inhomogeneities. This is most evident in the SiC semiconductor industry, which requires wafers of high quality for the fabrication of a variety of devices. SiC crystals grown using different techniques can contain crystalline imperfections such as growth dislocations of screw character with closed cores and hollow cores (micropipes), deformation induced basal plane dislocations, parasitic polytype inclusions, planar defects (stacking faults, microscopic twins, and small angle boundaries), hexagonal voids, and so forth. These defects affect the device performance; in particular, growth dislocations with hollow cores are detrimental to power devices. It is essential to study these defects and understand their origins to develop better crystal growth strategies. The techniques that are commonly used for imaging defects are based on electron and optical microscopy and X-ray diffraction. Each has its own range of capabilities and shortcomings. When it comes to actually solving the problems associated with crystal growth, it is not always obvious which technique is the most appropriate for a particular problem. However, recent developments in defect characterization of SiC crystals have clearly established that X-ray topography, particularly synchrotron white beam X-ray topography (SWBXT) [79,86,87], is superior to other techniques such as chemical etching, AFM, SEM, TEM, and optical microscopy based methods, although these techniques can be used in a complementary manner.

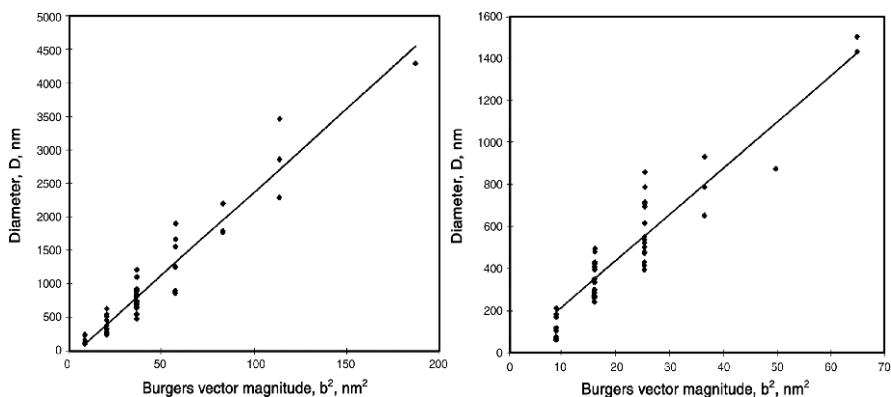
### 6.7.1 Micropipes and closed core screw dislocations

#### *Origin of the hollow core and Frank's theory*

Among the various defects that exist in SiC crystals, screw dislocations lying along the [0001] axis are the most significant and are generally considered to be one of the major factors limiting the extent of the application of SiC. These screw dislocations have been shown to have Burgers vectors equal to  $nc$  (where  $c$  is the lattice parameter along the [0001] direction in the hexagonal coordinate space and  $n$  is an integer), with hollow cores becoming evident with  $n \geq 2$  for 6H SiC and  $n \geq 3$  for 4H SiC [79]. These latter screw dislocations are generally referred to as micropipes, and their hollow cores can be understood from Frank's theory [78]. This theory predicted that a screw dislocation whose Burgers vector exceeds a critical value in crystals with large shear modulus should have a hollow core with the equilibrium diameter  $D$  related to the magnitude of the Burgers vector  $b$  by

$$D = \frac{\mu b^2}{4\pi^2 \gamma}, \quad (6.1)$$

where  $\mu$  is the shear modulus and  $\gamma$  is the specific surface energy. Experimentally, the diameter  $D$  can be directly measured by SEM or AFM, while the Burgers



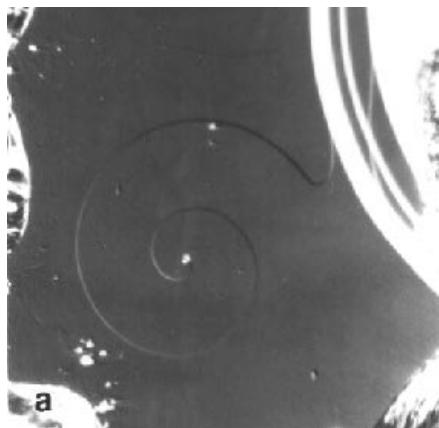
**Fig. 6.7.** Relationship between the magnitudes of screw dislocation Burgers vectors,  $b$ , and the diameters of the associated hollow cores,  $D$ . (a) 6H SiC, (b) 4H SiC [79]

vector magnitude  $b$  can be obtained by determining the step height of the growth spiral on the as-grown surface using optical interferometry or AFM, or directly using the X-ray topography. Detailed experimental results indicate a direct proportional relationship between  $D$  and  $b^2$  for micropipes in both 6H- and 4H-SiC [79, 86, 87]. In these studies, the magnitudes of the Burgers vectors were obtained using a set of SWBXT methods including back-reflection topography, transmission topography, and section topography, as described in the following. The  $D$  versus  $b^2$  correlation obtained experimentally for 6H SiC and 4H SiC is given in Fig. 6.7, this both explicitly verifies Frank's theory and simultaneously reveals that micropipes in SiC are screw dislocations with large Burgers vectors (super-screw dislocations).

### Growth spirals and screw dislocations

Growth spirals have been observed on habit faces of as-grown crystals, but not much attention was paid until Frank [78] proposed the dislocation theory to explain the growth of crystals at very low supersaturations. Spirals observed on the habit faces of the as-grown crystal are a clear manifestation of screw dislocations emerging on the surface contributing to the growth by providing everlasting steps for the attachment of units. Hence they are called growth spirals.

Verma [76] and Amelinckx et al. [77] have studied the growth spirals from SiC polytypes in detail. In fact, their study is the direct experimental evidence of Frank's theory suggesting the role of screw dislocations in crystal growth, particularly at very low supersaturations. These spirals have been studied using the phase contrast microscope [88], the scanning electron microscope (SEM) [88], and recently by the atomic force microscope (AFM) [89]. The spirals had different shapes ranging from circular shape (Fig. 6.8) to hexagonal. Often, these spirals show crystallographic symmetry. The center of the spiral coincides with the core



**Fig. 6.8.** Optical micrograph of a growth spiral on (0001) face of 6H SiC [93]

of the dislocation emerging out of the habit face. The spiral spins either clockwise or anticlockwise depending on the sign of the dislocation. The elementary spiral is of circular shape matching the theoretical shape, and the step height (Burgers vector) equals the lattice parameter along the  $c$  direction. Often it is possible to observe steps which are equal to several times the lattice parameter along  $c$  axis. When the Burgers vector is more than the unit cell parameter it will be energetically unfavorable unless it has an open core. These open cores have been observed as black dots with phase contrast microscopes [88,90–91]. As the step height increases the spacing of interlaces increases. The spirals interact with each other depending on the sign of the spiral and the pattern of interlace changes, and they have been studied in detail [88]. When two screw dislocations of the same sign are present very close to each other their spirals spin without intersecting each other, which are called cooperative spirals. If the distance between the two screw dislocations is more than the critical value, the shape of the resultant spirals changes because of the interaction. Two dislocations of opposite sign can form a closed loop.

In hexagonal SiC polytypes the step height (Burgers vector of the screw dislocation) is equal to  $nc$ , where  $n$  is an integer (where as in rhombohedral polytype the step height is  $1/3$  of the unit cell parameter  $c$ ). Tanaka et al. [92] have shown by optical microscopic study that the core radius of the spiral increased with the step height. Dudley et al. [93] have established that the micropipes are hollow core screw dislocations with Burgers vector 3–7 times that of the lattice parameter along  $c$ , to be discussed in more detail later. This was also confirmed by Giocondi et al. [89] by studying the step height of the spiral by AFM study. It is possible to observe giant spirals containing a micropipe at the center as well as minute spirals having no micropipes [94]. It is interesting to note that this study of the growth spiral can also be extended to find out the polytype by calculating the step height [90,91,95].

**Back-reflection observation of screw dislocations: Intersections with (0001) substrate surface.** Screw dislocations in (0001)SiC wafers, both closed core and hollow core (micropipes), can be characterized effectively using back-reflection geometry in synchrotron white beam X-ray topography (SWBXT) [96]. Figure 6.9, a typical back-reflection topograph taken from a (0001) SiC wafer (grown by Cree Research, Inc.) clearly reveals the screw dislocations, both hollow core or closed core, as white circular spots surrounded by black rings. The distribution of the micropipes and screw dislocations as well as their detailed structures can be obtained from such images.

It is noticeable that the circular white spots in Fig. 6.9 are not the images of the hollow cores of the micropipes, because the dimensions of these white spots range from several tens to hundreds of microns, while the actual dimensions of micropipes observed by SEM and AFM are on the order of several microns or less.

On the other hand, the smallest white spots in Fig. 6.9 are images of closed core screw dislocations. These two facts indicate that the circular images of micropipes and closed core screw dislocations are related to the diffraction effects associated with the long-range strain fields of the screw dislocations. In fact, the formation mechanism of the circular images can be described using a simple geometric X-ray diffraction model [97–100].

As indicated in Fig. 6.10(a), due to the lattice displacement of the screw dislocation, the normal  $\mathbf{n}$  to the (0001) lattice plane varies from point to point near the dislocation core. Consider a screw dislocation coinciding with the  $z$  axis (perpendicular to the (0001) surface). The displacement field  $\mathbf{u}$  can be expressed in the  $xyz$  coordinate space as:

$$u_x = u_y = 0, \quad u_z = \frac{b}{2\pi} \tan^{-1} \frac{y}{x} \quad (6.2)$$

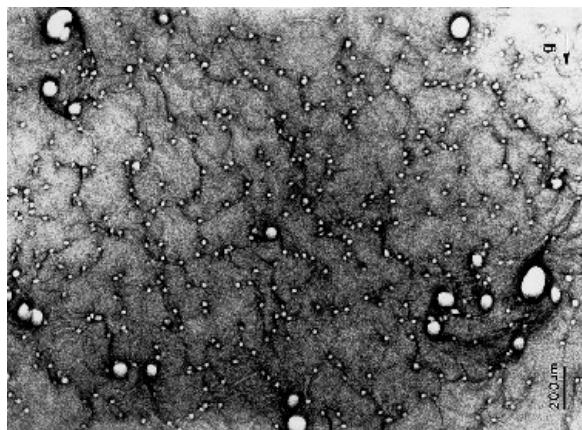
where  $b$  is the Burgers vector of the screw dislocation. Due to this displacement field, the distorted diffraction vector becomes [101],

$$\bar{\mathbf{g}} = \bar{\mathbf{g}}_0 - \nabla(\bar{\mathbf{g}}_0 \bullet \bar{\mathbf{u}}), \quad (6.3)$$

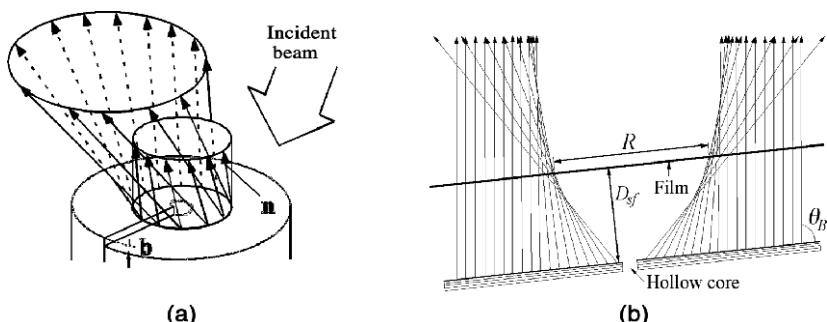
where  $\mathbf{g}_0$  is the undistorted diffraction vector of the perfect lattice. Eqs. (6.2) and (6.3) lead to the position-dependent  $\bar{\mathbf{n}} = \bar{\mathbf{g}} / |\bar{\mathbf{g}}|$  as:

$$\begin{aligned} n_x &= \frac{by}{r(b^2 + 4\pi^2 r^2)^{1/2}} \\ n_y &= \frac{-bx}{r(b^2 + 4\pi^2 r^2)^{1/2}}, \\ n_z &= \frac{2\pi r}{(b^2 + 4\pi^2 r^2)^{1/2}}, \end{aligned} \quad (6.4)$$

where  $r = (x^2 + y^2)^{1/2}$ .



**Fig. 6.9.** SWBXT back-reflection images of close core (smaller white spots) and hollow core (large white spots) screw dislocations in a (0001) 6H SiC wafer. The faint lines connecting these screw dislocation images are basal plane dislocation images [93]



**Fig. 6.10.** The contrast formation mechanism of micropipes on SWBXT back-reflection topographs. (a) Diffraction geometry:  $b$  is the Burgers vector;  $\bar{n}$  is the position-dependent normal to the (0001) lattice plane; (b) Schematic representation of overlap of the twisted cones in space

In SWBXT, as the effective divergence of the synchrotron radiation beam is usually around  $10^{-5}$  or less, it is accurate enough to assume that all the incident X-rays have the same direction  $s_0$ . Therefore, the continuous variation of  $\bar{n}$  in the distorted lattice makes both the directions and the wavelengths of the diffracted X-rays vary continuously from point to point. However, the direction  $\bar{s}_g$  of the diffracted X-rays from an arbitrary point on the surface can be simply described by the geometrical diffraction principle:

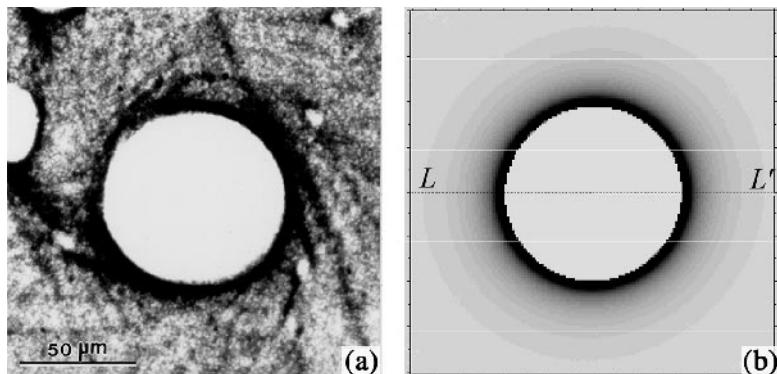
$$\bar{s}_g(x, y) = \bar{s}_0 + 2\sin\theta_B(x, y) \bar{n}(x, y), \quad (6.5)$$

where  $\theta_B(x, y) = \pi/2 - \cos^{-1}[-\vec{s}_0 \bullet \vec{n}(x, y)]$  is the Bragg angle. Thus, we can divide the crystal surface into a set of small squares of constant area and calculate the direction  $\vec{s}_g$  for each square. Since the intensity variation of the incident synchrotron spectrum is slow within the small wavelength range of diffraction, all the squares may be assumed to have the same diffraction power. In order to determine how the diffracted rays intersect the X-ray film, we can further divide this film into a set of squares. Then the computing process is to project the intensities from all the squares on the crystal surface onto the corresponding squares on the X-ray film according to the diffraction direction  $\vec{s}_g$ . The sum of the intensities of each square on the film received after the projection represents the local contrast level.

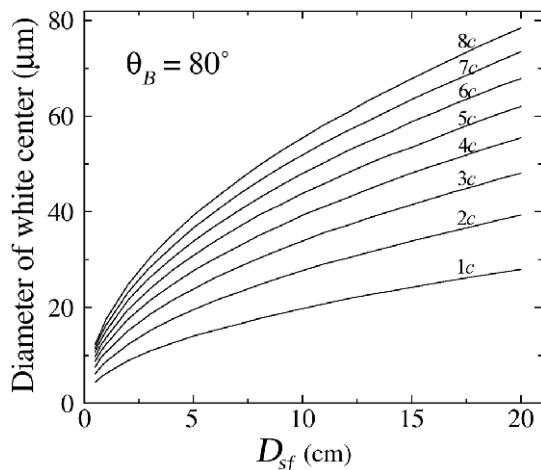
Detailed calculations based on this simulation principle indicate that when a nearly parallel white synchrotron beam is incident on the surface, the X-rays diffracted from successive circular regions surrounding the core form numerous twisted cones [one of these cones is schematically shown in Fig. 6.10(a)]. The overlap of these cones in space results in the formation of the circular images [see Fig. 6.10(b)]. Based on this principle, the images of micropipes and screw dislocations can be rigorously simulated. Fig. 6.11(a) shows a magnified image of an 8c micropipe in 6H SiC, while Fig. 6.11(b) is the simulated image of screw dislocation with the Burgers vector being 8c ( $b \approx 12.1$  nm). It is apparent that the simulation is in excellent agreement with the recorded micropipe image. This proves that micropipes in SiC are indeed pure screw dislocations.

Back-reflection SWBXT images of micropipes or close-core screw dislocations contain abundant information concerning the dislocation structures. The most important information is that the diameter of a screw dislocation image quantitatively indicates the magnitude of the Burgers vector. From Fig. 6.10(b) one can see that two factors determine the image diameter: one is the Burgers vector magnitude of the dislocation and the other is the film-to-sample distance ( $D_{sf}$ ). The relationship between these three quantities is shown in Fig. 6.12. From the curves in this figure it is easy to estimate the Burgers vector magnitude of any micropipe or screw dislocation revealed in the back-reflection topograph taken at a specific film-to-sample distance. For example, the smallest white spots, which have the highest density in Fig. 6.9, can be determined to be the images of 1c screw dislocations (elementary screw dislocations), while the larger spots are images of micropipes with Burgers vectors ranging from 2c to 8c (micropipes with Burgers vector as large as several tens of the  $c$  lattice parameter can also occasionally be found in low-quality SiC crystals).

The other kind of structural information that can be obtained by back-reflection SWBXT is that the twist direction of the diffraction cones unambiguously indicates the dislocation sense, that is, the direction of the Burgers vector. The clockwise twist of the diffracted X-rays (viewed toward the surface) in Fig. 6.10(a) actually results from a right-handed screw dislocation. For a left-handed dislocation, the twist direction is opposite. Figure 6.13(a) shows a back-reflection section topographic image of a micropipe obtained by a slit-limited synchrotron beam of about 20  $\mu\text{m}$  in width, while Fig. 6.13(b) is the corresponding simulation. Compared with Fig. 6.11(a), only two “tails” of the overall dislocation image remain in



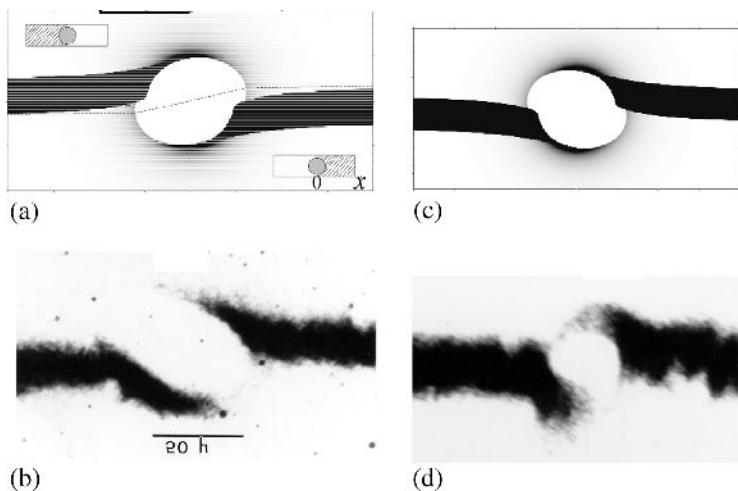
**Fig. 6.11.** (a) Back-reflection SWBXT image of an 8c micropipe taken from a (0001) surface of a 6H-SiC crystal. Sample-to-film distance 20 cm; (b) Simulation of a screw dislocation with Burgers vector  $|b| = 8c$  [98]



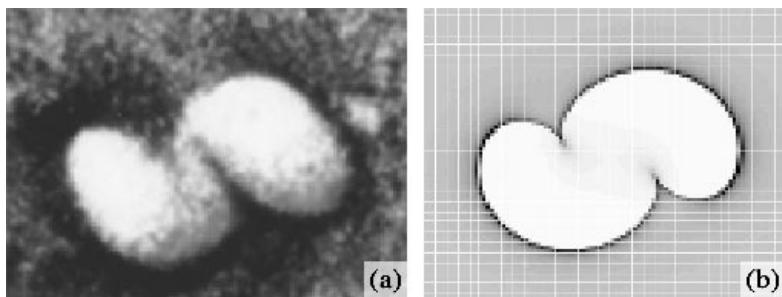
**Fig. 6.12.** Variation of the diameter of the circular micropipe white contrast as a function of the sample-to-film distance ( $D_{sf}$ ) and the Burgers vector magnitude [99]

the section topograph. The presence of the tails stretching in directions out of their illuminated sides indicates that the diffracted rays are indeed twisted. Since the twist is along the clockwise direction, the actual micropipe is a right-handed screw dislocation. Figures 6.13(c) and 6.13(d) show the section topograph and the corresponding simulation of a micropipe that is a left-handed screw dislocation.

An isolated micropipe appears as a circular black ring surrounding a white center under the symmetric back reflection, but noncircular white spots are also frequently observed (see Fig. 6.9). Observations of etched crystal surfaces using



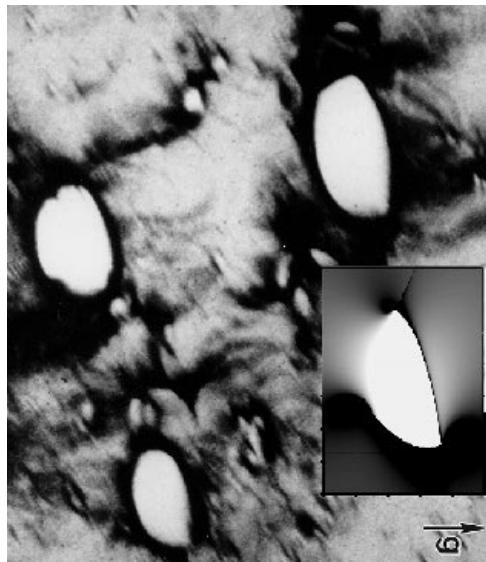
**Fig. 6.13.** Section topographs showing the senses of screw dislocations associated to micropipes. (a) and (b) are the simulated and recorded images of a right-handed screw dislocation; (c) and (d) are the simulated and recorded images of a left-handed screw dislocation [98]



**Fig. 6.14.** Recorded (a) and simulated (b) images of a micropipe with the same dislocation Burgers vector magnitude and sense [99]

SEM show that the noncircular white regions generally contain several micropipe etch pits close to each other, indicating that these images correspond to groups of micropipes.

Figure 6.14(a) shows a SWBXT image of two identical micropipes ( $b_1 = b_2 = 4c$ , 6H-SiC) separated by a distance of  $25 \mu\text{m}$ , and Fig. 6.14(b) is the image simulated on the basis of the superimposition of the two independent strain fields of the two micropipes. It is apparent that the two images exactly coincide with each other. The corresponding image and simulation of two opposite-sense screw



**Fig. 6.15.**  $11\bar{2}6$  grazing-reflection topograph of micropipes. Inset is the simulated contrast of a  $4c$  screw dislocation with surface relaxation effect considered [97]

dislocations ( $b_1 = -b_2$ ) will be presented below. From this principle, one can actually simulate images of arbitrarily distributed micropipe groups so as to extract the configurations of the individual dislocations.

**Grazing incidence imaging of screw dislocations.** In addition to the above SWBXT methods, another useful diffraction geometry is the grazing-reflection geometry. In this geometry the incident beam makes an extremely small angle (less than  $1^\circ$ ) with respect to the  $(0001)$  surface, but there is no limitation for the exit angle of the diffracted beam. This is an especially useful geometry for characterizing micropipes and screw dislocations in SiC films since one can control the penetration depth of X-rays at will by adjusting the incidence angle. Figure 6.15 is a  $1126$  topograph taken with the recording X-ray film parallel to the  $(0001)$  surface, in which the three oval-shaped white spots are images of micropipes. The simulated image based on the geometrical diffraction principle is shown in the inset of Fig. 6.15. Evidently, the shape of the simulated white contrast is similar to that of the recorded images.

**Defects revealed by etching.** One of the complementary techniques that has been used for evaluating the dislocation density is chemical etching, which is based on the preferential dissolution around the dislocation core due to the stress field. This can also provide information about the kind [102], configuration [103], and inclination [104]. The important task is to find out suitable etchant and etching conditions, and ensure that the etch pits are due to dislocations [105]. Numerous etchants have been reported in the literature for etching of SiC. The most widely

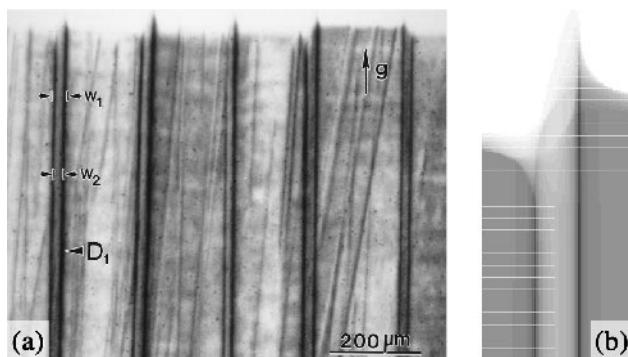
used etchant is KOH in the temperature range of 600–800°C [95]. This has become a routine technique used for the analysis of micropipes in industries. The (0001)Si face reveals the etch pits very clearly compared to poor etching on the (0001)C face [95]. Normally, the etching in SiC is optimized with the help of proven back reflection synchrotron white beam X-ray topography (BR-SWBXT) and is used for quick in-house evaluation of wafers. Depending on the sizes of the etch pits, one can classify them as: (a) large size hexagonal pits that are due to micropipes, (b) medium size pits caused by small spirals that have closed core screw dislocations, or (c) small pits due to edge dislocations [94]. It is also possible to observe process-induced dislocations in the form of dislocation pile-ups and polygonization [91]. Tuominen et al. [72] have revealed domain boundaries and micropipes using etching and SEM study. The domains are of the order of a millimeter with slight misorientation, which can result from the interaction of micropipes.

### **Transmission Observation of Screw Dislocations of $\{11\bar{2}0\}$ Substrate Wafers.**

The true nature of the screw dislocations in SiC is readily revealed by examining longitudinally cut  $\{11\bar{2}0\}$  wafers in transmission geometry, that is, wafers cut parallel to the [0001] growth axis [86,87,93]. In one such topograph, long straight segments of dislocation are observed, with line directions close to the growth axis (Fig. 6.16a). These dislocations have clearly not been created by plastic deformation in the classic sense, that is, via the operation of dislocation sources (such as Frank-Read sources) under the action of stress. Rather they are the dislocations produced during growth via phenomena occurring on the growth surface. These phenomena can include replication of dislocations intersecting the growth face, or dislocation nucleation processes involving incorporation of inclusions onto the growth face, or other “growth accidents”. Such “grown-in” dislocations are often observed in crystals grown from solution, vapor, or flux, and typically propagate at a small angle (usually not greater than  $\sim 15^\circ$ ) to the growth axis [106].

Examples of SWBXT images of growth dislocations, recorded using the symmetric 0006 reciprocal lattice vector, from a  $(11\bar{2}0)$  6H-SiC wafer (cut from a boule grown by Cree Research, Inc.) are shown in Fig. 6.16(a). Each screw dislocation image along the [0001] axis exhibits double contrast with a bimodal intensity profile. Micropipes with Burgers vectors  $b \geq 2c$  (for 6H-SiC), tend to run exactly parallel to [0001]; while closed core screw dislocations ( $b = 1c$ , for 6H-SiC) are only approximately parallel to [0001] (deviating by up to  $\sim 15^\circ$ ). This is due to the fact that deviation from [0001] for the micropipes would cost too much energetically due to the much higher line energy. Such transmission images make it possible to observe the nucleation (and potentially, annihilation) and propagation of the screw dislocations during the growth process.

Again, the transmission image can be rigorously simulated using the geometrical diffraction method, as plotted in Fig. 6.16(b). It should be noted that the vertical shift of the double contrast columns is related to the fact that the diffracting planes besides the dislocation center are tilted in opposite senses in the plane of incidence (the plane containing both the incident beam and the principal diffracted



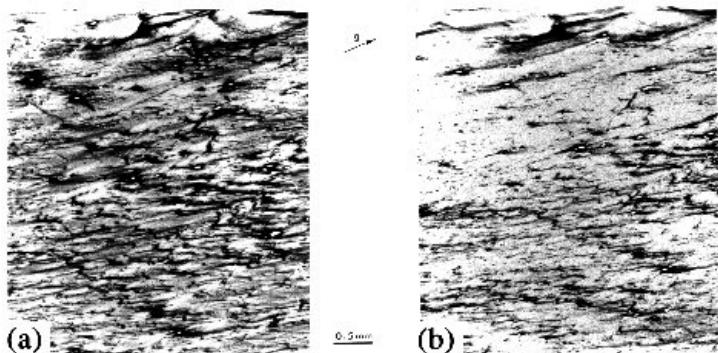
**Fig. 6.16.** Synchrotron transmission topograph showing the double contrast images of micropipes in a longitudinally cut SiC wafer; (b) simulated image of a micropipe in the transmission geometry [99]

beam), and the distance and direction of this shift are determined by the magnitude of the Burgers vector and the dislocation sense, respectively. This enables us to obtain both the dislocation distributions as well as the Burgers vector magnitudes of individual dislocations. Moreover, the vertical shift of the double contrast of each dislocation image unambiguously indicates the dislocation sense. For example, micropipes 1, 2, 3, and 4 in Fig. 6.16(a) are right-handed screw dislocations while micropipe 5 is a left-handed screw dislocation [87,99].

Micropipes and other defects like thermally decomposed voids running parallel to the surface have also been studied using transmission optical microscopy. Using optical microscopy, Sanchez et al. [66] have shown that thermal decomposition cavities in the bulk can be minimized by using a graphite coating on the seed. It is also possible to observe micropipes and other dislocations on (0001) surface under crossed polarizers [107]. The interference contrast in the image reveals the strain associated with the dislocations through the photoelastic effect. If the micropipe is filled with certain laser dyes, it can be easily observed by the fluorescence using laser scanning confocal microscopy.

### ***Dislocations in epilayers and device structures***

SWBXT can also be used to examine dislocation configurations in epilayers and in substrate/epilayer systems that have devices fabricated upon them. Such epilayer and device structures are typically fabricated upon (0001) oriented wafers. In reflection geometry, SWBXT samples defect structures down to the effective penetration depth of the X-ray beam, integrating all the information gathered into a single image. The effective penetration depth, which is controlled in large part by absorption, can be varied by changing the incident grazing angle. By recording images at successively greater penetration depths, one can look for the appearance of new contrast features, and in this way perform a depth profile of the

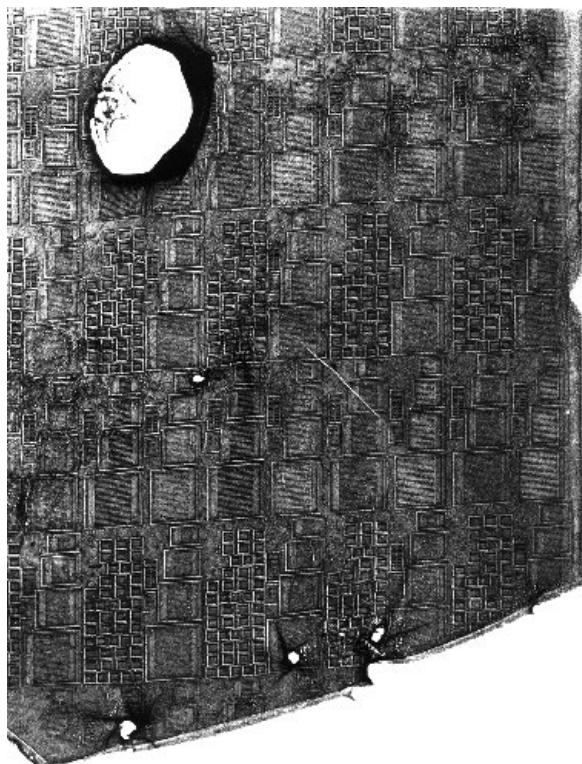


**Fig. 6.17.** Grazing incidence reflection topographs ( $g = 11\bar{2}6$ ,  $\lambda = 0.70 \text{ \AA}$ ) recorded from (a) a 6H-SiC substrate before epilayer growth; (b) the same region after growth of a  $6 \mu\text{m}$  thick epilayer [109].

defect structure [108]. Limiting the penetration depth through control of the grazing angle also makes it feasible to record images exclusively from an epilayer. Figure 6.17 shows an example where images were recorded in grazing incidence geometry from a (0001)6H-SiC crystal before and after the growth of a  $6 \mu\text{m}$  thick epilayer [109]. The penetration depth in each case is around  $6 \mu\text{m}$ , and so one can compare the microstructure in the epilayer to that in the substrate. Close examination of this figure reveals that all of the threading screw dislocations present in the substrate [see Fig. 6.17(a)], which appear as white elliptically shaped rings with white centers, are replicated, as expected, in the epilayer [Fig. 17(b)]. On the other hand, the basal plane dislocations, some of which are visible in Fig. 6.17(a) appear not to be present in Fig. 6.17(b). This is to be expected since most of these dislocations do not thread the surface (note that a finite number will, due to the offcut angle of the crystal). This also can be interpreted to provide some insight as to the mechanism of formation of the basal plane dislocations.

The CVD epilayer growth process is carried out at temperatures several hundred degrees lower than the PVT substrate growth. Since the basal plane dislocations are clearly generated by plastic deformation processes, as evidenced by the dislocation morphology comprising concentric loops piling up on the (0001) slip plane, this suggests two things: (1) that the temperature of CVD growth is not sufficiently high to provide the thermal stresses necessary to drive dislocation motion, and (2) the temperature is not high enough to sufficiently depress the yield stress to a level that is exceeded by the extant thermal stresses. Detailed stress modeling is required to determine the most significant factors controlling the appearance of basal plane dislocations.

Reflection geometry can also be used to examine substrate/epilayer systems that have devices fabricated upon them. The features that make up the device topology typically provide contrast on X-ray topographs. The contrast usually



**Fig. 6.18.** SWBXT back reflection image recorded from a 6H-SiC single crystal that has thyristors fabricated upon it (devices fabricated at U.S. Army Research Laboratory). The small white spots distributed over the image are  $1c$  and larger screw dislocations. The location of these dislocations with respect to the device topology can be clearly discerned, enabling the influence of the defects on device performance to be determined. The large white feature corresponds to damage inflicted by a probe.

originates from the strain experienced by the crystal at the edges of growth mesas, or metallization layers, although some absorption contrast may also superimpose on this. Topographs recorded from such structures provide an image of the defect microstructure superimposed on the backdrop of the device topology. This means that direct comparisons can be drawn between the performance of specific devices and the distribution of defects within their active regions. This has made it possible to determine the influence of threading screw dislocations (closed core and hollow core) on device performance [110,111]. The back reflection geometry is particularly useful here, since it gives a clear image of the distribution of screw dislocations on the background device topology that is imaged with sufficient clarity to unambiguously identify the device. An example of a back reflection image recorded from a crystal with devices fabricated on it is shown in Fig. 6.18.

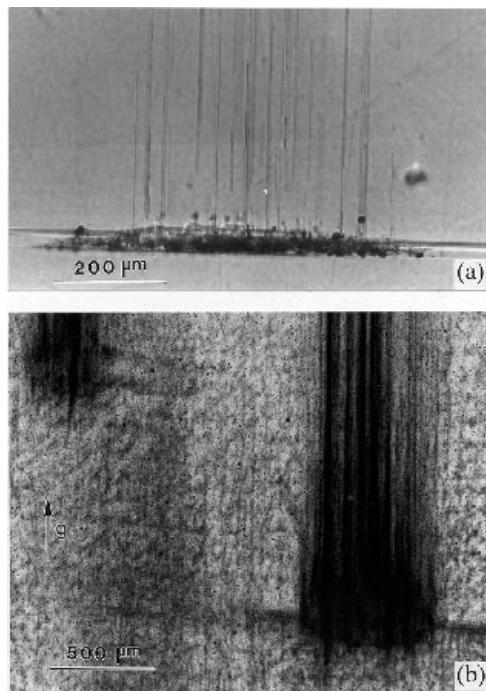
### ***Model for the origin of screw dislocations and micropipes***

It has been frequently observed that screw dislocation (including micropipe) nucleation can occur at foreign material inclusions incorporated into the SiC crystal during growth. However, the general mechanisms by which these inclusions, which could be, for example, graphite particles, silicon droplets, or even voids, can lead to screw dislocation nucleation are not clear. Dudley et al. [112] recently proposed a model for the mechanism of screw dislocation nucleation at such inclusions. This model is based on the previously proposed theory for nucleation of screw dislocations at foreign material (solvent, impurity, or void) inclusions during the growth of crystals from solution [113].

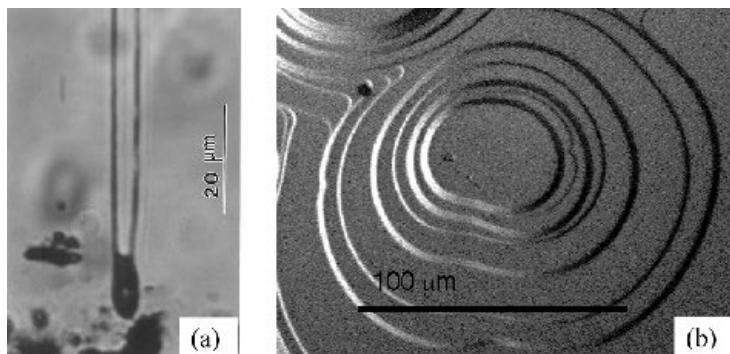
A typical example of the nucleation of screw dislocations (including micropipes) at inclusions in SiC can be clearly seen in Fig. 6.19(a), which is a transmission optical micrograph recorded from a (1-100) thin longitudinal-cut section from a *c*-axis 6H-SiC boule grown by the PVT method at Advanced Technology Materials, Inc. (in 1995). Here it is apparent that a group of micropipes has nucleated at the site of a group of what appears to be overlapping inclusions or voids. This phenomenon was observed to occur throughout this crystal, and many other similar crystals, with nucleation being observed at inclusions of various sizes. While optical microscopy is only able to reveal large micropipes, SWBXT can be employed to image screw dislocations in all their forms (including those with closed cores). A SWBXT image recorded in transmission geometry from the same sample is shown in Fig. 6.19(b). Here the total (micropipe and closed-core) dislocation density is much higher than that observed in Fig. 6.19(a), indicating that a large number of  $1c$  dislocations have also nucleated at these inclusions.

Due to the close proximity of the micropipes shown in Figs. 6.19(a) and 6.19(b), it is difficult to discern the details of the nucleation process. However, these details can be clearly revealed in the nucleation of micropipes at isolated inclusions. Figure 6.20(a) shows a pair of micropipes emanating from a small isolated inclusion, and this phenomenon can be frequently observed in PVT grown SiC crystals. In a reverse process, inclusions are also observed to terminate micropipe pairs. Evidence for the production of opposite sign, screw dislocation pairs can also be found from the frequent observation of mesa structures on the (0001) growth surface in the early stages of PVT-growth of SiC crystals. A typical mesa developed through the interaction between the growth spirals of two closely spaced screw dislocations on the as-grown surface is shown in Fig. 6.20(b). This type of mesa structure indicates the presence of two screw dislocations with the same Burgers vector magnitude but opposite signs [114].

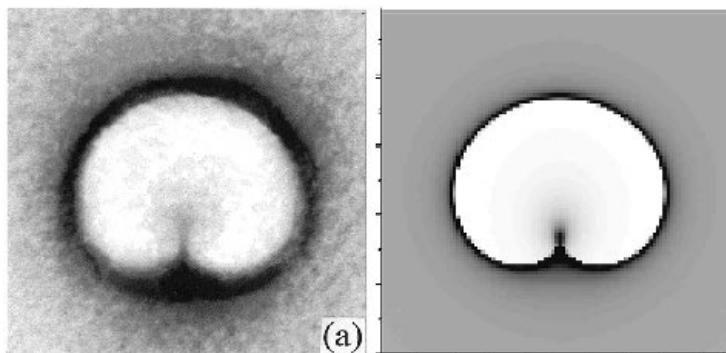
The formation of micropipe pairs is also observable in Lely platelets of SiC. Figure 6.21(a) is an enlarged back-reflection SWBXT image of one of a number of screw dislocation pairs on the (0001) surface of a 6H-SiC Lely platelet. Here the equal Burgers vector magnitudes and the opposite senses of the two dislocations can be verified by the corresponding simulation shown in Fig. 6.21(b) (for comparison, see the images of two screw dislocations with the same sense in Fig. 6.14) [98,99]. It should be noted that in Lely platelets, both the micropipe density



**Fig. 6.19.** (a) Optical micrograph of a part of a (1-100) 4H-SiC wafer showing the nucleation of micropipes at a group of inclusions during growth. (b) SWBXT image recorded in transmission geometry showing the same region as Fig. 6.1(a). (The upper-left region is another group of inclusions at which micropipes nucleate) [112].



**Fig. 6.20.** (a) Nucleation of a pair of micropipes at an inclusion in 4H-SiC; (b) AFM image showing a typical mesa structure on the growth face of a 4H SiC crystal [112]

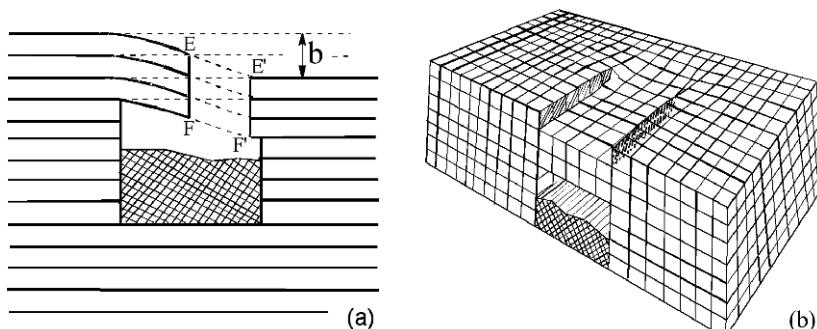


**Fig. 6.21.** (a) SWBXT image recorded in back-reflection geometry from a (0001) Lely platelet showing a pair of opposite-sign screw dislocations; (b) simulation of the image of two opposite-sign screw dislocations ( $b_1 = -b_2 = 12c = 18.2 \text{ nm}$ ) with  $30 \mu\text{m}$  spacing. Image dimensions  $200 \times 200 \mu\text{m}^2$  [112]

and  $1c$  dislocation density are very low, and the occurrence of isolated dislocation pairs indicates that the two closely spaced dislocations are most likely produced simultaneously, for example, at the same inclusion, and their close proximity cannot be attributed to the merging of two dislocations generated from different sites.

Systematic observations of screw dislocation (micropipe) formation processes using a variety of techniques thus suggest, in agreement with earlier reports [85, 89, 115–117], that a possible mechanism for nucleation of micropipes in SiC involves the incorporation of inclusions into the crystal lattice. In the case of small isolated inclusions, it is found that the screw dislocations (micropipes) nucleate in pairs.

The nucleation of screw dislocations at inclusions has been observed in several systems [118–120]. The formation of screw dislocation pairs from inclusions has been briefly proposed by Chernov [113] for the crystals grown from solution. Here we extend this approach in detail to explain the observed nucleation of screw dislocations in SiC. As shown in Fig. 6.22(a), this model assumes that two macrosteps of different height, approaching each other on the growth surface, trap a layer of foreign material (solvent, void, or impurity) on the growth surface. As a result of the higher rate of feeding of the protruding edge than the re-entrant edge, an overhanging ledge can subsequently be produced as the crystal attempts to overgrow the inclusion and incorporate it into its lattice. This overhanging ledge is vulnerable to deformation and vibrations and when the macrostep EG meets the approaching macrostep E'F', horizontal atomic planes which were at the same original height may no longer meet along the line where the two steps meet. If the layer of foreign material constituted a void (or transport gases), downward depression of the overhanging ledge may be expected, whereas if it constituted impurity, deformation of the opposite sense dislocations might be expected. In order to accommodate this misalignment, screw dislocations of opposite sign are created



**Fig. 6.22.** Schematic diagram illustrating the creation of a pair of opposite-sign screw dislocations during the process of inclusion overgrowth. (a) Sectional view through the inclusion parallel to the dislocation line. (b) Perspective view from above [112]

which have Burgers vector magnitudes equal to the magnitude of the misalignment. The configurations of the two created dislocations can be seen more clearly in Fig. 6.22(b). Since the degree of misalignment depends on the relative size of the two approaching steps and the lateral and vertical extent of the inclusion, the production of dislocations with a range of Burgers vectors becomes possible. In fact, micropipe-related screw dislocations in SiC can have Burgers vectors as large as several tens times the basic lattice constant along the  $c$  axis [121]. It seems more likely that these very large Burgers vector screw dislocations are created by this kind of mechanism rather than one involving the merging of groups of same-sign dislocations.

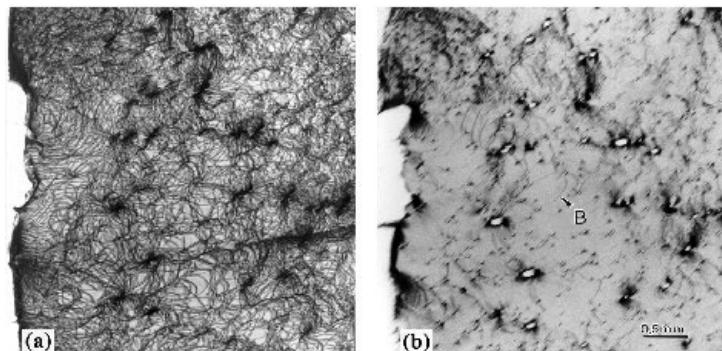
In addition, in cases of large inclusions or groups of inclusions, the deformation of the protruding ledge may be spread over the length of the line along which they meet, resulting in the creation of distributed groups of opposite-sign screw dislocations. These groups may not necessarily be distributed symmetrically, but in all cases, the sum of all the Burgers vectors of the dislocations created must equal zero.

In SiC, the sources of the growth steps involved in the above model can be the vicinal nature of the growth surface (which tends to be slightly dome-shaped), 2D nucleation, as well as spiral steps associated with the intersections of screw dislocations with the surface. Differences in step height are certainly conceivable when a vicinal step meets a spiral step and can even occur when two spiral steps associated with screw dislocations of different Burgers vector magnitude meet or if step bunching occurs for a group of dislocations. Moreover, the merging of 2D-grown islands also play an important role in the formation of growth steps as well as voids. These various sources in conjunction with the formation of inclusions thus provide opportunities for micropipes as well as closed-core screw dislocations to be created during growth.

### 6.7.2 Basal plane dislocations

The primary slip plane for hexagonal 4H and 6H SiC is the basal plane. It is therefore not surprising that deformation-induced dislocations on the basal plane are observed in both structures [122,123]. An example is shown in Fig. 6.23, a transmission topograph recorded from a 6H-SiC basal plane wafer (grown by Cree Research, Inc.). Also shown in this figure is a reflection topograph recorded from the same region of the 6H-SiC crystal.

Detailed Burgers vector analysis of these dislocations can be easily performed. Observation of the morphologies of the basal plane dislocation loops clearly indicates that they are deformation-induced and appear to have been nucleated both at the crystal edges and at the sites of micropipes. This is an interesting phenomenon and is the subject of ongoing study.

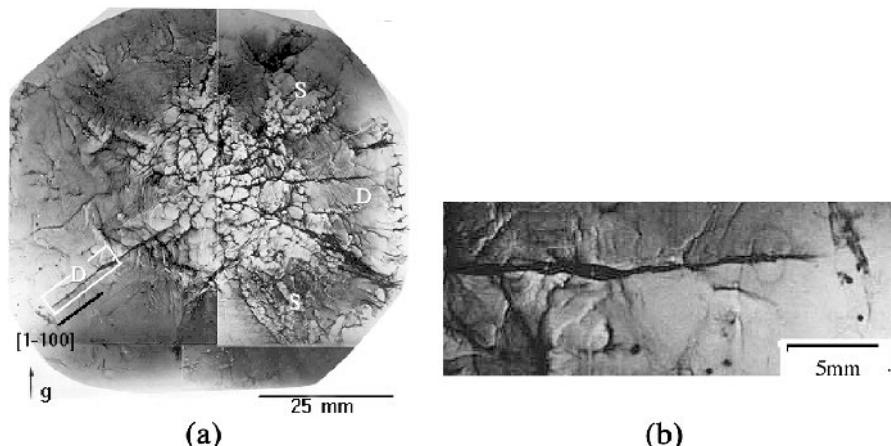


**Fig. 6.23.** (a) Transmission topograph recorded from a basal plane wafer, showing basal plane dislocation loops; (b) the corresponding reflection image, revealing the screw dislocations as well as a few basal plane dislocations [93,122]

### 6.7.3 Small angle boundaries

Another defect, which is receiving increasing attention in 4H-SiC, is the small angle boundary. Preliminary characterization using X-ray topography indicates that the tilt angles associated with these boundaries are only a few seconds of arc, although detailed analysis of the nature of these defects has not yet been completed [124]. Examples of this kind of defect are shown in Fig. 6.24.

Detailed studies carried out by Ha et al. [125], suggest that the small angle boundaries are composed of edge dislocations running approximately along the growth axis. These edge dislocations are believed to have been originally produced by plastic deformation processes occurring on nonbasal planes. These edge dislocations are postulated to subsequently undergo polygonization to form the small

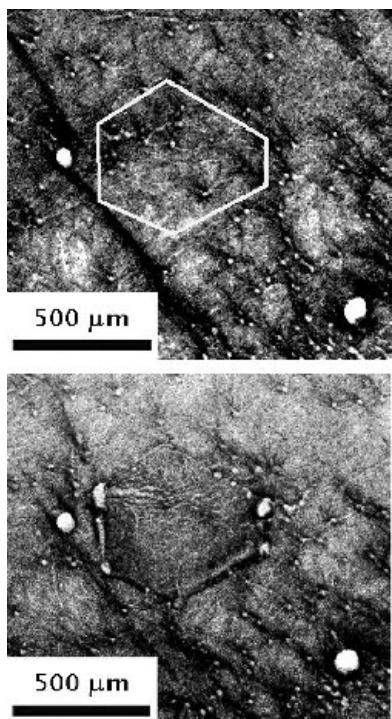


**Fig. 6.24.** (a) Back-reflection topograph of experimental 3-inch 4H-SiC wafer [(00016),  $\lambda = 1.26 \text{ \AA}$ ] showing several small angle boundaries; (b) enlargement from framed section on Fig. 6.17(a), clearly showing the orientation contrast (image overlap) from one of the boundaries [122]

angle boundary structures. The spacing between dislocations within the boundaries is shown by etching to be on the order of 1 micron. This is just below the resolution limit for SWBXT, but while the individual dislocations within the boundaries cannot be resolved, the tilt associated with the boundaries is clearly revealed.

#### 6.7.4 Hexagonal voids

Another defect that is sometimes observed in PVT-grown SiC boules is the hexagonal void; a flat, hexagonal, platelet-shaped cavity oriented parallel to the basal plane (with lateral sizes between 50 and 750  $\mu\text{m}$  and thickness along the  $c$ -axis between 5 and 25  $\mu\text{m}$ ). As shown by Kuhr et al. [126], these voids are nucleated at imperfections in the attachment layer between the seed and crucible cap. Growth steps are observed on the void facets closest to the seed, and evaporation steps are found on void facets closest to the growth surface, providing evidence for void movement during the growth. AFM images have revealed that the growth steps, nucleated at the sidewall of the void, flow across the bottom of the void and terminate in a trench-like depression. KOH etching of wafers between the void and seed further reveal the dislocations lining up along the trace of the void path, often with higher densities corresponding to the location of the trench. In addition, the SWBXT images recorded from wafers above and below the void show a random distribution of screw dislocations in the crystal volume above the void, and an absence of screw dislocations in the volume directly below the void, except for hollow core superscrew dislocations, which are found at the corners of the void trace



**Fig. 25.** Back-reflection X-ray topographs ( $\mathbf{g} = 00024$ ,  $\lambda = 1.24 \text{ \AA}$ ) of the area above (a) and below (b) a hexagonal void (a). The projected passage of the void has been traced in white. The screw dislocations visible above the void in (a) are not visible beneath the void in (b) [126]

(see Fig. 6.25). In this way, groups of closed core dislocations, intersected by the hexagonal voids as they sweep through the crystal, are forced to coalesce to produce fewer, larger Burgers vector screw dislocations (whilst conserving the Burgers vector).

## 6.8 Summary

An extraordinary combination of physical and electronic properties makes silicon carbide a unique material for devices in high power, high frequency, high temperature, and intense-radiation applications. Recent developments in SiC bulk growth and epitaxial film technology have greatly advanced the SiC-based device technology. Although the device potential of SiC was realized long ago from the SiC platelets grown by Acheson and Lely methods, the breakthrough occurred only when the seeded sublimation growth was demonstrated by Tairov and Tsvet-

kov in 1978. Since then research in the area of SiC crystal growth and device fabrication has increased substantially all over the world. The modified Lely method has now become a standard process for industrial production of SiC boules. Wafers of 50 mm diameter are commercially available, and 75 mm and 100 mm diameter wafers have also been grown on an experimental basis. It is expected that 75 mm SiC wafers will be commercially available soon in the market. This has been made possible by optimizing the crystal growth technology in conjunction with modeling and computer simulation. Details on process physics, modeling development, and simulation schemes, together with the description of the effects of various process parameters, are presented in Chapter 7.

The defects, particularly micropipes, have been significantly reduced by improving the growth technique, optimizing the process parameters, and developing better understanding of the defect generation and propagation. The undesirable polytype inclusions have been understood reasonably well, and now it is possible to grow a single polytype using the modified Lely method. Today, wafers of micropipe density as low as  $0.5/\text{cm}^2$  are available commercially. This development is considered quite important for most of the nonpower devices. Indeed, a remarkable advancement has been made in crystal growth technology for both 6H- and 4H-SiC crystals. Now efforts are being devoted to grow 15R SiC, which has a great potential for MOSFET applications. The other common polytype, 3C, is predominantly grown using heteroepitaxy.

With the availability of 6H-SiC wafers, research on epitaxial growth has increased tremendously. High quality films are being produced for different device applications using CVD techniques; in particular, HTCVD and hot-wall CVD have yielded films of good uniformity. Even though LPE of SiC is not as successful as CVD, recent developments such as container-free LPE growth show promise for better quality films. In addition, the quality of the epitaxial film and thereby the functioning of the device have been improved greatly by step-controlled epitaxy. High dopant incorporation can be achieved using the site-competition technique.

Defects present in the SiC crystals have been characterized using X-ray topography, and microscopy-based techniques such as chemical etching, AFM, SEM, TEM, reflection and transmission optical microscopy. Even though many of these techniques are used in a complementary manner to obtain detailed information on defects present in the crystal, X-ray topography, particularly SWBXT, is quite superior to other methods in revealing defects present in the SiC crystals. Indeed, SWBXT has provided complete quantitative characterization of both closed core and hollow core (micropipes) screw dislocations as well as basal plane dislocations. It has also given insights into the formation mechanisms of these defects. Since SWBXT is capable of imaging defects in a full size wafer with devices fabricated on it, the technique can be successfully used to study the influence of various defects on device performance.

The challenge in SiC growth still remains the quality, size, and cost. For widespread use of SiC as a semiconductor, it is important that further progress is made in all of these areas. Since the presence of micropipes is detrimental for device performance, micropipe density must be brought down to a much lower value.

Also, other defects such as basal plane dislocations, inclusions, and voids need to be reduced substantially. Another area that is important is the control of polytype and infringement of polycrystalline growth directly under the seed. Since different polytypes of SiC have different properties and also polytype inclusions can become a potential source for defect generation, it is critical that a single polytype is maintained throughout the growth of the boule.

Control of the growth process requires sensing, measurement, and control strategies. However, the process does not allow much measurement, in fact, nothing inside the growth zone. Measurement of temperatures at only two locations, far away from the growth surface and the bulk of the SiC charge, gives very little information on the actual growth temperature and temperature gradient, two critical growth parameters. Also, it is difficult to experimentally find out the rate of sublimation, chemical composition of vapor, and growth interface shape, etc., which make the control of the process very difficult.

Further, it is well known that the size of the semiconductor wafer has great influence on the cost of the device fabrication. Any improvement in the size of the wafer increases its use by a large factor. For widespread use of SiC, it is believed that 100 mm wafers should be made available immediately followed by 150 mm within five years. Indeed, an increase in SiC boule size and reduction in its price are essential if the SiC semiconductor market is to reach its forecast of \$4 billion by 2004 and \$8 billion by 2008.

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# 7 Silicon Carbide Crystals — Part II: Process Physics and Modeling

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## Nomenclature

$a$	activity
$A$	area ( $\text{m}^2$ )
$\mathbf{A}$	magnetic vector potential ( $\text{W b / m}$ )
$A_{SiC}$	growth area ( $\text{m}^2$ )
$\mathbf{B}$	magnetic flux density (T)
$c_p$	isobaric specific heat, ( $\text{J/kg/K}$ )
$d_p$	mean diameter of the charge particles (m)
$D$	diffusion coefficient ( $\text{m}^2/\text{s}$ )
$D_c$	diameter of crucible (m)
$f$	frequency (Hz)
$F$	radiation view factor
$g$	gravitational acceleration ( $\text{m/s}^2$ )
$Gr$	Grashof number, $\rho^2 g \beta R^3 \Delta T / \mu^2$
$G_{SiC}$	growth rate (m/s), dissolving rate of particles (m/s)
$\Delta G_T^0$	isobaric-isothermal Gibbs-function
$h$	heat transfer coefficient ( $\text{W/m}^2/\text{K}$ )
$\Delta h_{f, 298}^0$	heat of formation
$H$	latent heat (J/kg)
$I$	current (A)
$J$	current density ( $\text{A}/\text{m}^2$ )
$k$	thermal conductivity ( $\text{W/m/K}$ )
$K$	equilibrium constant of a chemical reaction
$L$	gap between the charge and seed (m)
$M$	molecular weight ( $\text{kg/mol}$ )
$p$	pressure (Pa)
$P$	partial pressure (Pa)
$Pe$	mass Pélet number ( $UL/D$ )

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$Pr$	Prandtl number ( $\mu c_p / k$ )
$q$	heat flux ( $\text{W}/\text{m}^2$ )
$q''_{eddy}$	heat generated by eddy currents ( $\text{W}/\text{m}^3$ )
$q''_{radi}$	radiative heat flux ( $\text{W}/\text{m}^2$ )
$Q$	heat flux (W)
$r$	radial coordinate (m)
$R$	universal gas constant, 8.314 (J/mol/K); heat resistance (K/W)
$R_s$	radius of susceptor (m)
$Ra$	Rayleigh number ( $Gr \cdot Pr$ )
$t$	time (s)
$T$	temperature (K)
$\Delta T$	temperature difference between the charge and seed (K)
$u$	displacement component
$U$	advective velocity (m/s), activation energy (J/mol)
$v$	displacement component
$z$	axial coordinate (m)

## Greek Symbol

$\alpha$	absorptivity, thermal expansion coefficient, sticking coefficient
$\beta$	volumetric expansion coefficient ( $1/\text{K}$ )
$\varepsilon$	emissivity, strain
$\varepsilon_m$	permittivity ( $F/\text{m}$ )
$\varepsilon_p$	porosity of SiC charge
$\mu$	viscosity ( $\text{kg}/\text{m}/\text{s}$ )
$\mu_m$	magnetic permeability ( $H/\text{m}$ )
$\rho$	density ( $\text{kg}/\text{m}^3$ )
$\rho_c$	density of crystal ( $\text{kg}/\text{m}^3$ )
$\sigma_c$	electrical conductivity ( $1/\Omega/\text{m}$ )
$\sigma$	Stefan-Boltzmann constant $5.670 \times 10^{-8}$ ( $\text{W}/\text{m}^2/\text{K}^4$ ), stress
$\omega$	angular frequency (rad/s)

## Subscripts

$\infty$	ambient
$boun$	boundary
$coil$	induction coil
$cond$	conductive
$conv$	convective
$eddy$	eddy current
$eff$	effective
$gas$	gas
$insu$	insulation material

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<i>radi</i>	radiative
<i>real</i>	real part of a complex quantity
<i>s</i>	solid
<i>Ste</i>	Stefan
$\theta$	angular direction

## 7.1 Introduction

Silicon carbide crystals of 50–100 mm diameter are now commercially grown using the method of physical vapor transport, commonly known as the modified Lely method. A detailed review of the historical development of SiC growth, micropipes and other defects in as-grown crystals, issues and challenges of the current process technology, and characteristics of the present industrial growth systems is presented in a companion article (Chapter 6) by Dhanaraj et al. [1]. Any advancement in crystal growth technology in terms of the boule size (diameter and length) and defect density strongly depends on the understanding of the process physics, better design of the growth system and effective control of the growth process. Since direct measurement of temperature, flow, species concentration, and growth rate is extremely difficult, if not impossible, physics-based modeling is the only way that one can develop an understanding of the transport mechanisms in a SiC growth system. The models can also help in process optimization and system design.

Modeling and simulation of SiC crystal growth has attracted significant research interests in last five years or so, and growth models have been developed by several investigators, namely, Hofmann et al. [2,3], Pons et al. [4,5], Egorov et al. [6], Müller et al. [7,8], Karpov et al. [9], Chen and co-workers [10–15], Selder et al. [16], and Räback et al. [17–19]. Various degrees of system complexity have been considered by these authors, such as electromagnetic field produced by RF heating, generated heat power in the graphite susceptor, conduction and radiation heat transfer, temperature distribution, and growth kinetics.

Hofmann et al. [2,3] modeled the temperature distributions for a growth temperature of 2573 K and system pressure of up to 3500 Pa. Pons et al. [4,5] calculated the electromagnetic field and temperature distribution, and found that the predicted temperatures for the seed and powder surface (2920 K and 3020 K) are much larger than the external temperatures measured at the top and bottom of the crucible (2390 K and 2500 K), while the maximum temperature of the insulation foam on its periphery is about 1000 K. The total pressure is around 30 Torr (4000 Pa) and the growth rate is 1.55 mm/h. Egorov et al. [6] modeled the global heat transfer inside the system for SiC growth in a tantalum container. Müller et al. [7,8] calculated the temperature distributions in inductively heated SiC growth reactors at temperatures of 2373–2673 K, and found that the temperatures in the powder are highly nonuniform, and predicted radial variations of 30–50 K along the powder surface. Karpov et al. [9] predicted growth rate in the growth of SiC in a tantalum container.

Ma et al. [10] performed an order-of-magnitude analysis of parameters in the SiC PVT growth, and used a one-dimensional network model and two-dimensional finite-volume model to predict the temperature distribution in a 75 mm growth system. Chen and co-workers [11–15] proposed a kinetics model for SiC vapor growth, predicted growth rate as a function of temperature, temperature gradient, and inert gas pressure, and obtained a growth rate profile across the seed surface from the temperature distribution in a 75 mm growth system. The powder charge is modeled as a solid matrix with a porosity and an effective conductivity that accounts for both the conduction and radiation in the powder.

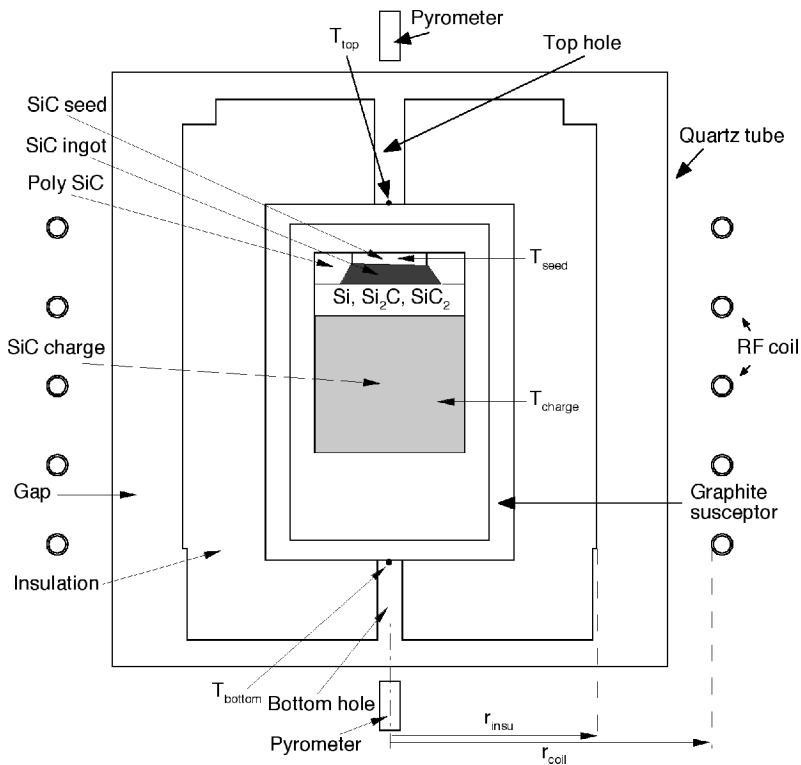
Selder et al. [16] introduced a modeling approach for the simulation of heat and mass transfer during SiC bulk crystal growth and compared calculated results with the experimental data. Räback et al. [17–19] presented a model for the growth rate of the SiC sublimation process and estimated the parametric dependencies of the growth rate.

## 7.2 Modeling of Heat and Mass Transfer and Growth Rate

### 7.2.1 Growth process

A typical SiC growth system consists of an RF copper coil, quartz tube, graphite susceptor, graphite insulation, crucible, and some other components (Fig. 7.1). The graphite crucible is filled with a SiC powder charge, and a SiC seed is placed on the bottom of the lid of the crucible as shown in Fig. 7.1. The seed is cooled by heat loss through the top hole. The SiC powder charge is heated by RF induction heating that is generated by passing through the coil a radio-frequency current. The current required depends on the number of turns of coil and distance between the coil and the susceptor. The time-harmonic electromagnetic field induces eddy currents in the graphite susceptor that has a high electrical conductivity, and heat is generated in a thin (skin) layer of the susceptor. Sometimes a double-walled water-cooled quartz tube is used to seal the system [5,20,21] that enables us to reduce the thickness of the insulation, and enhance the coupling between the coil and the susceptor. The system is maintained at a very low pressure using a vacuum pump, and an argon container is linked to the end plate to control the pressure inside the quartz tube and create an inert gas environment. Two holes are bored in the graphite insulation above and below the crucible to monitor the temperatures of the seed and the charge using pyrometers. The temperature inside the top hole is controlled, which is lower than the seed temperature.

The growth process consists of several steps [22,23]: (a) *vacuum degassing stage*—a low gas pressure ( $10^{-3}$  Pa) and an evacuation temperature of  $1073 \text{ K} < T < 1273 \text{ K}$  are applied to reduce the background nitrogen contamination; (b) *pre-heating stage*—temperature is gradually increased in high-purity argon environment (about  $10^5$  Pa) to the growth temperature and stabilized to achieve an optimum  $\Delta T$  between the source and the seed; (c) *growth stage*—a programmed



**Fig. 7.1.** Schematic of an RF-heated furnace for the growth of single SiC crystals by PVT

pressure reduction is used to achieve low-defect nucleation and uniform epitaxy on the oriented seed crystal, and argon pressure is decreased to  $10 < p < 2.66 \times 10^4$  Pa, and boule growth begins; and (d) *cooling stage*—the temperature is reduced. The temperature difference between the charge and the seed during the growth stage depends on the system configuration. According to Lilov [24], SiC dissociates completely into liquid silicon and solid carbon at  $T > 3150$  K and therefore the growth temperature must lie below 3150 K. Various growth systems used by industry employ different growth temperatures depending on the temperature gradient in the growth chamber; a higher growth temperature is usually associated with a lower temperature gradient and a higher pressure. Although a model can account for various stages of the growth as outlined above, those reported in the literature have thus far primarily focused on step (c), the growth stage.

## 7.2.2 Flow and heat transfer parameters

The flow in a silicon carbide growth system is induced by: (a) the buoyancy force that is produced by the variations in temperature on crucible walls, and (b) the ad-

vection due to sublimation of SiC charge. The flow is essential to bring the SiC vapor and other species from the charge at the bottom to the growth surface at the top. The effect of buoyancy can be determined by the Grashof number,

$$Gr = \frac{\rho^2 g \beta D_c^3 \Delta T}{\mu^2} = \frac{\rho^2 g D_c^3}{\mu^2} \frac{\Delta T}{T}, \quad (7.1)$$

where the isobaric expansion coefficient,  $\beta = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} = \frac{1}{T}$ , if the argon-vapor mixture is considered as an ideal gas, and the Prandtl number,

$$Pr = \frac{\mu c_p}{k} \quad (7.2)$$

For a typical process condition of  $3 \times 10^4$  Pa as the system pressure, 2900 K as the growth temperature, 30 K as the temperature difference ( $\Delta T$ ), the Prandtl number is obtained as 0.66 while the Grashof number is estimated to be 3 and 24 for crucible (inner) diameters of 50 mm and 100 mm, respectively. These values of the Grashof number are far below the threshold at which natural convection can be considered appreciable [4,10]. Even though in the case of a cylinder heated on the outer wall natural convection can occur at any Rayleigh number,  $Ra$  must be above 1707 for the onset of convection in an enclosure heated from below and cooled at the top (Bénard convection). The present configuration does not conform to any of these two classical cases. It is still reasonable to consider that buoyancy flow plays a far less important role than radiative and conductive heat transfer in a SiC growth system. However, in the next generation systems for large diameter SiC crystal growth, the Grashof number may not remain this small. For example, if the crucible (inner) height becomes 500 mm,  $Gr$  based on height will increase to about 3000 leading to appreciable buoyancy effects. Even though  $Gr = 3000$  is not very large, the complex temperature boundary conditions can lead to complex flows, a combination of Bénard convection and vertical boundary layer flows. For such convective flow analysis, a model based on fluid-superposed porous layer theory as outlined by Prasad [25] and Chen et al. [26,27] can be used.

The Stefan flow on the other hand is caused by volumetric expansion of silicon carbide species due to dissolving and sublimation of the charge. The species mainly include gaseous Si,  $Si_2C$ ,  $SiC_2$ , and SiC. The partial pressure of each species in the charge reaches an equilibrium value, which is a strong function of temperature. The transport of species from the charge to seed is determined by the Stefan flow and growth kinetics. The Stefan flow is therefore very important for mass transfer and growth rate.

If leakage and diffusion are neglected, the advective velocity of SiC vapor flow can be estimated from,

$$U = \rho_{SiC} G_{SiC} A_{SiC} / \alpha \rho_{gas} A_{gas}, \quad (7.3)$$

where the vapor density is  $\rho_{gas} = pM/RT$ ,  $A_{SiC}$  is the growth area, and  $\alpha$  is the sticking coefficient. This leads to the mass Pécelt number,

$$Pe = UL/D, \quad (7.4)$$

where the diffusion coefficient can be obtained from  $D = D_0(T/T_0)^n (p_0/p)$  [28], with  $D_0 = 5 \times 10^{-6} \sim 2 \times 10^{-4} \text{ m}^2/\text{s}$ ,  $n = 1.8$ ,  $T_0 = 273 \text{ K}$ , and  $p_0 = 1 \text{ atm}$ . Using  $D_0 = 5 \times 10^{-6} \sim 1 \times 10^{-5} \text{ m}^2/\text{s}$  and  $L = 50 \text{ mm}$ , Chen et al. [13] have calculated the advective velocity, diffusion coefficient, density, and Péclet number for two operating conditions, one with a low growth temperature and low gas pressure and another with a high growth temperature and high gas pressure (Table 7.1).

If the buoyancy effects are neglected, the heat transfer in the SiC growth system will depend on the latent heat released during the deposition (or absorbed during the sublimation), heat transfer by Stefan flow (advective mass transport), and radiative heat transfer inside the growth system. These three heat transfer quantities can be estimated from,

$$Q_{latent} = \rho_{SiC} G_{SiC} A_{SiC} \Delta H_{vs}, \quad (7.5a)$$

$$Q_{Stefan} = \rho_{SiC} G_{SiC} A_{SiC} c_p \Delta T, \quad (7.5b)$$

$$Q_{radi} = \varepsilon A_{SiC} \sigma (T_{charge}^4 - T_{seed}^4) \quad (7.5c)$$

For a growth rate of  $G_{SiC} = 1 \text{ mm/h}$ , a diameter of  $50 \text{ mm}$ ,  $\Delta T = 30 \text{ K}$ ,  $\varepsilon = 0.8$ , and  $T_{seed} = 2900 \text{ K}$ ,  $Q_{latent}$ ,  $Q_{Stefan}$ , and  $Q_{radi}$  are estimated to be  $0.01 \text{ W}$ ,  $0.1 \text{ W}$ , and  $1000 \text{ W}$ , respectively. It is therefore reasonable to neglect the latent heat released and heat transfer by Stefan flow while calculating the temperature distribution. It should, however, be noted that the temperature distribution inside the crucible will depend on the temperature conditions on the inner surfaces of the crucible and conduction and radiation in the SiC charge. As shown later, these heat transfer mechanisms can be easily included in a physics-based mathematical model for the system. Another important issue to keep in mind is the effect of latent heat release on the growth phenomena since a small change in temperature gradient (due to condensation) in the vicinity of the growth interface can significantly affect the growth behaviors. It has also been commonly assumed that the chemical reaction, both exothermic and endothermic, does not contribute much to the heat transfer and temperature distribution [4].

**Table 7.1.** Advective flow parameters for two different operating conditions [13]

	U [m/s]	D [m <sup>2</sup> /s]	$\rho$ [kg/m <sup>3</sup> ]	$\alpha$	Pe
2600 K, 20 Torr (2666 Pa)	0.178	$2.16 \times 10^{-2}$	$4.92 \times 10^{-3}$	1	0.41
2900 K, 200 Torr (26,666 Pa)	0.0199	$3.98 \times 10^{-4}$	$4.41 \times 10^{-2}$	1	2.5

### 7.2.3 One-dimensional network model

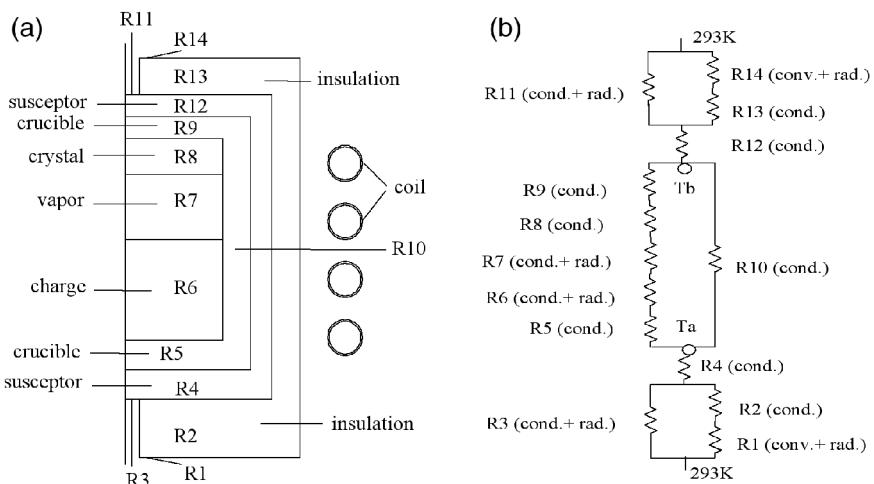
As a first approximation, a heat resistance network analysis can be very useful in developing a basic understanding of the thermal behavior of a SiC growth system [10]. In the absence of convective heat transfer, the thermal field in a SiC growth system is dominated by the interplay of conduction and radiation within and between the different components.

A typical SiC system, as shown schematically in Fig. 7.2(a), can be easily represented by a heat resistance network (Fig. 7.2b). For this simple analysis, the inner surfaces of the upper and lower graphite susceptors can be treated at fixed temperatures,  $T_a$  and  $T_b$ . The heat resistances for conduction, convection, and radiation are given by

$$R_{cond} = \frac{L}{kA}, \quad R_{conv} = \frac{1}{hA}, \quad (7.6a, b)$$

$$R_{radi} = \frac{1}{\varepsilon\sigma(T_1 + T_2)(T_1^2 + T_2^2)A} \approx \frac{1}{4\varepsilon\sigma T_{av}^3 A}, \quad (7.6c)$$

where  $L$  is the thickness,  $k$  is the thermal conductivity,  $A$  is the area,  $h$  is the heat transfer coefficient,  $\varepsilon$  is emissivity,  $\sigma$  is the Stefan-Boltzmann constant, and  $T_{av}$  is the average temperature of two surfaces under consideration,  $T_{av} = \frac{T_1+T_2}{2}$ , where  $T_1$  and  $T_2$  are the temperatures of the two surfaces.



**Fig. 7.2.** (a) Schematic and (b) thermal network of a SiC growth system (cond. — conduction, conv. — convection, rad. — radiation) [10]

It is necessary to consider both conduction and radiation from particle to particle to account for the heat transfer within the SiC charge. Several correlations for

the effective heat transfer coefficient due to radiation in a porous matrix have been reported in the literature [29]. One of these correlations valid for spherical particles is given by Kansa et al. [30],

$$h_{radi, porous} = \frac{8}{3} \varepsilon \varepsilon_p \sigma 4 T_{av}^3 d_p \quad (7.7)$$

where  $\varepsilon_p$  is the porosity for a randomly packed spherical bed,  $T_{av}$  is the average temperature of the charge, and  $d_p$  is the average particle diameter.

Figure 7.2(b) shows the thermal network diagram for a typical SiC growth system using the electrical circuit analogy. The resistances in various components of a typical growth system have been calculated by Ma et al. [10], which give a good indication of the magnitude of heat transfer through various components.

## 7.2.4 Thermal transport model

In developing a thermal transport model for SiC growth, it is important to consider the electromagnetic field generated by RF heating, heat generation, conduction and radiation in various parts of the growth system, and appropriate boundary conditions. The effects of convective heat transfer as discussed in Section 7.2.2 have been neglected by almost all investigators thus far. However, they may need to be considered as the PVT growth system is upscaled. A short description of the major components of the model is given below.

### ***Calculation of electromagnetic field***

The electromagnetic field produced by an RF induction coil can be calculated by using Maxwell equations, and the generated heat power in the graphite susceptor can be predicted by low frequency eddy current theory ( $f < 1$  MHz). For the present problem, the Maxwell equations can be simplified using the quasi-steady approximation. It is commonly assumed that the current in the coil is time-harmonic, and heat in the graphite susceptor is generated only by eddy currents [31]. Under such conditions, the magnetic flux density can be expressed as the curl of a magnetic potential vector,  $\mathbf{B} = \nabla \times \mathbf{A}$ , and the Maxwell equations can be written in terms of the vector potential,  $\mathbf{A}$ , as,

$$\nabla \times \left( \frac{1}{\mu_m} \nabla \times \mathbf{A} \right) + \varepsilon_m \frac{\partial^2 \mathbf{A}}{\partial t^2} + \sigma_c \frac{\partial \mathbf{A}}{\partial t} = \mathbf{J}_{coil} \quad (7.8)$$

Assuming that the coil and the electromagnetic field are axi-symmetric, such that both  $\mathbf{A}$  and the current density,  $\mathbf{J}_{coil}$ , have only one angular component each with an exponential form,

$$\mathbf{A} = \begin{Bmatrix} 0 \\ A_0 e^{i\omega t} + cc \\ 0 \end{Bmatrix}, \quad \text{and} \quad \mathbf{J}_{coil} = \begin{Bmatrix} 0 \\ J_0 e^{i\omega t} + cc \\ 0 \end{Bmatrix}, \quad (7.9)$$

where  $i$  is the complex unit, and  $cc$  denotes the complex conjugate. The final equation for  $\mathbf{A}$  is obtained by substituting Eqs. (7.9) in Eq. (7.8),

$$\left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{r^2} + \frac{\partial^2}{\partial z^2} \right) \left( \frac{A_0}{\mu_m} \right) + \epsilon_m \omega^2 A_0 - i\omega\sigma_c A_0 = -J_0 \quad (7.10)$$

In an axisymmetric system, the following boundary conditions can be used to solve equation (7.10),

$$A_0 = 0, \quad \text{at } r = 0, \text{ and } (r^2 + z^2) \rightarrow \infty \quad (7.11)$$

After solving equations (7.10) for  $A_0$ , the generated heat power by eddy currents in the graphite susceptor can be obtained from [31,32],

$$q''_{eddy} = \frac{1}{2} \sigma_c \omega^2 A_0 A_0^* \quad (7.12)$$

where  $*$  denotes the complex conjugate. Further details of the electromagnetic field formulation can be found in Bíró and Preis [31], Pons et al. [4] and Chen et al. [13].

### **Energy transport**

In the absence of convective flows, temperature distribution in the growth system can be calculated using an energy transport equation,

$$(\rho c_p)_{eff} \frac{\partial T}{\partial t} = \nabla \cdot (k_{eff} \nabla T) + q''_{eddy} - (q''_{radi} + q''_{insu}) \delta A / \delta V, \quad (7.13)$$

where  $q''_{radi}$  is the radiative heat flux normal to the inner surface of the radiation enclosure, and  $\delta A$  and  $\delta V$  are the area over a finite-volume face and finite volume near the gas/solid interface (see Fig. 7.3a), respectively. In Eq. (7.13),  $q''_{insu}$  is the radiative heat flux on the outer surface of the insulation,

$$q''_{insu} = \epsilon_{eff} \sigma (T^4 - T_\infty^4), \quad (7.14)$$

where  $\epsilon_{eff}$  is effective emissivity. For surfaces exposed to the ambient air, the effective emissivity can be chosen as that of the material,  $\epsilon_{eff} = \epsilon_{insu}$ . On the other hand, for surfaces exposed to the copper coil, the effective emissivity can be calculated from [33],

$$\epsilon_{eff} = \frac{1}{1/\epsilon_{insu} + r_{insu}/r_{coil}(1/\epsilon_{coil} - 1)}, \quad (7.15)$$

so that the reflection of energy by the inner surface of the copper coil can be included in the formulation [13]. Here  $\epsilon_{insu}$  and  $\epsilon_{coil}$  are the emissivities of graphite insulation and copper coil, respectively, and  $r_{insu}$  and  $r_{coil}$  are the radii of the outer surface of insulation and inner surface of coil (as shown in Fig. 7.1).

Suitable boundary conditions must be used to solve Eq. (7.13). The computational domain for the energy equation is set as inside the quartz tube (Fig. 7.1), and the temperature on the quartz tube is set as 293 K. If it can be assumed that the three-dimensional effects are negligible, the symmetric condition

$$\frac{\partial T}{\partial r} = 0, \quad \text{at } r = 0 \quad (7.16)$$

can be used at the central axis. This condition is certainly applicable for good quality, slow growth as is evident from the symmetric growth striations reported in the literature (Selder et al., [16]). However, three-dimensional effects can become important if the growth system becomes larger, the material uniformity cannot be maintained, and/or there are fluctuations in power supply.

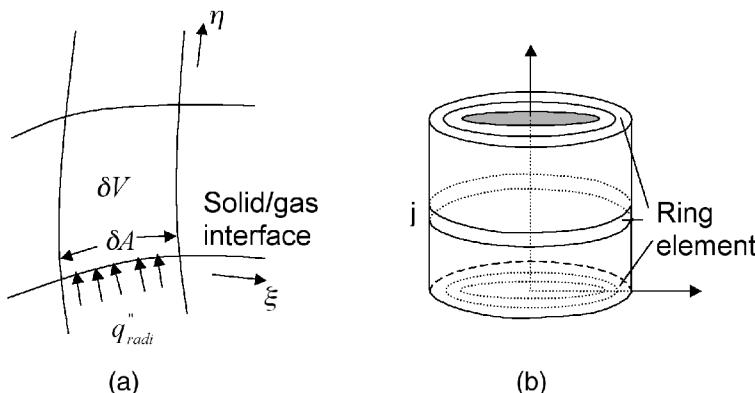
The thermal properties of various components (i.e., graphite susceptor, graphite insulation, crucible, and SiC charge) in the growth system should be considered as a function of temperature. Although most of the modeling studies consider SiC charge as a solid, Chen et al. [11,13] have considered the porosity of the charge and radiation from particle-to-particle. The effective heat capacity of the SiC powder charge can be estimated using the mixture theory,

$$(\rho c_p)_{\text{eff}} = (1 - \varepsilon_p)(\rho c_p)_{\text{SiC}} + \varepsilon_p(\rho c_p)_{\text{gas}}, \quad (7.17)$$

whereas the thermal conductivity can be obtained by considering the conduction-radiation heat transfer among the particles [30],

$$k_{\text{eff}} = (1 - \varepsilon_p)k_{\text{SiC}} + \varepsilon_p(k_{\text{gas}} + \frac{8}{3}\varepsilon\sigma 4T^3 d_p) \quad (7.18)$$

Many other correlations for  $k_{\text{eff}}$  can be found in Kaviany [29].



**Fig. 7.3.** (a) Heat flux on the radiation surface and curvilinear grid system, and (b) schematic of ring elements on radiative surfaces. The ring elements coincide with the finite volume grids for conduction calculation [13].

### Radiative heat transfer

Radiation is the dominant mode of heat transfer inside the crucible and requires special attention while developing a model for the SiC growth.

Pons et al. [4] have not considered the wall-to-wall radiation in the gas region, but assumed an apparent conductivity, greatly simplifying the energy equation [13] in their model. On the other hand, Hoffman et al. [2], Egorov et al. [6], and Chen and co-workers [13] have considered grid-to-grid gray-diffuse radiation together with appropriate view factors. This approach requires that all radiation surfaces be divided into grids and radiation view factors between each pair of these grids be calculated. In two-dimensional calculations, this, however, reduces to circular rings as shown in Fig. 7.3(b). It is also important that radiation heat transfer is calculated not only in the growth chamber but also in the bottom and top holes, as emphasized by Chen et al. [13].

Here, we describe the radiation model as adopted by Chen and co-workers [13], which is based on the method of discrete exchange factors (DEF) [34–36]. It is assumed that the radiation surfaces are gray, diffusely emitting and reflecting, and opaque. The radiation surface is broken into a number of rings each with uniform properties, and view factors between each pair of rings are calculated using appropriate relations [37]. The absorptivity  $\alpha_j$  is assumed to be equal to the emissivity  $\varepsilon_j$  in each ring. The integral equation for radiative heat transfer is then obtained as [33],

$$\frac{q''_{radi,j}}{\varepsilon_j} - \sum_{k=1}^N F_{j,k} \frac{1-\varepsilon_k}{\varepsilon_k} q''_{radi,k} = \sigma T_j^4 - \sum_{k=1}^N F_{j,k} \sigma T_k^4 \quad (7.19)$$

where  $F_{j,k}$  is the view factor from ring  $j$  to ring  $k$  [37]. The above equations can be solved numerically by writing,

$$(A_{jk}) \cdot (q''_{radi,k}) = (B_{jk}) \cdot (\sigma T_k^4), \quad (7.20)$$

where  $A_{jk} = \frac{\delta_{jk}}{\varepsilon_k} - F_{j,k} \frac{1-\varepsilon_k}{\varepsilon_k}$ ,  $B_{jk} = \delta_{jk} - F_{j,k}$ , and  $\delta_{j,k}$  is Kronecker's delta. The radiative heat flux can be written in the tensor form as,

$$q''_{radi,j} = (\mathbf{A}^{-1} \cdot \mathbf{B})_{jk} \cdot (\sigma T_k^4) \quad (7.21)$$

The radiative heat flux is used as a source term in each computational element when solving the energy equation (7.13).

It should be noted that the spectral (wavelength dependence) behavior of radiation heat transfer is not accounted for in the above model although the radiative properties of SiC surfaces may be spectral. Secondly, the decomposition of SiC and accumulation/deposition of carbon particles can change the radiative properties inside the crucible significantly as the growth proceeds. Finally, the chemical species in the gas/vapor region may also participate in heat transfer by volumetric radiation. Since nothing is known of the participating behavior of any species other than carbon, this is a difficult task at present.

### 7.2.5 Mass transport model

Once the temperature field inside the crucible is obtained, a mass transport model can be used to calculate the distribution of species in the system. Hofmann et al.

[2], Pons et al. [4], and Chen et al. [11–14] have all considered the transport of species with various degrees of complexity. Since sublimation of SiC particles is associated with decomposition in various species and chemical reactions, a thermodynamic analysis is necessary for the calculations of partial pressures and species transport.

### **Equilibrium processes**

Mass spectrometric investigations conducted by Drowart and De Maria [38] have shown that the basic components of the evaporation of SiC are Si,  $\text{Si}_2\text{C}$ ,  $\text{SiC}_2$ , and SiC. The content of the other components of evaporation ( $\text{Si}_2$ , C,  $\text{C}_2$ ,  $\text{C}_3$ ) in the vapor is insignificant and can be neglected. The following reactions are considered [38,24]:



The equilibrium constant of a chemical reaction can be calculated from,

$$K_i = \exp(-\Delta G_T^0 / RT). \quad (7.27)$$

The change in isobaric-isothermal Gibbs-function  $\Delta G_T^0$  for the reaction is given by,

$$\Delta G_T^0 = \sum_{\text{prod}} v_i (\Delta h_{f,298}^0 + h_T - h_{298} - T s_T^0) - \sum_{\text{reac}} v_i (\Delta h_{f,298}^0 + h_T - h_{298} - T s_T^0), \quad (7.28)$$

where  $\Delta h_{f,298}^0$  is the heat of formation,  $v_i$  is the stoichiometric coefficient, and  $h_T$  is the enthalpy of the reacting species.

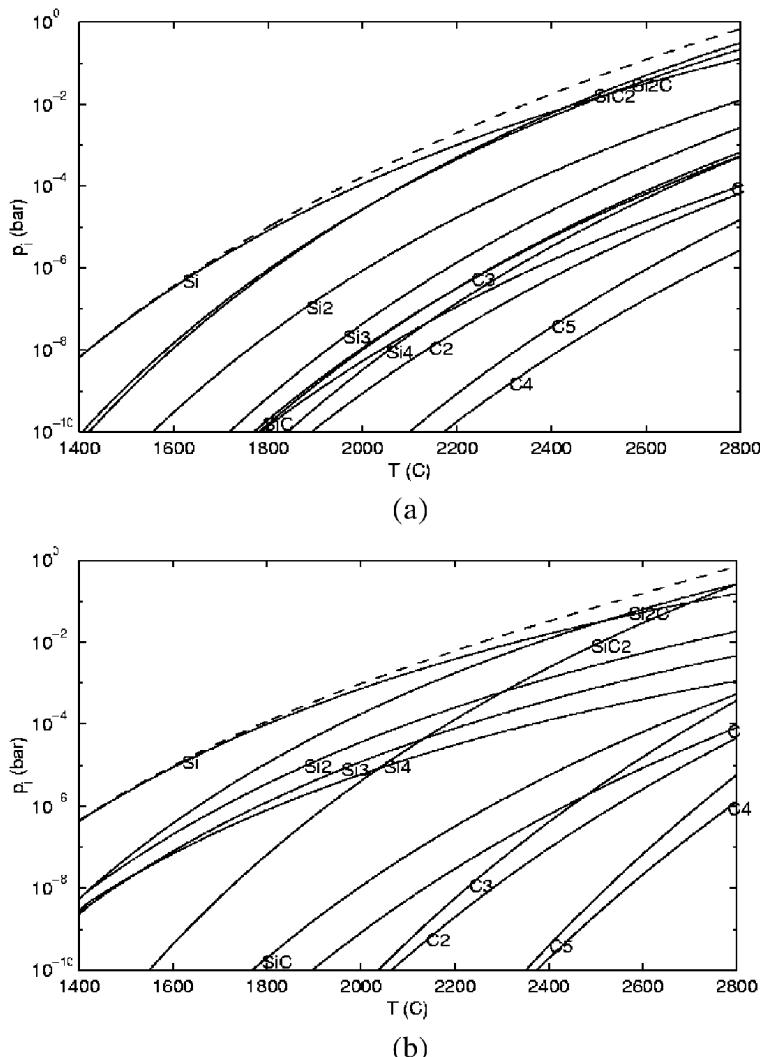
Lilov [24] has conducted a thermodynamic study on the partial pressure of each species. Up to 2546 K the pressure of silicon vapor above the silicon carbide is determined only by reaction (7.23) because the pressure of silicon ensured by (7.25) is less than the pressure of Si due to reaction (7.23). Therefore, in the temperature interval of 1500–2546 K, both reactions (7.23) and (7.25) take place simultaneously and the partial pressures of Si and  $\text{SiC}_2$  are determined by,  $P_{\text{Si}} = K_2$ ,  $P_{\text{SiC}_2} = K_4 / P_{\text{Si}}$ , respectively. In Table 7.2, the underlined values represent the real pressures at equilibrium; from 1500–2546 K, the silicon partial pressures due to reaction (7.23) are the real ones. The pressures of silicon vapor under these conditions are less than the pressure at saturated conditions, and therefore, in this temperature interval the dissociation takes place in the gas phase. As a result of reactions (7.23) and (7.25), carbon gradually accumulates in the silicon carbide charge.

At temperatures above 2546 K, the partial pressure of silicon due to reaction (7.25) becomes greater than that by reaction (7.23). Therefore, reaction (7.23) cannot take place ( $\Delta G_T^0 > 0$ ) and the pressure of silicon above SiC is regulated only by reaction (7.25). In Table 7.2, the values due to reaction (7.25) are underlined from 2546–2900 K, which represent the real ones. According to Lilov [24], above 2546 K, silicon is separated in the form of the solution saturated with carbon. In this case, the activity of Si in the solution is equal to the equilibrium constant of reaction (7.22),  $K_1 = a_{Si}$ . The partial pressure of silicon can be obtained according to Henry's law  $P_{Si} = P_{Si}^{sat} a_{Si}$  and the partial pressure of  $SiC_2$  can be determined from the equation,  $P_{SiC_2} = \frac{K_4}{K_1 P_{Si}^{sat}}$ .

**Table 7.2.** Partial pressures of Si and  $SiC_2$  (Pa) (Lilov [24])

T [K]	$P_{Si}^{sat} a_{Si}$	$P_{Si}$ reaction (7.23)	$P_{Si}$ reaction (7.25)	$P_{SiC_2}$ reaction (7.25)
1500	$3.5 \times 10^{-5}$	<u><math>3.0 \times 10^{-6}</math></u>	$3.9 \times 10^{-7}$	$5.1 \times 10^{-8}$
1600	$4.4 \times 10^{-4}$	<u><math>4.2 \times 10^{-5}</math></u>	$7.6 \times 10^{-6}$	$1.4 \times 10^{-6}$
1700	$4.0 \times 10^{-3}$	<u><math>4.3 \times 10^{-4}</math></u>	$1.0 \times 10^{-4}$	$2.5 \times 10^{-5}$
1800	$2.5 \times 10^{-2}$	<u><math>3.4 \times 10^{-3}</math></u>	$1.0 \times 10^{-3}$	$3.2 \times 10^{-4}$
1900	0.11	<u><math>2.2 \times 10^{-2}</math></u>	$8.3 \times 10^{-3}$	$3.2 \times 10^{-3}$
2000	0.47	<u>0.11</u>	$5.3 \times 10^{-2}$	$2.5 \times 10^{-2}$
2100	1.8	<u>0.52</u>	0.28	0.16
2200	5.8	<u>2.0</u>	1.3	0.84
2300	17	<u>7.0</u>	5.2	3.8
2400	47	<u>22</u>	18	15
2500	116	<u>61</u>	58	56
2546	173	<u>97</u>	96	96
2600	270	161	<u>170</u>	170
2700	588	391	<u>456</u>	456
2800	1210	890	<u>1138</u>	1138
2900	<u>2366</u>	1914	2659	2659
3000	<u>4419</u>	3904	5855	5855
3100	<u>7922</u>	7604	12250	12250
3150	<u>10477</u>	10477	17418	17418

At temperatures above 2900 K, the partial pressure of Si determined by the equilibrium constant of reaction (7.25) becomes more than the pressure of silicon saturated vapor and therefore the dissociation of SiC takes place in the condensed phase accompanied by the separation of liquid silicon. In Table 7.2, these values are underlined in the column  $P_{Si} = P_{Si}^{Sat} a_{Si}$ , that are obtained using Henry's law.



**Fig. 7.4.** Equilibrium partial pressures for various species in a Si-C system assuming (a) condensed SiC and carbon, (b) condensed SiC and silicon. The dashed line is the total pressure [19].

At 3150 K,  $K_1 = a_{Si} = 1$  and  $P_{SiC_2} = K_4/P_{Si}^{Sat}$ , the solution of C in Si becomes mutually saturated. At  $T > 3150$  K,  $\Delta G_T^0$  of reaction (7.22) is less than zero, and therefore, SiC under these conditions dissociates completely. Hence, 3150 K is the limiting temperature for the existence of SiC in the condensed phase.

Figure 7.4(a) shows the equilibrium pressures of a Si-C system at constant pressure. The gaseous species include C,  $C_2$ ,  $C_3$ ,  $C_4$ , Si,  $Si_2$ ,  $Si_3$ , SiC,  $SiC_2$ , and  $Si_2C$ , and the condensed species are SiC and carbon. Among individual species gaseous silicon dominates at temperatures below 2673 K, while  $SiC_2$  and  $Si_2C$  have larger partial pressures at higher temperatures. Figure 7.4(b) shows the system with condensed SiC and silicon. Since liquid silicon is energetically less favorable, it only occurs when there is excess of silicon and no carbon source. The partial pressures are higher as shown in Fig. 7.4(b).

### Growth kinetics

As explained above, reaction (7.25) is considered most important for the deposition process (Lilov [24]). The vapor pressure of silicon is larger than that of  $SiC_2$  at temperatures below 2546 K, and less than that of  $SiC_2$  at temperatures above 2900 K. The rate-determining species, A, is therefore chosen as  $SiC_2$  at  $T < 2546$  K, and as Si at  $T > 2900$  K. A can be either of the two at  $2546 K < T < 2900$  K, since they have the same vapor pressure (Table 7.2). Introducing  $z'$  coordinate, which is set as 0 at the charge and L at the seed, vapor pressures of various species can be considered as a function of  $z'$ .

To develop a growth kinetics model, Chen et al. [11,13] have assumed that the species transport rate near the seed is proportional to supersaturation of A, such that [39],

$$J_A = \chi_A (p_A(L) - p_A^*(L)), \quad (7.29)$$

where  $p_A^*$  is the equilibrium vapor pressure of A,  $\chi_A = \frac{1}{\sqrt{2\pi M_A RT}}$ . If  $SiC_2$  and Si vapors can be assumed to have an identical transport rate, i.e.,  $J_{SiC_2} = J_{Si}$ , the growth rate of SiC crystal will become,

$$G_{SiC} = \frac{2M_{SiC}}{\rho_{SiC}} \chi_A [p_A(L) - p_A^*(L)] \quad (7.30)$$

A multiple 2 is introduced on the right side of Eq. (7.30) since one  $SiC_2$  molecule and one Si molecule form 2 SiC molecules.

Assuming that advective velocities of the species  $SiC_2$  and Si are the same, the distribution of vapor pressure can be obtained from a one-dimensional mass transfer equation for Stefan flow as,

$$p_{SiC_2}(z') + p_{Si}(z') = p - [p - p_{SiC_2}(0) - p_{Si}(0)] \exp(Pe \cdot z'/L) \quad (7.31)$$

The advective velocity, U, in  $Pe$  can be expressed as a function of transport rate of  $SiC_2$  and Si,

$$U = J_{SiC} RT / p = 2\chi_A (p_A(L) - p_A^*(L))RT/p \quad (7.32)$$

From the above equation, one can obtain,

$$p_A(L) = p_A^*(L) + Up/(2\chi_A RT) \quad (7.33)$$

If  $Si_2C$  and Si can be assumed to have an identical vapor pressure in the growth chamber, equation (7.31) will reduce to,

$$U = D/L \ln((p - 2p_A(L))/(p - 2p_A(0))) \quad (7.34)$$

Even if there exists a difference between the equilibrium vapor pressures of the two species at the charge, the above equation is still valid.

Furthermore, if the vapor pressure at the source is assumed to be the same as the equilibrium vapor pressure, such that  $p_A(0) = p_A^*(0)$ ,  $U$  and  $p_A(L)$  can be obtained from Eqs. (7.33) and (7.34) by solving them in an iterative fashion. First, by setting  $U$  as 0,  $p_A(L)$  can be calculated using (7.33), the advective velocity  $U$  can then be obtained by substituting (7.33) in (7.34), and finally the growth rate can be calculated using (7.30). Here the equilibrium vapor pressures of species Si,  $SiC$ ,  $Si_2C$ , and  $Si_2C_2$  can be taken from (7.24) as partly shown in Table 7.2.

## 7.2.6 Numerical method

The transport equations for electromagnetic field, heat transfer, and species transport can be solved by using a numerical scheme based on either finite element (Pons et al. [4]; Egorov et al. [6]) or finite volume method (Hofmann et al. [2]; Chen et al. [13]). Pons et al. [4] have used an FEM package “Flux-Expert”, which alternately solves the electromagnetic and thermal equations without an external iterative scheme. Once the temperature field is obtained, the mass transfer equations are solved in an uncoupled manner. The computer model developed by Hofmann et al. [2] uses the basic finite volume code FASTEST (developed at the University of Erlangen) that also employs multigrid techniques.

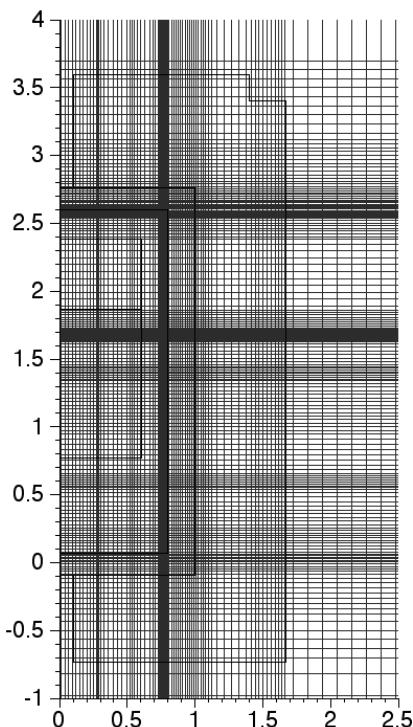
Chen and co-workers [13], on the other hand, have developed their computer model for  $SiC$  growth using MASTRAPP (Multizone Adaptive Scheme for Transport and Phase Change Processes). MASTRAPP employs high-resolution schemes for grid refinement and clustering for phase-change and moving boundary problems and has been extensively used for crystal growth modeling by Zhang et al. [40,41] and many others. MASTRAPP-based crystal growth simulations have been well tested against the experimental data, and the model is being used for a variety of industrial problems.

The integrated radiative heat transfer equations using the DEF method require special treatment. The coupling between the solvers of energy Eq. (7.13) and radiation Eq. (7.21) is obtained through nodal temperatures and heat fluxes in an iterative fashion. Refer to Chen et al. [13] and Naraghi et al. [34,35] for details on the solution scheme.

A suitable grid distribution with finer mesh in the regions of large temperature and species gradients needs to be used for accurate predictions. For example, Chen

et al. [13] have used a grid of  $198 \times 147$  for most of their calculations (Fig. 7.5). Other investigators have also used very fine grids to perform the growth simulation [2,4,6]. Furthermore, since the electrical and thermal conductivities of the graphite susceptor strongly depend on the temperature (Table 7.3), the heat power generated in the graphite susceptor changes significantly with time. It is therefore necessary to use a small time step, e.g., 2 s for the transient calculations.

A typical solution procedure is adopted as follows: The electromagnetic field (Eq. 7.10) is solved to obtain the heat generated by induction heating (Eq. 7.12), which is added as a heat source term in the energy equation (Eq. 7.13) to obtain the temperature distribution solved together with Eq. (7.21). After obtaining the temperature field, mass transfer, and vapor species concentration, growth rate can be obtained using a one-dimensional mass transfer model coupled with a growth kinetics model (Section 7.2.5). The radial variation of growth rate is considered by taking into account the temperature variation in the radial direction. The model can therefore predict two-dimensional growth interface profile except that mass transfer and thermal coupling are not allowed in the lateral direction.



**Fig. 7.5.** Computational grids for finite volume method [13]. Grids are highly clustered in the regions of large temperature gradients.

**Table 7.3.** Material properties of various components [13]

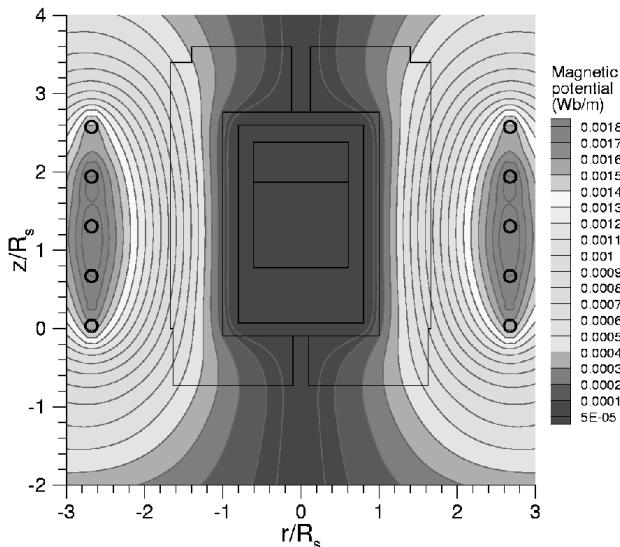
Components	Electrical resistivity [ $\Omega\text{m}$ ] [500–3000°C]	Thermal conductivity [W/m/K] [500–3000°C]
Graphite	$0.8 \times 10^{-5}$ – $1 \times 10^{-5}$	50–20
Insulation	0.001	0.1–3
SiC crystal	1–0.001	100–50
SiC charge	1–0.001	20–5
Argon	—	0.03–0.05

## 7.3 Growth Simulation

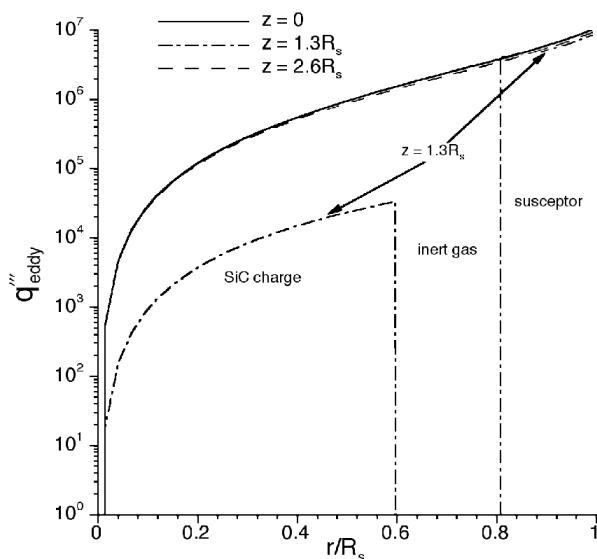
### 7.3.1 Electromagnetic field and heat generation

In calculating the electromagnetic field, it is necessary to consider reasonable axial and radial distances in the computational domain such that most of the contours of magnetic potential vector,  $A$ , remain within the field of simulation. This is important for application of the boundary condition [11] and accurate calculation of the heat generated in the graphite susceptor. For example, Chen et al. [13] have taken the computational domain as  $-20R_s < z < 20R_s$  and  $r < 20R_s$  with the radius of the outer surface of the susceptor  $R_s = 70$  mm for a 75 mm diameter crystal growth. In this case, the magnetic potential is diminished at a distance of  $20R_s$  from the coil. Many times, it is necessary to perform calculations with different sizes of the computational domains to make an appropriate choice. Typical contours of magnetic vector potential for 5 turns of coil and current of 1200 A as obtained by Chen et al. [11] are shown in Fig. 7.6. The contour lines are concentrated along the outer portion of the graphite susceptor, and the contour of  $(A_0)_{real} = 5 \times 10^{-5}$  Wb/m bends in the bottom and top portion of the susceptor and passes through the outer portion of the cylindrical susceptor. The graphite susceptor with a high conductivity serves as a shield, such that a large amount of energy is generated by eddy currents in the susceptor within a small skin depth, leaving less energy to be generated in the parts inside the susceptor (like the crucible, crystal, and charge).

The generated heat per unit volume for the case considered by Chen et al. [13] is shown in Fig. 7.7. Clearly,  $q''_{eddy}$  in the susceptor is several orders of magnitude larger than that in the SiC charge. The total amount of energy generated in the skin depth is much larger because of the volume for the same radial width becomes larger (second power) away from the central axis.



**Fig. 7.6.** magnetic potential contours,  $(A_0)_{real}$ , in a system with a coil of five turns, current of 1200 A and frequency of 10 kHz [13]. Only a portion of the computational domain,  $r \leq 3R_s$  and  $z \leq 4R_s$ , is shown in this figure.

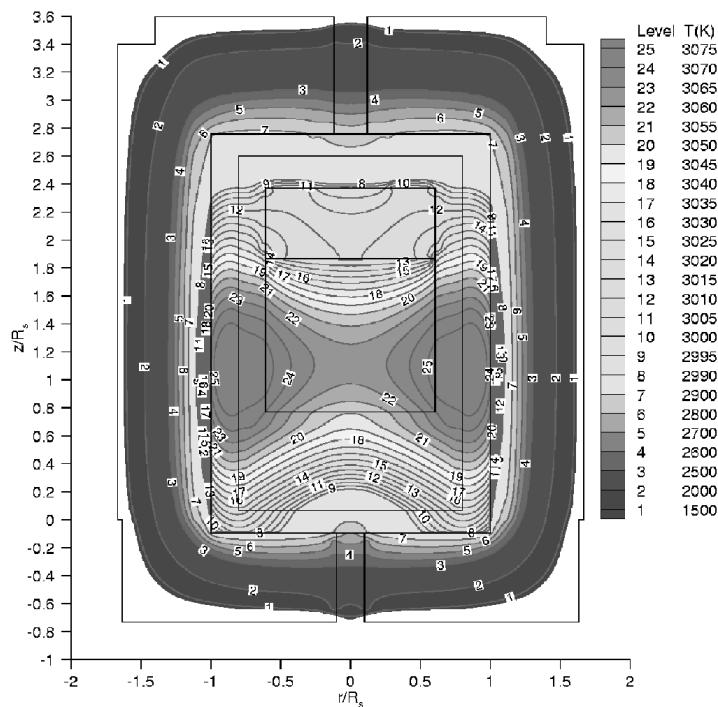


**Fig. 7.7.** Generated heat power,  $q'''_{eddy}$ , along the radial direction at different heights  $z = 0$ ,  $1.3R_s$ , and  $2.6R_s$ . The profile at  $z = 1.3R_s$  has an inert gas gap between the powder charge and the susceptor [13].

### 7.3.2 Temperature field

Axial and radial temperature gradients are crucial for the successful growth and enlargement of SiC crystals. The SiC charge sublimes in the bottom of the container where the temperatures are higher than that in the seed, and saturation of the SiC vapor is thus produced in the SiC charge region. Since temperature on the seed surface is lower than that in the powder charge, the SiC vapor becomes supersaturated near the seed. The supersaturation of vapor species acts as a driving force for the deposition of SiC. The growth rate is therefore not only related to the temperature at the seed but also to the axial temperature gradient. Balkas et al. [42] have found that for a given seed temperature, the growth rate is a linear function of the temperature gradient in the growth chamber.

A positive radial temperature gradient at the seed surface can initiate an outward growth especially when a Lely seed is used to grow large size crystals, and depress the polytype growth on the graphite lid near the seed. The lower temperature at the center of the seed can ensure a higher growth rate on the seed than that on the graphite lid, because the supersaturation of the vapor species is higher on the seed.

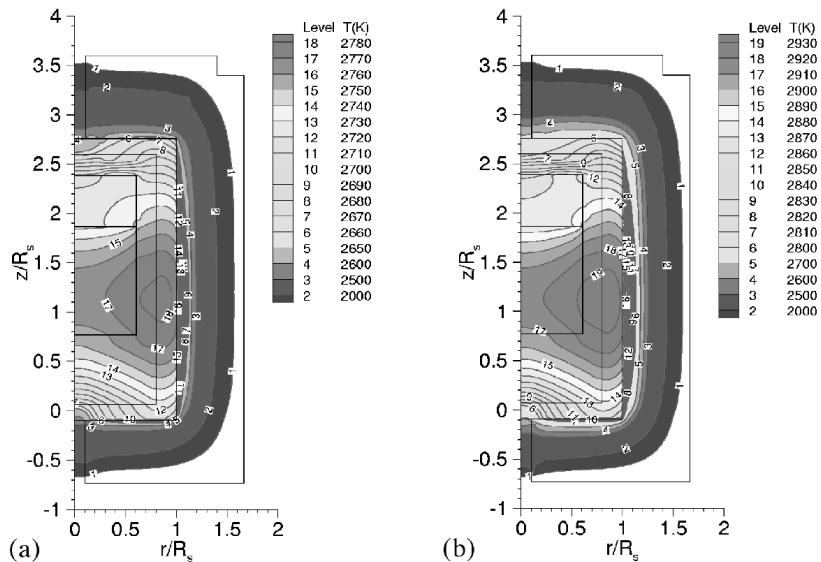


**Fig. 7.8.** Temperature contours for a system with a coil of five turns, current of 1200A, frequency of 10 kHz, and inert gas pressure of 26,666 Pa [11]

As shown by Chen and other investigators (Fig. 7.8), the maximum temperature exists in the graphite susceptor and always at the level of the geometric center of the induction coil. The positive temperature difference between the SiC charge and the seed allows the sublimation of SiC in the charge and deposition of SiC on the seed. A positive radial temperature gradient is also formed at the seed surface, which ensures an outward growth of the crystal [43]. As can be seen in Fig. 7.8, the temperature difference is less than 10 K at the seed surface. A proper radial temperature gradient at the seed has to be obtained to ensure a convex shape of the crystal interface and keep thermal stresses low in the crystal as well as low dislocation and micropipe densities.

### **Temperature distribution for different currents**

The temperature distribution strongly depends on the power supply to the RF coil (see Fig. 7.9 for  $I = 1000$  A and 1100 A and Fig. 7.8 for  $I = 1200$  A). The magnitude of the temperature increases with the current. The growth temperature for the modified Lely method ranges from 1800 K to 2900 K as reported by Tairov and Tsvetkov [44,45]. The temperature distribution for the case of  $I = 1200$  A corresponds to an upper limit growth condition for the modified Lely method in the system considered by Chen et al. [11]. The growth temperature depends on the temperature gradient that is related to the system design. For systems with a large temperature gradient, the growth temperatures are low (2100–2800 K) (Tairov and Tsvetkov [44,45]; Barrett et al. [22,23]; Hofmann et al. [2,3]; Müller et al. [7]),



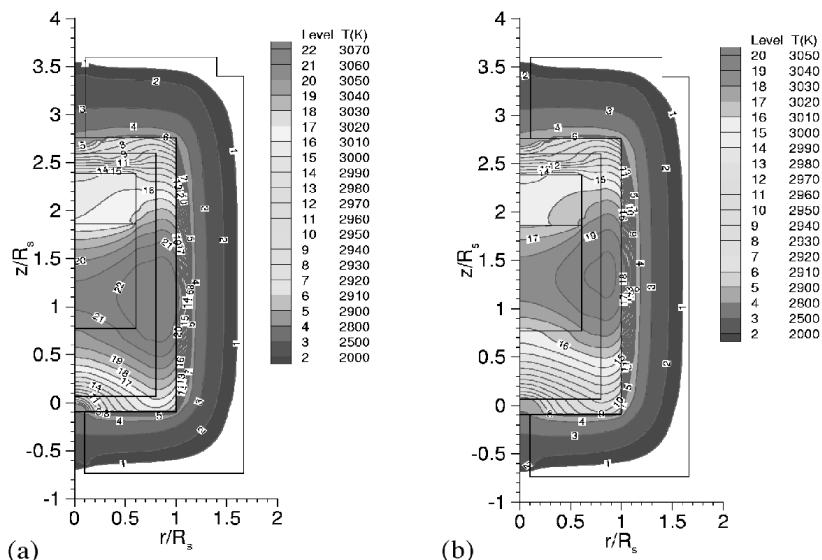
**Fig. 7.9.** Temperature distributions for different currents, (a)  $I = 1000$  A, and (b)  $I = 1100$  A [13]

while the growth temperatures range from 2700 K to 2900 K for systems that have smaller temperature gradients (Pons et al. [4,5]). For a low growth temperature, the inert gas pressure required is lower than that required for the high temperature growth.

As can be seen in Figs. 7.8 and 7.9, the temperature has a lower value at the center of the seed because of the cooling effect of the upper hole. The temperature increases along the radial direction on the seed surface, reaches a high value before the inner wall of the growth chamber. The lower temperature at the center of the seed can ensure an outward growth in radial direction, because of higher supersaturation of the vapor species at the center of the seed than that near the edge of the seed. Management of heat loss is crucial to control the growth of SiC crystals. However, it is not an easy task since thermal characteristics of the upper portion of the crucible change significantly as the growth proceeds and thermal resistance due to as-grown crystal increases. This task is made further difficult because currently the heat loss system used for PVT growth is passive.

### **Temperature for different coil positions**

As is well known, by moving the induction coil upward/downward, the temperature difference between the charge and the seed can be easily changed. Figure 7.10 presents the temperature distributions for two different positions ( $z_{coil} = 0, 10 \text{ mm}$ ), while the temperature on the top of the crucible is kept at 2400 K. A PID (propor-

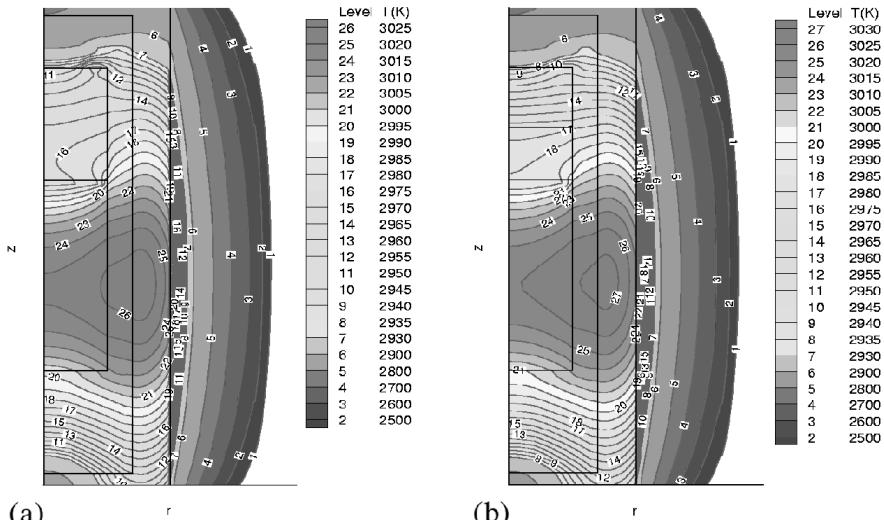


**Fig. 7.10.** Temperature distributions for different coil positions. The coil positions are (a)  $z_{coil} = 0$  and (b)  $0.01 \text{ m}$ , respectively. The temperature on top of the crucible is kept at 2400 K for all the cases [13].

tional, integral, and derivative) control strategy has been used numerically to keep the temperature on top of the crucible constant by changing the current. With the coil moved up, the location of the maximum temperature in the charge moves up and the temperature difference between the charge and the seed decreases. In Figs. 7.10(a–b), the temperature difference between the charge and the seed,  $T_{charge} - T_{seed}$ , is a linear function of the coil position,  $z_{coil}$ . It should be noted that the temperature difference may not remain a linear function of the coil position if the coil is moved further up. Since the growth rate depends on the temperature difference between the charge and the seed (Eq. 7.35), the change in coil position will certainly affect the growth rate.

### Temperature distribution for different ingot length

The temperature distribution also changes with the growth of crystal (Fig. 7.11). A large radial temperature gradient during the initial growth is important for enlargement of the crystal. After the ingot length of the crystal reaches 5 mm for the system considered here, the radial temperature gradient decreases (Figs. 7.11a–b). A small radial temperature gradient ensures a constant diameter of the crystal and relatively flat growth interface. More importantly, the thermal stress in as-grown crystal caused by temperature gradient decreases after the ingot length exceeds 5 mm. The axial temperature gradient in the ingot crystal is about 15 K/cm after the ingot of 25 mm has been grown (Figs. 7.11a–b).



**Fig. 7.11.** Temperature distributions in a 35mm system when  $I = 1350$  A, and ingot length (a)  $L_m = 0$  and (b)  $L_m = 25$  mm

Simulations reported by various investigators demonstrate that the temperature and temperature gradient inside the crucible are strong functions of system design, coil position, power supply, charge size, and ingot length. In addition, the temperature field continuously changes with an increase in the crystal length. The simulations reported in literature thus far give a good qualitative understanding of the effect of these parameters. However, simulations need to be performed every time a change in the design of the system is contemplated.

### 7.3.3 Growth rate calculations

The experimental data of Balkas et al. [42] indicate that the growth rate is a linear function of the temperature difference between the seed and source,  $\Delta T$ , and an exponential function of the inverse of growth temperature with the following expression,

$$G_{SiC} = A(p, S, t) \Delta T \exp(-U/RT), \quad (7.35)$$

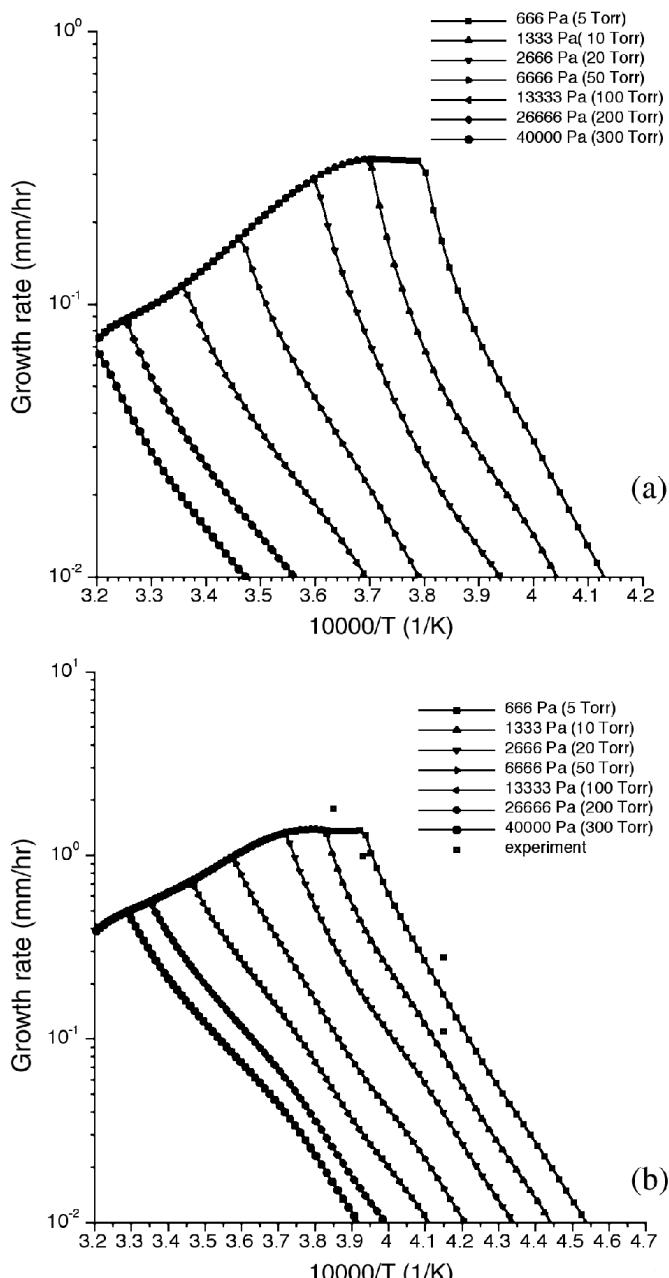
where  $U$  is the activation energy,  $A(p, S, t)$  is a coefficient that depends on the inert gas pressure  $p$ , the effective source surface area  $S$ , and the duration of the growth,  $t$ . Balkas et al. [42] found that  $U = 5.99 \times 10^5$  J/mol based on their experiment data.

#### ***Dependence of growth rate on growth temperature***

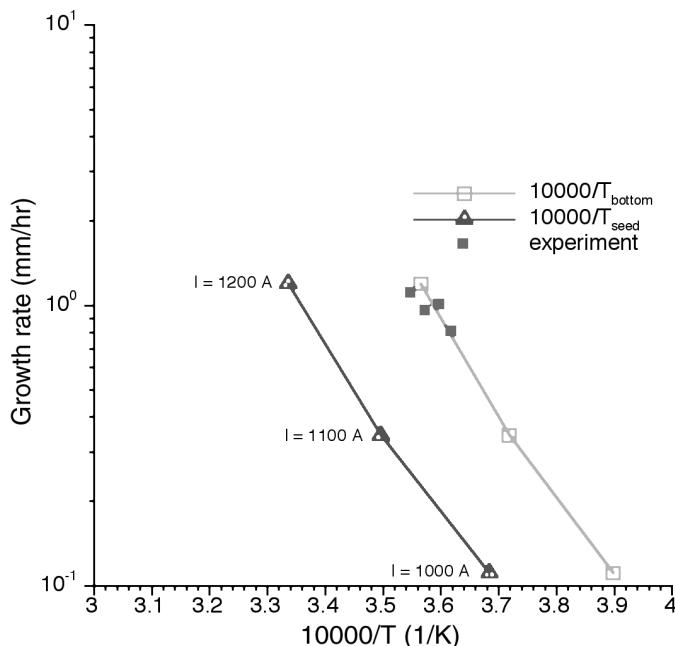
Chen et al. [11] have investigated the dependence of growth rate on growth temperature for a range of axial temperature gradients. They have considered two cases, one with a small axial temperature gradient of 2 K/cm, and the other with a large axial temperature gradient of 20 K/cm. The distance between the seed and the charge surface is taken as 5 cm (2 inch).

The growth rate predicted by Chen et al. [11] shows an Arrhenius-type dependence on the growth temperature for inert gas pressures ranging from 666 Pa (5 Torr) to 40,000 Pa (300 Torr) (Fig. 7.12). The growth rate curves, however, deviate from the Arrhenius behavior when the temperature becomes too high. The Arrhenius-type growth curve for a given pressure shifts towards the low temperature region when the axial temperature gradient increases (compare Fig. 7.12b with 7.12a). The low temperature growth, that is usually associated with small-scale systems, therefore, requires a larger axial temperature gradient (Fig. 7.12b). The experimental data for 700 Pa argon pressure in Fig. 7.12b taken from Nakata et al. [46] support the prediction of Chen et al. [11] at low pressures.

In the growth rate–growth temperature map, the curves merge at high temperatures where the total vapor pressure of species is larger than the inert gas pressure (Fig. 7.12). In this case, if the crucible is not properly sealed, the pressure inside the crucible will fluctuate since the pressure inside the crucible will be higher than the system pressure. The fluctuation of pressure inside the crucible can cause unsteady species transport in the growth chamber by Stefan flow and growth fluctuations.



**Fig. 7.12.** Predicted growth rate versus inverse of growth temperature for different gas pressures for axial temperature gradients of (a) 2 K/cm and (b) 20 K/cm [11]. Experimental data for inert gas pressure of 700 Pa in (b) are taken from Nakata et al. [46]

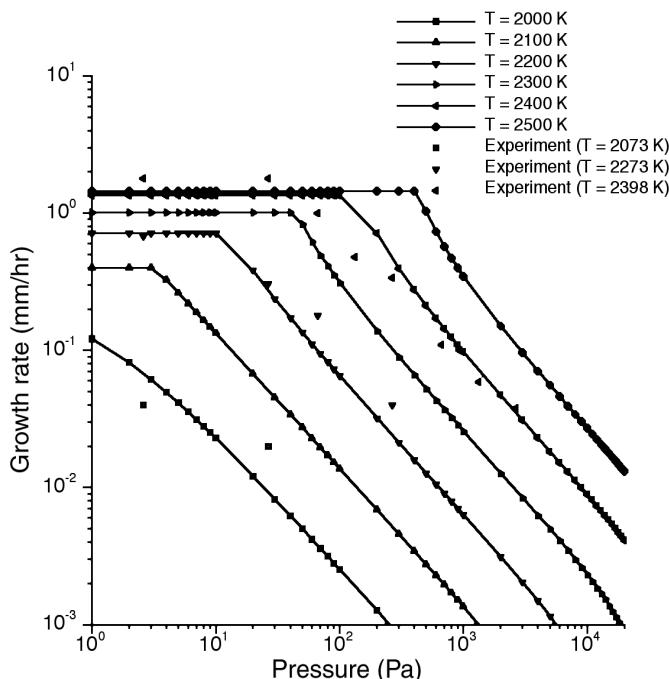


**Fig. 7.13.** Dependence of the growth rate on the seed temperature,  $T_{\text{seed}}$ , and the temperature on the bottom of the crucible,  $T_{\text{bottom}}$  in a 75 mm system [15]. The symbols from top to bottom correspond to currents of 1200 A, 1100 A, and 1000 A, respectively. Experimental data are taken from Balkas et al. [42]

The growth rate versus growth temperature curve in Fig. 7.13 is an Arrhenius-type curve and yields an activation energy of  $5.5 \times 10^5 \text{ J/mol}$ , close to  $5.44 \times 10^5 \text{ J/mol}$  as reported by Syväjärvi et al. [47]. The growth rate versus the inverse of the temperature at the bottom is also plotted in Fig. 7.13 and yields the same activation energy as the previous curve. The predicted growth rate at high pressures strongly depends on the diffusion coefficient  $D_0$ , which is in the range of  $5 \times 10^{-6} \sim 2 \times 10^{-4}$ , taken as  $1 \times 10^{-5} \text{ m}^2/\text{s}$  by Chen et al. [13] to better correlate the prediction with experimental data of Balkas et al. [42].

### Influence of inert gas pressure on growth rate

Chen et al. [11] have also examined the dependence of growth rate on inert gas pressure for the previous two cases. The growth rate curves become flat when the inert gas pressure is low. Although the growth rate of about 1 mm/h cannot be achieved for an axial temperature gradient of 2 K/cm (Fig. 7.12a), it is possible to obtain such a growth if the axial temperature gradient of 20 K/cm can be maintained at  $T_{\text{seed}} > 2400 \text{ K}$  (Fig. 7.12b). From Fig. 7.14, it is evident that it is theoretically



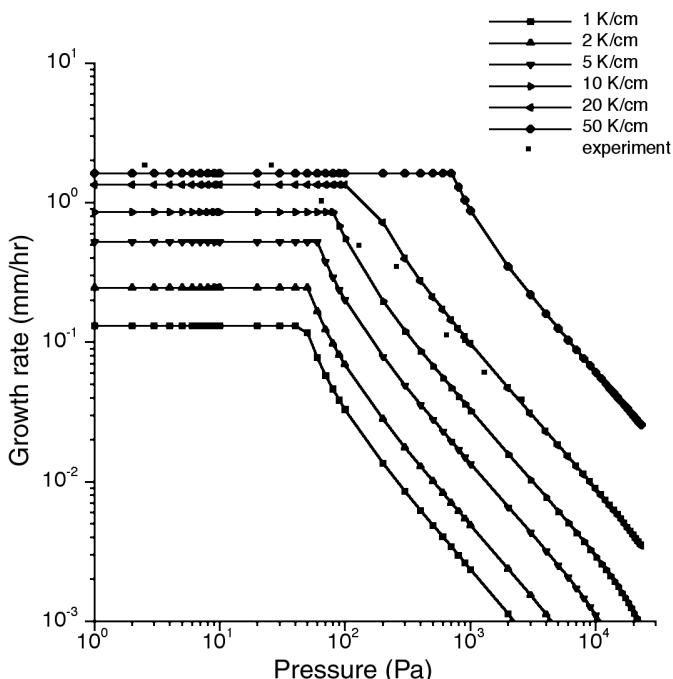
**Fig. 7.14.** Growth rate versus gas pressure for different growth temperatures at axial temperature gradient of 20 K/cm [11]

possible to grow SiC crystals at elevated inert gas pressures, such as 26,666 Pa (200 Torr), if the growth temperature is high. On the other hand, the growth at pressures less than 133 Pa (1 Torr) and temperatures below 2500 K is also possible, as shown in Fig. 7.14.

Figure 7.14 also shows that when the inert gas pressure is low, the growth rate does not increase as the pressure is decreased. This is because the total vapor pressure of SiC species is larger than the inert gas pressure. The growth is therefore unstable in this case, and a leak in the crucible will cause fluctuations in the pressure inside the crucible and unsteady growth conditions.

### **Dependence of growth rate on temperature gradient**

As is well known, the temperature gradient in the substrate region is an important parameter for CVD growth, but in the PVT growth of SiC crystals, the effect of this parameter has not been examined carefully. Chen et al. [11] have made the first attempt to study the importance of temperature gradient as presented in Fig. 7.15 where the growth rate versus inert gas pressure is presented for several different temperature gradients, for the growth temperature of 2400 K. With an increase

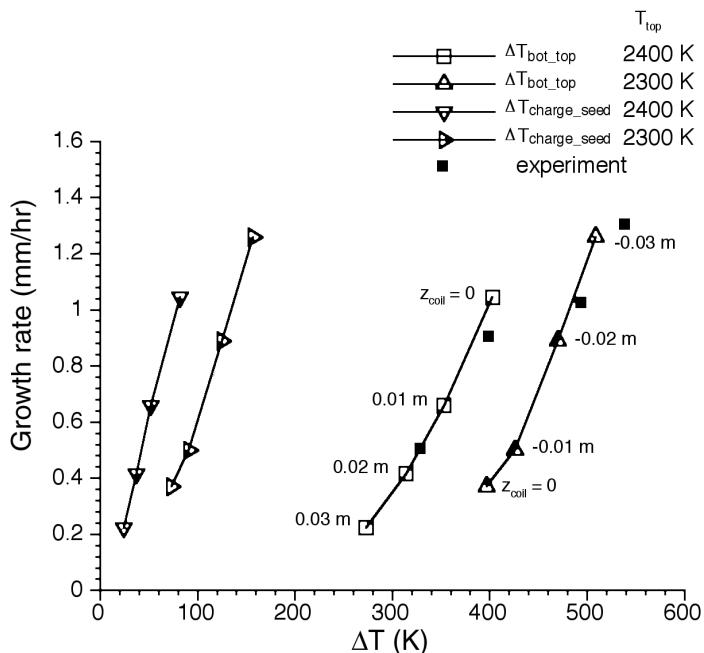


**Fig. 7.15.** Growth rate versus gas pressure for different axial temperature gradients at growth temperatures of 2400 K [11]. Experimental data are taken from [17]

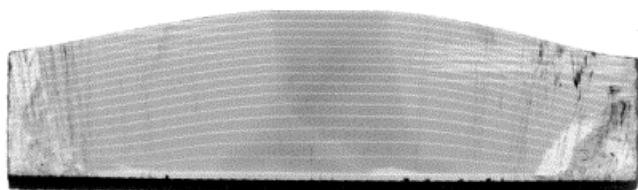
in temperature gradient, the growth rate curve moves upward towards the high growth rate region. Again, in the growth rate–inert gas pressure map, the region where the growth rate curves become flat will have unstable growth, since the total vapor pressure of SiC species will be higher than the inert gas pressure.

### ***Effect of coil position on temperature distribution and growth rate profile***

Since  $T_{charge} - T_{seed}$  is related to the coil position, the growth rate can be changed by moving the coil upward or downward. There are different control strategies, such as keeping the temperature on the top of the crucible,  $T_{top}$ , constant (Chen et al. [13]), or by keeping the power supply constant (Selder et al. [16]). The growth rate versus temperature difference between the charge and the seed is shown in Fig. 7.16 for different coil positions when  $T_{top}$  is kept constant, at 2400 K or 2300 K. In a certain range of coil position, the growth rate is a linear function of coil position,  $z_{coil}$ . For example, for  $T_{top} = 2400$  K, the growth rate is almost a linear function of  $z_{coil}$  when  $0 < z_{coil} < 0.03$  m; and for  $T_{top} = 2300$  K, the growth rate is a linear function for  $-0.03 \text{ m} < z_{coil} < 0$ . The growth rate can be less than zero representing etching of the seed (not shown here), if the coil is moved further up.

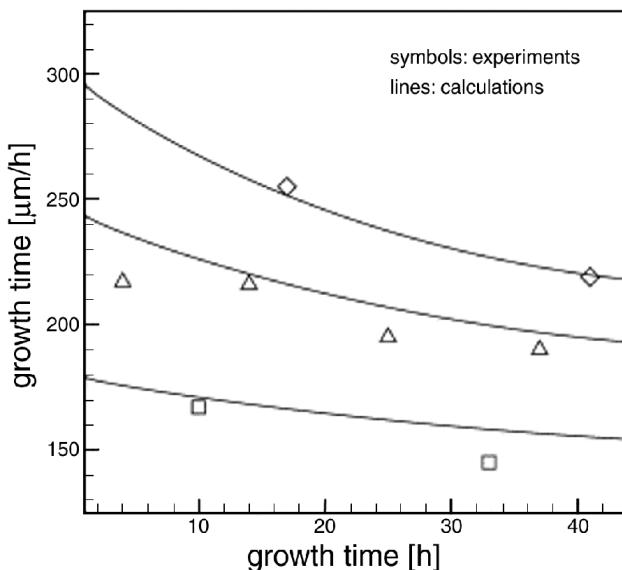


**Fig. 7.16.** Dependence of growth rate,  $G_{SiC}$ , on temperature difference between the charge and seed,  $T_{charge} - T_{seed}$ , and on temperature difference between the bottom and top of the crucible,  $T_{bottom} - T_{top}$ . The coil positions,  $z_{coil}$ , are denoted besides the symbols on the curve of  $G_{SiC} \sim T_{bottom} - T_{top}$ . The temperature on the top of the crucible,  $T_{top}$ , is maintained at either 2400 K or 2300 K [13]. Experimental data are taken from Balkas et al. [42]



**Fig. 7.17.** Slice of a SiC crystal marked during growth by interface demarcation technique. The seed is positioned at the bottom. Dark horizontal regions are nitrogen-rich SiC material, undoped regions exhibit a bright contrast (Selder et al. [16])

The effect of coil position has also been studied by Selder et al. [16] who used an interface demarcation technique to achieve the experimental surface shape. During the growth experiment, nitrogen was added to the inert gas in the growth cell at fixed time steps. After the growth experiment, a slice was cut from the grown crystal along its growth direction as shown in Fig. 7.17.



**Fig. 7.18.** Measured and predicted growth rates for different coil positions. Starting from a symmetrical coil position (upper curve), the coil is successively shifted downwards (Selder et al. [16])

Growth rate evolution in the center of the crystal was measured and computed for different coil positions while keeping the induction power constant. Figure 7.18 shows that the growth rate decreases with increasing crystal length. As can be seen, the growth rate also decreases by shifting the coil downward while the power supply is held constant. This is because the growth temperature,  $T_{seed}$ , decreases although  $T_{charge} - T_{seed}$  may increase.

### 7.3.4 Thermally induced stress

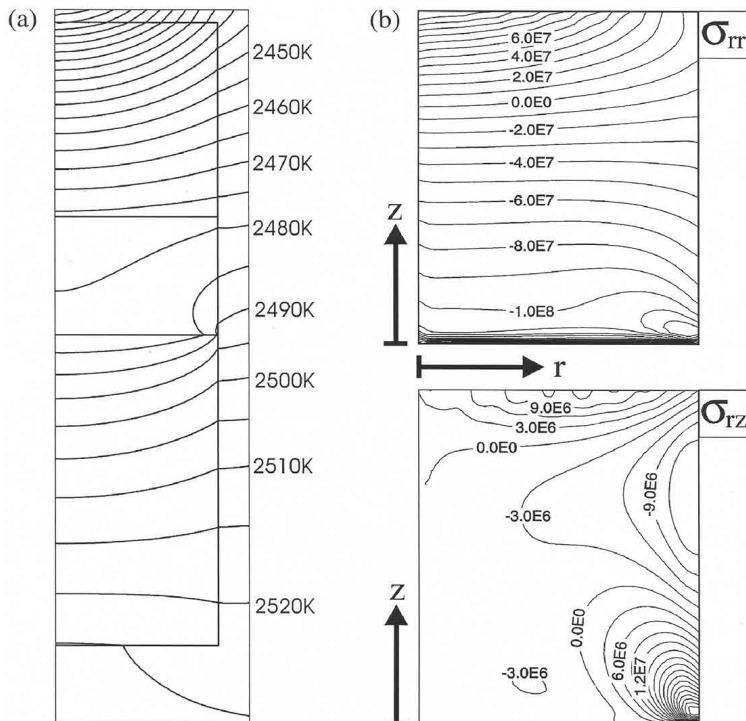
Thermal stresses in SiC crystal with nonuniform temperature gradient can cause plastic deformation and generation of dislocations during the growth. Müller et al. [8] have used a thermoelastic model to calculate the thermal stress based on the temperature field from their 2D model. The stress-strain relation for a thermoelastic anisotropic solid body is taken as [48,49]:

$$\begin{pmatrix} \sigma_{rr} \\ \sigma_{\varphi\varphi} \\ \sigma_{zz} \\ \sigma_{rz} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & 0 \\ c_{12} & c_{22} & c_{23} & 0 \\ c_{13} & c_{23} & c_{33} & 0 \\ 0 & 0 & 0 & c_{44} \end{pmatrix} \begin{pmatrix} \varepsilon_{rr} - \alpha(T - T_{ref}) \\ \varepsilon_{\varphi\varphi} - \alpha(T - T_{ref}) \\ \varepsilon_{zz} - \alpha(T - T_{ref}) \\ \varepsilon_{rz} \end{pmatrix} \quad (7.36)$$

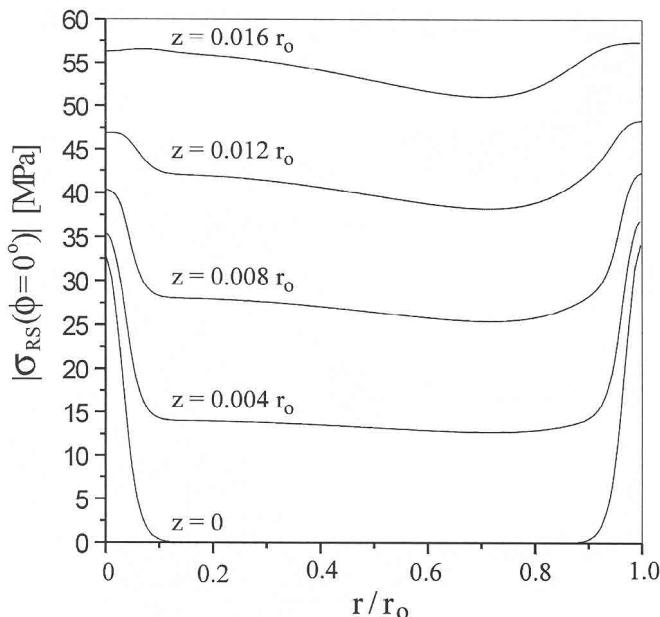
In the above equation,  $\alpha$  is the thermal expansion coefficient,  $T_{ref} = 0.5(T_{\min} + T_{\max})$  is a reference temperature, and

$$\varepsilon_{zz} = \frac{\partial u}{\partial z}, \quad \varepsilon_{rr} = \frac{\partial u}{\partial r}, \quad \varepsilon_{\varphi\varphi} = \frac{v}{r}, \quad \varepsilon_{rz} = \frac{\partial v}{\partial z} + \frac{\partial u}{\partial r}, \quad (7.37)$$

$c_{ij}$  are the elastic material constants in the Voigt notation and  $u, v$  are the displacement components in axial and radial direction, respectively. Figure 7.19 shows the calculated 2D temperature distribution and the corresponding 2D distribution of the normal component  $\varepsilon_{rr}$ , and shear stress  $\varepsilon_{rz}$  in the crystal area, with positive values corresponding to tension and negative values to compression [8]. The calculated level of thermoelastic stress up to  $\sim 100$  MPa in the SiC crystal during growth is well above the critical resolved shear stress  $\sigma_{CRS}$ ,  $\sim 8$  MPa (4H-SiC) and  $\sim 13$  MPa (6H-SiC) at  $1300^{\circ}\text{C}$  (Samant and Pirouz [50]). The resolved shear stress at  $2200$ – $2500^{\circ}\text{C}$  is  $< 1$  MPa by extrapolating the experimental values according to Müller et al. [8]. The generated dislocations are estimated to be  $N \propto (|\sigma_{RS}| - \sigma_{CRS})$ .



**Fig. 7.19.** (a) Numerical simulation of the axisymmetric temperature distribution inside a growth cell, and (b) resulting thermoelastic stress inside a 6H-SiC crystal: normal stress,  $\sigma_{rr}$ , and shear stress,  $\sigma_{rz}$  (Müller et al. [8])



**Fig. 7.20.** Radial dependence of the resolved shear stress in the  $<11\bar{2}0>$  direction at different distances from the growth interface ( $z = 0$ ) (Müller et al. [8])

For the three primary (0001)  $<11\bar{2}0>$  slip systems  $\sigma_{RS}$  is given by  $\sigma_{RS} = (\sigma_{rr} + \sigma_{rz}) \cos\phi - \sigma_{\phi\phi} \sin\phi$ . Figure 7.20 shows the radial dependence of  $|\sigma_{RS}|$  for  $\phi = 0^\circ$ , corresponding to the  $<11\bar{2}0>$  direction, for different  $z$ -positions within a thin boundary layer ( $\sim 500 \mu\text{m}$ ) at the growth interface.

Modeling of stresses during the growth of SiC crystals is quite challenging and not much has been reported on this problem except the work of Müller et al. [8]. It is expected that this topic will receive significant attention in the near future because of the direct relationship between the stresses and defects.

## 7.4 Summary

The vapor transport growth of silicon carbide crystals involves induction heating, electromagnetic field, radiative and conductive heat transfer, sublimation and condensation, chemical reaction, stoichiometry, mass transport, thermal stresses, as well as defect and micropipe generation and propagation. The irregular geometry, complicated boundary conditions, and lack of information on thermophysical properties at high temperatures make this process very difficult to understand, model, and control. Since defects and micropipes in SiC crystals are directly related to transport phenomena, it is critical to develop better understanding of these

phenomena to grow crystals of higher quality and larger size and to examine the effects of various parameters individually and collectively.

Models of sufficient complexity have been developed to simulate the sublimation SiC growth [2–19]. These models account for the RF heating, heat generation in graphite susceptor by eddy currents, heat transfer by conduction and radiation, species transport, growth kinetics, and stress analysis. The predictions made by these models are generally in good agreement with experimental data. The growth kinetics and mass transport from the charge to seed determine the growth rate and the shape of the crystal. The growth rate is a strong function of the interface temperature, temperature gradient, inert gas pressure, and the gap between the charge and seed, as well as the charge properties (particle size, height).

Modeling and simulation has been widely used in industry to optimize the system geometry and growth processes. The components of the growth system can be redesigned in order to grow crystals with low thermal stresses. Industry has used the model to design the furnace for growing 50–100 mm diameter SiC crystals. It is observed that a convex shape of interface can ensure an outward growth to expand a small size seed into a large diameter crystal. However, it can generate large thermal stresses and cause higher defect density. The mechanism of defects and screw dislocations is still not well understood and requires a strong coupling among modeling, growth, and characterization. Only then can a direct correlation among the process conditions, transport phenomena, chemistry, growth behavior, stresses, and defects be developed.

## Acknowledgments

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# 8 Thermodynamics of Multicomponent Perovskite Synthesis in Hydrothermal Solution

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## 8.1 Introduction

In this chapter, we will focus on the hydrothermal synthesis of smart ceramic materials with a perovskite-type structure. Perovskite compounds have the general formula  $\text{ABO}_3$ , where the A cation is relatively large and of low valence (such as  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{K}^+$ , and the B cation is relatively small (such as  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{4+}$ ,  $\text{W}^{6+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ).

Hydrothermal synthesis involves numerous simultaneous reactions between dissolved and solid species in an aqueous system to form anhydrous multicomponent oxides. Hydrothermal media may provide an effective reaction environment for the synthesis of numerous smart ceramic materials from a variety of precursor reagents (e.g., water-soluble salts, hydroxides, oxides) in the form of polycrystalline solids [1–15], thin films [16–22], and single crystals [23–25].

In particular, phase-pure ceramic materials with controlled stoichiometry and morphology can be hydrothermally synthesized in a single experimental step from simple and inexpensive precursors at moderate temperatures and pressures [26] far below those required for conventional techniques. To take advantage of the opportunities offered by hydrothermal synthesis, it is important to select a precursor system that is both reactive and cost-effective. However, the reactivity of a precursor system can only be judged by optimizing the processing variables such as reagent (precursor) concentrations and ratios, pH, temperature, and pressure, which can be extremely time consuming due to the large number of variables involved. To improve the efficiency of evaluating a precursor system, a comprehensive thermodynamic model that simulates hydrothermal reactions has been developed [27–29]. This model is a part of the OLI software [30]. Our simulation approach has been validated for numerous perovskite-type multi-component oxide systems, which include alkaline-earth titanates and zirconates [11,13,15], lead titanate [12], various solid solutions of lead zirconate titanate [14], lead magnesium niobate [31], and lead zinc niobate [31]. In this chapter, modeling and experimental validation of selected hydrothermal systems will be presented.

## 8.2 Thermodynamic Model

Prior to utilizing the thermodynamic model, we select candidate-starting materials (i.e., an appropriate precursor system) for hydrothermal synthesis. The thermodynamic model is used subsequently to predict the concentrations and activities of both ionic and neutral species in multicomponent systems that may contain an aqueous phase, any number of solid phases, and, if necessary, a vapor and a nonaqueous liquid phase. The starting point for the equilibrium calculations in the hydrothermal system is the computation of speciation in the investigated system. For this purpose, a realistic model of electrolyte systems is used. This model combines information about standard-state properties of all species of interest with a formulation for the excess Gibbs energy, which accounts for the solution nonideality. The model has been described in detail by Zemaitis et al. [28] and Rafal et al. [27].

In a multicomponent system, the partial molal Gibbs energy of the *i*-th species is related to the molality ( $m_i$ ) by

$$\overline{G}_i = \overline{G}_i^0 + RT \ln m_i \gamma_i \quad (8.1)$$

where  $\overline{G}_i^0$  is the standard-state partial Gibbs energy and  $\gamma_i$  is the activity coefficient. Thus, the thermodynamic properties of the system can be calculated if the standard-state Gibbs energies are available for all species as functions of temperature and pressure [i.e.,  $\overline{G}_i^0(T, P)$ ] and the activity coefficients are known as functions of the composition vector  $m$  and temperature [i.e.,  $\gamma_i(m, T)$ ]. From basic thermodynamics, the standard-state Gibbs energy of formation  $\overline{G}_i^0(T, P)$  can be calculated as a function of temperature and pressure if the following data are available:

1. Gibbs energy of formation at a reference temperature  $T_r$  and pressure  $P_r$  (usually 298.15 K and 1 bar, respectively)
2. Enthalpy of formation at  $T_r$  and  $P_r$
3. Entropy at  $T_r$  and  $P_r$
4. Heat capacity as a function of temperature and pressure
5. Volume as a function of temperature and pressure

The key to representing the standard-state properties over substantial temperature and pressure ranges is the accurate knowledge of the heat capacity and volume. For this purpose, the Helgeson-Kirkham-Flowers-Tanger (HKFT) equation of state [32–33] is used. This equation accurately represents the standard-state thermodynamic functions for aqueous, ionic, and neutral species as functions of both temperature and pressure. In its revised form [33], the HKFT equation is capable of reproducing the standard-state properties up to 1000°C and 5 kbar.

The HKFT equation is based on the solvation theory and expresses the standard-state thermodynamic functions as sums of structural and solvation contributions, the latter being dependent on the properties of the solvent (i.e., water). The standard partial molal volume ( $\overline{V}^0$ ) and heat capacity ( $\overline{C}_p^0$ ) are given by

$$\bar{V}_0 = a_1 + \frac{a_2}{\Psi + P} + \left( a_3 + \frac{a_4}{\Psi + P} \right) \left( \frac{1}{T - \Theta} \right) - \omega Q + \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{\partial \omega}{\partial P} \right)_T \quad (8.2)$$

$$\bar{C}_P^0 = c_1 + \frac{c_2}{(T - \Theta)^2} - \left( \frac{2T}{(T - \Theta)^3} \right) \left( a_3(P - P_r) + a_4 \ln \frac{\Psi + P}{\Psi + P_r} \right) + \omega TX + 2TY \left( \frac{\partial \omega}{\partial T} \right)_P - T \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{\partial^2 \omega}{\partial T^2} \right)_P \quad (8.3)$$

where  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $c_1$ , and  $c_2$  represent species-dependent nonsolvation parameters,  $T_r$  is the reference temperature of 298.15 K,  $P_r$  is the reference pressure of 1 bar,  $\Psi$  and  $\Theta$  refer to solvent parameters equal to 2600 bars and 228 K, respectively.  $Q$ ,  $X$ , and  $Y$  denote the Born functions given by

$$Q = \frac{1}{\varepsilon} \left( \frac{\partial \ln \varepsilon}{\partial P} \right)_T \quad (8.4)$$

$$X = \frac{1}{\varepsilon} \left[ \left( \frac{\partial^2 \ln \varepsilon}{\partial T^2} \right)_P - \left( \frac{\partial \ln \varepsilon}{\partial T} \right)_P^2 \right] \quad (8.5)$$

$$Y = \frac{1}{\varepsilon} \left( \frac{\partial \ln \varepsilon}{\partial T} \right)_P \quad (8.6)$$

where  $\varepsilon$  is the dielectric constant of water and  $\omega$  stands for the Born coefficient, which is defined for the  $j$ -th aqueous species by

$$\omega_j \equiv \omega_j^{abs} - Z_j \omega_{H^+}^{abs} \quad (8.7)$$

In Eq. (8.7),  $Z_j$  is the charge on the  $j$ -th aqueous species,  $\omega_{H^+}^{abs}$  refers to the absolute Born coefficient of the hydrogen ion and  $\omega_j^{abs}$  designates the absolute Born coefficient of the  $j$ -th species given by

$$\omega_j^{abs} = \frac{N^0 e^2 Z_j^2}{2r_{e,j}} \quad (8.8)$$

where  $N^0$  is the Avogadro number,  $e$  is the electron charge and  $r_{e,j}$  denotes the effective electrostatic radius of the  $j$ -th species, which is related to the crystallographic radius  $r_{x,j}$  by

$$r_{e,j} = r_{x,j} + |z_j|(k_z + g) \quad (8.9)$$

where  $k_z$  represents a charge-dependent constant equal to 0.0 for anions and 0.94 for cations, and  $g$  denotes a generalized function of temperature and density. Thus, the HKFT equation expresses the heat capacity and volume as functions of pure water properties and seven empirical parameters, which have been tabulated for large numbers of ions, complexes, and both inorganic and organic neutral molecules. The remaining thermodynamic properties are obtained by thermodynamic integration using the values of the Gibbs energy, enthalpy and entropy at reference temperature and pressure as integration constants.

The activity coefficient model used for representing the solution nonideality is an extended form of an expression developed by Bromley [34]. The Bromley

equation is a combination of the Debye-Hückel term for long-range electrostatic interactions and a semi-empirical expression for short-range interactions between cations and anions. In a multicomponent system, the activity coefficient of an ion  $i$  is given by

$$\log \gamma_i = \frac{-Az_i^2 I^{1/2}}{1+I^{1/2}} + \sum_j^N \left[ \frac{|z_i| + |z_j|}{2} \right]^2 \left[ \frac{(0.06 + 0.6B_{ij})|z_i z_j|}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} + B_{ij} + C_{ij}I + D_{ij}I^2 \right] m_j \quad (8.10)$$

where  $A$  is the Debye-Hückel coefficient that depends on temperature and solvent properties,  $z_i$  is the number of charges on ion  $i$ ,  $I$  is the ionic strength (i.e.,  $I = 0.5 \sum z_i^2 m_i$ ),  $N$  is the number of ions with charges opposite to that of ion  $i$ , and  $B_{ij}$ ,  $C_{ij}$  and  $D_{ij}$  are empirical, temperature-dependent cation-anion interaction parameters. Bromley's [34] original formulation contains only one interaction parameter,  $B_{ij}$ , which is sufficient for systems with moderate ionic strength. For concentrated systems, the two additional coefficients  $C_{ij}$  and  $D_{ij}$  usually become necessary. The three-parameter form of the Bromley model is capable of reproducing activity coefficients in solutions with ionic strength up to 30 mol/kgH<sub>2</sub>O. The temperature dependence of the  $B_{ij}$ ,  $C_{ij}$  and  $D_{ij}$  parameters is usually expressed using a simple quadratic function.

The Bromley model is restricted to interactions between cations and anions. For ion-molecule and molecule-molecule interactions, the well-known model of Pitzer [35] is used. To calculate the fugacities of components in the gas phase, the Redlich-Kwong-Soave [36] equation of state is used.

In the absence of sufficient experimental data, reasonable predictions can be made using a method due to Meissner [37], which makes it possible to extrapolate the activity coefficients to higher ionic strengths based on only a single, experimental or predicted, data point.

### 8.2.1 Computational method

The thermodynamic model is formulated for  $k$  independent reactions, each of which can be written as

$$\sum_{i=1}^{n_j} v_i^{(j)} A_i^{(j)} = 0 \quad (j = 1, \dots, k) \quad (8.11)$$

where  $A_i^{(j)}$  is the  $i$ -th chemical species participating in the  $j$ -th reaction,  $v_i^{(j)}$  is the stoichiometric number of species  $A_i^{(j)}$ , and  $n_j$  is the total number of species undergoing the  $j$ -th reaction.

The equilibrium state of the  $j$ -th reaction is defined by the standard Gibbs energy change of the reaction

$$\Delta G_j^\circ = \sum_{i=1}^{n_j} V_i^{(j)} \Delta G_f^\circ(A_i^{(j)}) = -R T \ln K_j(T, P) \quad (j = 1, \dots, k) \quad (8.12)$$

where  $\Delta G_f^\circ(A_i^{(j)})$  is the standard Gibbs energy of formation of species  $A_i^{(j)}$  and  $K_j$  is the equilibrium constant of the  $j$ -th reaction. Since molality  $m$  is used in this work as the concentration unit, the equilibrium constant is expressed as

$$K_j = \prod_{i=1}^{n_j} (m_{A_i^{(j)}} \gamma_{A_i^{(j)}})^{V_i^{(j)}} \quad (j = 1, \dots, k) \quad (8.13)$$

where  $\gamma_{A_i^{(j)}}$  is the activity coefficient of species  $A_i^{(j)}$ .

**Table 8.1.** Reaction equilibria in the Pb-Ti hydrothermal system with  $\text{TiO}_2$  and  $\text{PbAc}_2$  and/or  $\text{Pb}(\text{NO}_3)_2$  as starting materials

$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$\text{PbAc}_{2(\text{aq})} = \text{PbAc}^+ + \text{Ac}^-$
$\text{H}_2\text{O}_{(\text{g})} = \text{H}_2\text{O}$	$\text{PbAc}_3^{2-} = \text{Pb}^{2+} + 3\text{Ac}^-$
$\text{TiO}_{2(\text{s})} + \text{OH}^- = \text{HTiO}_3^-$	$\text{PbAc}_{2(\text{s})} = \text{Pb}^{2+} + 2\text{Ac}^-$
$\text{Ti}^{4+} + \text{H}_2\text{O} = \text{TiOH}^{3+} + \text{H}^+$	$\text{PbNO}_3^+ = \text{Pb}^{2+} + \text{NO}_3^-$
$\text{TiOH}^{3+} + \text{H}_2\text{O} = \text{Ti}(\text{OH})_2^{2+} + \text{H}^+$	$\text{Pb}(\text{NO}_3)_{2(\text{aq})} = \text{PbNO}_3^+ + \text{NO}_3^-$
$\text{Ti}(\text{OH})_2^{2+} + \text{H}_2\text{O} = \text{Ti}(\text{OH})_3^+ + \text{H}^+$	$\text{Pb}(\text{NO}_3)_{2(\text{s})} = \text{Pb}^{2+} + 2\text{NO}_3^-$
$\text{Ti}(\text{OH})_3^+ + \text{H}_2\text{O} = \text{Ti}(\text{OH})_{4(\text{aq})} + \text{H}^+$	$\text{HAc}_{(\text{g})} = \text{HAc}_{(\text{aq})}$
$\text{Ti}(\text{OH})_{4(\text{aq})} + \text{OH}^- = \text{HTiO}_3^- + 2\text{H}_2\text{O}$	$\text{HAc}_{(\text{aq})} = \text{H}^+ + \text{Ac}^-$
$\text{TiO}_2$ (rutile) + $2\text{H}_2\text{O} = \text{Ti}(\text{OH})_{4(\text{aq})}$	$\text{Ac}_{2(\text{aq})} = 2\text{HAc}_{(\text{aq})}$
$\text{TiO}_2$ (anatase) + $2\text{H}_2\text{O} = \text{Ti}(\text{OH})_{4(\text{aq})}$	$\text{Ac}_{2(\text{vap})} = \text{Ac}_{2(\text{aq})}$
$\text{PbO}$ (litharge) + $\text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	$\text{HNO}_3(\text{g}) = \text{HNO}_3(\text{aq})$
$\text{PbO}$ (massicot) + $\text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^-$	$\text{HNO}_3(\text{aq}) = \text{H}^+ + \text{NO}_3^-$
$\text{PbO}_{(\text{aq})} + \text{H}_2\text{O} = \text{PbOH}^+ + \text{OH}^-$	$\text{KOH}_{(\text{s})} = \text{K}^+ + \text{OH}^-$
$\text{Pb}(\text{OH})_{2(\text{s})} = \text{Pb}^{2+} + 2\text{OH}^-$	$\text{KOH} \cdot \text{H}_2\text{O} = \text{K}^+ + \text{OH}^- + \text{H}_2\text{O}$
$\text{PbOH}^+ = \text{Pb}^{2+} + \text{OH}^-$	$\text{KOH} \cdot 2\text{H}_2\text{O} = \text{K}^+ + \text{OH}^- + 2\text{H}_2\text{O}$
$\text{Pb}^{2+} + 2\text{OH}^- = \text{HPbO}_2^- + \text{H}^+$	$\text{KAc}_{2(\text{aq})} = \text{K}^+ + \text{Ac}^-$
$\text{Pb}_2\text{OH}^{3+} + \text{H}^+ = 2\text{Pb}^{2+} + \text{H}_2\text{O}$	$\text{KNO}_3(\text{s}) = \text{K}^+ + \text{NO}_3^-$
$\text{PbTiO}_{3(\text{s})} + 3\text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{OH}^- + \text{Ti}(\text{OH})_{4(\text{aq})}$	$\text{K}_2\text{TiO}_{3(\text{s})} + 3\text{H}_2\text{O} = 2\text{K}^+ + \text{Ti}(\text{OH})_{4(\text{aq})} + 2\text{OH}^-$
$\text{PbAc}^+ = \text{Pb}^{2+} + \text{Ac}^-$	

The chemical equilibrium Eqs. (8.12) and (8.13) are solved simultaneously with mass and electroneutrality balance equations. To solve this system of equations, the standard Gibbs energies of formation and activity coefficients are calculated as described above.

For example, let us consider a system obtained by mixing soluble salts of lead (e.g., lead acetate or lead nitrate) with titanium dioxide. Table 8.1 contains equilibrium equations between 42 aqueous and solid species that may exist in the Pb-Ti-H<sub>2</sub>O system. The presence of nitric acid and potassium hydroxide (cf. Table 8.1) results from the fact that the formation of ceramic materials (e.g., lead titanate) may require pH-adjusting agents such as acids, alkaline hydroxides, or ammonia. For completeness, the data for gaseous species are also included even though the gas phase plays a secondary role in perovskite synthesis under the *T-P* conditions of interest. As we can see in Table 8.1, even a relatively simple hydrothermal system such as Pb-Ti-H<sub>2</sub>O contains a large number of species and a correspondingly large number of equations to be solved.

## 8.2.2 Standard-state properties

The standard Gibbs energy of formation at the temperature and pressure of interest is calculated from the standard Gibbs energy  $\Delta G_f^\circ$  and enthalpy  $\Delta H_f^\circ$  of formation, and entropy  $S^\circ$  at a reference temperature (usually 298.15 K) as well as the partial molar volume  $V^\circ$  and heat capacity  $C_p^\circ$  as functions of temperature. The OLI data bank contains information for many aqueous, gaseous, and solid compounds. Whenever possible, data should be taken from critically evaluated and consistent sources. These compilations were discussed previously along with criteria for selecting the most reliable data [29]. Extensive works on the application of the HKFT equation [38–39] serve as a main source of data for aqueous species. Data for solid compounds are usually taken from the compilations of NBS [40–41], JANAF [42], Medvedev et al. [43], and Robie and Hemingway [44]. For ceramic materials, especially double oxides (e.g., lead and alkaline-earth titanates), most of the data are available in the book of Barin [45].

In the case of solid compounds, solubility data in pure water as well as in alkaline or acidic solutions at different temperatures are the best source of data for standard-state properties. These data are available in books of Seidell and Linke [46–47] and in the current literature. Whenever possible, regression of solubility data are performed using the OLI software [30] to obtain accurate and consistent thermochemical data for solid compounds.

In many cases, no experimental data are available for aqueous and solid species of interest; therefore predictive methods are necessary. If the HKFT equation parameters are not available from the regression of experimental data, they can be estimated. For this purpose, Shock and Helgeson [38–39] presented correlations for most solution species except for complexes. Sverjensky [48] developed an estimation method for several classes of complexes. In addition to the HKFT equation parameters, these methods make it possible to predict the reference-state en-

enthalpy and entropy if the reference-state Gibbs energy is known. These and other estimation techniques have been reviewed in detail by Rafal et al. [27].

At the same time, empirical procedures for calculating the standard-state properties of perovskite-type multicomponent (double) oxides of the general formula  $\text{ABO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$ , etc.;  $\text{B} = \text{Ti}, \text{Zr}$ , etc.) have been developed [49]. They are based on a family analysis [50–51] or group contribution methods [52]. In our work, unavailable thermochemical properties for lead zirconate and lead, magnesium, zinc niobates, and lead zirconate were estimated using these methods.

For solid solutions (e.g., PZT, PMN, PZN), no thermodynamic properties are available and no experimental solubilities were measured. Therefore, estimation methods are necessary. They include calculations of thermochemical data based on the ideal-solid solution approximation. A less sophisticated alternative is the use of group contribution methods. A more rigorous approach is based on the analysis of the thermodynamic properties of solid solutions in terms of the thermodynamic functions of mixing. This approach was applied to calculate standard-state properties of the PZT solid solutions [14].

It should be noted that the number of potentially stable solid phases in some multicomponent systems can be very large. For example, in the  $\text{Pb}-\text{Mg}-\text{Nb}-\text{K}$  hydrothermal system we are dealing with a large number of solid phases (i.e., oxides, hydroxides, niobates, etc.). Therefore, in the case of such a complicated system for which a great deal of estimation is necessary, it is useful to utilize the model interactively with experimentation to establish the solid phases that are likely to form. Experiments may greatly suppress or increase the number of phases included in the model, whose properties can be estimated as mentioned earlier. Furthermore, experimentation can provide feedback for adjusting the magnitude of certain thermochemical data, which may have questionable origin.

### 8.2.3 Stability and yield diagrams

The purpose of our work was to calculate the optimum synthesis conditions for the formation of phase-pure materials. This information can be obtained from the knowledge of stability and yield diagrams calculated for hydrothermal systems involving ceramic materials. In the past, stability diagrams were considered for a limited number of hydrothermal systems by assuming that the aqueous solutions were ideal [8,53].

Repetitive application of the model for different input concentrations of the A-site and B-site precursors as well as pH-adjusting agents (mineralizers) makes it possible to construct stability and yield diagrams. Stability diagrams show the ranges of equilibrium conditions for which various aqueous and solid species are stable in the hydrothermal system. Equilibrium conditions include the total molality of a selected aqueous metal precursor, solution pH, and temperature. The total molality of the aqueous metal precursor is the sum of the equilibrium concentrations of all dissolved metal species and does not include the species that precipitate from the solution as solids. While the stability diagrams provide information about the conditions for incipient precipitation of various solid phases, they do not

specify the reaction conditions required for an assumed yield of a reaction product. To accomplish this goal, the idea of yield diagrams was conceived [12]. In contrast to stability diagrams, yield diagrams are shown with the total input concentration of the metal precursor as the independent variable instead of the equilibrium (total) concentration of all dissolved metal species. The metal precursor can be converted to the desired product (e.g.,  $\text{ABO}_3$ ) with a certain yield, while the remainder of the metal precursor can remain in the solution. For the purpose of yield analysis, it is necessary to use the input concentration because we are concerned not only with the equilibrium concentration of species in saturated solution but also with the conversion of the precursor system into a phase-pure product. Thus, the input concentration of the metal precursor takes into account all metal-containing solution and solid species. In our previous papers [11–14], yield diagrams were constructed point by point, whereas later, a computer program has been developed for the automatic generation of these diagrams [15].

As the *y*-axis variable of yield diagrams, the program uses the input concentrations of one or more starting materials, which is equal to the initial concentration of the metal precursor. To simplify the graphical output in multicomponent metal oxide systems, the ratios of the input precursor concentrations are held constant at a predetermined value. As the *y*-axis variable of stability diagrams, the program uses the total concentrations of one or more metal precursors. As the *x*-axis variable, the program can use either pH or the input concentration of a mineralizer. All concentrations are expressed in molalities because such units are easily measurable. Also, temperature can be used as the *y*-axis variable and all precursor concentrations can be used as the *x*-axis or *y*-axis variables. If pH is chosen as the *x*-axis variable, the program changes the equilibrium pH by adding varying amounts of a selected acid (e.g.,  $\text{HNO}_3$ ) and a base (e.g., KOH). It should be noted that the pH values are calculated at the temperature of an experiment at equilibrium. For example, pH values in alkaline solutions at 433–473 K are smaller by about 2–3 pH units than those for the same solutions at room temperature.

If the input concentration of a pH-adjusting agent is chosen as the *x*-axis variable, it is varied by the program on a linear or logarithmic scale. It should be noted that the diagrams developed in previous papers [29,11–14] were constructed always with the total or input concentration of the metal precursor, equilibrium pH or temperature as the *y*-axis variable and with equilibrium pH or temperature as the *x*-axis variable. The automatic generation of diagrams allows us to be more flexible in the choice of independent variables. This is particularly useful when it is necessary to determine the amount of a pH-adjusting agent that is needed to obtain a certain yield of the product.

The stability diagrams include two types of lines: the solid lines denote the states of incipient precipitation of solids, whereas the dotted lines show the loci where two aqueous species have equal concentrations. In practice, an equilibrium point is assumed to lie on the solid-aqueous species boundary (solubility curve) when less than 0.25% of the precursor is found to be in the form of a solid phase. The yield diagrams show the areas where the desired product precipitates with a yield greater than or equal to an assumed value (e.g., 99%). At the solubility curve (shown in both stability and yield diagrams), the yield is very small because the

solubility curve corresponds to incipient precipitation of the desired product. The yield increases as we move beyond the solubility curve into the solid-liquid region. This yield is calculated by dividing the number of moles of the product by the total number of moles of the input metal precursor. The yield areas are shown in the diagrams as shaded fields. Usually, the boundaries between aqueous species are not shown in the yield diagrams. It should be noted that yield diagrams provide direct guidance for the experimental synthesis, because the shaded area of the yield diagram shows the range of input precursor concentrations that can produce a phase-pure product.

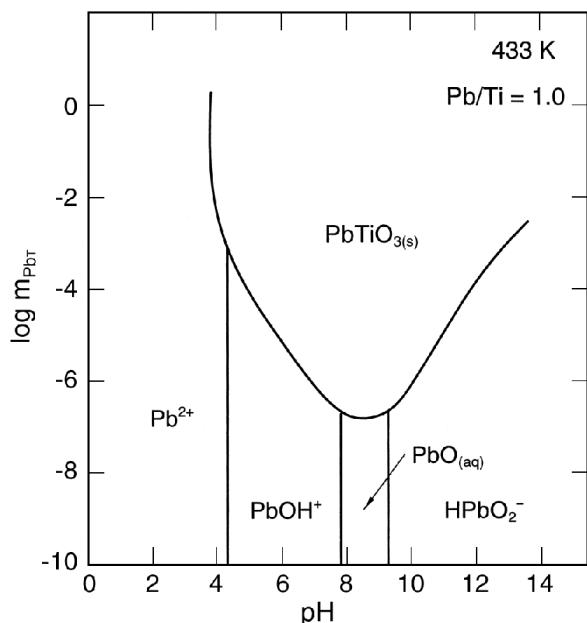
A certain ratio of metals in the starting materials (i.e., A/B) is assumed by choosing the precursor system for hydrothermal synthesis. It may correspond to the stoichiometric ratio in the formula of the perovskite (i.e.,  $\text{ABO}_3$ ) or can be greater or lower than one. If the ratio is lower than one, the formation of the perovskite phase does not go to completion. If it is greater than one, the formation of the perovskite and possibly additional phases containing A-site metals takes place. If the ratio is equal to one, we may expect the formation of phase-pure  $\text{ABO}_3$  if thermodynamics drives the following reaction to completion, i.e., if reaction (8.14) has a large equilibrium constant:



Thus, for making phase-pure  $\text{ABO}_3$ , reaction conditions where the ratio A/B equals or exceeds one are the most useful to optimize. In the section that follows, we will present examples where we have achieved this.

### 8.2.4 Stability and yield diagrams for the stoichiometric ratio of precursors (A/B = 1)

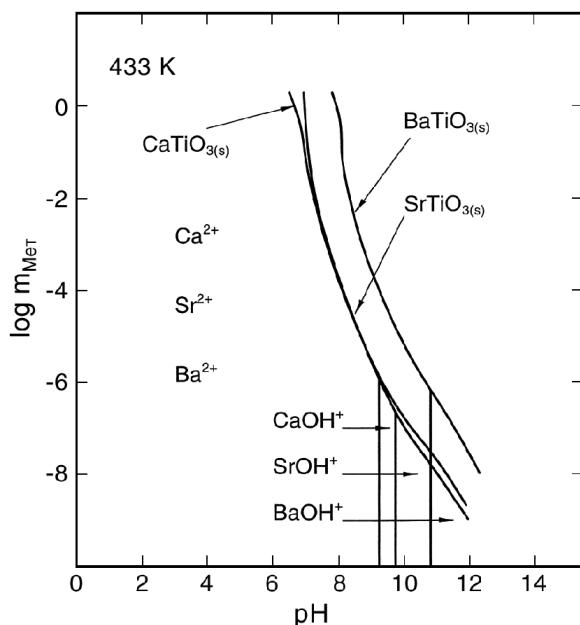
Figure 8.1 shows the stability diagram calculated for the hydrothermal system obtained by mixing lead nitrate or lead acetate and titanium dioxide at  $T = 433$  K. The stoichiometric molar ratio  $\text{Pb}/\text{Ti} = 1$  is employed. The total molality of all lead species that may occur in the solution and the solution pH are used as independent variables. The solid curved line on the stability diagram corresponds to the states of incipient precipitation of  $\text{PbTiO}_3$ . On the other hand, the vertical straight lines correspond to the loci where two aqueous species have equal concentrations. As shown in Fig. 8.1, the chemical identity of these species varies with pH. While  $\text{Pb}^{2+}$  dominates at pH below 4.3, it becomes hydrolyzed to  $\text{PbOH}^+$  at  $4.3 < \text{pH} < 7.8$ . Further, the neutral species  $\text{PbO}_{(\text{aq})}$  becomes predominant at  $7.8 < \text{pH} < 9.2$  and is, in turn, replaced by  $\text{HPbO}_2^-$  at pH above 9.2. The formation of the desired product,  $\text{PbTiO}_3$ , is strongly dependent on pH. Crystalline  $\text{PbTiO}_3$  can be obtained at pH higher than ca. 4.0. The stability of  $\text{PbTiO}_3$  increases with rising pH and reaches a maximum at pH equal to 8.5. In this range of pH,  $\text{PbTiO}_3$  precipitates when the concentration of lead in solution is as low as  $10^{-7}$  m. The stability of  $\text{PbTiO}_3$  somewhat decreases at pH above 10 because of the amphoteric character of lead. Thus, the solubility curve of  $\text{PbTiO}_3$  has a parabolic shape.



**Fig. 8.1.** Calculated stability diagram for the Pb-Ti system at 433 K.  $\text{PbAc}_2$  and  $\text{TiO}_2$  are used as starting materials and the ratio of total molalities is equal to 1.0

The incipient precipitation line of  $\text{PbTiO}_3$  is practically insensitive to the chemical identity of lead precursors. A very small shift in pH (about 0.2 units) is caused by the existence of various lead nitrate and lead acetate complexes in this system (cf. Table 8.1).

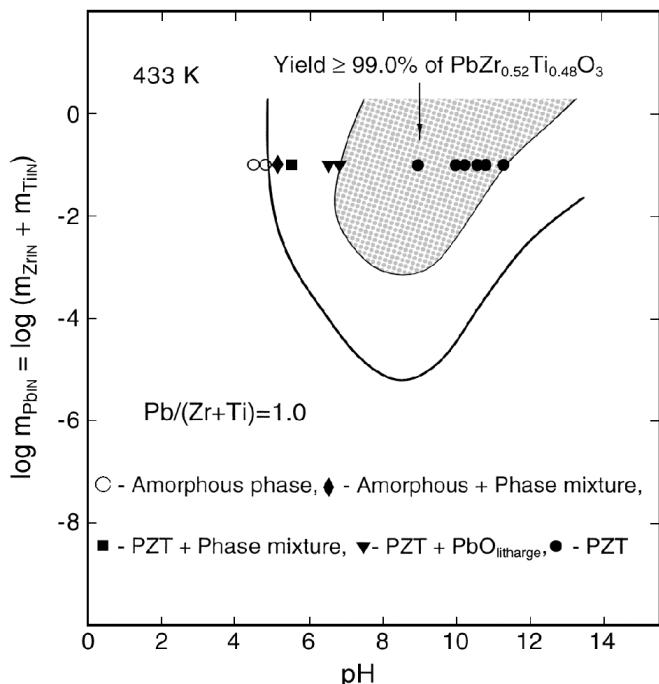
Figure 8.2 shows the comparison of the conditions for the synthesis of the alkaline-earth titanates,  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{BaTiO}_3$ . It combines the calculated phase stability diagrams for three hydrothermal systems Ca-Ti, Sr-Ti, and Ba-Ti at 433 K. The diagrams are qualitatively similar because of the chemical similarity of the Ca, Sr, and Ba cations. The total molality of the alkaline-earth metal precursor and the pH of the solution adjusted by KOH are chosen as independent variables. Three incipient precipitation lines are shown in this figure. The beginning of precipitation lines of  $\text{CaTiO}_3$  and  $\text{SrTiO}_3$  are very close to each other. The  $\text{BaTiO}_3$  line is located at somewhat higher pH. Its distance from the  $\text{SrTiO}_3$  line is about 1.2 pH units. The relative location of the incipient precipitation lines is a result of an interplay of several independent factors. Among them, most important are the relative magnitude of standard-state thermodynamic functions, alkalinity of the Ba, Sr, and Ca species as well as specific interactions between ions that determine the activity coefficients. It is apparent that the incipient precipitation line for the titanate of the most alkaline metal (i.e., Ba) lies at higher pH values. The differences between the  $\text{CaTiO}_3$  and  $\text{SrTiO}_3$  lines become visible only at relatively high



**Fig. 8.2.** Comparison of calculated phase stability diagrams for the hydrothermal systems Ca-Ti, Sr-Ti, and Ba-Ti at 433 K for the stoichiometric molar ratios of precursors

or low (but not intermediate) concentrations. The  $\text{CaTiO}_3$  and  $\text{SrTiO}_3$  lines cross each other. If the input concentration of titanium dioxide is 0.1 M, barium titanate precipitates at pH above 8, strontium titanate begins to form at pH above 7.5 and calcium titanate occurs at pH above 7.3 at 433 K. The predominant areas of alkaline-earth cations and their hydroxycomplexes are also shown in this figure.

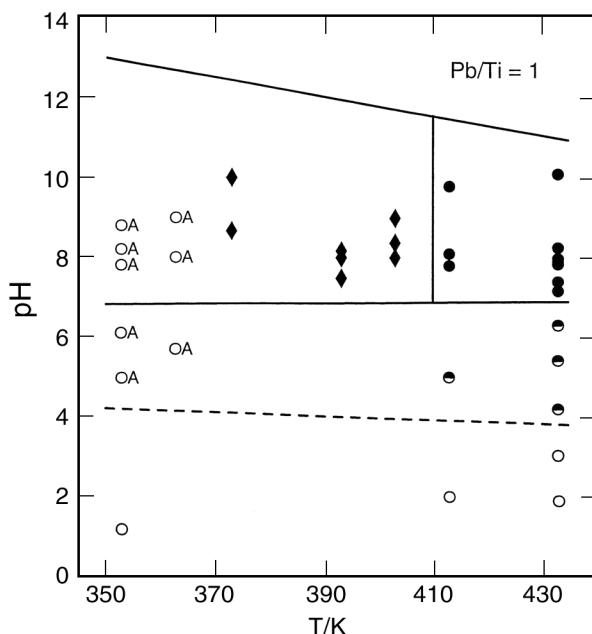
Figure 8.3 shows a yield diagram for the Pb-Zr-Ti hydrothermal system calculated at 433 K [14]. Lead acetate and zirconium and titanium dioxide with a molar ratio equal to 0.52/0.48 were used as precursors. KOH was used to adjust pH and the  $\text{Pb}/(\text{Zr}+\text{Ti})$  ratio was equal to one. The area of stability of a solid solution  $\text{Pb}_{0.52}\text{Zr}_{0.48}\text{TiO}_3$  (PZT) is encompassed by a parabolic-shaped solid line. The exact pH value at which precipitation begins depends on the total concentration of Pb in the aqueous phase. For example, if the concentration of lead precursor is equal to 0.1 M, the precipitation of the solid solution starts at pH values above 4.9. If lead nitrate is used, the left boundaries are shifted toward lower pH values by about 0.3–0.4 pH units while the right boundaries remain the same. The area of PZT solid solution stability increases with higher concentration. For relatively concentrated solutions, dissolution of solid PZT phases occurs at pH values above 14.0. The effect of temperature on the diagram is minimal in the range from ca. 433 K to 573 K. At 573 K, the incipient precipitation lines shift toward lower pH values by about 0.2–0.4 units. The area of PZT yield greater than 99.0% is much smaller



**Fig. 8.3.** Calculated yield diagram of  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  at 433 K.  $\text{PbAc}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  are used as starting materials for the calculations. Symbols denote various solid phases that were experimentally obtained using  $\text{PbAc}_2$  and coprecipitated the Zr-Ti hydrous oxide  $\text{Zr}_{x}\text{Ti}_{1-x}\text{O}_2\text{nH}_2\text{O}$

than the stability region. It is illustrated in Fig. 8.3 as a shaded region encompassed by a solid line. For the input concentration of lead and, subsequently, the sum of the input concentrations of Ti and Zr equal to 0.1 m, phase-pure PZT forms at pH values above 6.8 and below 11.4. Since the yield diagrams are somewhat sensitive to the chemical identity of precursors [12], calculations were performed with lead nitrate as a precursor. In this case, the area of PZT yield greater than 99% is shifted toward lower pH values by about 0.8–0.9 pH units.

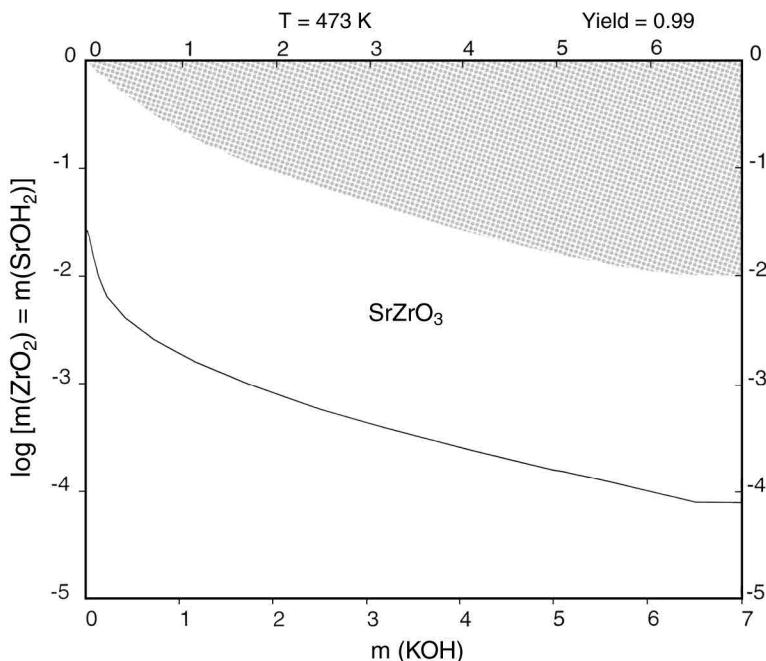
One of the possible ways of presenting yield diagrams is by performing calculations of stability and yield of ceramic materials at different temperatures as a function of the solution pH. Figure 8.4 summarizes theoretical findings pertaining to the synthesis of  $\text{PbTiO}_3$  from lead acetate or lead nitrate and titanium dioxide for the  $\text{Pb}/\text{Ti}$  ratio equal to 1. Figure 8.4 is valid for the input reagent concentrations ranging from 0.05 to 0.2 m, which are convenient for carrying out the reactions in practice. The dashed line corresponds to the beginning of precipitation of lead titanate. The solid lines encompass the region of greater than 99.99% yield of  $\text{PbTiO}_3$ , which is appropriate for performing practical syntheses. The areas



**Fig. 8.4.** Solid products of hydrothermal reactions of  $\text{PbAc}_2$  and/or  $\text{Pb}(\text{NO}_3)_2$  and  $\text{TiO}_2$  for the input molality of lead equal to 0.05–0.2  $m$  at different temperatures and pH values: solid circles — crystalline  $\text{PbTiO}_3$ , A — amorphous  $\text{PbTiO}_3$ , hollow circles —  $\text{TiO}_2$ , semi-solid circles —  $\text{PbTiO}_3 + \text{TiO}_2$ , solid diamonds —  $\text{PbTiO}_3 + \text{TiO}_2 + \text{PbO}$  (massicot) +  $\text{Pb}_2\text{Ti}_2\text{O}_6$ . The dashed line denotes the beginning of precipitation of  $\text{PbTiO}_3$  and the solid lines encompass the region where the yield of  $\text{PbTiO}_3$  exceeds 99.99%

between the dashed and lower solid lines and upper solid line and pH = 14 correspond to the precipitation of  $\text{PbTiO}_3$  along with unreacted solid titanium dioxide. The region between the pH = 0 axis and the dashed line shows the conditions for which the synthesis reaction does not occur. In this region, unreacted solid titanium precursor and aqueous species coexist. For clarity, aqueous lines are not shown in the yield diagrams.

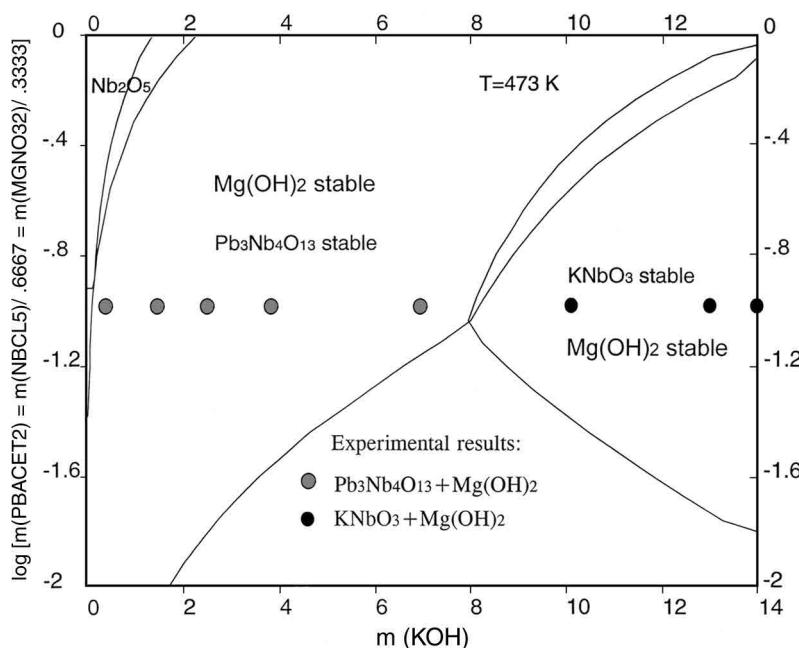
The stability and yield diagrams with pH as an independent variable (i.e., Figs. 8.1–8.4) do not indicate the concentration of a pH-adjusting agent necessary to synthesize the desired product. Figure 8.5 shows calculated phase stability and yield of strontium zirconate obtained by mixing strontium hydroxide and zirconium oxide at 473 K. In this figure, the Sr and Zr precursors, with a fixed molar ratio (i.e.,  $\text{Sr/Zr} = 1$ ), are used as y-axis variables and pH is replaced with the molality of a base (i.e., KOH) as an x-axis variable. The solid line in Fig. 8.5 denotes the beginning of precipitation of strontium zirconate. In the area above the solid line, strontium zirconate and zirconium oxide coexist. As we move closer to the shaded area, the yield of strontium zirconate increases while the amount of



**Fig. 8.5.** Calculated phase stability and yield diagram as a function of the input amount of KOH at 473 K for Sr/Zr = 1 using Sr(OH)<sub>2</sub> as a source of strontium

zirconium dioxide decreases. The shaded region shows the optimum synthesis conditions (i.e., input molality of strontium hydroxide and potassium hydroxide) for the formation of phase-pure strontium zirconate (yield greater than 99%) at 473 K. The amount of KOH necessary to form phase-pure SrZrO<sub>3</sub> from Sr(OH)<sub>2</sub> is much smaller than that from strontium nitrate [15] but cannot be completely eliminated (cf. Fig. 8.5). The minimum amount of KOH is as low as 0.2 m when the input concentration of Sr(OH)<sub>2</sub> is 1 m but rises to 1.6 m for an input concentration of 0.1 m.

All the above diagrams showed that it is possible to synthesize phase-pure titanates and zirconates if the synthesis conditions are carefully chosen. Compositions in the perovskite family with the general formula Pb(B<sub>1</sub>,B<sub>2</sub>)O<sub>3</sub> are known as ferroelectric relaxors and are of considerable interest. It has been reported in the literature [54] that these materials are difficult to fabricate reproducibly without the appearance of a pyrochlore phase that can be detrimental to the dielectric properties. Lead magnesium niobate [Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> or PMN] attracted our attention because it has never been obtained hydrothermally at moderate temperatures. An analysis of the stability of perovskite materials in vacuum based on quasi-thermodynamics and crystal chemical arguments performed by Shrout and Halliyal [55] showed that the problem of pyrochlore formation in the preparation



**Fig. 8.6.** Stability of various solid phases in the Pb-Mg-Nb-K-H<sub>2</sub>O system at 473 K

of PZN and PMN is primarily thermodynamic in nature. Therefore, it was of interest to study whether high stability of pyrochlores (such as  $\text{Pb}_{1.83}\text{Mg}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$  or  $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ ) in the Pb-Mg-Nb-H<sub>2</sub>O system is also responsible for the failure of obtaining phase-pure tetragonal PMN hydrothermally. One of the main steps in calculating the stability of the phase of interest (i.e., PMN) is to find or estimate thermochemical data for solid phases that are likely to form at hydrothermal conditions. It should be noted that the number of potentially stable solid phases in this system is very large and consists of oxides and hydroxides of lead, magnesium, and niobium; various niobates of magnesium, lead, and potassium; and solid solutions, which include a tetragonal and a cubic PMN pyrochlore phase and possibly a solid solution between potassium niobate and lead magnesium niobate.

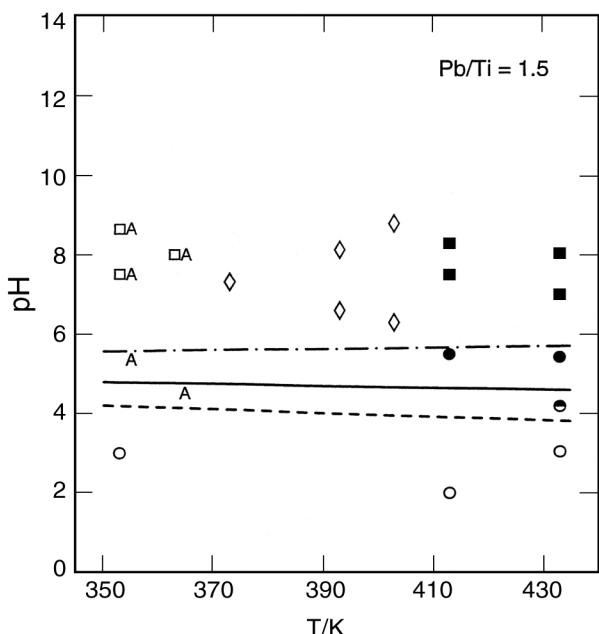
Our original databank did not contain thermochemical properties of most of the above solids except for magnesium and lead oxides and hydroxides. Therefore, thermochemical data for  $\text{Nb}_2\text{O}_5$ ,  $\text{Pb}(\text{NbO}_3)_2$ , and  $\text{KNbO}_3$  were calculated from the reported solubilities of these species in aqueous solutions [46–47,31]. Thermochemical properties of multicomponent oxides (niobates) were calculated using a group contribution method [30,51]. Then, based on the new values for the end-members, thermochemical properties of the solid solutions were calculated using an ideal solid solution approximation. Figure 8.6 shows the calculated stability of various solid phases in the Pb-Mg-Nb-K-H<sub>2</sub>O system at 473 K. Input molality of lead, magnesium, and niobium precursors with a ratio corresponding to the

stoichiometry of tetragonal PMN is shown on the  $y$ -axis and the KOH concentration is shown on the  $x$ -axis. The solid lines encompass the regions where various solid materials are stable. For example,  $\text{Nb}_2\text{O}_5$  is stable in an acidic environment at low amounts of KOH and at relatively high concentration of niobium in the solution. Lead niobate,  $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ , is extremely stable and starts to precipitate at very low concentrations of KOH. At high concentrations of KOH, lead niobate dissolves to release Nb ions into the solution to form potassium niobate ( $\text{KNbO}_3$ ). The stability regions of  $\text{Mg}(\text{OH})_2$  and the  $\text{Pb}_3\text{Nb}_4\text{O}_{13}$  pyrochlore phase overlap at low pH values, but magnesium hydroxide is very stable at highly alkaline solutions and overlaps in this region with  $\text{KNbO}_3$ . These calculations are summarized in Fig. 8.6, which shows that tetragonal PMN is not thermodynamically stable. This is because magnesium hydroxide and lead niobate are more stable than tetragonal PMN in basic aqueous solutions. Furthermore, the use of KOH mineralizer causes the formation of  $\text{KNbO}_3$ . Organic mineralizers such as tetramethylammonium hydroxide ( $\text{Me}_4\text{NOH}$ ) do not form niobates but they still cause the formation of  $\text{Pb}_3\text{Nb}_4\text{O}_{13}$  and  $\text{Mg}(\text{OH})_2$  instead of tetragonal PMN [31]. It should be noted that standard-state properties for many solid compounds in this system were estimated. Therefore, this is a preliminary phase and stability diagram of the Pb-Mg-Nb-K hydrothermal system, which may be fine-tuned in the future.

### 8.2.5 Stability and yield diagrams for the nonstoichiometric ratio of precursors ( $\text{A}/\text{B} > 1$ )

When the A/B ratio is above one, we expect the area of phase-pure product in the yield diagrams to increase. This is because an excess of A-site metal in solution shifts the equilibrium so that pure perovskite phase precipitates at lower pH values, which also reduces the amount of required mineralizer. However, an excess amount of metal A can also cause the precipitation of secondary phases. In the lead-containing hydrothermal systems, an excess of lead will form lead hydroxide or lead oxide (litharge) [12]. Hydrated and nonhydrated forms of hydroxides can precipitate together with desired ceramic material in the systems containing alkaline-earth metal [29,13,15]. While some of these impurities can be eliminated with washing, the leaching of A-site ions from the perovskite lattice is also an important concern [56]. Thus, an excess of A metal is useful provided that syntheses are performed in the pH region where additional solid phases do not precipitate.

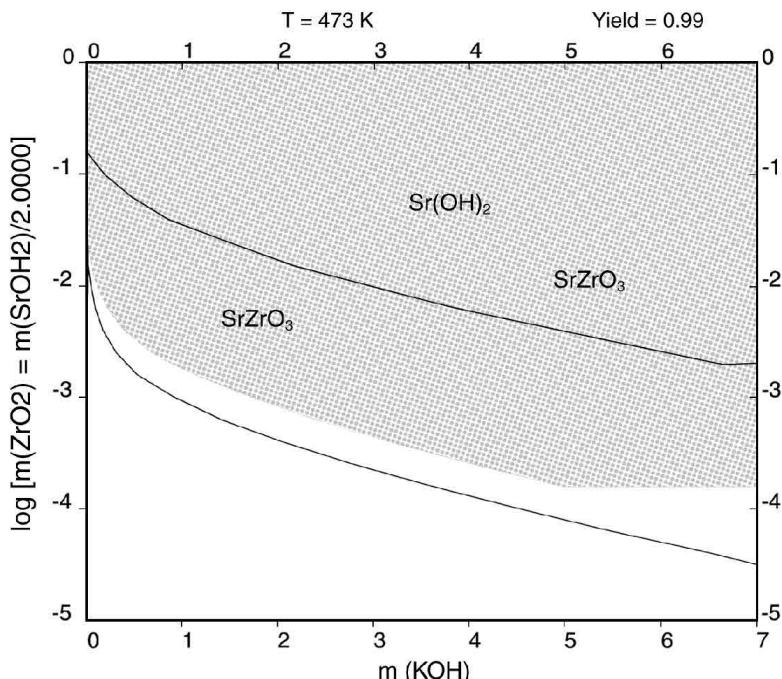
Figure 8.7 shows a yield diagram in the  $\text{Pb}-\text{Ti}-\text{H}_2\text{O}$  system constructed using lead acetate and titanium oxide with the  $\text{Pb}/\text{Ti}$  ratio equal to 1.5. This figure shows the pH-T regions where different solid phases can be obtained for the input concentration of lead precursor equal to 0.1 m. The dashed line represents the beginning of precipitation of  $\text{PbTiO}_3$ . The region between the axis  $\text{pH} = 0$  and the dashed line shows conditions where the reaction does not occur. In the area between the dashed and solid lines,  $\text{PbTiO}_3$  will precipitate along with unreacted  $\text{TiO}_2$ . In Fig. 8.7, the dot-dashed line shows the beginning of precipitation of  $\text{PbO}$  (litharge). Phase-pure perovskite precipitates between the solid and dot-dashed



**Fig. 8.7.** Solid products of hydrothermal reactions of  $\text{PbAc}_2$  and  $\text{TiO}_2$  for the input concentration of lead equal to  $0.1\text{ m}$  at different temperatures and pH values: solid circles — crystalline  $\text{PbTiO}_3$ , A — amorphous  $\text{PbTiO}_3$ , hollow circles —  $\text{TiO}_2$ , semi-solid circles —  $\text{PbTiO}_3 + \text{TiO}_2$ , open diamonds —  $\text{PbO}$  (litharge and massicot) +  $\text{Pb}_2\text{Ti}_2\text{O}_6 + \text{TiO}_2$ , hollow squares —  $\text{PbO}$  (litharge and massicot), solid squares —  $\text{PbTiO}_3 + \text{PbO}$  (litharge and massicot). The dashed line denotes the beginning of precipitation of  $\text{PbTiO}_3$ , the solid and dot-dashed lines encompass the region where the yield of  $\text{PbTiO}_3$  exceeds 99.99%, and the dot-dashed line denotes the beginning of precipitation of  $\text{PbO}$ .

lines. Thus, the area above the dot-dashed line corresponds to the region where phase-pure  $\text{PbTiO}_3$  cannot be obtained because of the presence of an additional solid phase,  $\text{PbO}$ . A comparison of Figs. 8.4 and 8.7 shows that an excess of Pb decreases the pH for the formation of phase-pure  $\text{PbTiO}_3$  by about 2 pH units. Consequently, less mineralizer is necessary to obtain pure phase. However, the region of phase-purity is relatively small and limited to one pH unit. At higher alkalinities, lead oxide precipitates along with lead titanate. The extent of the phase-purity region depends strongly on the  $\text{Pb}/\text{Ti}$  ratio [12,57–58].

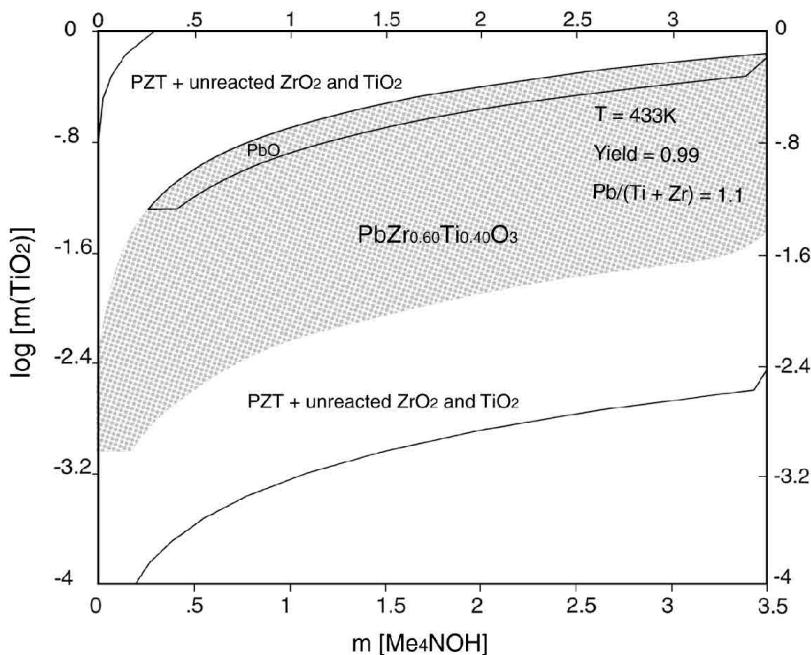
Figure 8.8 shows calculated phase stability and yield diagram as a function of the input molality of KOH at 473 K for the  $\text{Sr}/\text{Zr}$  ratio equal to 2.0 in the Sr-Zr hydrothermal system. Strontium hydroxide and zirconium dioxide were used as precursors. In comparison with the  $\text{Sr}/\text{Ti}$  ratio equal to 1.0 (cf. Fig. 8.5), the beginning of precipitation of  $\text{SrZrO}_3$  shifts very slightly towards lower concentrations of the input metal precursors thus suggesting that a slightly lower pH is necessary



**Fig. 8.8.** Calculated phase stability and yield diagram as a function of the input amount of KOH at 473 K for  $\text{Sr}/\text{Zr} = 2.0$  using  $\text{Sr}(\text{OH})_2$  as a source of strontium. The solid circle denotes experimental conditions for which phase-pure  $\text{SrZrO}_3$  was obtained.

for the formation of pure strontium zirconate. The region of nearly complete yield of  $\text{SrZrO}_3 (> 99\%)$  is much greater than for  $\text{Sr}/\text{Zr} = 1.0$  and starts at lower amounts of KOH (cf. Fig. 8.5) and correspondingly lower pH values [15]. No mineralizer is necessary when the input concentration of Zr exceeds 0.02 m. The upper solid line in Fig. 8.8 represents the incipient precipitation line of strontium hydroxide. In the area above this line,  $\text{SrZrO}_3$  is always contaminated with  $\text{SrOH}_2$ .

Our work has also examined the possibility of utilizing organic mineralizers [58]. The next diagram shows the calculated yield of lead zirconate titanate ( $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$ ) at 433 K with the ratio of lead acetate to a sum of titanium and zirconium dioxide equal to 1.1. In Fig. 8.9, the input molalities of Ti precursor are plotted against the molality of tetramethylammonium hydroxide ( $\text{Me}_4\text{NOH}$ ). The upper left and lower solid lines encompass the region of stability of rhombohedral PZT. They belong to the incipient precipitation line. Phase-pure  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  can form in a relatively wide region of input precursor and mineralizer molalities (cf. shaded area in Fig. 8.9).  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  precipitates along with  $\text{PbO}$  in the small region shown on the top of the phase-purity region. The stability area of  $\text{PbO}$  is



**Fig. 8.9.** Calculated yield diagram of  $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$  at 433 K.  $\text{PbAc}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$  are used as starting materials for the calculations

relatively small and limited to a high concentration of precursors. In highly alkaline solutions, lead oxide dissolves. When the ratio of metals in precursor materials is greater than one, the area of the perovskite phase-purity region widens. However, at some reaction conditions it causes contamination of ceramic materials with additional phases.

### 8.2.6 Carbon dioxide contamination

There are three general ways to introduce  $\text{CO}_2$  into a hydrothermal product. They are as follows:

1. Contaminated starting materials (e.g., alkaline and alkaline-earth hydroxides, hydrous oxides)
2. Synthesis unit operation into a high pH precursor solution (the absorption of  $\text{CO}_2$ )
3. Post-synthesis unit operations (i.e., during washing, filtration, etc.)

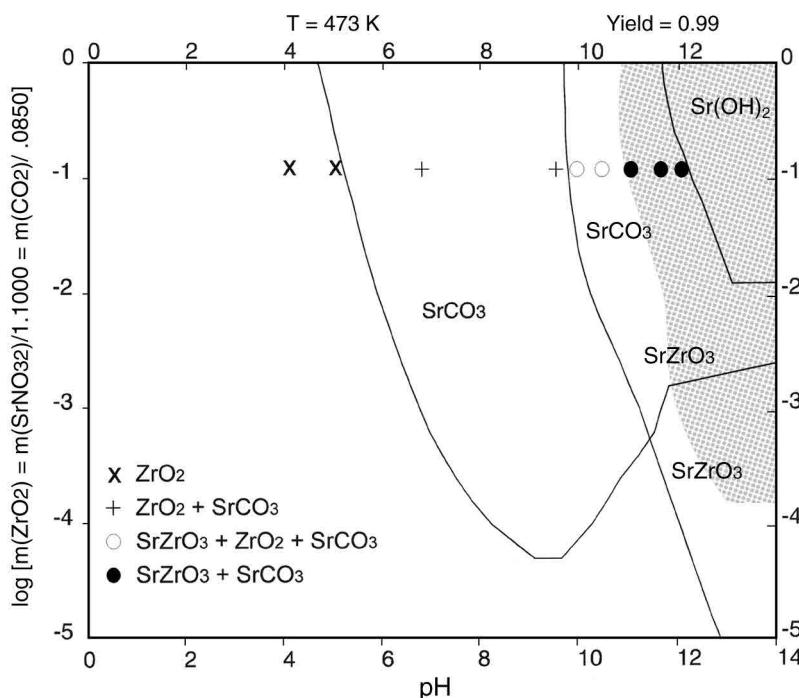
To eliminate the risk of carbonate contamination with starting materials, all reagents should be free from carbonates. However, carbonate-free alkaline-metal hydroxides (i.e., precursors) and alkaline hydroxides (i.e., mineralizers) are not

available commercially. For example, according to the manufacturer (Aldrich), the 99.99% (adjusted to cation) electronic grade KOH contains 0.4 wt% of  $K_2CO_3$ . On the other hand, commercially available alkaline-earth hydroxides usually contain 0.5–3 wt% of  $CO_2$ . The weight percent of alkaline-earth carbonate in the final product can be calculated assuming that all  $K_2CO_3$  contained in KOH converts to  $ACO_3$  ( $A = Ba, Sr, Ca$ ). In principle, carbonates can be removed from the final product by washing with a weak acid but the risk of dissolving ceramic materials with acids is very high as suggested in the stability and yield diagrams (cf. Figs. 8.1–8.10). Therefore, it is advisable to purify commercial hydroxides and hydrates. It can be done by filtering metal carbonate contaminants from a hot stock solution of the corresponding hydroxide and hydrate.

The problem of contamination of the solution with carbonates during preparation of starting materials has been discussed in our previous papers [11,13]. Unless the system is isolated from the atmosphere, contact with  $CO_2$  may occur during precursor solution preparation. The effect of atmospheric  $CO_2$  on the purity of alkaline-earth titanates and zirconates is different for the Ca-, Sr-, and Ba-containing hydrothermal systems. It is directly correlated with the碱alities of Ca, Sr, and Ba because the absorption of  $CO_2$  is facilitated by the alkalinity of the solution. Accordingly, the metal concentration thresholds above which carbonates precipitate are different for the three systems. For example, the contact of alkaline strontium precursors with an open  $CO_2$ -containing air atmosphere will lead to a contamination with  $SrCO_3$  when the input concentration of Sr is above about  $10^{-4}$  m [11,15]. Thus, it is beneficial to avoid contact with atmosphere during the preparation of reagents. This is also the case when alkaline-earth metal salts (e.g., nitrates or acetates) are used as precursors in conjunction with NaOH or KOH as mineralizers because the presence of the mineralizers makes the solutions alkaline. However, our practical observations show that the absorption of atmospheric  $CO_2$  may require a substantial amount of time, which could be much longer than the time required for experimental manipulations.

Washing and vacuum filtering of the synthesis products in air may cause additional contamination, especially when an excess amount of the A-site cation is present in alkaline environments. However, our study [15] shows that the existing carbonate content of the starting materials appears to be the major determinant of the purity of the product.

For our thermodynamic simulations, we assume that the carbonate contamination results primarily from the  $CO_2$  content of the starting materials. We have constructed stability diagrams for the Sr-Zr- $CO_2$ - $H_2O$  system in which the amount of  $CO_2$  is varied proportionally to the amount of the Sr and Zr precursors [15]. This simulates a real-world situation in which  $CO_2$  is a fixed fraction of a reactant. Figure 8.10 shows the effect of  $CO_2$  on the stability and yield diagram plotted against the pH when the input amount of  $CO_2$  is equal to 0.085 times the amount of  $ZrO_2$ . This amount corresponds to the average concentration of carbon dioxide typically found in hydrous  $ZrO_2$  and KOH in our reactions [15]. In Fig. 8.10, the stability region of strontium carbonate has a parabolic shape. Despite the small  $CO_2$  content of the system,  $SrCO_3$  is very stable and its stability range almost overlaps with



**Fig. 8.10.** Calculated phase stability and yield diagram at 473 K for  $\text{Sr}/\text{Zr} = 1.1$  using  $\text{Sr}(\text{NO}_3)_2$  as a source of strontium when the amount of  $\text{CO}_2$  in the starting materials is equal to 0.085 times the amount of  $\text{ZrO}_2$ . The symbols denote experimental conditions for which the following products were obtained: (x)  $\text{ZrO}_2$ , (+)  $\text{SrCO}_3 + \text{ZrO}_2$ , (Y)  $\text{SrZrO}_3 + \text{ZrO}_2 + \text{SrCO}_3$ , (○)  $\text{SrZrO}_3 + \text{SrCO}_3$

the nearly complete yield range of strontium zirconate denoted by the shaded area. At very high pH values, strontium hydroxide is stable and its stability region overlaps with those of strontium zirconate and strontium carbonate. Thus,  $\text{SrZrO}_3$  is predicted to be carbonate-free only in dilute solutions at high pH values.

The hydrothermal equilibrium systems discussed in this chapter provide representative examples of what can be achieved using our methodology. These examples show that for a given precursor system, thermodynamic calculations can be used to specify the optimum synthesis conditions for the formation of phase-pure smart perovskite materials. However, electrolyte thermodynamics computations alone are not sufficient. Sluggish reaction kinetics at low temperatures as well as the limited availability of thermochemical data for some species in the hydrothermal system can render questionable conclusions derived from computations. Therefore, experimental evaluation of the thermodynamic predictions is necessary.

### 8.3 Validation and Applications of Thermodynamic Modeling

In order to validate the theoretical predictions, experiments are performed using the calculated stability and yield diagrams as a guide. In particular, hydrothermal syntheses are carried out at various metal precursor concentrations and ratios (A/B) for a wide pH range (mineralizer concentration) at each temperature. Thus, hydrothermal reactions are performed to investigate whether the location of the various stability and yield regions agrees with the experimental findings. Soluble salts of lead and alkaline-earth metals are used as sources of the A-site cation in the hydrothermal synthesis. Such starting materials are inexpensive and easy to handle. Also, alkaline-earth metal hydroxides can be used for this purpose [11,13,15]. However, they usually contain carbonates [15] and, therefore, should be purified prior to use. Also, their low solubility is of concern [15]. As a convenient source of the B-site cation, commercial anhydrous or freshly precipitated hydrous oxides are used, the latter considered more reactive [12,14–15]. From a practical point of view, the starting material concentration above 0.02 m is recommended. Reaction products are identified using X-ray diffraction technique. To further verify phase purity, other techniques such as wet chemical methods, thermogravimetric analysis, electron diffraction, energy dispersive spectroscopy, and other methods are employed. These tools are important if X-ray diffraction patterns are inconclusive. Experimental points are plotted in the corresponding regions of the yield diagrams (cf. Figs. 8.4, 8.7, 8.10).

Our simulation approach has been validated for numerous perovskite systems, which include BaTiO<sub>3</sub> [59], CaTiO<sub>3</sub> [13], SrTiO<sub>3</sub> [11], SrZrO<sub>3</sub> [15], PbTiO<sub>3</sub> [12,57–58], various solid solutions of PZT [14,60], PMN [31], and PZN [31]. The results indicate a very good agreement between theoretical predictions and experimental results for all investigated systems.

It is noteworthy that in some cases this agreement takes place only above a certain temperature that is characteristic for a precursor system (cf. Figs. 8.4, 8.7) or in certain regions of the stability and yield diagrams (e.g., in the phase-pure region or at high pH values, cf. Fig. 8.3). For example, there is an excellent agreement between predictions and experiments at temperatures above 410 K in the Pb-Ti-H<sub>2</sub>O system [12] (cf. Fig. 8.4). However, the same agreement can be reached even at lower temperatures (above 363 K) in the same system with complexing agents [57]. The discrepancies at lower temperatures may be caused by sluggish reaction kinetics that can lead to the formation of metastable crystalline or amorphous products (cf. Figs. 8.4 and 8.7) that cannot be inferred from thermodynamic computations. Also, the lack of thermodynamic data (e.g., for Pb<sub>2</sub>Ti<sub>2</sub>O<sub>6</sub> or amorphous precursors) and inaccurate data may contribute to the disagreement.

Possible sources of disagreement may also result from a fact that the complexity of the thermodynamic system depends on the scale of mixing of all reagents. It is worth noting that thermodynamic calculations assume that all reagents are mixed on a microscopic scale. This is especially important in the case of solid solutions. In practice, the mixture may not be homogenous. Thus, instead of a phase-

pure product, phase separation results [14] such as precipitation of the end-members of the solid solution system (e.g., PT and PZ instead of PZT) or formation of multiple phases (e.g.,  $\text{CaTiO}_3$  and  $\text{Ca}(\text{OH})_2$ ), which are likely far from equilibrium [12,14].

To validate the thermodynamic predictions with greater accuracy, a special option called “an expert system” has been developed as a part of the OLI program. It makes it possible to design experiments that test the position of the yield boundary (cf. the shaded areas in Figs. 8.3–8.10). For this purpose, the expected yield and amount of ceramic material as well as the number of tests inside and outside the yield boundary is specified by the user in conjunction with the allowed variation in temperature and precursor concentration. As a result, the recommended metal precursor and mineralizer concentrations at each temperature are calculated.

Our computations for numerous systems have uncovered a series of thermodynamic trends. The systems investigated so far belong to two categories: alkaline-earth metal and lead-containing perovskites. Stability diagrams for alkaline-earth titanates (i.e.,  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{BaTiO}_3$ ) are qualitatively similar because of the chemical similarity of the Ca, Sr, and Ba cations. Their stability and yield regions are limited by lower boundaries with respect to pH [11,13] (cf. Figs. 8.2, 8.10). In other words, alkaline-earth titanates and zirconates are stable in alkaline solutions and dissolve in either acids or  $\text{CO}_2$ -containing water, or both. The formation of phase-pure alkaline-earth titanates from metal hydroxides instead of metal nitrates or acetates at high input metal concentrations (above 0.1 m) does not require the addition of a mineralizer because the necessary concentration of  $\text{OH}^-$  groups is readily provided by the hydroxide precursor [13]. The presence of excess A-site ions in precursor reagents (i.e.,  $A/B > 1$ ) expands the width of the yield region closer to the incipient precipitation line. Thus, phase-pure products can form at less alkaline solution, which is very important from economic and environmental points of view. However, if the pH becomes too high, alkaline-earth hydroxides precipitate as an impurity phase (cf. Fig. 8.10). Alkaline-earth metal-Ti-Zr-H<sub>2</sub>O systems also proved to be very vulnerable to contamination with carbonates [11,13,15] (cf. Fig. 8.10).

In contrast to the alkaline-earth metals, lead is amphoteric. Its hydroxy complexes are relatively stable in highly alkaline environments. Therefore, the stability areas of PT, PZ, and PZT are parabolic in shape (cf. Figs. 8.1, 8.3, 8.10). In other words, the stabilities of lead-containing perovskites are bounded by lower and upper pH limits. Although the presence of excess lead widens the yield region, it can also cause the precipitation of an unwanted PbO phase in the middle of the yield region [12]. However, this problem has been solved with the aid of complexing agents and our simulation-based approach [57]. In contrast to alkaline-earth perovskites, carbonate contamination is not an issue in the Pb-Ti-Zr-H<sub>2</sub>O systems because lead-containing carbonates (i.e.,  $2\text{PbO}\cdot\text{PbCO}_3$ ,  $\text{PbO}\cdot\text{PbCO}_3$ ,  $\text{PbCO}_3$ ,  $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ , and  $\text{PbCO}_3$ ) are less stable than their corresponding perovskites.

## 8.4 Summary

A thermodynamic model of heterogeneous aqueous electrolyte systems, coupled with a facility for the automatic generation of stability and yield diagrams, provides a powerful tool for predicting the effect of various process conditions on the synthesis of smart ceramic materials. In particular, it makes it possible to determine the optimum conditions (T, pH, input precursor concentrations, and ratios) for the synthesis of various perovskite-type materials from simple precursors. The model is particularly valuable for analyzing the effects of changing the chemical identity and relative amounts of starting materials as well as for predicting the possibility of contamination with carbonates. The theoretical predictions allow us to formulate synthesis guidelines. In order to validate the results of theoretical predictions, experimental syntheses were performed in the whole temperature and pH range and for various input amounts of starting materials. Experience has demonstrated that this first-principles based approach provides a very successful means to find optimum synthesis conditions for the formation of perovskite-type multicomponent oxides.

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# **9 Growth of Multicomponent Perovskite Oxide Crystals: Synthesis Conditions for the Hydrothermal Growth of Ferroelectric Powders**

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## **9.1 Introduction**

In this chapter a general description of the hydrothermal process and ferroelectric materials will be presented. An overview of the approaches used for the synthesis will be outlined in table form. In addition, the specifics of the synthesis for controlled chemical and phase purity, kinetics and rate controlling mechanisms, controlled morphology, and controlled particle size will be discussed. Finally, conclusions about the synthesis of the hydrothermal growth of ferroelectric powders will be made.

## **9.2 General Overview**

### **9.2.1 Description**

Hydrothermal synthesis is accomplished by the use of suspensions or homogeneous solutions subjected to temperature and pressure to induce rapid phase transformation kinetics. This synthesis method falls under the category of wet chemical methods that includes sol-gel and coprecipitation. The wet chemical routes achieve purer and finer powders than the conventional solid-state calcination route. Unlike other wet chemical methods, the hydrothermal method can be used to prepare anhydrous phase-pure oxides in a single step synthesis route from inexpensive precursors. During the process, no hazardous volatiles are produced. Furthermore, the water-based solvent can be recycled. All of these advantages make hydrothermal processing an environmentally friendly manufacturing process. The method has been used to prepare powders as reviewed in Dawson [1] and Riman [2]. Crystals have been discussed by Yanagisawa et al. [3–5], and films by Bendale et al. [6], Chien et al. [7–8], Kajiyoshi et al. [9], Pilleux et al. [10], Roeder et al. [11], and Yoshimura et al. [12].

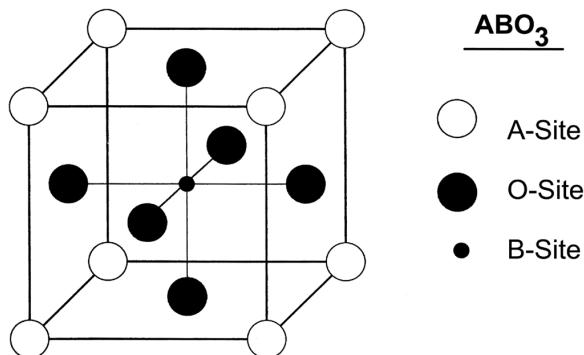
Hydrothermal processes can further be categorized into oxidation, precipitation, decomposition, and crystallization processes as described by Somiya [13]. The oxidation requires a metal powder to transform to an oxide while in water (e.g., an oxidation equation:  $\text{PbO} + \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{PbZrO}_3 + 2\text{H}_2$  (Somiya [13])). In the precipitation process, two metal salts dissolve in water and coprecipitate under hydrothermal conditions (e.g., a precipitation equation:  $\text{Pb}(\text{NO}_3)_2 + 0.5\text{ZrOCl}_2 + 0.5\text{TiCl}_4 + \text{KOH} + \text{H}_2\text{O} \rightarrow \text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3 + \text{H}_2\text{O} + \text{ions}$  (Lee et al. [14])). In the decomposing process a precursor (e.g., an oxalate or carboxalate) decomposes under hydrothermal conditions (e.g., a decomposition equation:  $\text{SrTiO}_{(2-x/2)}(\text{OH})_{1+x}\text{OOC-}n\text{-C}_7\text{H}_{15} (0 < x < 2) + \text{H}_2\text{O} \rightarrow \text{SrTiO}_3 + \text{H}_2\text{O} + \text{other species}$  (Riman et al. [15])). In the crystallization process a hydrous precursor crystallizes to form a crystallite while in water (e.g., a crystallization equation:  $\text{PbO} + \text{ZrO}_2 \cdot n\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{PbZrO}_3 + n\text{H}_2\text{O}$  (Somiya [13])).

## 9.2.2 Perovskite ferroelectrics

The perovskites are of interest to the electronics industry because of their structure that gives them unique electronic properties. The  $\text{ABO}_3$  perovskite unit cell is illustrated in Fig. 9.1. Each ‘A’ site ion is surrounded by twelve nearest neighbor oxygen ions, while, each ‘B’ site ion has six oxygen ions in an octahedral coordination. The ‘A’ site ions and oxygen ions together form a face centered cubic lattice, with ‘B’ site ions fitting into octahedral interstices. Since the ‘B’ site ion is much smaller than the ‘A’ site ion, the ‘B’ site ion can rattle within the octahedral interstices which suggests minimum energy positions for the ‘B’ site that are off-center and consequently give rise to an electric dipole. When a stress is applied, the dipoles align in one direction to provide a polarization that is called the piezoelectric effect. The ferroelectric state is when the crystals contain a spontaneous reversible electric dipole moment. The paraelectric state is when the dipoles in neighboring cells are randomly oriented relative to each other. The change from paraelectric to ferroelectric state occurs at the Curie temperature and corresponds to the change in dielectric constant. Therefore, many perovskite materials are used for applications in electronics (e.g., nonvolatile memories, transducers, actuators, and capacitors) based on their special electronic properties. Jaffe et al. [16] provides a more detailed description of ferroelectrics in his book on piezoelectrics.

The hydrothermal method allows for the tailoring of electronic properties of the ferroelectric materials by varying the composition of the ‘A’ and ‘B’ site cations and allows for a controlled dopant distribution. Furthermore, the production of more reactive-controlled, nano-sized particles allows for lower temperature sintering so that co-firing can be accomplished with less expensive electrodes (e.g., 30%Pd with 70%Ag). The control of particle size also prevents exaggerated grain growth and allows for thinner layers of materials for a better control of electronic materials and better mechanical stability.

### **Perovskite Crystal Structure**



**Fig. 9.1.**  $\text{ABO}_3$  perovskite unit cell [20]

#### **9.2.3 History**

Flaschen [17] in 1955 was the first to publish an article written about the hydrothermal synthesis of the ferroelectric materials. Flaschen [17] prepared  $\text{BaTiO}_3$  from titanium ester and soluble barium salt at a pH of 11–14 at a temperature greater than 80°C for 1–2 h. Since then many other perovskite ferroelectric materials have been prepared by the hydrothermal method by many others (cf. Table 9.1).

The conditions of the preparation however have varied. Tables 9.2–9.4 outline some of the conditions used in the hydrothermal synthesis of  $\text{PbTiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , and  $\text{BaTiO}_3$ , respectively. These variables include time, temperature, pH, mineralizer type, mineralizer concentration, type of ‘A’ site precursor, type of ‘B’ site precursor, ‘A’/‘B’ molar ratio in the precursor, concentration of ‘A’ site precursor, and the use of additives or stirring.

**Table 9.1.** Ferroelectric Powders Prepared by the Hydrothermal Method

$\text{SrTiO}_3$ [18–24]	$\text{BaTiO}_3$ [6–8,17–19,20,23,25–65]	$\text{PbTiO}_3$ [18,20,23,28,45,66–84]
$\text{CdTiO}_3$ [18]	$\text{CaTiO}_3$ [18,24,45,85–86]	$\text{BaSnO}_3$ [87]
$\text{SrZrO}_3$ [23,88]	$\text{BaZrO}_3$ [18,23,89]	$\text{CaZrO}_3$ [18]
$\text{PbZrO}_3$ [20]	$(\text{Ba},\text{Sr})\text{TiO}_3$ [11,20,23,90,11]	$\text{Ba}(\text{Ti},\text{Zr})\text{O}_3$ [33,60]
$\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ [91]	$(\text{Ba},\text{Sr})(\text{Ti},\text{Zr})\text{O}_3$ [34]	$\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ [20,23,92–102]
$\text{Pb}(\text{Zr},\text{Ti})\text{O}_3\text{--Nb}_2\text{O}_5$ [3]	$\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$ [5]	$(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ [4,100]
$\text{Pb}(\text{Zr},\text{Ti})\text{O}_3\text{--MnO}$ [3]		

**Table 9.2.** Synthesis Conditions for PbTiO<sub>3</sub>

Author	Time [h]	T [°C]	pH	Min. [type]	[Min] [M]	'Pb'	'Ti'	Pb/Ti	[Pb] [M]	Stir
Kaneko & Imoto [76]	5	100–500				oxide	SO <sub>3</sub>	1–1.8		No
Takai et al. [77]	1–3	100–160				oxide	NO <sub>3</sub>			Yes
Suzuki et al. [75]	6–8	100–220	11–14	KOH		acetate	Cl	1	0.15	Yes
Walton et al. [74]	1	200–300	9.5–9.6	NH <sub>3</sub>		acetate	isopropoxide	1	0.5–1	Yes
Rossetti et al. [80]	0–367	225–250	9.5–9.6	NH <sub>3</sub>		acetate	isopropanol	1	0.1–1	Yes
Li & Yao [79]	1–4	180–200	13.6–13.8	KOH	0.4–1	acetate	butoxide	1.2–2	0.1–0.5	No
Lencka & Riman [66]	24–72	90–160	9–11	KOH NH <sub>3</sub>		acetate NO <sub>3</sub>	oxide, isopropoxide	1–1.5	0.05–0.2	No
Sato et al. [70]	2–8	150–300		K, Na, Li-OH NH <sub>3</sub>		NO <sub>3</sub>	Cl	1		Yes
Ohara et al. [69]	24	150				OH	K-Ti	1		No
Cheng et al. [68]	2	220		KOH	4	oxide	oxide	0.5–1.05	5	Yes
Choi et al. [28]	16	220		KOH		acetate	Cl	1	0.15	Yes
Moon et al. [72–73]	0–18	150	> 14	KOH	1	acetate	acetylacetone	1.5	0.025–0.125	Yes
Gersten et al. [67]	72	70–200	7–14	KOH	0–10	acetate	oxide, isopropoxide	1–2	0.05–0.1	No
Gelabert et al. [78]	96–144	200		KOH KF		NO <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> C H <sub>2</sub> O	2		No

**Table 9.3.** Synthesis Conditions for Pb(Zr,Ti)O<sub>3</sub>

Author	Time [h]	T [°C]	pH	Min. [type]	[Min] [M]	'Pb'	'B'	Pb/'B'	[Pb] [M]	Stir
Kutty et al. [92]	6–8	150–350				oxide	Cl	1		Yes
Lee et al. [14]	0.5–96	70–200		KOH, NaOH	2–10	NO <sub>3</sub>	Cl	1	1	No
Beal [75]	0.5	300	> 12	Many	0.1–0.66	oxide	Cl	1.1	0.5	Yes
Lencka et al. [93]	24–48	90–200	8.5–12	KOH		acetate NO <sub>3</sub>	pro- panoide	1	0.1	Yes
Ichihara et al. [98]	0.5–48	70–200		KOH	4–10	NO <sub>3</sub>	Cl	1–1.2		Yes
Cheng et al. [97]	2	150		KOH	1–5	acetate	Cl, butyl	1–1.9	0.5	No
Ohba et al. [99]	4	150, 180		KOH	0.001–10	NO <sub>3</sub>	hydrous	1.1	0.0275–0.55	Yes
Su et al. [102]	6	350		KOH, NaOH	1	acetate	acetylacetone			Yes
Lee & Yen [100]	2–48	160–260		KOH	0.5	NO <sub>3</sub>	Cl	1	0.05	No
Chen et al. [96]	35–70	160–240				acac	hydrous	1	0.13	No
Traianidis [101]	2	265		KOH	1–10	NO <sub>3</sub>	hydrous	1–2	0.13	No

**Table 9.4.** Synthesis Conditions for BaTiO<sub>3</sub>

Author	T [h]	T [°C]	pH	Min. [type]	[Min] [M]	'Ba'	'Ti'	Ba/ Ti	[Ba] [M]	Stir
Flaschen [17]	1–2	80		KOH		Salt	ester	1		No
Christensen et al. [18]	70– 125	350– 490		NaOH, KF	1–4	OH	O <sub>2</sub> *H <sub>2</sub> O	1–2	0.05– 0.24	No
Yamamura et al. [62]		120				OH	Cl	1		No
Kaneko & Imoto [39]	0.5– 12	200– 600				OH	oxide	1–2		No
Matsuoka et al. [48]	0– 1.5	78– 370				OH	oxide	1– 1.2		Yes
Ovramenko et al. [52]	0–40	200– 500			0.4– 1	OH	oxide			Yes
Hertl [35]	12– 72	70– 103				OH	oxide	>1	0.2– 6.94	No
Kutty et al. [44]	3–10	180– 280				OH	hydrous, oxide	1	0.23	Yes
Klee et al. [41]	Many	80– 150		TMAH, NH <sub>3</sub>		OH	hydrous	1–2		No
Bagwell et al. [26]	1–24	90	13.6– 13.9			OH	oxide	1/ 1.23	0.64– 0.16	No
Gersten et al. [20]	8	150– 300	7–14	KOH		acetate	oxide, alk	1–2	0.05– −1	Yes
Hu et al. [37]	24	90– 100	10– 12	KOH		OH	Cl	1	0.2	No
Um et al. [56]	0–12	150– 300				OH	alkoxide			Yes
Wada et al. [59]	4	150	>13	KOH		OH	Ti- Chelate oxide	5		Yes
Shi et al. [55]	4–72	75– 200		NH <sub>3</sub>		OH		1		No
Asiaie et al. [25]	1–8	240		NaOH	0.3–4	Cl	isopro- poxide oxide, alk	>1	.005	No
Kumazawa et al. [42–43]	8	150– 300				OH		1–4		Yes
Viveka- nandan et al. [60]	2–10	90– 180				OH	hydrous	1	0.2, 1	Yes
Fukai et al. [33]	5	200				OH	Cl	1.5	0.9	No
Pfaff [53]	6–36	60– 250				OH	oxide, Cl	1– 1.2	0.25	Yes
Hennings et al. [36]	10– 15	150	>13	TMAH	25 wt%	acetate	acetate, alkoxide	1	0.03	No
Dutta & Gregg [31]	12– 168	240		NaOH	0.01	OH, Cl	oxide	1	0.25	No
Hung et al. [38]	4–56	90				OH	oxide	1		No
Lencka et al. [45]	72	100– 200	7–17	KOH, NaOH		NO <sub>3</sub>	hydrous, oxide	1	0.05– −0.1	Yes
Komarneni et al. [23]	0.5– 2	109– 194	>13	KOH	10	NO <sub>3</sub>	Cl	1–2	0.35	micro- wave

Some authors have written papers [1–2,13,89,103] that reviewed the synthesis method. This chapter will review the hydrothermal synthesis of complex perovskite powders with an emphasis on the variables that control chemical phase, morphology, and size. Discussion of the rate controlling mechanism will also be addressed.

## 9.3 Synthesis Conditions for Controlled Chemical and Phase Purity

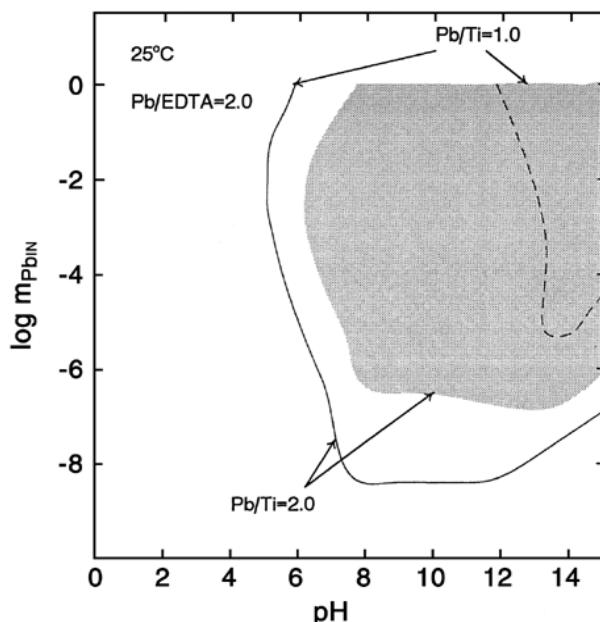
Chemical purity and phase purity of the perovskite ferroelectric is of the utmost importance to control since it will directly influence the electronic properties (e.g., dielectric constant, Curie temperature, etc.). The synthesis conditions (e.g., pH, temperature, and concentration) as well as the purity of the precursor materials significantly affect the chemical and phase purity of the resultant powders. The variables and strategies to control phase and chemical purity of hydrothermally synthesized ferroelectric powders will be discussed in this section.

### 9.3.1 Thermodynamic conditions

The optimal approach to control the chemical phases of the ferroelectric perovskite under equilibrium conditions is to calculate the stability and yield conditions of the perovskite by a thermodynamic model. Lencka et al. [19,93] described a thermodynamic model for aqueous solutions. Calculations were performed using software from OLI systems, Inc. [104] for many perovskite systems:  $\text{PbTiO}_3$  [45,66,67],  $\text{BaTiO}_3$  [45],  $\text{SrTiO}_3$  [45],  $(\text{Ba},\text{Sr})\text{TiO}_3$  [20],  $\text{CaTiO}_3$  [45],  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  [20,93], and  $\text{SrZrO}_3$  [88]. The model requires the following information for all species in the solution: the standard Gibbs energies  $\Delta G_f^\circ$  and enthalpies  $\Delta H_f^\circ$  of formation, entropies  $S_\circ$  at a reference temperature (298.15 K), and the partial molar volumes  $V_\circ$  and heat capacities  $C_p^\circ$  as functions of temperature. Equilibrium equations for all the species in the solution are set up. For example, Table 9.5 lists all the reaction equilibria for the system with feedstocks of titania, Ba-acetate, Sr-acetate, and ethylene diamine tetra acetic acid (EDTA), hereafter referred to as the EDTA-Ba-Sr-Ti hydrothermal system [20]. The model considers all the activity coefficients of aqueous species [104]. When the thermodynamic values are not known, estimation methods can be used to obtain the values [20,93].

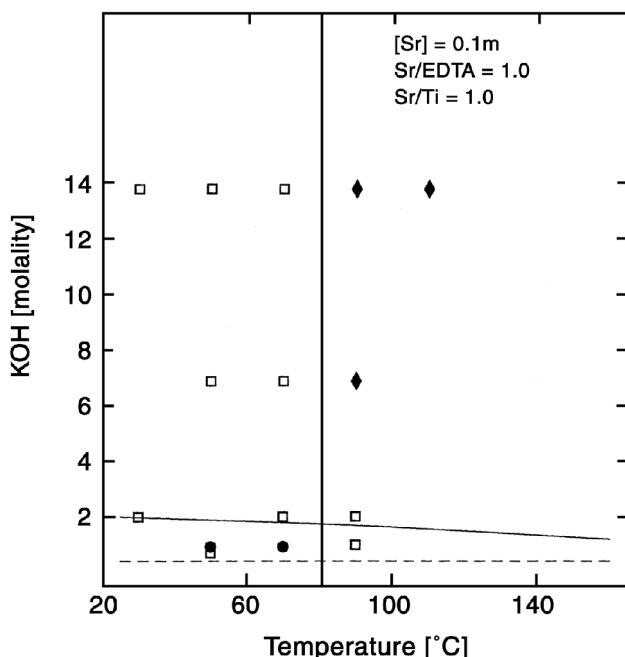
**Table 9.5.** Reaction Equilibria in the EDTA-Ba-Sr-Ti Hydrothermal System with  $\text{TiO}_2$ ,  $\text{BaAc}_2$ , and  $\text{SrAc}_2$  as Feedstocks

(1) $(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8)^{-2} = \text{H}^+ + (\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)^{-3}$	(2) $(\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_8)^{-1} = \text{H}^+ + (\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8)^{-2}$
(3) $(\text{C}_{10}\text{H}_{17}\text{N}_2\text{O}_8)^{+1} = \text{H}^+ + \text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8{}_{(\text{aq})}$	(4) $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8{}_{(\text{s})} = \text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8{}_{(\text{aq})}$
(5) $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8{}_{(\text{vap})} = \text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8{}_{(\text{aq})}$	(6) $(\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_8)^{+2} = \text{H}^+ + (\text{C}_{10}\text{H}_{17}\text{N}_2\text{O}_8)^{+1}$
(7) $(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)^{-3} = \text{H}^+ + (\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-4}$	(8) $\text{K}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-2} = \text{K}^+ + (\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)^{-3}$
(9) $\text{Ba}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-2} = \text{Ba}^{+2} + (\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)^{-3}$	(10) $\text{Ba}(\text{HC}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-1} = \text{H}^+ + \text{Ba}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-2}$
(11) $\text{Sr}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-2} = \text{Sr}^{+2} + (\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_8)^{-3}$	(12) $\text{Sr}(\text{HC}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-1} = \text{H}^+ + \text{Sr}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^{-2}$
(13) $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	(14) $\text{H}_2\text{O}_{(\text{g})} = \text{H}_2\text{O}$
(15) $\text{TiO}_{2(\text{s})} + \text{OH}^- = \text{HTiO}_3^-$	(16) $\text{Ti}^{4+} + \text{H}_2\text{O} = \text{TiOH}^{3+} + \text{H}^+$
(17) $\text{TiOH}^{3+} + \text{H}_2\text{O} = \text{Ti}(\text{OH})_2^{2+} + \text{H}^+$	(18) $\text{Ti}(\text{OH})_2^{2+} + \text{H}_2\text{O} = \text{Ti}(\text{OH})_3 + \text{H}^+$
(19) $\text{Ti}(\text{OH})_3^+ + \text{H}_2\text{O} = \text{Ti}(\text{OH})_4{}_{(\text{aq})} + \text{H}^+$	(20) $\text{Ti}(\text{OH})_4{}_{(\text{aq})} = \text{TiO}_{2(\text{s})} + 2\text{H}_2\text{O}$
(21) $\text{BaO}_{(\text{s})} + 2\text{H}^+ = \text{Ba}^{+2} + \text{H}_2\text{O}$	(22) $\text{BaOH}^+ = \text{Ba}^{+2} + \text{OH}^-$
(23) $\text{Ba}(\text{OH})_{2(\text{s})} = \text{Ba}^{+2} + 2\text{OH}^-$	(24) $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}_{(\text{s})} = \text{Ba}^{+2} + 8\text{H}_2\text{O} + 2\text{OH}^-$
(25) $\text{Ba}(\text{OH})_2 \cdot 3\text{H}_2\text{O}_{(\text{s})} = \text{Ba}^{+2} + 3\text{H}_2\text{O} + 2\text{OH}^-$	(26) $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}_{(\text{s})} = \text{Ba}^{+2} + \text{H}_2\text{O} + 2\text{OH}^-$
(27) $\text{BaTiO}_{3(\text{s})} + \text{H}_2\text{O} = \text{Ba}^{+2} + 2\text{OH}^- + \text{TiO}_{2(\text{s})}$	(28) $\text{Ba}_2\text{TiO}_{4(\text{s})} + 2\text{H}_2\text{O} = 2\text{Ba}^{+2} + 4\text{OH}^- + \text{TiO}_{2(\text{s})}$
(29) $\text{Ba}(\text{NO}_3)_{2(\text{s})} = \text{Ba}^{+2} + 2\text{NO}_3^-$	(30) $\text{CO}_{2(\text{g})} = \text{CO}_{2(\text{aq})}$
(31) $\text{CO}_{2(\text{aq})} + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	(32) $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$
(33) $\text{BaCO}_{3(\text{s})} = \text{Ba}^{+2} + \text{CO}_3^{2-}$	(34) $\text{BaCO}_{3(\text{aq})} = \text{Ba}^{+2} + \text{CO}_3^{2-}$
(35) $\text{BaHCO}_3^+ = \text{Ba}^{+2} + \text{HCO}_3^-$	(36) $\text{BaAc}_2 \cdot 2\text{H}_2\text{O} = \text{Ba}^{+2} + 2\text{H}_2\text{O} + 2\text{Ac}^-$
(37) $\text{BaAc}_2 \cdot 3\text{H}_2\text{O} = \text{Ba}^{+2} + 3\text{H}_2\text{O} + 2\text{Ac}^-$	(38) $\text{BaAc}^+ = \text{Ba}^{+2} + \text{Ac}^-$
(39) $\text{BaAc}_{2(\text{s})} = \text{Ba}^{+2} + 2\text{Ac}^-$	(40) $\text{BaAc}_{2(\text{aq})} = \text{Ba}^{+2} + 2\text{Ac}^-$
(41) $\text{SrO}_{(\text{s})} + 2\text{H}_2\text{O} = \text{Sr}^{+2} + 2\text{OH}^-$	(42) $\text{SrOH}^+ = \text{Sr}^{+2} + \text{OH}^-$
(43) $\text{Sr}(\text{OH})_{2(\text{s})} = \text{Sr}^{+2} + 2\text{OH}^-$	(44) $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}_{(\text{s})} = \text{Sr}^{+2} + 8\text{H}_2\text{O} + 2\text{OH}^-$
(45) $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}_{(\text{s})} = \text{Sr}^{+2} + \text{H}_2\text{O} + 2\text{OH}^-$	(46) $\text{SrTiO}_{3(\text{s})} + \text{H}_2\text{O} = \text{Sr}^{+2} + 2\text{OH}^- + \text{TiO}_{2(\text{s})}$
(47) $\text{Sr}_2\text{TiO}_{4(\text{s})} + 2\text{H}_2\text{O} = 2\text{Sr}^{+2} + 4\text{OH}^- + \text{TiO}_{2(\text{s})}$	(48) $\text{Sr}(\text{NO}_3)_{2(\text{s})} = \text{Sr}^{+2} + 2\text{NO}_3^-$
(49) $\text{Sr}(\text{NO}_3)_{2(\text{aq})} = \text{SrNO}_3^+ + \text{NO}_3^-$	(50) $\text{SrNO}_3^+ = \text{Sr}^{+2} + \text{NO}_3^-$
(50) $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} = \text{Sr}^{+2} + 4\text{H}_2\text{O} + 2\text{NO}_3^-$	(51) $\text{SrAc}_2 \cdot 4\text{H}_2\text{O} = \text{Sr}^{+2} + 4\text{H}_2\text{O} + 2\text{Ac}^-$
(52) $\text{SrAc}_2 \cdot 0.5\text{H}_2\text{O} = \text{Sr}^{+2} + 0.5\text{H}_2\text{O} + 2\text{Ac}^-$	(53) $\text{SrAc}^+ = \text{Sr}^{+2} + \text{Ac}^-$
(54) $\text{SrCO}_{3(\text{s})} = \text{Sr}^{+2} + \text{CO}_3^{2-}$	(55) $\text{SrCO}_{3(\text{aq})} = \text{Sr}^{+2} + \text{CO}_3^{2-}$
(56) $\text{SrHCO}_3^+ = \text{Sr}^{+2} + \text{HCO}_3^-$	(57) $\text{HAc}_{(\text{g})} = \text{HAc}_{(\text{aq})}$
(58) $\text{HAc}_{(\text{aq})} = \text{H}^+ + \text{Ac}^-$	(59) $\text{HNO}_{3(\text{g})} = \text{HNO}_{3(\text{aq})}$
(60) $\text{HNO}_{3(\text{aq})} = \text{H}^+ + \text{NO}_3^-$	(61) $\text{KOH}_{(\text{s})} = \text{K}^+ + \text{OH}^-$
(62) $\text{KOH} \cdot \text{H}_2\text{O}_{(\text{s})} = \text{K}^+ + \text{OH}^- + \text{H}_2\text{O}$	(63) $\text{KOH} \cdot 2\text{H}_2\text{O}_{(\text{s})} = \text{K}^+ + \text{OH}^- + 2\text{H}_2\text{O}$
(64) $\text{KNO}_{3(\text{s})} = \text{K}^+ + \text{NO}_3^-$	(65) $\text{KAc}_{(\text{aq})} = \text{K}^+ + \text{Ac}^-$
(66) $\text{KAc}_2^- = \text{K}^+ + 2\text{Ac}^-$	(67) $2\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 + 2\text{H}_2\text{O} = \text{Ba}^{+2} + \text{Sr}^{+2} + 2\text{HTiO}_3^- + 2\text{OH}^-$



**Fig. 9.2.** Yield diagram for  $\text{PbTiO}_3$ . The yield diagram depicts the input concentration of Pb on the y-axis and pH on the x-axis at the particular temperature of  $25^\circ\text{C}$ . The shaded region denotes greater than 99% phase-pure  $\text{PbTiO}_3$  yield for  $\text{Pb}/\text{Ti}$  molar ratio equal to 2 and  $\text{Pb}/\text{Ti}$  molar ratio equal to 1. The lines represent the beginning of precipitation of  $\text{PbTiO}_3$  [20].

The results of the calculation of the model are the equilibrium concentrations of all species as a function of pH, temperature, and initial reagent concentrations. The conditions for phase-pure perovskites can be represented in a yield diagram as shown in Fig. 9.2 for  $\text{PbTiO}_3$ . This yield diagram depicts the input concentration of lead on the y-axis and pH on the x-axis at the particular temperature of  $25^\circ\text{C}$ . The shaded region denotes greater than 99% phase-pure  $\text{PbTiO}_3$  yield for  $\text{Pb}/\text{Ti}$  molar ratio equal to 2 and  $\text{Pb}/\text{Ti}$  molar ratio equal to 1. The lines represent the beginning of precipitation of  $\text{PbTiO}_3$ . In this case, the input reagent included EDTA in a  $\text{Pb}/\text{EDTA}$  molar ratio equal to 2.0. Apparent from the diagram is that there is a larger area in the yield diagram for the phase pure region of  $\text{PbTiO}_3$  with the  $\text{Pb}/\text{Ti}$  molar ratio equal to 2 rather than 1. This highlights the influence of the molar ratios of the input reagent concentrations on the reaction conditions for obtaining chemically pure material. A second variable is the actual reagents used in producing the yield diagram. In this case, EDTA, lead acetate, titania, and potassium hydroxide were used as the initial reagents. However, reactions without the additive of EDTA would have produced a yield diagram with  $\text{PbO}$  precipitate [20]. Another yield diagram is shown in Fig. 9.3 with the y-axis as temperature and the x-axis as KOH concentration [20]. The input variables are Sr concentration



**Fig. 9.3.** Yield diagram for  $\text{SrTiO}_3$ . The input variables are Sr concentration of 0.1  $m$ , the Sr/Ti molar ratio is 1 and the Sr/EDTA molar ratio is 1. The dashed line represents the beginning of precipitation of  $\text{SrTiO}_3$ . The horizontal solid line represents the beginning of greater than 99% yield of  $\text{SrTiO}_3$ . The vertical line represents the minimum reaction temperature for  $\text{SrTiO}_3$  synthesis. The experimental points are denoted by points as follows:  $\lambda\text{TiO}_2$ ,  $\text{SrTiO}_3 + \text{TiO}_2$ , and  $\tau\text{SrTiO}_3$  (After [20])

of 0.1  $m$ , the Sr/Ti molar ratio is 1, and the Sr/EDTA molar ratio is 1. The dashed line represents the beginning of precipitation of  $\text{SrTiO}_3$ . The horizontal solid line represents the beginning of greater than 99% yield of  $\text{SrTiO}_3$ . The vertical line represents the minimum reaction temperature for  $\text{SrTiO}_3$  synthesis. The experimental points are denoted with points as follows:  $\lambda\text{TiO}_2$ ,  $\text{SrTiO}_3 + \text{TiO}_2$ , and  $\tau\text{SrTiO}_3$ .

The yield diagram is only useful in obtaining pure materials if pure precursors are used. If carbon dioxide from the air or are in the mineralizers during or after the hydrothermal reaction, the product can contain a layer of carbonate contamination. Urek et al. [57] found that carbonate contamination is reduced by increasing the pH. Similarly, Gersten [20] found that the use of chelating agents such as EDTA could reduce the carbonate contamination. For example, from thermodynamic calculations of the hydrothermal preparation of  $\text{BaTiO}_3$  from  $\text{TiO}_2$ , Ba-acetate, and KOH without EDTA,  $\text{BaCO}_3$  will form with only 0.001 mol%  $\text{K}_2\text{CO}_3$  present. However, with EDTA present 4.5 mol%  $\text{K}_2\text{CO}_3$  must be present before  $\text{BaCO}_3$  will appear [20].

Often when a carbonate-rich perovskite or a nonstoichiometric phase with excess ‘A’ site is produced the situation is “fixed” by washing the perovskite with acid (Li and Yao [79] in preparing  $\text{PbTiO}_3$ ; Kutty and Balachanadran [92] in preparing  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ; and Ovramenko et al. [52] in preparing  $\text{BaTiO}_3$ ). However, this approach without guidance from equilibrium conditions may also leach away the desired perovskite phase causing exaggerated grain growth on sintering as described in Hung et al. [38] and Pinceloup et al. [54].

### 9.3.2 Mineralizers and additives

The type of mineralizer (pH adjusting agent) can affect the final purity of the perovskite powders. For example, in the case of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , Beal [95] used several different mineralizers (i.e.,  $\text{NaF}$ ,  $\text{NaCl}$ ,  $\text{NaOH}$ ,  $\text{KF}$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KOH}$ ,  $\text{LiF}$ ,  $\text{LiCl}$ , and  $\text{LiOH}$ ). He found that the ionic radius of the alkali mineralizers of Na, K, and Li correlated directly to the impurity concentrations. The smaller Li ion was retained in the structure of the powders at higher levels (i.e., 0.4–0.5 mol%) compared with the K ion (0.03 mol%) that is twice as large [95]. It was also found that fluoride-based mineralizers contaminated greater than the other halides. He suggested that there was a stronger bonding of the F ion to the structure. The presence of Zr increased the contamination potential of the F ion. However, fluoride-based mineralizers do promote the formation of pure perovskite [95]. Yanagisawa and Kanai [3] also found the incorporation of K ion (i.e., 0.37 wt%) from the KF mineralizer used (i.e., 25–45 wt%) to prepare  $(\text{Pb}, \text{La})(\text{Zr},\text{Ti})\text{O}_3$  and  $(\text{Pb}, \text{Mn})(\text{Zr},\text{Ti})\text{O}_3$ . The contamination by the K ion was significantly higher in the preparation of  $\text{Pb}(\text{Nb},\text{Zr},\text{Ti})\text{O}_3$  (i.e., 1.1–1.5 wt%) since the K ion incorporates in the ‘A’ site of the perovskite, while the Nb is in the ‘B’ site [3]. The larger incorporation of K ion in the Nb-Pb( $\text{Zr},\text{Ti}$ ) $\text{O}_3$  may be a result of the charge neutrality.

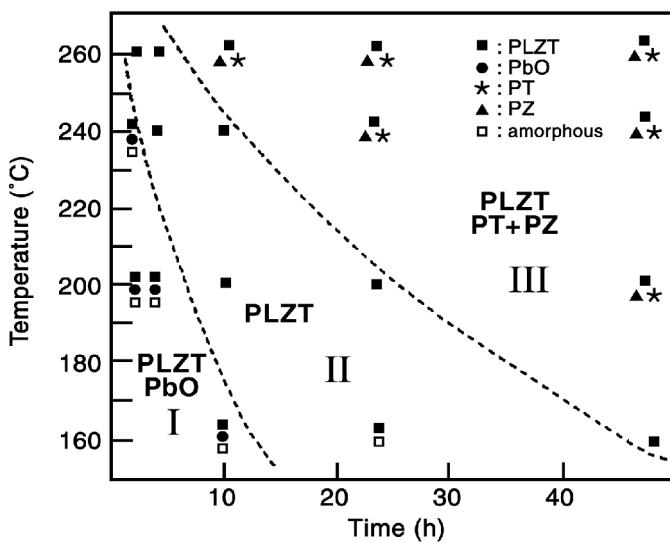
To avoid the impurity from the alkali mineralizer, either no mineralizer [96], an organic mineralizer (e.g., tetramethylammonium hydroxide (TMAH) [36,46,41,57]) or another base (e.g.,  $\text{NH}_3$ ) have been used. The use of no mineralizer has been used extensively in the preparation of  $\text{BaTiO}_3$ ; for example, Flaschen [17] and Eckert et al. [32] used  $\text{Ba}(\text{OH})_2$  to raise the pH for the hydrothermal synthesis of  $\text{BaTiO}_3$ . However, when the source of pH and concentration are coupled, it is not possible to independently evaluate the effects of these variables. Furthermore, the unreacted hydroxide requires washing that can leach the  $\text{BaTiO}_3$ , as discussed by Hennings et al. [36]. Instead, Hennings et al. [36] used TMAH to increase the pH and a stoichiometric BaTi-acetate gel was used as the precursor for pure phase  $\text{BaTiO}_3$  at 150°C within 10–15 h. However, Urek et al. [57] found that TMAH requires a burnout step at 800°C before the sintering of a ceramic material. Another limitation is that it will decompose above 150°C. Therefore, when the minimum reaction temperature of some of the hydrothermal synthesis conditions for preparing perovskites approach these temperatures alternative methods need to be found. One alternative is to find other precursors. For example, Chen [96] used precursors of 0.03 m Pb-acetylacetone and Zr-Ti hydrous gel to form  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ .

at 160°C within 70 h and at 200°C within 30 h. However, when Pb-acetate was used instead of the Pb-acetylacetone, the perovskite would not form [96].

If additives are used during the hydrothermal reaction, the reaction could be hindered. For example, Kiss et al. [40] found that Cynamer P-250 and Elvanol 50-42 prevented the complete reaction of BaTiO<sub>3</sub>.

### 9.3.3 Homogeneity

Another variable in the final product is the homogeneity of the starting precursor. The starting precursor for the synthesis of Pb(Zr,Ti)O<sub>3</sub> [93,96] or (Pb,La)(Zr,Ti)O<sub>3</sub> [100] requires molecular scale mixing in order for the pure-phase product to occur. For example, Lencka et al. [93] found that a hydrous ZrO<sub>2</sub>-TiO<sub>2</sub> prepared from a coprecipitate of titanium isopropoxide and zirconium propoxide in 2-propanol mixed with Pb-acetate and heated for 3 days at 150°C resulted in pure phase Pb(Zr,Ti)O<sub>3</sub>. However, when precursors of hydrous TiO<sub>2</sub> and ZrO<sub>2</sub> were prepared separately and then mixed with Pb-acetate under the same conditions, PbTiO<sub>3</sub> and PbZrO<sub>3</sub> precipitated out separately. The same results were corroborated with the hydrothermal procedure used by Chen et al. [96]. Similarly, in the preparation of (Pb,La)(Zr,Ti)O<sub>3</sub>, Lee and Yen [100] found that the precursor prepared from a coprecipitated stoichiometric gel resulted in pure phase (Pb,La)(Zr,Ti)O<sub>3</sub>, while the mixture of individually precipitated Pb, La, Zr, and Ti gels resulted in a phase mixture of PbTiO<sub>3</sub> and PbZrO<sub>3</sub> (cf. Fig. 9.4). The reason



**Fig. 9.4.** TTT (fraction transformation, temperature, time) diagram of (Pb,La)(Zr,Ti)O<sub>3</sub> (PLZT) phase formation under hydrothermal conditions [100]

for this required homogeneity may be explained on the basis of kinetics:  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  are more stable than  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$  [100]. Further evidence for the metastable nature of  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$  is that powders prepared from coprecipitated gel at high temperatures (e.g., 200 to 240°C) or long times (e.g., 10 to 40 h) will phase separate [100].

### 9.3.4 Reaction time and temperature

Reaction time is another variable that affects the chemical purity of the perovskite. Although the thermodynamic model predicted the possibility of the phase-pure perovskites at all temperatures greater than 25°C, in reality, temperatures greater than 25°C were required for phase pure synthesis. In the case of  $\text{PbTiO}_3$ , Gersten [20] found that the minimum reaction temperatures varied between 140 and 70°C. In the case of  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$  however, the minimum reaction temperature was found to be 90°C (cf. Fig. 9.3). Below the minimum reaction temperature, incomplete reactions resulted probably due to sluggish reaction kinetics (e.g., short reaction time).

### 9.3.5 Hydroxyl groups

An unavoidable contaminant of the hydrothermal process is the hydroxyl groups that attach to the lattice of the crystal structure and adsorb on the surface. There has been some disagreement in the literature [25,27,58–60,91] as to the affect of the lattice hydroxyls on the phase structure of hydrothermally prepared  $\text{BaTiO}_3$ . Vivekanandan and Kutty [91] found the cubic-tetragonal transformation of hydrothermally prepared  $\text{BaTiO}_3$  was a function of hydroxyl concentration. In agreement with this study, Wada et al. [59,105] studied these water groups for a particular size of hydrothermally prepared  $\text{BaTiO}_3$  (89.72 nm) and found that they contribute to the crystal structure (being cubic rather than tetragonal) and defects. The hydroxyls can be removed by heat treatments up to 600°C. Shi et al. [55] also supposed that a cubic phase rather than a tetragonal phase is stabilized by defects from OH ions and Ba ion vacancies. He based his supposition on his findings that at a Ba/Ti molar ratio equal to 1 a cubic phase was formed, while Ba/Ti equal to 3 gave tetragonal phase and higher synthesis temperatures stabilized the tetragonal phase. Kaneko and Imoto's [39] studies agreed with the findings of Shi et al. [55].

However, Begg et al. [27] argues that the structure transformation is a function of particle size. Below 0.19  $\mu\text{m}$  the particles are cubic and above 0.27  $\mu\text{m}$  the particles are completely tetragonal [27]. In support of this argument, Dutta and Gregg [31] synthesized tetragonal  $\text{BaTiO}_3$  of particle size 1  $\mu\text{m}$  stabilized with chloride ions, but synthesized metastable cubic phase  $\text{BaTiO}_3$  of particle size 0.2  $\mu\text{m}$  without the chloride. Asiaie et al. [25] is in agreement that the hydroxyl defects do not induce the tetragonal–cubic transformation and it is not an effect of strain, or the presence of amorphous impurities. After analysis of tetragonal particles of various

sizes (i.e., 0.3 and 0.5  $\mu\text{m}$ ) they support the transition being particle size dependent [25].

### 9.3.6 Summary

In summary, the variables that can affect the purity and phase of the hydrothermally grown ferroelectric can be divided into categories of thermodynamics and kinetics. The thermodynamic variables include the following: temperature, pH, precursor type, mineralizer type, precursor concentration, purity of precursors, and ratios of the precursor concentrations (including additives). The kinetic variables include all the above, as well as time and homogeneity of the initial precursors. The unavoidable impurities that result in the product are the hydroxyls in the crystal lattice, impurities in the precursors, and impurities that result from the mineralizer to adjust the pH.

## 9.4 Kinetics and Rate Controlling Mechanisms

As already mentioned, the reaction time actually contributes to the phase-purity of the hydrothermal reaction. Without the appropriate length of time, the reaction will not be complete even with the correct synthesis conditions (i.e., pH, temperature, initial reagent concentration). Furthermore, the reaction time will also contribute to the resulting powder morphology and size of the product. Therefore, before further discussing some of the variables that control morphology and size, a discussion on the kinetics and possible rate controlling mechanisms will be presented.

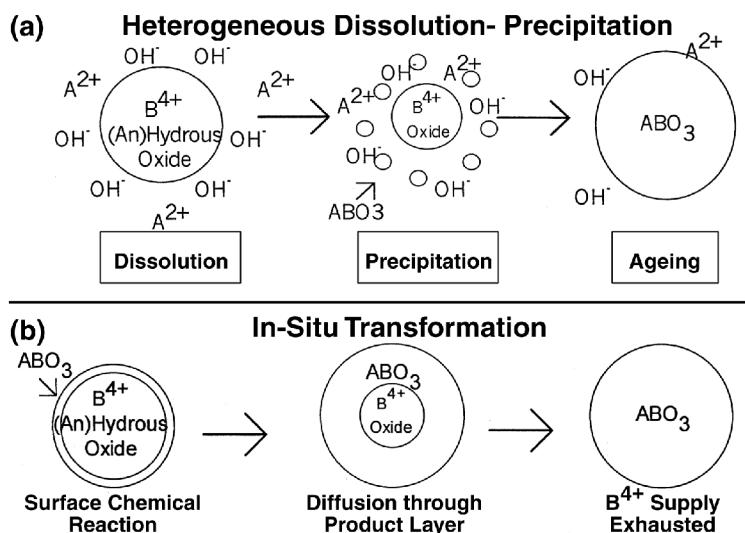
Some of the rate-controlling mechanisms have been hinted at in the introduction in the classification of hydrothermal reactions. These include oxidation, decomposition, coprecipitation, and crystallization. However, most of the synthesis conditions (cf. Tables 9.2–9.4) used for the synthesis of the ferroelectric powders have been through the coprecipitation or crystallization routes. Therefore, the discussion of the mechanisms will focus on these.

### 9.4.1 Rate determining step in the mechanisms

Two main mechanisms or a combination of these mechanisms have been suggested in the literature as rate determining for the hydrothermal reaction of ferroelectric powders: dissolution-precipitation and *in situ* transformation [2,32] (cf. Fig. 9.5). A dissolution-precipitation mechanism occurs when soluble reactants are heated over time. As a result, the concentration in the hydrothermal solution increases. When there is sufficient dissolution of the ions, supersaturation is achieved and the product is formed. On the other hand, an *in situ* transformation mechanism assumes a surface (topochemical) reaction of cations (i.e., Ba) with a

less soluble species (i.e.,  $\text{TiO}_2$ ) in water. The reaction proceeds by the diffusion of cations through the structure of insoluble species until the completion of the reaction.

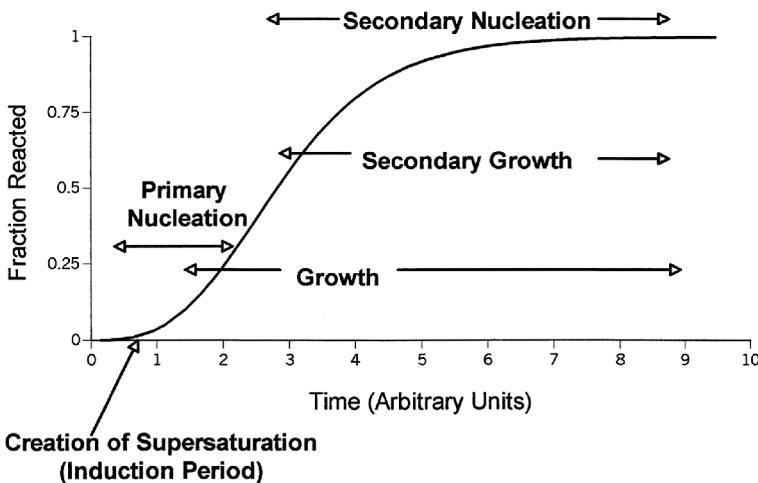
The rate limiting process for dissolution and precipitation is either the dissolution of the oxide phase and/or the precipitation from solution, or both. However, these processes are only broad descriptions that can be divided into other mechanisms. For example, within the dissolution mechanism, mass transport (i.e., diffusion or convection) or surface mechanisms may control the rate. Furthermore, within the surface chemical mechanism the following mechanisms can be rate controlling: nucleophilic or electrophilic attack, surface reconstruction, or transfer of charge reactions [106]. Once the conditions of supersaturation of a critical nuclei is obtained, precipitation may occur. The supersaturation is the metastable state of a solution in which soluble species remain in solution even though their thermodynamic equilibrium limit is exceeded. Nuclei may form homogeneously or heterogeneously. Growth of the nuclei may be limited by the following mechanisms: mass transport of the ions from solution to the nuclei, adsorption of ions on the crystal surface, diffusion of the ions through the adsorption layer of the crystal, dissolution of the nuclei, nucleation on the crystal surface, and by surface spiral growth of the crystals [107]. Also growth can be limited by continuous precipitation of new nuclei [108–110]. There also may be more than one mechanism that can control the rate [107].



**Fig. 9.5.** Two mechanisms: (a) dissolution-precipitation and (b) *in situ* transformation (After [2])

### 9.4.2 Precipitation

A typical kinetic process for precipitation is shown in Fig. 9.6. The process (cf. Fig. 9.6 in ref. [111]) includes an initial induction time due to the creation of supersaturation, primary and secondary nucleation, and growth stages. In the primary stage, critically sized nuclei form by homogenous or heterogeneous nucleation. In the secondary stage, Ostwald ripening occurs, where dissolution is followed by re-deposition. Additionally, in the secondary stage an aggregation process dominates, where agglomeration and coagulation of particles occur. The final effect of this growth stage is the redistribution of solid phase of the precipitate to form a low energy morphology.



**Fig. 9.6.** A typical kinetic process for precipitation (fraction reacted vs. time) (After [111])

### 9.4.3 Reaction rate

The reaction rate for the hydrothermal synthesis can be described as a function of the concentration of species in the aqueous environment and the reaction temperature. The part of the rate equation that is dependent on concentration is expressed as fraction reacted with time. There are many different rate equations depending on the physical model. One model is the Johnson-Mehl-Avrami (JMA) [108–110] where growth and nucleation are simultaneous given by

$$\frac{df}{dt} = kt^m(1-f), \quad (9.1)$$

where  $t$  is time,  $f$  is the fraction reacted, and  $k$  and  $m$  are fit parameters. The JMA equation can be solved for time as

$$t = t_{ind} + [-1/k (\ln(1-f))]^{1/m} \quad (9.2)$$

where,  $t$  is the time for  $f$  fraction perovskite to react, and  $t_{ind}$ ,  $k$ , and  $m$  are the three fit parameters.  $t_{ind}$  represents the induction time,  $m$  represents a geometric constant, and  $k$  represents a constant that depends on nucleation frequency and rate of grain growth. Hancock and Sharp [112] generalized the approach and used the value of  $m$  to differentiate between various possible mechanisms (cf. Table 9.6).

**Table 9.6.** Reaction Rate Slope  $m$  for the Johnson-Mehl-Avrami Equation  $-\ln \ln(1-f) = \ln(k) + m \ln(t)$  (After Hancock and Sharp [112])

Implied Mechanism	$m$
Diffusion controlled	0.54–0.62
Phase boundary	1.07–1.11
Nucleation and growth	2.00, 3.00
Zero order	1.24
First order	1.00

**Table 9.7.** Rate Determining Mechanisms

Material	Mechanism	Evidence	Condition [cf. Tables 9.2–9.4]	Reference
$\text{BaTiO}_3$	Surface Reaction	H&S, size	$\text{Ba}(\text{OH})_2 > 0.1\text{M}$	Hertl [35]
	Diffusion	H&S, size	$\text{Ba}(\text{OH})_2 < 0.1\text{M}$	Hertl [35]
	Combination	H&S, size & morphology	$\text{Ba}(\text{OH})_2 > 0.1\text{M}$	Eckert [32]
	Diffusion	Size & morphology	$\text{Ba}(\text{OH})_2 = 0.1\text{M}$	Hu [37]
	Dissolution	H&S, comparison of $E_a$		Ovramenko [52]
	Dissolution	Size with time	$\text{Ba}(\text{OH})_2 > 0.1\text{M}$	Kumazawa [42]
$\text{PbTiO}_3$	Dissolution	H&S, size & morphology	$\text{Ba}(\text{OH})_2 > 0.1\text{M}$	Bagwell [26]
	Dissolution	H&S, size & morphology	$[\text{PbAc}_2] = 0.1, 1.0\text{M}$	Rossetti [80]
	Dissolution	H&S, size & morphology	$[\text{PbAc}_2] = 0.025, 0.125; \text{KOH} = 1.0\text{M}$	Moon [73]
	Ion exchange	Morphology & size		Ohara [69]
	Dissolution	H&S, Nielsen, size & morphology	$[\text{PbAc}_2] = 0.1\text{M}, \text{KOH} = 2.5, 7.8\text{M}$	Gersten [20]
	Precipitation	Size & morphology	$[\text{PbAc}_2] = 0.1\text{M}$	Gelabert [78]
$\text{Pb}(\text{Zr,Ti})\text{O}_3$	Combination	H&S, morphology		Lee & Yen [100]
	Dissolution	Same morphology as precursor		Kutty [92]
	Dissolution		$\text{KOH} > 5\text{M}, \text{Pb} = 0.5\text{M}$	Cheng [97]

Many have used the method of Hancock and Sharp (H&S) [112] (cf. Table 9.6) along with particle characterization (size or morphology or both) to suppose a rate determining mechanism for synthesis of perovskites (cf. Table 9.7).

Most authors that suggested a dissolution rate determining mechanism also pointed out the very low solubility of  $\text{TiO}_2$  (and  $\text{ZrO}_2$ ) precursor. Therefore, instead the precursor may not fully dissolve, but A (where A = Ba, Pb) ions may cause structural rearrangement within the precursor followed by dehydration [24,92,100].

Hertl [35] used a Hancock and Sharp (H&S) [112] type method and suggested that the rate-determining step for the hydrothermal synthesis of  $\text{BaTiO}_3$  above a  $\text{Ba}(\text{OH})_2$  concentration of 0.1 m may be the reaction of  $\text{Ba}(\text{OH})_2$  with  $\text{TiO}_2$  at the solid-liquid interface. However, below 0.1 m [ $\text{Ba}(\text{OH})_2$ ] the rate-determining step is diffusion through the product layer. Eckert et al. [32] points out that the change in kinetic mechanism may be a result of the OH ions that changes the solubility of the  $\text{TiO}_2$  rather than the influence of the Ba ions. They suggested a combination mechanism of diffusion and dissolution control based on H&S results and micro-structure. Bagwell et al. [26] suggested a dissolution reprecipitation mechanism for the synthesis of  $\text{BaTiO}_3$  after using the H&S method and evaluating the micro-structure. However, the reaction slowed due to polymers adsorbed on the  $\text{TiO}_2$  precursor. These polymers inhibit the dissolution of the  $\text{TiO}_2$ . Kumazawa et al. [42] also suggested a dissolution rate limiting mechanism based on evidence from differences in the particle size of the resulting  $\text{BaTiO}_3$  powders from amorphous and crystalline precursors. Rossetti et al. [80] supposed a mechanism of dissolution-precipitation from homogeneous solution for the hydrothermal synthesis of  $\text{PbTiO}_3$ . Support for this mechanism was the data from the H&S method along with microstructure data that showed that the particle size decreased with a decrease in feedstock concentration. Particle size should decrease with an increase in feedstock concentration in order to support a nucleation and growth mechanism. From the crystallization fraction as a function of time and a microscope study, a dissolution rate determining mechanism was suggested. Similarly Moon et al. [72] used this approach and confirmed a dissolution-precipitation mechanism. However, they suggested a chemical reaction at the interface of the growing particles is the rate-limiting step. They recommend increasing the lead concentration and alkalinity to increase the solubility that results in an increase in supersaturation, thereby promoting  $\text{PbTiO}_3$  precipitation.

Support for the “shrinking core” diffusion reaction mechanism was also presented. For example, Hu et al. [37] aged 0.1 M  $\text{Ba}(\text{OH})_2$  solution and 0.1 M monodispersed  $\text{TiO}_2$  0.1–1  $\mu\text{m}$  for 24 h at 100°C to form  $\text{BaTiO}_3$  monodispersed microspheres of the same size and shape indicating a diffusion-reaction mechanism. Su et al. also suggest an *in situ* transformation mechanism for the synthesis of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  from an amorphous zirconia-titania gel by the diffusion of  $\text{PbO}$  into the amorphous network, which by expulsion of water will crystallize [102]. Somewhat like the diffusion rate limited reaction, Ohara [51,69], suggested an ion exchange mechanism to predominate for the transformation of fibrous potassium titanate into fibrous  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  under hydrothermal conditions.

**Table 9.8.** Rate Controlling Mechanisms for the Nielsen Equation  $df/dt = kf^q(1-f)^p$  [107,113–115] for Different Values of  $q$  and  $p$ 

Implied mechanism	$q$	$p$	$E_a$ [kJ/mol]
Growth by diffusion through the solution	0.33	1.0	~6–20
Surface adsorption growth	0.67	1.0	~45
Integration growth			~30–75
Mononuclear growth	1.33	$\geq 0.0$	
Spiral growth	0.67	2.0	
Polynuclear growth	0.67	$\geq 1.0$	
Surface diffusion controlled growth			

Recently, Gersten [20] showed that a Nielsen [107] growth model could equally be applied to rate data to distinguish between physical mechanisms. The growth model presented by Nielsen [107] is represented by the differential equation

$$df/dt = kf^q(1-f)^p \quad (9.3)$$

where  $f$  is the fraction reacted,  $t$  is the time, and  $k$ ,  $p$ , and  $q$  are fit parameters. For diffusional growth  $q$  is equal to 1/3 and  $p$  is equal to 1. For mononuclear surface growth,  $q$  is equal to 4/3 and  $p$  is an integer. For polynuclear surface growth,  $q$  is equal to 2/3 and  $p$  is an integer [107]. The various mechanisms based on this model are presented in Table 9.8. The model assumes all the growth occurs after a nucleation step.

Gersten [20] used the H&S method along with a Nielsen [107] approach (cf. Tables 9.6 and 9.8) to determine the rate determining mechanism for the hydrothermal synthesis of  $PbTiO_3$  in the  $Pb$ - $Ti$ -K-EDTA- $H_2O$  system and  $(Ba,Sr)TiO_3$  in the  $Ba$ - $Sr$ - $Ti$ -K-EDTA- $H_2O$  system. Both systems were found to be of the dissolution-precipitation type. They exhibited an induction time indicative of the creation of a supersaturation. Furthermore, the reaction time, as a function of the fraction reacted, best fit a Nielsen's equation for adsorption and integration by polynuclear controlled growth (i.e.,  $p = 0.75$ ,  $q = 0.67$ ). This can include adsorption (via electrostatic, chemical, and “ligand-like” effects), and integration by dehydration. The values for  $E_a$  also agreed with this mechanism (i.e.,  $E_a \sim 50$ –100 kJ/mol). The presence of 1 nm particles on the surface of the precursor after 1 min also confirmed this mechanism.

The part of the function that is dependent on temperature can be written as the Arrhenius equation. The Arrhenius equation is given by

$$k(T) = A \exp(E_a/RT), \quad (9.4)$$

where  $R$  equals 8.314 J/mol K,  $T$  is temperature,  $A$  is a constant, and  $E_a$  is the apparent activation energy.

Gersten [20] found that the activation energy was dependent on the KOH concentration. It was found to decrease from 101 to 47 kJ/mol with an increase in KOH from 2.5 to 7.8 *m*. Rossetti et al. [80] found an even lower magnitude of apparent activation energy, 30.1 kJ/mol, under varied conditions (cf. Table 9.3). Other apparent activation energies for hydrothermally-formed BaTiO<sub>3</sub> were 105.5 kJ/mol [35], 107 kJ/mol [20], 56 kJ/mol [52], and 20.9 kJ/mol [48]; for SrTiO<sub>3</sub> it was 72 kJ/mol [22] and 91 kJ/mol [20]. Gersten [20] attributed the variations in the apparent activation energies for each system to the different synthesis conditions (cf. Tables 9.3, 9.5).

#### 9.4.4 Variables affecting the reaction rate

The reaction time can be affected by the types of precursors, concentrations of the precursors, proportions of the concentrations of precursors, concentrations of mineralizers, type of mineralizer, types of additives, and temperature. Gersten [20] found that the rank of importance of the variables studied for the hydrothermal preparation of PbTiO<sub>3</sub> from Pb-acetate, titania, EDTA, and KOH were (1) the change in titanium species precursor, (2) an increase in temperature, (3) the concentration of KOH, (4) the Pb/Ti molar ratio, and (5) the concentration of Ti and Pb species.

As expected, the larger the precursor, the longer the reaction will take. This is due to the longer time required for dissolution or diffusion in larger sized precursors. Also, if the precursor is more reactive (e.g., higher surface area, more defects in the precursor, metastable phase of the precursor) the reaction will be shorter. Pfaff [53] found that the larger sized rutile titania would not form as much BaTiO<sub>3</sub> compared with the more reactive anatase titania under hydrothermal conditions. Also as expected, if there is a hindering material (e.g., polymer, ion) adsorbed on the surface of the precursor, the reaction will take longer. For example, Li and Yao [79] found that the type of mineralizer (LiOH vs. KOH) influences the reaction time of PbTiO<sub>3</sub> powders. Li<sup>+</sup> easily absorbs on the surface of the particles, and because of its small radius it resists crystal growth so that the reaction time is longer. Beal et al. [95] found that the reaction time was hindered by chloride-containing mineralizers compared with sodium and lithium fluoride mineralizers.

A way to increase the reaction time is to increase the heat up rate of the reaction. This can be accomplished by the novel microwave approach as developed by Komarneni et al. [23] and Abthu et al. [94] for the preparation of a wide variety of perovskite materials (cf. Table 9.1). Another modification of the hydrothermal process is the electrochemical-hydrothermal method that combines the hydrothermal process with an electric field [12]. Yoo et al. [63] used an electric field (50 mA/cm<sup>2</sup>) for the anodic oxidation of a Ti metal plate in the formation of BaTiO<sub>3</sub> powders at 250°C with 0.5 N Ba(NO<sub>3</sub>)<sub>2</sub>.

## 9.5 Synthesis Conditions for Controlled Morphology

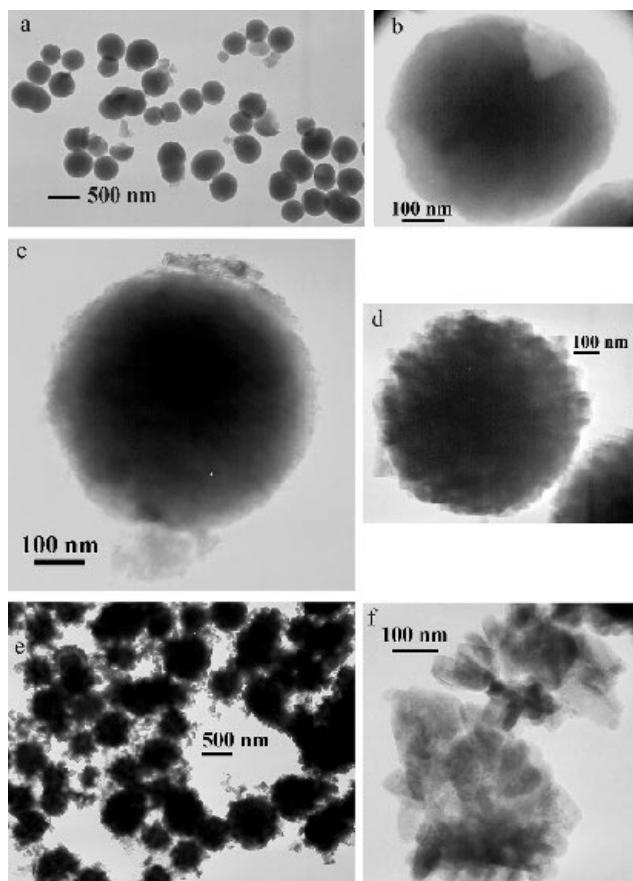
The control of the morphology of hydrothermally grown powders is closely related to the growth mechanism of the reaction, which in turn is a function of the supersaturation [106,113–116]. Walton [116] provided a summary of the effects of initial supersaturation and interfacial energy on the growth mechanism and morphology crystal growth of a general material. He summarizes as follows: with an initial supersaturation ( $S$ ) 1–2 and a low interfacial energy (IE) the morphology will be discrete, well formed crystals with no agglomerates. The nucleation is heterogeneous, and the growth is slow and predominantly occurs by screw dislocation. However, with  $S$  between 2–5 and a high IE, the growth changes to surface nucleation. With a low IE or a high IE, but with  $S$  between 10–50 the growth changes to dendritic and the morphology changes to poorly formed dendritic crystals. With  $S$  between 10–50 and a low IE or with a  $S > 1000$  and a high IE, the nucleation becomes homogeneous and the morphology would be both stability-dependent and agglomerated [116].

Although the supersaturation is the driving force for the growth of the powders, there are many related factors that contribute as well to the morphology of the final hydrothermal product. These include initial reagent, initial reagent concentration, pH, temperature, stir rate, and time. The supersaturation increases with a decrease in temperature and an increase in concentration of soluble species. In the presence of low-soluble species (e.g.,  $TiO_2$ ), the supersaturation may be increased by the pH that will increase the dissolution of the mostly insoluble species. Additives also prevent or enhance the dissolution of the essentially nondissolving species by either surface adsorbing or chelating the species, respectively. Additives or mineralizers occupy reaction sites necessary for the product formation. Stirring and time also increase the rate of dissolution thereby increasing the supersaturation. The initial morphology of the precursor may also greatly contribute to the final morphology because dissolution may be limited, thereby a diffusion mechanism may result. The resultant mechanism could be the diffusion of the soluble species, the structural rearrangement within the precursor, followed by dehydration. The contributions of these variables to the particle morphology will be discussed in detail in the following sections.

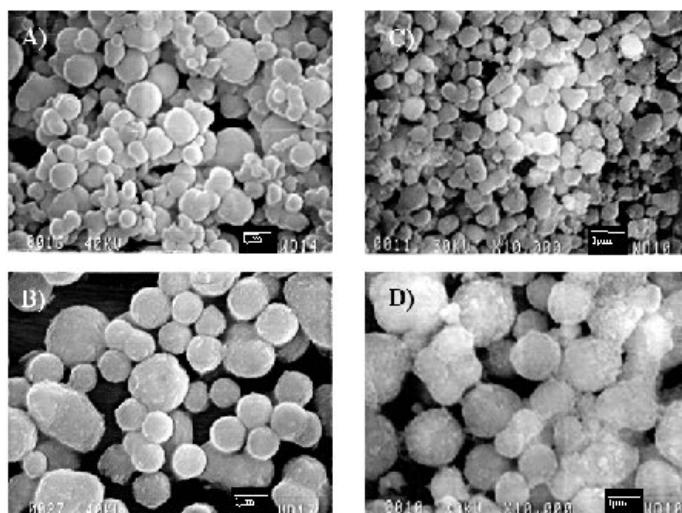
### 9.5.1 Precursor

The initial shape and size of the essentially nondissolving initial precursor reactants (such as  $ZrO_2$  or  $TiO_2$  in the case of zirconates and titanate perovskites) can play an important role in the final morphology and size of the perovskite. These precursors can act as templates for the final product. For example, Choi et al. [28] found that spherical perovskite powders of  $PbTiO_3$ ,  $BaTiO_3$ ,  $SrTiO_3$ ,  $Pb(Zr,Ti)O_3$ ,  $PbZrO_3$ , and  $Ba(Zr,Ti)O_3$  were hydrothermally prepared from precursors of spherical gel powders of hydrous titania and zirconia hydrolyzed from titanium tetrachloride and zirconium oxychloride, lead acetate trihydrate, barium hydrox-

ide, and strontium hydroxide. Hu et al. [37] found that monodispersed microspheres of  $\text{TiO}_2$  under hydrothermal conditions reacted with barium to form  $\text{BaTiO}_3$  with the same size and shape as the initial powders. Similarly, Gersten et al. [20,90] prepared spherical  $\text{PbTiO}_3$  (cf. Fig. 9.7) and  $(\text{Ba},\text{Sr})\text{TiO}_3$  powders (cf. Fig. 9.8) from spherical precursors of hydrous titania. Furthermore, Ohara et al. [51] synthesized  $\text{BaTiO}_3$  from a precursor of fibrous potassium titanate hydrate and barium hydroxide with  $\text{Ba}/\text{Ti}$  molar ratio equal to 1 at 150°C for 24 h. The fibrous potassium titanate was 1 to 10 mm long and 1–100  $\mu\text{m}$  in diameter, whereas the  $\text{BaTiO}_3$  product was 100  $\mu\text{m}$  to 1 mm long and 1–10  $\mu\text{m}$  in diameter composed of fine crystals of average 270-nm size. A similar method was used to prepare fibrous  $\text{PbTiO}_3$  [69].



**Fig. 9.7.** TEM micrographs of (a) and (b) spherical hydrous titania precursor, (c) and (f) partially reacted spherical  $\text{PbTiO}_3$  powder, (d) and (e) fully reacted spherical  $\text{PbTiO}_3$  powder [20]



**Fig. 9.8.** SEM micrographs of precursors of spherical titania with particle size of (a) 1  $\mu\text{m}$ , (b) 1.5  $\mu\text{m}$ , and respective product of  $(\text{Ba},\text{Sr})\text{TiO}_3$  with corresponding particle sizes (c) 1  $\mu\text{m}$ , (d) 1.5  $\mu\text{m}$

### 9.5.2 Temperature

The influence of temperature on the morphology of the perovskite has been demonstrated in preparation of  $\text{BaTiO}_3$  by MacLaren et al. [46] from Ba-acetate, TMAH, and hydrous  $\text{TiO}_2$ ; after 2 h at 120 or 160°C, the particles were round, whereas at 200°C the powder formed a facet on low index planes towards cubic morphology (cube faces parallel to {100} planes). In another study, Xia et al. [61] found a similar progression occurred from spherical clusters at 75°C to cubes or spheres at 400°C after a 4 h reaction with equimolar amounts of  $\text{Ba(OH)}_2$  and  $\text{TiO}_2$ . Kuttty and Balachandran [92] studied the effects of temperature and  $\text{Pb}/(\text{Ti}+\text{Zr})$  molar ratio on the morphology in the precipitation of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  from  $\text{PbO}$ , and on hydrous- $\text{TiO}_2$ - $\text{ZrO}_2$  derived from chlorides after 8 h. The crystallites formed a tabular shape (0.3  $\mu\text{m}$ ) at 300°C with  $\text{Pb}/(\text{Ti}+\text{Zr})$  equal to 1 but were cubic (0.4  $\mu\text{m}$ ) at 400°C with a molar ratio of 1.2. Gelabert et al. [78] found that dendritic growth occurred in the preparation of  $\text{PbTiO}_3$  from homogeneous mixture of precursors. They attributed the growth to inefficient heat dissipation or a high supersaturation. Dendritic growth could be minimized by more accurate temperature control, prevention of thermal gradients by agitation, or incorporation of stronger ligands [78].

### 9.5.3 Reagent concentration

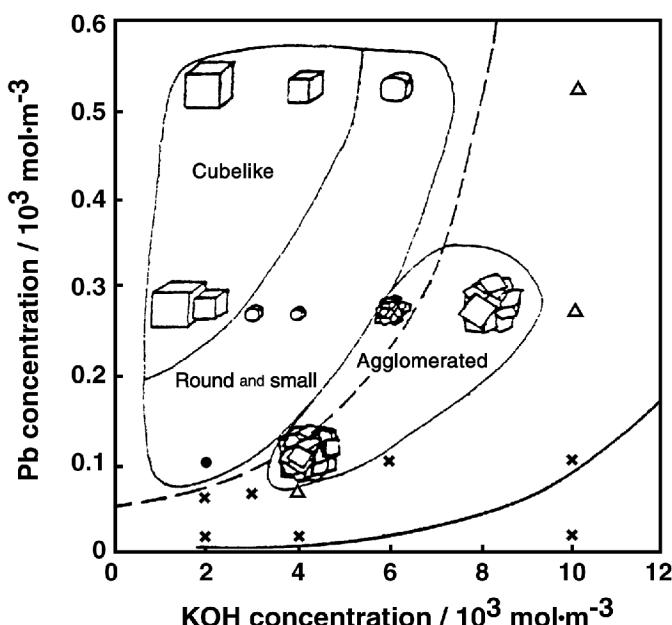
The reagent concentration can significantly change the morphology. For example, Moon et al. [73] found that tabular  $\text{PbTiO}_3$  was produced at 0.05 M feedstock concentrations, whereas cubic particles were prepared at 0.1 M and aggregate tabular particles were synthesized at 0.125 M. The feedstock was Pb-acetate, Ti-isopropoxide acetylacetone, and KOH or NaOH with 1.5 molar ratio of Pb/Ti, and was heated to 150°C for 12 h. Bagwell et al. [26] also found that the concentration of the precursor in the synthesis of  $\text{BaTiO}_3$  influenced the final morphology. As an example, a change in concentration from 1.62 to 0.64 M changed the particle morphology from round to octahedral for particles synthesized at 90°C for 24 hrs from solution containing  $\text{TiO}_2$ ,  $\text{Ba(OH)}_2$ ,  $\text{NH}_3$ , and polymers adsorbed on the  $\text{TiO}_2$  (i.e., polyacrylic acid and polyethylene oxide-block-polymethacrylic acid). This also may be the result of the adsorbed polymers that reduce the surface energy of various growth planes [26].

### 9.5.4 Additives

Polymeric additives such as polyacrylic acid and polyethylene oxide-block-polymethacrylic acid make  $\text{BaTiO}_3$  particles more round [26]. Li and Yao [79] used water-soluble polymers (e.g., PVP, PEG, etc.) as protecting agents during hydrolysis in the preparation of  $\text{PbTiO}_3$  between 180–240°C for 1–4 hours. With the addition of PVP, the powders synthesized were tabular perovskite powders. Under similar synthesis conditions, PEG formed acicular powders of an unknown lead titanate phase. Kutty et al. [44,85,87] and Vivekanandan et al. [60,91] used poly-vinyl-alcohol (PVA) in the synthesis of  $\text{BaTiO}_3$ ,  $\text{BaZrO}_3$ ,  $\text{BaSnO}_3$ ,  $\text{Ba(Sn,Ti,Zr)O}_3$ , and  $\text{CaTiO}_3$ ; they found that the polymer changed the morphology of the growth of the perovskite. For example, irregular, acicular-shaped crystals of  $\text{CaTiO}_3$  formed without PVA, but in its presence rectangular platelets formed [87]. This was attributed to the steric hindrance due to the polymers on the surface of the precursor that prevented aggregation, so that the small particles could be more reactive. Also the polymers could act as growth modifiers on certain habits of the crystals to limit crystal size (and growth directions). In general, the polymer molecular structure may also act as a morphology template for the crystal.

### 9.5.5 Mineralizer type and concentration

The type and concentration of mineralizer was also found to affect the morphology of the powders. In a study conducted by Beal [95] on the synthesis of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  from KBr, KOH, and KF, it was determined that KBr and KOH produced random morphologies (1  $\mu\text{m}$ –10  $\mu\text{m}$  elongated) and KF produced cubic. However, for KF the mineralizer concentration influenced the morphology. With low concentrations, rounded ( $\mu\text{m}$ ) particles grew, while with greater concentrations



**Fig. 9.9.** Schematic representation of the morphology of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  powders synthesized at  $150^\circ\text{C}$  for 4 hours. Solid line and dashed line are for the Pb concentration saturated with  $\text{PbO}$  and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  powder, respectively. Phases of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  ( $\lambda$ ), and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  with other crystalline solids (triangles), and amorphous ( $\times$ ) [99]

cube-like (mm) particles grew [95]. Gelabert et al. [78] also found that the mineralizer concentration influenced the morphology. They found that  $\text{PbTiO}_3$  changed from spherical agglomerates with dendrites at 0.8 M KOH to square platelets with dendrites at 1.2 M KOH. In another study of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , Ichihara et al. [98] formed  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  powders with complicated folded cubes at high concentrations of KOH (4 M) which became dice shaped forms with small folded cubes at low concentrations of KOH (< 4 M). In another study of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , Cheng et al. [97] found that an increase in 1–2 M KOH to 5 M KOH transformed cubic-like particles to a smaller random morphology that formed larger aggregates. In yet another study, Traianidis et al. [101] found that in the synthesis of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  powder from  $\text{Pb}(\text{NO}_3)_2$  and hydrous  $\text{TiO}_2\text{-ZrO}_2$  at  $265^\circ\text{C}$  with  $\text{Pb}/\text{Ti}$  molar ratio equal to 2, after 2 h cubic shaped particles were made with 1 M KOH and turned platelet with KOH concentrations greater than 2 M. Ohba et al. [99] found the morphology conditions of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  were outlined as a function of Pb concentration and KOH concentration (cf. Fig. 9.9). For values between 0.3 and 0.6 m Pb concentration and 2 and 4 m KOH a cubic-like morphology was dominant. For values between 0.1 and 0.2 m Pb and 2 and 6 m KOH a rounded morphology was dominant. For values of 0.1 Pb m and between 4 and 8 m KOH an agglomerated

morphology was dominant. This was found correlated with the solubility of PbO [99]. Zhao [65] suggested that BaTiO<sub>3</sub> formed {111} octahedrons under the high alkaline processing conditions from Ba-hydroxide, and titania (anatase) powder at 90°C under hydrothermal conditions, and suggested this is the only stable surface under these processing conditions.

### 9.5.6 Summary

In summary, the morphology of perovskite powders produced by the hydrothermal method has been shown to be controllable by the initial reagent types, initial reagent concentration, pH, temperature, stir rate, and time that are parameters of the supersaturation. Polymer additives may control the morphology by acting as growth modifiers, steric stabilizer, and/or template. The insoluble precursor may also act as a template assisting to preserve the morphology for the product.

## 9.6 Synthesis Conditions for Controlled Particle Size

The particle size and morphology is also dependent on the supersaturation and the growth mechanism. This can be affected by initial precursor, ratio of precursors, temperature, time, additives, mineralizer type, and mineralizer concentration. Under the mechanism of nucleation and growth, the particle size is expected to decrease with an increase in supersaturation. Therefore, the particle size is expected to decrease with a decrease in temperature and an increase in concentration of soluble species. However, in the presence of slightly soluble species, particle size is expected to increase with an increase in pH (mineralizer concentration) and an increase in reaction time. However, if the reaction proceeds by a diffusion-limited mechanism, the starting size of the precursor should be the main contribution to the final particle size.

Just as expected from nucleation and growth kinetics, the parameters that effect the particle size in the hydrothermal synthesis of BaTiO<sub>3</sub> and SrTiO<sub>3</sub>, were noted by Um, Kumazawa, and others [42,43,56]. These parameters included an increase in size with temperature and time and a decrease with Ba/Ti or Sr/Ti molar ratio and Ba(OH)<sub>2</sub> concentration.

### 9.6.1 Precursor

As discussed previously, the size, shape, and phase of the initial precursor of the mostly nondissolving precursor can greatly influence the resultant product size and shape with almost any perovskite. Hu et al. [37] found that monodispersed microspheres of TiO<sub>2</sub> under hydrothermal conditions reacted with barium to form BaTiO<sub>3</sub> with the same size and shape as the initial powders. Likewise, Gersten et

al. [90] prepared  $(\text{Ba},\text{Sr})\text{TiO}_3$  powders (cf. Fig. 9.8) from spherical precursors of hydrous titania with the same size and shape.

In the hydrothermal preparation of  $\text{BaTiO}_3$  powders from  $\text{Ba}(\text{OH})_2$  and amorphous titania (particle size 0.65  $\mu\text{m}$ ), Kumazawa et al. [42] found that the particle ranged in size from 0.03 to 0.11  $\mu\text{m}$  depending on the hydrothermal conditions. However, when a rutile  $\text{TiO}_2$  precursor (particle size 0.49  $\mu\text{m}$ ) was used in the synthesis, the resultant particles were 0.2–0.7  $\mu\text{m}$ . Similarly, Klee et al. [41] found that powders of  $\text{BaTiO}_3$  prepared from hydrous titania had a higher surface area ( $56 \text{ m}^2/\text{g}$ ) than the particles prepared from titania ( $10.6 \text{ m}^2/\text{g}$ ).

### 9.6.2 Concentration and molar ratio

Concentration can affect the particle size. For example, Moon et al. [72] found that the particle size decreased from 3 mm to 1.5 mm for  $\text{PbTiO}_3$  with an increase in concentration from 0.05 M and 0.1 M feedstocks of Pb-acetate and Ti-acetyl acetone. The molar ratio of the precursors can affect the particle size. In the case of hydrothermally prepared  $\text{BaTiO}_3$ , Wada et al. [59] found that the particle size decreased with increasing Ba/Ti molar ratio of the precursors of Ba-hydroxide and titania; however, above a Ba/Ti molar ratio of 20, the size remained a constant 20 nm. Wada et al. [58] also found that with a different set of precursors using Ba-hydroxide and Ti chelated with nitrilotriacetic acid (NTA) and with a Ba/Ti molar ratio equal to 5, the average particle size of the  $\text{BaTiO}_3$  that formed remained at 19 nm.

### 9.6.3 Mineralizer type and concentration

The mineralizer type or additives of organic materials may stabilize smaller particles by the steric effect. For example, Urek et al. [57] found a smaller particle size for the hydrothermal synthesis of  $\text{BaTiO}_3$  from Ba-acetate, Ti-ethoxide, and TMAH compared with synthesis from Ba-hydroxide, Ti-ethoxide, and ammonia. Similarly, Kutty, Vivekanandan and others [44,85,87,60,91], found that small amounts of poly-vinyl-alcohol (PVA) (0.01–0.05 wt%) decreased the particle size for the preparation of  $\text{BaTiO}_3$ ,  $\text{BaZrO}_3$ ,  $\text{BaSnO}_3$ ,  $\text{Ba}(\text{Sn},\text{Ti},\text{Zr})\text{O}_3$ , and  $\text{CaTiO}_3$ . Kiss et al. [40] also noticed that the addition of isopropyl alcohol for the hydrolysis of Ti-ester in highly alkaline solutions of  $\text{Ba}(\text{OH})_2$  decreased the particle size due to the decrease in polarity of the suspension that hindered the condensation of neighboring particles.

The concentration of mineralizer affects the particle size. In the preparation of  $\text{BaTiO}_3$  from  $\text{NaOH}$ ,  $\text{BaCl}_2$ , and Ti-isopropoxide, Asiaie et al. [25] found that an increase in  $\text{NaOH}$  concentration from 0.003 to 0.005  $m$  increased the particle size from 0.09 to 0.3  $\mu\text{m}$ . In the synthesis of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , Ohba et al. [99] found an increase in the concentration of mineralizer resulted in larger particles as expected from a mechanism of nucleation and growth. Similarly, Beal et al. [95] found that when the concentration of mineralizer was increased and the pH was raised, the particles grew larger.

Dutta and Gregg [31] noticed a decrease in particle size from 1  $\mu\text{m}$  to 0.2  $\mu\text{m}$  of hydrothermally prepared  $\text{BaTiO}_3$  and attributed it to the presence of Cl ion from the synthesis of  $\text{BaCl}_2$ ,  $\text{TiO}_2$ , and  $\text{NaOH}$  compared with the preparation from  $\text{Ba}(\text{OH})_2$ . However, for both syntheses the concentration of Ba and NaOH was kept a constant, 0.25 m and 1 m, respectively, without considering an increase in pH due to an increase in the hydroxide concentration from the  $\text{Ba}(\text{OH})_2$ .

#### **9.6.4 Reaction time**

The particle size of the hydrothermally prepared perovskite was found to increase as a function of time. For example, Asiaie et al. [25] found that  $\text{BaTiO}_3$  particles increased from 0.3 to 0.5  $\mu\text{m}$  by increasing the reaction time from 1 week to 2 weeks.

#### **9.6.5 Temperature**

The crystallite size is affected by temperature. For example, MacLaren et al. [46] studied hydrothermal  $\text{BaTiO}_3$ , and found the powders formed with TMAH, Ba-acetate, and hydrous  $\text{TiO}_2$  after 2 h at 120 and 160°C were 15–50 nm, but were larger at 200°C (the size increase was not noted). Ichihara et al. [98] also found that the grain size of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  prepared by reacting  $\text{Pb}(\text{NO}_3)_2$  with  $\text{ZrOCl}_2$  and  $\text{TiCl}_4$  with 4 M KOH for 4 h decreased from 2–3  $\mu\text{m}$  to 1–2  $\mu\text{m}$  with an increase in reaction temperature from 180 to 200°C. However, Ohba [99] found that an increase in temperature can increase or decrease the size of the  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  particles depending on the synthesis conditions. For example, the particle size increased for an increase in temperature from 150 to 180°C when KOH was 4 m and Pb was 0.1 and 0.275 m. However, the particles became smaller for an increase in temperature from 150 to 180°C when the Pb concentration was 0.5 m and the KOH concentration was 2–4 m [99]. The suggested reason for the change in particle size with respect to conditions is due to the degree of saturation of  $\text{PbO}$ . At higher temperatures, there is a decrease in the degree of  $\text{PbO}$  saturation that results in a decrease in size and a higher degree of agglomeration [99].

#### **9.6.6 Summary**

Particle size has been shown mostly to follow trends expected for supersaturation under the conditions for precipitation. Therefore, as expected with increases in temperature, time, and mineralizer concentration, the particle size increases, but the particle size decreases with an increase in concentration. Any additive that enhances the supersaturation decreases the particle size and vice versa.

## 9.7 Summary

The processing parameters for the synthesis of ferroelectric perovskite powders by the hydrothermal method have been reviewed. In conclusion, the first step in processing of chemically phase pure materials is the thermodynamic verification of the correct processing conditions for the reaction of the desired product. The chemical purity of the precursors should be high, and the pH adjusters or other additives should be decomposable at calcination temperatures. For multicomponent oxides (e.g.,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ), the starting precursors must be intimately mixed. The reaction time must be long enough for complete reaction. The time can be predicted if the mechanism is known, but can be shortened by an increase in concentration or temperature. Knowledge of the supersaturation can be helpful in the control of the morphology and particle size. The supersaturation is influenced by the initial reagent concentration, pH, temperature, stir rate, and time. An increase in supersaturation will result in a decrease in particle size. Therefore, to obtain fine particles, the temperature should be kept at a minimum and the concentration at a maximum. Other variables to keep in mind when trying to produce nano-sized particles are the mineralizer concentration, reaction time, and additives.

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# **10 Crystal Growth, Size, and Morphology Control of Nd:RVO<sub>4</sub> Under Hydrothermal Conditions**

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## **10.1 Introduction**

Growth of solid-state laser host crystals is an attractive field in solid-state science owing to its technological significance. Laser diode pumped solid-state lasers have a wide variety of applications in military, industrial, medical treatment, and scientific fields due to their advantages of high stability, compactness, high efficiency, and long life time and have become one of the frontier areas of research [1]. There exists a large number of solid-state laser host crystals. In this context, the rare earth vanadates are of great interest due to their useful luminescent and magnetic properties [2]. These materials have been employed as highly efficient laser diode pumped microlasers [3], an efficient phosphor [4], and as very attractive polarizer materials [5]. The rare earth vanadates are known as the high temperature materials and their synthesis by any technique insists on high temperature conditions. That is the reason why most of the earlier workers have obtained these laser crystals by flux or melt methods at elevated temperatures [6–9]. In spite of its excellent physical properties, the high-tech applications have not been realized due to crystal growth difficulties. One of the major problems encountered in RVO<sub>4</sub> crystals is the presence of oxygen imperfections (color centers and inclusions) introduced during the crystal growth processes. Although YVO<sub>4</sub> melts congruently [10], certain vanadium oxides vaporize incongruently, causing changes in Y/V ratio and oxygen stoichiometry in the melt. These undesired effects could generate additional phases and oxygen defects in YVO<sub>4</sub> crystals especially those grown from the melt [11]. Efforts to eliminate these defects did not yield significant success in the flux and melt techniques. Rubin and Van Uitert (1966) were the first to obtain large bulk crystals of Nd:YVO<sub>4</sub> using the Czochralski (Cz) technique [12]. But problems related to the oxygen deficiency and inclusions could not be eliminated. This is emphasized by the numerous reports of Cz growth [12–14] and

other melt growth methods like Verneuil [15], modified floating zone [16,17], laser heated pedestal growth [18,19], and Bridgman [13]. The flux growth experiments did not yield adequate results due to inclusion and size problems. The hydrothermal method was not attempted to grow these crystals and it might be due to the fact that their growth insists on high temperature and high-pressure conditions and also, a strong belief that their growth under mild hydrothermal conditions will introduce water into the structure or interstices. There is a growing tendency in recent years to obtain crystals under mild hydrothermal conditions. The method involves the use of aqueous solvent or mineralizers under lower temperature and pressure to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions.

The hydrothermal method has an advantage over the earlier methods because of its suitability and perfection in obtaining a desired polymorphic modification. It is well known that in vanadate crystals grown at much higher temperature, there is a rapid fall in the fluorescent lifetime because of various physical defects.

This motivated the present authors to obtain rare earth vanadates under lower pressure and temperature conditions by the hydrothermal method. Detailed studies of the growth mechanism, role of pH, morphology control, X-ray diffraction, and luminescent properties are discussed here.

## 10.2 Technologically Important Vanadates

The synthesis of vanadates began in the 19th century [20]. In recent years several new rare earth vanadates have been reported from time to time. Among these, Nd:YVO<sub>4</sub> and Nd:GdVO<sub>4</sub> are the prominent ones. YVO<sub>4</sub> was first synthesized by Goldschmidt and Harldsen in 1928 [20]. However, the growth of Nd:YVO<sub>4</sub> crystals of high optical quality encounters a lot of difficulties, which hinder their application. Nd:GdVO<sub>4</sub> crystal was first introduced by Zagumennyi et al. (1992) as a new laser material [21]. This material offers large effective absorption and emission cross-sections coupled with a relatively broad absorption line. The laser performance is expected to be much more tolerant to diode wavelength variation than Nd:YAG, and is therefore an interesting material for future applications [22–25].

## 10.3 Phase Equilibria

The study of the phase equilibria of a given system helps to understand the phases crystallizing and their crystallization boundaries. This is one of the first and foremost requirements for the successful growth of any compound in the form of single crystals. Failures in the growth of single crystals are largely due to the lack of phase equilibria data for the corresponding systems and also the growth technology. Although the study of vanadate systems started as far back as the 1950s, the systems bearing V<sub>2</sub>O<sub>5</sub> studied up to now are the following: Y<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> [10], Y<sub>2</sub>O<sub>3</sub>-

V<sub>2</sub>O<sub>5</sub>-V<sub>2</sub>O<sub>3</sub> [26], and Y<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5-y</sub> [27]. It is known that among the vanadium oxides V<sub>2</sub>O<sub>5</sub> has the highest equilibrium O<sub>2</sub> partial pressure, while V<sub>2</sub>O<sub>3</sub> has the lowest. V<sub>2</sub>O<sub>3</sub> is the most stable form in the V<sub>2</sub>O<sub>5</sub>-V<sub>2</sub>O<sub>3</sub> system, and is the only congruently vaporizing phase. Other vanadium oxide phases vaporize incongruently, transforming in a stepwise manner into V<sub>2</sub>O<sub>3</sub>. Since high-temperature systems containing V<sub>2</sub>O<sub>5</sub> always have intermediate vanadium oxide phases, it is more appropriate to consider Y<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> as a ternary system Y<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub>-V<sub>2</sub>O<sub>3</sub> [18]. Although an equilibrium phase diagram cannot be constructed due to the incongruent vaporization of the metastable vanadium oxides, a ternary depiction of the quasi-equilibrium system representing the various yttrium-vanadium compounds involved is useful for better understanding of the processes. Figures 10.1 and 10.2 show the binary and ternary systems of YVO<sub>4</sub> [10,26]. The phase relations can be interpreted through the ternary system (Fig. 10.2) where the direction of melt composition modification is indicated by a small arrow. Although a number of black YVO<sub>4-x</sub> phases have not yet been identified precisely, the existence of a minimum of two kinds of black crystal phases along the YVO<sub>4</sub>-YVO<sub>3</sub> line has been confirmed.

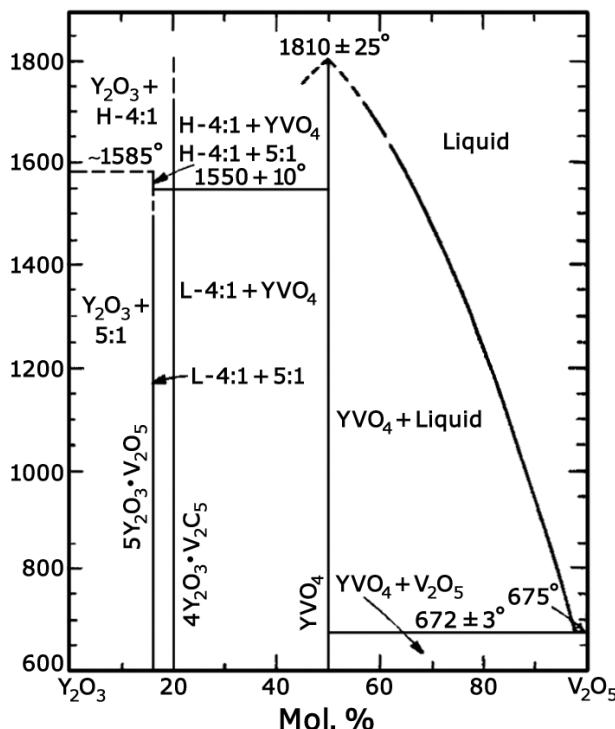
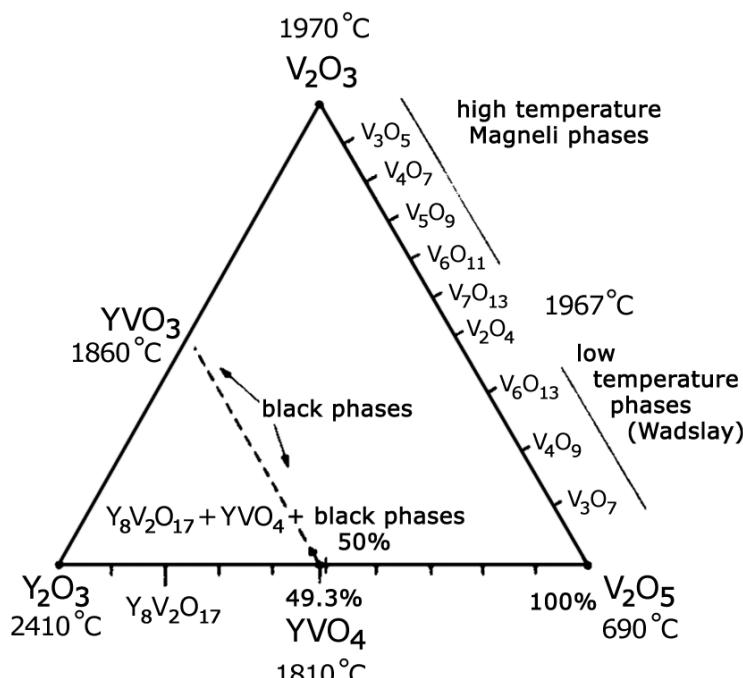


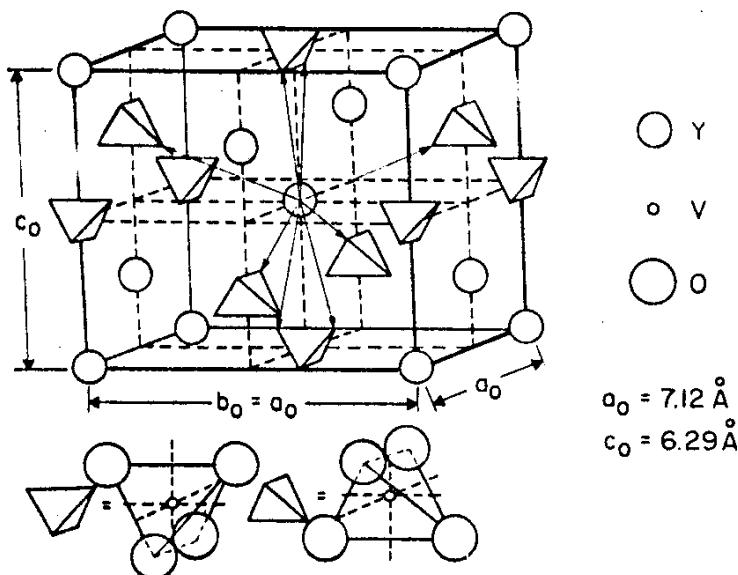
Fig. 10.1. Y<sub>2</sub>O<sub>3</sub> - V<sub>2</sub>O<sub>5</sub> binary system [10]



**Fig. 10.2.**  $\text{Y}_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{V}_2\text{O}_3$  ternary system [26]

## 10.4 Structure of Nd:RVO<sub>4</sub>

RVO<sub>4</sub> belongs to a large family of tetragonal compounds with the I4<sub>1</sub>/amd space group [28]. The rare earth ions occupy the positions with D<sub>2d</sub> symmetry and the vanadium ions have tetrahedral symmetry. Theoretically, rare earth ions in these compounds are trivalent and the valency of vanadium ions is equal to five. Therefore, the external electronic configuration of rare earth ions can be ascribed to 4f<sup>n</sup> 5s<sup>2</sup>5p<sup>6</sup> and the vanadium ions to 3p<sup>6</sup>. The rare earth bonds are realized by the 6s and 5d orbitals because of the fact that 4f and 5d levels are energetically close to each other and 4f-5d electronic transfers may take place. Energetic separations between 4f and 5p levels are in the range of 20 eV. Then the 4f electrons participate in the chemical bonds. The values of the lattice parameters of RVO<sub>4</sub> crystals are close to 7.2 Å (*a* parameter) and 6.35 Å (*c* parameter). Both parameters decrease with the atomic number of the rare earth ion. The tetragonal unit cells containing four YVO<sub>4</sub> molecules are shown in Fig. 10.3. The principal structural unit of YVO<sub>4</sub> is a chain of alternating edge sharing VO<sub>4</sub> tetrahedra and YO<sub>8</sub> polyhedra,



**Fig. 10.3.** Tetragonal unit cell of YVO<sub>4</sub>. VO<sub>4</sub> arrangements are represented by schematic tetrahedra: eight arrows indicate oxygen positions around the central Y of the YO<sub>8</sub> polyhedron [28]

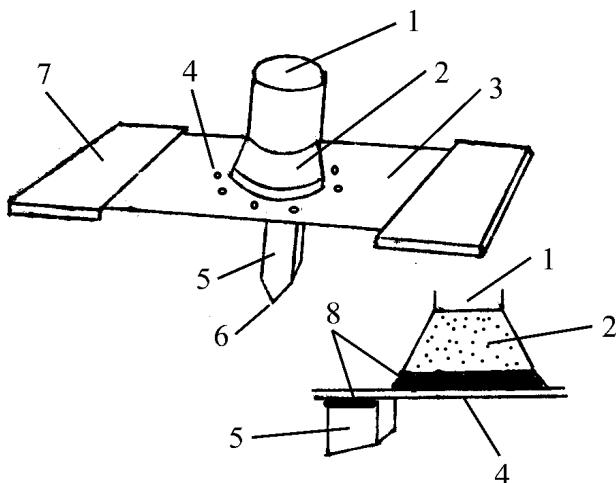
which can be best described as a triangular dodecahedron [29]. Two edges are shared with VO<sub>4</sub> groups and four with dodecahedra. Nevertheless, 12 (8+4) edges are unshared. The chains are joined laterally by the edge sharing YO<sub>8</sub> dodecahedra, causing specific cleavage characteristics in YVO<sub>4</sub> crystals [29].

## 10.5 Synthesis and Growth of Rare Earth Vanadates

The methods used in the synthesis and growth of rare earth vanadates are discussed below.

### 10.5.1 Zone melting

Good quality rare earth orthovanadate crystals have been prepared by the relatively inexpensive method of zone melting with dynamic immersion by means of an iridium plate heater [16,17]. The growth of rare earth vanadates by this technique is a complex combination of physicochemical incongruent evaporation and crystallization from a multicomponent Y<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> system. The process requires a careful maintenance and control of oxygen partial pressure.

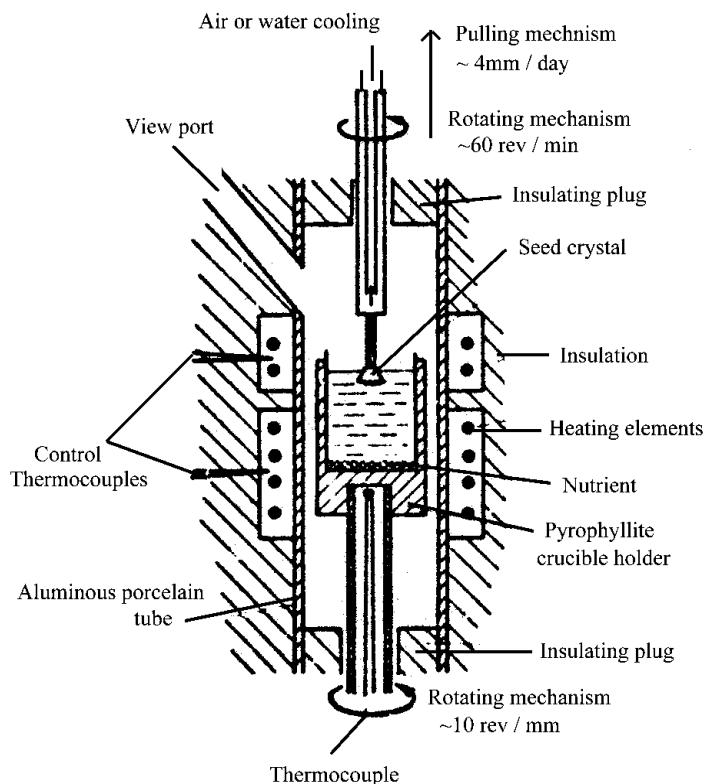


**Fig. 10.4.** Experimental set up for zone melting [17]: (1) polycrystalline feed rod, (2) rod section impregnated by the melt, (3) opening for melt passage, (4) iridium plate, (5) crystal, (6) seed crystal, (7) platinum leads, (8) melt

The single crystal synthesis was carried out in a universal vacuum/compression chamber (type T-935) constructed by the Kharkov Physicotechnical Institute of the Academy of Sciences of the Ukrainian SSR. A  $8.0 \times 1.4 \times 0.05$  cm iridium plate was fastened to water-cooled copper leads (Fig 10.4). The chamber was first evacuated under oxygen partial pressure control followed by admission of argon to yield a total pressure equal to atmospheric pressure. Pentavalent vanadium is known to be unstable at high temperature [30,31]. So the initial composition obviously becomes enriched with  $V_2O_5$  due to the selective volatility of vanadium oxides. The crystal develops colors immediately during and after growth varying from a light honey yellow to a dark brown. Therefore, preparation of colorless crystals evidently requires tighter control as to oxygen partial pressure, excess  $V_2O_5$ , and geometric parameters of the molten zone, along with its rate of movement.

### 10.5.2 Czochralski technique

Rare earth vanadates were obtained by the Czochralski technique of pulling from the melt [32,33]. For high melting oxides, iridium crucibles are generally used to hold and directly or indirectly heat the melt. The heating arrangements are such that the central region of the surface of the melt is its coolest part. For vanadates, the melt is not stable under atmospheric conditions. Temperature in excess of 2000°C is required to keep the material molten. At these temperatures, there is a continuous evolution of oxygen from the depths of the melt. The crystals are annealed for 12 hours to remove any discoloration.



**Fig. 10.5.** Pulling furnace [32]

Though this method produced the layered and relatively highest quality crystals, oxygen loss and inclusion problems could not be eliminated [30,34]. The crystals grown by the conventional Cz method exhibited severe spiral growth, which retarded the continuing growth; no more than 20% of the melt was consumed at the onset of spiral growth. However, nearly 50% of the melt was consumed for the growth without a spiral mode [3]. The schematic diagram of the pulling furnace is shown in Fig. 10.5.

### 10.5.3 Flux growth

The flux method is popular to grow rare earth vanadates [35]. It can be defined as high temperature solution growth, which allows the growth of materials in the form of single crystals of sufficiently large size. The experiments were carried out in a specially designed crystallization chamber. The crucible-containing nutrient

**Table 10.1.** Starting Composition and Experimental Conditions for the Growth of Nd:RVO<sub>4</sub> under Flux Growth

Nutrient	Flux	Initial temp [°C]	Duration [h]	Final temp [°C]	Compound	Ref.
Y <sub>2</sub> O <sub>3</sub> + Nd <sub>2</sub> O <sub>3</sub>	PbO + V <sub>2</sub> O <sub>5</sub> + PbF <sub>2</sub>	1350	20	1000	Nd:YVO <sub>4</sub>	[36]
Dy <sub>2</sub> O <sub>3</sub> + Nd <sub>2</sub> O <sub>3</sub>	PbO + PbF <sub>2</sub> + V <sub>2</sub> O <sub>5</sub>	1350	20	950	Nd:DyVO <sub>4</sub>	[37]
Gd <sub>2</sub> O <sub>3</sub> + Nd <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> O <sub>3</sub> + V <sub>2</sub> O <sub>5</sub>	1320	14	950	Nd:GdVO <sub>4</sub>	[38]
Pr <sub>2</sub> O <sub>3</sub> + Nd <sub>2</sub> O <sub>3</sub>	PbO + V <sub>2</sub> O <sub>5</sub>	1360	12	980	Nd:PrVO <sub>4</sub>	[39]

Cooling rate = 1°C/h

material was placed inside the crystallization chamber. The mixture was heated up to 1200°C at the rate of 300°C/h and held for 20 to 24 hours until the complete dissolution of the oxide took place. Later on, the temperature was slowly decreased at the rate of 1°C/h up to 800°C followed by a fast cooling. The crystals obtained were cleaned using hot dilute 1:5 HNO<sub>3</sub>.

In most of the experiments, lead vanadate (Pb<sub>2</sub>V<sub>2</sub>O<sub>7</sub>) was used as the flux agent rather than bismuth vanadate. Although, this method gives fairly good quality crystals, the method lacks popularity because of:

- Difficulties in maintaining the oxygen stoichiometry and controlling the loss of vanadium oxide,
- The presence of mixed phases,
- The presence of ions of the flux impurities in the crystals,
- Problems in removing flux agents.

YVO<sub>4</sub> melt continuously transforms into a multiphase system during the growth process, since undesired Y<sub>8</sub>V<sub>2</sub>O<sub>17</sub> and black YVO<sub>4-x</sub> ( $0 < x \leq 1$ ) phases are formed by incongruent vanadium oxide vaporization [26].

#### 10.5.4 Top seeded solution growth (TSSG)

Rare earth vanadate single crystals were grown using lithium meta vanadate (LiVO<sub>3</sub>) flux, dissolved and purified in hot water. Since LiVO<sub>3</sub> has excellent water solubility, its dissolution in water and subsequent filtering and drying minimized impurities in TSSG. The TSSG pulling rate was approximately 0.02 mm/h.

The UV absorption edge of RVO<sub>4</sub> crystals grown by Cz and TSSG was compared by Erdei et al. (1997) [40]. TSSG–RVO<sub>4</sub> crystal grown from LiVO<sub>3</sub> flux has a broader optical transmittance in UV than the Cz crystal, implying that the TSSG–YVO<sub>4</sub> has better Y–V–O stoichiometry than the Cz crystal. Since, the crystal grown by this method is at 1800°C, appearance of the metastable phase relations, precipitates, and oxygen deficiency could not be eliminated.

Thus the rare earth vanadates obtained by flux, Cz, TSSG, zone melting belong to high temperature growth techniques and are relatively poor in crystal quality. This prompted the present authors to an alternative technique, wherein most of these problems have easily been overcome.

In spite of a very long history behind the development of the hydrothermal technique and its adoptability to modern technological requirements, still it remains as a recent technique, especially for the growth of vanadates.

## 10.6 Solubility Study

This is one of the most important aspects of the hydrothermal growth of crystals. Due to the lack of proper data on the type of solvents, the solubility and solvent-solute interaction, the hydrothermal growth of a specific compound initially failed. Despite the large amount of literature data available, still it is a highly attractive field in hydrothermal research not only for crystal growers, but also for the corrosion scientists, hydro metallurgists, geoscientists, and so on. Unfortunately, most of the studies have been performed only at the saturated vapor pressure of the system and very few combined high-temperature high-pressure experiments have been designed to yield thermodynamical data.

The real hydrothermal solutions are different from the ideal solutions and their understanding relies upon the knowledge of the influence of the solvent in the process of dissolution and crystallization of various compounds. Obviously, as shown in most of the experiments, the type of solvent and its concentration determine the specific hydrothermal process and its important characteristics, such as the solubility of the starting materials, quantity of the phases, their composition, output of the phases, kinetics, and growth mechanism of single crystals.

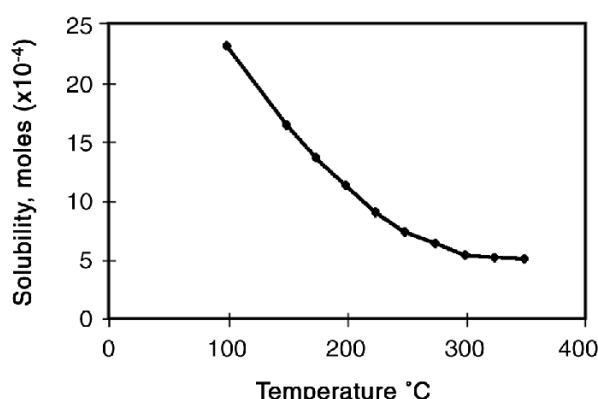
The synthesis of a specific compound is carried out using different solvents on the basis of physicochemical considerations. The following conditions are adopted in selecting the most suitable mineralizers:

1. Congruence of the dissolution of the test compounds
2. A fairly sharp change in the solubility of the compounds with changing temperature or pressure
3. A specific quantitative value of the absolute solubility of the compound being crystallized
4. The formation of readily soluble mobile complexes in the solution
5. A specific redox potential of the medium ensuring the existence of ions of the required value.

Besides, the solvent should have a desired viscosity, insignificant toxicity, and very weak corrosion activity with respect to the apparatus. These factors may fulfil the requirement of the hydrothermal mineralizers in addition to determining the values of solubility of the compound under investigation.

A successful growth of any crystal relies on the availability of solubility data. In fact, the earlier workers did not attempt the hydrothermal growth of rare earth

vanadate crystals due to the lack of solubility data on these compounds. The authors [41] carried out a systematic study of the solubility of Nd:RVO<sub>4</sub>. Several mineralizer solutions like HCl, HNO<sub>3</sub>, HCOOH, H<sub>2</sub>SO<sub>4</sub>, NaOH, NaF, and NH<sub>4</sub>Cl were tried. Since the Nd:RVO<sub>4</sub> compounds did not have any solubility data under hydrothermal conditions, the authors have selected the solvents on the empirical basis and found that Nd:RVO<sub>4</sub> shows good solubility essentially in the acidic solvents. However, HCl or HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> or HCOOH alone did not show considerable solubility. The resultant products obtained were essentially fine crystalline mass without any morphology. It is interesting to note that the use of alkaline solvent did not result in the crystallization of rare earth vanadates, but instead rare earth hydroxides, R(OH)<sub>3</sub>, or hydrous rare earth vanadates, RVO<sub>4</sub>•nH<sub>2</sub>O (where R = rare earths) were formed. These results provided a stimulus for the authors to carry out the growth of M:RVO<sub>4</sub> (where M = Nd, Eu; R = Y, Gd) using mainly the acidic solvents. The use of a single acid solvent with a varying molarity did not substantially enhance the solubility. Therefore, attempts were made to use the mixed acid mineralizers. The acids like HCl+HNO<sub>3</sub>, HCl+HCOOH, HNO<sub>3</sub>+HCOOH were mixed in different molarity and ratios in order to find the most suitable mineralizer for Nd:RVO<sub>4</sub>. The solubility measurements were carried out by the weight loss method. Here a crystal is kept in equilibrium with an appropriate solution at the desired pressure and temperature conditions for a period of time greater than that necessary to establish equilibrium. All the solubility measurements were carried out in Morey type autoclaves. The experimental temperature to study the solubility was up to 350°C. Nd:RVO<sub>4</sub> shows negative solubility. The enthalpy of dissolution calculated from an Arrhenius plot, log S vs. 10<sup>3</sup>/T, for Nd:YVO<sub>4</sub> was found to be 16.345 kJ /mole. The solubility of Nd:RVO<sub>4</sub> has been studied with reference to temperature, pressure, concentration of the solution, and so forth. The corresponding solubility curves are represented in Figs. 10.6–10.8. The study of the complexation process with reference to the solvent–solute interaction is of great importance in understanding the crystallization of rare earth



**Fig. 10.6.** Solubility curve of Nd:RVO<sub>4</sub> in 1.5 M HCl + 3.0 M HNO<sub>3</sub>

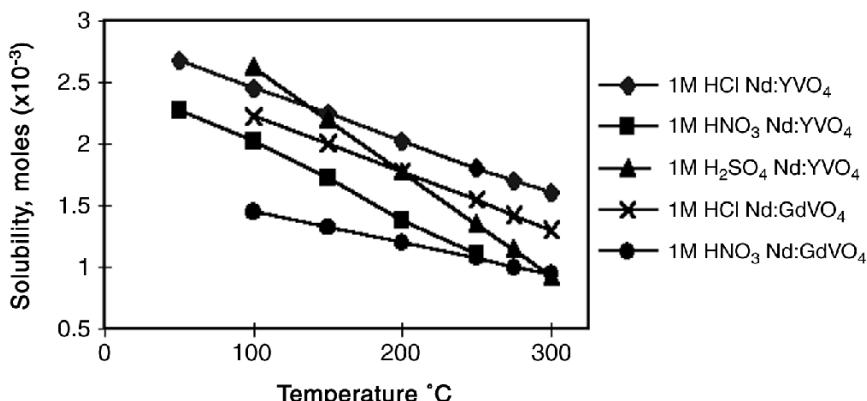


Fig. 10.7. Solubility of Nd:RVO<sub>4</sub> in different solvents

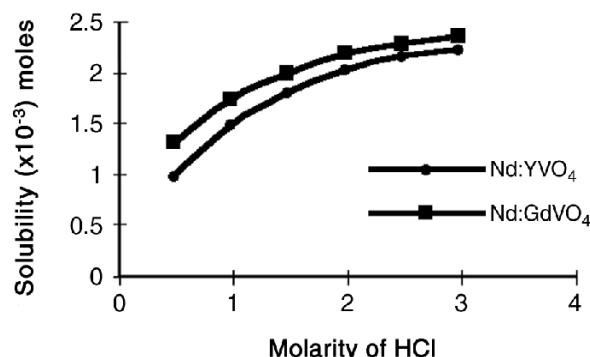


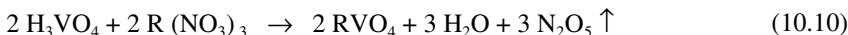
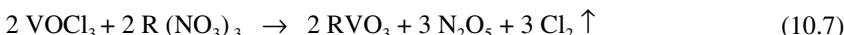
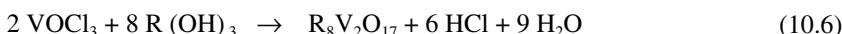
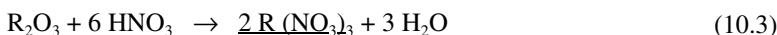
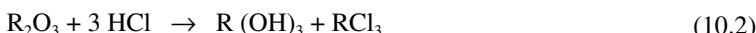
Fig. 10.8. Solubility curves for Nd:RVO<sub>4</sub> in HCl

vanadates. Reports on such studies are seldom found in the literature for rare earth vanadates. The authors [42] have made an attempt to study the solvent-solute interaction, complexation, and related physicochemical aspects of crystallization.

In the experiments to grow Nd:RVO<sub>4</sub> (where R = Y, Gd) crystals, concentrated HCl and HNO<sub>3</sub> were used as the solvent. Con. HCl and Con. HNO<sub>3</sub> (1.5 M : 3.0 M) in the ratio 2:1 is the best solvent to grow Nd:YVO<sub>4</sub>. Con. HCl and Con. HNO<sub>3</sub> (1.0 M : 1.0 M) in the ratio 1:2 is the best solvent for Nd:GdVO<sub>4</sub>.

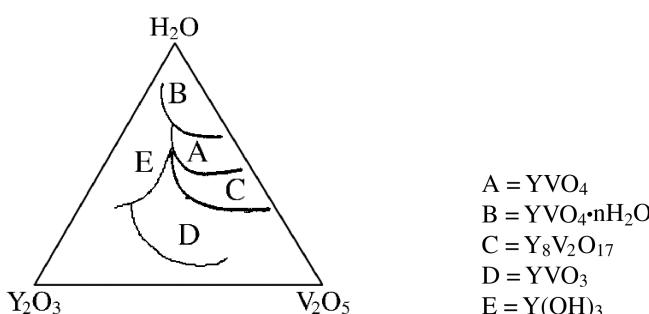
The choice of the solvent was determined by the solubility of the components of the most complex equilibrium systems. The solvent and solute are essentially linked by the coordination type and hence varied complexes of independent existence occur. In the complex systems considered here, consisting of more than four components, it is extremely difficult to precisely understand the formation of such coordination compounds and the interpretation given here is based on the compositions of the starting materials. The hard bases H<sub>2</sub>O, OH<sup>-</sup>, NO<sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> act in de-

terminating the solubility of the final resultant stable complex [43]. The following reaction series can be proposed for the formation of Nd:RVO<sub>4</sub> (R = Y, Gd):



Note: Underlined formulas represent the solid precipitation

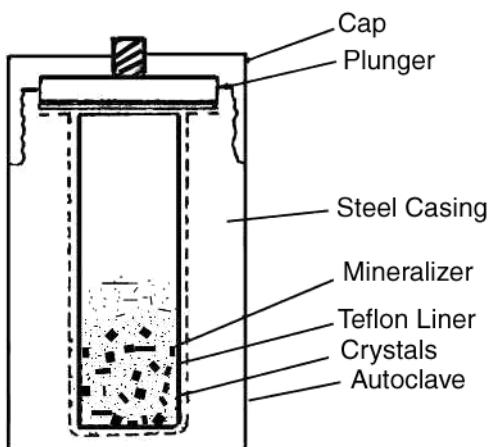
It is further presumed that the formation of a stable complex, Nd:RVO<sub>4</sub> at 240°C and 100 bars pressure must have undergone several intermediate stages of solvation, forming stable and unstable solvated complexes, at different temperatures (room temperature to 240°C) and pressures between 1 bar and 100 bars. It is not possible to write precisely all the intermediate stages of solvation taking place in such a complex system. Figure 10.9 is the composition diagram showing the crystallization boundaries. In general the crystallization fields for various phases are rather narrow, and a slight change in the nutrient will give rise to other phases shown in the diagram.



**Fig. 10.9.** Composition diagram for Y<sub>2</sub>O<sub>3</sub> – V<sub>2</sub>O<sub>5</sub> – H<sub>2</sub>O system at T = 240°C and 60% fill

## 10.7 Crystal Growth

The authors [43] have obtained Nd:RVO<sub>4</sub> crystals under hydrothermal conditions using Morey type autoclaves provided with teflon liners of capacity 25 ml. The use of teflon liners has helped in overcoming the entry of inclusions from the autoclave material. Figure 10.10 shows the schematic diagram of the hydrothermal autoclave used in the present work. The starting materials such as R<sub>2</sub>O<sub>3</sub> (where R = Y, Gd), V<sub>2</sub>O<sub>5</sub>, and Nd<sub>2</sub>O<sub>3</sub> were taken in appropriate proportions in teflon liners. A suitable mineralizer solution of known concentration was added into the teflon liners and the entire mixture was stirred well until a homogeneous and less viscous solution was obtained. The temperature was kept constant at 240°C and the pressure generated depended on the fill (usually 50–60%). The pH of the growth medium was measured before and after each experiment and crystallization was carried out through spontaneous nucleation. Hence, an effort was made to reduce the number of nucleation centers by increasing the temperature of the crystallization reactor slowly at the rate of 10°C/h up to 100°C and beyond at the rate of 3°C/h. The nutrient materials were held at 240°C for a period of 3 days without any fluctuations in the temperature. From the fourth day onwards the temperature fluctuation to the tune of ±10°C to ±20°C was introduced periodically in order to reduce the number of nucleation centers. By this means, small crystallites, which had developed earlier, dissolve leaving only bigger crystallites to grow. The authors [8] had previously employed an oscillating temperature technique to obtain bigger crystals (3 × 0.5 × 7 mm) of yttrium orthovanadates from high temperature solution. In these experiments, it was observed that as the size of the crystal increases, the crystal quality reduces (4.2 × 4.2 × 4 mm).



**Fig. 10.10.** Schematic diagram of the hydrothermal autoclave

**Table 10.2.** Experimental Conditions for the Growth of Nd: YVO<sub>4</sub> Crystals

Sl. No	Nutrient Composition	Mineralizer	P/bar	% fill	pH [i]	pH [f]	Size [mm]	Remarks
1.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	0.75 M HCl: 1.5 M HNO <sub>3</sub> 2:1	100	60	0.33	0.39	—	amorphous powder
2.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	0.75 M HCl: 0.75 M HNO <sub>3</sub> 2:1	100	60	0.30	4.70	0.1–0.25	tiny plate-like thin crystals
3	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 10 wt% 1:2	1.0 M HCl: 2.0 M HNO <sub>3</sub> 2:1	100	60	0.25	5.20	0.5–1.0	bulk crystals, plate-like, hexagonal
4.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 10 wt% 1:2	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	100	60	0.18	4.12	1.0–1.5	bulk crystals, plate-like, rhombohedral, thicker crystals
5.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	130	80	0.13	4.09	1.5–2.5	well developed, plate-like, rhombohedral, thicker crystals
6.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 10 wt% 1:2	2 M HCl: 4 M HNO <sub>3</sub> 2:1	100	60	0.08	3.02	2.5–3.0	irregular shaped thicker crystals
7.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	123	75	0.05	2.56	1.0–2.0	light brown, thick, not well developed, crystals
8.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.0 M HCl: 1.0 M HNO <sub>3</sub> 2:1	115	70	0.03	1.56	0.5–1.0	tiny irregular, light brown crystals
9.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	0.5 M HCl: 1.0 M HNO <sub>3</sub> 2:1	115	70	0.01	0.46	—	crystalline powder

T = 240°C, t(duration) = 8 days, pH (i) = initial, pH (f) = final

The rare earth concentrations are in the range 3–10 wt%. After the experimental run, the autoclaves were quenched initially using an air jet and then water, and the products were washed thoroughly in distilled water and ultrasonic cleaner to separate single crystals from the solution. The products obtained were well-faceted single crystals of 0.1 to 4 mm size. Tables 10.2 and 10.3 give experimental conditions for the growth of Nd:RVO<sub>4</sub> crystals.

**Table 10.3.** Experimental Conditions for the Growth of Nd: GdVO<sub>4</sub> Crystals

Sl. No	Nutrient Composition	Mineralizer	t [days]	pH [i]	pH [f]	Size [mm]	Remarks
1.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.0 M HCl: 1.0 M HNO <sub>3</sub> 1:1	8	0.01	0.50	—	amorphous powder
2.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.5 M HCl: 1.5 M HNO <sub>3</sub> 2:1	8	0.03	1.42	—	very fine crystalline powder
3	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.0 M HCl: 2.0 M HNO <sub>3</sub> 1:2	6	0.05	3.02	0.5–1.0	bulk plate-like, hexagonal crystals
4.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.5 M HCl: 1.5 M HNO <sub>3</sub> 1:2	8	0.14	3.15	1.0–1.5	bulk crystals, small plate-like, rhombohedral
5.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	0.75 M HCl: 1.5 M HNO <sub>3</sub> 1:2	6	0.23	3.35	1.5–2.5	bulk crystals, plate-like, hexagonal
6.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.0 M HCl: 1.0 M HNO <sub>3</sub> 1:2	8	0.30	3.73	2.5–3.0	plate-like, rhombohedral, thick crystals
7.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	0.75 M HCl: 0.75 M HNO <sub>3</sub> 1:2	8	0.38	3.90	1.0–2.0	bulk plate-like, rhombohedral
8.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	1.5 M HCl: 0.75 M HNO <sub>3</sub> 1:2	8	0.46	2.90	0.5–1.0	bulk plate-like, rhombohedral
9.	Gd <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2	0.75 M HCl: 0.75 M HNO <sub>3</sub> 1:2	8	0.50	1.90	—	fine crystalline powder

T = 240°C, P = 100 bars, pH (i) = initial, pH (f) = final

Here, the nutrient materials were taken directly in the teflon liners. The size of the crystals obtained was not more than 3 mm. R<sub>2</sub>O<sub>3</sub>+V<sub>2</sub>O<sub>5</sub>+Nd<sub>2</sub>O<sub>3</sub> interact first with each other in the presence of a mineralizer to form Nd:YVO<sub>4</sub>. Here structural units/growth units are formed first, followed by the further interaction of these growth units with the mineralizer to from bulk growth units or single crystals.

Table 10.4 gives experimental conditions for the growth of Nd:YVO<sub>4</sub> crystals using sintered nutrient. The starting materials such as Y<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Nd<sub>2</sub>O<sub>3</sub> were taken in an appropriate ratio (with a slight surplus of V<sub>2</sub>O<sub>5</sub>) and sintered at 900°C for 24 hours in a nitrogen atmosphere. In such a nutrient the Nd:YVO<sub>4</sub> structural

**Table 10.4.** Experimental Conditions for the Growth of Nd: YVO<sub>4</sub> Crystals Using Sintered Nutrient

Sl. No	Nutrient Composition	Mineralizer	P/bar	% fill	pH [i]	pH [f]	Size [mm]	Remarks
1.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	0.5 M HCl: 1.0 M HNO <sub>3</sub> 2:1	90	55	1.1	1.4	—	amorphous powder
2.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	1.0 M HCl: 1.0 M HNO <sub>3</sub> 2:1	100	60	0.9	2.01	0.25–0.5	small, light brown, cubic crystals
3	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 10 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	115	70	0.58	2.78	1.0–1.5	bulk crystals, small hexagonal, thick crystals
4.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	115	70	0.42	3.21	1.5–2.0	light brown, well developed, hexagonal, thick crystals
5.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	115	70	0.31	3.83	2.0–2.5	small plate-like, rhombohedral, thicker crystals
6.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	1.5 M HCl: 3.0 M HNO <sub>3</sub> 2:1	115	70	0.15	4.10	2.5–3.5	well developed, plate-like, rhombohedral, light brown, thick crystals
7.	Y <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub> Nd <sub>2</sub> O <sub>3</sub> – 5 wt% 1:2.5 H <sub>2</sub> O <sub>2</sub> 1 ml	1.5 M HCl: 1.5 M HNO <sub>3</sub> 2:1	115	70	0.04	4.73	3.0–4.2	light brown, thicker crystals, plate-like, rhombohedral

T = 240°C, t (duration) = 8 days, pH (i) = initial, pH (f) = final

units pre-exist. During the crystal growth process under hydrothermal conditions, these structural units directly interact with the mineralizer solution at a higher growth rate. This facilitated the present authors to obtain fairly large size single crystals (4.2 × 4.2 × 4 mm) through a spontaneous nucleation process. If these large crystals are used as seed crystals, we can grow large crystals (size up to 1 cm) of rare earth vanadates under mild hydrothermal conditions. Such work would facilitate the growth of large high quality single crystals under milder hydrothermal conditions without going into the high temperature solution or melt techniques.

## 10.8 Morphology

The study of morphology is an important aspect in crystal growth, particularly in crystals carrying device potential. It also helps to understand the defects in crystals and their growth mechanism. The defects are directly revealed by the micro- and macro-morphology of crystals. The slowest growing faces having the lowest surface energy determine the habit of a crystal. A number of factors such as degree of supersaturation, type of solvent, pH of the mineralizer, and so forth affect the habit of a crystal.

The morphological analysis of these Nd:RVO<sub>4</sub> crystals show platelike, pseudo-cubic, or hexagonal habits. The size of the crystals varies from 0.1 to 4.2 mm from a typical experimental run of 8 days duration. The crystal faces are very well developed with highly polished surfaces in most of the cases and vitreous luster. The morphological forms of Nd:RVO<sub>4</sub> mainly depend upon the % fill, molarity of the mineralizer, and pH of the media (Figs. 10.11 to 10.15).

Figures 10.11 and 10.12 clearly show how the growth rate changes with pH of the growth media. As pH increases, the crystal morphology also varies. As evident from Table 10.5, plate-like rhombohedral Nd:YVO<sub>4</sub> crystals were obtained in the pH range 0.15 to 0.30 and Nd:GdVO<sub>4</sub> in the range 0.25 to 0.40. As pH increases, the morphology and also the growth rate of the crystals decline.

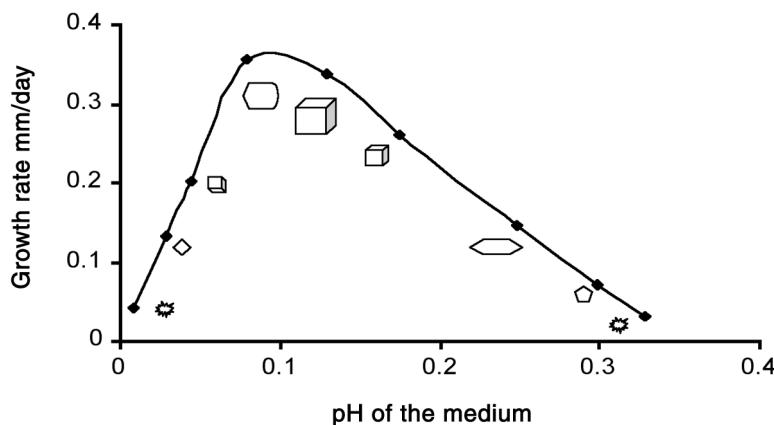
Figures 10.13 and 10.14 show the variation of morphology with pressure. As the pressure increases, morphology of rare earth vanadates changes from hexagonal plate-like to rhombohedral shape and also the growth rate increases. As the pressure increases beyond 125 bars, irregular shaped crystals are obtained.

Figure 10.15 shows morphology variation with pH for Nd:YVO<sub>4</sub> crystals obtained using sintered nutrient. The growth rate gradually decreases as the pH of the medium increases. The growth rate increases as the reaction involves direct interaction of Nd:YVO<sub>4</sub> with mineralizer. Figure 10.16a shows the characteristic photograph of Nd:YVO<sub>4</sub>. When the initial pH is 0.25 in 1 M HCl + 2 M HNO<sub>3</sub> (2:1) solution, Nd:YVO<sub>4</sub> crystallizes as hexagonal platelets. Crystals are honey yellow colored with a vitreous surface. Figure 10.16b shows the characteristic

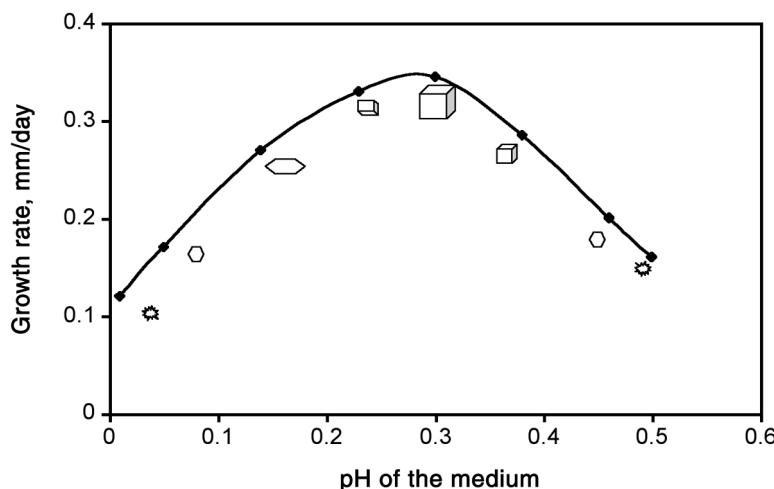
**Table 10.5.** Morphology of Rare Earth Orthovanadates

Composition	Initial pH	Common faces	Growth rate
Nd:YVO <sub>4</sub>	0.15 to 0.30	(001) (010) (110)	$\gamma(110) > \gamma(010)$
Nd:YVO <sub>4</sub>	0.13 to 0.08	(001) (100) (010)	$\gamma(100) > \gamma(010)$
Nd:GdVO <sub>4</sub>	0.05 to 0.20	(100) (010) (011)	$\gamma(011) > \gamma(010)$
Nd:GdVO <sub>4</sub>	0.25 to 0.40	(100) (001) (010)	$\gamma(001) > \gamma(010)$

T = 240°C, P = 100 bars



**Fig. 10.11.** Dependence of growth rate and pH of the media for Nd:YVO<sub>4</sub> 1.5 M HCl + 3.0 M HNO<sub>3</sub>



**Fig. 10.12.** Dependence of growth rate and pH of the growth media for Nd:GdVO<sub>4</sub> 1.0 M HCl + 1.0 M HNO<sub>3</sub>

photograph of Nd:GdVO<sub>4</sub>. When the initial pH is 0.05 in 1 M HCl + 2 M HNO<sub>3</sub> (1:2) solution, Nd:GdVO<sub>4</sub> crystallizes as hexagonal platelets. Crystals are honey yellow colored with a vitreous surface. When the initial pH is 0.13 in 1.5 M HCl + 3 M HNO<sub>3</sub> (2:1) solution, Nd:YVO<sub>4</sub> crystallizes as thick rhombohedral crystals. Crystals are honey yellow colored with a vitreous surface. The well-developed faces are: (100), (010), (001) (Fig. 10.16c). The schematic diagrams of the crystals are shown in Fig. 10.17.

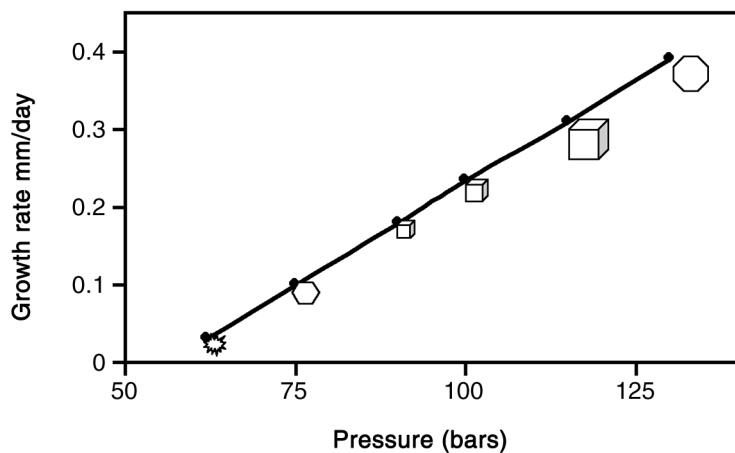


Fig. 10.13. Morphology variation with pressure for Nd:YVO<sub>4</sub> crystals

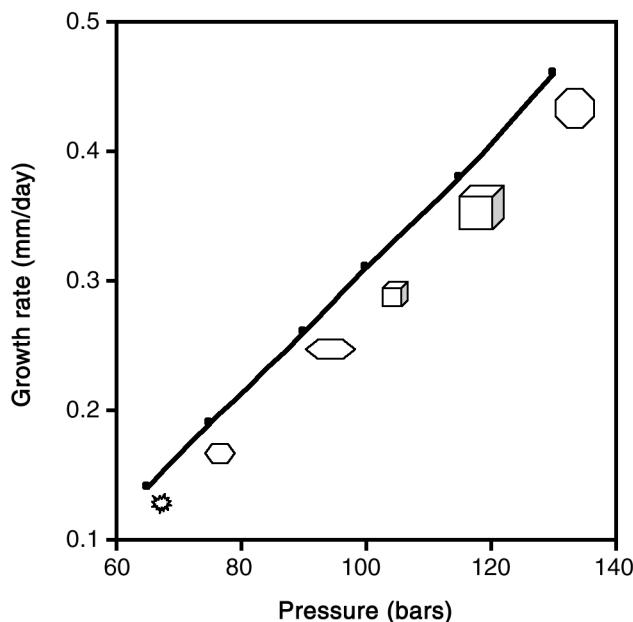
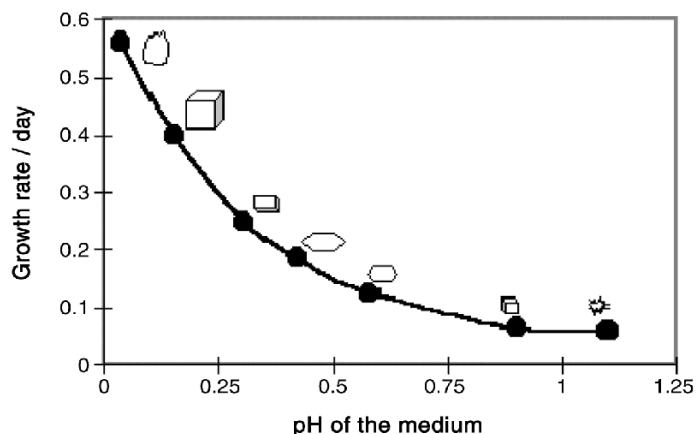
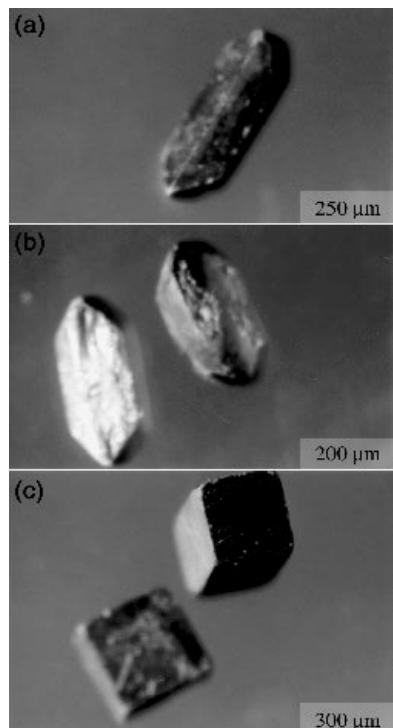


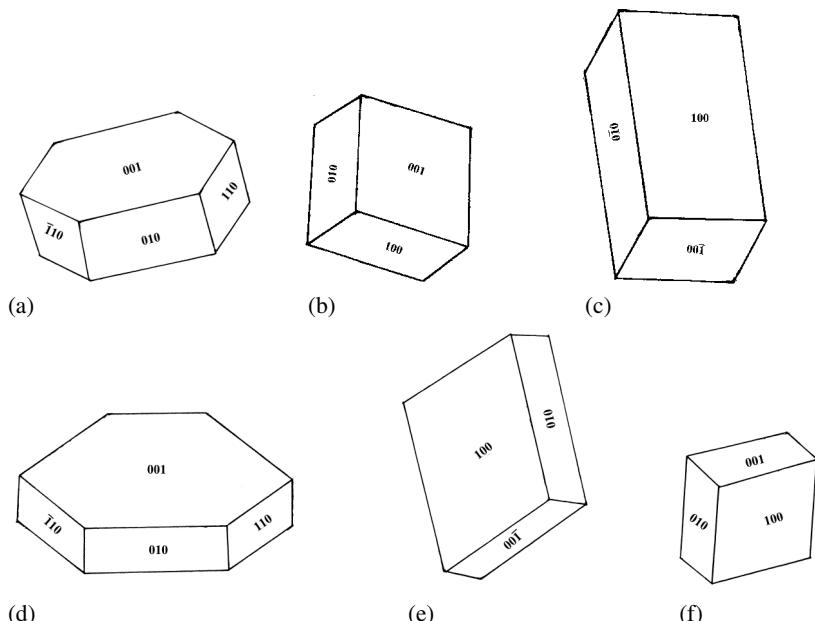
Fig. 10.14. Morphology variation with pressure for Nd:GdVO<sub>4</sub> crystals



**Fig. 10.15.** Morphology variation with pH for Nd:YVO<sub>4</sub> crystals obtained from sintered nutrient



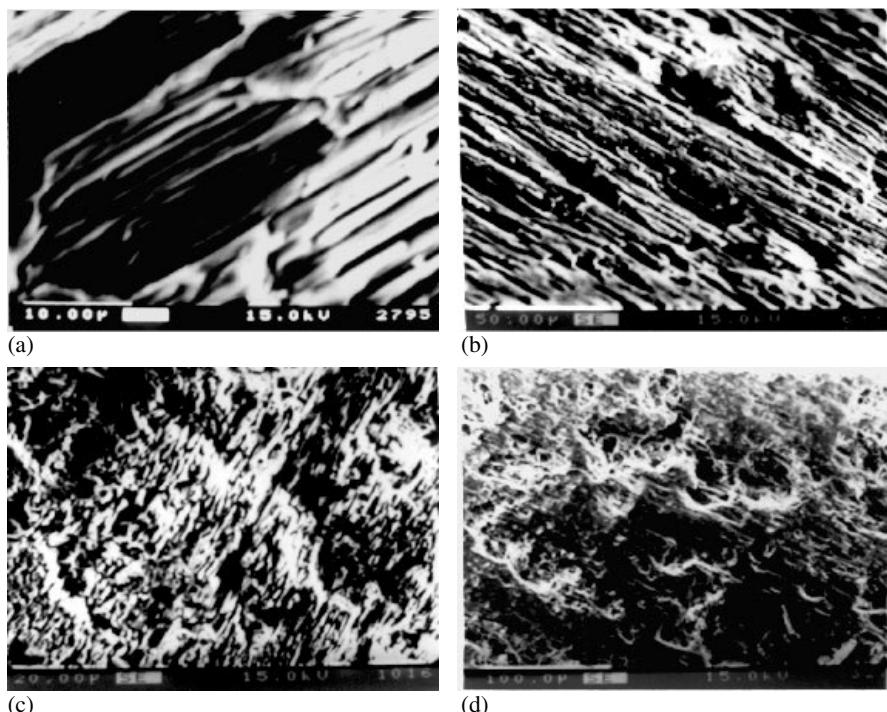
**Fig. 10.16(a-c).** Characteristic photographs of rare earth vanadate crystals obtained under mild hydrothermal conditions



**Fig. 10.17.** Schematic diagrams of Nd:RVO<sub>4</sub> crystals

### 10.8.1 Surface morphology

Although, there are several reports on the growth and characterization of Nd:RVO<sub>4</sub> crystals, there are hardly any reports on the defect studies like surface morphology and micro-morphology of as-grown surfaces. The as-grown surfaces of Nd:RVO<sub>4</sub> crystals exhibit thick kinked layers; arrays of parallel layers on certain faces, isolated etch pits and etch pitch clusters. Crystals obtained from both slowly cooled and suddenly quenched autoclaves showed these characteristic features. However, as expected, the crystals obtained from quenched autoclaves showed less dissolution morphology in comparison with those from slowly cooled autoclaves. Figure 10.18(a-d) shows the surface morphology of slowly cooled rare earth vanadates. It is well known that rare earth vanadates show negative temperature coefficient of solubility. During cooling the crystals undergo dissolution and hence dissolution features are observed in most of the rare earth vanadates. Dissolution is seen more in the center on the surface of the (001) face than at the edge. The middle void surface corresponds to the dissolution pit (Fig. 10.18a). Consequently, the rare earth vanadates do not require further etching to study the surface morphology. The study of the surface morphology clearly indicated the requirement of rapid cooling of autoclaves after the experimental run, moderate supersaturation and a slow rate of growth to obtain high quality single crystals of rare earth vanadates.



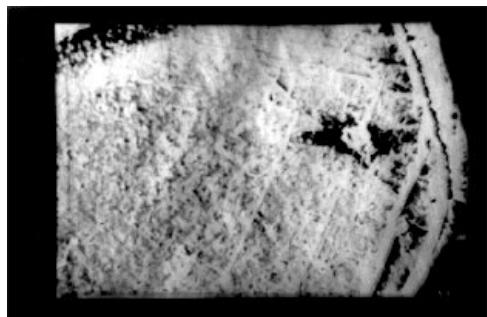
**Fig. 10.18(a-d).** Surface dissolution features in rare earth orthovanadate crystals

Crystals obtained from quenched autoclaves showed less dissolution morphology in comparison with those from slowly cooled autoclaves. Figure 10.19(a-c) shows the morphology of the crystals obtained from rapid quenching of autoclaves.

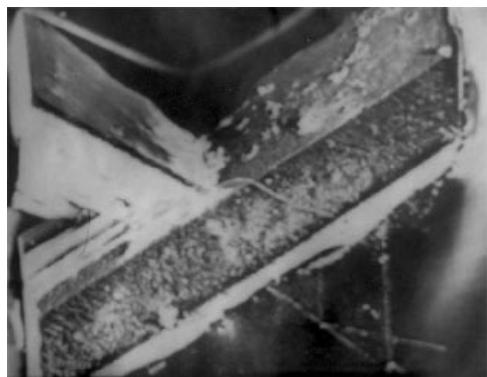
The surface morphology of the as-grown surfaces of rare earth vanadates consists of striations, micro steps, growth layers, block structures, and so forth. The surface morphology varies with pH, pressure, and molarity of the mineralizer. Figure 10.19a shows the striations at the edge. This surface morphology was obtained when the pH of the media was 0.05 and pressure 100 bars in 8 days of experimental duration. Figure 10.19b shows micro steps on the (001) surface. This morphology was obtained when the concentration of the mineralizer was 1.5 M HCl + 3 M HNO<sub>3</sub>, pressure 130 bars, pH = 0.13 in an experimental duration of 10 days. Figure 10.19c shows twinning morphology. This was observed when the concentration of the mineralizer was low (0.75 M HCl + 0.75 M HNO<sub>3</sub> in the ratio 1:2), pressure 100 bars, pH = 0.05 in an experimental duration of 10 days. The temperature in all the experiments was maintained at 240°C.



(a)



(b)



(c)

**Fig. 10.19(a-c).** Surface morphology of rare earth vanadates after a rapid quenching of autoclaves

## 10.9 Characterization

### 10.9.1 XRD and IR studies

The authors [44] have carried out X-ray and infrared studies. The cell parameters were calculated for the representative samples and depicted in Table 10.6. These values are in correspondence with the reported values [45,46].

The infrared spectrum of rare earth vanadates shows more fineness and multiple splitting in the region of lower wave numbers. The most interesting feature of this spectrum is the absence of  $(OH)^-$  bands in the region 3000–3500  $Cm^{-1}$ . This shows that water is not incorporated in the interstices of vanadates grown by hydrothermal technique in spite of the mild hydrothermal experimental conditions. In the range 950–1050  $Cm^{-1}$  and 400–600  $Cm^{-1}$ , the compound shows 4 sharp absorption bands, which were formed by  $[VO_4]^{3-}$  [47].

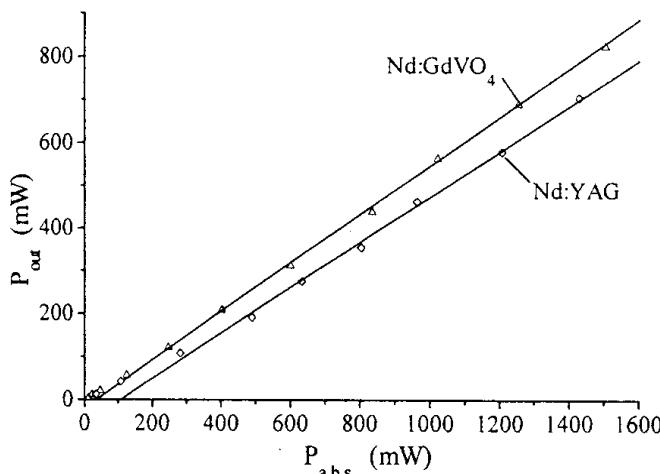
Compound vanadate	Coordination	$\gamma(A_1)$	$\gamma(E)$	$\gamma(F_2)$	$\gamma(F_2)$
	$[VO_4]^{3-}$	870	345	825	480

**Table 10.6.** Cell Parameters for Rare Earth Vanadates Obtained Under Hydrothermal Conditions

Compound	a, Å	c, Å	V, $\text{\AA}^3$
YVO <sub>4</sub>	7.118(3)	6.289(8)	318.64
Nd:YVO <sub>4</sub> (3% Nd)	7.127(4)	6.297(5)	319.85
GdVO <sub>4</sub>	7.214(2)	6.348(4)	330.36
Nd:GdVO <sub>4</sub> (3% Nd)	7.223(7)	6.359(7)	331.76

### 10.9.2 Laser spectroscopy

Laser spectroscopic experiments at 1.06  $\mu m$  were performed on a 2 mm thick crystal sample. The crystal was oriented with the c-axis parallel to the polarization direction of the diode laser. Pump source was a SDL-2482 diode with an emitting area of 500  $\mu m \times 1 \mu m$  and a CW power of 2.3 W at 808.4 nm. The pump beam was first collimated in one direction using a collimating optic with 5 mm focal length. The higher slope efficiency and the lower pump threshold of Nd:GdVO<sub>4</sub> result in an output power surplus of 100 mW at an absorbed pump power of 1500 mW [23]. Figure 10.20 shows an input-output curve of Nd:GdVO<sub>4</sub> and for comparison, a measurement with an identical Nd:YAG setup is shown (slope efficiency 53%).



**Fig. 10.20.** Diode-laser pumped lasing of Nd:GdVO<sub>4</sub> and Nd:YAG at 1.06  $\mu\text{m}$  under identical conditions [23]

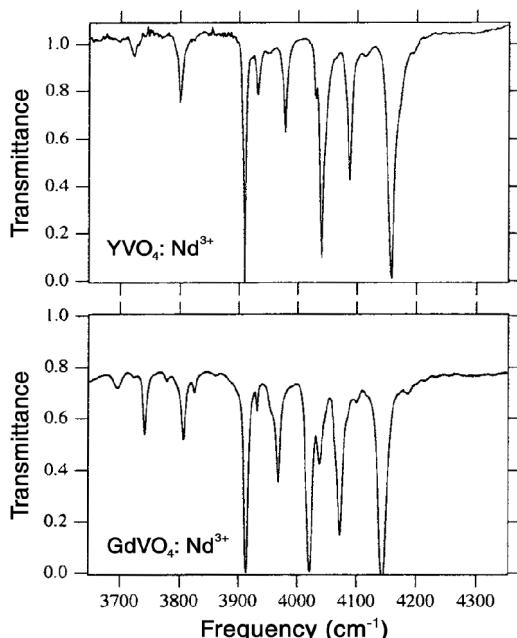
The substitution of Gd for Y in these various crystals leaves the crystal field felt by the Nd ion largely unchanged and does not alter greatly the spectra that arise from doping of these crystals with Nd. However, as Gd<sup>3+</sup> is closer in size to Nd<sup>3+</sup> than Y<sup>3+</sup>, a larger concentration of Nd can be incorporated into the crystals, thereby enhancing the absorption coefficient [23]. Since this leads to an increased pumping efficiency, Gd-based crystals are good candidates for future use in miniaturized Nd lasers.

For Nd:YVO<sub>4</sub> and Nd:GdVO<sub>4</sub>, accurate stark levels for  $^4\text{I}_j$  ( $J = 9/2, 11/2, 13/2, 15/2$ ) and  $^4\text{F}_{3/2}$  multiplets have been determined from the spectra [48]. Representative spectra are shown in Fig. 10.21. The lines shown in these spectra arise from the  $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{13/2}$  transitions. The spectra are nearly identical between the Y and Gd counterparts with respect to peak position, relative strengths, and polarization dependence.

Table 10.7 shows the norms of the parameters for the Gd-based crystals, and are slightly less than those for the Y-based crystals. This suggests that the Nd ions experience a weaker average crystal field in the Gd-based crystals, and is consistent with the larger radius of Gd<sup>3+</sup> ion compared to the Y<sup>3+</sup> ion [49], which is expected to result in an increase in the lattice constants for the Gd-based crystals. For the vanadates, the lattice constants of GdVO<sub>4</sub> are larger than those of YVO<sub>4</sub> [50]. Thus, due to the increased distance between the Nd impurity and the neighboring host atoms, the strength of the crystal field is reduced, giving rise to (slightly) smaller crystal field parameters.

The parameters  $\beta$  and  $\gamma$  give energies of the  $t_2$  and  $t_1$  triplets respectively, resulting from the tetrahedral field B ( $t_2$ ) and C ( $t_1$ ); and Y ( $t_2-t_1$  mixing) results from the tetragonal distortion.

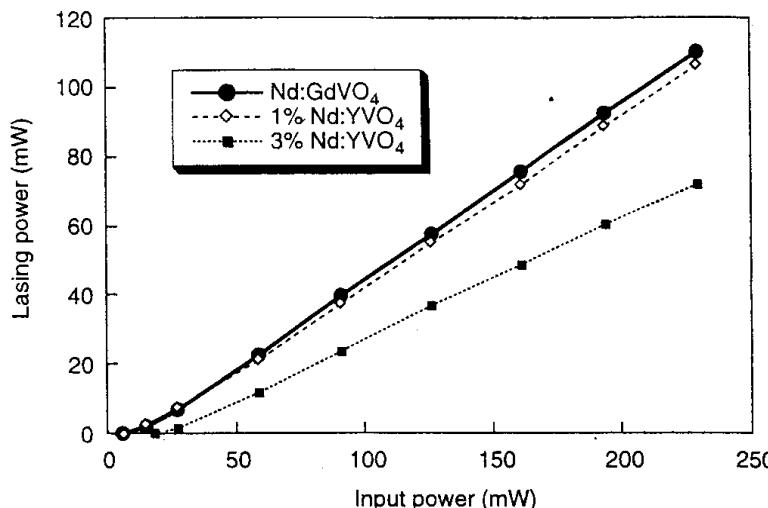
The absorption coefficient of 1% Nd:GdVO<sub>4</sub> was 59.3 cm<sup>-1</sup>, twice that of 1% Nd:YVO<sub>4</sub>, and approximately the same as that of 3% Nd:YVO<sub>4</sub> [3]. Slope efficiency, threshold pump power and output power of Nd:GdVO<sub>4</sub> exceeded those of Nd:YVO<sub>4</sub>.



**Fig. 10.21.** Transmittance spectra for Nd-doped YVO<sub>4</sub> and GdVO<sub>4</sub> showing  $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{13/2}$  transitions [48]

**Table 10.7.** Crystal Field Parameters for the Nd Impurity (values are in  $\text{Cm}^{-1}$ )

Parameter	YVO <sub>4</sub>	GdVO <sub>4</sub>
beta	190.6	157.3
gamma	-59.6	-37.6
B	-386.2	-384.5
C	30.4	76.2
Y	-99	-97.5
E(11/2)	1866	1866
E(13/2)	3836	3836
E(15/2)	5872	5872



**Fig. 10.22.** Input–output CW characteristics of Nd:GdVO<sub>4</sub> compared with Nd:YVO<sub>4</sub> [3]

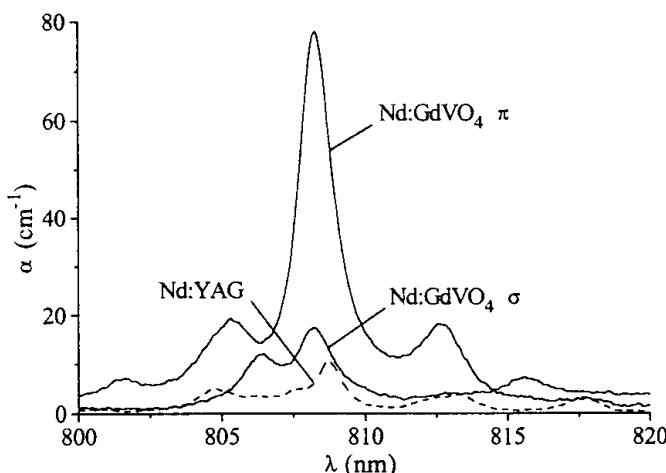
### 10.9.3 Absorption measurements

The uniaxial crystal Nd:GdVO<sub>4</sub> shows strong polarization dependent absorption transitions due to the anisotropic crystal field [23]. At 808.4 nm, the peak absorption cross section was  $5.2 \times 10^{-19} \text{ cm}^2$ . For  $\sigma$ -polarization the absorption coefficient is only  $17 \text{ cm}^{-1}$ . The absorption spectrum as a function of wavelength for both polarizations is shown in Fig. 10.23. The half width of the absorption at 808.4 nm is 1.6 nm. For comparison with Nd:YAG and Nd:YVO<sub>4</sub> some data are listed in Table 10.8 for active ion densities of  $1.5 \times 10^{20} \text{ cm}^{-3}$ .

At the same neodymium concentration, the absorption coefficient of Nd:GdVO<sub>4</sub> is seven times higher and the transition line is 80% broader in comparison with Nd:YAG.

**Table 10.8.** Comparsion of Absorption in YAG, YVO<sub>4</sub>, and GdVO<sub>4</sub> for Diode-laser Pumping near 808 nm

Crystal	Crystal ion density [1020 cm <sup>-3</sup> ]	Polarization direction	Absorption Coefficient [cm <sup>-1</sup> ]	Eff. Absorption cross section [10 <sup>-19</sup> Cm <sup>2</sup> ]	Half width [nm]
1.1% Nd:YAG	1.5	Unpolarized	11	0.7	0.9
1% Nd:YVO <sub>4</sub> [51]	1.5	E  c	40	2.7	2
1.2%Nd:GdVO <sub>4</sub>	1.5	E  c	78	5.2	1.6



**Fig. 10.23.** Absorption spectra from the ground state  $^4I_{3/2}$  into the  $^4F_{5/2}$  multiplet for Nd:GdVO<sub>4</sub> in  $\pi$ - and  $\sigma$ -polarization [23]

## 10.10 Summary

The hydrothermal growth of rare earth vanadates has several advantages. Although, the rare earth vanadates have very high melting points ( $> 1800^\circ\text{C}$ ) and very low solubility, these crystals could be obtained under mild hydrothermal conditions ( $T = 240^\circ\text{C}$ ,  $P \sim 100$  bars). One of the major problems encountered in the growth of rare earth vanadates is the presence of oxygen imperfections (color centers and inclusions) introduced during the crystal growth processes. Also a certain amount of vanadium oxide vaporizes incongruently, causing changes in Y/V ratio and oxygen stoichiometry in the melt. Further, vanadium is highly corrosive at high temperature. Adoption of the hydrothermal technique could eliminate all these problems. We have studied the ternary system  $\text{Y}_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{H}_2\text{O}$  under hydrothermal conditions at  $T = 240^\circ\text{C}$ , with 60% fill, and identified the crystallization field for the RVO<sub>4</sub> crystals. The problems encountered by melt and flux techniques have been completely eliminated by the authors by using hydrothermal technique. A systematic study of the growth rate and morphology has been carried out with respect to the type of mineralizer, % fill, pH of the growth media, and the nutrient type. Rare earth vanadates usually exhibit pseudo-cubic, rhombohedral, and prismatic habits, and the authors have succeeded in introducing the hexagonal and rectangular plate-like habit through careful controlling of the growth parameters. Such an *in situ* fabrication of the morphology is highly useful for device applications, which do not need further cutting, polishing, and so forth. Although spontaneous nucleation was used for the growth of these rare earth vanadates, a higher growth rate was accomplished to obtain large size single crystals.

of  $4.3 \times 4.3 \times 2$  mm in an experimental run of 8 days. The use of these spontaneously grown large crystals as seeds would facilitate the growth of bulk single crystals of rare earth vanadates up to 1 cm size in about 8 to 10 days. The infrared spectroscopic studies did not show the presence of any hydroxyl molecules in these crystals in spite of the mild hydrothermal growth conditions adopted. The laser spectroscopic properties of these crystals are found to be highly encouraging.

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# 11 Hydrothermal Growth of Quartz Under Specific Conditions and the Raman Spectra of Ion Species in a Hydrothermal Growth Solution

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## 11.1 Introduction

Hydrothermal growth is suitable for synthesizing a material which cannot exist in stable form or which is highly soluble at a high temperature. The most typical example of electronic components synthesized by this method is synthetic quartz. Synthetic quartz is most often used as a quartz oscillator for frequency generators and as a filter for frequency controllers. They are used in both industrial electronic components and consumer electronic components.

The first to discover the method of using seed crystal for growing quartz crystal was an Italian crystal grower, G. Spezia from the University of Torino. H. Iwasaki and F. Iwasaki confirmed that the following three publications of Spezia have greatly contributed to the development of electronic components today.

1. G. Spezia: Contribuzioni di Geologia Chimica, La pressione e chimicamente inattiva nella solubilità e ricostituzione del quarzo, *Atti. Accad. Sci. Torino*, 40:254–262 (1905).
2. G. Spezia: Contribuzioni sperimentali alla cristallogenesi del quarzo, *Atti. Accad. Sci. Torino*, 41:158–165 (1906).
3. G. Spezia: Sull’ accrescimento del quarzo, *Atti. Accad. Sci. Torino*, 44:95–107 (1909).

The achievements of Spezia were described in detail by F. Iwasaki and H. Iwasaki [4]. According to the report, while the dissolved lasca is transported from the nutrient side to the seed crystal side by convection in the current growth method of synthetic quartz, the lasca is transported mainly by diffusion in Spezia’s method. The growth rate in the  $z$ -direction is supposed to have been 0.02 mm/day on one side because the growth was realized by diffusion. British researchers, Wooster et al. [5], conducted their experiments applying Spezia’s method. In Germany also, Nacken [6] carried out his studies on the growth of crystal on the basis of Spezia’s method, by placing the nutrient and the seed crystal in isothermal conditions. After

World War II, on the basis of these achievements, studies were carried out in the United States to develop the hydrothermal temperature gradient method currently used, which consists of using the difference in solubility. This method, which consisted of placing the seed crystal on the upper part of an autoclave and the nutrient, i.e., lasca, in the lower part with a temperature gradient between such parts, was highly suited to mass produce quartz of good quality. The earliest studies in this field in Japan started at Yamanashi University in 1953. Currently, Japan is the largest producer of synthetic quartz in the world.

$\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  are used as solvents to grow quartz on an industrial scale. Typical solvents other than alkaline solutions that have been used to grow quartz include  $\text{NaCl}$  developed by Corwin and Swinnerton [7] and Hosaka and Taki [8],  $\text{RbOH}$  developed by Kopp and Clark [9],  $\text{NH}_4\text{F}$  developed by Balitsky [10] and Hashimoto et al. [11], including experiments under isothermal conditions and those using a temperature gradient method. The grown crystal shows morphology specific to the solvent used.

A factor other than the solvent that influences the sound growth of  $\alpha$ -quartz is the filling of the solution. Usually, at room temperature, the solution fills more than 75% of the free volume of the vessel. As the percentage of the solution at room temperature decreases the quality of grown quartz declines, and when the filling rate drops below 50%, the seed crystal suspended in the upper part of the autoclave dissolves. Even at such low filling below about 50%, however, quartz has been successfully grown by applying the so called hydrothermal reverse temperature gradient method, which consists of placing the nutrient on the lower temperature side and the seed crystal on the higher temperature side [12]. The pressure inside the autoclave at a high temperature varies with the rate at which the solution fills the vessel at room temperature. Kennedy's isobaric and isovolumic solubility curves [13] for a  $\text{SiO}_2\text{-H}_2\text{O}$  system shows that, when the pressure is over 75 MPa, the temperature coefficient of solubility is positive at a constant pressure. The temperature coefficient of solubility is negative, however, below about 70 MPa. One realizes that in the ordinary temperature gradient method quartz is grown at a pressure of 75 MPa or more, where the temperature gradient of solubility is positive. On the other hand, at a lower pressure, one can grow quartz by placing the seed on the higher temperature side and the source material on the lower temperature side, since the temperature gradient of solubility is negative. The authors [12] have succeeded in growing quartz in a  $\text{NaCl}\text{-H}_2\text{O}$  system with a filling rate of less than 50% by using the hydrothermal reverse temperature method. The growth of quartz with a low rate of filling can be explained by the temperature gradient of solubility. However, the problem of existing species should be studied further since it is expected that ion species present in the solution are different between a high rate of filling (i.e., a high pressure) and a low rate of filling (i.e., a low pressure), at a high temperature. If it was possible to mass produce high-quality quartz with a low filling rate, it would make an excellent industrial method with lower heating costs, but crystals thus produced were often imperfect with crevice flawing in the  $z$ -direction. However, in natural quartz crystal, two phase fluid inclusions have less than 50% of liquid phase in some cases. Crystal with such a proportion of liquid phase in fluid inclusions is formed

in dike- and pike-like veins and may have been grown by the transport of silicic ions from the low temperature side to the high temperature side. Natural quartz crystal rarely has crevice flawing and achieves transparency, since it grows mainly in directions perpendicular to the *r*- and *z*-faces.

When a small amount of impurity is added into the solvent, the impurity enters into the structure of the quartz crystal as substitutional or interstitial type. The crystal gives various colors according to the quantity and type of such impurity. Lehmann and Bambauer [14] reported, for instance, that the purple color of amethyst is attributable to the presence of paramagnetic holes formed by exposure to radiation when  $\text{Fe}^{3+}$  is incorporated into the structure of quartz crystal as a substitute for  $\text{Si}^{4+}$  or an interstitial type filling the interstices in the structure. As is amethyst, smoky quartz which incorporated  $\text{Al}^{3+}$  substitutionally also has a hole color center formed by radiation. The color of citrine is attributable to substitutional  $\text{Fe}^{3+}$ . As for the color cause of rose quartz, Hosaka et al. [15] stated that it was attributable to charge transfer between interstitial  $\text{Fe}^{2+}$  and substitutional  $\text{Ti}^{4+}$ , and Balitsky et al. [16] reported that it was a complex color center attributable mainly to the phosphorous element, both based on their experiments. However, colored quartz obtained by the addition of impurities is used only as jewelry stone and is produced only in small quantity. Industrially, there are more demands today for synthetic quartz without impurities such as  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , which is used for the development of electronic components.

Today, the improvements in growing method allows the production of high quality quartz with less impurities and microscopic solid phase inclusions such as acmite ( $\text{NaFeSi}_2\text{O}_6$ ) and emeleusite ( $\text{Na}_4\text{Li}_2\text{Fe}_2\text{Si}_{12}\text{O}_{30}$ ) [17].

As there are a lot of technical reports written since Spezia about the growth of synthetic quartz used as electronic components and for the characterization of grown quartz crystals, the discussion is limited to the following studies carried out by the author.

### 11.1.1 Growth of quartz with small content of $\text{Al}^{3+}$

It is supposed that when  $\text{Al}^{3+}$  incorporated in synthetic quartz is of substitutional type, alkaline metal ions are incorporated for charge compensation and that, when such crystal is exposed to radiation, defects are caused in the form of holes or  $\text{H}^+$  traps in the oxygen orbit neighboring the substitutional  $\text{Al}^{3+}$  and this affects the frequency change of oscillators. Concerning the effects of  $\text{Al}^{3+}$  on the growth of synthetic quartz, Brown and Thomas [18] reported that  $\text{Al}^{3+}$  enters into the crystalline structure as substitutional type when its concentration is low, while it fills the crystal lattice as interstitial type, and the unevenness on the *Z*-face increases as the concentration increases. Martin and Armington [19] also reported that the amount of the incorporated  $\text{Al}^{3+}$  increases and *Q*-value decreases as the growth rate increases. Further, Taki and Hosaka [20] reported that, when the concentration of  $\text{Al}^{3+}$  is 100 ppm or less, the *S*-region develops on the boundary between the *+X*-region and the *Z*-region. The relation of  $\text{Al}^{3+}$  contents in these regions may be

written as  $Z < X < S$ . Iwasaki et al. [21] have stated that Al contents in Y-bar synthetic quartz may be expressed by the following formula:

$$\text{Al} = a \cdot \exp(b \cdot \text{Al}_{\text{lasca}}) \quad (11.1)$$

The values of  $a$  and  $b$  are dependent upon the growth conditions. The formula shows clearly that  $\text{Al}^{3+}$  impurities in synthetic quartz are largely dependent on the lasca used as nutrient.

The authors [22] have synthesized high purity  $\alpha$ -quartz using powdered synthetic, high purity  $\alpha$ -cristobalite containing 3.1 ppm of  $\text{Al}^{3+}$ .

### 11.1.2 Synthesis of micro $\alpha$ -quartz crystals by hydrothermal hot-pressing method

This experiment was conducted by the author [23] to see if quartz crystal can be synthesized by the hydrothermal hot-pressing method, which requires neither large vessels nor high temperatures/high pressures, but cannot produce a large single quartz crystal. Its advantage consists rather in its ability to synthesize in short time micro crystals, which can be used as filler.

### 11.1.3 Growth of quartz crystals above transition temperature and morphology of synthetic crystals

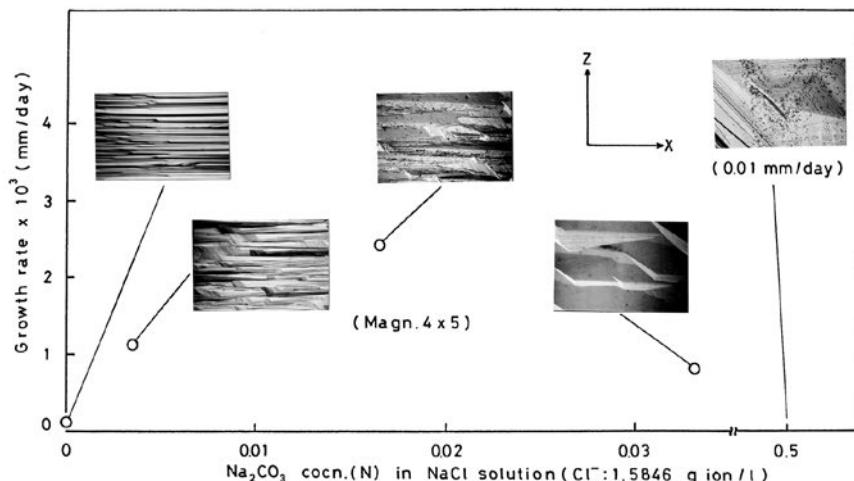
The transition from low quartz ( $\alpha$ -quartz) to high quartz ( $\beta$ -quartz) takes place at a temperature of 573°C. The  $\alpha$ -quartz belongs to the trigonal crystal system and exhibits a hexagonal prismatic habit with major and minor rhombohedral faces and prism faces. The  $\beta$ -quartz belongs to the hexagonal crystal system and exhibits a hexagonal dipyramidal habit which usually does not have prism faces, but may have extremely small faces in some rare cases. The sharp transition temperature between the  $\alpha$ - and  $\beta$ -quartz is easily expected because they are of a framework structure consisting of  $\text{SiO}_4$  tetrahedra, and the only difference between them is the angle between neighboring  $\text{SiO}_4$  tetrahedra.

The structural similarity contradicts the long-held belief and observation that prism faces usually do not appear on  $\beta$ -quartz. The authors [24] have synthesized quartz crystals at a temperature higher than the transition temperature by applying the hydrothermal method and checked whether the morphologies of the as-grown crystals varied with temperature, as well as the validity of the long-held belief that prism faces do not appear on  $\beta$ -quartz and observed a hexagonal dipyramidal habit, and in a few cases, a hexagonal dipyramidal habit without prism faces. Swanson and Fenn [25] have synthesized  $\beta$ -quartz in silicate melts and observed only a hexagonal dipyramidal habit, but hydrothermal synthesis of quartz at a temperature higher than the transitional temperature has never been performed before.

### 11.1.4 Raman spectral studies of $\text{SiO}_2\text{-NaOH-H}_2\text{O}$ and $\text{SiO}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ system solutions under hydrothermal conditions

The morphology and the surface microtopography of a grown crystal reflect the environment in which the crystal grew. For example, on synthetic quartz grown in an alkaline solution, the rhombohedrons are usually composed of three rhombohedral faces. Pyramidal growth hillocks are observed on the prism faces.

These pyramids may have been developed by spiral growth or two-dimensional spread. On the other hand, natural quartz usually has six rhombohedral faces while the prism faces show striations running perpendicularly to the *c*-axis. The striations are relatively a few in number and flat or steep in shape. The distance between respective striations varies from crystal to crystal. In surface microtopography on their rhombohedrons, natural quartz and synthesized quartz grown in an alkaline solution differ from each other. The surface microtopography of natural quartz shows small growth hillocks and mosaic-like growth patterns which vary between places of origin, while, on the rhombohedrons of quartz grown in an alkaline solution, relatively large growth hillocks are observed. Figure 11.1 illustrates an experiment to show the surface microtopography varying with an alkaline concentration. The horizontal axis of the graph represents the concentration of  $\text{Na}_2\text{CO}_3$  added into  $\text{NaCl}$  solution. The prism faces of quartz synthesized in  $\text{NaCl}$  solution simulating the growth conditions of natural quartz present fine parallel striations [26]. One realizes from the figure that, as the alkali content increases, the striations widen their respective distances to gradually form a pyramid as shown in the figure. When an alkaline solution such as  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  was added into 10 wt%  $\text{NaCl}$  solution, no remarkable difference has been observed in



**Fig. 11.1.** Relation between the surface topography on the prism face and  $\text{Na}_2\text{CO}_3$  conc. (N) in  $\text{NaCl}$  solution. Growth temp.: 400°C, Dissolving temp.: 425°C, Degree of fill: 70%

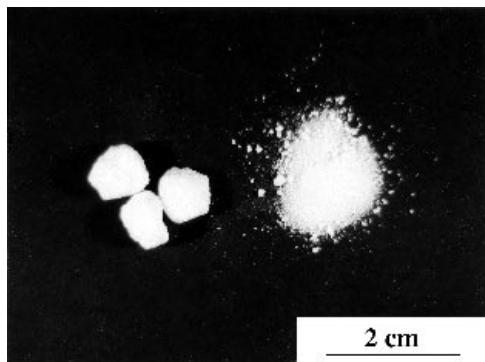
the distance between respective striations, but, when each of such alkaline solutions was added into H<sub>2</sub>O, the distance between striations on the prism faces of the crystals grown in Na<sub>2</sub>CO<sub>3</sub> became somewhat wider compared to that shown by the crystals grown in a solution to which the same content of NaOH had been added. The surface microtopography is largely dependent upon the nature of the growth solution or solvent, that is to say, upon dissolved silicic ion species. As silicic ion species, there are SiO<sub>4</sub>, Si<sub>2</sub>O<sub>7</sub>, Si<sub>3</sub>O<sub>10</sub>, (SiO<sub>3</sub>)<sub>4</sub>, and (SiO<sub>4/2</sub>)<sub>x</sub>. The ratio of these ions varies between the types of solution. For example, based on the measurements of solubility Laudise [27] and Taki [28] performed, they supposed that Si<sub>3</sub>O<sub>7</sub> occupies a large part in the NaOH solution, because 3 mol of SiO<sub>2</sub> is dissolved into 2 mol of NaOH there; and that SiO<sub>3</sub> is predominant in the Na<sub>2</sub>CO<sub>3</sub> solution because there 1 mol of SiO<sub>2</sub> was dissolved in 1 mol of Na<sub>2</sub>CO<sub>3</sub>. Under hydrothermal conditions, silicic ions other than these ions or amorphous sodium silicate (Na<sub>x</sub>Si<sub>y</sub>O<sub>z</sub>) are supposed to be present. Lentz [29] analyzed trimethylsilyl derivatives of silicic ions in sodium silicate solutions by gas chromatography to examine the degree of polymerization of silicic ions. He reported that, when Na<sub>2</sub>O/SiO<sub>2</sub> ≥ 2.0, the proportion of monomers increases as the alkali content increases; when Na<sub>2</sub>O/SiO<sub>2</sub> ≤ 1.0, the proportion of chain or ring polysilicic ions increases as the alkali content decreases.

Hosaka and Taki [30] have designed an autoclave with optical windows resistant to high temperature and pressure as a means for *in situ* observation of solutions at high temperature and pressure. Using a Raman spectrometer, they tried to measure directly and optically the conditions of solutions at high temperature and pressure to check the correspondence between the previously confirmed chemical species [27,28,29] and Raman spectra.

## 11.2 Growth of Quartz with Poor Al<sup>3+</sup> Content

### 11.2.1 Experimental method

The α-cristobalite used as the nutrient was amorphous silica particles sintered at 1,000–1,300°C with less than 1 ppm of Al<sup>3+</sup> impurities [31]. Two compacted forms of α-cristobalite of 30–40 μm particle size were used in these experiments. One was sintered at more than 1,300°C into grains of 0.5–1.0 mm in diameter. The other one was also sintered at more than 1,300°C and compacted into lumps of about 1 cm in diameter. Figure 11.2 [22] shows the α-cristobalite used as nutrient. It would be possible to use high-purity glass as nutrient once it is transformed into α-quartz at high temperature and pressure [7], but, in such a case, transparent crystals could not be obtained until the glass is completely transformed into α-quartz, because glass is highly soluble. The advantage of α-cristobalite over glass is that it can be used as nutrient in an autoclave from the beginning of the experiment, because it has much lower solubility [32] and transforms into α-quartz at a temperature of about 300°C (measured on the outer wall of the autoclave). As seed



**Fig. 11.2.**  $\alpha$ -cristobalite used as the source material. Right: compacted into lumpus (about 1 cm). Left: compacted into grains (0.5–1.0 mm)

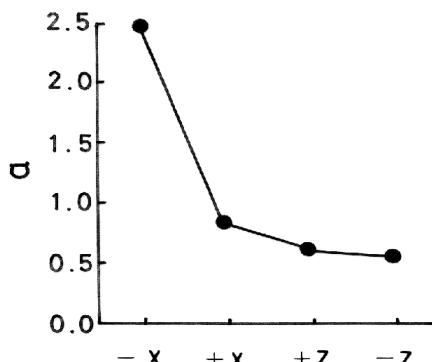
crystal, Y-bar crystal was used. As solvent, 1 N NaOH solution was used. The experiment was performed at a growth temperature of 315°C, a dissolving temperature of 340°C, and a degree of filling of 83%.

### 11.2.2 Experimental results

Synthesized crystals were transparent and did not present any inclusions of microscopic size ( $\times 100$ ) in their growth regions. The rate of growth was 0.20–0.60 mm/day in the Z-direction, but did not show any significant difference compared to the previous experiments conducted using lasca as nutrient.

The Al<sup>3+</sup> content analyzed with inductively coupled plasma atomic emission spectrometry (ICAP-88, Nippon Jarrell-Ash Co., Ltd.) in each of both sides of the Z region, the +X, and -X regions, the Al<sup>3+</sup> content was 2.9, 2.1, and 2.1 ppm, respectively. The Al<sup>3+</sup> content included both substitutional and interstitial types. The low Al<sup>3+</sup> content of the substitutional type in the Z and X regions was suggested, however, by the facts that the irradiation of CO<sup>60</sup>  $\gamma$ -rays of 10 Mrad did not cause any coloration and that the absorption coefficients for 3304 cm<sup>-1</sup> and 3364 cm<sup>-1</sup> which were stated by Halliburton et al. [33] to be absorbed by Al-H<sup>+</sup>.....OH<sup>-</sup> (Al in this case was a substitutional type) was extremely small except for in the -X direction. The release of Al<sup>3+</sup> from the nutrient into the solution upon the dissolution of the nutrient does not mean that all of the released Al<sup>3+</sup> is incorporated into the grown seed crystal: They are “purified,” so to speak [21]. The fact that the Al<sup>3+</sup> content of the grown crystal was about 2 ppm in each region when  $\alpha$ -cristobalite of less than 1 ppm of Al<sup>3+</sup> content was used as nutrient suggests a contamination from the NaOH solution or the inner wall of the vessel.

The generation of the S-region was not observed between the Z- and X-regions of the synthetic quartz. Previous studies [20] have made it clear that with less than 10 ppm of Al<sup>3+</sup> content, the S-region was not generated.



**Fig. 11.3.** Absorption coefficient at  $3407\text{ cm}^{-1}$

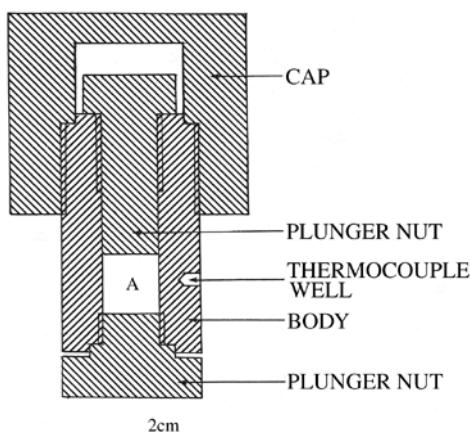
Figure 11.3 shows for each region the absorption coefficient ( $\alpha$ ) of  $3407\text{ cm}^{-1}$  attributable to the presence of  $\text{H}_2\text{O}$  or its ion species. The measurement of infrared absorption spectra was performed in the region not affected by the change of  $\text{Al}^{3+}$  content, that is to say, at a distance of 0.3 mm apart from the seed crystal remaining in the grown crystal. The fact that the absorption coefficient for the  $-X$ -region is larger than those in other regions seems to reflect the fact that  $\text{H}_2\text{O}$  particles, which are easily absorbed on the  $-X$  face, are included in the crystal.

After the experiment, it was confirmed by means of X-ray diffraction that the  $\alpha$ -cristobalite used as nutrient had recrystallized into  $\alpha$ -quartz at a temperature of  $300^\circ\text{C}$ . The  $\alpha$ -cristobalite remained as it was, however, at a temperature of  $260^\circ\text{C}$ . This suggests that when the temperature in the nutrient side was  $270^\circ\text{C}$  or less, the  $\alpha$ -cristobalite does not recrystallize into  $\alpha$ -quartz, but directly dissolves into silicic ions and that such dissolved silicic ions are transported to the seed crystal side. The fact that at a temperature of  $300^\circ\text{C}$  or more, the transformation from  $\alpha$ -cristobalite to  $\alpha$ -quartz takes place within 24 hours seems to suggest that, in this case, silicic ions dissolved from the transformed  $\alpha$ -quartz are transported to the seed side. There was no evidence that the difference between the two forms of  $\alpha$ -cristobalite used as nutrient had any particular effect on the grown crystal.

## 11.3 Synthesis of Micro $\alpha$ -Quartz Crystals by Hydrothermal Hot-Press Method

### 11.3.1 Experimental method

Figure 11.4 shows the hydrothermal hot-press used in the experiment [34]. The mixture of the nutrient and the solvent filled the space A of the figure. As nutrient [31], nonsintered  $\alpha$ -cristobalite 200  $\mu\text{m}$  in diameter and 0.5–1.0 mm in length was



**Fig. 11.4.** Schematic diagram of hydrothermal hot-press

used. As solvent, 1 N NaOH, 1 N Na<sub>2</sub>CO<sub>3</sub>, and sodium formate were used. The NaOH and Na<sub>2</sub>CO<sub>3</sub> were used in the state of aqueous solutions. The sodium formate was mixed with the nutrient in a ratio of 1:1 without water before being used. After the space A was filled with solvent and nutrient, the plunger nuts B and C were put in place and tightened with a constant torque of 500–1,000 kg·f·cm with a torque wrench. The device was set in an electric furnace and left for the reaction for 24–30 hours. After the experiment, the device was quenched and the reactant was examined by means of SEM and X-ray diffraction.

### 11.3.2 Experimental results

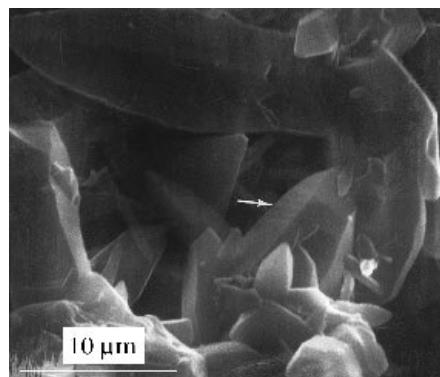
In the experiment using 1 N NaOH, 1 N Na<sub>2</sub>CO<sub>3</sub>, and sodium formate, a 100% crystallization was observed at a temperature of 300°C. The crystal thus grown was hexahedral and had a rhombohedron at one end or at both ends. The micro quartz was 20 µm in length and 5–8 µm in thickness. On the prism faces of the crystals synthesized in sodium formate, striations were observed running parallel to the boundary between the rhombohedron and the prism faces. Figure 11.5 shows the micro quartz synthesized from sodium formate. Table 11.1 shows the results of the experiment [34].

At a high temperature, sodium formate is supposed to decompose into sodium oxalate. Considering that the sodium oxalate may decompose secondarily, it seems quite probable that the solution contains complex ion species at temperatures above the melting point (253°C).

Sodium formate is a kind of fused salt. Probably, the experiment was the first to have used sodium formate as a solvent to grow quartz. When observed through SEM, the morphology of the micro quartz synthesized in each of 1 N NaOH and 1

**Table 11.1.** Results of Synthetic Micro Quartz Crystals

Solvent	Reaction temp. [°C]	Reaction time [h]	Results [X-ray diffraction]
1 N NaOH	250	24	$\alpha$ -cristobalite
Sodium formate	255	24	$\alpha$ -cristobalite
1 N NaOH	300	24	100% $\alpha$ -quartz
Sodium formate	300	30	100% $\alpha$ -quartz
1 N $\text{Na}_2\text{CO}_3$	300	30	100% $\alpha$ -quartz

**Fig. 11.5.** SEM photograph of micro  $\alpha$ -quartz crystals synthesized from sodium formate at a temperature of 300°C

N  $\text{Na}_2\text{CO}_3$  solutions had no significant difference from that of crystals synthesized by convection. This suggests that the ion species present in each of 1 N NaOH and 1N  $\text{Na}_2\text{CO}_3$  solutions used in this experiment were similar to those previously examined [27,28].

## 11.4 Growth and Morphology of Quartz Crystals Synthesized Above Transition Temperature

### 11.4.1 Experimental method

The nutrient and the solvent were initially made to react for 58 hours at a soaking temperature exceeding the transition temperature, then were cooled down slowly to the quenching temperature at a constant speed (0.07°C/mm), and finally

**Table 11.2.** Experimental Data

Nutrient	$\alpha$ -cristobalite: 0.5 g (grains of 0.5–1.0 mm)
Solvent	10 wt% NaCl, 1 N NaOH 0.89 cm <sup>3</sup>
Filling	30%
Soaking temperature	600–750°C, at every 50°C
Soaking duration	58 h
Quenching temperature	600–750°C, at every 50°C
Cooling rate	0.07°C/mm
Cooling duration	12 h
Quenching speed from a quenching temp. to 50–60°C	About 5.5°C/s, by running water

quenched at a speed of 5.5°C/s. The  $\beta$ -quartz is considered to grow principally during the slow cooling period. Table 11.2 summarizes part of the experimental conditions [24].

As nutrient, high-purity  $\alpha$ -cristobalite was used to prevent the influence of impurities. The solvent filled 30% of the free volume of the reaction vessel. At this filling rate and high temperature, it takes the form of a fluid of very low density, i.e., vapor phase. In the growth of natural quartz, the same phenomenon is observed. This is evident from the observation of two phase fluid inclusions found in natural quartz. In some cases, the proportion of the liquid phase to the vapor phase in such two phase fluid inclusions reaches to 20–30% [35,36]. It is understood that quartz with inclusions of such a high proportion of vapor phase, or such a low proportion of liquid phase, grows under vapor phase at a high temperature. Therefore, one may consider that the growth of  $\beta$ -quartz in this experiment also took place under vapor phase. Considering this method similar to or an extension of the hydrothermal growth method, the author named it “hydrothermal vapor growth.”

The effects of the filling density in liquid phase, i.e., fluid density at a high temperature, upon the growth of quartz at a high temperature of 600°C or more is not yet clear.

As the temperature rises, the solvent reacts with  $\alpha$ -cristobalite used as nutrient. Dissolved silicic ions dissolve into the vapor phase and grow during the slow cooling period. That is to say, the  $\beta$ -quartz grew during the period through which these ions were slowly cooled down from the soaking temperature. Since the transition from  $\alpha$ -quartz to  $\beta$ -quartz occurs at a temperature of 573°C, one might suppose that quenching at a temperature sufficiently higher than 573°C allows one to see that the morphology of  $\beta$ -quartz is unchanged, in the same way as  $\beta$ -quartz in volcanic rocks is observed. The authors observed that the crystals thus quenched and characterized through SEM and X-ray diffraction are  $\alpha$ -quartz transformed from  $\alpha$ -cristobalite.

### 11.4.2 Experimental results

Table 11.3 summarizes the results of the experiment [24]. Crystals are roughly classified into the following two groups:

- Type 1: Most of these crystals show a long prismatic habit and rounded terminations. The hexagonal pyramidal faces of this type show  $\{10\bar{1}\bar{1}\}$ .
- Type 2: These crystals show a hexagonal or stout prismatic habit. They are larger than those of type 1. The photograph in Fig. 11.6 shows both types 1 and 2. The type 1 crystals have a thickness of 3  $\mu\text{m}$  and a length of less than 25  $\mu\text{m}$ . The type 2 crystals may be further classified into the following three subgroups:
  - Type 2N: As in Fig. 11.7, these crystals show a hexagonal dipyramidal habit without prismatic faces.
  - Type 2F: As in Fig. 11.8, these crystals show a stout prismatic habit with flat prismatic faces.
  - Type 2C: As in Fig. 11.9, these crystals show a spindle-like habit with tapering faces. Their prismatic faces tend to curve as their size grows.

Most of the hexagonal pyramidal faces of these Type 2N, Type 2F, and Type 2C crystals were  $\{\text{hohl}\}$  faces, with  $\{10\bar{1}1\}$  faces appearing only as small faces at the terminations.

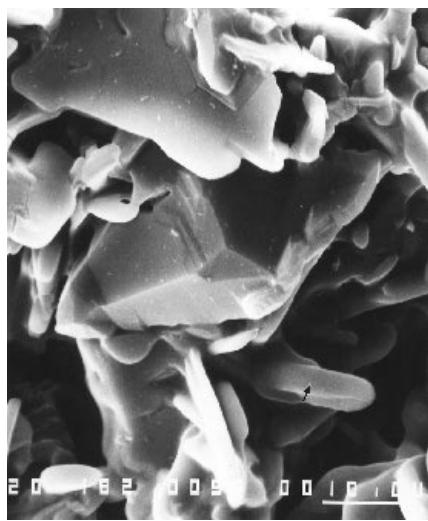
As is shown clearly in Table 11.3, there are more Type 1 crystals than Type 2 crystals. The table also shows that as the temperature rises (above 700°C), the Type F crystals increase and the Type N crystals decrease in number. At a soaking temperature of less than 700°C, Type C and F crystals were observed, but there were no Type N crystals. At a soaking temperature of 600°C and a quenching temperature of 550°C, the crystals showed a habit like  $\alpha$ -quartz. No significant difference of morphology was observed that was attributable to the difference of solvent, but in the experiment with NaCl solution, striations were observed on the prismatic faces. While in the experiment with NaOH solution, pyramidal growth hillocks were observed on the prismatic faces. This indicates that, even at such a

**Table 11.3.** Summary of the Experiment Results

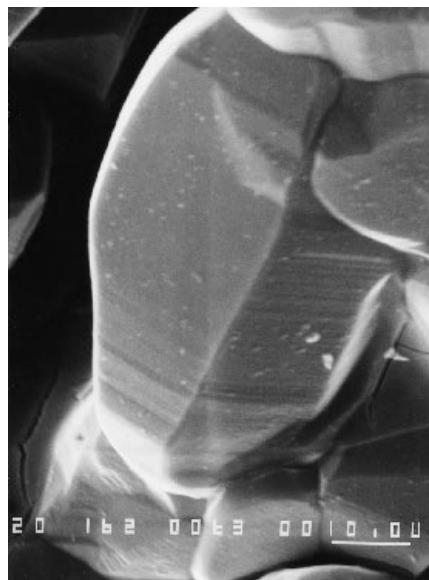
Soaking temperature [°C]	Quenching temperature [°C]	Solvent 10 wt% NaCl	Solvent 1 N NaOH
750	700	Type 1 > Type 2 (F > C >> N)	Type 1 > Type 2 (F > C >> N)
700	650	Type 1 > Type 2 (C > F)	Type 1 > Type 2 (C ~ F)
650	600	Type 1 > Type 2 (C ~ F)	Type 1 > Type 2 (C ~ F)
600	550	As $\alpha$ -quartz	As $\alpha$ -quartz



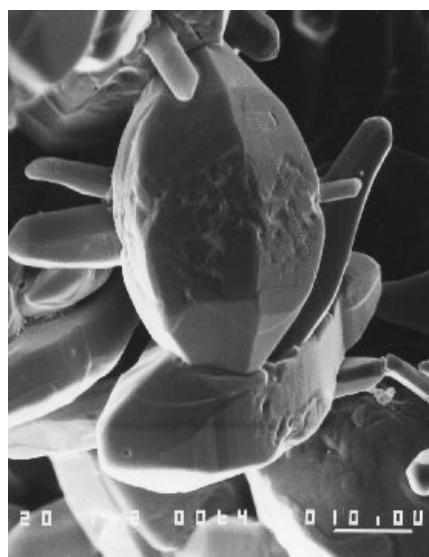
**Fig. 11.6.** SEM photograph of a crystal group showing Type 1 habit (larger crystals) and Type 2 habit (smaller crystals). 10 wt% NaCl solution, soaked at 700°C and quenched at 650°C



**Fig. 11.7.** SEM photograph of  $\beta$ -quartz crystal (Type 2N) without prism faces. 10 wt% NaCl solution, soaked at 750°C and quenched at 700°C. A black arrow indicates co-existing Type 1 crystal



**Fig. 11.8.** SEM photograph of  $\beta$ -quartz crystal (Type 2F). 1 N NaOH solution, soaked at 750°C, and quenched at 700°C



**Fig. 11.9.** SEM photograph of  $\beta$ -quartz crystal (Type 2C). 10 wt% NaCl solution, soaked at 700°C, and quenched at 650°C

high temperature as allows the growth of  $\beta$ -quartz, dissolved ion species are different from solution to solution.

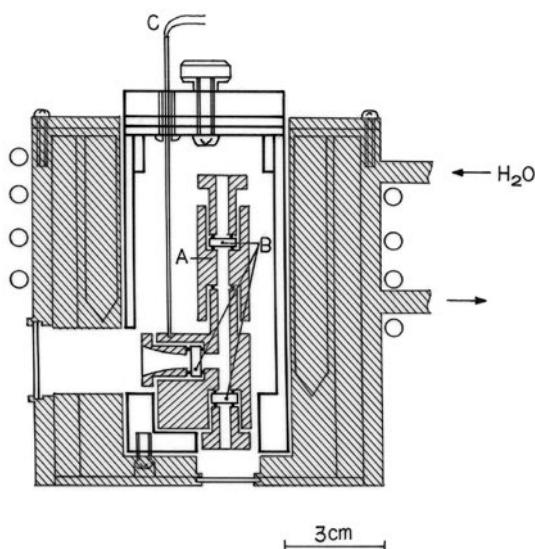
In this experiment,  $\beta$ -quartz grown under “hydrothermal vapor phase” above the transitional temperature showed, in most cases, a hexagonal dipyramidal habit and, in few cases, a hexagonal dipyramidal habit without prism faces. Another remarkable morphological characteristic is that hexagonal dipyramidal faces were not  $\{10\bar{1}1\}$  faces, but fundamentally  $\{h0\bar{h}1\}$  faces. With the appearance of such highly indexed hexagonal pyramidal faces, crystals showed a tendency to show round forms as their size increased.

These observations and the discussions that followed suggest the following about the growing process of  $\beta$ -quartz: The habits shown by the Type 1 and Type 2 crystals represent the morphology of  $\beta$ -quartz.  $\beta$ -quartz starts with Type 1 habit and transforms into a stout Type 2 crystal. In other words, as the crystal grows, the growth rate perpendicular to the prism faces increases much faster than the growth rate perpendicular to the dipyramidal faces. As a result, hexagonal pyramidal faces and tapered prism faces of high indexes appear.

## 11.5 Raman Spectral Studies of the Solution Chemistry of $\text{SiO}_2\text{-NaOH-H}_2\text{O}$ and $\text{SiO}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ Systems Under Hydrothermal Conditions

### 11.5.1 Experimental method

In order to observe directly the state of an aqueous solution under hydrothermal conditions, it is necessary to construct an autoclave with optical windows. Figure 11.10 illustrates an autoclave with optical windows constructed of Cr-Mo steel. A small type autoclave (A) is placed in an electric furnace. The autoclave has a reaction chamber with an internal diameter of 3 mm and a total capacity of 0.5 cm<sup>3</sup>. At the upper and lower sides and a lateral side, the autoclave has mirror-finished, sapphire-plate optical windows (B) 9 mm in diameter and 7 mm in thickness. The material for such windows must not only resist high temperature and pressure, but also must satisfy many other conditions: They must have a high transmittance in an adequate range of light transmittance; the reflective index and its dispersion must be small; its own fluorescent characteristics must be low when Raman spectra is measured, and so forth. Diamond would be best suited as such a material considering all these requirements, but the authors [24] used sapphire plates in the experiment because it had been proven in preliminary experiments that they are quite satisfactory for the purpose. The electric furnace was made in a size, which can be placed in the sample room for the spectrophotometer. The heating in the electric furnace was realized by means of three 300 W and two 100 W parallel nichrome wires wound around the core tube. Around the outer surface of the electric furnace of the autoclave, a copper tube was wound to circulate cooling water



**Fig. 11.10.** Autoclave having optical windows for the measurement of Raman spectra at high temperature and high pressure and electrical furnace. (A) autoclave; (B) sapphire windows; (C) thermocouple

during the spectrophotometric measurement. Temperature was measured by inserting the tip of a thermocouple (C) into a well made on the top of the autoclave to a depth of about 2 mm.

Argon ion laser (Toshiba Co., Ltd.) with a wavelength of 514.5 nm, enabling the control of spontaneous emission in the range of 0–1,000  $\text{cm}^{-1}$ , was used in these experiments. The laser beam was led into the reaction chamber through the lower window of the small autoclave shown in Fig. 11.10. Scattered Raman light generated in the reaction chamber of the autoclave was picked up by a spectrophotometer (Nihon Denshi Co., Ltd.) through the left side window of the autoclave.

When put in direct reaction in the autoclave shown in Fig. 11.10, the quartz and the solution might form heavy cake, which would stick to the inner surface of the sapphire plates of the small autoclave, and reduce the intensity of the laser beam. The scattered laser beam from heavy cake might be picked up, too. For this reason, in the experiment, the author grew quartz for 3 days preliminarily by an ordinary temperature gradient method in an autoclave having an internal volume of 350  $\text{cm}^3$  and a platinum vessel having an internal volume of 100  $\text{cm}^3$ , with a filling rate of 60% and at a dissolving temperature of 350°C and a growing temperature of 330°C. The autoclave was then quenched. The solution was filtered and the filtered solution used as the sample solution, which was supposed to retain silicic ions present at the time the quartz crystals grew up. As solvent, aqueous solutions of 1 N NaOH and 0.5 N  $\text{Na}_2\text{CO}_3$  were used. After having the solution and quartz made to react, the concentration of  $\text{Na}_2\text{O}/\text{SiO}_2$  was calculated from each solution

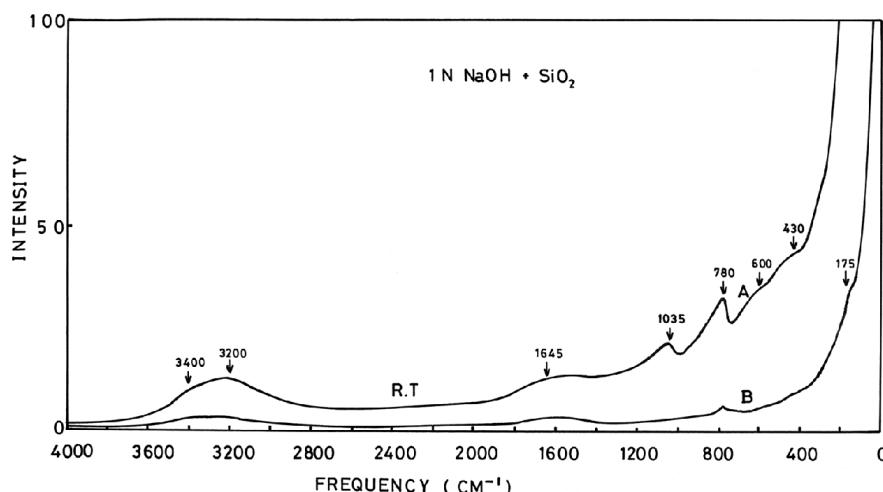
filtered, respectively. The concentration was about 0.56 for the 1 N NaOH solution and about 2.50 for the 0.5 N Na<sub>2</sub>CO<sub>3</sub> solution.

Spectrophotometric measurement was performed in the range of 50–4,000 cm<sup>-1</sup>, maintaining the specimen at a measurement temperature for sometime and gradually increasing the temperature of the autoclave. The filtered solution filled 60% of the inner capacity of the small autoclave shown in Fig. 11.10. The spectra at each temperature were integrated 20 to 30 times with a Raman data analyzer and then averaged.

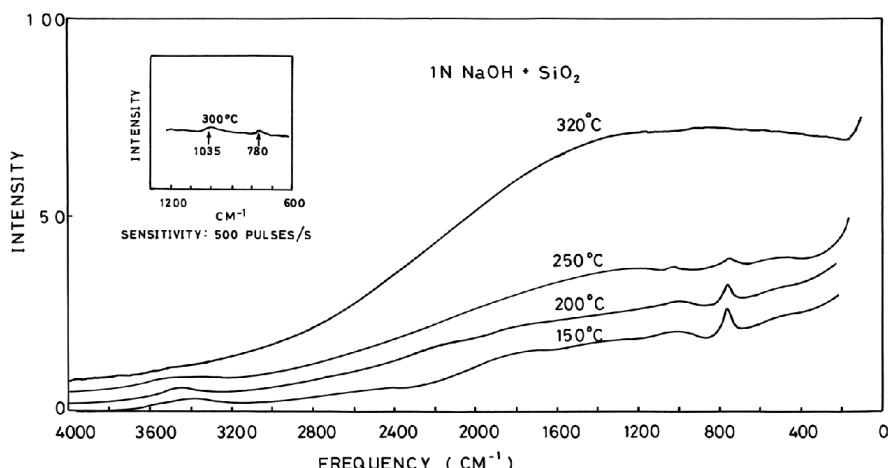
### 11.5.2 Experimental results

#### *SiO<sub>2</sub>-NaOH-H<sub>2</sub>O system [37, 38]*

Figure 11.11 shows the Raman spectra at room temperature. Raman spectra were observed at 175, 430, 600, 780, 1035, 1645, 3200, and 3400 cm<sup>-1</sup>. The Raman spectra shown in Fig. 11.12 were measured at temperatures of 150, 200, 250, 300, and 320°C. At each of the temperatures of 150, 200 and 250°C, spectra were observed at 430, 780, 1035, 3200, and 3400 cm<sup>-1</sup>. Each of these spectra became feebler as the temperature was increased. At a temperature of 300°C, it was confirmed at 780 and 1035 cm<sup>-1</sup>. At a temperature of 320°C, the spectral broadening centering around 1200 cm<sup>-1</sup> was observed. The spectral pattern observed during temperature decrease was the same as that observed during temperature increase. Shifting of the spectral bands with temperature increase and temperature decrease was not observed.



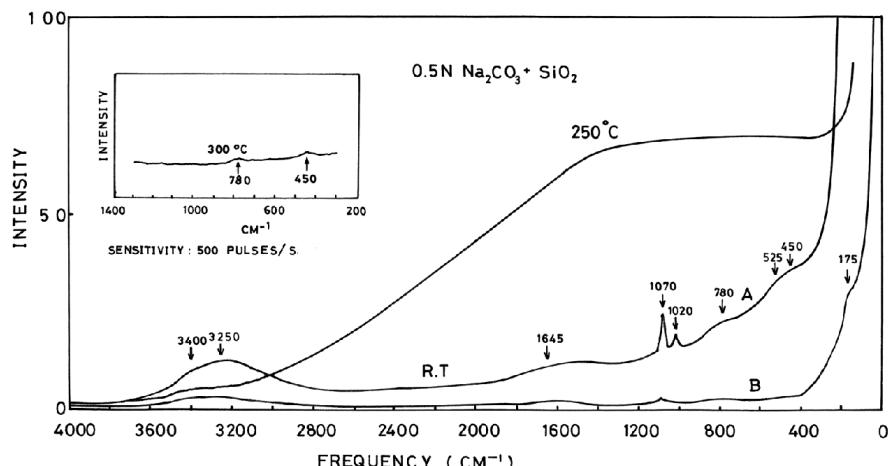
**Fig. 11.11.** Raman spectra of SiO<sub>2</sub>-NaOH-H<sub>2</sub>O system at room temperature. Sensitivity: (A) 1,000 pulses/s; (B) 10,000 pulses/s



**Fig. 11.12.** Raman spectra of  $\text{SiO}_2\text{-NaOH}\text{-H}_2\text{O}$  system at a series of temperatures. Sensitivity: 1,000 pulses/s

### $\text{SiO}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ system [37]

Figure 11.13 shows Raman spectra recorded at room temperature, 250, and 300°C. At room temperature, Raman spectral bands were observed at 175, 450, 525, 780, 1020, 1070, 1645, 3250, and 3400  $\text{cm}^{-1}$ . The spectrum at 780  $\text{cm}^{-1}$  was broad, different from the one shown with NaOH. Under hydrothermal conditions at 300°C,



**Fig. 11.13.** Raman spectra of  $\text{SiO}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$  system at room temperature and a series of temperatures. Sensitivity: (A) 1,000 pulses/s; (B) 10,000 pulses/s

broad spectra were observed at 450 and 780  $\text{cm}^{-1}$ . Spectral patterns observed during temperature decrease was the same as that observed during temperature increase. Shifting of the spectra with temperature increase and temperature decrease was not observed.

### 11.5.3 Discussion

There are several reports on the Raman spectra of sodium silicate solution, like Fortnum and Edwards [39], and Earley et al. [40]. Fortnum and Edwards [39] observed Raman spectra at 448, 607, 777, and 935  $\text{cm}^{-1}$  with 2.5 M sodium silicate solution. With 0.5–2.5 M sodium silicate solutions, Earley [40] observed Raman spectra at 616, 782, and 929  $\text{cm}^{-1}$  at an  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio of 2.0 and at 456, 614, 779, 937, and 1030  $\text{cm}^{-1}$  at an  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio of 1.0. The difference in the  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio caused the slight difference in wavelengths. In the experiment performed by the author with the  $\text{SiO}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$  system at an  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio of 0.56, the Raman spectra observed at 430, 600, 780, and 1035  $\text{cm}^{-1}$  correspond to those reported by Fortnum and Edwards, and Earley et al. Other spectra correspond to those of water. The Raman spectrum observed at 780  $\text{cm}^{-1}$  also corresponds to that of water. However, such a sharp and intensified spectrum of 780  $\text{cm}^{-1}$  as is shown in the figure should not be attributed to water but to silicic ions, since water has a very broad pattern of spectra due to the hydrogen bond between the water molecules. Lentz reported that the proportion of monomers increases as the alkaline concentration increases when the molar ratio is  $\text{Na}_2\text{O}/\text{SiO}_2 \geq 2.0$ , and the proportion of chain or ring type polysilicic ions increases as the alkaline concentration decreases when the molar ratio is  $\text{Na}_2\text{O}/\text{SiO}_2 \leq 1.0$  [29]. Therefore, the concentration of silicic ions in a solution of  $\text{Na}_2\text{O}/\text{SiO}_2$  with a molar ratio of 0.56 ( $\text{Na}: \text{Si} \approx 1:1$ ) is supposed to be in the following relation [29]:



The compliance between the Raman spectra of sodium silicate measured at room temperature with those measured under hydrothermal conditions, and the absence of shifting observed when Fig. 11.11 was compared to Fig. 10.10, shows that the Raman spectra with solutions of  $\text{Na}_2\text{O}/\text{SiO}_2$  with a molar ratio of 0.56 measured under hydrothermal conditions below 300°C (Fig. 11.10, Fig. 11.11) represent Raman spectra of solutions which contain, in the order of appearance in the above relation, monomers, dimers, trimers, and polysilicic ions.

Raman spectra of reaction solution between a 0.5 N  $\text{Na}_2\text{CO}_3$  solution and a  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio of 2.50, and quartz did not show any remarkable characteristics, as were shown with  $\text{NaOH}$ , and in most cases corresponded to those of water. According to Earley et al. [40], the Raman spectra at room temperature of sodium silicate with a  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio of 2.0 or more appear at 454, 614, 784, and 932  $\text{cm}^{-1}$ . The spectra at 454 and 784  $\text{cm}^{-1}$  thus correspond to the results of this experiment. The results of the experiments reported by Lentz [29] suggest the predominance of monomer ions for compositions of  $\text{Na}_2\text{O}/\text{SiO}_2 \geq 2.0$ .

Based on the measurement of the solubility [27,28], it is supposed that ring type  $\text{Si}_3\text{O}_7^{2-}$ , in the case of NaOH, and monosilicic ions of  $\text{SiO}_3^{2-}$ , in the case of  $\text{Na}_2\text{CO}_3$ , exist in each solvent. This corresponds roughly to the results of the experiments performed by Lentz [29]. Raman spectra decreased their intensity as the temperature was increased and were observed at 780 and  $1035\text{ cm}^{-1}$  at a temperature of  $300^\circ\text{C}$  in a  $\text{SiO}_2\text{-NaOH-H}_2\text{O}$  system and at 450 and  $780\text{ cm}^{-1}$  at the same temperature in a  $\text{SiO}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$  system. At a temperature of  $320^\circ\text{C}$ , a broad pattern of spectra were observed in both solutions. This may be attributable to the following:

1. As a result of temperature change, the change of equilibrium constant altered the ratio of existing silicic ions.
2. As a result of temperature change, the vibration level of the Si-O bond altered.
3. Background light increased.

#### 11.5.4 Summary

In the experiment, an autoclave, with optical windows resistant to high temperature and pressure of  $350^\circ\text{C}$  and 400 psi, respectively (at a filling rate of 60%), was constructed and used to measure Raman spectra under high temperature and pressures. The types of silicic ions present in aqueous solutions of sodium silicate vary with the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio of such solutions. As the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio increases, the chain of Si-O-Si is cut to generate monosilicic ions. As the  $\text{Na}_2\text{O}/\text{SiO}_2$  molar ratio decreases, chain or ring type polysilicic ions are generated. A change in the type of these silicic ions causes some shifting or change in intensity of the Raman spectra specific to silicic ions. For example, the spectra of silicic ions with chain-like structure appear at the slightly lower frequency side, but such difference in wave number is small. Therefore, it may be supposed that spectra of silicic ions usually appear around 450, 600, 700, and  $1035\text{ cm}^{-1}$ .

In this experiment, Raman spectra were measured for a  $\text{SiO}_2\text{-NaCl-H}_2\text{O}$  system with a filtered solution obtained after the interaction between a quartz crystal and a NaCl solution at a temperature of  $350^\circ\text{C}$ , but no characteristic Raman spectra were observed. This might be because the solubility of quartz in NaCl solution at this temperature is too small to generate a large amount of silicic ions.

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# **12 Growth and Characterization of Technologically Important Oxide Single Crystals**

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## **12.1 Introduction**

There is a wide variety of technologically important oxide single crystals, which find applications in diverse fields. These are employed as laser hosts, in nonlinear optical devices, optical wave guides and other components in optical communications, in memories, and numerous other applications. Many of the oxide crystals had been extensively used as substrates to prepare high T<sub>c</sub> superconductors, blue light emitting lasers, magnetic bubble memories, and so forth. Lithium niobate [1–2], cadmium tungstate, sapphire, ruby, garnets [3], lithium tantalate, lead molybdate [4], bismuth germanate, potassium niobate, barium titanate [5], bismuth silicate [6], and others are being extensively used for making important devices. We shall discuss recent advances in growth and structural characterization of lithium niobate and bismuth germanate (BGO) crystals.

Lithium niobate ( $\text{LiNbO}_3$ ) is an opto-electronic material.  $\text{LiNbO}_3$  crystals with high degree of perfection, optical homogeneity, correct stoichiometry, and single ferroelectric domain are required for fabrication of surface acoustic wave devices (SAW), optical wave guides, photonic switches in telecommunication, as piezoelectric materials in tomography, and as second harmonic generators (SHG) [1].  $\text{LiNbO}_3$  single crystals have large electro-optic coefficients and do not need application of a high voltage. These crystals have received much attention as phase conjugate wave generators and real-time read-write holograms using the photorefractive effect [7]. Generally, to improve properties,  $\text{LiNbO}_3$  crystals have been doped with transition metals. Iron doping has been utilized for making devices like second harmonic generators. Crystals grown from congruent melts are inherently metastable at room temperatures. Therefore, a strict control on composition of the charge for crystal growth experiments and physical parameters like temperature are very crucial for growing good quality single crystals.

Bismuth germanate is widely used as a scintillator due to its attractive properties like nonhygroscopic nature, high atomic number (Z), short decay time, and extremely short afterglow [8–15]. BGO scintillators are being widely used for positron emission tomography [16,17], mammography [18], X-ray computed to-

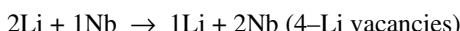
mography [19,20], calorimetry [21,22], and oil well logging [23]. Only colorless crystals grown from high purity oxides are useful as scintillators [9]. Crystals grown from low purity  $\text{Bi}_2\text{O}_3$  and  $\text{GeO}_2$  are yellowish in appearance. Study of influence of doping elements on sensitivity has shown that Gd and Ti improved sensitivity by 4% above that of pure BGO [24–26]. The fluorescence from BGO is similar to that reported for other materials where bismuth is present as a dilute activator ion. The BGO luminescence is assigned to  ${}^3\text{P}_1 \rightarrow {}^1\text{S}_0$  transitions of  $\text{Bi}^{3+}$  [8]. Fluorescence spectra of BGO gives a peak at a wavelength of 483.3 nm.

High resolution X-ray diffraction topography and diffractometry have been found to be useful for the direct observation of lattice defects in single crystals and provide valuable feedback for improving structural perfection of crystals [27].

In this chapter, we review recent advances made in growth and characterization of nearly perfect lithium niobate and bismuth germanate crystals.

## 12.2 Crystallographic Structure

At room temperature  $\text{LiNbO}_3$  has rhombohedral structure. It belongs to the  $3m$  point group and  $\text{R}3c$  space group. In the  $\text{R}3c$  space lattice Nb atoms occupy  $(0,0,0)$  positions, Li atoms occupy  $(0,0,1/4)$  positions and O atoms occupy  $(4,1/3,1/2)$  positions. The unit cell dimensions are:  $a = 5.1494 \text{ \AA}$  and  $c = 13.8620 \text{ \AA}$ . At  $1160^\circ\text{C}$ ,  $\text{LiNbO}_3$  undergoes a first order phase transition. The polar ferroelectric  $3m$  symmetry transforms into nonpolar paraelectric  $3\bar{m}$  symmetry above the Curie temperature. There is a substantial change in the volume of the unit cell at the phase transition due to which strain is produced in the crystals as these cross the Curie temperature. This strain has to be handled very carefully during growth experiments as it can lead to cracking or a high level of residual stress in the crystals. Lithium niobate is known to grow with lithium deficiency. The model for Li deficiency is as follows:



This results in a total of 5.9% Li missing from its regular sites and this is called antisite defects.

Menzer (1931) showed that  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) is isomorphous with  $\text{Bi}_4\text{Si}_3\text{O}_{12}$  (eulytine) [28]. Eulytine belongs to the  $\text{I}43d$  space group [29,30]. Durif and Averbuch-Pouchot (1982) refined the atomic positions of BGO [30]. The cubic unit cell has a lattice constant,  $a_0 = 10.497 \text{ \AA}$  and contains four formula units.  $\text{Ge}^{4+}$  with site symmetry  $\bar{4}$  has an almost regular tetrahedral coordination of  $\text{O}^{2-}$  ions at distance  $1.740 \text{ \AA}$ .  $\text{Bi}^{3+}$ , site symmetry 3, is coordinated by three  $\text{O}^{2-}$  ions at  $2.160 \text{ \AA}$  and three  $\text{O}^{2-}$  ions at  $2.605 \text{ \AA}$ , in a highly deformed octahedron. One tetrahedron shares points with eight octahedra. One octahedron shares edges with three other octahedra and shares points with six tetrahedra. An interesting aspect of BGO is the presence of “holes” in its structure. These are empty sites with point symmetry

4 and are enclosed tetrahedrally by O<sup>2-</sup> ions at 2.47 Å [31]. No cleavage planes have been observed for BGO [32]. The atomic absorption coefficient for X-rays of wavelength 0.7 Å is very high and calculated as 710 cm<sup>-1</sup>.

### 12.3 Growth of Lithium Niobate Crystals: Earlier Work

Reisman and Holtzberg (1958) gave the first phase diagram of the system Li<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub> [33]. However, Svaasand et al. (1973) worked out the phase diagram of LiNbO<sub>3</sub>, which was widely accepted [34]. Lerner et al. (1968) made a substantial improvement, showing that LiNbO<sub>3</sub> has a fairly large solid solution ranging from 44 to 55 mol % of Li<sub>2</sub>O. The maximum melting temperature does not occur at the stoichiometric composition but rather at 48 to 49 mol % of Li<sub>2</sub>O and tends to grow with variable stoichiometry [35]. Starting with Ballman in 1965, several investigators have carried out the growth of single crystals of LiNbO<sub>3</sub> [36]. The LiNbO<sub>3</sub> crystals were generally grown by the Czochralski (Cz) method, although other methods such as Verneuil, Bridgman/Stockbarger, and Stepanov techniques are possible and have been tried [37,38]. The materials aspect of LiNbO<sub>3</sub> were dealt with in the well-known series of five papers from the Bell Laboratories by Nassau et al. (1966) [39] and Abrahams et al. (1966) [40]. They could grow successfully single domain crystals by *in situ* poling during the growth. Baumann et al. (1993) had grown crystals with melt composition varying from 48.46–48.49% Li<sub>2</sub>O [41]. They determined the congruent melt composition as 48.470 ± 0.005 mol % Li<sub>2</sub>O for the [00.1] growth direction. They have analyzed the compositional homogeneity along the crystal by analyzing the orthoscopic fringe patterns and found that the composition of the congruent melting point shifts from the stoichiometrical composition towards the niobium rich side. The precise congruent composition reported in the literature varies between 48.3 to 48.6 mol % Li<sub>2</sub>O. Different methods were used to determine the exact value of the congruent composition by investigation of compositional variation on physical properties like Curie temperature [42,43], surface acoustic wave velocity [44], refractive index [45–48], birefringence [49], and phase matching temperature of the second harmonic generation [48,49].

Single crystals of high structural perfection without compositional inhomogeneities are required for device fabrication. The most serious problem concerning the quality of LiNbO<sub>3</sub> is the spatial variation of birefringence, which is considered to be related to thermal stress and compositional variation during crystal growth. Studies on spatial variations of the birefringence using optical techniques have been made by several workers [48,49]. Reich et al. (1991) studied the effect of electrical field on the growth of LiNbO<sub>3</sub> crystals [50]. Stoichiometry control plays a key role in property tailoring. To optimize the stoichiometry and grow nearly perfect crystals, we have grown LiNbO<sub>3</sub> crystals with variable composition from 45 to 55 mol % Li. X-ray diffractograms were recorded for each composition. It was seen that for a small change in Li/Nb ratio there was an appreciable change in the peak intensity particularly for 11.1 type reflections. Though

the bulk powder was  $\text{LiNbO}_3$ , only Nb concentration varied in the different composition powders. The excess Nb concentration in the crystals gave different colors to the crystals.

## 12.4 Growth of Bismuth Germanate Crystals: Earlier Work

Nitsche (1965) had grown for the first time bismuth germanate ( $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ) single crystals as a replacement for the bismuth silicon oxide (eulytite) [32]. Nitsche used a crucible-free technique as it was found to react with platinum. BGO crystal rods with a diameter of 4–5 mm and lengths of 10–12 mm were grown successfully. These were yellow in color and X-ray Laue patterns established that these were single crystals. It was found that the crystal was stable in air but dissolved easily in concentrated HCl. Research on the growth of good quality and large size BGO crystals was started after this initial work [51–53]. Dickinson et al. (1972) grew BGO crystals by the Cz method in air, thereby, suppressing the corrosion of the platinum crucible [54]. They could grow BGO crystals of 15 mm diameter and 25–38 mm length. These crystals were transparent and nearly colorless with a slightly yellowish tinge. Seed rotation rate was optimized at 30 rpm and the pulling rate was kept in the range of 3–4 mm/h. They used X-ray diffraction analysis to confirm the crystallinity. Mass spectrographic analysis showed that the total impurity concentration in the crystals ranged from 35 to 85 ppm. They found silicon was the major cation contaminant, and chlorine was the major anion impurity. In addition, aluminum, potassium, and calcium were detected in the 1–20 ppm range. Platinum contamination was below 1 ppm level.

Weber and Monchamp (1973) showed BGO as a laser host crystal for rare earth and iron group activator ions and also as a scintillator material [8]. This was the first paper to propose that BGO can be used as a scintillation material. The group compared  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  with  $\text{Bi}_{12}\text{GeO}_{20}$  and showed its superiority. Takagi et al. (1981) studied the influence of crystalline defects on scintillation conversion efficiency [24]. It was found that the efficiency decreases by shrinkage voids and impurities. This work suggested that shrinkage voids may be eliminated by making the growth interface flat and purifying the crystals. It was shown that the sensitivity can be brought up to 12% of that of NaI (Tl) by eliminating voids and purifying the crystals. Later, Barnes (1984) studied the influence of impurities on the quality of bismuth germanate, particularly on the scintillation property [55]. Al, Ca, Fe, Mg, Si, and Pt were among the major impurities investigated in Cz grown crystals. The impurity tolerance in the raw material was set at 1 ppm level.

Schmid et al. (1984) grew BGO crystals by the heat exchanger method (HEM) [56]. They compared their crystals with those grown by the Cz method. The crystals were transparent and free of dislocations. Control of stoichiometry was found to be a problem in the Cz grown crystals as there are a few more stable  $\text{Bi}_2\text{O}_3$  -  $\text{GeO}_2$  phases according to the phase diagram [54,57]. Schmid and co-workers suggested that variations in stoichiometry of the melt is less in the HEM method than that found in the case of the Cz method. In the Cz method, the melt surface had a

local temperature gradient and, therefore, secondary phases could be trapped in the grown crystal. These were not present in the crystals grown by the HEM method.

Van Hoof et al. (1985) characterized Bridgman grown crystals by X-ray diffractometry and topography techniques [58]. They found that the half width of the diffraction curves in the central region was only 10 arc sec, and for the entire crystal it was ~20 arc sec. They found that the Bridgman grown BGO crystals were dislocation free except at the outer edges. The dislocation density was estimated as less than  $10 \text{ cm}^{-2}$  at the center and about  $10^2\text{--}10^3 \text{ cm}^{-2}$  at the outer edges. However, for Cz grown BGO crystals half widths of the diffraction curves were about 16 arc sec for the central region. Low angle boundaries were observed in the crystals. For the entire crystal the half width was 500 arc sec and the dislocation density was found to be in the range:  $1\text{--}1.5 \times 10^4 \text{ cm}^{-2}$ , which was almost 100 times of that observed with the Bridgman grown BGO crystals. X-ray diffraction topographs recorded with crystals grown by the Bridgman as well as Cz methods supported the results obtained by diffractometry [58]. Allegretti et al. (1989) also showed that the Bridgman grown BGO crystals exhibit less dislocation density than the Cz grown BGO single crystals [59]. Smet et al. (1988) found that the yellowish color of crystals was due to change in stoichiometry and also caused by impurities [60]. The formation of voids and inclusions was also observed in Bridgman grown BGO crystals. They characterized the crystals by the etching method. BGO crystals grown from the melt were always bounded by {112} and {112} crystallographic facets. The formation of inclusions was concentrated at the edges of the growth facets and impurity segregation was maximum near the center of the facets. Van Enckevort et al. (1990) had also characterized Bridgman grown BGO single crystals by the etching method [61]. 1N–4N HCl etchant was used in this case. They also used the birefringence microscopy technique. Edge dislocations were observed in the Bridgman grown BGO single crystals.

Takagi et al. (1986) studied the effect of growth conditions on the shape of BGO single crystals [62]. They used the Cz method to grow BGO crystals. The rotation rate was varied from 27 rpm to 50 rpm. They observed an optimized rotation rate of 40 rpm to achieve a stable shape of the crystal. Otherwise the crystals were twisted and imperfect. By varying the position of the rf coil it was observed that the crystal shape could be improved by making the upper part of the crucible hotter than the lower part. They also suggested that the use of an after-heater on a crucible is an effective way of suppressing the heat loss from the melt and the crystal surfaces, and also prevented twisting of the crystal. Horowitz et al. (1986) studied the effect of precipitates and yellow color on crystal performance [63].

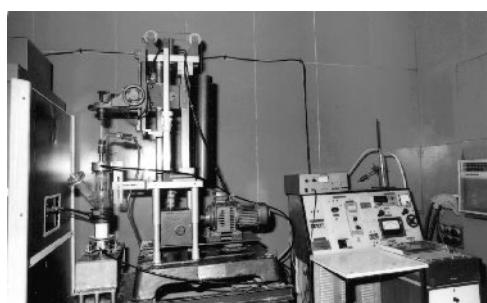
Ivleva et al. (1987) grew some of the multi-oxide single crystals like  $\text{LiNbO}_3$ ,  $\text{Ca}_3(\text{VO}_4)_2$ ,  $\text{Bi}_{12}\text{SiO}_{20}$ ,  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , and  $\text{Bi}_{12}\text{GeO}_{20}$  by Stepanov's technique [38]. In this method the melt is transported via a feed capillary to the meniscus on the top plane of a shaper. By this technique crystals of desired shapes can be grown. However, the quality of these crystals was not found to be high enough for device applications. Gopalkrishnan et al. (1994) made an attempt to grow BGO crystals by the Float zone method [64]. Later, this group made XPS studies on BGO and BSO crystals grown by the Cz and Float zone methods and found that the surfaces

of these crystals were contaminated [65]. The eulytite crystals are chemically more robust to degradation than the sellinite crystals. A research group at IIC, Novosibirsk (1996), (2001) has grown very large size BGO single crystals, weighing more than 30–50 kg, by the Low Thermal Gradient Cz (LTG Cz) technique [66]. They suggested that the LTG Cz method may be a suitable method for growing bismuth germanate single crystals of device quality. We have used this technique to grow nearly perfect BGO crystals [67–71]. These crystals have been extensively characterized by high-resolution X-ray diffraction techniques.

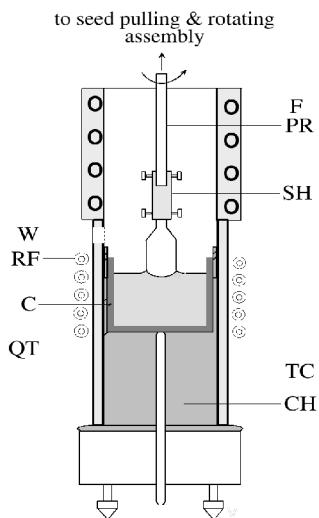
## 12.5 A Crystal Growth System for Cz Growth of Nearly Perfect Crystals

A versatile crystal puller designed, developed, and fabricated in our laboratory is shown in the Fig. 12.1. It has been extensively used for growth of single crystals using a resistance heating furnace as well as an rf induction heating system [72,73]. It is possible to continuously vary the seed pulling rates by a factor of ten around a given nominal growth rate. Different absolute values of growth rates can be obtained by selecting an appropriate set of gears. A high level of uniformity and smoothness of pulling motion is ensured by employing two stainless steel rods with surface flatness within  $\pm 5 \mu\text{m}$  as guides to the motion.

The salient features of the crystal growth system are shown schematically in Fig. 12.2. The platinum crucible (C), ceramic holder (CH), and Pt / Pt-10% Rh thermocouple (TC) are enclosed in a quartz tube (QT). A window (W) had been provided in the quartz tube for viewing the crystal while it is being grown. The crucible assembly is surrounded by an rf coil (RF) for melting the charge. A platinum seed holder (SH) was fixed at one end of a ceramic rod (PR). The other end of the ceramic rod is fixed to a seed pulling and rotating assembly. A resistive furnace (F) was placed above the crucible set-up to ensure controlled post-growth cooling of the crystals.



**Fig. 12.1.** A photograph of a crystal growth system designed and developed at NPL (National Physical Laboratory, New Delhi, India)



**Fig. 12.2.** A schematic line diagram of the crucible set-up of the crystal growth system developed at NPL

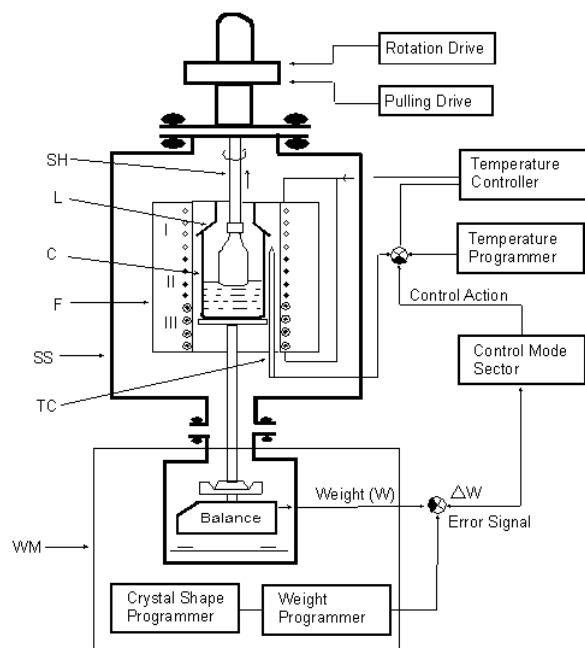
### 12.5.1 A crystal growth system for low thermal gradient Czochralski (LTG Cz) technique

The LTG Cz method employed for successful growth of high quality BGO crystal is a modification of the conventional Cz method [74]. It is well-known that in the usual Cz growth of crystals the temperature gradient across the seed–melt interface is important in deciding the rate of growth and the perfection of the grown crystals. The temperature gradient is particularly important for the growth of oxide single crystals [75]. For the growth of crystals like BGO, a low thermal gradient has enhanced the perfection of the crystals to the state-of-the-art level [68]. To achieve a low thermal gradient in Cz growth, special features have to be incorporated in the growth system. Figure 12.3 shows such a crystal growth system designed and developed at the Institute of Inorganic Chemistry, Novosibirsk, Russia. A block diagram of the crystal growth system is shown in Fig. 12.4. The main subassemblies of this system are: (1) the growth chamber SS; (2) the furnace F; (3) the crucible C; (4) the crystal pulling and rotation mechanism SH; and (5) the power supply and electronic controls [67].

The crystal growth chamber (SS) is essentially a double-walled stainless steel vertical cylinder 600 mm in diameter and 900 mm high. The crucible and the resistance furnace are housed in this chamber. Doors are provided to this chamber on two opposite vertical sides for taking out and putting in crucibles. For viewing the interior of the chamber, two windows, one on each door, are fixed. The chamber is mounted on a base plate. A weighing mechanism (WM) consisting of an electronic balance to weigh the crucible and charge is located below the base plate.



**Fig. 12.3.** A photograph of the crystal growth system employed for growth of crystals by the low thermal gradient Cz method



**Fig. 12.4.** A block diagram of the crystal growth system used for growth of crystals by the low thermal gradient Cz method

A three-zone muffle furnace (F) has been used. The electrical power fed to all the zones is controlled independently. The temperature of each zone is monitored by positioning the thermocouples (TC) radially to the furnace.

Cylindrical-shaped platinum crucibles (C) are employed. In some of the experiments for the growth of BGO crystals, crucibles with diameters of ~70 mm and lengths of ~150 mm were used [68]. The crucible is placed on one arm of the microbalance of the weighing mechanism. A tightly fitting platinum lid (L) was employed to cover the top of the crucible. This arrangement helps in maintaining the low temperature gradient above the melt.

A pull rod made of ruby, with a diameter of ~10 mm and length of ~35 cm, is fixed to the pulling assembly. A cylindrical platinum seed holder is attached to the other end of the pull rod. By varying the frequency of the input power of the motor, the pulling rates can be varied. Six different pull rates in the range of 0.1 mm/h to 6 mm/h and three different seed rotation speeds in the range of 7.5 rpm to 100 rpm are possible.

The central electronic control unit consists of: (1) a Seed Rotation Control Unit (SRCU); (2) a Seed Pulling Control Unit (SPCU); (3) an Electronic Weight Balancing Unit (EWBU); (4) a Crystal Weight Programmer Unit (CWPU); (5) an Error Signal Feedback Unit (ESFU); (6) Recording Instruments (RI), and (7) Temperature Controller-cum-Programer Units (TCPU). These units are employed to control all the essential functions.

## 12.6 High Resolution X-ray Diffractometers

High resolution X-ray diffraction techniques are being extensively employed to evaluate crystalline perfection of single crystals and to characterize crystal defects [76]. In these experiments, the exploring X-ray beam is required to be highly collimated and monochromated. The divergence of the beam has to be reduced, keeping in view the theoretical half widths of the diffraction curves to be recorded. Ideally, it should be much lower than the theoretically expected half widths. Such systems are now available [77]. However, even if the divergence is comparable to the half width, the system can be used effectively. To achieve nearly parallel X-ray beams, combinations of X-ray sources with small sizes (microfocus or fine focus), long collimators, slits with small openings, and monochromator-collimator crystals are used.

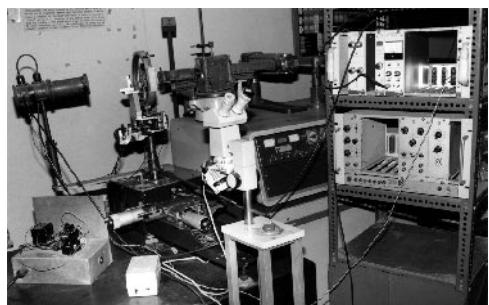
Essential features of a double crystal X-ray diffractometer and a five crystal X-ray diffractometer, which were employed to characterize BGO and LiNbO<sub>3</sub> crystals, respectively, in the authors' laboratory are described in the following.

### 12.6.1 Double crystal X-ray diffractometer

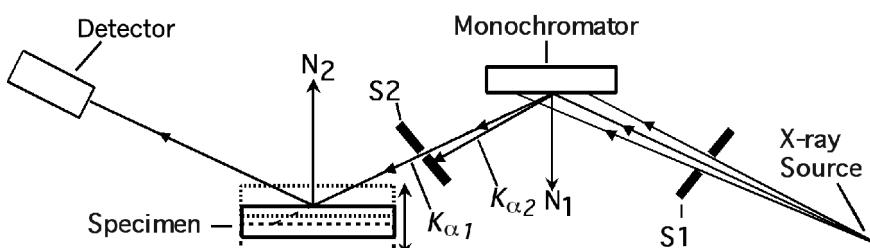
Figures 12.5 and 12.6 show a photograph and a schematic line diagram of the double crystal X-ray diffractometer, respectively. The diffractometer has been de-

signed and developed at NPL [78]. It consists of: (1) an X-ray source; (2) the monochromator stage; (3) the specimen stage; (4) the traversing mechanism, and (5) the detector and the counting systems. A fine focus X-ray source was employed as the source of X-rays. The source size was  $0.4 \times 0.4 \text{ mm}^2$  after foreshortening. A 50 cm long collimator fitted with a slit (S1) is used to reduce the divergence of the beam to  $\sim 300$  arc sec in the horizontal plane, which is the plane of diffraction. One of the slits is vertical and is used to reduce the divergence in the horizontal plane. The other slit is horizontal and controls the vertical divergence. The jaws of both the slits are made of  $\sim 1.6$  mm thick tantalum sheet. The edges of the jaws are prepared carefully by grinding and lapping.

The X-ray beam emerging from the first collimator slit (S1) falls on a plane (111) silicon monochromator-collimator. The crystal was mounted on a tilt stage, which in turn is fixed on the top of a turntable, which is essentially an optical spectrometer. The diffracting (111) planes of silicon were oriented to lie in a vertical plane. The angular orientation of the monochromator with respect to the collimated beam was adjusted for Bragg diffraction from (111) planes, which were nearly parallel to its surface. The diffracted beam from the monochromator contained well resolved  $K_{\alpha 1}$  and  $K_{\alpha 2}$  components of the characteristic  $K_{\alpha}$  doublet. A



**Fig. 12.5.** A photograph of the double crystal X-ray diffractometer designed and developed at NPL



**Fig. 12.6.** A schematic diagram of the double crystal X-ray diffractometer developed at NPL

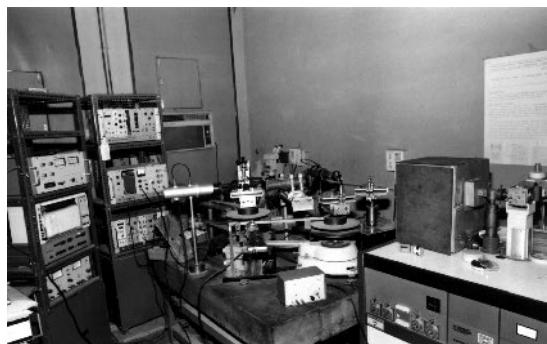
second collimator slit (S2), is placed in the path of the diffracted beam. The vertical slit was positioned to allow only the  $K_{\alpha 1}$  beam to pass through. The  $K_{\alpha 2}$  beam and the residual direct beam were blocked. The  $K_{\alpha 1}$  beam so isolated was used as the exploring beam. The height of the exploring beam can be fixed as per the requirements of an experiment.

The specimen occupied the second crystal stage of the diffractometer. In all the experiments reported in the present work, the specimens were oriented for diffraction in (+, -) symmetrical Bragg geometry. However, this stage can be used to perform the experiments in Laue geometry also. The specimen was mounted on a tilt stage or a vertical circle goniometer, which is fixed on top of a traversing mechanism. This entire assembly is mounted on a central turntable, which has been designed and developed at NPL. This turntable is able to give small angular rotations of about 0.06 arc sec to the crystal around a vertical axis. The angular rotation of the crystal in the plane of diffraction ( $\theta$ -motion) is measured accurately from the deflection of a graticule fixed at the end of a 1 m long radial arm of the turntable. The diffractometer was placed on a heavy granite surface plate. The top surface of the granite plate is flat within  $\pm 8 \mu\text{m}$ .

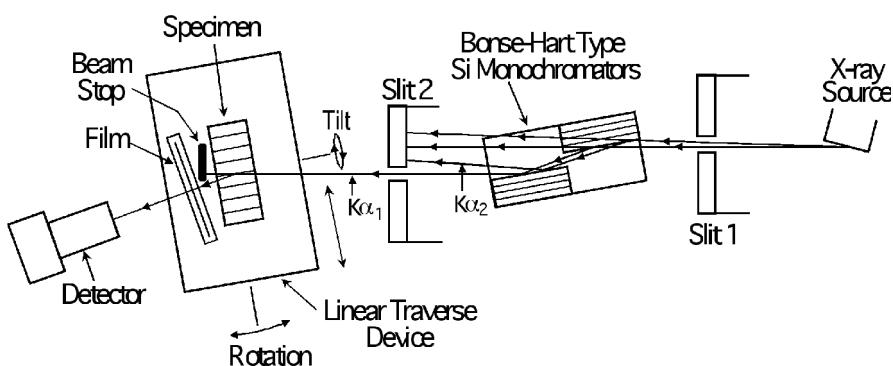
A scintillation counter designed, developed, and fabricated at NPL was used as the X-ray detector. In this counter a NaI (Tl) crystal was used as the scintillator. The diffractometer can be used for recording high resolution X-ray diffraction (rocking) curves and topographs, making absolute integrated intensity measurements and for measuring the radius of curvature of specimen crystals [67,68,71,79,80].

## 12.6.2 Five crystal X-ray diffractometer

A five crystal X-ray diffractometer, designed, developed, and fabricated at NPL (National Physical Laboratory, New Delhi, India) has been used for the high resolution X-ray diffractometric and topographic evaluation of crystalline perfection [77]. Figure 12.7 shows a photograph of this diffractometer. The results reported in this article were obtained by employing the diffractometer in a three crystal configuration. A schematic line diagram of the diffractometer in the three crystal configuration is shown in Fig. 12.8. The diffractometer was set in (+, -, +) geometry. A well collimated X-ray beam was achieved by employing a combination of a fine focus X-ray source, a long collimator, and two plane silicon monochromator-collimator crystals, which were set in (+, -) geometry of Bonse-Hart type [81]. The X-ray source and collimator details are the same as in the case of the double crystal X-ray diffractometer described above. With this arrangement, the  $K_\alpha$  characteristic radiation is resolved into  $K_{\alpha 1}$  and  $K_{\alpha 2}$  components. Highly monochromated and well collimated  $K_{\alpha 1}$  beam was isolated with the help of a fine slit and was used as the exploring X-ray beam. In the present set of investigations Mo  $K_{\alpha 1}$  radiation was used. The specimen crystals formed the third crystal of the diffractometer. For X-ray diffractometric and topographic studies of crystals in



**Fig. 12.7.** A photograph of the five crystal X-ray diffractometer, designed, developed, and fabricated at NPL

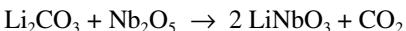


**Fig. 12.8.** A schematic diagram of the five crystal X-ray diffractometer in the three crystal configuration

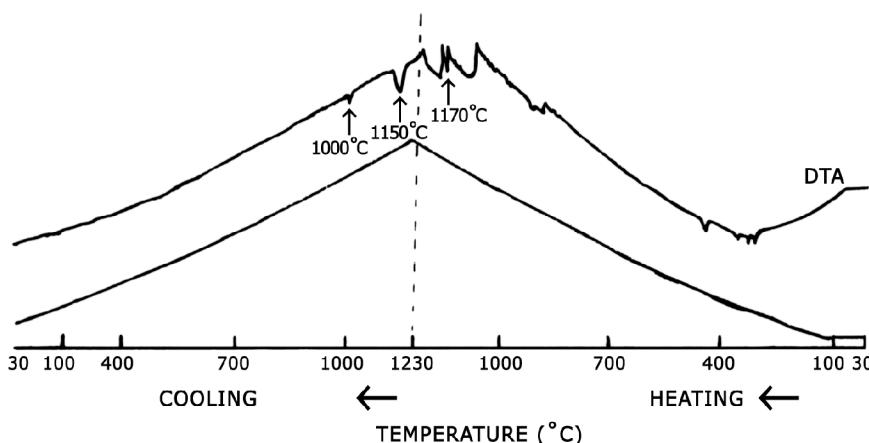
transmission geometry, these were thinned down to 0.4 mm. Great care has been taken in mounting these thin wafers so that no appreciable strain is introduced during the mounting process [82]. Diffraction from (11.0) lattice planes was studied in symmetrical Laue geometry. These planes are normal to the growth direction [00.1]. The exploring X-ray beam had a width of 0.2 mm in the plane of diffraction and the height was adjusted according to the size of the sample.

## 12.7 Synthesis of Lithium Niobate and Bismuth Germanate Powders

The LiNbO<sub>3</sub> charge was prepared by the solid state reaction of Li<sub>2</sub>CO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> at 1000°C for 24 h according to the reaction:



To optimize the correct stoichiometry,  $\text{Li}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  varying from 45 mol % to 55 mol % were mixed to prepare the charge. X-ray diffractograms were recorded for each charge composition. The phase change during the heating as well as the cooling cycle until the melting point were confirmed by DTA and TGA curves. A typical DTA curve is shown in Fig. 12.9.



**Fig. 12.9.** A typical DTA curve recorded for lithium niobate powder

Bismuth germanate powder was prepared by high temperature solid-state reaction of  $\text{Bi}_2\text{O}_3$  and  $\text{GeO}_2$  powders. The binary system of  $\text{Bi}_2\text{O}_3$  and  $\text{GeO}_2$  can produce several stable compounds on reaction [31,53,57]. The molar ratios of the two constituents in these compounds are 1:1, 2:3, 6:1, 7:1, and 1:3. For the present series of experiments, the two powders were carefully weighed with molar ratio of 2:3 to achieve the desired phase with the composition  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ . The chemical reaction is given by:

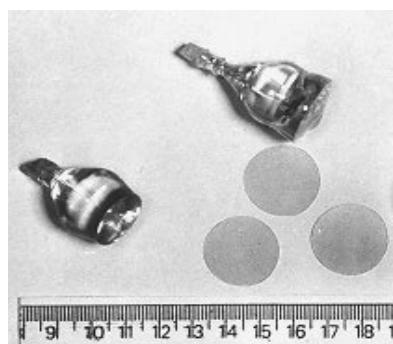


The two powders in the molar ratio 2:3 were thoroughly mixed for 24 h. The purity of both the chemicals were 99.99%. The mixture was sintered at 850°C for 8 h. After the reaction, charge was cooled and once again powdered, remixed, and again sintered at 850°C for 8 h. The crystallographic phase was confirmed by powder X-ray diffraction. For the crystal growth experiments this powder was used as the charge material.

## 12.8 Growth of Nearly Perfect Crystals of LiNbO<sub>3</sub> and BGO

### 12.8.1 LiNbO<sub>3</sub> single crystals

LiNbO<sub>3</sub> single crystals were prepared by varying the molar fractions of Li<sub>2</sub>CO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub>. The mol % of Li was varied from 45% to 55%. X-ray diffraction patterns were recorded to confirm all the compositions. Single crystals were grown with different Li to Nb ratios. The crystals were grown along the [00.1] direction in air using platinum crucibles 50 mm in diameter and length of about 55 mm [73]. Experimental parameters were optimized for growth of nearly perfect crystals. The seed pulling rate was kept at ~10 mm/h and the rate of seed rotation was maintained at 30 rpm. Since these crystals have a first-order phase transition below melting point, these can easily crack during cooling to room temperature after the growth. The post-growth cooling rates were optimized in the following manner. After the growth, the crystals were first cooled down to about 900°C at the rate of 20°C/h over a period of 10–15 h in rf heating. Thereafter, the crystals were pulled up into the resistive furnace (F), which was positioned above the crucible set-up, and was preheated to 900°C. The crystal boules were cooled down to room temperature in about 30–40 h. The grown crystals were about 20 mm in diameter and 40 mm in length. The colors of the as-grown crystals for different compositions were slightly different. The colors of the as-grown crystals in the lower Li percentage side were light green, whereas when Li percentage was high the crystals were dark brown in color. Colorless and transparent crystals of LiNbO<sub>3</sub> were obtained for the charge composition of 48.6 mol % lithium oxide. In the as-grown stage these were pale yellow in color. The crystals grown under air are known to be deficient in oxygen. To remove oxygen deficiency, the crystals were heated under flowing oxygen at 1000°C for about 48 h. The crystals became colorless and transparent after annealing. Fig. 12.10 shows some of the typical crystals grown in these experiments.

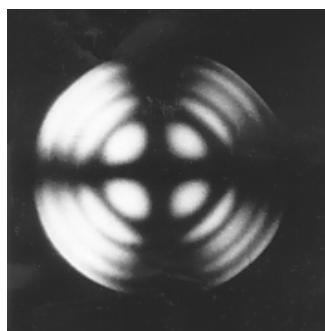


**Fig. 12.10.** LiNbO<sub>3</sub> crystals grown along the [00.1] direction. A few polished wafers cut perpendicular to the growth direction are also shown.

Thin wafers with surfaces perpendicular to the [00.1] growth direction were cut using a diamond ID cutter. These wafers were lapped and polished to a thickness of ~0.4 mm for characterization by X-ray diffraction and optical examination. The mechanically damaged surface layers were etched off in a hot mixture of two parts of HF and one part of  $\text{HNO}_3$  for about 2–5 min. at 100°C. This was found to be adequate to get damage-free crystals. High resolution X-ray diffractometry helps in giving the feedback in these experiments.

Iron doped  $\text{LiNbO}_3$  crystals are particularly useful for nonlinear optical applications, such as in second harmonic generators. They were grown by using the technique described above. 5 N pure  $\text{Fe}_2\text{O}_3$  powder was used as a dopant. Single crystals with doping level of 0.05 mol % iron have been grown. The doped crystals were pinkish in color. A doping level of more than 0.05 mol %  $\text{Fe}_2\text{O}_3$  resulted in complete blackening of the crystal boules.

Special steps are needed to grow  $\text{LiNbO}_3$  crystals, which have a single ferroelectric domain in their entire volume. Generally, as-grown crystals contain several small ferroelectric domains. As described later, high resolution X-ray diffraction topography has been employed to reveal ferroelectric domains. To obtain mono-domain crystals, poling was carried out *in situ*, by applying a high DC electric field across the crystal–melt system along the growth direction [00.1]. The crucible was connected to the positive polarity, whereas the seed holder was maintained at negative voltage. Experiments were performed with electric current densities in the growing crystal varying from 1.5 mA/cm<sup>2</sup> to 2.5 mA/cm<sup>2</sup>. X-ray topographs provided the feedback on the mono-domain nature of grown crystals. The results of investigations reported above have shown that colorless transparent pure crystals and iron doped crystals can be grown along the [00.1] direction in air for the charge composition of 48.6 mol % lithium. The crystalline perfection of  $\text{LiNbO}_3$  crystals was found to be quite good, as indicated by the small half width of their diffraction curves. The traverse topographs of these crystals show the presence of ferroelectric domains if these are present. Adequate poling, however, enables growth of nearly perfect mono-domain crystals.



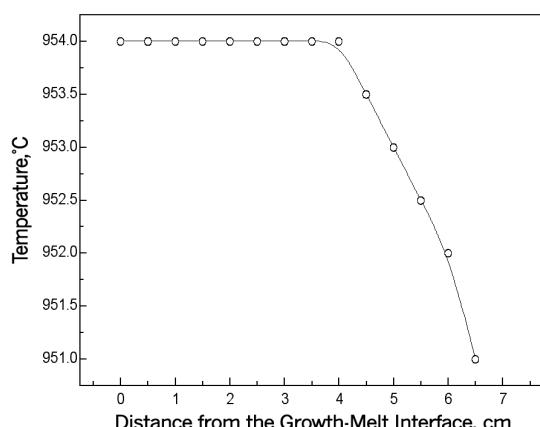
**Fig. 12.11.** A conoscopic interferogram for white light of  $\text{LiNbO}_3$  sample cut perpendicular to the growth axis

To assess the optical quality of the crystals, conoscopic interferograms or optic-axis pictures were recorded using a high-resolution microscope. These were recorded with monochromatic as well as white light. The specimens were cut perpendicular to the growth axis [00.1]. Figure 12.11 shows a typical interferogram recorded with white light. The conoscopic interferogram recorded showed perfect symmetry and were quite sharp. This implies that the crystals exhibit pronounced birefringence and the optic axis is perpendicular to the wafer surface. This property is required for phase matching conditions in devices.

### 12.8.2 Bismuth germanate single crystals

For growing BGO crystals, the temperatures of the three zones of the LTG furnace were set near the melting point of the BGO ( $1040^{\circ}\text{C}$ ) in TCPU of control panel. The temperature of the middle zone was kept a little bit higher than that of the other two zones. The temperature profile of the furnace above the melt was measured to ensure a low thermal gradient. A typical temperature profile is shown in Fig. 12.12. The melt surface was taken as a reference point. The temperature is nearly constant over a length of  $\sim 4$  cm above the melt surface and after that a temperature gradient of nearly  $1.2^{\circ}\text{C}/\text{cm}$  is observed. It can be seen that the thermal gradient is quite low. This enables one to grow crystals in low thermal gradient conditions, a salient feature of these experiments.

The crystal growth experiments were started by weighing of the crucible carrying the charge. This weight was balanced by appropriate electronic weights in the other arm (EWBU). The powder was heated at a rate of  $250^{\circ}\text{C}/\text{h}$  till the entire powder was melted at  $1040^{\circ}\text{C}$ . The melt temperature was stabilized for a few hours. Initially, only the platinum seed holder without the seed crystal was dipped into the melt to optimize the temperature of the melt for crystallization. The



**Fig. 12.12.** A typical temperature profile of the low thermal gradient furnace

temperature was adjusted until crystallization was possible at its tip. The seed holder was pulled up slightly above the melt after dipping to cool the drop of melt at its tip. It was dipped again and the temperature of the melt was optimized by observing the growth of the drop. If the temperature of the melt is higher than the desired one, the drop will melt. If on the other hand, the temperature of the melt is lower than the optimum value many nucleation points will be created. So, the temperature of the melt was adjusted carefully to ensure that the droplet starts growing in a controlled manner. At this stage, the platinum seed holder was pulled out and a T-shaped Z-cut bismuth germanate seed crystal was fixed in the platinum seed holder with its axis along [001]. The growth experiment was initiated after dipping the seed and attaining the thermal equilibrium.

During the crystal growth experiment, the diameter of the crystal was controlled by the automatic diameter control mechanism of the crystal growth system. The rate of increase in crystal weight ( $\Delta g/\Delta t$ ) had been programmed for a pre-set desired diameter of the crystal to be grown.

If  $S_k$  is the area of crystal cross-section (in  $\text{cm}^2$ ),  $\rho$  is the density of the melt (in  $\text{g}/\text{cm}^3$ ),  $V_p$  is the seed pulling rate (in  $\text{cm}/\text{h}$ ),  $\Delta H/\Delta t$  is the rate of decrease of melt height in the crucible (in  $\text{cm}/\text{h}$ ). The value of  $\Delta H/\Delta t$  is given by:

$$\frac{\Delta H}{\Delta t} = \frac{\Delta g / \Delta t}{\rho S_c} \quad (12.1)$$

Here  $S_c$  = cross-sectional area of the crucible. It can be easily shown that  $S_k$  is given by:

$$S_k = \frac{\Delta g / \Delta t}{\rho(V_p + \Delta H / \Delta t)} \quad (12.2)$$

Before the start of the crystal growth experiment, the growth rate ( $\Delta g/\Delta t$ ) was calculated and the system was programmed accordingly. The rate of increase in crystal weight ( $\Delta g/\Delta t$ ) for growing crystals of diameter 40 mm, has been worked out as 30  $\text{g}/\text{h}$ . This growth rate was set in the CWPU module of the crystal growth system. During the growth, if there is any deviation in the cross-section of the crystal from the desired size, the error feedback control system ESFU modifies the power to the furnace and hence the crystal cross-section. For example, if there is an increase in cross-section of the crystal from the desired value, the temperature of the melt is increased suitably. Similarly, if the actual cross-section of growing crystal is smaller than that of the desired size, the temperature of the melt is decreased. The cross-section of the crystal can also be controlled by changing the seed pulling rate. However, in these experiments, the seed pulling rate was kept constant and the cross-section of the crystal was controlled by controlling the temperature of the melt. It may be mentioned that the weighing mechanism is quite sensitive and its limit of detection is 10 mg in 1 kg or 10 ppm level.

In a typical experiment, target diameter of crystal was kept as ~40 mm and the length aimed at ~80 mm. The growth experiments were programmed to run for nearly 33 h. The first five hours were utilized for growing the cone portion after the seed growth condition was attained. This stage is over once the desired di-

ameter of ~40 mm is reached. Thereafter, the growth experiment was continued for 28 h and the diameter was maintained at this value. The seed pull rate was fixed at the optimum value of 2.5 mm/h. The seed rotation rate was 38 rpm, which had been optimized separately. After the growth was over, the crystal was cooled to room temperature at a rate of 150°C/h.

Figure 12.13 shows a photograph of a typical boule grown under these conditions. This crystal was ~40 mm in diameter and ~80 mm in length. The crystal was colorless in appearance. Further, it can be seen that the shape is nearly circular at the top and almost rectangular at the bottom without any twist. The upper portion of the crystal towards the seed appears to be slightly bigger than the rest of the crystal. As mentioned above, initially the crystal diameter is increased gradually to attain the desired size of ~40 mm diameter. Thereafter, the automatic weight control feedback loop was utilized to maintain the diameter. This system essentially ensures a constant rate of weight addition. The cross-sectional area of the crystal remained reasonably constant. However, the cross-section is not absolutely circular due to faceting and appears to be of different dimensions when viewed from different directions. This is the primary reason why the diameter appears to be smaller in the middle region of Fig. 12.13. Depending upon this faceting, different crystals have slightly different appearance when viewed from different directions in spite of good weight control.



**Fig. 12.13.** A typical BGO crystal grown by low thermal gradient Czochralski method along the [001] direction

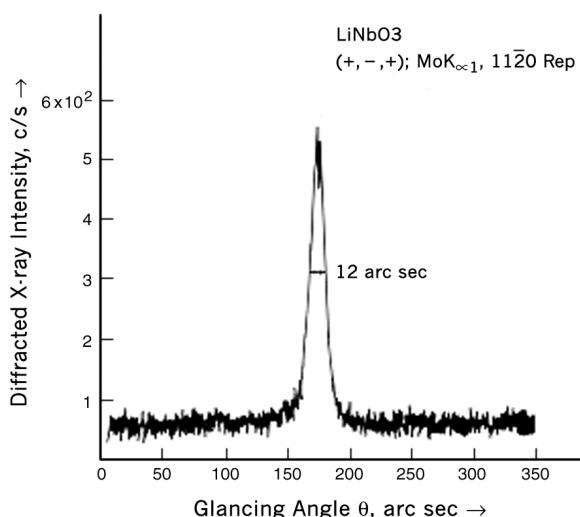
## 12.9 Evaluation of Perfection of Lithium Niobate and Bismuth Germanate Single Crystals by High Resolution X-ray Diffractometry and Topography

High resolution X-ray diffractometry and topography experiments were performed to evaluate the crystalline perfection of lithium niobate and bismuth germanate

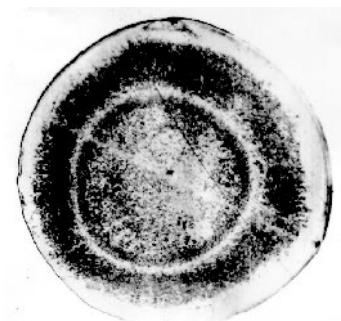
single crystals and to directly observe and characterize defects in the same by employing multi-crystal X-ray diffractometers.

### 12.9.1 Characterization of lithium niobate crystals

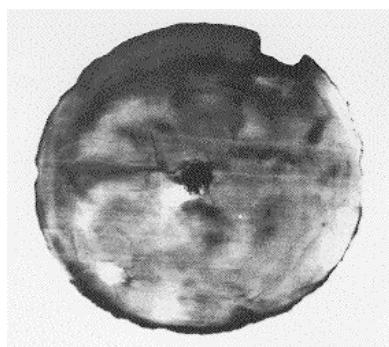
For evaluation of the perfection of  $\text{LiNbO}_3$  crystals a five crystal X-ray diffractometer was employed in a three crystal mode as described above (Figs. 12.7 and 12.8). The high resolution diffraction curves were quite sharp with half widths in the range of 10–30 arc sec [73]. Figure 12.14 shows a typical diffraction curve recorded with (11.0) diffracting lattice planes in symmetric Laue geometry in (+, -, +) configuration of the diffractometer. The specimen was at the third crystal stage. It is a single sharp peak with a half width of 12 arc sec. The theoretical half width of the diffraction curve calculated on the basis of plane wave dynamical diffraction theory for an ideally perfect lithium niobate crystal is 3.3 arc sec [83–86]. Under identical experimental conditions, half widths of diffraction curves of nearly perfect silicon single crystals are in the range of 5–10 arc sec [87,88]. A part of the broadening of such curves was due to the difference in lattice spacing of the diffracting planes of the specimen and those of the monochromator crystals. Also, the finite angular divergence and wavelength spread of the exploring  $K_{\alpha 1}$  beam led to some broadening. Considering these factors, the diffraction curves of the specimens are quite sharp. Therefore, it can be concluded that these crystals possess a high degree of crystalline perfection. Results of high resolution X-ray topography experiments gave similar results.



**Fig. 12.14.** A typical high resolution X-ray diffraction curve of a (00.1)  $\text{LiNbO}_3$  crystal recorded with (11.0) diffracting planes in symmetrical Laue geometry.  $\text{MoK}_{\alpha 1}$  radiation used



**Fig. 12.15.** A typical high resolution X-ray diffraction traverse topograph of an unpoled (00.1)  $\text{LiNbO}_3$  crystal recorded in symmetrical Laue geometry with (11.0) diffracting planes and  $\text{MoK}_{\alpha 1}$  radiation



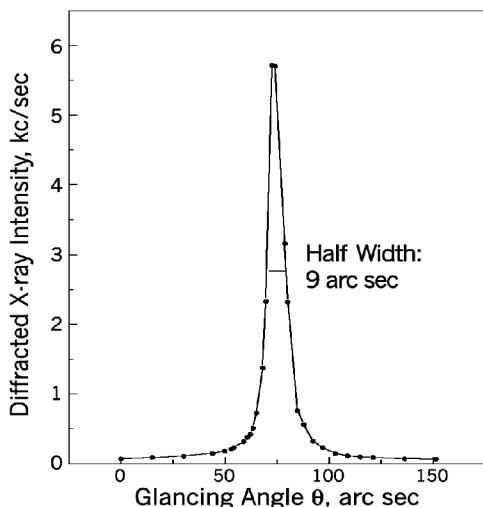
**Fig. 12.16.** A typical high resolution X-ray diffraction traverse topograph of a poled (00.1)  $\text{LiNbO}_3$  crystal. Experimental conditions were the same as in Fig. 12.15.

High resolution X-ray topographs were recorded for both poled and unpoled crystals. Figure 12.15 shows a typical topograph recorded for an unpoled crystal sample and Fig. 12.16 for a poled crystal sample, using  $\text{Mo K}_{\alpha 1}$  radiation with (11.0) diffracting planes. In the unpoled sample ferroelectric domains are randomly oriented. There is a concentric distribution of defects in an otherwise uniform intensity background. These may be due to segregation of impurity defects. The dark rings are due to ferroelectric domain boundaries with the opposite polarity to that of the matrix. Sugii et al. (1973) have also observed similar ferroelectric domain boundaries [89]. We have found experimentally that the strong contrast is independent of diffraction vectors. In the topograph of a poled sample the dark rings have disappeared and have nearly uniform intensity throughout, which clearly depicts absence of multiple domains. The domain vectors are now perfectly aligned along the electric field.

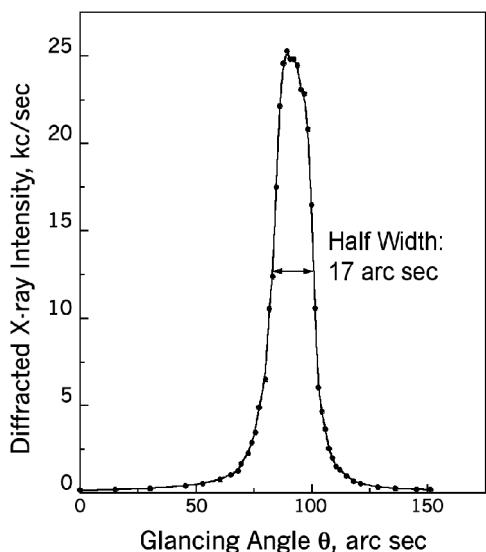
### 12.9.2 Characterization of bismuth germanate single crystals

A double crystal X-ray diffractometer described above was employed to characterize the BGO single crystals. Some of the specimens were rectangular in shape and a few nearly circular specimens were also used. Disk-shaped specimens with diameters of ~25 mm had been examined in detail. The exploring beam size was kept small:  $\sim 5 \text{ mm} \times \sim 0.4 \text{ mm}$ . The height of the beam was  $\sim 5 \text{ mm}$  in the vertical direction, the plane of diffraction being horizontal. In a few experiments, the exploring beam height was increased to 30 mm so that it irradiated the entire specimen along the vertical direction. Different regions of the specimen surface were examined by selective irradiation.

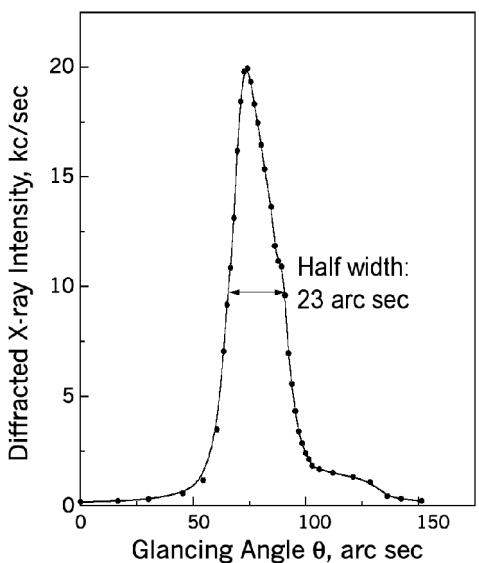
Figure 12.17 shows a typical high resolution X-ray diffraction curve of a (001) BGO crystal. In this experiment, (004) planes, which were nearly parallel to the specimen surface, were selected for diffraction. The beam height was  $\sim 5 \text{ mm}$  and it irradiated the central region of the specimen. The diffraction curve is quite sharp with a half width of  $\sim 9 \text{ arc sec}$ . The theoretical value of the half width for the diffraction curve for (004) diffracting planes of an ideally perfect BGO crystal, calculated by using the plane wave dynamical theory is 3.8 arc sec [83–86]. Since the monochromator in the diffractometer was a (111) silicon crystal, some broadening is expected due to dispersion caused by the lattice mismatch ( $d_{\text{Si}} = 3.1355 \text{ \AA}$ ,  $d_{\text{BGO}} = 2.6307 \text{ \AA}$ ). Keeping this fact in view, the observed value of the half width is quite close to the theoretical value for a perfect BGO crystal. This indicates that the quality of the explored region of the specimen crystal is quite good.



**Fig. 12.17.** A typical high resolution X-ray diffraction curve of a (001) BGO single crystal recorded with (004) planes from the central part of the specimen in symmetrical Bragg geometry



**Fig. 12.18.** A typical high resolution X-ray diffraction curve of a (001) bismuth germanate single crystal recorded with (004) diffracting planes in Bragg geometry when the exploring X-ray beam irradiated the entire specimen along the vertical direction on right hand side of the center.



**Fig. 12.19.** A typical high resolution X-ray diffraction curve of a (001) bismuth germanate single crystal recorded with (004) diffracting planes in Bragg geometry from a region on the left hand side of the center.

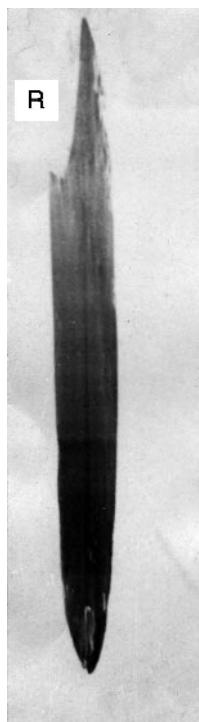
The exploring beam height was increased from 5 mm to ~30 mm to observe overall perfection along the vertical direction. Figure 12.18 shows a typical diffraction curve recorded when the exploring beam was irradiating the right side of the central area of the specimen. It can be seen that the curve is considerably broader than the curve of Fig. 12.17. The half width of the diffraction curve has increased to 17 arc sec. A single peak was observed in the diffraction curve. Therefore, one can conclude that no boundary is present in the irradiated region. Figure 12.19 shows a typical diffraction curve recorded under conditions similar to those in Fig. 12.18. This curve was recorded from the left side of the central region of the specimen. The half width of this diffraction curve is 23 arc sec. This curve is broader than that shown in Fig. 12.18. Further, a slight hump is observed on the right hand side of the main peak. This indicates the presence of another smaller peak, and hence the presence of a low angle boundary in the specimen crystal. The changes in half widths and shapes of the diffraction curves from different regions of the specimen (Figs. 12.18 and 12.19) suggest that there is a variation in degree of perfection of the specimen from region to region. Also, there is a possibility of low angle boundaries being present in the specimen. For a detailed study, X-ray diffraction traverse topography was combined with diffractometry.

Figure 12.20 shows a typical X-ray diffraction traverse topograph of the BGO specimen of Figs. 12.17–12.19, recorded with (004) diffracting planes in symmetrical Bragg geometry. It is seen that in the top region (marked as R), a part of the crystal is not diffracting. This shows the presence of a low angle boundary. In the lower portion also the intensity is not uniform, which indicates variations in degree of perfection from region to region, broadly similar to the results of diffractometric experiments. The region marked as R in Fig. 12.20, indicating a low angle boundary, has been studied in detail.

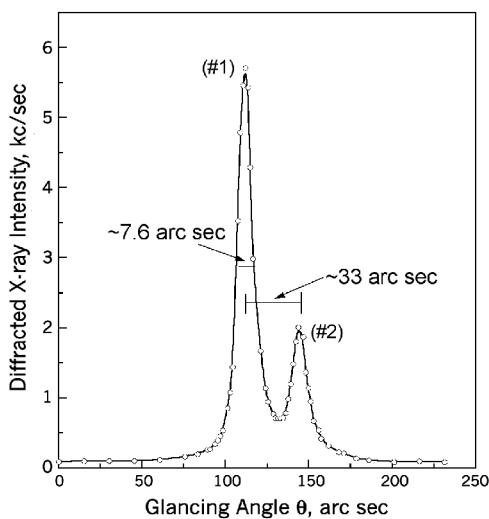
To examine the peripheral region of the specimen the height of the exploring X-ray beam perpendicular to the plane of diffraction was reduced to ~9 mm, and its position relative to the crystal was adjusted in such a manner that it irradiated the region R of the specimen (Fig. 12.20). A typical diffraction curve recorded from this region is shown in Fig. 12.21. This curve consists of two well resolved peaks. The angular separation between the two peaks is only ~33 arc sec. The splitting of the diffraction curve into two peaks clearly shows that the specimen contains a low angle boundary. However, the tilt angle between the two subgrains is very small, less than one arc min. Boundaries with such low tilt angles have been termed *very* low angle boundaries [68]. The high sensitivity of the X-ray diffraction technique employed in these experiments enabled direct observation of such *very* low angle boundaries. Subgrains on either side of the boundary, however, give sharp diffraction curves. Indeed, the half width of the larger peak is only ~7.6 arc sec. This peak is even sharper than that obtained from the central region, which was 9 arc sec (Fig. 12.17). High resolution X-ray traverse topographs were also recorded under identical conditions after orienting the specimens at the two peak positions of Fig. 12.21. Figures 12.22 (a) and (b) show topographs recorded respectively with subgrains of the larger and the smaller peaks. Both the topographs are found to be complementary to each other and enabled direct im-

aging of the two subgrains. Further, the intensity in the topographs is not uniform. This is due to small strains present in this region of the specimen. A lower degree of perfection towards the edges is expected because of the high thermal gradient existing between the crystal surface and the surrounding area. However, large central parts of the specimen were nearly perfect. Also, detailed topographic investigation carried out by Lal et al. (1979) on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals grown by the Cz method showed the presence of low angle boundaries with tilt angles of a few arc minute towards the periphery [90].

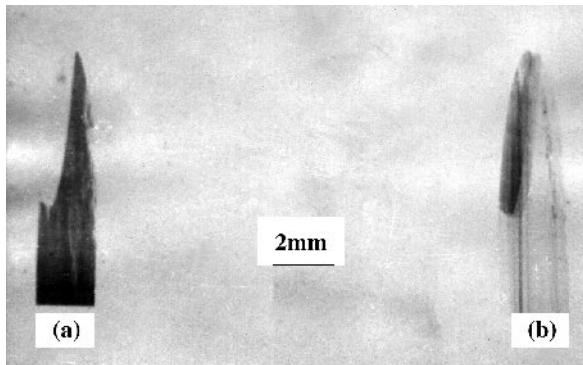
Bismuth germanate crystals containing *very* low angle boundaries have been investigated in considerable detail [67,69]. Pinning of very low angle boundaries due to decoration by traces of impurities like silicon has been demonstrated [69]. Also, prominent point defect clustering has been observed in the crystals having a yellow tinge [70]. Van Hoof et al. (1985) investigated BGO crystals grown by the Bridgman technique using X-ray diffractometry [58]. They obtained sharp diffraction curves from the central region with half width of  $\sim$ 10 arc sec when the irradiated area was  $\sim$ 1.3 mm<sup>2</sup>. The half width increased to  $\sim$ 20 arc sec when the whole area of about 300 mm<sup>2</sup> was irradiated. Our results are quite similar to these. In the present study,



**Fig. 12.20.** A typical high resolution X-ray traverse topograph of the (001) BGO specimen of Figs. 12.17 to 12.19 recorded with (004) diffracting planes in symmetrical Bragg geometry.



**Fig. 12.21.** A typical high resolution X-ray diffraction curve of a (001) BGO single crystal recorded from the peripheral region of the specimen. (004) diffracting planes were employed



**Fig. 12.22.** Typical high resolution X-ray traverse topographs of the (001) BGO specimen of Figs. 12.17 to 12.21 recorded with (004) diffracting planes in symmetrical Bragg geometry. (a) and (b) were recorded after orienting the specimen on peak #1 and #2, respectively, of Fig. 12.21.

diffraction curves with half width of  $\sim 9$  arc sec were obtained from the central region. They had reported the presence of dislocations predominantly at the outer edge of the Bridgman grown specimen. The presence of grain boundaries and high dislocation density in the Cz grown specimen was reported. However, we have observed very low angle grain boundaries at the periphery of the specimen. The Cz specimen of Van Hoof et al. had a mosaic structure with a large angular spread

of  $\sim 0.15^\circ$ . Chemical etching of {112} faces of the Bridgman specimens revealed dislocations occurring in rows representing low angle grain boundaries [61].

Brandle and Miller (1974) studied the effect of liquid temperature gradient on the distribution of dislocations in large diameter LiTaO<sub>3</sub> single crystals [75]. Typical radial temperature gradient of their system was minus 3–5°C/cm above the crucible and plus 3–5°C/cm between the crucible lid and the liquid surface. They suggested that a lower temperature gradient would be required for the growth of good quality single crystals of LiTaO<sub>3</sub>. Takagi et al. (1976) also suggested that a small temperature gradient would be desirable for the growth of gadolinium gallium garnet single crystals [91]. According to their results, when the temperature gradient is small it is easy to grow facet less crystals. All these investigations indicated that improvements in crystalline perfection of oxide single crystals were possible through the maintenance of a small temperature gradient across the melt. The present work has shown that the low thermal gradient Cz technique is quite appropriate to grow nearly perfect single crystals of bismuth germanate. These results are consistent with earlier findings, and also demonstrate that the LTG Cz method can be employed to grow high quality BGO crystals [68] and the degree of their perfection is nearly the same as that reported for Bridgman grown crystals.

## 12.10 Summary

The recent advances made in the growth and characterization of two technologically important crystals, lithium niobate and bismuth germanate, have been reviewed. Essential features of Cz growth experiments employed for the preparation of mono-domain nearly perfect lithium niobate have been discussed. High resolution X-ray diffraction evaluation gave valuable feedback for the growth of such high quality single crystals.

It has been shown that the LTG Cz method can be employed to grow nearly perfect bismuth germanate crystals. Interesting results concerning direct observation and characterization of *very* low angle boundaries have been described.

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# **13 Growth and Development of Nonlinear Optical Borate Crystals for Generation of Visible and UV Light**

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## **13.1 Introduction**

### **13.1.1 Coherent solid-state light source in the visible and UV regions by nonlinear optical crystals**

The coherent and monochromatic photon flux of laser light is viewed as a clean energy source for the synthesis and processing of materials. Because of their high photon energies and ability to be tightly focused, radiations at short wavelengths are desired. For instance, photon energy in the UV region is sufficient enough to induce bond-breaking processes in many materials. High-power UV output is currently available only from the rare-gas halide excimer lasers (e.g., XeCl, KrF, and ArF). However, these lasers use corrosive gases, have high voltage gaseous discharges, require regular maintenance, and have bulky dimensions. A compact, maintenance-free, all-solid-state alternative is therefore desired.

An effective technique for UV generation is cascaded sum-frequency generation pumped by the output of near-IR ( $\lambda \sim 1 \mu\text{m}$ ) solid-state lasers by using nonlinear optical (NLO) crystals. For instance, the fundamental wavelength ( $\lambda = 1064 \text{ nm}$ ) of Nd:YAG lasers is first converted to SHG (Second Harmonic Generation) ( $2\omega, \lambda = 532 \text{ nm}$ ) and then to UV wavelengths by third, fourth, fifth ... harmonic generations ( $3\omega, 4\omega, 5\omega \dots$  at  $\lambda = 355 \text{ nm}, 266 \text{ nm}, 213 \text{ nm} \dots$ , respectively). Thus, NLO crystals that generate visible and UV lights effectively are important for the realization of a high-power, all-solid-state UV light source. For the purpose of reliable laser frequency conversion, NLO crystals need to have properties like: (1) large NLO coefficient, (2) moderate birefringence, (3) small walk-off effect, (4) large angular, spectra and temperature bandwidths, (5) wide transparency range for operating wavelength, (6) high laser-induced damage threshold, (7) ease of growth, (8) low material cost, (9) good chemical stability, and (10) good mechanical stability.

Until 1975, most NLO crystals were based on the P-O, I-O, and Nb-O bonds like those in KDP ( $\text{KH}_2\text{PO}_4$ ) [1,2],  $\text{LiIO}_3$  [3,4], and  $\text{LiNbO}_3$  [5]. KDP meets conditions (5) to (8) and thus is used for frequency conversion in high-power lasers. It is particularly suitable for the purpose of a laser fusion system involving NLO devices with large dimensions of several tens of cm. Likewise, because of properties (1), (2), and (9), crystals like  $\text{LiNbO}_3$  and  $\text{KNbO}_3$  [6] are frequently used for frequency conversions in semiconductor lasers. The KTP ( $\text{KTiOPO}_4$ ) [7] crystals developed later provide properties that merely combined those of KDP and  $\text{LiNbO}_3$ . This makes KTP popular for both high-power and semiconductor laser operations. Comprehensive references on these materials are compiled in the handbook on NLO crystals prepared by Dmitriev et al. (1999) [8].

### 13.1.2 NLO borate crystals

#### ***Borate crystals for UV light generation***

NLO crystals with B-O bonds are often employed for high-power UV light generation because of the relatively high resistance against laser-induced damage and higher transparency in the UV region. The first borate crystal described for UV generation was  $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$  (KB5) [9]. However, intense research on borate crystals was initiated only after the development of  $\beta\text{-BaB}_2\text{O}_2$  (BBO) [10]. After BBO, Chen et al. have developed several other borate crystals like  $\text{LiB}_3\text{O}_5$  (LBO) [11],  $\text{KBe}_2\text{BO}_3\text{F}_2$  (KBBF) [12], and  $\text{Sr}_2\text{Be}_2\text{BO}_7$  (SBBO) [13]. The present authors have been involved in the development of several borate crystals like  $\text{CsB}_3\text{O}_5$  (CBO) [14],  $\text{CsLiB}_6\text{O}_{10}$  (CLBO) [15–17],  $\text{YCa}_4\text{O}(\text{BO}_3)_3$  (YCOB) [18,19],  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  (GdYCOB) [20,21], and  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  (KAB) [22,23]. Recently, lithium tetraborate  $\text{Li}_2\text{B}_4\text{O}_7$  [24,25] was also reported as a possible NLO crystal for UV light generation. Note that NLO properties of BBO, LBO, as well as KB5 have been described elsewhere [26]. A recent review on borate crystals like BBO, LBO,  $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{GdCa}_4\text{O}(\text{BO}_3)_3$  (GdCOB) [27,28], and YCOB were prepared by Becker (1998) [29]. Our discussions on borate materials are concentrated on the latest progress with CLBO, GdYCOB, and KAB, which are not well compiled in any review articles available to date. Discussions on other NLO borate crystals are included for comparison. For example, the latest progress on CBO is mentioned in the section on CLBO and new data on GdCOB and YCOB are included in the discussion of GdYCOB. Likewise, properties of KBBF and SBBO are considered together in the section on KAB crystals.

#### ***Relation between the anionic borate group and optical properties***

The optical properties of borate crystals appeared to be related to their molecular structure. Several borate crystals mentioned earlier are taken as examples and listed in Table 13.1. These crystals are constructed from three basic structural units:  $(\text{B}_3\text{O}_6)^{3-}$ ,  $(\text{B}_3\text{O}_7)^{5-}$ , and  $(\text{BO}_3)^{3-}$  anionic groups. The anionic group is thought

**Table 13.1.** Properties of some NLO borate crystals

Crystals	Space group	Transparency range [nm]	Nonlinear coefficient [pm/V]	Birefringence $\Delta n$	Shortest SHG [nm]	Basic structural unit
$\beta\text{-BaB}_2\text{O}_4$ (BBO)	R 3c	190-3300	$d_{11}=1.844$	0.12 at 1064 nm	205	$\text{B}_3\text{O}_6$
$\text{LiB}_3\text{O}_5$ (LBO)	Pna 2 <sub>1</sub>	160-2600	$d_{31}=0.94$ $d_{32}=1.13$ $d_{33}=0.256$	0.04 at 1064 nm	277	$\text{B}_3\text{O}_7$
$\text{CsB}_3\text{O}_5$ (CBO)	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	167-3400	$d_{14}=0.863$	0.053 at 1064 nm	273	$\text{B}_3\text{O}_7$
$\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF)	R 32	155-3660	$d_{11}=0.8$	~0.072 at 589 nm	185	$\text{BO}_3$
$\text{Sr}_2\text{Be}_2\text{BO}_7$ (SBBO)	P 6 <sub>3</sub>	155-3780	$d_{15}=\sim 2$	~0.062 at 589 nm	200	$\text{BO}_3$
$\text{CsLiB}_6\text{O}_{10}$ (CLBO)	I 42 d	180-2750	$d_{36}=0.95$	0.050 at 1064 nm	237	$\text{B}_3\text{O}_7$

to determine the nonlinear optical coefficient of borate crystals according to the anionic group theory [26]. Two fundamental assumptions are considered in the calculation of complete neglect of differential overlap (CNDO) approximations: (1) the macroscopic NLO coefficient of the crystal is the geometrical superposition of the microscopic second order susceptibility tensor ( $\chi^{(2)}$ ) of the relevant anionic groups, and has nothing to do with essentially spherical cations; and (2) the microscopic second order susceptibility can be determined from the localized molecular orbitals of the anionic group using quantum chemical calculation.

Due to the planar hexagonal structure of the  $(\text{B}_3\text{O}_6)^{3-}$  anionic group, borate crystals constructed from this basic unit have larger  $\chi^{(2)}$  compared to crystals composed of  $(\text{B}_3\text{O}_7)^{5-}$  and  $(\text{BO}_3)^{3-}$  groups. Thus, in terms of NLO coefficient, the  $(\text{B}_3\text{O}_6)^{3-}$  group is most suitable as the basic structural unit of NLO borate materials, followed by the  $(\text{B}_3\text{O}_7)^{5-}$  group and then the  $(\text{BO}_3)^{3-}$  group. However, the UV absorption edge of some borate crystals containing the  $(\text{B}_3\text{O}_6)^{3-}$  group occurred at a longer wavelength (e.g., BBO) as compared to those constructed from the  $(\text{B}_3\text{O}_7)^{5-}$  group (LBO, CBO, and CLBO). Calculations show that  $\pi$ -conjugated orbitals of planar  $(\text{B}_3\text{O}_6)^{3-}$  tend to shift the UV absorption edge toward the red [26]. As one of the boron atoms in  $(\text{B}_3\text{O}_6)^{3-}$  changed from trigonal to tetrahedral coordination, thereby forming nonplanar  $(\text{B}_3\text{O}_7)^{5-}$  groups, the  $\pi$ -conjugated orbital system is weakened, as in the case of LBO and CBO, and the UV absorption edge shifts to 160-170 nm. Both CBO and LBO are constructed from a continuous network of nonplanar  $(\text{B}_3\text{O}_7)^{5-}$  groups with interstitial cesium and lithium cations, respectively. Based on the absorption edge, therefore, the  $(\text{B}_3\text{O}_7)^{5-}$  group is ideal as the basic structural unit of deep UV NLO materials. Likewise, if the dangling bonds of the three terminated oxygen atoms of  $(\text{BO}_3)^{3-}$  groups are interlinked with

cations, an absorption edge appearing at wavelengths as short as 155 nm is also possible, as is the case with KBBF and SBBO [13].

### ***Crystal growth of some NLO borate crystals***

Borate crystals containing the  $(\text{BO}_3)^{3-}$  anionic group like KBBF and SBBO tend to grow in a layered structure. To date, KBBF crystals available for laser experiments are still less than 0.5 mm thick [30]. In fact, there is no detailed evaluation of the performance in laser frequency conversion from both KBBF and SBBO, despite their good transparency in the vacuum UV region. Some supplementary discussions on the growth of KBBF and SBBO are included in section 4. Likewise, the BBO crystal has a high temperature phase ( $\alpha$ -BBO) that is centrosymmetric. Thus, the melt growth of BBO crystals is relatively difficult because of the phase transition near the melting point. BBO crystals can be grown by flux but suffer from flux inclusions [31,32]. Czochralski (Cz) growth that involved stoichiometric melts avoids flux inclusions but requires a high temperature gradient near the melt surface [33,34]. The Cz grown BBO has a relatively low laser-induced damage threshold. Quality of Cz-BBO crystal can be improved by annealing [35]. On the other hand, LBO crystals do not melt congruently. The LBO is grown by a top-seeded solution growth (TSSG) / top-seeded Kyropoulos method. Both the growth rate and optical quality of LBO seem to be degraded by the high viscosity and low diffusion rate of the flux solution. It takes more than two months for a crystal with a dimension of several cm to grow, and special care is required for thermal homogeneity [11]. Information on growing BBO and LBO was discussed in Ref. [29] and thus is not repeated here.

## **13.2 CLBO Crystals for High-Power Generation of Deep-UV Light**

### **13.2.1 The search for $\text{CsLiB}_6\text{O}_{10}$ (CLBO)**

As discussed, the development of NLO borate crystals is desired for high-power UV light generation like  $4\omega$  and  $5\omega$  of Nd:YAG lasers. The BBO crystals were widely evaluated for producing  $4\omega$  and  $5\omega$  of Nd:YAG lasers because of their relatively large nonlinearity. Laser frequency conversion in BBO is limited by the large walk-off angle (due to a large birefringence), as well as the relatively small angular, spectra, and temperature acceptance bandwidths. Its absorption edge at 189 nm also decreased the conversion efficiency because of thermal dephasing initiated by the optical absorption. As mentioned in the previous section, other NLO crystals like the KBBF and SBBO are still not available for practical application. LBO crystals can only generate UV SHG radiation down to 277 nm due to their small birefringence and are thus unable to produce  $4\omega$  radiation by SHG of green light. They can generate UV light at shorter wavelengths by SHG, but the effective NLO coefficient is reduced by a factor of  $\cos \theta$  or  $\cos \phi$  [11,36]. All

these crystals are not easy to grow like the nonborate KDP and KTP crystals. Thus, finding a new borate material for UV light generation is desirable.

The discovery of CLBO is related to CBO and LBO crystals. Properties of LBO crystals are rather well known and have been discussed in many papers since 1989. The first CBO bulk crystal was grown from a stoichiometric melt in Osaka University during 1992 [14]. The CBO crystallizes in an orthorhombic space group  $P2_12_12_1$  with unit cell dimensions:  $a = 6.213$ ,  $b = 8.521$ ,  $c = 9.170$  Å, and  $Z = 4$  [37]. This crystal is constructed of the  $(B_3O_7)^{5-}$  group with the  $Cs^+$  cation. Unlike LBO, which is also comprised of the  $(B_3O_7)^{5-}$  group, CBO is relatively easy to grow. The CBO crystals melt congruently and thus can be grown from both a stoichiometric melt and a solution. Wu grew CBO from a nearly stoichiometric melt [38]. The starting charges were prepared from a mixture of  $Cs_2CO_3$  and  $H_3BO_3$  by the following chemical reaction:



The mixture was reported to be slightly rich in  $Cs_2CO_3$ , and a crystal as large as  $40 \times 25 \times 25$  mm<sup>3</sup> was obtained after two weeks of growth. Likewise, Kagebayashi et al. (1999) reported the growth of CBO crystals from a  $Cs_2O$ -enriched melt [39]. The starting materials were  $Cs_2CO_3$  and  $B_2O_3$  powders. The melt composition was 26.6 mole %  $Cs_2O$  and 73.3 mole %  $B_2O_3$ . The melting temperature was 821.4°C, as compared to 824.7°C of the stoichiometric melt. A colorless, crack-free, and inclusion-free single crystal of CBO as large as  $45 \times 41 \times 44$  mm<sup>3</sup> can be obtained in 14 days. This crystal is transparent from 170 to 3400 nm.

According to the Sellmeier equation prepared by Kato (1995) [40], the shortest possible SHG wavelength producible from type-1 CBO is 272.8 nm, slightly shorter than that of LBO. The CBO crystal can generate UV light as short as ~185 nm, which could not be realized using BBO and LBO crystals [40]. The NLO coefficients of CBO and LBO are almost the same [ $d_{14}(CBO) \sim d_{31}(LBO) \sim d_{32}(LBO)$ ] [11]. The marked advantage of CBO over LBO is a larger effective NLO coefficient for UV light generation. The effective NLO coefficients of CBO are given by  $d_{eff} = d_{14}\sin 2\theta$  or  $d_{14}\sin 2\phi$  [41] in contrast to that of LBO, which is reduced by a factor of  $\cos \theta$  or  $\cos \phi$ . In particular,  $d_{eff}$  of CBO for type-2 third harmonic generation (1064 nm + 532 nm → 355 nm) or type-1 SHG (1064 nm + 355 nm → 266 nm) is close to its maximum.

The  $(B_3O_7)^{5-}$  network reported so far is connected with one type of cation, that is Li or Cs of LBO and CBO, respectively. We attempted to search for new NLO borate crystals based on the  $(B_3O_7)^{5-}$  network. Instead of one, we tried to include two alkali metals into the borate network. Many combinations of various alkali metals were attempted and several of them crystallized [42]. Most of these phases are either not SHG active or weak in SHG. By this method, we found a new phase:  $CsLiB_6O_{10}$ , from the melted mixtures of  $Cs_2CO_3$ ,  $Li_2CO_3$ , and  $B_2O_3$  powders [43].

The relationship between composition and melting temperature in the  $(Cs_2O + Li_2O)-(B_2O_3)$  system was investigated. In this case, the ratio of  $Cs_2O$  relative to  $Li_2O$  was fixed at 1:1 while the proportional ratios of  $(B_2O_3)$  to  $(Cs_2O + Li_2O)$

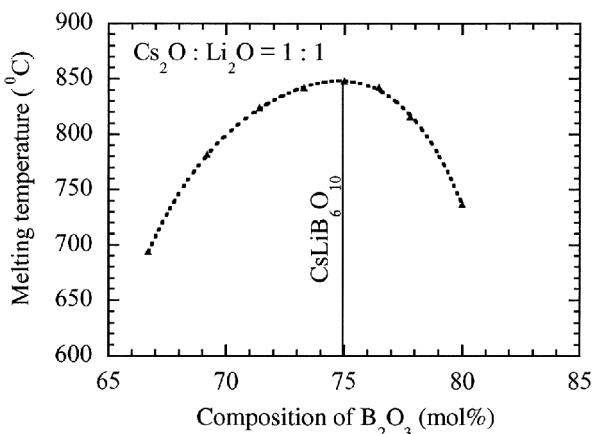


Fig. 13.1. Melting temperatures of the (Cs<sub>2</sub>O + Li<sub>2</sub>O)-(B<sub>2</sub>O<sub>3</sub>) system

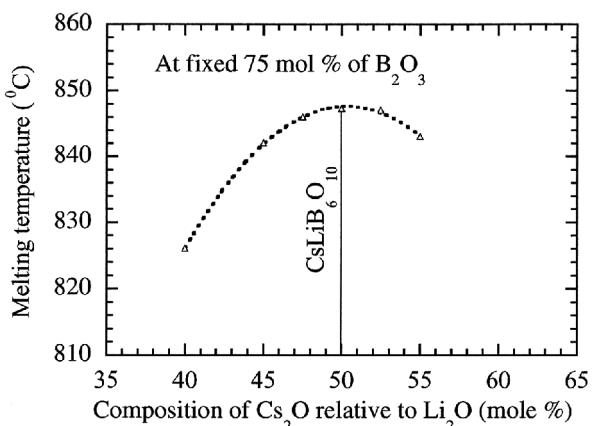
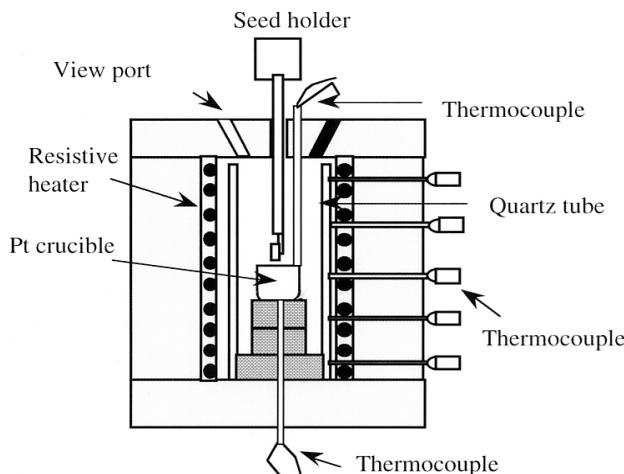


Fig. 13.2. Melting temperatures of the (Cs<sub>2</sub>O)-(Li<sub>2</sub>O) system at 75 mole % of B<sub>2</sub>O<sub>3</sub>

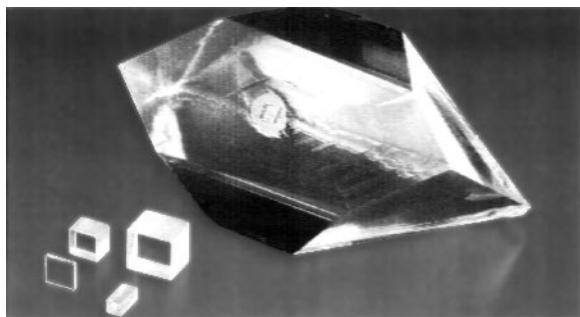
were varied from 80.0 to 66.7 mol %. As shown in Fig. 13.1, CLBO was found to melt congruently at 848°C. The recognized phase was CLBO for all indicated data points except at 66.7 mole % of B<sub>2</sub>O where CBO coexisted. Next, the system of (Cs<sub>2</sub>O)-(Li<sub>2</sub>O) was studied by fixing the B<sub>2</sub>O<sub>3</sub> content at 75 mole %. In this case, the ratio of Cs<sub>2</sub>O to Li<sub>2</sub>O was varied from 40.0 to 55.0 mole %. The procedure described for the (Cs<sub>2</sub>O + Li<sub>2</sub>O)-(B<sub>2</sub>O<sub>3</sub>) system was repeated. As shown in Fig. 13.2, CLBO was found to melt congruently at 848°C. From these results, the stoichiometric melt must contain Cs<sub>2</sub>O:Li<sub>2</sub>O:B<sub>2</sub>O<sub>3</sub> at a ratio of 1:1:6 to grow CLBO at ~848°C.

### 13.2.2 Growth of CLBO

Like the CBO crystals, CLBO crystals are relatively easy to grow. Bulk crystals can be grown from both the stoichiometric melt and a solution by TSSG [44]. A five-zone vertical furnace, as shown in Fig. 13.3 was used due to its high spatial temperature uniformity. The seed rod was rotated at a rate of 15 rpm and inverted to the opposite direction every three minutes. The growth temperature was decreased at a rate of  $0.1^{\circ}\text{C/day}$  during crystal growth. The CLBO crystal with dimensions of  $29 \times 20 \times 22 \text{ mm}^3$  was grown from a stoichiometric melt in four days [44]. Solution growth was carried out from a starting mixture of  $\text{Cs}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{B}_2\text{O}_3$  at a ratio of 1:1:5.5 (73.3%  $\text{B}_2\text{O}_3$ ). The self-fluxed solution poor in  $\text{B}_2\text{O}_3$



**Fig. 13.3.** Schematic of a five-zone vertical furnace for top-seeded solution growth of CLBO crystals



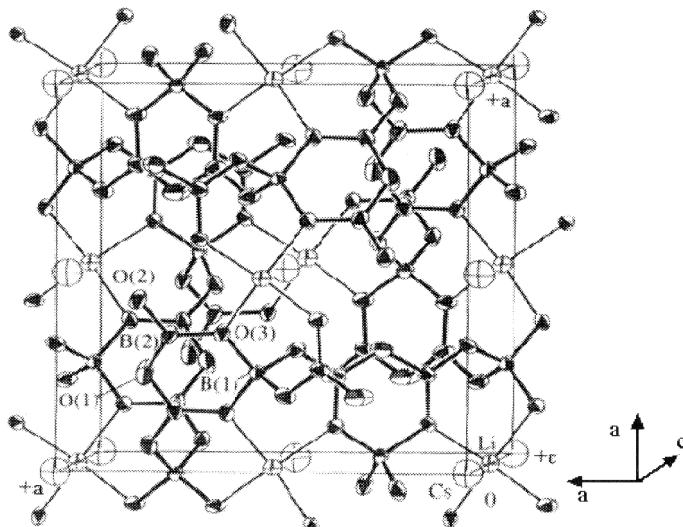
**Fig. 13.4.** Photograph of a large CLBO crystal with dimensions of  $14 \times 11 \times 11 \text{ cm}^3$

was chosen due to its relatively low viscosity. The estimated saturation temperature was 845°C. High-quality CLBO crystal as shown in Fig. 13.4 can be grown this way.

### 13.2.3 Structural and optical properties of CLBO

The CLBO crystal has a tetragonal structure with a space group of  $I\bar{4}2d$  (#122) and cell dimensions of  $a = 10.494$ ,  $c = 8.939$  Å, and  $Z = 4$ , totally different from that of CBO and LBO crystals. The structure is composed of eight-coordinated Cs and four-coordinated Li atoms within the borate network. The basic structural unit of this network is the  $(B_3O_7)^{5-}$  anionic. Likewise, the molecular packing of CLBO in a three-dimensional framework is shown in Fig. 13.5. A detailed description of the crystal structure is provided elsewhere [17].

Properties of CLBO that relate to its abilities of high-power laser frequency conversion are listed in Table 13.2. The angular, spectral, and temperature ( $\Delta\theta l$ ,  $\Delta\lambda l$ ,  $\Delta T l$ , respectively) bandwidths are compared to other frequently used NLO crystals like  $KD_2PO_4$  (DKDP or  $KD^*P$ ), KDP, and BBO. In general, CLBO exhibits a relatively high bulk laser-induced damage threshold [24 GW/cm<sup>2</sup> and 26 GW/cm<sup>2</sup> along (001) and (100) directions, respectively] at 1.064 μm with 1.1 ns pulse width. For UV light generation, CLBO has an effective NLO coefficient between BBO and KDP, moderate birefringence between that of LBO and BBO (Table 13.1), and possess a smaller walk-off angle and larger angular, spectral, and temperature bandwidths than KDP and BBO.



**Fig. 13.5.** Molecular packing of CLBO in a three-dimensional framework

**Table 13.2.** Properties of CLBO crystals for harmonic generation of Nd:YAG lasers as compared to other NLO crystals

Wavelength [nm]	NLO crystal	Phase matching angle [θ/deg.]	$d_{eff}$ [pm/V]	$\Delta\theta l$ [mrad-cm]	$\Delta\lambda l$ [nm-cm]	$\Delta Tl$ [°C-cm]	Walk-off angle [deg.]	Damage threshold [GW/cm <sup>2</sup> ]
1064 + 1064 = 532	CLBO (Type-2)	41.9	0.95	1.7	5.6	43.1	1.78	26
	KDP (Type-2)	59	0.38	3.4	11.5	19.1	-	~20
	KD*P (Type-2)	53.5	0.4	5.0	5.6	6.7	1.38	-
	BBO (Type-1)	22.8	2.06	0.92	2.1	37.1	3.2	13.5
1064 + 532 = 355	CLBO (Type-2)	48.4	0.94	0.82	0.84	21.3	2.1	-
	KDP (Type-2)	58	0.38	1.06	0.95	-	-	-
532 + 532 = 266	CLBO	61.9	0.84	0.49	0.13	8.3	1.83	6.4
	KDP	78	0.51	1.7	0.13	1.2	-	-
	BBO	47.5	1.32	0.27	0.07	4.5	4.8	-
1064 + 266 = 213	CLBO	67.4	0.87	0.42	0.16	4.6	1.69	-
	KDP	51.1	1.26	0.19	0.08	3.1	5.34	-

### 13.2.4 Degradation of CLBO crystallinity and solution

CLBO possesses good combinations of NLO properties for UV light generation. However, CLBO is hygroscopic and this distorts the refractive index of the CLBO crystal. Many NLO borate crystals are hygroscopic, including CBO and LBO. Hydration of CLBO crystals ( $Cs_2B_{10}O_{16} \cdot 8H_2O$ ) was detected with X-ray diffraction (XRD) and occurs at a relatively faster rate at high humidity (>45%), which eventually leads to crystal cracking [45]. Such hydration is eliminated at ~120°C. Basically, one can solve the hydration problem by keeping the crystal dry.

The main problem with CLBO is distortion of the refractive index of the crystal. Such distortions are indicated by the degradation of device performance and are detectable by using a laser transmission interferometer (LTI). Distortion of refractive index is generally induced by mechanical stress arising from various factors. Reduction of distortion rate at low ambient humidity [45] revealed that hydration is one of the origins of stress. However, distortion can still happen if a

device is subjected to dry conditions during use, which indicates that thermal shock introduced during laser operation can also cause crystalline degradation. We have attempted to stabilize the crystallinity of CLBO.

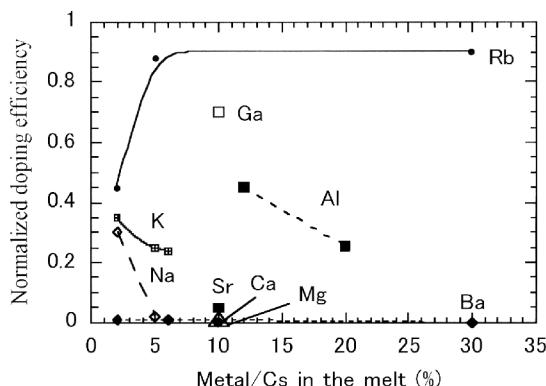
### ***Effect of doping in CLBO***

Doping can modify properties of a given material. For borate crystals, systematic investigation of doping has not been reported. We found that various metals can be used to dope CLBO [46]. As shown in Fig. 13.6, the doping efficiency of metal atoms is dependent on ionization number. Doping efficiency is defined as the ratio of dopant concentration in the crystal to that in the growth solution, that is, the ratio between “Metal/Cesium” in the crystal and “M/Cs” in the growth solution, where M = metal. Composition was measured by ICP (inductive coupled plasma) analysis.

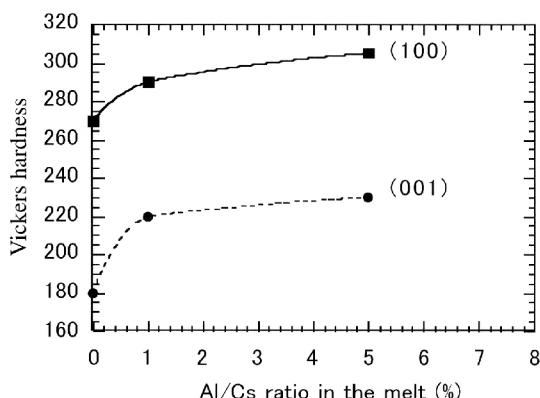
For alkali metals, the highest doping efficiency was observed for Rb as compared to K and Na. This is explained by the radii of the  $Rb^+$  cation closest to that of the  $Cs^+$  cation. The doping efficiency of Rb atoms increases with increasing dopant concentration in the melt. Almost 100% of the Rb atoms in the melt can be incorporated into CLBO crystals. Single crystals of CLBO:Rb up to a doping concentration as high as 10 mole % can be obtained without inclusions and cracking. Four-circle X-ray diffraction (XRD) analysis revealed that Rb is incorporated by substitution for Cs.

A much lower doping efficiency was observed for alkali earth metals (Mg, Ca, Sr, Ba) compared to that for alkali metals. This might be due to the differences in the ionization number between alkali and alkali earth metals. Despite this, CLBO:Mg crystals with doping concentration as high as 10 mole % can be obtained without inclusions and cracking. On the other hand, it is interesting that Al and Ga can also be used to dope CLBO despite the fact that they are group III elements. The XRD analysis showed that the a-axis expanded while the c-axis contracted as the doping concentration increased. High-quality single CLBO:Al crystals can be obtained up to a doping concentration of about 5 mole %. The doping sites of these elements are not clear.

The effects of doping on various properties of CLBO have been studied [46]. We found that Rb doping could reduce the shortest SHG wavelength that can be phase-matched ( $\lambda_c$ ) by CLBO. For example, the  $\lambda_c$  is 2 nm shorter for a CLBO:Rb crystal of 10 mole %. The Rb doping, however, makes CLBO fragile. This was also the case for K and Na doping. On the other hand, Al doping gives rise to an enhancement of mechanical properties of CLBO. Figure 13.7 shows the Vickers hardness as a function of the Al/Cs ratio in the melt. Each data point represents an average value obtained from several indentations. The hardness of undoped CLBO was 270 and 180 for (100) and (001) planes, respectively. The values for 1% Al-doped and 5% Al-doped CLBO were 290 and 310 for (100) and 220 and 230 for (001) surfaces. A similar enhancement of hardness was observed from the doping of Ga. Note that the hygroscopic nature of CLBO is also suppressed by doping with Al. The undoped and 2 mole % Al-doped CLBO crystals were dissolved in a



**Fig. 13.6.** The doping efficiency of various impurities in CLBO crystals as a function of dopant concentration in the melt



**Fig. 13.7.** Vickers hardness of Al-doped CLBO (100) and (001) surfaces as a function of Al/Cs ratio in the growth melt

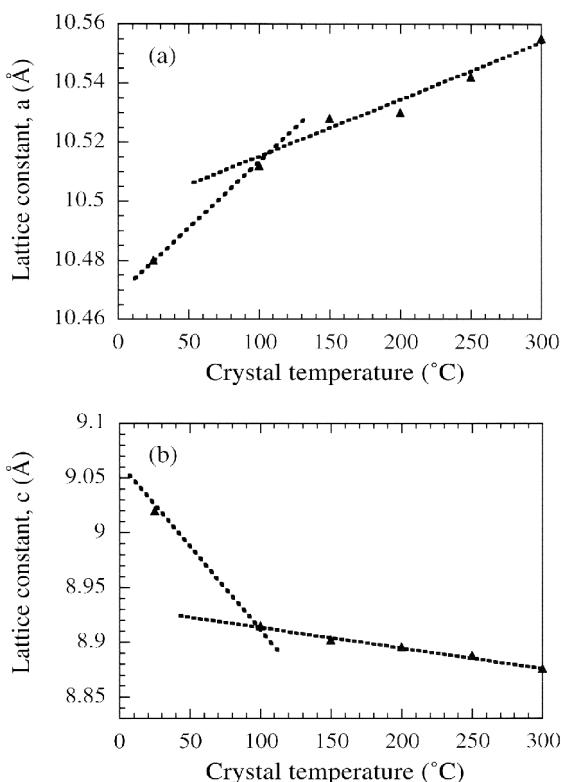
solution of  $\text{H}_2\text{O}$  (20%) and glycerin (80%) for investigation. The samples were dipped in the solution during the experiment. We found that the Al-doped CLBO is less soluble than undoped CLBO [46,47].

### ***Stabilizing CLBO at elevated crystal temperature***

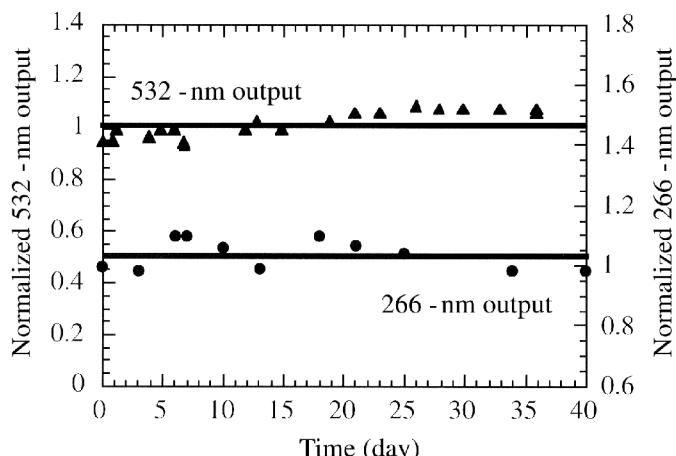
Doping with Al improves both mechanical and chemical properties of CLBO. However, these enhancements are insufficient to protect CLBO from crystalline degradation [48]. Thus another attempt was introduced. In fact, it is known that the lattice constants of CLBO crystals are sensitive to changes in the crystal temperature [49]. As shown in Fig. 13.8, an extraordinary behavior of CLBO is ob-

served, where (a) an elongation along the  $a$ -axis occurs together with (b) a contraction along the  $c$ -axis. A careful interpretation reveals that such changes are relatively larger within the range of room temperature to  $\sim 100^\circ\text{C}$  [50]. Note that above  $120^\circ\text{C}$ , stress from hydration can be relieved by elimination of CLBO hydrates. Thus, stabilizing a CLBO device at an elevated crystal temperature well above  $120^\circ\text{C}$  stabilizes its crystallinity and relieves the crystal distortion from hydration. A detailed investigation was carried out to verify this argument [51–53].

The CLBO crystals were continuously kept at  $160^\circ\text{C}$  for long-term observation [52]. The performance of CLBO was examined by measuring the  $2\omega$  output of a doubler and  $4\omega$  output of a quadrupler. Degradation of crystallinity, if any, was indicated by a decrease in the corresponding harmonic output. As shown in Fig. 13.9, CLBO crystals maintained their crystalline conditions for more than 1 month when exposed to ordinary room humidity. Note that cracking sometimes happened within one week when crystals were continuously exposed to room humidity at room temperature even without being subjected to laser operation [48].



**Fig. 13.8.** (a) Elongation of CLBO lattice constant along the  $a$ -axis and (b) contraction of CLBO lattice constant along the  $c$ -axis



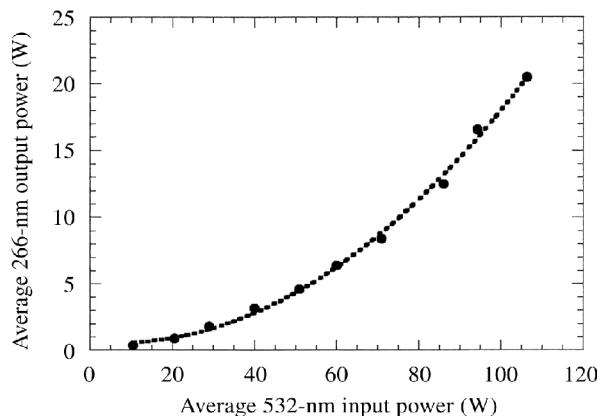
**Fig. 13.9.** Normalized output energy at 532 and 266 nm from CLBO crystals at 160°C. Stable performance was obtained for more than one month with continuous exposure to ordinary room humidity.

From the point of view of nature, a crystal is most stable in its intrinsic physical structure. For the purpose of applications, NLO crystals are shaped beyond such a stable structure. Thus mechanical stress on a device is always introduced, particularly on the surrounding edges. This effect is very obvious for CLBO crystals due to the existence of large interstitial spaces surrounding the sides of Cs ions [52]. Thus, stress from crystal processing is sufficient to cause crystalline distortions in CLBO. Note that the space is relatively large along the *c*-axis or <001> (vertical direction of the figure), and this tends to contract when the neighboring borate network is subjected to thermal vibration. The borate rings joined by the Li ion appeared like a pantograph network. Such a crystalline structure allows active vibration of the Cs ions and their surrounding borate network even at moderate crystal temperatures. This vibration is likely to promote crystal annealing even at temperatures well below the crystal's melting point. At an elevated crystal temperature, such as 160°C, hydration stress on CLBO crystals is prevented. Under this condition, physical stress from crystal processing and thermal shock from laser power absorption can be relieved by activated phonon vibration. Thus, the long-term stability of a CLBO crystal is maintained at an elevated crystal temperature. Note that, as shown in Fig. 13.8, an elevated temperature as low as 80–100°C should be sufficient to obtain long-term operation of CLBO crystals in dry ambient air. In fact, CLBO is currently employed in several commercial solid-state UV laser systems.

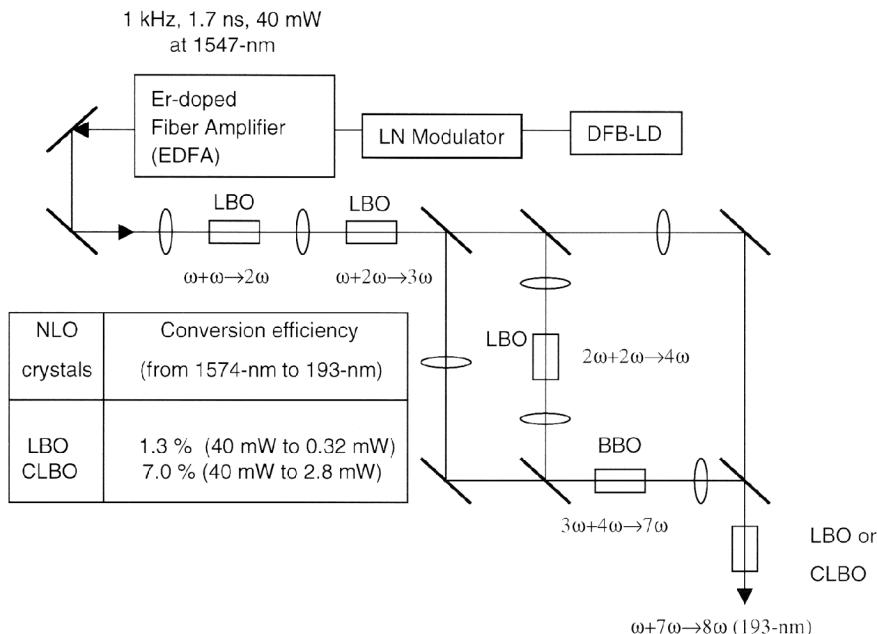
### 13.2.5 Performance of CLBO for generation of deep-UV light

The superior abilities of CLBO crystals for generating UV radiation ( $4\omega$  and  $5\omega$  Nd:YAG laser) were clearly demonstrated at 10 Hz [54], 100 Hz [55], and 1 kHz [56]. For example, the 266 nm output from CLBO is 2.5 times higher than that generated from high-quality BBO (super-BBO/ S-BBO) [56]. An average output of 20.5 W at  $\lambda = 266$  nm was recently generated at 10-kHz by means of CLBO crystals [57–59]. The CLBO crystal is no doubt the most effective NLO crystal for deep-UV light generation. This is due to the relatively small walk-off angle of CLBO (related to its moderate birefringence) that produces better spatial overlapping of the mixing beams. Its relatively large angular, spectral, and temperature acceptance bandwidths favor CLBO for stable UV light generation [54]. These properties, in addition to its shorter absorption edge at 180 nm, eventually lead to a high conversion efficiency and stable output of UV radiation. The output-input relation of the 20.5 W UV light ( $\lambda = 266$  nm) generation is shown in Fig. 13.10.

Note that CLBO crystals have also been characterized for the operation of continuous-wave [60], picosecond [61,62], femtosecond [63,64], and various schemes of UV lasers [65–72]. High-power UV light at  $\lambda = 213$  nm was also used as the pump source for vacuum ultraviolet (VUV) Raman lasers to generate radiation at wavelengths as short as 124.7 nm [73]. It is noteworthy that CLBO was demonstrated to produce deep-UV light at  $\lambda = 193$  nm by  $8\omega$  generation of the Er<sup>3+</sup>-doped fiber amplifier [74]. The conversion efficiency from the fundamental wavelength of 1547 nm was 7% by using the CLBO crystal as the eighth harmonic generator ( $\omega + 7\omega$ ). The conversion efficiency was 1.3% when CLBO was replaced by LBO crystal. The schematic layout of this experiment is shown in Fig. 13.11. This is the most effective generation of 193 nm light from an all-solid-state system.



**Fig. 13.10.** Average UV ( $\lambda = 266$  nm) output power as a function of average green input power at 10 kHz. The dotted line is to guide the eyes.



**Fig. 13.11.** Schematic of experimental set-up for deep-UV light generation at 193 nm

### 13.2.6 Relation between crystal quality and resistance to bulk laser-induced damage

Laser-induced damages and UV absorption of NLO crystals are among the limitations of the development of solid-state UV radiation by NLO crystals. Microscopic crystal defects inside the NLO devices are the important factors that cause laser-induced damage and UV light absorption. The improvement of bulk quality NLO crystals can effectively reduce the UV absorption, suppress the thermal dephasing, enhance the bulk laser damage threshold, and thus improve the performance of solid-state UV lasers. We have developed a modified crystal growth technique to obtain high-quality CLBO crystals. We found that resistance to bulk laser-induced damage can be enhanced by upgrading crystal quality. This was achieved by the implementation of a stirred solution technique [75]. The bulk laser-induced damage threshold was measured using the 0.75 ns FWHM fourth harmonic generation (266 nm) of a Nd:YAG laser employed in the experiment described previously. The bulk laser-induced damage threshold for CLBO grown by the conventional TSSG method and that grown by the stirred solution technique are shown in Table 13.3. The data from a fused quartz sample was taken as a reference. As shown, the maximum bulk laser-induced damage threshold of CLBO grown by the stirred solution technique increased from 10.4 to 25.4 GW/cm<sup>2</sup>.

**Table 13.3.** The bulk laser-induced damage threshold of CLBO grown by a conventional TSSG method and by a stirred solution technique. The damage threshold of fused quartz is shown for comparison

CLBO crystals			
	Stirred solution technique	Conventional TSSG	Fused quartz
Damage threshold (GW/cm <sup>2</sup> )	10.4-25.4	8.8-10.4	10.4

The CLBO grown from the stirred solution technique exhibits a bulk laser-induced damage threshold ~2.5 times higher than the conventional CLBO and fused quartz. This result simply implies the improvement of CLBO crystallinity by our stirred solution technique. The details of this technique will be discussed in the future.

### 13.3 GdYCOB Crystal for Noncritical Phase-Matching (NCPM) of Visible and UV Light

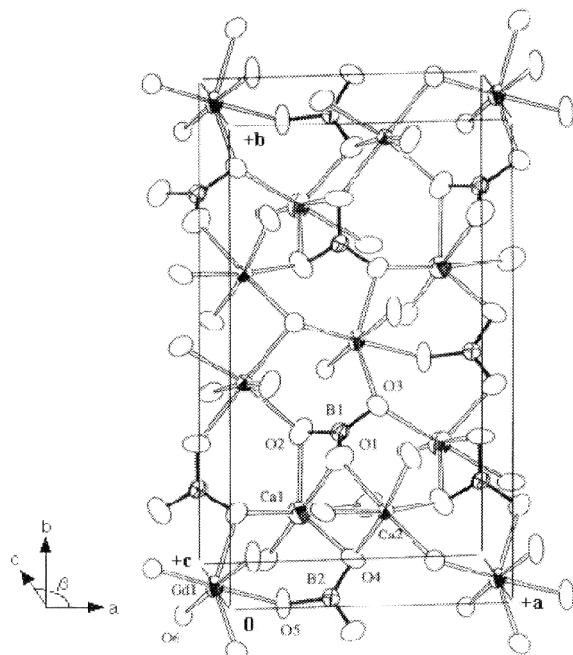
#### 13.3.1 The search for $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ (GdYCOB)

The GdYCOB crystal belongs to the so-called rare-earth (Re) calcium oxyborate family, with a general composition of  $\text{ReCa}_4\text{O}(\text{BO}_3)_3$ . This crystal family is called oxyborate because not all the oxygen atoms are directly bonded to the boron. The first compound in this series,  $\text{SmCa}_4\text{O}(\text{BO}_3)_3$  was studied by Khamaganova et al. (1991) [76]. One year later, a series of compounds from this family were examined by Norrestam et al. with Re = La, Nd, Sm, Gd, Er, and Y [77]. Ilyukhin and Dzhurinskii investigated compounds with Re = Gd, Tb, and Lu [78]. The space group of this family is monoclinic noncentrosymmetric Cm with  $Z = 2$ . In 1996, Aka et al. grew a single crystal of  $\text{GdCa}_4\text{O}(\text{BO}_3)_3$  (GdCOB) by the conventional Cz method and reported its NLO properties [27,28]. The GdCOB melts congruently at 1480°C. In addition, Y and La were indicated to be alternative rare-earth atoms (Re) for  $\text{ReCa}_4\text{O}(\text{BO}_3)_3$  NLO crystals [27]. One year later, Iwai et al. (1997) reported on the growth of GdCOB and YCOB single crystals and investigated their differences in terms of linear and nonlinear optical properties [18]. Furthermore,  $\text{ReCa}_4\text{O}(\text{BO}_3)_3$  (Re = Gd, Lu, Yb, Tm, Y, Sm, Nd, La) were confirmed to be SHG active [79]. Total substitution of the Ca site by Mg, Sr, and Ba was also attempted, but these compounds did not produce SHG [79].

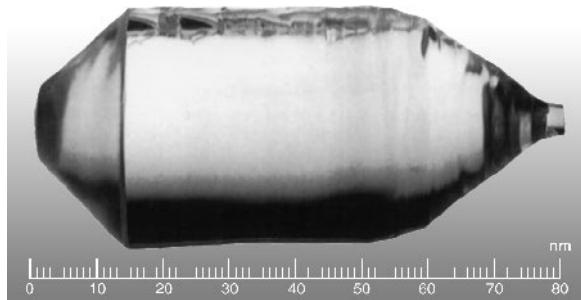
The detailed linear and NLO properties of GdCOB crystals were reported in 1997 [18,80]. This crystal appeared to be effective for SHG of Nd:YAG lasers. The main advantages of GdCOB compared to other borate crystals are the ease of crystal growth and that they are absolutely nonhygroscopic. This crystal has a

relatively small birefringence ( $\Delta n = 0.033$  at  $\lambda = 1064$  nm) and has a significant effective NLO coefficient of 1.3 pm/V [18]. The crystal structure of GdCOB is shown in Fig. 13.12 with  $a = 8.0937$ ,  $b = 16.013$ ,  $c = 3.5579$  Å and  $\beta = 101.27^\circ$  [18].

The properties of the YCOB crystal are significantly different from those of GdCOB [18]. The YCOB melts congruently at 1510°C and was grown by conventional Cz using an Ir crucible in an Ar atmosphere. The YCOB crystal has a slightly smaller NLO coefficient (1.1 pm/V). Note that GdCOB has several absorption lines within 240 to 320 nm that are characteristic of  $Gd^{3+}$ . The YCOB has a UV cut-off at 210 nm and is highly transparent up to 2500 nm [20]. The structure of YCOB is identical to that of GdCOB with slightly smaller lattice constants  $a$ ,  $b$ ,  $c$  and  $\beta$  angle [18]. The most important property of YCOB is the relatively larger birefringence of 0.041 at  $\lambda = 1064$  nm. This allows UV generation by YCOB by third harmonic generation (THG) of a Nd:YAG laser (1064 nm + 532 nm  $\rightarrow$  355 nm) that is not possible using GdCOB [18,81]. The shortest type-1 SHG wavelengths phase-matchable along the  $y$ -axis of YCOB and GdCOB are estimated at  $\sim 360$  nm and 420 nm [82], respectively, by the Shellmeier equations proposed by Mougel et al. [83]. The difference in birefringence between GdCOB and YCOB is related to the higher lattice constant ratio ( $a/c$ ) of YCOB ( $\sim 2.288$ ) compared to that of GdCOB ( $\sim 2.275$ ) [82].



**Fig. 13.12.** Molecular packing of GdCOB in a three-dimensional framework



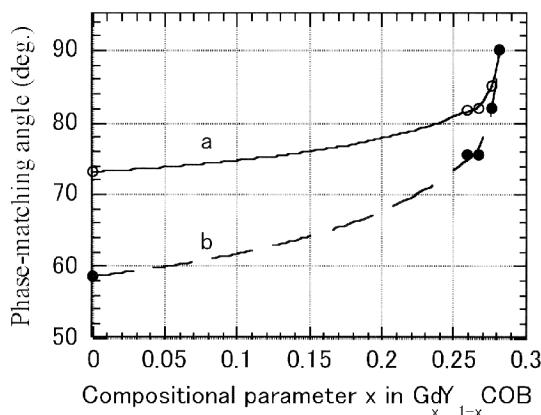
**Fig. 13.13.** Photograph of the Cz-grown GdYCOB crystal

The total substitution of Gd in GdCOB by Y results in YCOB that is larger in birefringence for producing THG of Nd:YAG lasers. This result simply implies the possibility of modifying crystal birefringence by changing the ratio of Gd:Y in the crystals [81,84]. Single crystals of  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  were grown like those of GdCOB and YCOB. The as-grown crystal of  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  ( $x = 0, 0.48, 1$ ) crystals were measured using a four-circle X-ray diffractometer. The ratios of lattice constants ( $a/c$ ,  $a/b$ ) in  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  ( $x = 0, 0.48, 1$ ) crystals were measured using a four-circle X-ray diffractometer. The ratios of lattice constants  $a/c$  and  $a/b$  in GdYCOB were linearly changed with the increase compositional parameter  $x$  [20]. This result confirms that GdYCOB is a substitutional solid solution and that it is possible to vary its refractive indices continuously.

### 13.3.2 Noncritically phase-matched THG for Nd:YAG lasers by GdYCOB

It is known that laser frequency conversion by noncritical phase-matching (NCPM) along the principle axes is advantageous because of a larger angular acceptance and the elimination of the walk-off effect. The phase-matching angles for type-1 THG in YCOB were experimentally determined as  $(\theta, \phi) = (90^\circ, 73.2^\circ)$  and  $(58.7^\circ, 90^\circ)$  in the  $xy$  and  $yz$  planes, respectively. In general, as the birefringence of a NLO crystal decreases, the phase-matching angles shift towards a larger value. Partial substitution of Gd for Y in YCOB crystals makes the birefringence small; therefore, we expect to achieve NCPM THG along the  $y$  axis by introducing appropriate Gd atoms into the sites of Y atoms of YCOB; i.e. phase-matching of THG in the  $xy$  and  $yz$  planes should shift toward  $(\theta, \phi) = (90^\circ, 90^\circ)$ .

We examined the phase-matching angles on the principal planes ( $xy$ ,  $yz$ ) for various GdYCOB compounds. The experiments were carried out at room temperature. Type-1 GdYCOB crystals were cut at the  $y$ -axis or phase-matching direction for THG. Figure 13.14 represents the phase-matching angles for type-1 THG as a function of the compositional parameter  $x$  in  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ .



**Fig. 13.14.** Changes of phase-matching angles for THG as a function of the compositional parameter x

**Table 13.4.** Properties of GdYCOB for THG of Nd:YAG lasers compared to those of YCOB, LBO, and KDP

	$d_{\text{eff}}$ [pm/V]	External angular Acceptance bandwidth [mrad cm]		Temperature bandwidth [°C cm]	Walk-off angle [mrad]
		$\Delta\theta l$	$\Delta\phi l$		
YCOB (type I, xy)	0.52	-	3.2	9.7	8.5
GdYCOB (type I, y)	0.55	114 mrad cm <sup>1/2</sup>	65.6 mrad cm <sup>1/2</sup>	6.6	0
LBO (type I, xy)	0.68	-	1.71	19.0	18.3
LBO (type II, yz)	0.50	5.02	-	3.7	9.30
KDP (type II)	0.35	1.58	-	5.20	26.5

crystals. For curve a, the wave vector  $k$  is in the  $xy$  plane and the phase-matching angle is  $\phi$  from the  $x$ -axis. Similarly, for curve b the phase-matching angle is  $\theta$  from the  $z$ -axis in the  $yz$  plane. The phase-matching angles gradually change to 90° due to increasing of  $x$  in  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$ . At  $x = 0.28$ , the phase-matching angle reaches  $(\theta, \phi) = (90^\circ, 90^\circ)$ , which is the type-1 noncritical phase-matching at room temperature.

The phase-matching properties for THG of  $\text{Gd}_{0.28}\text{Y}_{0.72}\text{Ca}_4\text{O}(\text{BO}_3)_3$  are summarized in Table 13.4 together with those of YCOB, LBO, and KDP. As indicated, we have improved the angular properties of YCOB for THG by the substitution of Gd for Y in YCOB. Furthermore, the zero walk-off effect in  $\text{Gd}_{0.28}\text{Y}_{0.72}\text{Ca}_4\text{O}(\text{BO}_3)_3$  allowed perfect spatial overlapping of the mixing beams for THG. These advantages contribute to a THG output from  $\text{Gd}_{0.28}\text{Y}_{0.72}\text{Ca}_4\text{O}(\text{BO}_3)_3$  five times higher than that by YCOB [85,86]. These results suggest that  $\text{Gd}_{0.28}\text{Y}_{0.72}\text{Ca}_4\text{O}(\text{BO}_3)_3$  is suitable for THG generation and that a longer crystal can be utilized for higher frequency conversion efficiency.

### 13.3.3 Noncritically phase-matched SHG for Nd:YAG lasers by GdYCOB

We found that the phase-matching angles for type-2 SHG in  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  also changed to  $90^\circ$  with an increase in the compositional parameter  $x$ , and the angles reached  $(\theta, \phi) = (90^\circ, 90^\circ)$  at  $x = 0.275$  [87,88]. In addition,  $\text{Gd}_{0.28}\text{Y}_{0.72}\text{Ca}_4\text{O}(\text{BO}_3)_3$  was also confirmed to generate SHG along the same direction. That is, the  $\text{Gd}_{0.28}\text{Y}_{0.72}\text{Ca}_4\text{O}(\text{BO}_3)_3$  crystal is NCPM for both type-2 SHG and type-1 THG at room temperature.

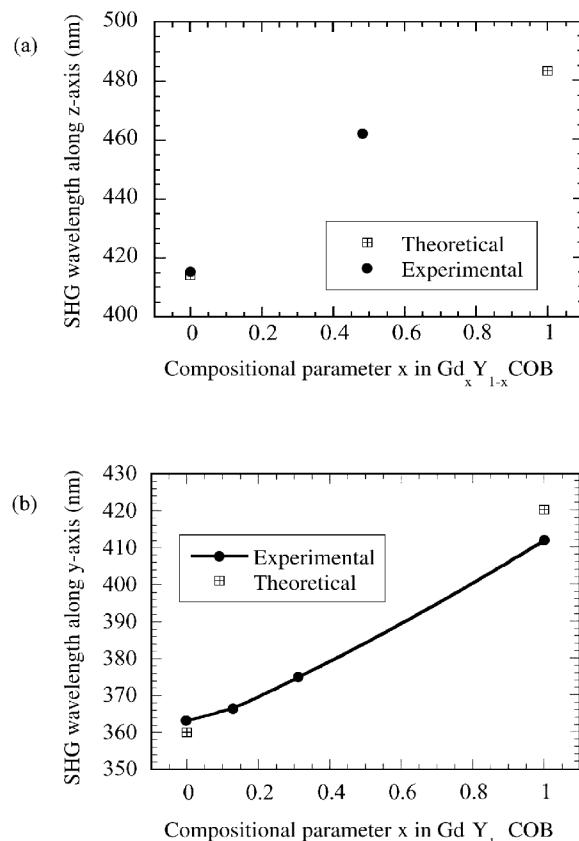
The phase-matching properties of type-2 SHG in a  $\text{Gd}_{0.275}\text{Y}_{0.725}\text{Ca}_4\text{O}(\text{BO}_3)_3$  crystal were measured and are summarized in Table 13.5, together with those of KDP and LBO. We found that  $d_{\text{eff}}$  of  $\text{Gd}_{0.275}\text{Y}_{0.725}\text{Ca}_4\text{O}(\text{BO}_3)_3$  is 0.35 pm/V, smaller than that of LBO and comparable to that of KDP. The angular acceptance bandwidths of  $\text{Gd}_{0.275}\text{Y}_{0.725}\text{Ca}_4\text{O}(\text{BO}_3)_3$  are broader than those of the NCPM type-1 LBO [89]. The temperature bandwidth for type-2 SHG in  $\text{Gd}_{0.275}\text{Y}_{0.725}\text{Ca}_4\text{O}(\text{BO}_3)_3$  is significantly larger than those of KDP and LBO. A detailed description of these measurements has been presented elsewhere [88].

**Table 13.5.** Properties of GdYCOB for SHG of Nd:YAG lasers compared to those of YCOB, LBO, and KDP

	$d_{\text{eff}}$ [pm/V]	External angular Acceptance bandwidth [deg cm $^{1/2}$ ]		Temperature bandwidth [°C cm]	Walk-off angle [mrad]
		$\Delta\theta l$	$\Delta\phi l$		
GdYCOB (type II, y axis)	0.35	11.5	6.8	32.4@27°C	0
KDP (type II)	0.35	0.2 deg cm	-	18.3@25°C	24.5
LBO (type I, x axis, 148°C)	0.85	4.1	5.7	4.8@149°C	0

### 13.3.4 Noncritically phase-matched SHG for Ti:sapphire lasers by GdYCOB

Tailoring the atomic ratio of Gd/Y adjusts the birefringence of GdYCOB crystals for NCPM type-2 SHG and type-1 THG of Nd:YAG lasers. We examined the range of NCPM type-1 SHG of Ti:sapphire using GdYCOB. As shown in Fig. 13.15 (a), the type-1 SHG wavelengths phase-matchable along the  $z$ -axis for  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  at  $x = 0$  (i.e., YCOB) and  $x = 1$  (i.e., GdCOB) are estimated theoretically as 414 nm and 483 nm, respectively, using the Shellmeier equations proposed by Mougel et al. [83]. Experimentally, the NCPM type-1 SHG wavelengths at  $x = 0$  and  $x = 0.48$  are 415 nm and 462 nm, respectively. Thus, NCPM of type-1 SHG from ~415 to 483 nm can be obtained along the  $z$ -axis of GdYCOB.



**Fig. 13.15.** Phase-matched wavelength produced by NCPM type-1 SHG along the (a)  $z$ -axis and (b)  $y$ -axis of  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  as a function of compositional parameter  $x$

Note that shorter SHG wavelengths can be produced by type-1 NCPM along the  $y$ -axis with a higher effective NLO coefficient. Several GdYCOB samples with various  $x$  compositions were examined using a Ti:sapphire laser. As shown in Fig. 13.15 (b), the NCPM type-1 SHG wavelengths are experimentally estimated to be ~363 nm, 366 nm, 375 nm, and 412 nm for cases in which  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  at  $x = 0$  (i.e., YCOB), 0.13, 0.31, and 1 (i.e., GdCOB), respectively. Thus, type-1 SHG wavelengths from ~363 to 412 nm can be obtained along the  $y$ -axis of GdYCOB. The effective NLO coefficient for type-1 SHG in this direction is estimated to be 0.55 pm/V.

### 13.3.5 Optical damage of GdYCOB and its solution

#### *Gray-track and photorefractive damage in GdYCOB*

The crystals of GdCOB, YCOB, and GdYCOB have several desired NLO properties for laser frequency conversion. The most interesting features offered by GdYCOB are the ability to generate visible and UV light by means of NCPM. All these crystals appeared to be promising for actual applications in high-power all-solid-state laser systems in the visible and near-UV regions. However, during the high-power THG operation of GdYCOB, optical damages were generated inside the crystals. In fact, two kinds of damages were identified: (1) gray-track and (2) photorefractive damage. Such damages also happened in other  $\text{ReCa}_4\text{O}(\text{BO}_3)_3$  crystals like GdCOB and YCOB when irradiated by UV (355 nm) light. Furthermore, we found that these damages can be recovered by annealing at temperatures above 100 to 150°C. The minimum crystal temperature required to avoid gray-track seems to be lower for YCOB and higher for GdCOB. Details of these results were discussed elsewhere [90]. In addition, gray-track in these crystals was investigated by electron paramagnetic resonance (EPR) [91].

#### *Prevention of optical damage in GdYCOB at elevated crystal temperature*

We think that it is possible to use GdYCOB for high-power THG operation at elevated temperature without formation of gray-track and photorefractive optical damage. Laser experiments were carried out to verify this idea. As shown in Fig. 13.16, a diode-pumped high repetitive Nd:YVO<sub>4</sub> laser was used for the experiment. The fundamental power was measured before the type-1 LBO doubler, C<sub>1</sub>. For frequency tripling, we compared GdYCOB to type-2 LBO. Note that birefringence of GdYCOB decreases with crystal temperature. Thus, GdYCOB crystal with a smaller composition of Gd/Y ( $x < 0.28$ ) was grown for this experiment. The NCPM condition for THG in GdYCOB was fine-tuned by temperature and happened to perform NCPM at 240°C [92]. This crystal was 18 mm in length while the LBO crystal was 12 mm. Note that LBO crystal has AR coating while GdYCOB crystal does not.

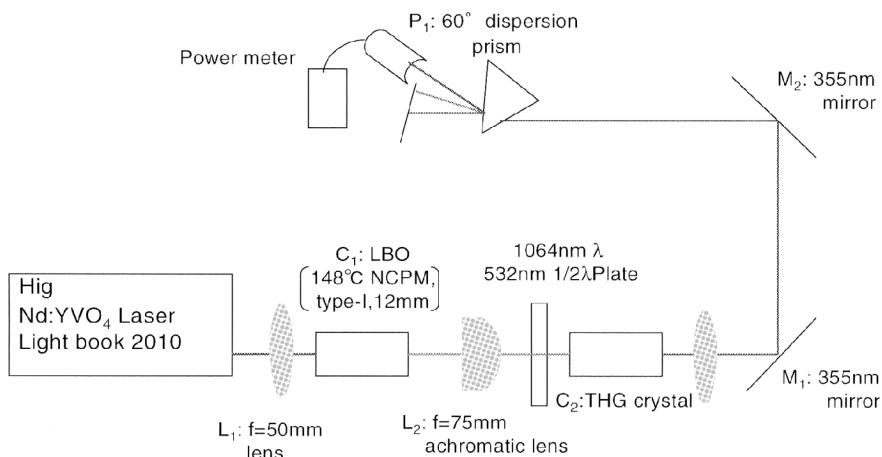


Fig. 13.16. Experimental set-up for high-repetition rate THG measurement

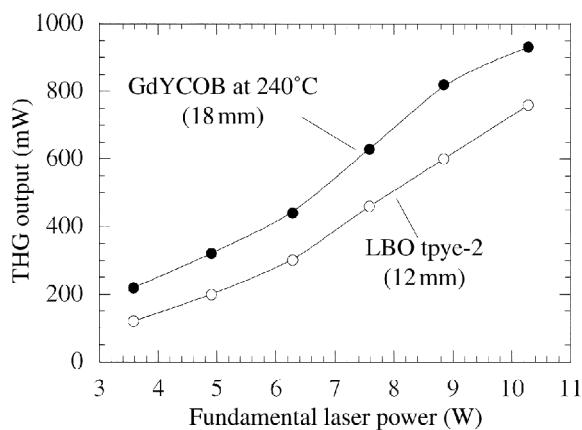


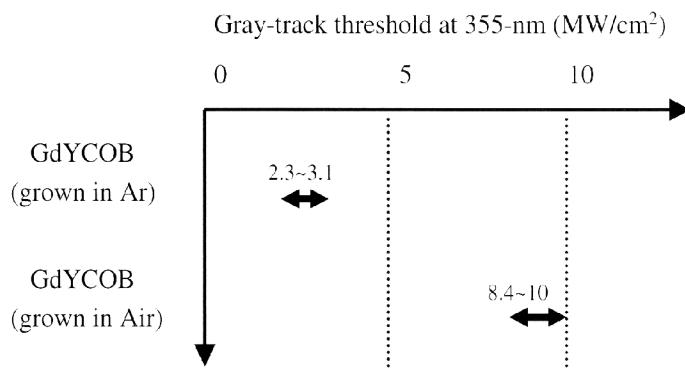
Fig. 13.17. UV output power at 355 nm for two NLO crystals

Figure 13.17 represents the relationship between the output power at 355 nm and the fundamental input power at a repetition rate of 62.5 kHz. For the case of LBO, the third-harmonic power was increased steadily up to 0.74 W. On the other hand, THG output of GdYCOB at 240°C is 0.93 W. Thus, performances of GdYCOB are comparable to that of LBO. Output stability at elevated temperature was excellent (< 1%) with nondistorted beam profile. Both photorefractive damage and gray-track were not formed after experiment. As indicated from this preliminarily result, GdYCOB at elevated temperature is suitable for practical generation of high-average power UV light at 355 nm.

### **Dependence of gray-track threshold of GdYCOB on the crystal growth atmosphere**

Single crystals of GdYCOB were grown by the conventional Czochralski technique. The GdYCOB starting material was prepared by solid-state reaction of  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and  $\text{B}_2\text{O}_3$  [20]. In fact, oxygen or oxygen-containing atmosphere is required for the growth of oxyborate crystals like the GdCOB, YCOB, and GdYCOB. Due to the high growth temperatures ( $\sim 1500^\circ\text{C}$ ), an Ir crucible is used instead of a Pt crucible because of its higher melting point (2457°C for Ir, 1772°C for Pt). However, oxygen must be avoided when using an Ir crucible in order to prevent oxidization. Thus, Ar atmosphere was employed when the Ir crucible was used. By this means, oxygen defects can be created in the crystals. We suspect that optical damages discussed so far are related to such crystal defects. Thus, GdYCOB crystals were grown in both Ar and ambient air. The sintered material of GdYCOB was melted in the Ir crucible (in the case of Ar atmosphere) or the Pt crucible (in the case of ambient air) by induction heating. The <010>-oriented seed crystal was used for crystal growth. For all cases, the pulling rate was 1–4 mm/h and the seed rotation rate was 10–15 rpm.

We examined the threshold of gray-track for GdYCOB grown in Ar and ambient air. Note that all GdYCOB crystals were optically polished without AR coating. Figure 13.18 represents the relationship between the growth atmosphere and gray-track damage threshold. For the case of GdYCOB grown in Ar atmosphere, the damage threshold at 355 nm was 2.3–3.1 MW/cm<sup>2</sup>. On the other hand, in the case of GdYCOB grown in ambient air, the damage threshold was 8.4–10.0 MW/cm<sup>2</sup>, about three-fold larger than that grown in Ar atmosphere.



**Fig. 13.18.** Gray-track threshold of GdYCOB at laser wavelength of 355 nm

## 13.4 KAB Crystal: Difficulty of Growing Borate Crystal with Layered Structure

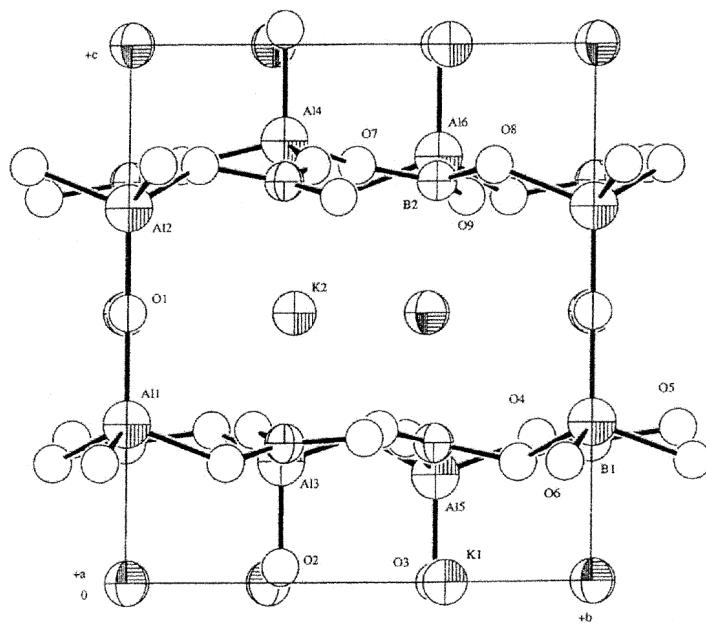
### 13.4.1 The search for $K_2Al_2B_2O_7$ (KAB)

In this section, we describe the search for a new NLO borate crystal:  $K_2Al_2B_2O_7$  (KAB). In general, a good NLO crystal that can generate deep-UV light effectively is required to have a birefringence between that of BBO ( $\Delta n = 0.12$  at  $\lambda = 1064$  nm) [96] and LBO ( $\Delta n = 0.04$  at  $\lambda = 1064$  nm) [11]. This allows the expansion of the phase-matching range for SHG at a reasonably low walk-off effect and significantly large phase-matching bandwidths. The success of CLBO for high-power deep-UV light conversion is a good example. The CLBO has a birefringence of  $\Delta n = 0.052$  at  $\lambda = 1064$  nm, slightly larger than that of LBO, and thus can produce the shortest possible SHG wavelength of  $\sim 237$  nm [94,95] as compared to 277 nm for LBO and 205 nm for BBO. Thus, more NLO crystals like CLBO that possesses a birefringence between that of BBO and LBO are desired for effective UV light conversion.

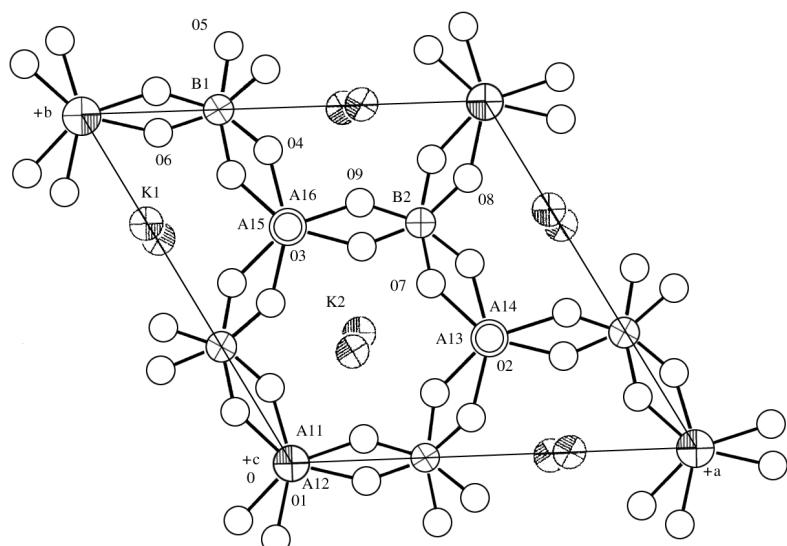
At a wavelength of 589 nm, the KBBF has  $\Delta n = 0.072$  while the SBBO has  $\Delta n = 0.062$  [96]. However, because of the weak binding between the layered structural units, KBBF is difficult to grow and is mechanically fragile [13]. The SBBO has strong covalent bonds between Be atoms and oxygen atoms in adjacent layers. This makes SBBO mechanically stronger and relatively easy to grow compared to the KBBF. However, Be is toxic, which makes crystal growth inconvenient. Thus, it is important that Be atoms in SBBO be replaced by a nontoxic element. We have attempted to replace  $(BeO_4)^{6-}$  with  $(AlO_4)^{5-}$  and to replace  $Sr^{2+}$  with  $M^+$  ( $M^+ = Li^+, Na^+, K^+, Rb^+,$  and  $Cs^+$ ) according to the concept of ionic compensation ( $Al^{3+} + K^+ \rightarrow Be^{2+} + Sr^{2+}$ ) [22,23]. In this way, we discovered the potassium aluminum borate crystal:  $K_2Al_2B_2O_7$  (KAB), which possesses a spatial arrangement similar to that of SBBO.

The structure of KAB was analyzed by 4-axis X-ray diffraction (Rigaku AFC5R diffractometer). The KAB crystallizes in the trigonal space group P321 (#150) with  $a = 8.5657$ ,  $c = 8.463$  Å,  $V = 537.7$  Å<sup>3</sup>, and  $Z = 3$  [97]. As illustrated in Fig. 13.19, the basic structural features of the KAB crystal are  $K^+$  cations,  $(BO_3)^{3-}$  triangles, and distorted  $(AlO_4)^{5-}$  tetrahedra. The triangular and tetrahedral anions form a three-dimensional  $Al_2(BO_3)_2O$  framework which houses  $K^+$  cations. This framework is constructed of nearly planar  $[BO_3]-[AlO_4]$  units with oxygen connecting the Al atoms between two adjacent layers at an Al-O-Al bond angle of 180°.  $K^+$  cations are arranged in the spaces formed between the layers. Compared to SBBO, the major NLO active group of KAB is also the  $(BO_3)^{3-}$  group, with its three terminal oxygen atoms linked to Al atoms. The KAB crystal possesses a spatial arrangement similar to SBBO. The powder of  $K_2Al_2B_2O_7$  was previously studied by Kaduk and Sate (1996) [98].

(a)



(b)



**Fig. 13.19.** Projection of the KAB crystal along the (a)  $a$ -axis and (b)  $c$ -axis

### 13.4.2 Growth of KAB

The structures of KBBF, SBBO, and KAB consist of layered structures. There are no detailed descriptions of the procedure for growing crystals of KBBF (or more accurately MBe<sub>2</sub>BO<sub>3</sub>F<sub>2</sub> with M = Na, K) and SBBO. Crystals of KBBF [96,99,100] and NBBF [101] with dimensions of  $10 \times 10 \times 0.3$  mm<sup>3</sup> and  $0.1 \times 0.4 \times 0.6$  mm<sup>3</sup> were reported, respectively. The growth of SBBO is much easier but also not well described, although a crystal with dimensions of  $7 \times 7 \times 3$  mm<sup>3</sup> was reported to be of good optical quality [13]. In this section, we provide a detailed procedure for the growth of KAB crystals. This may provide some references for the growth of borate crystals with layered crystalline structures.

#### ***Growth of KAB crystals by self-flux***

The KAB crystals were grown by TSSG in a five-zone vertical furnace like that employed to grow CLBO crystals (Fig. 13.3). The single-phase powders of KAB were prepared from a mixture of a stoichiometric ratio of analytical reagent grade K<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and B<sub>2</sub>O<sub>3</sub>. The mixture was first heated at 650°C for one day, followed by further heating at 800°C for two days. The solid-state reaction involved in this case is: K<sub>2</sub>CO<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> + B<sub>2</sub>O<sub>3</sub> → K<sub>2</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub> + CO<sub>2</sub>. The powders were ground at room temperature between heating. The final mixtures were ground and compressed into a Pt crucible and melted at 1100°C. The melt was cooled at a constant rate of 5°C/hour for 50 hours, followed by a cooling rate of 40°C/hour to room temperature. Many triangular and transparent crystals could be physically selected and used as seed crystals.

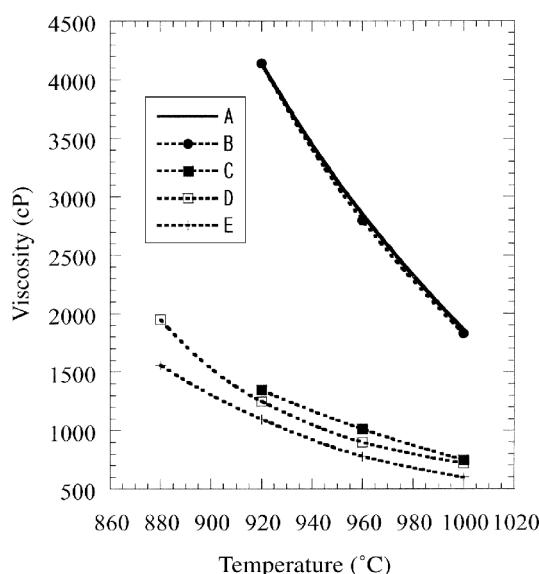
An additional flux must be employed for crystal growth because of the high viscosity of the stoichiometric KAB liquid. The B<sub>2</sub>O<sub>3</sub> flux alone made the solution very viscous, while using K<sub>2</sub>CO<sub>3</sub> alone led to high saturation temperatures and marked volatility of the solution. Thus, a mixture of K<sub>2</sub>CO<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> was attempted. In short, the increase in B<sub>2</sub>O<sub>3</sub> content increased the viscosity and decreased the crystal growth temperature. In such a case, mass transport in the solution is too slow for crystal growth. The condition is reversed for cases with increased K<sub>2</sub>CO<sub>3</sub> content. Crystals of KAB with dimensions as large as  $18 \times 14 \times 3$  mm<sup>3</sup> can be obtained using K<sub>2</sub>CO<sub>3</sub>:B<sub>2</sub>O<sub>3</sub> (1:1.8) fluxes. These dimensions are significantly larger than those reported for SBBO and KBBF crystals [13,96,99–101]. The KAB tends to grow in a plate-like structure that seems to relate to its crystalline structure.

#### ***Growth of KAB crystals with the addition of alkali metal halides***

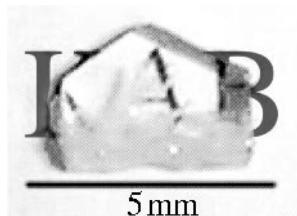
Crystals of KAB grown from K<sub>2</sub>CO<sub>3</sub>:B<sub>2</sub>O<sub>3</sub> (1:1.8) fluxes have many inclusions. Additional solvents that can decrease the viscosity of the solution without significantly increasing the growth temperature and volatility are desired. For cases of B<sub>2</sub>O<sub>3</sub>-containing solutions, it is well known that the addition of alkali metals and halide ions can reduce the viscosity of the solution by breaking the –O–B–O–

chains in the solution [102,103]. We have investigated the effects of these ions on the viscosity of KAB solutions, as summarized in Fig. 13.20. The viscosity is reduced significantly from 4140 to 1327 cP at 920°C as the ratio of  $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3$  is increased from 1:1.8 (case A) to 1:1.5 (case C). The addition of 0.2 KF in KAB solutions with  $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3$  fluxes at a ratio of 1:1.8 do not obviously change the viscosity of the solution (case B). The addition of 0.2 NaF in KAB solutions with  $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3$  fluxes at a ratio of 1:1.5 decreases the viscosity further as shown in case E. The effect of NaF is stronger than that of LiCl (case D). Note that the reduction of viscosity is more significant in the low temperature range. The NaF appeared to work better because of its higher melting temperature compared to LiCl and KF.

We tried to grow KAB crystals by the procedure described as follows [104]. The starting materials for KAB were prepared using a two-step process. First, a mixture of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{B}_2\text{O}_3$  at a ratio of 2:1 was mixed and ground. The mixture was decomposed at 200°C for 12 hours and sintered at 600°C for 24 hours.  $\text{K}_2\text{CO}_3$  was then added and the mixture was heated again at 650°C for one day and at 800°C for two days. The KAB raw materials made from this procedure are better for KAB crystal growth. We think that  $\text{Al}_2\text{O}_3$  can be completely mixed and melted to form a highly homogeneous solution by this method. During crystal growth, we raised the rotation rate of the seed crystals from 20 rpm to 40 rpm to



**Fig. 13.20.** Viscosity of solution for KAB crystal growth as a function of temperature for various fluxes. A = ( $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3 = 1:1.8$ ), B = ( $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3:\text{KF} = 1:1.8:0.2$ ), C = ( $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3 = 1:1.5$ ), D = ( $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3:\text{LiCl} = 1:1.5:0.2$ ), and E = ( $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3:\text{NaF} = 1:1.5:0.2$ )



**Fig. 13.21.** Transparent KAB crystals grown from  $\text{K}_2\text{CO}_3/\text{B}_2\text{O}_3/\text{NaF}$  fluxes

improve the homogeneity of the solution. The flux composition was adjusted to  $\text{K}_2\text{CO}_3:\text{B}_2\text{O}_3:\text{NaF}$  at a 1:1.5:0.2 ratio to decrease the viscosity of solution and thus promote mass transport in the solution. This flux also decreases the supersaturation of the solution and suppresses spontaneous nucleation during growth. In this way, crystal growth can be carried out at relatively lower temperatures with reduced volatility. We further reduced the cooling rate to  $\sim 0.2^\circ\text{C}/\text{day}$ . Finally, we have grown transparent KAB crystals as shown in Fig. 13.21.

### 13.4.3 Optical properties of KAB

It is still difficult to grow transparent KAB to dimensions sufficient for laser experiments. Some optical properties of KAB have been determined. The UV absorption edge of KAB was estimated at a wavelength of 180 nm [22]. The SHG coefficient of KAB was estimated to be comparable to that of KDP ( $d_{36} = 0.38 \text{ pm/V}$ ) as obtained from powder samples. The refractive indices of the ordinary and extraordinary axes are  $n_o = 1.553$  and  $n_e = 1.479$  with a birefringence  $\Delta n = 0.074$  as determined by the oil immersion technique, as compared to 0.072 and 0.062 for KBBF and SBBO, respectively. The lower effective NLO coefficient of KAB compared to that of SBBO ( $= 1.52 \text{ pm/V}$  [105]) is probably due to the lack of identical spatial orientation of the  $(\text{BO}_3)^{3-}$  groups between adjacent layers. The fact that the UV absorption edge of KAB is longer than that of SBBO is due to the natural absorption of  $(\text{AlO}_4)^{5-}$ .

## 13.5 Summary and Perspective

We have reviewed the growth and recent development of borate NLO crystals for generation of high-power visible and UV light, especially that of  $\text{CsLiB}_6\text{O}_{10}$  (CLBO),  $\text{Gd}_x\text{Y}_{1-x}\text{Ca}_4\text{O}(\text{BO}_3)_3$  (GdYCOB), and  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  (KAB) crystals. No doubt, development of these new borate materials has stimulated significant progress in the generation of high-power UV light by NLO crystals. Continued efforts to search for new NLO crystals are necessary. The assistance of theoretical approaches to the prediction of crystal structure and properties is still insufficient.

Recently, cluster modeling was used to calculate the electronic structure and NLO properties of LBO, CBO, and CLBO [106]. The nonlinear response of these crystals was considered related to the interaction between the cation and the anionic group, as consistent with that reported earlier for KTP crystals [107]. The usage of such model on structural prediction is still not being demonstrated.

There is no doubt that the development of NLO borate crystals is promoted by the need for a high-power, coherent, all-solid-state UV light source. Under such circumstances, borate crystals of “perfect” quality are needed for minimizing linear and nonlinear optical absorption and thus suppressing the occurrence of laser-induced damage and thermal dephasing. Advances in crystal growth techniques and device processing are important. New approaches for growing crystals like KBBF and SBBO must also be considered for further progress in this area.

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# 14 Growth of High $T_c$ Crystals

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## 14.1 Introduction

Since the discovery of Ba-La-Cu-O compounds of high  $T_c$  superconductors by Bednorz and Muller [1], many papers have been published on the various types of high  $T_c$  superconductors containing copper oxides such as  $\text{LnBa}_2\text{Cu}_3\text{O}_y$  (123 type), where Ln is a rare earth atom and Y, and Bi-Sr-Ca-Cu-O (BSCCO) compounds. This chapter is made up of the following three parts:

1. Growth of the high  $T_c$  phase of BSCCO ( $T_c \sim 100$  K)
2. Liquid phase epitaxial growth of the low  $T_c$  phase of BSCCO ( $T_c \sim 80$  K)
3. Construction of phase diagrams by *in situ* observation and their application to crystal growth of oxide superconductors.

## 14.2 Growth of the High $T_c$ Phase of BSCCO

Three superconducting phases are known in the Bi-Sr-Ca-Cu-O compounds, which have the formula of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{x-1}\text{Cu}_x\text{O}_y$  ( $x = 1, 2, 3$ ). Their structures are similar, differing only in the spacing along the  $c$ -axis. The approximate values of  $c_0$  in order of  $x = 1, 2$ , and 3 are 24, 30, and 36 Å, and their superconducting tran-

sition temperatures  $T_c$  are 10, 80, and 105 K, respectively. Hereafter, we call the 30 Å ( $x = 2$ ) and 36 Å ( $x = 3$ ) phases low  $T_c$  and high  $T_c$  phases, respectively.

Among them, the high  $T_c$  phase (2223 phase) is very difficult to grow sizable single crystals. We made the following three experiments for growing the high  $T_c$  phase: (1) synthesis by sintering the powder of Bi-Sr-Ca-Cu, (2) annealing the solidified mass of Bi:Sr:Ca:Cu = 4:3:3:4, and (3) conversion of low  $T_c$  crystals to high  $T_c$  ones by annealing. Most of this part was reported in our papers [2–4].

#### **14.2.1 Synthesis of the high $T_c$ phase by sintering the powder of Bi-Sr-Ca-Cu**

Our ultimate purpose is to grow sizable single crystals of the high  $T_c$  phase of a BSCCO superconductor. This high  $T_c$  phase has a transition above 100 K. It was necessary to obtain fundamental data relating to the thermal stability of this phase before conducting an experiment on single crystal growth. Endo et al. [5] reported an excellent method for preparing sintered samples consisting of about 100% high  $T_c$  phase ( $T_{c(R=0)} = 107.5$  K). We also tried to synthesize the high  $T_c$  phase following their method. Attention was paid to the processes of synthesis and decomposition of this phase.

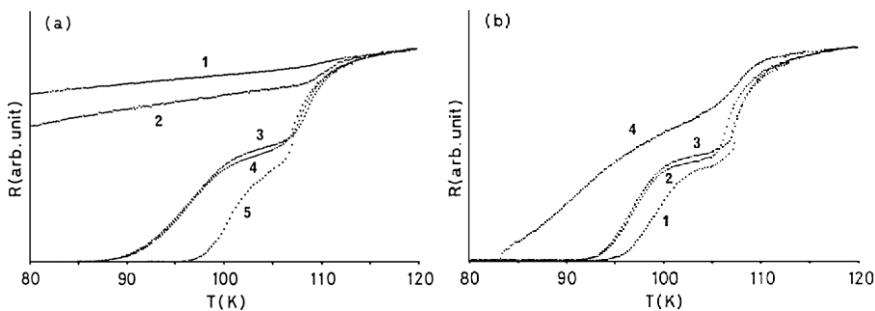
Powder with a cation ratio of Bi:Pb:Sr:Ca:Cu = 0.8:0.2:0.8:1.0:1.4 was prepared by a coprecipitation method. The powder thus prepared was ground and pressed into pellets 2–3 mm thick. They were heated at 790–880°C for 1–100 hours in a stream of Ar-O<sub>2</sub> gas mixture of about 1 atm with an oxygen partial pressure of 1/13 atm. After heating, they were cooled to 500°C at the rate of about 100°C/h. Their resistivity was measured with a standard four-probe technique. Hereafter, we shall refer to the phase with the lattice parameter  $c = 30$  Å as the low  $T_c$  phase and that with  $c = 36$  Å as the high  $T_c$  phase.

#### ***Effects of the sintering temperature***

Figure 14.1 shows the resistivity  $R$  versus temperature  $T$  curves for the specimens sintered at various temperatures for 30 h. The following observations were derived from these data.

(a) A single high  $T_c$  phase could not be obtained in any case for the sintering time of 30 h. The  $R$ - $T$  curves showed a two-step superconducting transition. This suggests a coexistence of the high  $T_c$  phase with the low  $T_c$  phase in these sintered specimens. This coexistence was confirmed by their X-ray powder diffraction patterns.

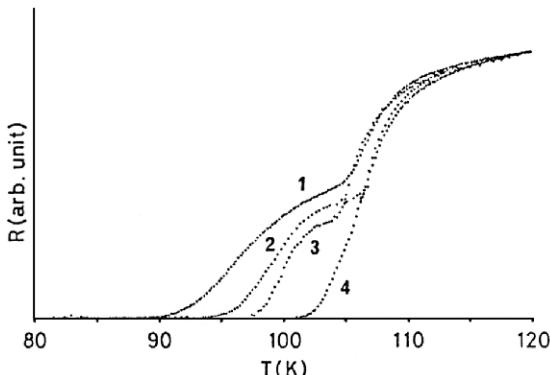
(b) The proportion of the high  $T_c$  phase increased with sintering temperature in the range of 790–830°C. This increase was significantly greater above 810°C (Fig. 14.1a), whereas the decomposition process of the high  $T_c$  phase was dominant at about 870°C (Fig. 14.1b).



**Fig. 14.1.** Sintering temperature dependence of the  $R$ - $T$  curves for specimens that were sintered at various temperatures for 30 h in a stream of Ar-O<sub>2</sub> gas of about 1 atm with an oxygen partial pressure of 1/13 atm: (a) (1) 790°C, (2) 800°C, (3) 810°C, (4) 820°C, (5) 830°C; (b) (1) 840°C, (2) 855°C, (3) 860°C, (4) 870°C. (From reference 2 by permission of *Jpn. J. Appl. Phys.*)

### Effects of sintering time

Figure 14.2 shows the  $R$ - $T$  curves for the specimens sintered at 840°C for various periods of time. The content of the high  $T_c$  phase increased with the sintering time, and single high  $T_c$  phase could be obtained after sintering for 100 h. This was also confirmed by the X-ray diffraction patterns. The  $T_{c(R=0)}$  for the low  $T_c$  phase gradually increased from 85 to 97 K with the sintering time (Fig. 14.2). Many authors have reported the values of  $T_{c(R=0)}$  for the low  $T_c$  phase to be 75–85 K [6–11]. But, some authors have reported that the values of  $T_{c(R=0)}$  were 87 K [12] and/or 92 K [13]. The reasons for the variety of  $T_{c(R=0)}$  values are not clear at present.

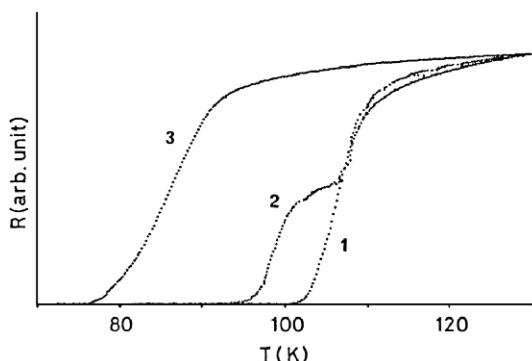


**Fig. 14.2.** Sintering time dependence of the  $R$ - $T$  curves for the specimens that were sintered at 840°C for various periods of time. (1) 1 h, (2) 30 h, (3) 48 h, (4) 100 h. (From reference 2 by permission of *Jpn. J. Appl. Phys.*)

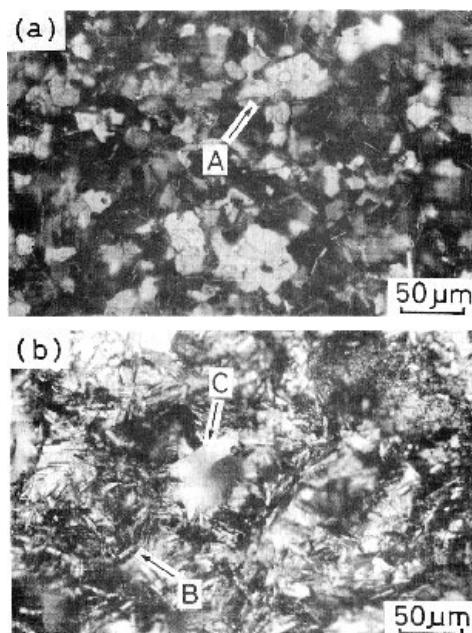
### Decomposition of the high $T_c$ phase

The decomposition process of the high  $T_c$  phase was studied by heating the single high  $T_c$  phase specimen, which had been prepared by the method mentioned above, at various temperatures for 1 h. The results are shown in Fig. 14.3. It was found that the low  $T_c$  phase starts to form as soon as the high  $T_c$  phase begins to decompose at around 870°C, and that most of the high  $T_c$  specimen was transformed into the low  $T_c$  phase around 880°C. Figures 14.4a and 14.4b show the grain structure on the surfaces of the sintered specimen of the single high  $T_c$  phase and its heat-treated structure at 880°C for 1 h, respectively. The heat-treated specimen was reduced in volume and a number of needlelike crystals were formed in addition to the low  $T_c$  phase, as shown in Fig. 14.4b. The composition of the needlelike crystal is shown in Fig. 14.5. This crystal was mainly composed of Ca and Cu. Figures 14.6a and 14.6b show the composition of the high  $T_c$  phase (before the heat treatment) and the low  $T_c$  phase (after the heat treatment), respectively. The content of Ca and Cu in the low  $T_c$  phase (Fig. 14.6b) was slightly poorer than in the high  $T_c$  phase (Fig. 14.6a). This shows that the high  $T_c$  phase incongruently melted and decomposed into the low  $T_c$  phase and liquid, and that the needle-like crystals were crystallized from the liquid in the cooling process.

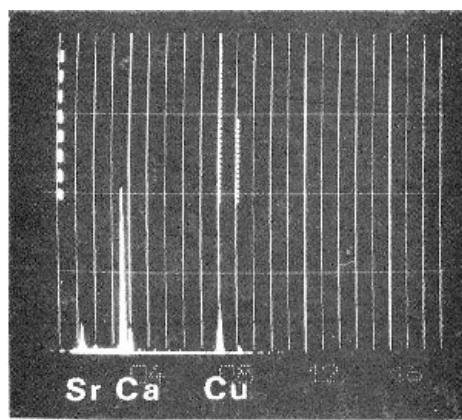
The above results are summarized as follows. (a) The low  $T_c$  phase was dominant at the early stage of the reaction at 840°C. The low  $T_c$  phase gradually transformed during sintering through a complicated reaction process [14] into the high  $T_c$  phase. These results were nearly the same as those reported by Hatano et al. [15] and Kim et al. [16]. (b) The values of  $T_c(0)$  in the low  $T_c$  phase varied from 80–97 K depending on the sintering conditions (Figs. 14.1–14.4). (c) The high  $T_c$  phase incongruently melted and decomposed into the low  $T_c$  phase and liquid around 870–880°C. Needlelike crystals formed from the liquid in the partially melted portion. These are very important results in terms of designing and improving the method of crystal growth.



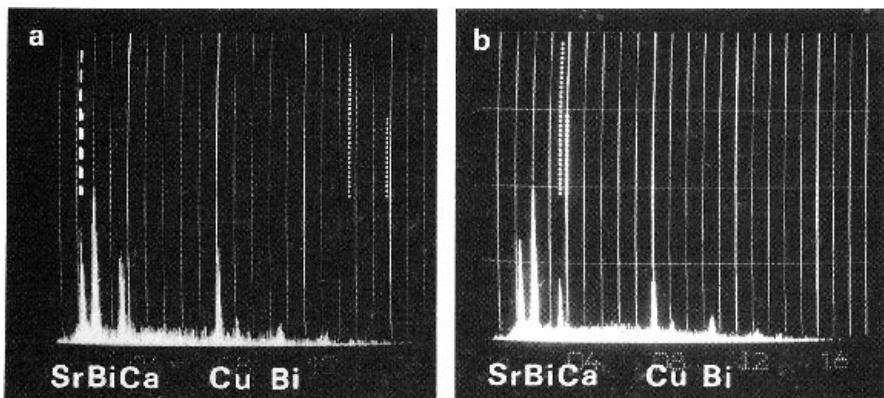
**Fig. 14.3.** Sintering temperature dependence of the  $R$ - $T$  curves for the single high  $T_c$  phase specimen. (1) the original high  $T_c$  phase specimen before heat treatment, (2) 870°C for 1 h, (3) 880°C for 1 h. (From reference 2 by permission of *Jpn. J. Appl. Phys.*)



**Fig. 14.4.** Photographs showing the decomposition of the single high  $T_c$  phase specimen by the heat treatment shown in Fig. 14.3 (3). (a) The surface structure of the original specimen of the single high  $T_c$  phase [before heat treatment, see Fig. 14.3 (1)]. A: high  $T_c$  platy crystals; (b) the surface structure after heat treatment at 880°C for 1 h [see Fig. 14.3 (3)]. B: Needle crystals that were crystallized from the partially melted portion, C: Low  $T_c$  platy crystals (optical reflection micrograph). (From reference 2 by permission of *Jpn. J. Appl. Phys.*)



**Fig. 14.5.** X-ray energy dispersive spectrum of the needle crystals in Fig. 14.4(b) (accelerated voltage: 15 kV). (From reference 2 by permission of *Jpn. J. Appl. Phys.*)



**Fig. 14.6.** Comparison of the composition of high  $T_c$  crystals with that of low  $T_c$  crystals using X-ray energy dispersive spectra. The X-ray system used 15 kV. a) High  $T_c$  (A in Fig. 14.4a); b) Low  $T_c$  (C in Fig. 14.4b). (From reference 2 by permission of *Jpn. J. Appl. Phys.*)

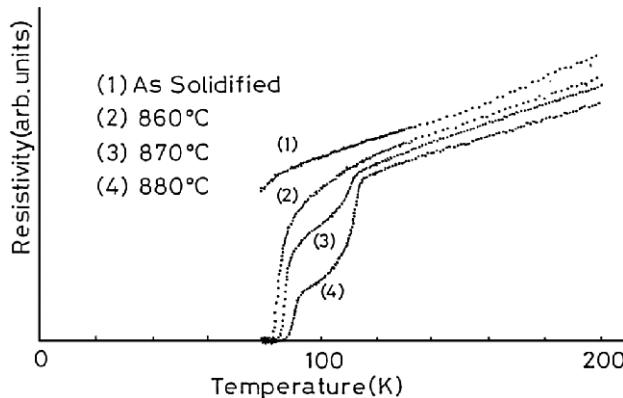
#### 14.2.2 Preparation of single crystals containing the high $T_c$ phase of a Bi-Sr-Ca-Cu-O superconductor

Ono et al. [17] synthesized a single crystal with  $T_c$  equal 105 K (0.5 mm  $\times$  0.5 mm) by sintering a pressed pellet with the cation ratio of Bi:Sr:Ca:Cu = 5:4:4:6 at 883°C in air for 24 hours. Strobel et al. [18] synthesized single crystals with  $T_c$  = 110 K (0.2 ~ 0.8 mm long) by sintering a pressed pellet of 2:1.5:2:3.4 at 846°C for 12 days in a reduced oxygen atmosphere ( $P(O_2)$  = 0.035 atm).

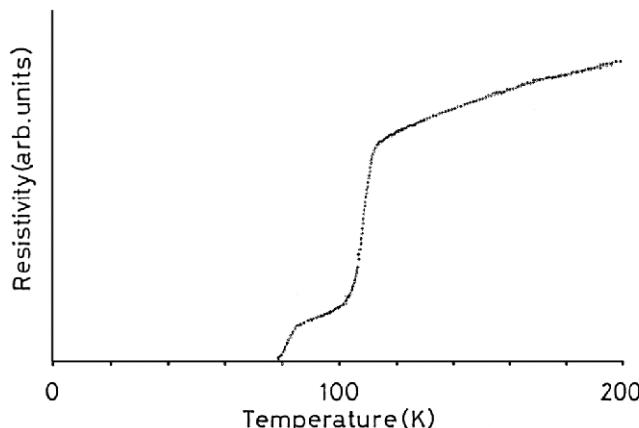
We grew single crystals with  $T_c(0)$  = 100 K by annealing solidified samples instead of pressed pellets, which were prepared by slowly cooling the melt of Bi:Sr:Ca:Cu = 4:3:3:4. Sizable single crystals could be more easily obtained by our method than by sintering a pressed pellet. Tarascon et al. [19] first used the composition of 4:3:3:4 for synthesizing the low  $T_c$  phase (85 K).

The starting materials were  $Bi_2O_3$ ,  $CaCO_3$ ,  $SrCO_3$ , and  $CuO > 99.9\%$ . Powder with a cation ratio of Bi:Sr:Ca:Cu = 4:3:3:4 was prepared by grinding the above materials in an alumina mortar. The mixed powder was pressed into a pellet (30 mm $\phi$   $\times$  5 mmH) and calcined in air at 800°C for 20 ~ 30 hours. The calcined pellet was melted at 1050°C for 2 hours in an alumina crucible, 23 mm $\phi$   $\times$  34 mmH. The temperature was then lowered to 500°C at a rate of 10°C/h, and then the sample was furnace cooled to room temperature. The alumina crucible that contained the solidified sample was cut into several pieces by means of a diamond cutter. We will hereafter call the pieces of the solidified sample the bulk sample. The bulk samples were annealed to investigate the effects of annealing upon the formation of the high  $T_c$  (>100 K) phase. The annealing conditions were as follows: (1) temperatures: 860 ~ 880°C, (2) annealing times: 50 ~ 100 h, (3) atmosphere: air.

Platy crystals ( $\sim 1$  mm in length), which were embedded in the mother medium, were picked up after breaking the bulk samples. The superconducting properties were determined by both resistivity and magnetization measurements. Resistivity was measured using a standard four-probe technique. The low-field d.c. magnetization measurement was performed using a semiconducting quantum interference device (SQUID) magnetometer. The phases formed were identified using either X-ray powder diffraction measurements or  $15^\circ$  oscillation photographs of single crystals.



**Fig. 14.7.** Annealing temperature dependence of the  $R$ - $T$  curves for the bulk samples that were prepared by slowly cooling the melt of  $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 4:3:3:4$ . The samples were annealed at  $860\text{--}870^\circ\text{C}$  in air for 50 h. (From reference 3 by permission of *Jpn. J. Appl. Phys.*)

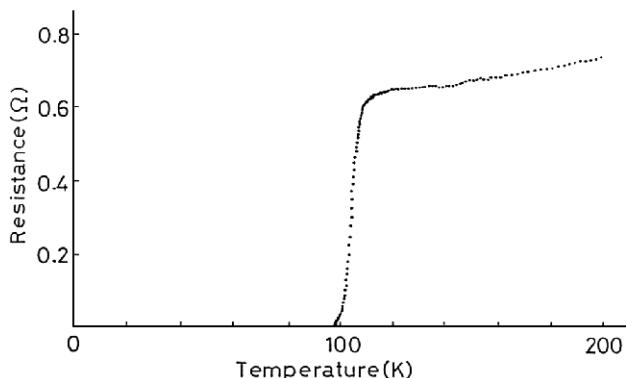


**Fig. 14.8.** Resistivity-temperature curve in the bulk sample that was annealed at  $870^\circ\text{C}$  for 100 h in air. (From reference 3 by permission of *Jpn. J. Appl. Phys.*)

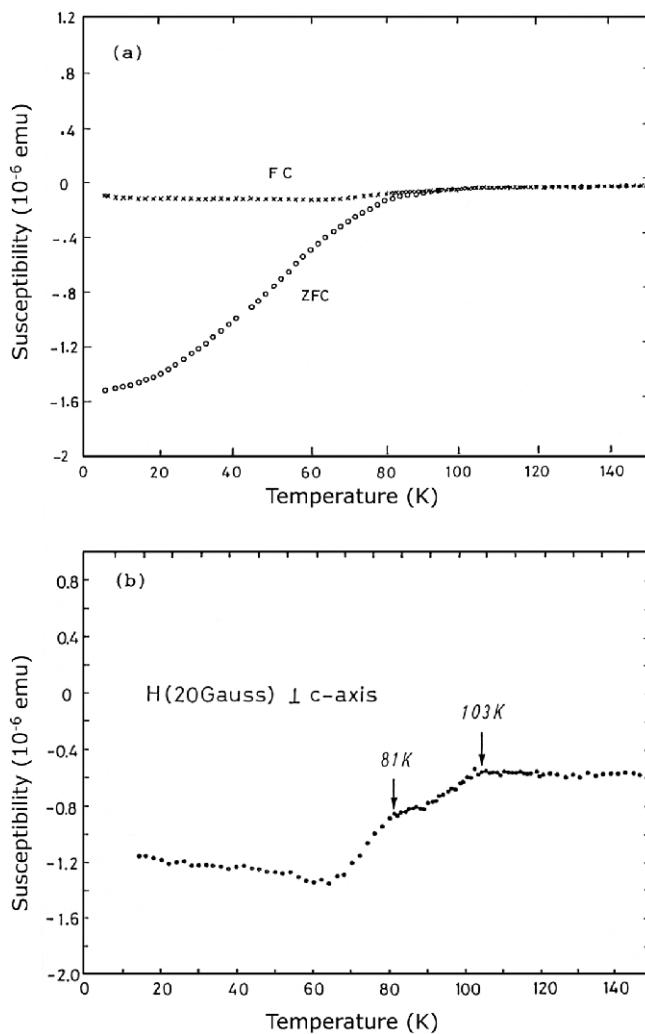
Figure 14.7 shows the resistivity  $R$  versus temperature  $T$  curves for the bulk samples before [as solidified, (1) in Fig. 14.7] and after [(2)–(4) in Fig. 14.7] annealing at various temperatures for 50 hours. The X-ray powder diffraction measurement on the sample before annealing [(1) in Fig. 14.1] showed the coexistence of the low  $T_c$  phase and the 24 Å ( $x = 1$ ) superconducting phase in equal amounts, but no high  $T_c$  phase was found in the sample. The major phase in the annealed samples [(2)–(4) in Fig. 14.7] was the low  $T_c$  phase. It was found from Fig. 14.7 that the fraction of high  $T_c$  phase ( $T_c > 100$  K) increased with the annealing temperature, especially above 870°C. The samples annealed above 870°C were partly molten and showed rounded edges. To investigate the effect of the annealing time upon the formation of the high  $T_c$  phase, the samples were annealed for a much longer time, 100 hours at 870°C and 880°C in air, respectively. The sample annealed at 880°C for 100 hours was mostly melted, and the high  $T_c$  phase could not be detected. A good result was obtained in the sample annealed at 870°C for 100 hours in air, as shown in Fig. 14.8; that is, the fraction of high  $T_c$  phase was larger than that in the case for the 50-h annealing time [compare the  $R$ - $T$  curve in Fig. 14.8 with (3) in Fig. 14.7].

Resistivities were measured on several single crystals ( $0.5 \times 0.7 \times 0.05$  mm<sup>3</sup>) that were picked up from the broken pieces of the sample annealed at 870°C for 100 h. A few single crystals showed  $T_{c(R=0)} = 100$  K, although most crystals showed two distinct superconducting transitions at  $T_{c1} = 110$  K and  $T_{c2} = 85$  K, respectively. A typical  $R$ - $T$  curve for a high  $T_c$  single crystal ( $T_{c(R=0)} = 100$  K) is shown in Fig. 14.9.

To ensure that the single crystals showing high  $T_c$  are bulk superconductors, we measured magnetization with a SQUID magnetometer. The measurements were done on the single crystals used in the resistivity measurement in Fig. 14.9. The result is shown in Fig. 14.10. It was found from the figure that this crystal was



**Fig. 14.9.** Resistivity-temperature curve in the high  $T_c$  single crystal that was found in the bulk sample annealed at 870°C for 100 h in air. (From reference 3 by permission of *Jpn. J. Appl. Phys.*)



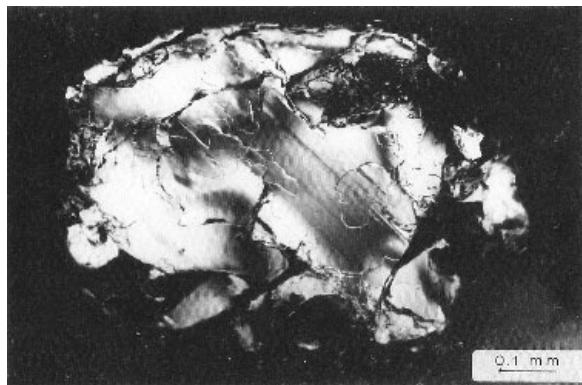
**Fig. 14.10.** Magnetization as a function of temperature for the high  $T_c$  single crystal in Fig. 9. (a) FC: cooling in a field of 20 Gauss, ZFC: cooling in a zero field. (b) This figure shows the same FC data as in (a) except for the units of the vertical axis. The vertical unit is changed from  $10^{-6}$  emu in (a) to  $10^{-7}$  emu in this figure. (From reference 3 by permission of *Jpn. J. Appl. Phys.*)

composed of high  $T_c$  ( $>100$  K) and low  $T_c$  ( $\sim 80$  K) phases with possible intergrowth. Because it was very difficult to estimate quantitatively the volume fraction of superconductive phase only from the magnetization data [20], the fraction of high  $T_c$  phase could not be estimated. A  $15^\circ$  oscillation photograph also showed the coexistence of high  $T_c$  and low  $T_c$  phases.

A surface microtopograph of single crystals showing  $T_{c(R=0)} = 100$  K in Fig. 14.9 is shown in Fig. 14.11, which was taken by a differential interference microscope. This photograph indicates that the crystal was grown by the layer-by-layer growth mechanism, which strongly suggests a solution growth mechanism.

The details of the formation mechanism of high  $T_c$  crystals are not clear at present. But the following two facts will be important in considering the formation mechanism: (1) the high  $T_c$  single crystals were grown in the bulk samples which were annealed at near their melting point and were partially molten, (2) the surface microtopograph of Fig. 14.11 shows a layer-by-layer growth pattern. These facts strongly suggest that the single crystals ( $T_{c(R=0)} = 100$  K) were grown from high-temperature solutions which were formed in the partially melted part, and that the composition and temperature ranges of the solution for the high  $T_c$  crystal growth were very narrow.

The above results were summarized as follows. High  $T_c$  ( $T_{c(R=0)} = 100$  K) single crystals were grown by annealing the bulk sample. This sample was prepared by slowly cooling the melt of Bi:Sr:Ca:Cu = 4:3:3:4, at 870°C for 100 hours in air. It was found from the SQUID magnetization measurement that these crystals were composed of a high  $T_c$  phase and a low  $T_c$  one with possible intergrowth.



**Fig. 14.11.** Photograph showing the surface microtopograph of the high  $T_c$  single crystal in Fig. 14.9. A differential interference micrograph was used. (From reference 3 by permission of *Jpn. J. Appl. Phys.*)

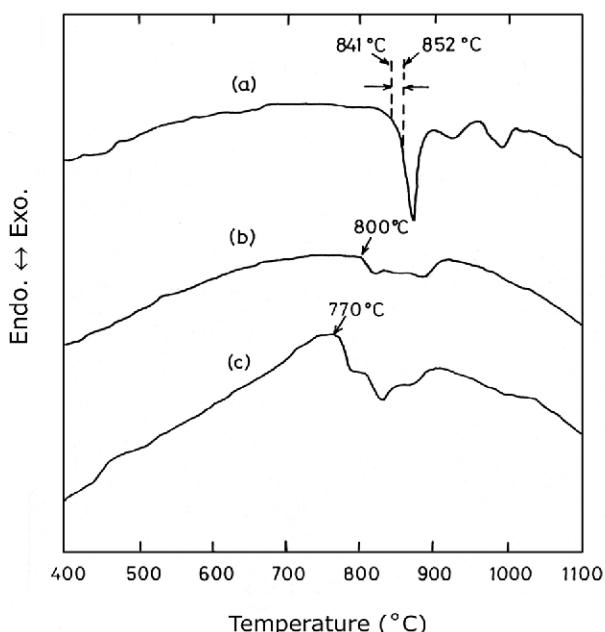
#### 14.2.3 Conversion of superconducting Bi-system single crystals from 2212 to 2223 by the annealing method

In the previous section [21], we reported the preparation of single crystals ( $T_{c(R=0)} = 100$  K) by annealing solidified samples containing 2212 single crystals. However, the fraction of 2223 phase was small in the annealed crystals. The purpose of this study is to re-examine the conversion of flux grown 2212 single crystals to 2223

crystals by the annealing method of Matsubara et al. [22], and thereby obtain a more complete understanding of the following points: (a) the dependency of 2223 formation upon the annealing temperatures, (b) the change of the surface microtopographs of the annealed crystals with increasing annealing temperatures, and (c) the change of the chemical compositions caused by annealing the crystals.

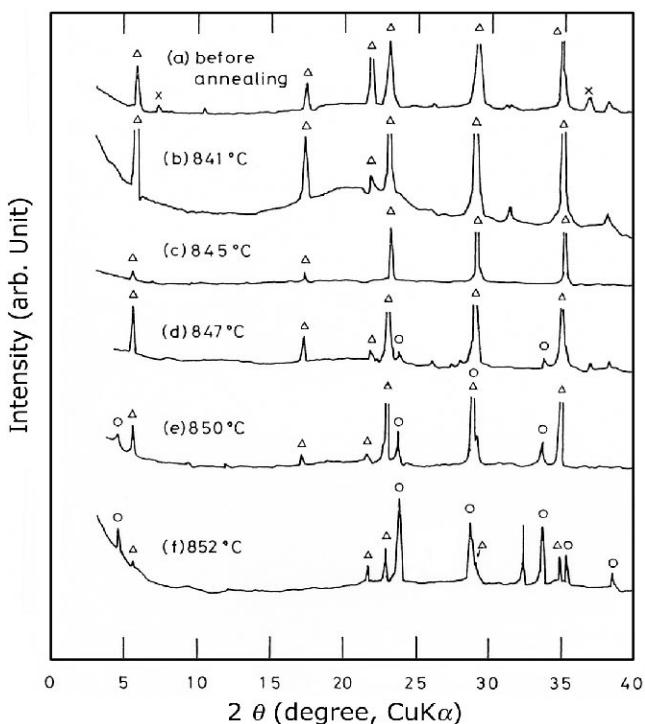
Two series of 2212 single crystals for the annealing experiments were grown from melts A and B as follows. The A series crystals were grown from a melt of Bi:Sr:Ca:Cu = 3.3:2.2:2.7, whereas the B series crystals were grown from a melt of Bi:Sr:Ca:Cu = 2:1:1:2. The chemical compositions of the series A and B crystals were  $\text{Bi}_{2.4}\text{Sr}_{2.4}\text{Ca}_{1.6}\text{Cu}_{3.6}$  and  $\text{Bi}_{2.4}\text{Sr}_{2.2}\text{Ca}_{1.8}\text{Cu}_{3.6}$ , respectively (EDX). The atomic ratio of Ca/Sr for the B crystals was slightly higher than that for the A crystals.

The 2212 single crystals thus obtained (2 mm × 2–3 mm) were buried in a powder with the composition of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1.6}\text{Cu}_{3.6}$ , which had been calcined at 820°C for 20 h. The powder containing the 2212 single crystals was annealed at 841, 843, 845, 847, 850, and 852°C for 150 h in air, respectively. The annealing temperatures were measured by the Pt/Pt-Rh (13%) thermocouple, which was directly put into the powder. The homogeneity of the temperature was within  $\pm 0.5^\circ\text{C}$  in the powder.

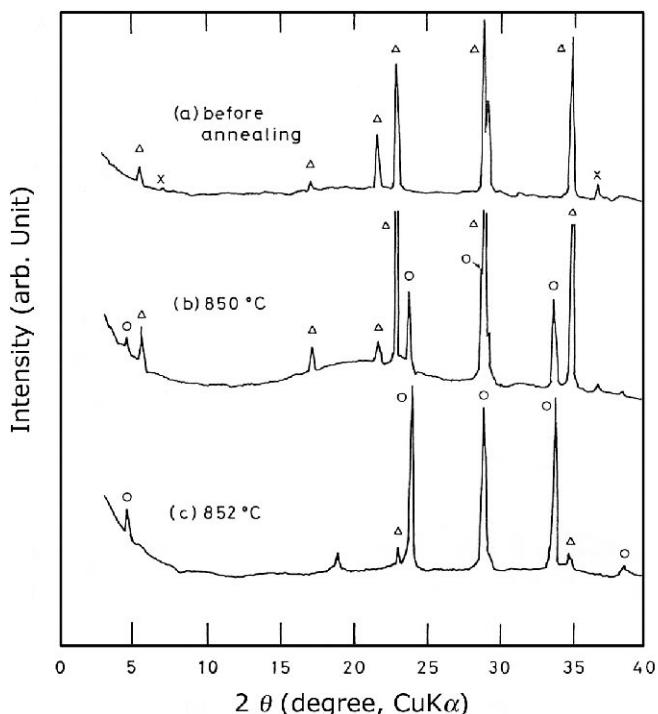


**Fig. 14.12.** DTA heating curves for (a) the calcined powder of  $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_y$ , (b) the series A crystals, and (c) the series B crystals before annealing experiments (heating rate; 10°C/min). Arrows indicate the range of annealing temperatures used in this study (841–852°C). (From reference 4 by permission of *Jpn. J. Appl. Phys.*)

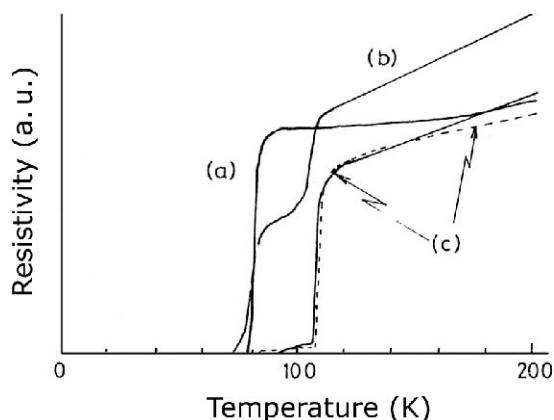
The following was found from the DTA curves in Fig. 14.12: (1) the partial melting of the calcined powder started around 840°C. (2) Some structural change occurred around 800°C in the series A and 770°C in the series B crystals, respectively. (3) The range of annealing temperatures (841~852°C) that were employed in this experiment is marked by arrows on the DTA curve for the powder. These annealing temperatures existed in the partial melting range of the powder. The dependency of the phase conversion from 2212 to 2223 upon the annealing temperatures is shown in Fig. 14.13 (series A crystals) and Fig. 14.14 (series B crystals), respectively. These figures indicate the following: (1) The conversion from 2212 to 2223 is very sensitive to the annealing temperature, that is, the temperature range of the formation of 2223 was probably within 2°C. (2) The best temperature for the conversion was 852°C. (3) The fraction of 2223 phase in the series B crystals, which were annealed at 852°C for 150 h, was a little higher than that in the series A crystals. (Compare Fig. 14.13f with Fig. 14.14c.) If the annealing temperature was raised above 852°C, the single crystals could not be separated



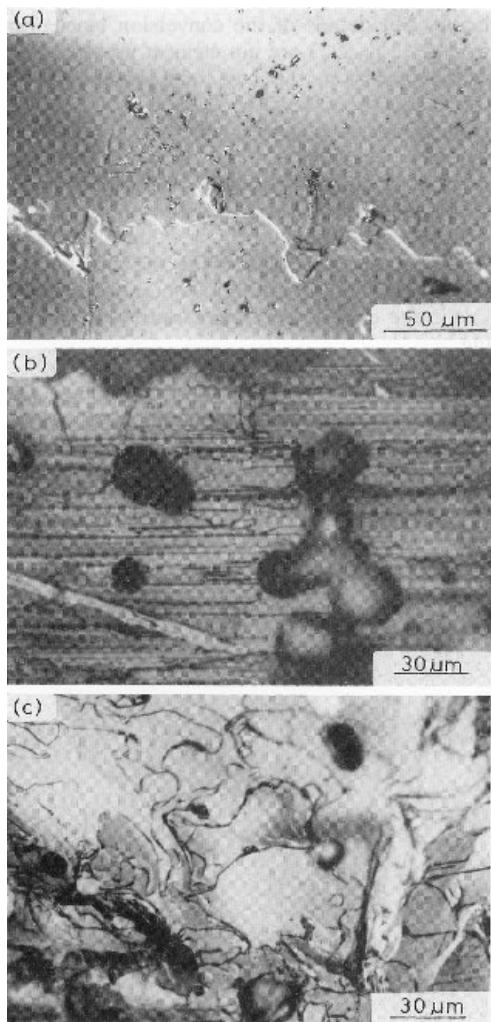
**Fig. 14.13.** X-ray diffraction patterns for the series A single crystals before (a) and after annealing in the calcined  $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_y$  powder at (b) 841°C, (c) 845°C, (d) 847°C, (e) 850°C, and (f) 852°C for 150 h in air. ( $\times$ ) 2201; ( $\Delta$ ) 2212; ( $\circ$ ) 2223. (From reference 4 by permission of *Jpn. J. Appl. Phys.*)



**Fig. 14.14.** X-ray diffraction patterns for the series B single crystals (a) before and (b, c) after annealing in the calcined powder at (b) 850°C and (c) 852°C for 150 h in air. (×) 2201; ( $\Delta$ ) 2212; ( $\Upsilon$ ) 2223. (From reference 4 by permission of *Jpn. J. Appl. Phys.*)



**Fig. 14.15.** Annealing temperature dependence of the  $R$ - $T$  curves for the series A crystals (a) before and (b, c) after annealing at (b) 841°C and (c) 852°C. (From reference 4 by permission of *Jpn. J. Appl. Phys.*)



**Fig. 14.16.** Photographs showing the surface microtopographs of the series B crystals (a) before and (b, c) after annealing at (b) 850°C and (c) 852°C. (From reference 4 by permission of *Jpn. J. Appl. Phys.*)

from the partially melted powder because the molten portion of the powder increased. The resistivity  $R$  versus temperature  $T$  curves showing the annealing effects for the series A crystals are summarized in fig. 14.15. This figure shows that the major phase converted from 2212 to 2223 in the crystals after annealing at 852°C, although a small amount of 2212 phase was still left, which is consistent with the X-ray diffraction data. The  $R-T$  curves for the series B crystals after annealing at 852°C for 150 h were the same as those for the series A crystals.

Figure 14.16 shows the change of the surface microtopographs with increasing annealing temperatures for the series B crystals. The cleaved surface which was flat and smooth became rough and stepwise after annealing above 847°C for 150 h in air. In the temperature range of 847 to 850°C, a structure consisting of straight steps that ran parallel to each other formed (Fig. 14.16b). However, the step structure suddenly changed from the parallel pattern to the circular one at 852°C, as shown in Fig. 14.16c. The same results were obtained in the series A crystals. As already mentioned, the fraction of 2223 was largest in the crystals annealed at this temperature. Thus it was found that there was a strong correlation between the formation of 2223 and the surface microtopograph.

The chemical compositions of the crystals were quantitatively examined by the energy-dispersive X-ray (EDX) analyzer. The compositions (cation ratio) of the series B crystals changed from  $\text{Bi}_{2.4}\text{Sr}_{2.2}\text{Ca}_{1.8}\text{Cu}_{3.6}$  to  $\text{Bi}_{2.0}\text{Sr}_{2.0}\text{Ca}_{1.9}\text{Cu}_{4.2}$  by annealing at 852°C for 150 h in air. It was found that the contents of Cu and Ca (especially Cu) increased, whereas those of Bi and Sr decreased by the annealing.

The range of the annealing temperatures employed in this experiment was in the partial melting region of the calcined  $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_y$  powder, as shown in the DTA curve in fig. 14.12. The microtopographs of the annealed crystals strongly suggest the reaction of the 2212 crystals with the liquid. But details of the conversion mechanism from 2212 to 2223 are not clear.

In conclusion, the best temperature for the conversion from 2212 to 2223 was 852°C. The surface microtopographs of the crystals were strongly dependent on the annealing temperatures. The surface structure changed from the straight and parallel step structure to the circular structure at 852°C, and the fraction of 2223 was largest in the crystals showing the circular step structure. The Cu and Ca contents (especially Cu) in the crystals were increased by the annealing.

The above results are summarized as follows. The composition and temperature ranges of the solution for the high  $T_c$  crystal growth were very narrow. The formation temperatures of the high  $T_c$  crystals were slightly different depending on the chemical compositions. The high  $T_c$  crystals were formed by reactions of the low  $T_c$  crystals with the liquid, which formed in the partially melted region of calcined Bi-Sr-Ca-Cu-Pb-O.

### 14.3 Liquid Phase Epitaxial Growth of Low $T_c$ Phase of BSCCO

The epitaxial films of the Bi-based superconductors,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ : 2223 phase,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ : 2212 phase, and  $\text{Bi}_2\text{Sr}_2\text{CuO}_z$ : 2201 phase, have usually been grown from the vapor phase and sometimes from the liquid phase. Liquid phase epitaxy (LPE), however, seems to be a promising method for growing the films of an atomically flat surface in a wide area because the LPE growth can be done at a considerably lower supersaturation than that from the vapor phase [23]. For example, in the case of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (or  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ ) superconducting system, extremely flat surfaces of wide area have been grown by the LPE method [23,24].

**Table 14.1.** Crystallographic data of the Bi-based superconductors and the substrates used in this study. (From reference 29 by permission of *J. Crystal Growth*)

	Lattice spacing <sup>a</sup> [Å]			Crystal system <sup>b</sup>
	a	b	c	
2212 phase	~5.4	~5.4	~30.8	Orthorhombic
2201 phase	~5.4	~5.4	~24.6	Orthorhombic
SrTiO <sub>3</sub>	3.91	—	—	Cubic
LaAlO <sub>3</sub>	3.79	—	—	Cubic
NdGaO <sub>3</sub>	5.43	5.50	7.71	Orthorhombic

<sup>a</sup> At room temperature<sup>b</sup> At 840°C

So far, many reports have been published on the preparation of Bi-based superconducting films by the LPE method [25–27]. However, most of the reports were limited to a brief description of the characteristics of the films, and almost no attention was paid to the growth mechanism or the flatness of the films. We report here results of the characterization and some growth mechanisms of the Bi-based superconductors grown on three types of substrates by the LPE method using a KC1 flux. Most of this section previously appeared in our papers [28,29].

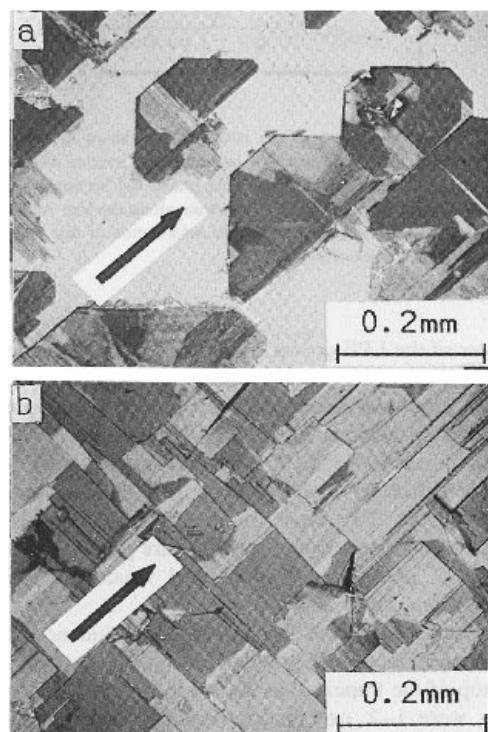
Well-reacted oxide powder having an atomic ratio of Bi:Sr:Ca:Cu = 2:2:1:2 was prepared from sintering powders of Bi<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub>, CaCO<sub>3</sub>, and CuO. The final reaction temperature was 850°C, and the total sintering time was 100 h. It was confirmed using the X-ray powder diffraction method that the sintered material was close to the 2212 single phase. This material was used as a nutrient in all experiments reported here.

The nutrient powder (5 g) was placed at the bottom of an alumina crucible (30 ml), and KC1 powder (20 g) was put on it as a flux [30,31]. These materials were heated at 925°C for 2 h. Then, the solution was cooled down to the growth temperature (840°C) in 30 min, and held at this temperature for 2 h. The substrate was fixed horizontally to the end of an alumina shaft, and dipped about 14 mm into the solution and rotated (20 rpm). Many experiments were conducted by varying the growth period and the substrate. At the end of each growth experiment, the substrate was pulled up about 10 mm above the liquid surface, and cooled to room temperature. Throughout the experiments, the upper part of the crucible was kept colder than the lower part to induce the natural convection and increase nutrient transport. SrTiO<sub>3</sub> (100), LaAlO<sub>3</sub> (100), and NdGaO<sub>3</sub> (001) were used as the substrates, whose crystallographic data together with the superconducting phases are shown in Table 14.1. The phase of each LPE-grown film was determined by X-ray diffraction (XRD). Back-reflection Laue photographs were taken to find out the crystallographic orientation of the film relative to the substrate [32]. The macroscopic surface morphology of the films was examined by polarizing light microscopy (PLM) and differential interference microscopy (DIM). The microscopic sur-

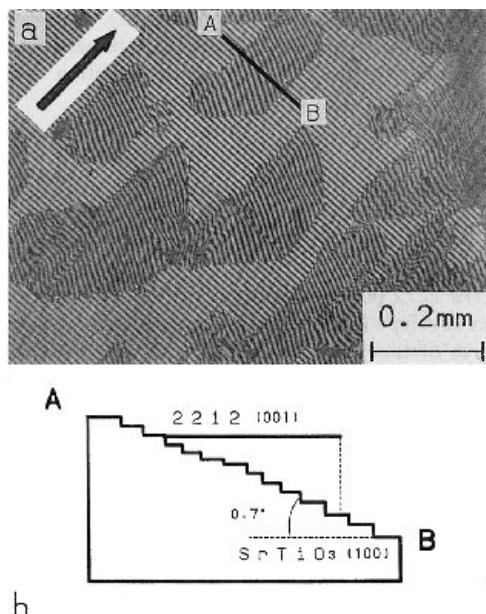
face morphology was observed by atomic force microscopy (AFM). Two-beam interferograms (TBI) were taken to measure the film thickness and the three-dimensional morphology of island layers. The temperature dependence of the electric resistivity was measured by an ordinary four-probe method to check the critical transition temperature of superconductivity ( $T_{c(R=0)}$ ), and the transition width ( $\Delta T_c$ ).

#### 14.3.1 SrTiO<sub>3</sub> (100) substrate [28]

The 2212 phase initially grew as island layers and then developed into a continuous single film in due course of time. Figure 14.17a and Fig. 14.17b are PLM photographs showing 2212 phase islands for the growth period of 10 h and a film grown continuously for 22 h, respectively. As is clear from the PLM photographs, the film thus obtained had twin structures. The diameter of the LPE-grown single

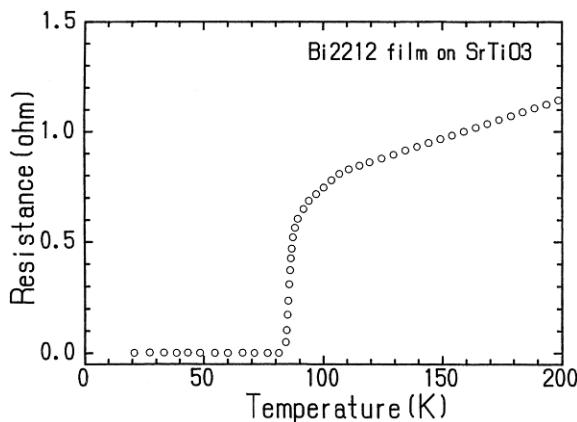


**Fig. 14.17.** PLM photographs (cross-nicols) of the 2212 phase on the SrTiO<sub>3</sub> (100) substrate. (a) Island layers grown in a period of 10 h, and (b) continuous film grown in a period of 22 h. The arrow indicates (011) of SrTiO<sub>3</sub> and [100] or [010] of the 2212 phase. (From reference 29 by permission of *J. Crystal Growth*)



**Fig. 14.18.** (a) Interferogram of the island layers shown in Fig. 14.1a (wavelength: 5470 Å). The arrow indicates the direction of either [100] or [010] with respect to the 2212 phase. (b) Sectional view of an island layer on the SrTiO<sub>3</sub> substrate along the line A-B in (a). The dashed line indicates that no information of that part is obtained from the interferogram. (From reference 29 by permission of *J. Crystal Growth*)

grains was estimated to be about 100 μm, which is larger than those grown from the vapor phase. The crystallographic relationship between the 2212 film and the SrTiO<sub>3</sub> substrate was (001)<sub>F</sub> || (100)<sub>S</sub>, [100]<sub>F</sub> or [010]<sub>F</sub> || {011}<sub>S</sub>, where suffixes F and S indicate film and substrate, respectively. Two types of orientation of the 2212 phase with respect to the substrate are possible since the 2212 phase has a modulated structure of Bi atoms along the *b*-axis [33]. It was found from the TBI that the thickness of the islands increased gradually from the bottom to the top of the trapezoid as shown in Fig. 14.18a. The topsides were 1–2 μm thicker than the bottom sides. This suggests that the substrate surface is a vicinal face that is inclined at an angle of a few tens of minutes from the exact (100) crystallographic plane. This was confirmed by a back reflection Laue photograph and XRD, which indicated that (001)<sub>F</sub> and (100)<sub>S</sub> are exactly parallel to each other. The schematic of Fig. 14.18b shows the geometrical relation of the LPE grown 2212 layer and the substrate. For this reason, when the 2212 island layers coalesced to form a continuous layer, a height difference of about 1 μm was formed. Thus the obtained film was not so flat from the microscopic point of view. Figure 14.19 shows a resistance curve as a function of temperature for the film grown for 20 hours. This film showed a superconducting transition with  $T_{c(R=0)} = 84$  K and  $\Delta T_c = 4$  K.



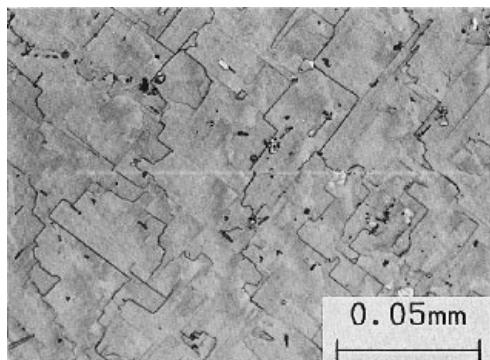
**Fig. 14.19.** Temperature vs resistance curve of the film grown for 20 hours. (From reference 28 by permission of the *Jpn. J. Appl. Phys.*)

### 14.3.2 LaAlO<sub>3</sub> (100) substrate

During the growth, numerous microcrystals of the 2212 phase were obtained in the solution. Then some of these microcrystals drifted with convection, and others formed a cloud in the lower part of the solution. When LaAlO<sub>3</sub> was used as a substrate, many microcrystals adhered randomly to the substrate and the film. However, the 2212 continuous film was grown only when the microcrystals coexisted in the solution. We checked this point repeatedly and arrived at a working hypothesis that the components of the 2212 phase were provided via the microcrystals, which might be a transient phase. The 2212 continuous film was composed of two types of domains whose *b*-axes were perpendicular to each other as in the case of the SrTiO<sub>3</sub> (100) substrate. In addition, this film had a similar morphology to the film grown on the SrTiO<sub>3</sub> (100) substrate. Its  $T_{c(R=0)}$  and  $\Delta T_c$  were 81 and 8 K, respectively.

Aiming at avoiding the adhesion of the microcrystals, we fixed the substrate to the rotating shaft vertically and rotated the substrate eccentrically. As a result, we could avoid the adhesion of the microcrystals, but the film had the 2201 phase. At present, we conjecture that the microcrystals have a significant role to supply solute to the growing film. If the growing film is kept far away from the microcrystals, the Ca atoms will be poorly supplied from the microcrystals because the solubility of Ca atoms in molten KC1 is very low. This is one reason why the 2201 phase formed instead of the 2212 phase. A DIM microphotograph of this film is shown in Fig. 14.20.

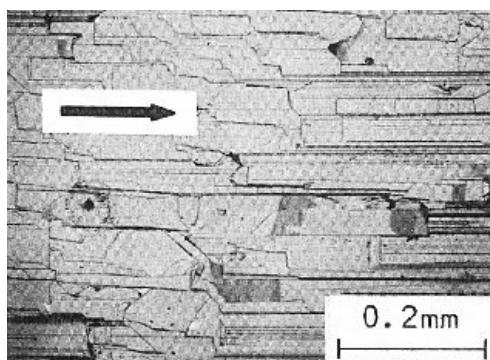
We also observed the microscopic flatness of this film by AFM, which showed flat terraces expanding up to several  $\mu\text{m}^2$ . This area is two orders of magnitude wider than the flat area of the films produced from the gas phase. The step height difference between the terraces was a few times that of the unit cell height (c-spacing) in the 2201 phase.



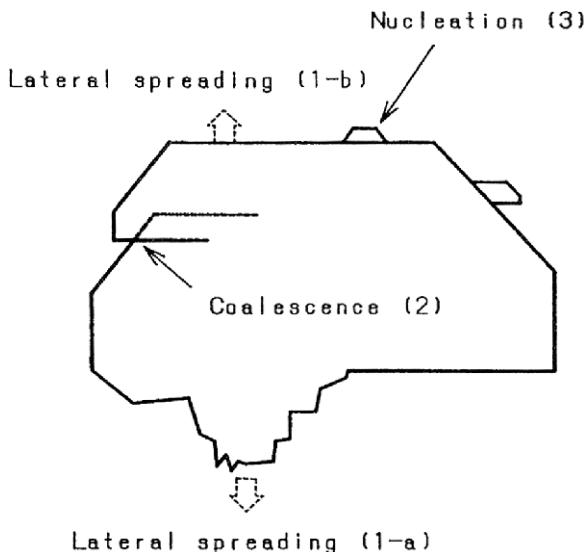
**Fig. 14.20.** Continuous film of the 2201 phase grown on the (100) face of the  $\text{LaAlO}_3$  substrate (DIM micrograph). The film thickness was about  $1 \mu\text{m}$ . (From reference 29 by permission of *J. Crystal Growth*)

### 14.3.3 $\text{NdGaO}_3$ (001) substrate

When  $\text{NdGaO}_3$  was used as a substrate, the adhesion of the microcrystals was remarkable as in the case of  $\text{LaAlO}_3$ . Figure 14.21 shows the surface of the 2212 phase film, which escaped from the adhesion of microcrystals. In contrast to the film grown on the  $\text{SrTiO}_3$  (100) substrate (Fig. 14.17b), this film shows a uniform tint except for a small area as shown in the PLM photograph (Fig. 14.21). This suggests that the film is nearly twin free, and we confirmed by a Laue photograph that the crystallographic  $a$ -axis of the film coincided with that of the substrate. The thickness of the film grown for 10 h was about  $1.5 \mu\text{m}$ , and there existed about a



**Fig. 14.21.** PLM photograph (cross-nicols) of a continuous film of the 2212 phase grown on the  $\text{NdGaO}_3$  (001) substrate in a period of 10 h. The arrow indicates [100] of  $\text{NdGaO}_3$  and [100] of the 2212 phase. (From reference 29 by permission of *J. Crystal Growth*)



**Fig. 14.22.** Schematic explanation of the enlarging processes of superconducting layers. (From reference 29 by permission of *J. Crystal Growth*)

0.5  $\mu\text{m}$  height difference among the grains. This film showed a superconducting transition with  $T_{c(R=0)} = 79$  K and  $\Delta T_c = 6$  K. However the resistivity exhibited an anomalous increase with decreasing temperature near the critical temperature, whereas a monotonous decrease was observed in the case of SrTiO<sub>3</sub> and LaAlO<sub>3</sub>. Furthermore, the resistivity at room temperature was one order of magnitude larger ( $\sim 20$  m $\Omega \cdot \text{cm}$ ) than that of the 2212 films grown on the other substrates ( $\sim 1$  m $\Omega \cdot \text{cm}$ ). These differences might be caused by contaminants from the substrate as suggested by Balestrino et al. [27].

From the present observations, we propose three processes that increase the island size as follows. (1) Nucleation of the crystals at the interface between the substrate and the island as seen in Fig. 14.17a. (2a) Lateral spreading toward the A direction in Fig. 14.18b. (2b) Lateral spreading toward the B direction. (3) Coalescence of the islands as a result of spreading. A schematic drawing to explain these processes is shown in Fig. 14.22. In this study, the highest wettability between the substrate and the 2212 phase was observed when NdGaO<sub>3</sub> (001) was used, whereas SrTiO<sub>3</sub> (100) had the lowest wettability. This result is consistent with the misfit ratios of each substrate. There are two barriers that must be overcome to produce a film having a macroscopically flat surface. One is solved by avoiding the random adhesion of the microcrystals to the film. The key to solving this problem will lie in the control of the liquid flow by rotating the substrate as mentioned in the case of the LaAlO<sub>3</sub> (100) substrate. The other problem is solved by changing the growth mode from three-dimensional island growth to the layer-by-layer growth mode. Reducing the supersaturation might solve this problem. This opera-

tion will make the spacing among steps larger and, microscopically as well as macroscopically, a flat surface in a wider area will form [23]. However, we presume that the wettability between the substrate and the solution and/or that between the solution and the film is a more significant factor than the supersaturation, because layer-by-layer growth has been observed in the gas phase system even on the  $\text{SrTiO}_3$  (100) substrate, which has the largest misfit ratio ( $\sim 2.4\%$ ) among the substrates used in this study, and the supersaturation in the gas phase system is higher than that in the liquid phase system.

The above results are summarized as follows. LPE growth of Bi-based superconductors was carried out on three types of substrates. Three-dimensional island growth was observed, irrespective of the type of substrate. The enlarging processes of the island layers were suggested. Because a difference in height is created when the islands coalesce to form continuous films on the vicinal surface, macroscopic flatness of the films was not attained in this study. However, reasonably flat surfaces which have an area of about  $1 \mu\text{m}^2$ , were confirmed to exist in the 2201 film grown on the  $\text{LaAlO}_3$  (100) substrate. This shows the possibility of obtaining an atomically flat and large terrace of Bi-based superconductors by the LPE method. It was shown that the  $\text{NdGaO}_3$ (001) substrate, which belongs to the orthorhombic crystal system, is effective in suppressing the formation of twins in the 2212 phase.

#### 14.4 Construction of Phase Diagrams by *In Situ* Observation and Their Application to Crystal Growth of Oxide Superconductors

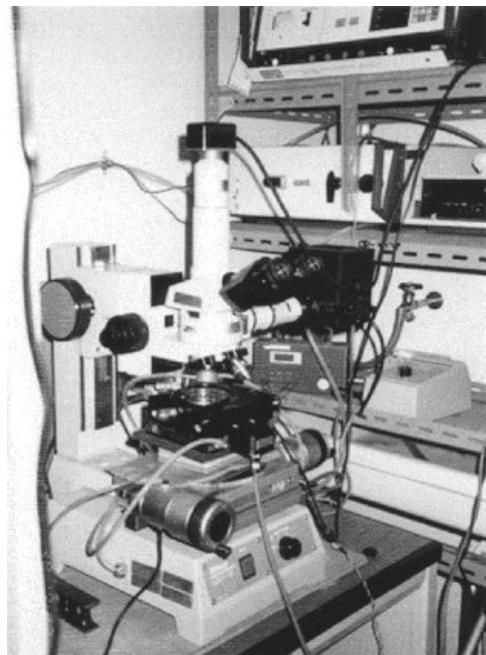
Growing single crystals without a phase diagram is just like making a voyage without a map. In crystallization from multicomponents systems, it is difficult to grow your target crystal as a single phase because there are many byproducts and the crystallization condition is complicated. Precise phase diagrams are therefore indispensable, especially for growing single crystals of incongruent-melt compounds by the traveling solvent floating zone method, the top-seeded solution growth method, the liquid phase epitaxy method, and other methods. The most important information for single crystallization is the condition in which your target crystal can crystallize from solution without any other solid phases. On the phase diagram, this is the liquidus line. From the liquidus line, we can evaluate the solubility and the driving force for crystallization. This driving force is the supersaturation.

Oxide superconductors are composed from many elements and their crystal structures are complicated. They incongruently melt when they are heated. To construct phase diagrams for these materials, it is difficult for us to precisely follow when the liquid-solid reaction process occurs by ordinary thermal analysis such as DTA. This is because such analysis needs a large heating or cooling rate to obtain large enough signals. Thus, techniques suitable for growth at very slow rates are needed. High-temperature microscopy is one such candidate. *In situ* ob-

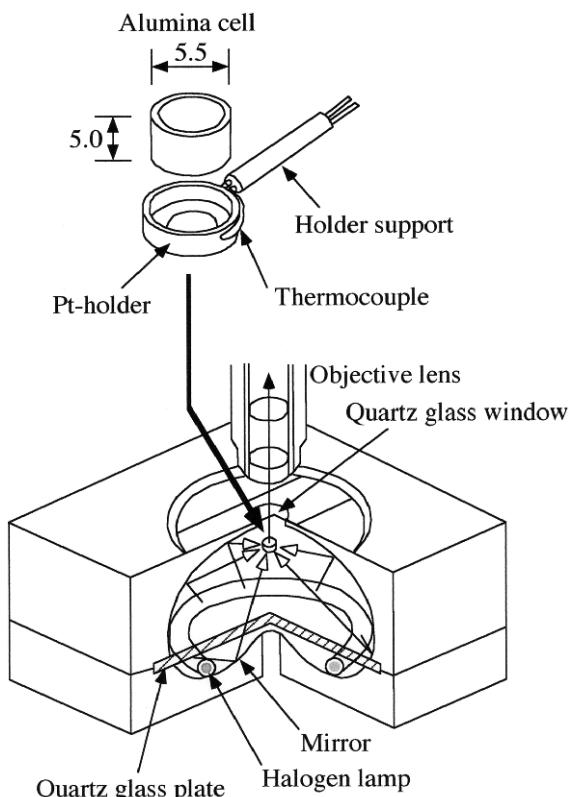
servations are convincing because seeing is believing. Using high-temperature optical microscopy, we observed crystallization and dissolution processes of oxide superconductor systems to make their phase diagrams. Here, we introduce this method and some results [34]. The main merits of this are that we can slow down the heating or cooling rate to the extent that the system is approximately in equilibrium, which are approximately the same conditions for actual solution growth experiments; furthermore, we can directly observe the processes contributing to crystal growth and dissolution to recognize the order of the phase formation.

#### 14.4.1 Apparatus

The apparatus used was composed of a reflection type optical microscope (Nikon Optiphot) and an infrared heating furnace (Sinkuriko model MS-E1R). Figure 14.23 is a photograph of the apparatus and Fig. 14.24 shows an illustration of the furnace. The latter was composed of a gold-plated mirror housed in the chamber. The mirror shape was ellipsoidal; a halogen lamp was placed on one focus and the sample cell sat on a thermocouple at the other focus. This chamber could be sealed and we could make a vacuum condition or change the gas atmosphere in it. The cup-shaped sample cell was made from alumina with a diameter of 5.5 mm and



**Fig. 14.23.** Photograph of the observation system



**Fig. 14.24.** Schematic of the infrared heating furnace and the sample cell (Reprinted from [34(c)], with permission of Elsevier Science)

height of 5 mm. Long working distance objectives (larger than 11 mm, magnification 5 $\times$ , 10 $\times$ , and 20 $\times$ ) enabled us to observe the high-temperature growth through a chamber window. The image of the sample was monitored by a CCD camera and recorded by a time-lapse video recorder because crystallization of multicomponent system takes a long time. The time and sample temperature were also recorded on the VTR. In the chamber, the light emitted from the halogen lamp was focused to the sample cell and heated it up to 1200°C. The sample temperature was regulated by a PID controller. The monitored temperature was calibrated by the melting points of standard materials such as Bi<sub>2</sub>O<sub>3</sub> (824°C), LiF (848°C), PbO (886°C), silver (961°C), and gold (1064°C). The error in the temperature measurement was estimated to be within about  $\pm 1.5^\circ\text{C}$ .

The volume of the chamber was about 150 cm<sup>3</sup>, and it had gas inlet and outlet ports. The oxygen partial pressure in the chamber was controlled by adjusting the mixing ratio of oxygen and argon gases by mass-flow meters. The oxygen concentration was measured by an oxygen meter (Iijima model G-101) with a gal-

vanic cell-type sensor that was precise to 0.1%. The total flow rate of the gas mixture was about 100 cm<sup>3</sup>/min. The total pressure was kept at atmospheric pressure (0.1 MPa).

Samples were prepared as follows. The raw materials were prepared by mixing powders of oxides. They were calcined several times in air in the temperature range from 750 to 800°C for one day. A small amount of sample powder was put on a cleaved thin plate of an MgO single crystal, which was put on the bottom of an alumina sample cell in the chamber. The cell was heated by focusing the light of the halogen lamp. This allowed us to heat and cool the cell rapidly between room temperature and 1200°C because the thermal capacity of the cell was small. As temperature increased, the sample powder melted and formed a tiny droplet. For the solution of oxide superconductors, the wettability between the substrate and the sample droplet was poor: the contact angle was less than 90°. Then, the droplet was halted on the substrate. Below 1200°C, no reaction with the substrate and the droplet seemed to occur from the observation of the interface.

The merits of this method to construct phase diagrams are summarized as follows:

1. We can choose heating and cooling rates arbitrarily and observe the sample *in situ*. The time-lapse video recording enables us to visualize very slow changes for a long time period.
2. We can recognize the existence of the new phase in the image even though it is too tiny to be detected by thermal or X-ray analysis.
3. Intermediate phases can be recognized. In the peritectic reaction, as temperature decreases, an intermediate phase tentatively crystallizes by a small amount and dissolves again. We think this method is a unique way to detect such a phase.
4. If there are many phases in the texture, direct observation enables us to recognize the order of crystallization.
5. We can seal the furnace chamber. Then we can study the effect of oxygen partial pressure on crystallization.
6. Only a small amount of sample will suffice for fundamental studies because the process is magnified by optical microscopy.
7. The volume of the sample is small and the solution cannot escape from the droplet. Thus, the composition of the solution is kept constant and homogeneous.

The demerits are as follows: we can only observe the surface process of the droplet. To observe inside, the droplet should be transparent. We can measure the growth rate under various conditions, but we cannot adjust the crystal orientation in the droplet by hand and it is difficult to study growth rates along a required direction. We cannot remove the crystal from the solution.

Here we introduce two examples of the construction of a phase diagram of oxide superconductors [SmBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  and Bi<sub>2</sub>(Sr,Ca)<sub>x+1</sub>Cu<sub>x</sub>O<sub>y</sub> (3 > x > 0)] and their application to real growth experiments.

#### 14.4.2 Phase diagram of $\text{SmBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and its application

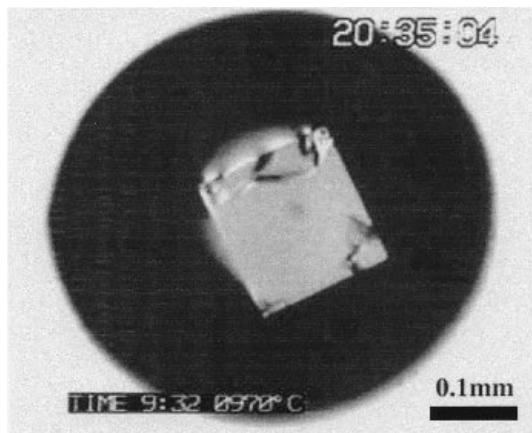
Here we describe how to determine the liquidus lines of oxide superconductor phases. The  $\text{Sm}_2\text{O}_3$ -BaO-CuO system is used as an example.  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (R is a rare earth element) is well known as a superconductor phase. Hereafter, we call it R123.

Phase diagrams of R123, especially Y123, have been widely made by thermal analysis and X-ray powder diffractometry after quenching, and using element analysis of the solution [35]. However, it was difficult to precisely determine the liquidus temperatures and compositions because only a small amount of R123 crystallizes from the solution. Furthermore, thermal analysis needs a large cooling and heating rate to obtain a clear signal. Meanwhile, *in situ* observation is a powerful technique to determine the phase diagram in such a system.

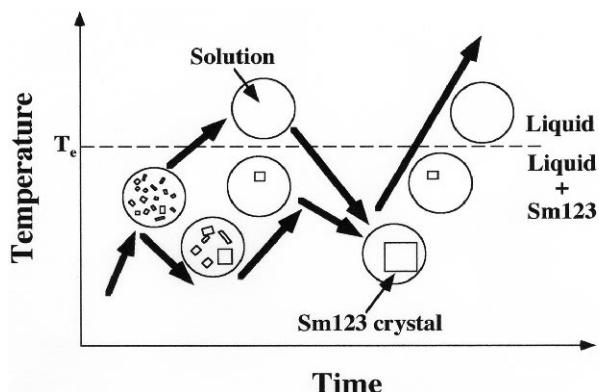
For the Sm123 system, the phase diagram at 950°C in the  $\text{Sm}_2\text{O}_3$ -BaO-CuO system made by the quenching method was reported, and the Sm123 phase is considered to crystallize in a triangle of Sm123-BaCuO<sub>2</sub>-CuO [36]. To determine precise liquidus lines, where primarily the Sm123 phase crystallizes, we made seven pseudo-binary phase diagrams in the region of Sm123-BaCuO<sub>2</sub>-CuO [37]. Here, we describe how to construct the phase diagram with this method by using the Sm123-“ $\text{Ba}_7\text{Cu}_{18}\text{O}_{25}$ ” pseudo-binary system as an example. The quotes are used because no such material exists. The liquidus lines should be, in principle, determined both by the crystallizing temperature and the dissolution temperature obtained by *in situ* observation. However, the liquidus temperature determined by the crystallizing temperature is lower than that by the dissolution temperature because the nucleation needs a large supersaturation. In this study, we observed the dissolution process and determined the liquidus temperature.

The procedure used in this study is as follows. Sample powders of systematically selected compositions were first prepared. The composition was expressed as a molar percentage of Sm123 in  $\text{Ba}_7\text{Cu}_{18}\text{O}_{25}$  as a solvent where BaO:CuO = 7:18 was reported to be a eutectic point of the BaO-CuO system [38], and the dissolution temperature was expected to be lowest near this point. All experiments were carried out in air. The prepared sample was heated up to 950°C–1000°C and formed a mixture of tiny crystals and high temperature solution. At this temperature, we increased and decreased the temperature several times. In this procedure, the tiny crystals coalesced, and finally only one crystal remained in the solution (Fig. 14.25). We call this the self-seeding method. After only one crystal was formed, we slowly increased the temperature (1°C per 30 minutes) and finally, the crystal was completely dissolved. We measured this temperature and adopted it as the liquidus temperature. This process is shown in Fig. 14.26. To check that no crystals remained in the solution, we decreased the temperature by 5°C–10°C. If tiny crystals had remained in the solution, they would soon grow to an observable size because the supercooling of 10°C is too small for nucleation. Conversely, a lack of observed crystals indicated that no crystals remained.

As temperature was increased, needle  $\text{Sm}_2\text{BaCuO}_5$  crystals [39], hereafter we call Sm211, sometimes crystallized before the Sm123 crystal completely dissolved.



**Fig. 14.25.** Optical micrograph of the Sm123 crystal coexisting with the liquid in air [37]



**Fig. 14.26.** Diagram of the self-seeding technique and determination of the liquidus temperature [37]

When this occurred, a peritectic reaction [29] of  $\text{Sm123} \rightarrow \text{Sm211} + \text{liquid}$  occurred at this composition, and from this composition, we could not directly grow the Sm211 crystals. We also determined this partial melting temperature. We measured the temperature at which the Sm211 crystals first appeared four times. The average temperature was adopted as the partial melting temperature for this composition. Figure 14.27 shows a constructed pseudo-binary phase diagram. It shows that the Sm123 phase primarily crystallizes in the composition range from 5 mol% to 40 mol%. Above 45 mol% concentration, the peritectic reaction  $\text{Sm123} \rightarrow \text{Sm211} + \text{liquid}$  occurs, and the Sm123 crystals decompose at about 1060°C to form the Sm211 phase. The liquidus line of the Sm211 phase lies above 1080°C.

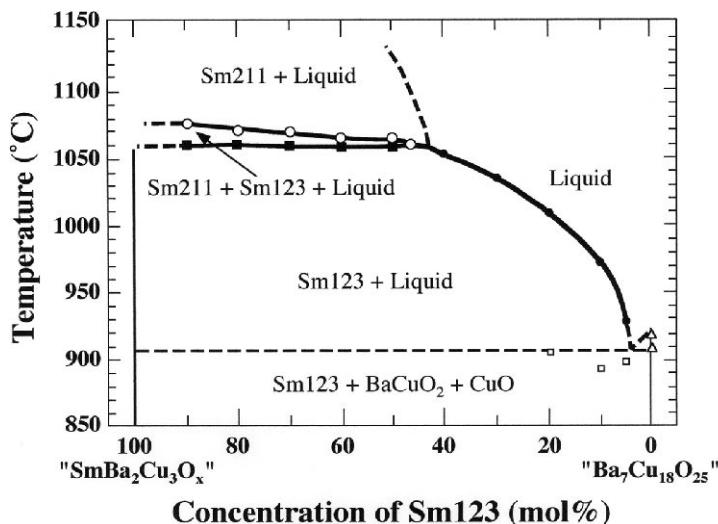
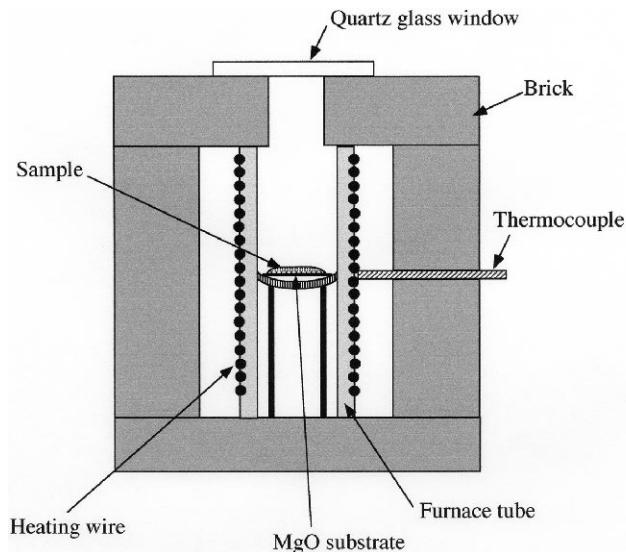


Fig. 14.27. Pseudo-binary phase diagram of the Sm123 system in air [37]

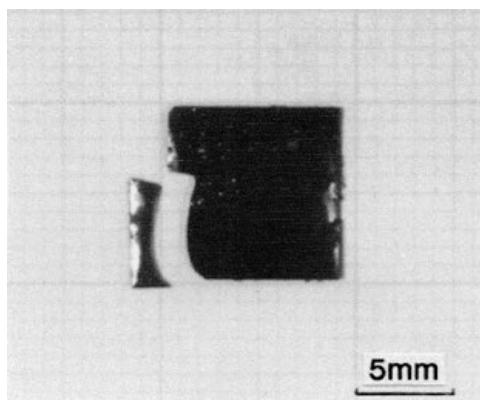
Three phases of Sm123, Sm211, and the liquid coexist in the composition range between 45 mol% and 90 mol%, and in the temperature range between 1060°C and 1080°C. As temperature increases in this region, the Sm123 crystal dissolves but the Sm211 grows. Conversely, as temperature decreases, the Sm211 dissolves and the Sm123 grows. These processes were directly observed.

A precise phase diagram enables us to calculate the supersaturation. Using the obtained phase diagram, we measured the dependence of the growth rate on supersaturation. Supersaturation was determined as follows. First, we let only one crystal remain in the solution in equilibrium; this temperature and solubility are denoted  $T_e$  and  $C_e(T_e)$ , respectively. In this state, the supersaturation is zero. We next increased the temperature to  $T$ , and the crystal dissolved by a certain amount. If the crystals remained in the solution after this operation and they were in equilibrium, the solubility of the solution could be expressed as  $C_e(T)$ . Then, we rapidly reduced the temperature to  $T_e$ . In this case, the supersaturation  $\sigma$  could be expressed as  $\sigma = [C_e(T) - C_e(T_e)]/C_e(T_e)$ . Under the microscope, we could measure the growth rate along the crystallographic *a*- and *c*-axis under various supersaturations. In this experiment, the composition of the sample was 35 mol% of Sm123 in the  $\text{Ba}_8\text{Cu}_{17}\text{O}_{25}$  solvent, and the growth temperature was kept constant at  $T_e = 1000^\circ\text{C}$ . Up to a supersaturation of 0.4, the growth rate along the *a*-axis gradually increased as the supersaturation increased. At the supersaturation of 0.4, it was about 12  $\mu\text{m}/\text{min}$ . Above 0.4, the growth rate rapidly increased with supersaturation. At the supersaturation of 0.7, it was about 70  $\mu\text{m}/\text{min}$ . On the other hand, the growth rate along the *c*-axis was one order of magnitude less than that along the *a*-axis, although it gradually increased with supersaturation. This growth rate anisotropy is probably caused by the strong anisotropy in crystal structure.

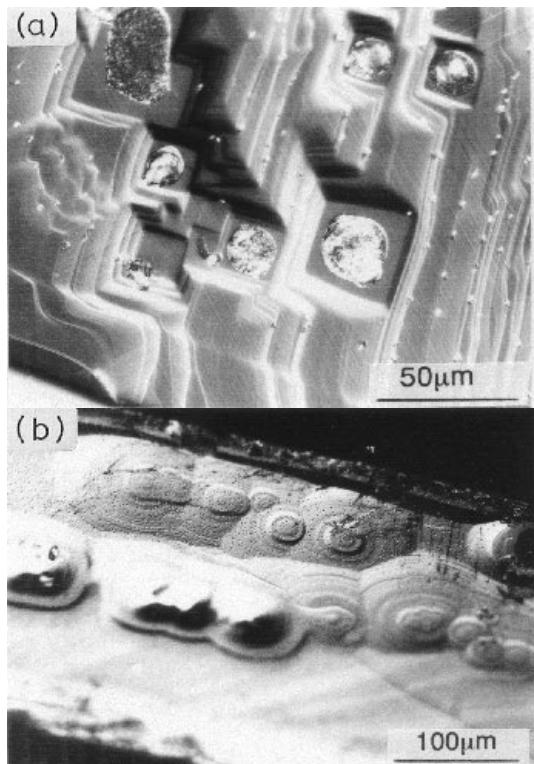
This method was also applied to study the effect of oxygen partial pressure on phase diagrams [41], to construct phase diagrams of other solvent compositions [42], to study the effect of rare earth elements [43], and to construct phase diagrams of other oxide systems [44]. This information was used to grow single crystals by the self-seeding method and by the traveling-solvent floating-zone method.



**Fig. 14.28.** Schematic of the furnace used to scale-up phenomenon under the microscope [37]



**Fig. 14.29.** Photograph of the Sm123 crystal grown by the self-seeding technique under the large furnace [37]



**Fig. 14.30.** Differential interference contrast optical micrograph of the as-grown Sm123 crystal [37]. (a) *c*-plane, (b) *a*-plane

The self-seeding growth technique mentioned above was achieved under the optical microscope in a droplet with diameter of several millimeters. This method, however, should be scaled up to obtain larger single crystals that are easier to handle. We then made a simple furnace, and tried to grow larger crystals using information obtained under the microscope. Figure 14.28 shows a schematic of this furnace. In principle, this system was similar to the high-temperature optical microscopy system except for the heating method. The size of the cleaved MgO plate was  $20 \times 20 \text{ mm}^2$  and the diameter of the sample droplet was about 15 mm. The temperature at the edge of the droplet was higher by  $3^\circ\text{C}$  than at the center. The composition of the sample was 40 mol% of Sm123 in the  $\text{Ba}_7\text{Cu}_{18}\text{O}_{25}$  solvent.

The procedure of the self-seeding method was just the same as that used under the microscope. When only one crystal remained in the solution, the temperature was decreased at a rate of  $1^\circ\text{C}/\text{h}$  to grow the crystal. We succeeded in obtaining a  $10 \times 10 \times 0.5 \text{ mm}^3$ -size single crystal, which showed that the phenomenon under the microscope could be scaled up. Figure 14.29 shows a photograph of the obtained crystal. Finally, the residual solution was sucked up into a porous alumina

rod, and then a sole crystal was obtained. The observed crystal surface was the  $c$ -plane. It is well known that oxide superconductors have strong anisotropy in growth rate between that in the  $c$ -plane and that along the  $c$ -axis. Figure 14.30a shows a differential interference contrast micrograph of the as-grown surface of the  $c$ -plane on the obtained crystal. Two-dimensional hillocks and many macro-steps were observed. The hillocks are rectangular with edges parallel to the  $a$ - and  $b$ -axes. Figure 14.30b is that of the  $a$ -plane. Round growth hillocks and fine steps are visible. The shapes of the hillocks were elliptic with major axis along the  $a$ -axis.

#### 14.4.3 Phase diagram of Bi-based oxide superconductors

Three types of Bi-based oxide superconductors,  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ ,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (the low  $T_c$  phase), and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (the high  $T_c$  phase) are known [45]. Their critical temperatures are 20, 80, and 110 K, respectively. Large single crystals of the low  $T_c$  phase have been grown from high temperature solutions using either the flux growth method or the traveling-solvent floating-zone method. But on the other hand, it has been difficult to grow the high  $T_c$  phase crystals even though this has the highest critical temperature and its application is expected. This phase is composed of five elements and is known as an incongruously melting compound. Therefore, it is difficult to recognize the phase relation at high temperatures. Especially, since it was not known whether this phase coexisted with the liquid phase. This information is essential to grow crystals from solution.

Shigematsu et al. [46] proposed a  $\text{Bi}_2(\text{Sr,Ca})\text{O}_4-(\text{Sr,Ca})\text{CuO}_2$  pseudo-binary phase diagram that had no liquidus coexisting with the high  $T_c$  phase. However, there were a few reports suggesting the possibility of growth of the high  $T_c$  phase from the liquid [47]. Thus, a reliable phase diagram is a key to growing single crystals of the high  $T_c$  phase. To determine whether or not the high  $T_c$  phase could be grown from solution, we studied the phase relation using high-temperature optical microscopy [34].

Samples were prepared as follows. The raw materials were prepared by mixing powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$ . Following the work of Shigematsu et al. [46], we chose their nominal composition  $\text{Bi}_2(\text{Sr,Ca})_{x+1}\text{Cu}_x\text{O}_y$  ( $3 > x > 0$ ). The samples were calcined in air in the temperature range from 750°C to 800°C for one day. These samples were then used for high-temperature optical microscopy.

We observed the crystal growth processes of  $\text{Bi}_2(\text{Sr,Ca})_{x+1}\text{Cu}_x\text{O}_y$  by slow cooling from high-temperature solutions with respect to the values of  $x$  of the starting material. The low  $T_c$  phase is  $x = 2$ , whereas the high  $T_c$  phase is  $x = 3$ . In the case of  $3 > x > 1.2$ , the first solids that appeared were needle crystals of  $(\text{Sr,Ca})\text{CuO}_2$  [48], and as the temperature decreased, thin plate crystals began to grow at 878°C.

In the case of  $1.2 > x > 0.9$ , the plate crystal of the low  $T_c$  phase appeared directly from the liquid. Another type of plate crystals of  $\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_6$  appeared directly from the liquid in the range of  $0.9 > x > 0.4$  and below 860°C. We could distinguish this crystal from other plate crystals by its striations. The low  $T_c$  crystal shows clear striations after crystallization was complete, whereas the crystal of

$\text{Bi}_2(\text{Sr,Ca})_2\text{CuO}_6$  has no striation. The striations are at an angle of 45° to the edges of the single crystal. The origin of this striation is not known.

In the case of the solution of  $x = 1.3$ , needle crystals and plate crystals (the first crystal) nucleated at the same time in the earlier stage of cooling. In the mean time, some of the plate crystals dissolved to form new crystals in spite of the cooling of the solution. The details of the processes observed under the microscope were as follows. After the growth of the first crystal (Fig. 14.31a), which kept its facet while dissolving (Fig. 14.31b), new thin plate crystals (the second crystals) formed at the expense of the first crystals at 865°C (Fig. 14.31c). When the furnace temperature reached 850°C, we quenched the sample and measured the electric resistance.

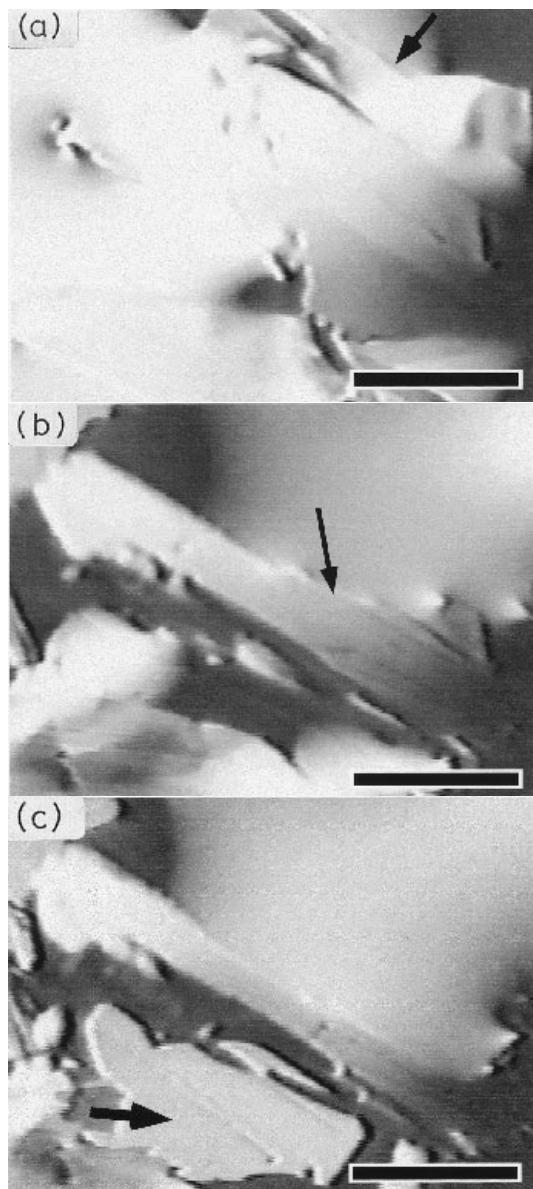
As the temperature decreased, the resistance began to decrease at about 110 K and it dropped to zero at 87–89 K as shown in Fig. 14.32a. We attributed the features of the resistivity curve to the oxygen deficiency [49] of the samples that were a mixture of the high and low  $T_c$  phases because of quenching. To supply oxygen, the samples were annealed under an oxygen atmosphere at 800°C for 24 h. We obtained the resistivity curve as shown in Fig. 14.32b. It clearly shows the existence of the high  $T_c$  phase. The analysis using an electron probe microanalyzer could not identify the high  $T_c$  phase because the thickness of the first crystal lying on other crystals was too small (5–10  $\mu\text{m}$ ) to identify the chemical composition.

Thus, growth experiments from high temperature solutions suggested the formation of the high  $T_c$  phase as a result of the peritectic reaction of the first crystals with the solution.

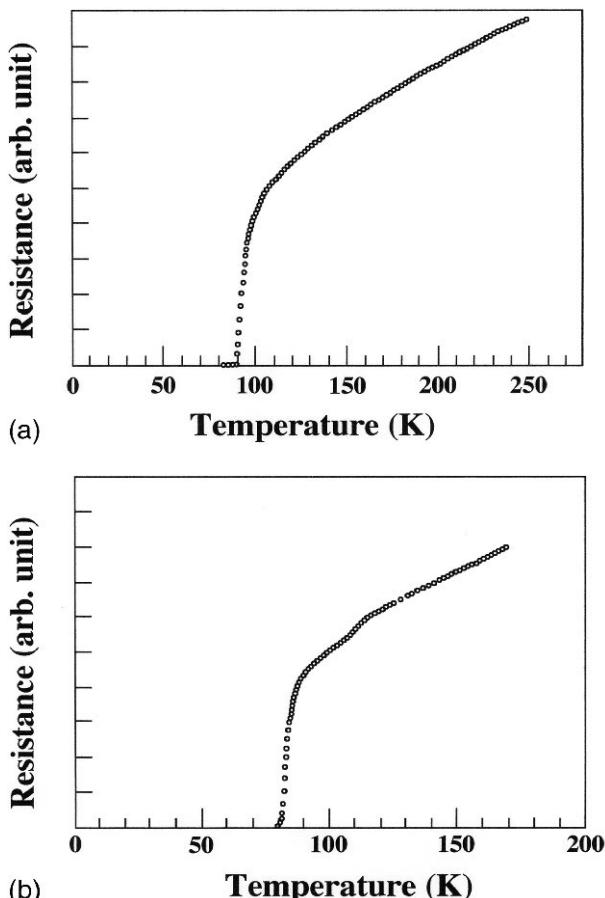
The partial melting of the low  $T_c$  phase was then examined. As the temperature increased, the low  $T_c$  phase single crystal began to decompose into liquid at 865°C. When we kept the sample at 870°C, needle crystals of  $(\text{Sr,Ca})\text{CuO}_2$  began to grow. Then, two kinds of solids (the needle and the low  $T_c$  phase) and a liquid coexisted for a while. Ten hours later, very thin plate crystals began to grow on the surface of the liquid and grew for 18 h. We quenched this sample and annealed it at 800°C for 24 h under an oxygen atmosphere. The resistivity of this sample is shown in Fig. 14.33, which clearly reveals the existence of the high  $T_c$  phase. This suggests that the thin plate crystal would be a crystal of the high  $T_c$  phase. But the size of this crystal was too small ( $100 \times 100 \times 2 \mu\text{m}^3$ ) to be identified by normal X-ray diffraction.

Following the results described above and our measurements of differential thermal analysis, we propose a modified phase diagram along the composition line of  $\text{Bi}_2(\text{Sr,Ca})_{x+1}\text{Cu}_x\text{O}$  as shown in Fig. 14.34, which indicates the possibility of obtaining high  $T_c$  phase single crystals from solution though the coexisting region of the high  $T_c$  phase and the liquid is narrow. This would explain why the high  $T_c$  phase was not detected by thermal analysis.

In order to confirm this phase diagram, we tried *in situ* observations of the partial melting of the low  $T_c$  phase because it was expected to decompose into the high  $T_c$  phase and the liquid according to the proposed pseudo-binary phase. The starting material consisted of the low  $T_c$  phase crystals obtained by slow cooling of the oxide flux of  $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 1.65:1:1:3.5$ . These crystals were heated in air at

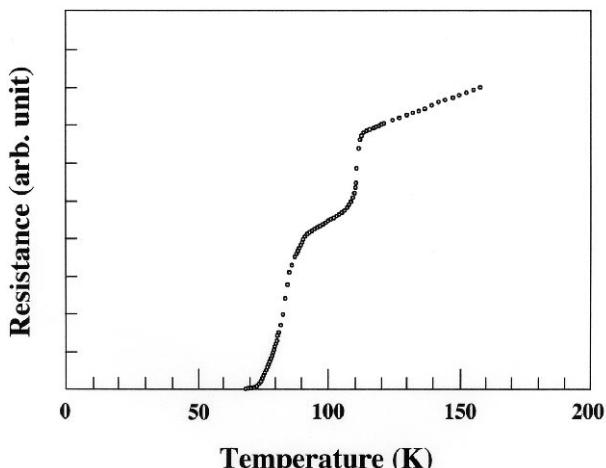


**Fig. 14.31.** Photographs of the plate crystals that appeared as the temperature decreased. The scale bar indicates  $100 \mu\text{m}$ . (a) The first crystals grown on the surface of a liquid (marked by an arrow) at  $865^\circ\text{C}$ . (b) The first crystals dissolved at  $860^\circ\text{C}$ . The solid-liquid boundary is marked by an arrow. (c) The second crystals (marked by an arrow) grew from the liquid at  $845^\circ\text{C}$ . (Reprinted from [34(a)], with permission of Elsevier Science)

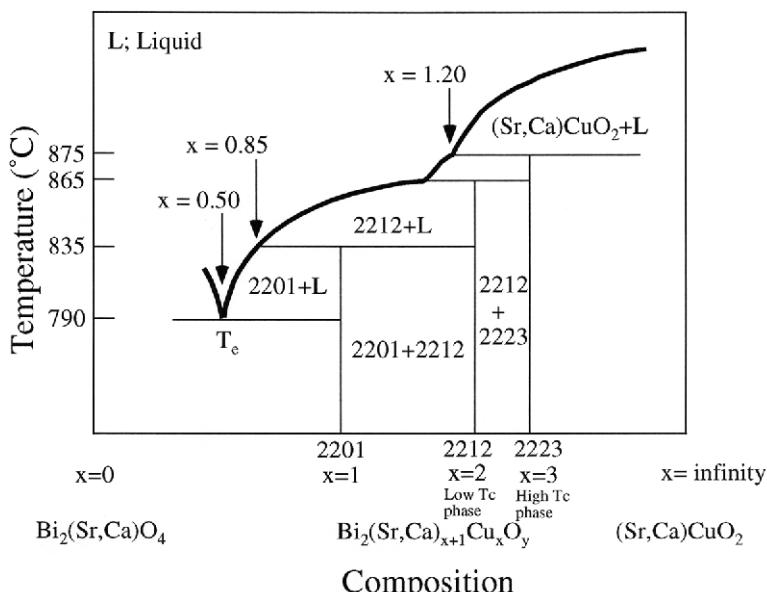


**Fig. 14.32.** Temperature dependence of the resistance of the sample grown from a high-temperature solution. a) As-grown sample. b) The sample annealed at 800°C in oxygen atmosphere for one day. (Reprinted from [34(a)], with permission of Elsevier Science)

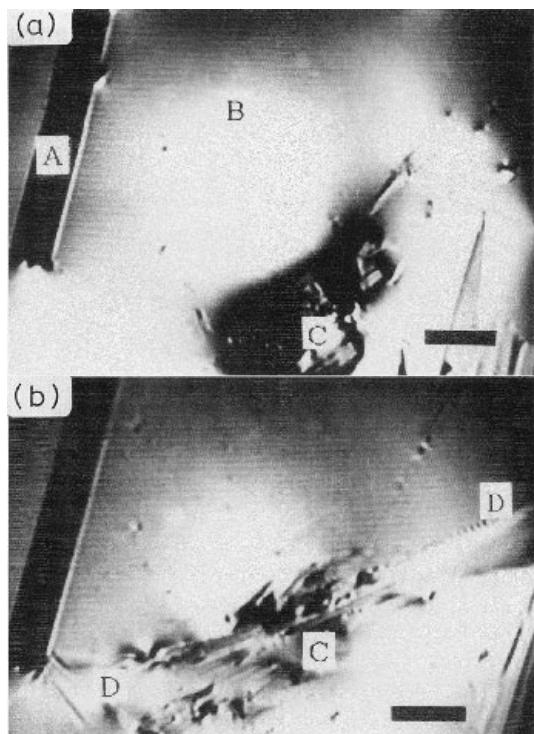
a rate of 3°C/min to find the partial melting temperature. At 860°C, small droplets began to emerge on the surface of the crystals [50]. These droplets grew large as the temperature increased. The crystals of the low  $T_c$  phase began to decompose into a viscous and opaque liquid at 865°C. When we kept the temperature of the sample at 870°C, needle crystals of  $(\text{Sr,Ca})\text{CuO}_2$  began to grow (Fig. 14.35a), then needle crystals, low  $T_c$  phase crystals, and a liquid coexisted for a while. The temperature was kept at 870°C for 10 h, after which it was noticed that very thin plate crystals began to grow on the liquid surface that grew for 20 h (Fig. 14.35b). The growth rate of these crystals was very small (80  $\mu\text{m}/\text{h}$ ). After keeping the temperature at 870°C for 50 h, we quenched them at a rate of 100°C/s. The rest of the solution quickly solidified and the surface of the droplet became wavy.



**Fig. 14.33.** Temperature dependence of the resistance of the sample annealed at 800°C in an oxygen atmosphere (Reprinted from [34(a)], with permission of Elsevier Science)

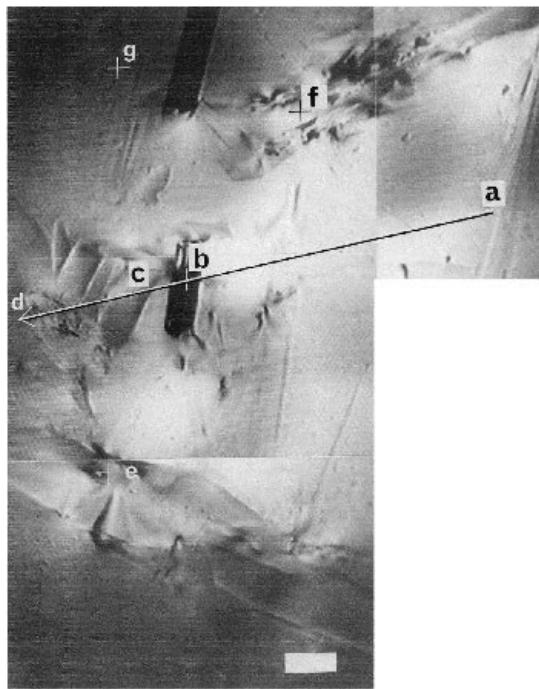


**Fig. 14.34.** The pseudo-binary phase diagram of  $\text{Bi}_2(\text{Sr,Ca})_{x+1}\text{Cu}_x\text{O}_y$  proposed after *in situ* observation.  $\text{Bi}_2(\text{Sr,Ca})\text{O}_4$  at  $x = 0$  and  $(\text{Sr,Ca})\text{CuO}_2$  at  $x = \infty$  (Reprinted from [34(a)], with permission of Elsevier Science)



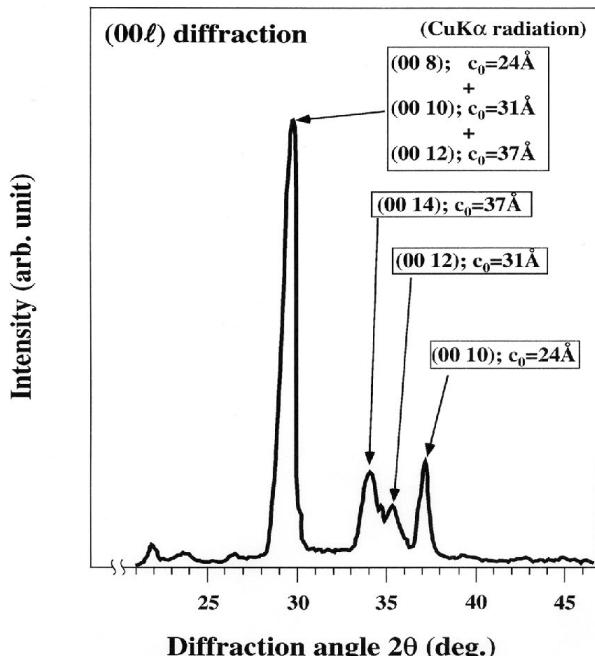
**Fig. 14.35.** Optical micrographs of the surface of the sample. Scale bars indicate 100  $\mu\text{m}$ . (a) After the temperature of the sample was kept at 870°C for 24 h. A: the needle crystal of (Sr,Ca)CuO<sub>2</sub>; B: surface of the liquid; C: crystals of the low  $T_c$  phase. (b) 18 h after (a). D: newly grown plate crystals. (Reprinted from [34(b)], with permission of Elsevier Science)

We then annealed them in oxygen flow at 800°C for 24 h to distinguish the high  $T_c$  phase from the low  $T_c$  phase. The annealing temperature was low enough and no phase change occurred. This sample showed electric resistance drops both at 110 K and 80 K, which clearly revealed the coexistence of the high  $T_c$  phase with the low  $T_c$  phase. It was assumed that the thin plate crystals grown after the partial melting were the high  $T_c$  phase. The size of these plate crystals was so small and thin ( $100 \times 100 \times 2 \mu\text{m}^3$ ) that we could not identify the high  $T_c$  phase by normal X-ray diffraction. Then we analyzed this thin crystal by micro-area X-ray diffractometry to identify a small area on the surface of the sample. The size of the incident beam was 50  $\mu\text{m}$  in diameter, and it struck the crystal surface at a low glancing angle. This crystal was grown after the partial melting. (See point c in Fig. 14.36, which is a micrograph of the surface of the sample.) The surface of this area was highly oriented and parallel to the  $c$ -planes of Bi-based oxide superconductors. The (001) X-ray profile obtained is shown in Fig. 14.37. Peaks attributed to the high  $T_c$  phase ( $c_0 = 3.7 \text{ nm}$ ) were found together with those of the other two superconducting phases.

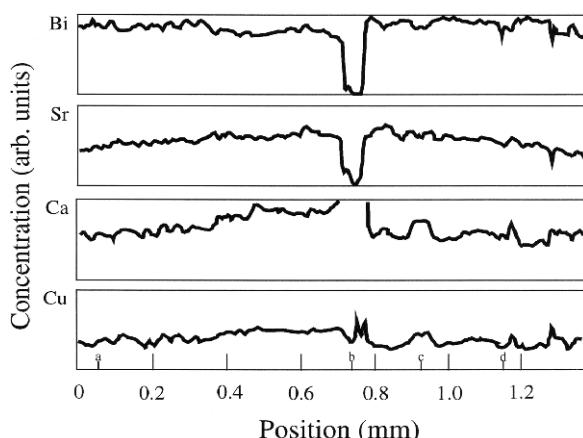


**Fig. 14.36.** Micrograph of the surface of the sample. The temperature of the sample was 870°C and had been kept constant for 18 h. The scale bar indicates 100  $\mu\text{m}$ . This sample was quenched 32 h later. After quenching, micro-area X-ray analysis was done at the point c (see Fig. 14.37). The concentration distribution of the cations measured along the line abcd are shown in Fig. 14.38. The ratios of cations measured at points c, e, f, and g are listed in Table 14.2. (Reprinted from [34(b)], with permission of Elsevier Science)

Thus, the existence of the high  $T_c$  phase was proved. EDX measurements with an acceleration voltage of 15 kV were also done to analyze the chemical composition of the sample. Distributions of concentrations of Bi, Sr, Ca, and Cu cations along line a-d in Fig. 14.36 are shown in Fig. 14.38. The sharp change at point b is attributed to the presence of the needle crystal of  $(\text{Sr,Ca})\text{CuO}_2$ . Bi concentrations varied with position and showed negative correlation with those of Ca and Cu. The concentrations of Ca and Cu at point c, where the high  $T_c$  phase was detected by the X-ray measurement, were larger than those in nearby regions. The ratios of cations at the points c, e, f, and g in Fig. 14.36 are listed in Table 14.2. In Fig. 14.36, there exist other thin plate crystals grown after partial melting at point e, and the low  $T_c$  phase crystals at point f. The liquid surface is revealed at point g. The ratio of cations at point c showed that this area was composed mainly of the low  $T_c$  phase although we found the high  $T_c$  phase by X-ray diffraction. Components of Sr, Ca, and Cu at points c and e, where thin crystals have been observed



**Fig. 14.37.** X-ray profile at the point c in Fig. 14.36 obtained by micro-area X-ray diffractometry. The size of the incident beam was 50  $\mu\text{m}$  in diameter. (Reprinted from [34(b)], with permission of Elsevier Science)



**Fig. 14.38.** Distributions of concentrations of Bi, Sr, Ca, and Cu cations along the line a-d in Fig. 36. EDX was used to obtain this result. A large variation at point b was attributed to the needle crystal of  $(\text{Sr,Ca})\text{CuO}_2$ . The high  $T_c$  phase was detected at point c by micro-area X-ray diffractometry. (Reprinted from [34(b)], with permission of Elsevier Science)

**Table 14.2.** Cation ratios obtained by EDX. They are normalized for bismuth content equal to 2.0. Points c, e, f, and g are indicated in Fig. 14.36

Points	Bi	Sr	Ca	Cu
c	2.00	1.21	1.37	2.03
e	2.00	1.10	1.67	2.34
f	2.00	0.97	1.01	1.73
g	2.00	0.72	0.71	0.91

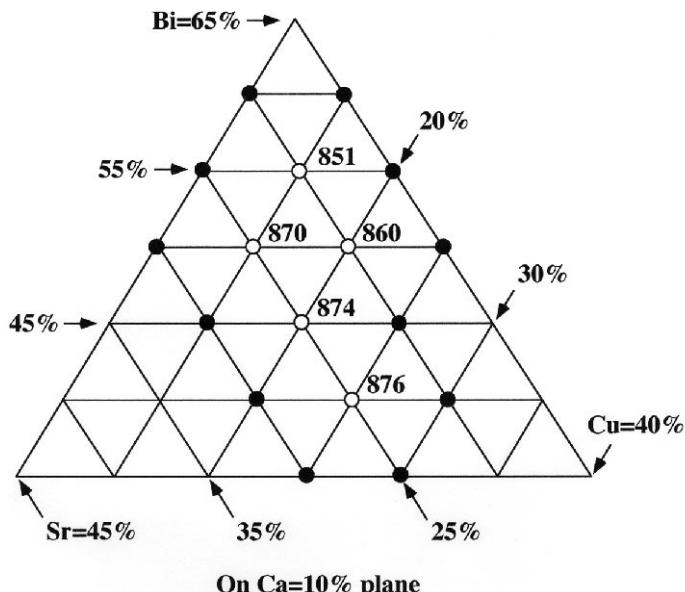
to grow, were larger than those at points f and g. The high  $T_c$  phase crystals were so thin that the EDX measured contributions from both the high  $T_c$  phase and the material beneath it (presumably, the low  $T_c$  phase).

We then heated the sample in Fig. 14.35 at a rate of 2°C/h. The high  $T_c$  phase crystals completely melted at 875°C. Up to this temperature, crystals of the low  $T_c$  phase had already melted, and only needle crystals of (Sr,Ca)CuO<sub>2</sub> and the liquid existed. This result showed that the high  $T_c$  phase and the liquid would coexist in the temperature range from 865°C to 875°C. Reprinted from [34(b)], with permission of Elsevier Science.

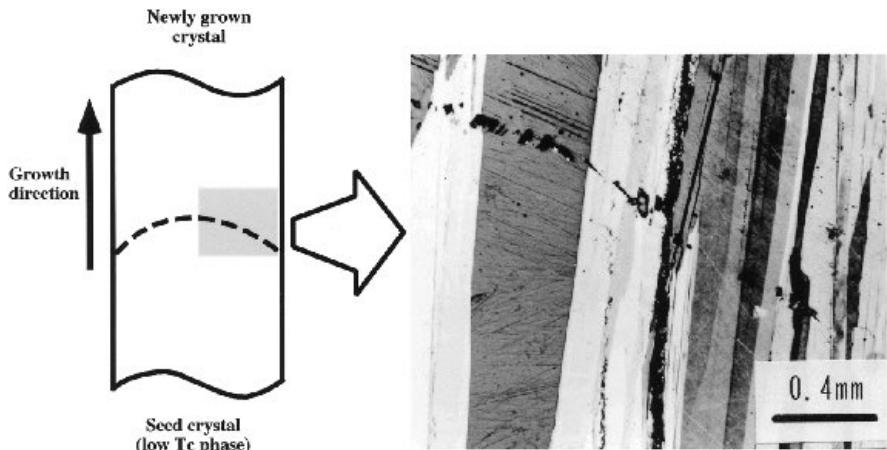
#### 14.4.4 Primary crystallization field of Bi-based oxide superconductors and its application

The composition in the phase diagram mentioned above represents the one along a line in a tetrahedron whose apices are BiO<sub>1.5</sub>, SrO, CaO, and CuO. In this tetrahedron, the composition in which primarily the superconductor phases grow (primary crystallization field) should be in regions having certain volumes. It would take, however, a long time to make many pseudo-binary phase diagrams to find the coexisting regions of the destiny phase and the liquid in this 4-dimensional space. In such a case, *in situ* high temperature optical microscopy is a powerful tool to find these regions. Here we introduce how to determine the primary crystallization field (PCF) by *in situ* observations of dissolution and crystallization over a wide composition range. The PCF consists of a part of the phase diagram and corresponds to the liquidus line in the binary phase diagram.

The procedure used here is similar to that for the Sm123 system mentioned above. The sample was heated up just before it changed to a uniform liquid. The remaining crystals were regarded as the primary crystal of that solution. The temperature that crystals of the superconductor phase completely dissolved was measured against the sample composition. Thus, the PCF was determined. In Fig. 14.39, the PCF was illustrated in the case of 10 mol% composition of Ca. Open circles indicate the composition belonging to the PCF of the superconductor phase. The dissolution temperatures are also labeled. Filled circles indicate that



**Fig. 14.39.** The PCF of the Bi-based oxide superconductors [51]. These crystals had a 10 mol% composition of Ca and were grown in air. Open circles indicate the composition belonging to PCF. The dissolution temperatures were written together. Filled circles indicate other phases remained.



**Fig. 14.40.** Optical micrograph of the section along the growth direction of the rod grown by the TSFZ method with the seed [51]. New crystals continued to grow from the seed crystals.

other phases remained. Similar results were obtained with 15 mol% of Ca composition. These results suggest that the composition belonging to the PCF of the superconductor phases lay in a long and narrow composition region where the composition of Sr + Ca is between 30 mol% and 35 mol%.

We applied the obtained PCF composition to the traveling-solvent floating-zone (TSFZ) method [52]. We prepared a seed crystal rod of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  by the TSFZ method using a sintered rod as a seed. Although this rod was polycrystalline, large single crystalline regions formed. A sintered rod whose composition belonged to the PCF was made and used as the solution part. These rods were used in the TSFZ growth experiments. As a result, newly grown crystals continued to grow from crystals in the seed keeping their crystallographic orientation without crystallizing other phases. Figure 14.40 shows an optical micrograph of a region near the interface of the seed and the newly crystallized crystals. Thus, the composition in the PCF was shown to be a good solution for the TSFZ method.

## Acknowledgments

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# 15 Growth of Zinc Chalcogenides

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## 15.1 Introduction

The fairly high ionic character of the II-VI chemical bond governs not only most of the physical properties of these semiconductors but also their crystal growth. Generally, the higher the ionicity, the lower the thermal conductivity will be. The thermal conductivity of II-VIs is then generally lower than that of more covalent compounds, making it difficult to control the growth interface in both melt and vapor growth. The characteristics of the highly ionic chemical bond also cause II-VI melts to remain highly associated at temperatures close to the melting point, leading to the presence of highly organized particles which influence the nucleation process and growth kinetics. Because of a stronger interaction between unlike particles arising from the considerable ionic contribution to the bond energy, the II-VI liquidus curve of the phase diagram shows a hyperbolic shape near the congruent melting point.

It has been shown that the higher the ionicity of the bond, the smaller will be the energy of formation of vacancies, which are the major defects in II-VIs. This accounts for the large II-VI nonstoichiometry, which is an additional complicating factor for their crystal growth.

The higher the ionicity, the smaller will be the energy of creation of dislocations and of stacking faults. This makes the highly ionic II-VI crystal lattice very sensitive to any strain and easily defective. Similarly, the higher the ionicity, the higher is the tendency to form hexagonal structure. As a result, the cubic II-VIs suffer from extensive twinning. Because of their high ionicity, ZnSe and ZnS show a phase transition in the solid state, from the hexagonal structure at high temperature to the zincblende one at lower temperature. This tendency to polymorphism is considered at the origin of twinning when cooling the crystals after melt growth: crossing the transition temperature during the cooling process induces a very high density of twins. All these factors clearly have a major impact on II-VI crystal growth.

**Table 15.1.** Ionicity  $\lambda$ , melting point  $M_p$ , energy gap  $E_g$ , enthalpy of formation  $\Delta H_f$ , thermal conductivity  $W$ , hexagonal to cubic transition temperature, lattice parameter of Zn chalcogenides

Material [structure @ RT]	$\lambda$	$M_p$ [°C]	$E_g$ @ RT [eV]	$\Delta H_f$ @ RT [kJ/mol]	$W$ [Wcm <sup>-1</sup> K <sup>-1</sup> ]	Hex.-cub. transition temperature	Lattice parameter [nm]
ZnTe (ZB)	0.49	1298	2.26	119	0.18	—	0.61034
ZnSe (ZB)	0.63	1526	2.67	159	0.19	1425	0.56690
ZnS (ZB)	0.77	1718	3.66	201	0.166	1020	0.54094
ZnO (W)	0.8	1880	3.4	350	0.54	—	$a = 0.32501$ $c = 0.52071$

RT = Room temperature

Zinc is the smallest atom of the second column of the periodic table of the elements. Among II-VI compounds, zinc chalcogenides thus present stronger bonding, and then higher energy gaps, higher enthalpies of formation, and higher melting points, as displayed in Table 15.1 in which the hexagonal to cubic transformation temperature for both ZnSe [1,2] and ZnS [3] is also given.

## 15.2 Zn Chalcogenide Growth

Given the difficulties arising from the high ionic character of their chemical bond – low thermal conductivity, associated melts, large nonstoichiometry, tendency to polymorphism – and because of their high melting points, Zn chalcogenides have been submitted to a wide variety of growth techniques: melt growth, solution growth using either homo- or hetero-solvent, growth from the vapor phase in open, semi-closed and closed systems by sublimation or by chemical vapor transport, and hydrothermal growth.

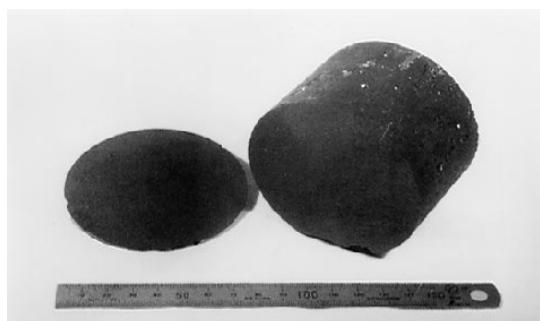
### 15.2.1 ZnTe

The interest in this compound has been recently renewed: ZnTe showed only *p*-type conductivity, impeding fabrication of *p-n* junctions, but low resistivity *n*-type layers have recently been demonstrated [4]. Moreover, intrinsic *p-n* junctions have been very recently realized by a simple thermal diffusion process, making possible strong pure green light emission [5].

Melt growth is generally preferred for the preparation of large volume single crystals. In spite of the ZnTe melting point lying in the temperature range where silica begins to soften, ZnTe melt growth by sealed ingot zone refining in specially treated silica tubes has been shown to be possible [6]. ZnTe can conveniently be grown by the Bridgman technique under pressure, according to two variants. In

the classical technique proposed by Fischer [7], an inert gas pressure reduces the loss of volatile components. This technique is still used today for the industrial growth of large high purity ZnTe ingots. In the sealed tube technique, sometimes called soft ampoule method, a silica ampoule, which is thermoplastic at the compound melting point, serves as a gas-tight liner. The decomposition pressure forces the silica against a tight-fitting graphite enclosure, which counteracts the mechanical forces. This last technique has been used [8] for the growth of In-doped ZnTe crystals. Excellent large diameter (70 mm) ZnTe crystals with average EPD less than  $2000/\text{cm}^2$  have also been grown by the vertical gradient freezing method (VGF) from a melt encapsulated by  $\text{B}_2\text{O}_3$  under 10 atm nitrogen [5]. More recently, 80-mm diameter single crystals (Fig. 15.1), which is the largest diameter reported so far for ZnTe single crystals, have been grown by the same group using the same VGF technique in a high pressure furnace (Fig. 15.2) under  $\text{B}_2\text{O}_3$  encapsulation [9]. The crystals are reported to present EPDs of  $5000\text{--}10,000 \text{ cm}^{-2}$  with rocking-curve FWHMs around 20 arcsec.

ZnTe solution growth, which allows a lower melting temperature, has been reported by the vertical Bridgman technique (VBT) [6,10–13] and by the traveling solvent method (TSM) according to two variants, the traveling heater method (THM) [6,14] and temperature gradient solution zoning (TGSZ) [15], using Te as the solvent. Crystals grown by THM show hole mobilities as high as  $8000 \text{ cm}^2/\text{V s}$  at 35 K (Fig. 15.3) attesting to their high purity level as a result of the low growth temperature, in addition to the efficient purification of solution zone refining [6]. Indium has been used as the solvent for the ZnTe growth by VBT [16] and by THM [17]. The possibility of hetero-seeding, using a (0001) sapphire substrate as a hetero-seed material, has been demonstrated for the first time in the ZnTe solution growth in a vertical Bridgman arrangement [12]. Very pure ZnTe crystals, have been obtained by the cold traveling heater method (CTHM), a modification of the classical THM, in which the source material is constituted of a Zn rod surrounded by Te powder (Fig. 15.4) [14]. The high purity of the crystals is attested to by photon spectroscopy experiments [18] and hole mobilities as large as  $7180 \text{ cm}^2/\text{V s}$  measured at 81 K, which is among the highest values reported so



**Fig. 15.1.** 80-mm diameter ZnTe single crystal (from Reference 9)

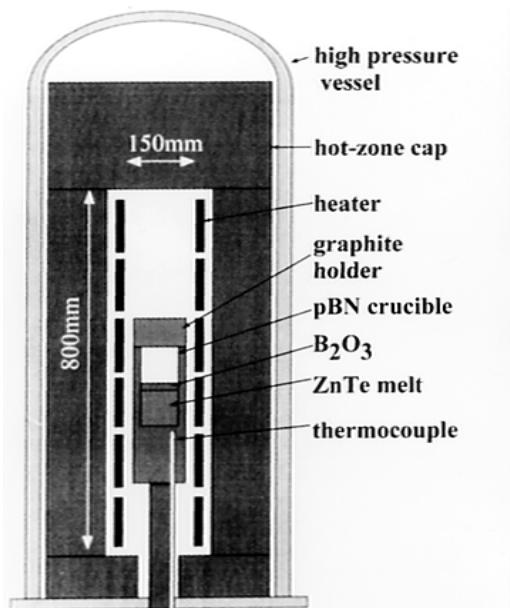


Fig. 15.2. High pressure VGF furnace (from Reference 9)

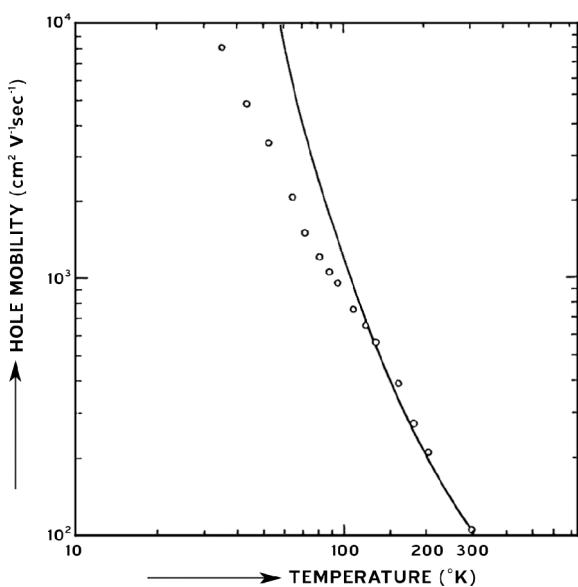
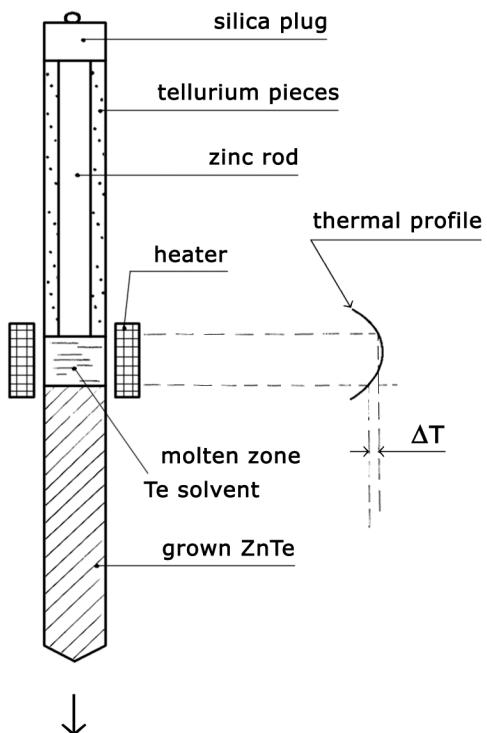


Fig. 15.3. Electron mobility versus temperature for a THM grown ZnTe crystal (from Reference 6)



**Fig. 15.4.** Schematic diagram of “cold THM” principle (from Reference 14)

far. Synthesis, purification, and growth are achieved in the same run, at the moderate temperature of 950°C.

According to the mode of transport used, vapor growth can be subdivided into static and dynamic techniques, or closed tube and open tube methods, respectively. In the closed tube method, the transport of the polycrystalline ZnTe charge occurs either by dissociative sublimation followed by diffusion to lower temperatures or by chemical vapor transport (CVT). In the first method, often called physical vapor transport (PVT), the charge is kept at temperatures ranging from 1050 to 1250°C, with an undercooling  $\Delta T$  of 10–20°C [19–21]. By CVT, generally carried out with iodine as a chemical agent, the ZnTe charge is kept at 700–800°C, and an undercooling  $\Delta T$  of 10–20°C is used [22,23]. The Sublimation Traveling Heater Method, with the solvent zone of classical THM replaced by an empty space, has also been used for the growth of ZnTe with the sublimation interface set at 815°C and the crystallization interface temperature at 785–800°C [24]. In order to release the excess volatile component until the total pressure in the ampoule has reached its minimum value, corresponding to congruent sublimation and then maximum growth rate, a new method has been disclosed [25] in which the elements are heated in an ampoule with a pinhole at one end. According to the

same principle, DeMeis and Fischer [26] attached a long capillary to one end of the ampoule, which extended to the room ambient air and acted as a cold trap for the excess vapor.

In the open tube method, the powder is heat-treated at 950–1000°C in a stream of H<sub>2</sub> or of inert gas like Ar, or in a low pressure system, with a difference between saturation temperature and equilibrium growth temperature  $\Delta T \sim 10\text{--}30^\circ\text{C}$  [27,28], or in a stream of iodine-hydrogen mixture with the source at 927–1008°C and a substrate temperature of 877°C [29].

Small (0.2 cm<sup>3</sup>) dark red ZnTe crystals have been obtained under hydrothermal conditions at a temperature of 350°C and a pressure of 150–200 MPa in (OH)<sup>-</sup> solutions, at a growth rate of 0.3 mm/day [30].

### 15.2.2 ZnSe

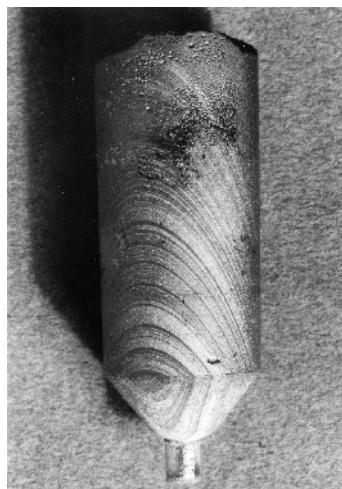
From the announcement in 1991 of the first ZnSe-based blue-green emitting laser diodes, ZnSe bulk growth has been considerably increased for fabricating epitaxial substrates. Like in the case of ZnTe, melt growth, solution growth using either homo- or hetero-solvent, vapor phase growth in open, semi-closed and closed systems by sublimation or by chemical vapor transport, and hydrothermal growth have been used for the growth of ZnSe crystals, as well as solid phase recrystallization.

Since Se is smaller than Te, the main differences between ZnSe and ZnTe lie in the higher melting point and in the ZnSe tendency to polymorphism, due to the higher ionicity of its chemical bond.

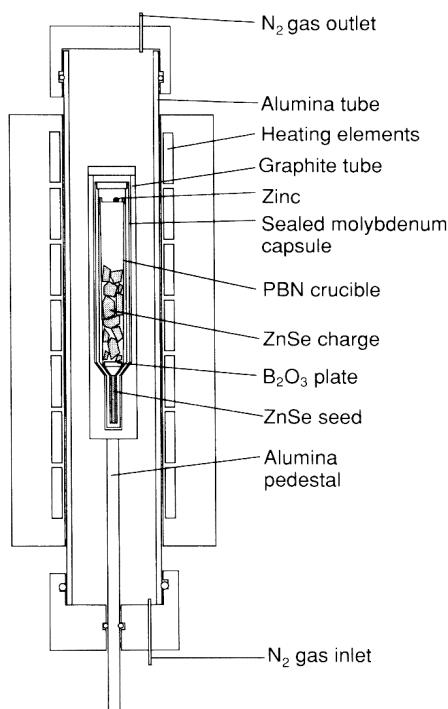
A review of the ZnSe melt growth is proposed by Rudolph [31]. After thermodynamic analysis and phase equilibria calculations of the Zn-Se system [(32)], the Zn-Se phase diagram, knowledge of which is necessary to achieve melt growth under well-controlled conditions, has been recently reanalyzed [33] and experimentally determined by DTA [34].

In order to grow large crystals at a high growth rate, numerous efforts have been concentrated on the melt growth of ZnSe by the vertical Bridgman technique under inert gas pressure, but this approach has up to now partly failed mainly because of the twinning tendency of ZnSe (Fig. 15.5). The inert gas, either Ar or N<sub>2</sub>, counter-pressure, dedicated to retain the volatile species in the melt, ranges usually between 5 to 10 MPa [31,35–42], but can reach up to 20 MPa [43]. With B<sub>2</sub>O<sub>3</sub> as the encapsulant, the counter-pressure can be reduced down to 1 MPa using a molybdenum capsule (Fig. 15.6) [2] and down to 0.8 MPa when sealing screwed caps on graphite containers using sealants like B<sub>2</sub>O<sub>3</sub> or Ti [31]. The growth rate ranges generally from 30 to 100 mm/day.

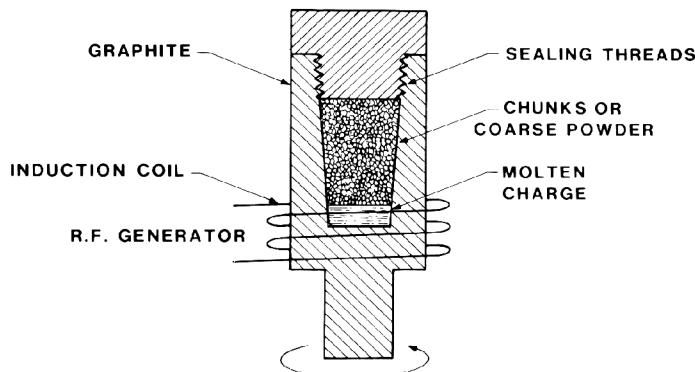
By applying the so-called soft ampoule method, either with a tight-fitted silica ampoule [44] or a molybdenum capsule [45,46], the pressure can be lowered down to less than 10<sup>-4</sup> Pa in this last case. A self-sealing technique in which a graphite crucible is sealed by the ZnSe vapors needs an outer pressure of only 0.5–0.7 MPa (Fig. 15.7) [47–49]. Lower pressure has been shown efficient in reducing the



**Fig. 15.5.** ZnSe crystal grown by high pressure Bridgman method (from Reference 41)



**Fig. 15.6.** Schematic diagram of the VGF system with the molybdenum Capsule (from Reference 2)



**Fig. 15.7.** Self-sealing system for the growth of ZnSe crystal (from Reference 48)

density of microvoids in the crystals [39]. The control of the crystal stoichiometry by applying a Zn partial pressure in the high-pressure chamber [50–52] or in the soft ampoule method [46] has also been reported.

The LEC technique, using  $\text{B}_2\text{O}_3$  as the encapsulant, has been attempted in order to obtain ZnSe crystals [46,53]. Although the growth of big cylindrical boules has been reported, no single crystals have been obtained so far by this technique. By the Kyropoulos technique, large cylindrical blocks with large grains have been obtained, but no structural feature of the crystals is given by the authors [54].

One of the major problems in the melt-grown ZnSe crystals is their high tendency toward twinning, essentially because of the presence of a first-order type phase transition from high temperature wurtzite to low-temperature zincblende structures.

The attempts to reduce this twinning tendency by reducing the supersaturation of the wurtzite phase either using a zincblende seed or grain boundaries in the first to freeze region have not fully succeeded [31]. A significant decrease in the twinning tendency has been observed after Mn doping ( $10^{18}$ – $10^{20}$  Mn/cm<sup>3</sup>), but not in a reproducible way [49]. Adopting a closed double crucible assembly and suitable growth conditions ( $G/R \sim 83$  Kh/cm<sup>2</sup>, with a typical gradient of 30 K/cm, a growth rate of 3.6 mm/h, a superheating temperature of 76°C, and a holding time of 6–8 h in the molten state) Wang et al. [55] have very recently demonstrated the growth of twin-free single crystals 12 mm in diameter and 55 mm in length by a seeded vertical Bridgman method (Fig. 15.8).

The difficulties inherent in the volatility of the constituents, in the microvoids constituted by inert gas inclusions, in the phase transitions, in the plastic deformations, and in the contamination from the environment so far have not allowed large melt-grown crystals exploitable for making epitaxy substrates to be obtained.

Vapor growth presents the frequently stressed drawbacks of low growth rate, crystals of limited thickness – because the initial optimal thermal conditions are progressively lost after about 2–3 cm of growth due to the low thermal conductivity of the material – and variable single crystal yield.

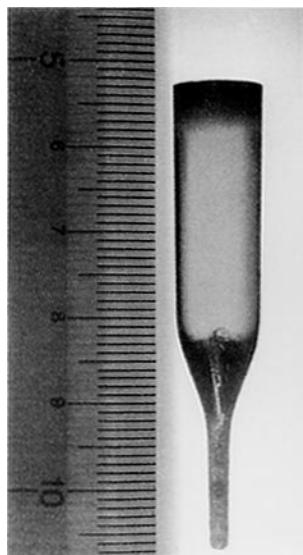
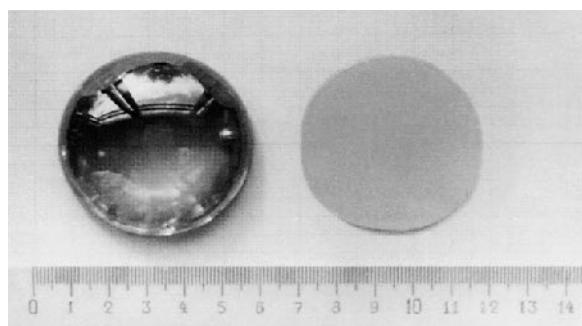


Fig. 15.8. Melt-grown twin-free ZnSe crystal (from Reference 55)

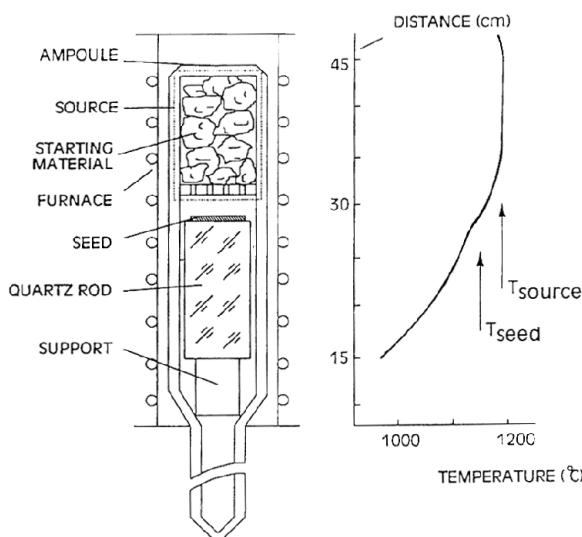
Apart from these drawbacks, crystallization from vapor by physical vapor transport (PVT) or dissociative sublimation presents some advantages over melt growth: 1) the lower processing temperature involved, 2) the purification effect as the result of the differences in the vapor pressures of the native elements and the impurities, and 3) the higher interfacial morphological stability of the solid-vapor interfaces. Sizable crystals of high quality can be obtained by PVT. In the PVT of II-VI compounds, the species found in the vapor phase are group II elements, Zn or Cd, and diatomic molecules of group VI elements, O<sub>2</sub>, S<sub>2</sub>, Se<sub>2</sub>, or Te<sub>2</sub>. The transport rate is controlled by the temperature of the source [56], the partial pressures of the species II and VI<sub>2</sub> in equilibrium with the II-VI compound, which can vary by orders of magnitude as the composition of the compound varies over the homogeneity range, and the enclosed gas nature and pressure [57]. The maximum transport rate occurs under the condition of congruent sublimation [58,59]. The mass fluxes of ZnSe by PVT have been measured in the temperature range 1050–1140°C using an *in situ* dynamic technique and have been found in good agreement with those calculated from a one-dimensional diffusion model [60]. Water has been shown to be an “activator” of ZnSe sublimation [61].

Many PVT closed and semi-open systems have been designed in order to reach the conditions of congruent sublimation. A method, in which a capillary connected to the ampoule is aimed at reaching the stoichiometry of the charge in order to adjust the total pressure to its minimum value corresponding to congruent sublimation, and then maximum growth rate, has been reported [26,62,63]. ZnSe crystals 40–55 mm in diameter have been grown using the Markov-Davydov technique [64] of seeded PVT on (111) seeds [65] and (100) seeds [66] (Fig. 15.9). In

this so-called free-growth method, the polycrystalline source is put in a chamber with perforated walls in the upper part of the ampoule as schematized in Fig. 15.10. A seed is placed below at a definite distance from the chamber on the center of a sapphire or quartz pedestal. The total pressure in the growth ampoule is about 1 atm. H<sub>2</sub> or its mixture with Ar is used as residual atmosphere in sealed ampoules, or He with the cold end of the ampoule connected to a He reservoir for gas refeeding. The presence of a cool end of the ampoule also allows the total pressure to be controlled in order to reach the conditions of congruent sublimation.



**Fig. 15.9.** ZnSe single crystal grown by a seeded vapor-phase free method in <100> direction and (100) substrate cut from such crystal (from Reference 66)



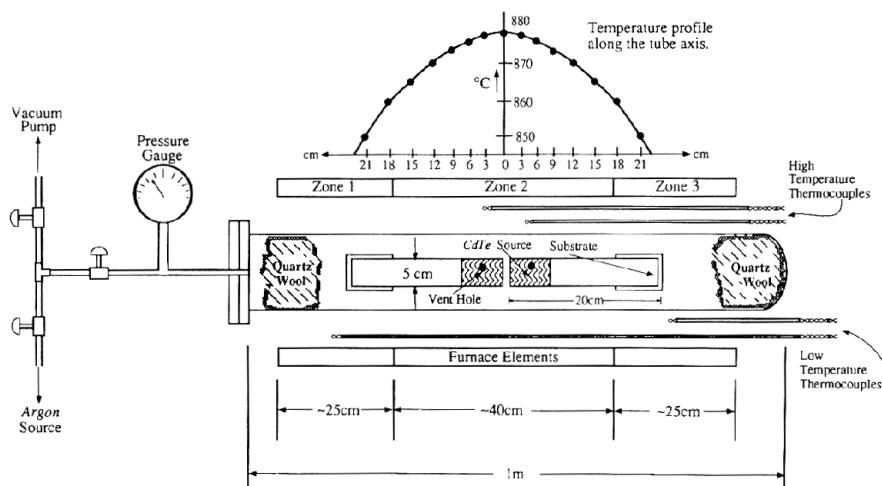
**Fig. 15.10.** Growth ampoule and temperature profile for the growth of ZnSe crystals by a seeded vapor-phase free growth (from Reference 65)

Another way of controlling the stoichiometry of the charge is the use of a Zn reservoir, either in a horizontal configuration [59,67–69] or in a vertical one [70]. In the classical method of Piper and Polich [71], successfully used for the growth of ZnSe single crystals [72–77], no control of the stoichiometry of the charge is used, but sometimes there is a preliminary treatment of the source [69,78,79]. Either seeding using the (111)B face of ZnSe crystals [80] or the selection of a seed crystal from a needle-shaped cavity in the cold finger attached to the growth end of the ampoule [74] were sometimes used in this simple Piper and Polich configuration. Like in the ZnTe case, ZnSe single crystals with rocking-curve full width half maximum (FWHM) as low as 20 arcsec have been grown by sublimation THM [80–82], at source temperatures ranging from 900 to ~1155°C,  $\Delta T$  of ~5–35°C, and pulling rates ranging from 0.04 to 0.26 mm/h depending on the growth temperature. Using some kind of semi-open system, in which the source is loaded in an ampoule, including a vent hole of 1–2 mm diameter, which is then placed in an outer quartz tube sealed off at one end and connected to a vacuum pump and an Ar supply connected in parallel, as described by Boone et al. [83] for CdTe (Fig. 15.11), excellent ZnSe substrates are industrially produced by Eagle Picher using seeded PVT: 2-in. diameter twin-free ZnSe crystals with lengths up to 25 mm and weighing up to 190 g are obtained under a residual Ar pressure adjusted to a value allowing congruent sublimation [84].

Introduction of Ar gas in a semi-closed horizontal ampoule has been shown to make the leakage of the excess component from the growth zone controllable [85,86]. The growth rate was then determined by the diffusion of component gases Zn and Se<sub>2</sub> in Ar with a constant nonstoichiometry. ZnSe single crystals weighing 25 g have been grown without seeding by a dynamic open system vapor growth technique, in which the flow of saturated vapor species is constricted [87].

Chemical vapor transport (CVT) using iodine as the chemical agent has been widely used, since it allows crystal growth far below melt and transition temperatures even more than PVT. While the crystals grown by CVT are of excellent crystalline quality, they are indeed generally of rather small size (Fig. 15.12). CVT is still used today for the growth of twin-free conductive ZnSe crystals in horizontal [22,88–91] or vertical [92–95] configuration. Growth conditions for preparing large single crystals are given by Fujita et al. [95]. Numerical studies have been carried out to evaluate the influence of typical growth parameters on heat and mass transport. The growth of crystals of good perfection requires the following conditions: a sufficiently high growth temperature ( $T_g > 750^\circ\text{C}$ ) to restrict condensation and source evaporation limitations;  $\Delta T < 100$  K between source and crystal;  $dT/dx < 10$  K/cm at the growth interface; a transport regime with the Rayleigh number up to 4000 with the aspect ratio of the ampoule ranging between 9 and 15 [96]; and share of convective transport lower than 20–30% [97]. NH<sub>4</sub>Cl has been used as a transport agent as well [98].

Solution growth of ZnSe crystals has been investigated in order to use normal silica tubes. The use of such solvents as Sn and Bi [99], Ga and In [100], Te [101], In-Zn alloys [102], PbCl<sub>2</sub> [92,103], ZnCl<sub>2</sub> [104], PbSe [103], As<sub>2</sub>Se<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub> [105], Se [103,106,107], Se/Te mixed solution [108,109], and SnSe [110] have

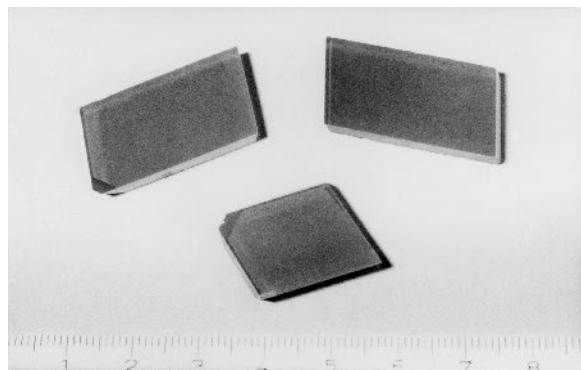


**Fig. 15.11.** SPVT system used by Eagle Picher for the growth of CdTe and ZnSe (from Reference 83)



**Fig. 15.12.** ZnSe crystal grown by chemical vapor transport with iodine as chemical agent (from Reference 92) (scale in mm)

been reported. In most cases, a vertical Bridgman configuration is used. Crystals with a minimum deviation from stoichiometry and then improved properties have been grown from a pre-annealed source crystal with an optimum vapor pressure of Zn in Se/Te solvent and of Se in Zn solvent [111]. The liquid encapsulated flux growth has been achieved using Se as the solvent with the evaporation suppressed using a liquid encapsulant and an Ar overpressure [103,106]. By the technique of temperature difference method under controlled vapor pressure (TDMCVP) [107], ZnSe crystals were grown at 1050°C from Se solvent under Zn pressure, and



**Fig. 15.13.** (100) ZnSe substrates grown by solid-state recrystallization (from Reference 114)

*p*-type crystals were obtained when adding lithium to the solution. THM has been used with  $\text{PbCl}_2$  [92,103],  $\text{PbSe}$  [103], and  $\text{SnSe}$  [110] as the solvents. Compared to the growth from  $\text{PbCl}_2$  solution, a drastically reduced density of inclusions was found in crystals grown with  $\text{SnSe}$  as the solvent.

Solid-state recrystallization (SSR), long used in the past for the growth of  $\text{HgCdTe}$ , has been extended to ZnSe [112,113]. Crystals of high crystallographic quality, with rocking curve FWHM  $\sim 14$  arcsec and a dislocation density  $\leq 10^2 \text{ cm}^{-2}$  have been grown by long annealing at  $1100^\circ\text{C}$  under high Se partial pressure (Fig. 15.13) [114], while low resistive *n*-type samples have been obtained by Al-diffusion from Al-doped molten zinc, with carrier concentrations reaching  $5 \times 10^{17} \text{ cm}^{-3}$  [115]. Twinning remains the main concern of this technique.

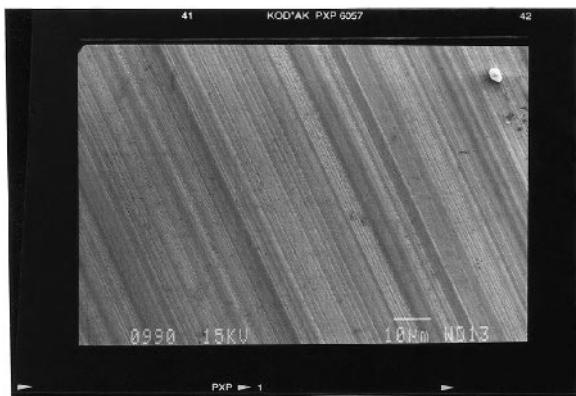
Good quality ZnSe seeded growth has been achieved under hydrothermal conditions from  $(\text{OH})^-$  solutions in the presence and in the absence of  $\text{Li}^+$  [116].

### 15.2.3 ZnS

Because of its highly ionic chemical bond, ZnS is known to crystallize in a large variety of crystallographically different structures (more than 80!), called polytypes, which are observed in natural as well as synthetic crystals grown from the vapor phase at temperatures above  $1100^\circ\text{C}$ . The growth of ZnS crystals has stimulated less effort than the growth of ZnSe.

Like for ZnSe, growth from the melt under high pressure by the Bridgman and Tamman (gradient freeze) techniques has been widely developed [117–120].

Growth from the vapor phase, either by PVT, with the charge at a temperature of  $1200$ – $1350^\circ\text{C}$  and an undercooling of  $10$ – $20^\circ\text{C}$  [19,22,65,121–129], or by the flow method in open tubes [130–132], or by chemical vapor transport, with either iodine (charge at  $850$ – $1000^\circ\text{C}$  and  $\Delta T$  of  $7$ – $20^\circ\text{C}$ ) [22,95], HCl [133,134], or  $\text{NH}_4\text{Cl}$  [98] as chemical agents, has been widely used.



**Fig. 15.14.** Micro-twins seen on SSR grown ZnS crystals by scanning electron microscopy (from Reference 141)

Solution growth of small ZnS crystals has been reported using KCl [135], ZnF<sub>2</sub> [136], Ga and In [137], or Te [101,138] as the solvents.

Crystals of several grams have been obtained using the hydrothermal method [139].

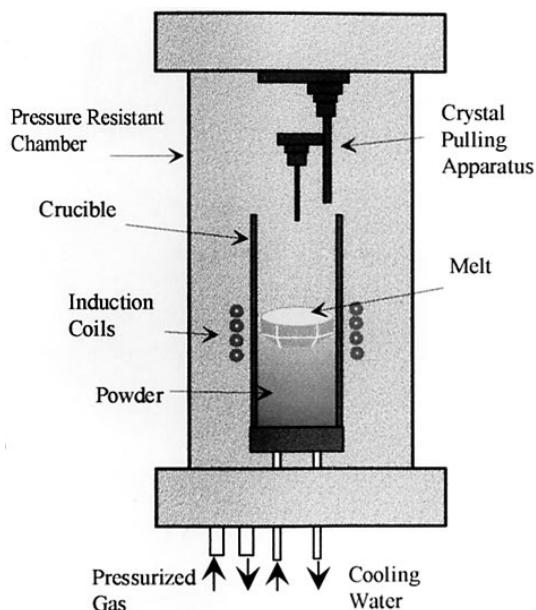
Tiny ZnS crystals have been even grown by directly interacting the component colloids in silica gels [140].

Large (~ 70 cm<sup>3</sup>) but highly twinned ZnS crystals (Fig. 15.14) of cubic structure have been obtained very recently by solid phase recrystallization (SPR) at 1100°C under sulfur pressure [141]. Cubic ZnS crystals with monocrystal area of 20 × 20 mm<sup>2</sup> and thickness of 2 mm have been obtained by SPR as well during hot pressing in the phase transition region [142]. Hot pressing was conducted in vacuum in the temperature range 900–1150°C and at pressures of 200 MPa from several minutes to several hours of In-doped ZnS with a grain size of about 1.5 µm. No indications are given by the authors on the crystallographic properties of the crystals and on their actual twinning state.

#### 15.2.4 ZnO

In spite of its very high melting point and its high reactivity with any surrounding material but platinum, cm-sized ZnO crystals with rocking-curve FWHM of ~125 arcsec have been grown from the melt using Cermet's melt growth apparatus with water-cooled crucible (Fig. 15.15) [143].

The hydrothermal method has been shown suitable for the growth of large ZnO crystals from (OH)<sup>-</sup> solutions at temperatures < 500°C under high pressure (15 to 50 MPa) with a temperature difference  $\Delta T \sim 3\text{--}40$  K and a growth rate in the range 0.05–0.3 mm/day [139,144–146]. More recently, high quality ZnO crystals, as



**Fig. 15.15.** Cermet's melt growth apparatus used for the ZnO growth (from Reference 143)

demonstrated by X-ray rocking curves in the 40 arcsec range and sharp PL peaks, have been grown hydrothermally at 355°C with a  $\Delta T$  of 10°C from  $(\text{OH})^-$  solutions [147].

Large diameter (2-inch diameter) boules have been recently reported to be grown by SPVT in a nearly closed horizontal tube using  $\text{H}_2$  as a carrier gas and a small amount of water to maintain the proper stoichiometry [148]. Furthermore, residual water, present in  $\text{H}_2$  or Ar, has been shown to act as sublimation activator of the vapor phase transport of ZnO [149].  $\text{Cm}^3$  size single crystals with rocking curve FWHM  $\sim 28$  arcsec have been obtained by chemical vapor transport using C as the transporting agent [150].

Smaller crystals have been obtained by CVT in closed tubes using such chemical transport agents as  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{NH}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{HgCl}_2$ ,  $\text{H}_2$ ,  $\text{Br}_2$ , and  $\text{ZnCl}_2$  at source temperatures ranging from 800 to 1150°C and  $\Delta T$  from 20 to 200°C [151–155].

Crystals of small size have been grown as well in open tube systems, either by oxidation of  $\text{ZnI}_2$  [156],  $\text{ZnS}$ ,  $\text{ZnSe}$  [157],  $\text{ZnBr}_2$  [158], and  $\text{Zn}$  [159–161] or by hydrolysis of  $\text{ZnF}_2$  [162],  $\text{ZnCl}_2$  [163,164], or  $\text{ZnI}_2$  [165]. The oxidation or hydrolysis character of the reaction can depend on the temperature range used for a same source. The temperature of the growth region ranges generally in such experiments from 900 to 1350°C.

Such solvents as  $\text{PbF}_2$  [166] and  $\text{V}_2\text{O}_5/\text{P}_2\text{O}_5$  mixtures [167] have been used for the flux growth of ZnO crystals. Using  $\text{PbF}_2$  as the solvent in sealed Pt crucibles, ZnO crystals have been grown by THM [168].  $\text{PbCl}_2$  has been found to be a very

good solvent of ZnO as well, but also shows a great reactivity with any surrounding material but platinum [169]. The same authors have found the Zn-In alloys to be good solvents of ZnO without reactivity with silica.

### 15.3 Properties and Defects of the Crystals

Sizable high quality crystals have been obtained for both ZnTe and ZnSe. The case of ZnSe, which has been the most studied Zn chalcogenide: very large ingots, up to 100 mm diameter, have been grown from the melt under high inert gas pressure [39] and crystals showing a crystallographic perfection close to the III-V's one have been obtained by SPVT, with an X-ray FWHM of 8.6 arcsec [83] and a dislocation density between 640 and 1300 cm<sup>-2</sup> [170]. Using solid-state recrystallization, a density of dislocations as low as 10<sup>2</sup> cm<sup>-2</sup> has been reported [171]. Crystalline perfection and size are lower for the other Zn compounds.

The presence of microvoids is reported in the crystals melt-grown under inert gas pressure, likely due to argon gas trapped during the melting process. These voids can completely disappear by reducing the gas pressure [39]. Inclusions and precipitates are frequently reported in the growth from nonstoichiometric melts, and Se or C inclusions are observed as well in the SSR ZnSe crystals [171]. In the ZnTe case, Te precipitates due to the retrograde solidus shape have been shown to act as a source of impurities, which can be released in the crystal by post-growth annealing [172].

As pointed out in the introduction, the highly ionic II-VI crystal lattice is very sensitive to any strain and is easily defective. Dislocations and subgrain boundaries are then frequently observed. Dislocation density generally exceeds 10<sup>5</sup> cm<sup>-2</sup> in the ZnSe Bridgman crystals and has been shown to depend on the impurity concentration through the effect of solution hardening [38]. ZnSe crystals free from rod-like low angle grain boundaries have been grown from the melt under Ar pressure under a small temperature gradient of 12–22°C/cm [40].

One of the major concerns in the growth of these highly ionic chalcogenides is their high tendency to twinning along the {111} planes. The occurrence of twinning and of both low and high angle grain boundaries appears to be reduced in the ZnSe PVT crystals which have been shown to present rocking curve FWHM as low as 10 arcsec compared with 60–70 arcsec for Bridgman grown material [84].

Zn interstitials and vacancies have been frequently pointed out in Zn chalcogenides. The Zn interstitial in ZnSe was the first isolated native interstitial directly observed in a semiconductor [173]. From theoretical calculation, Laks et al. [174] have concluded that the dominant defect in *p*-type ZnSe is the interstitial Zn<sub>i</sub><sup>2+</sup>. The double charged Zn vacancy has been reported to be the dominant intrinsic defect in ZnSe, the band gap energy position of which should be 0.66 eV above the valence band [175]. Their complexes with residual donors (V<sub>Zn</sub><sup>2-</sup>–D<sup>+</sup>) or with interstitials, like (V<sub>Zn</sub>, Li<sub>i</sub>) considered as an acceptor in ZnSe [176], have been frequently reported. Chalcogen vacancies and their complexes with acceptors, acting as deep electron traps, have been pointed out as well in ZnSe and ZnS [177]. Te

antisites acting as donor-like deep states have been considered from theoretical calculations to be prevalent in tellurides [178]. Such deep levels can compensate shallow dopants, resulting in a decrease of conductivity.

## 15.4 Purity, Contamination and Doping

The crystals grown by the Bridgman method under inert gas pressure are markedly contaminated by residual impurities due to the contact with the crucible over long periods of time at high temperature. There is thus a contamination of the starting charge in the case of the highest melting point compounds like ZnSe and ZnS. Such elements as Na, K, Cu, Al, Si, and Fe are generally found to be the major residual impurities [179]. Depending on the purity of the starting CVD charge, ZnSe crystals of extremely high purity have been obtained by SSR as assessed from photoluminescence measurements [180]. ZnTe crystals of very high purity as shown from two photon spectroscopy experiments [18], have been obtained by solution zone melting using the cold traveling heater method (CTHM) [14].

Zn oxide, sulphide, and selenide are generally *n*-type, and Zn telluride is *p*-type. *P*-type ZnO layers [181] and *n*-type ZnTe layers [4] have been nevertheless obtained using respectively N and Al as the dopants. Very recently, *p*-type ZnO layers showing a carrier concentration in the  $10^{19} \text{ cm}^{-3}$  range have been obtained by Ga+N co-doping [182], and the surface of ZnTe bulk crystals has been converted to *n*-type by a simple thermal diffusion process [5]. *P*-type ZnSe layers are now commonly grown by MBE and at lower doping level by MOCVD. *P*-type bulk ZnSe crystals have even been obtained using Li as the dopant by controlling the stoichiometry of the crystals either during the growth [183] or during a post-growth annealing process [184].

## 15.5 Applications and Perspectives

Bulk semiconductor crystals have been long privileged subjects for fundamental studies and applications. Much of the knowledge of the fundamental properties of II-VI semiconductors comes from studies on bulk crystals. Bulk material is now widely replaced by thin layers, even though it keeps some niches, like nuclear detectors or epitaxy substrates, and it is still used for some studies needing sizable samples.

Green emitting diodes have been recently realized on Bridgman grown bulk ZnTe crystals on which *p/n* junctions have been obtained by diffusion of a donor through the vapor phase [5].

In thin film form, ZnSe has been studied since 1991 for its potentialities in blue light emitting devices. Now, not only challenged but also clearly dominated by nitrides and mainly GaN for such blue light emitting devices, ZnSe nevertheless keeps some attractive niches and prospects, even in the domain of light emission.

While some progress can be expected for blue light emitting devices grown from ZnSe homoepitaxial layers, ZnSe-based white LEDs have been demonstrated in which the devices use a phenomenon unique to ZnSe homoepitaxy [185]. A portion of the main greenish-blue emission from the active layer of a *p/n* junction diode is absorbed by the conductive substrate, which in turn gives an intense broadband yellow emission. Both emission bands combine to give a light, which appears white to the naked eye. Lifetimes of such devices are said to exceed 800 h at room temperature by the authors [185]. This revolutionary new form of high-efficiency lighting opens the way to the fantastic market of compound semiconductor LEDs, which could replace incandescent light bulbs. Another attractive application of bulk ZnSe lies in the realization of tunable mid-infrared sources from alternate ZnSe stack quasi-phase matching overcoming the fact that ZnSe is isotropic, so that no birefringence phase-matching scenarios are available [186]. Such devices will benefit from the high optical nonlinear susceptibility  $\chi^{(2)}$  of ZnSe, its high threshold damage power density, its excellent transparency over the 1–15  $\mu\text{m}$  wavelength range, its good mechanical properties, and the possibility of future integration with the pumping source [187].

ZnS is presently used for making alternating-current electroluminescent (ACTFEL) displays. It presents, however, interesting possibilities as well for light emitting and detecting devices, mainly since high conductivity *p*-type doping has been recently demonstrated [188] which now paves the way to the realization of diodes.

ZnO, due to its unique combination of piezoelectric, conducting, thermal, and optical properties, is used for making piezoelectric transducers, optical wave guides, acoustooptic media, conductive gas sensors (detectors of gas like ammonia), and transparent conductive electrodes for use in efficient solar cells. It could be thought of also as a scintillator. Furthermore, ZnO, with an exciton binding energy (60 meV) well above the thermal energy at room temperature, has been shown to display excitonic stimulated emission up to 550 K, the highest temperature ever reported for any semiconductor [189]. This is a significant indicator for possible stimulated emission and lasing at room temperature with large gain. ZnO substrates are also in great demand for making homoepitaxial ZnO layers and as heterosubstrates of GaN.

The lack of commercial availability of large good quality Zn chalcogenide substrates at low price still limits their possibilities and use. Progress still needs to be made in the Zn chalcogenide growth area.

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# 16 Growth of Hydroxyapatite Crystals

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## 16.1 Introduction

*Hydroxyapatite* is a calcium orthophosphate containing water with a chemical composition of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . The composition and structure of hydroxyapatite closely resembles that of mineral components of vertebrate hard tissues. Body fluid is supersaturated with respect to hydroxyapatite under normal physiological conditions. Therefore, the growth and dissolution of hydroxyapatite has an important contribution to ossification, calculus formation, and the development of caries. However, the mechanism underlying biological apatite formation is still not sufficiently clear. In addition to the normal calcifications in bone and teeth, some of the pathological calcifications are also regulated by various factors including cells and matrix proteins.

In this chapter, we first briefly review the calcium orthophosphate family to which hydroxyapatite belongs, although detailed reviews on this subject have already been published by a number of authors [1–5]. Some calcium orthophosphates are formed as precursors that have chemical and structural similarities to hydroxyapatite, and others are used as raw materials for calcium phosphate cements and hydroxyapatite single crystals.

An important aspect of hydroxyapatite growth in modern technology is that, in many cases, the nucleation and subsequent growth of hydroxyapatite on the surface of biomaterials implanted in body tissues determine the performance and even lifetime of biomaterials. For biomaterials used in the repair of bone tissue, the formation of hydroxyapatite on the surface is a desirable property, leading to direct bonding between bone and biomaterials. On the other hand, the formation of hydroxyapatite must be avoided for biomaterials used in contact with blood, such as artificial blood vessels and artificial heart valves. Investigations of interfaces between bone and bone-bonding biomaterials have led to the development of a variety of techniques to form a bonelike apatite coating on biomaterial surfaces in aqueous solutions. These techniques have been used to modify the surfaces of metals, ceramics, and polymers to improve biocompatibility and bone-bonding ability. In this chapter we also review the mechanism and kinetics of hydroxyapa-

ite growth in solution, in addition to the aspect of hydroxyapatite growth associated with hardening of calcium phosphate cements, and the fabrication of hydroxyapatite ceramics and single crystals.

## 16.2 Calcium Orthophosphates

Besides hydroxyapatite, many kinds of calcium orthophosphate salts are listed in Table 16.1. The calcium orthophosphates are conventionally classified according to their Ca/P molar ratio, which varies from 0.5 to 2. These salts are insoluble except for  $\text{Ca}(\text{HPO}_4)_2$  and  $\text{Ca}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ . Hydroxyapatite is the most insoluble salt in neutral and alkaline solutions. Therefore, all of the calcium orthophosphate salts in Table 16.1 can be converted into hydroxyapatite at a pH higher than 5 [6]. Except for tricalcium and tetracalcium phosphates, these salts can be formed in aqueous solutions. However, when a small amount of divalent cation with an ionic radius of 0.07 nm, typically magnesium, is present in solution such as body fluid, whitlockite, that has a structure very similar to  $\beta$ -tricalcium phosphate, is precipitated [7].

*Dicalcium phosphate dihydrate* (DCPD) with the formula  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and *dicalcium phosphate anhydrous* (DCPA) with the formula  $\text{CaHPO}_4$  are stable phases at a pH lower than 4.5–4.3 at 25°C [6]. Dicalcium phosphate anhydrous is 0.680 times less soluble than dicalcium phosphate dihydrate. Dicalcium phosphate dihydrate gradually dehydrated in water at 60–100°C resulting in the formation of dicalcium phosphate anhydrous.

**Table 16.1.** Calcium Orthophosphate Family

Ca/P molar ratio	Abbreviation	Log (solubility product) at 25°C
0.50 $\text{Ca}(\text{HPO}_4)_2$	MCPA	—
0.50 $\text{Ca}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	MCPM	—
1.00 $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	DCPD	6.55 [8], 6.66* [9]
1.00 $\text{CaHPO}_4$	DCPA	6.90 [10]
1.33 $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	OCP	49.6** [11], 48.4**† [12]
1.50 Amorphous calcium phosphate	ACP	24.8‡ [13], 10.6§, 11.5§ [14]
1.50 $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$	$\beta$ TCP	28.92 [15]
1.50 $\alpha$ - $\text{Ca}_3(\text{PO}_4)_2$	$\alpha$ TCP	25.5 [16]
1.50 $\alpha'$ - $\text{Ca}_3(\text{PO}_4)_2$	$\alpha'$ TCP	—
1.50–1.67 Calcium-deficient apatite	—	—
1.67 $\text{Ca}_5(\text{PO}_4)_3\text{OH}$	HAP	58.5 [17], 57.5 [18]
2.00 $\text{Ca}_4(\text{PO}_4)_2\text{O}$	TeTCP	38 [19]

\* 37.5°C

\*\* pK<sub>sp</sub> on the basis of  $(\text{Ca})^4(\text{H})(\text{PO}_4)^3$

† 23.5°C

‡ pK<sub>sp</sub> on the basis of  $(\text{Ca})^3(\text{PO}_4)^{1.87}(\text{HPO}_4)^{0.2}$

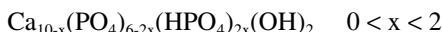
§ pK<sub>sp</sub> on the basis of  $(\text{Ca})(\text{PO}_4)^{0.74}(\text{H})^{0.22}$  at 30–42°C

*Octacalcium phosphate* (OCP) has the formula  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  and often occurs as a transient intermediate in the precipitation of the thermodynamically more stable hydroxyapatite. The crystal structure of octacalcium phosphate consists of two layers parallel to (100), an apatitic layer that corresponds very closely to that of hydroxyapatite and a hydrated layer that contains all the water molecules [20]. Octacalcium phosphate is transformed into calcium-deficient hydroxyapatite by hydrolysis at neutral pH [21].

*Tricalcium phosphate* (TCP) with the formula  $\text{Ca}_3(\text{PO}_4)_2$  has three polymorphs  $\beta$ ,  $\alpha$ , and super  $\alpha$ , with transition temperatures  $\beta \rightarrow \alpha$  at 1125°C and  $\alpha \rightarrow$  super  $\alpha$  at 1430°C [22,23]. The super  $\alpha$  phase is unable to survive quenching to room temperature. The crystal structure of the  $\alpha$  phase contains an atomic arrangement similar to that of hydroxyapatite [24]. Thus, the hydroxyapatite structure can be derived from that of the  $\alpha$  phase. The  $\alpha$  phase is transformed by hydrolysis into calcium-deficient hydroxyapatite, octacalcium phosphate, and dicalcium phosphate dihydrate depending on the pH and the temperature [25]. The reactivity toward hydrolysis of the  $\beta$  phase is much lower than that of the  $\alpha$  phase.

*Amorphous calcium phosphate* (ACP) is an amorphous phase with a typical Ca/P molar ratio of 1.50 [26]. Precipitation of calcium orthophosphate from a moderately or highly supersaturated solution at or above neutral pH tends to produce amorphous calcium phosphate as an initial phase. Subsequently, a more stable crystalline phase is formed, such as octacalcium phosphate or hydroxyapatite [27]. The Ca/P molar ratio of amorphous calcium phosphate is reported to be 1.50. However, a detailed study of the composition of amorphous calcium phosphate revealed that the Ca/P molar ratio ranged from 1.18 to 1.50 before washing and  $1.50 \pm 0.03$  after washing. The chemical composition  $\text{Ca}_9(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_x$  is proposed for amorphous calcium phosphate. Chemical compositions of  $\text{Ca}_3(\text{HPO}_4)_{0.66}(\text{PO}_4)_{1.56}$  and  $\text{Ca}_3(\text{HPO}_4)_{0.2}(\text{PO}_4)_{1.87}$  were reported with defined values of the solubility product [14,28].

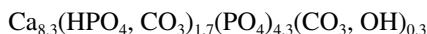
Hydroxyapatite with a Ca/P molar ratio lower than 1.67 is called *calcium-deficient hydroxyapatite*, although stoichiometric hydroxyapatite has a Ca/P ratio of 1.67. Calcium-deficient hydroxyapatite is formed with no difficulty from aqueous reactions between calcium and phosphate ions and/or by conversion from other calcium orthophosphates in water. Several chemical formulas have been proposed for calcium-deficient hydroxyapatite [29]. An example of a proposed formula is [30]:



Any calcium-deficient hydroxyapatite decomposes into hydroxyapatite and tricalcium phosphate at temperatures between 700 and 1200°C.

*Bone mineral* closely resembles hydroxyapatite in composition and structure. The difference between hydroxyapatite and bone mineral lies in the impurity content and crystallinity. Bone mineral is poorly crystalline apatite and contains sodium (0.5–0.7 wt%), magnesium (0.26–0.55 wt%), water (9.7 wt%), and carbonate (5.8 wt%) as major impurities, and zinc (164–217 ppm), strontium (138–155 ppm), aluminum (60–73 ppm), lead (29–34 ppm), and barium (18–19 ppm) as mi-

nor impurities [31–33]. The metallic ions substitute for calcium sites in the hydroxyapatite structure. Carbonate groups can substitute for both phosphate (so-called Type B substitution) and hydroxyl groups (Type A substitution). Neglecting the metallic impurities, the average composition of bone mineral is indicated by the following chemical formula:



corresponding to calcium-deficient hydroxyapatite with no detectable amount of OH<sup>-</sup> ions [34]. The carbonate group substitutes mainly for phosphate groups and minorly for hydroxyl groups in bone mineral. Moreover, bone mineral contains labile carbonate and phosphate and/or hydrogenphosphate groups with a nonapatitic environment [35,36]. These ions may be primarily located on the surface of the crystals.

*Tetracalcium phosphate* with the formula Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O is obtained under anhydrous conditions or under a low water vapor pressure typically at temperatures above 1300°C. Tetracalcium phosphate has a close structural relationship to hydroxyapatite [37].

## 16.3 *In Vivo Calcification of Biomaterials*

### 16.3.1 Calcification of biomaterials used in contact with bone

The growth of apatite crystals on the surface of biomaterials determines the characteristics and performance of a number of biomaterials. Because body fluid is highly supersaturated with respect to apatite, with the degree of supersaturation corresponding approximately to 23, apatite deposition may occur on any biomaterial implanted in the body. For biomaterials used in contact with bone, nucleation and growth of apatite on their surfaces are desirable properties, subsequently resulting in the formation of a bond between the bone and the biomaterial. Such a biomaterial is called a bioactive material and is defined as, “a material that elicits a specific biological response at the interface of the material, which results in the formation of a bond between the tissues and the material” [38]. The apatite grown on the surface of a bioactive material is poorly crystallized carbonate-containing hydroxyapatite because body fluid contains a high concentration of carbonate ions. The carbonate groups substitute mainly for phosphate groups in the carbonate-containing hydroxyapatite. The carbonate-containing hydroxyapatite promotes the differentiation of marrow stromal stem cells into osteoblasts that are bone-producing cells [39]. Because the osteoblasts form bone tissue on the bioactive materials, the material finally bonds to the bone.

The promotion of cell differentiation by the carbonate-containing hydroxyapatite is suggested to arise from its nonstoichiometric composition, high specific surface area, and high reactivity. As a result, the carbonate-containing hydroxyapatite can adsorb active proteins such as bFGF (basic fibroblast growth factor) which makes stromal cells differentiate to specific classes of cells [40]. IGFBP-5 (insulin

like growth factor bonding protein-5) that binds to IGF (insulin like growth factor) is well adsorbed to hydroxyapatite [41]. IGF also promotes the differentiation and proliferation of osteoblasts [42]. When the carbonate-containing hydroxyapatite is not formed on the biomaterial surface, no cell differentiation into osteoblasts occurs. Consequently, fibroblastic cells proliferate on the biomaterial surface and produce a fibroblastic membrane around it, which results in nonbonding between the biomaterial and the bone. Therefore, growth of carbonate-containing hydroxyapatite on the surface is an essential requirement for bioactive materials to bond to the bone.

Adsorption of bone matrix proteins (see Section 16.8) to the carbonate-containing hydroxyapatite is suggested to be another important factor in the bonding of bioactive materials to bone tissue [43]. *In vitro* bone cell cultures in association with observation by a field-emission transmission electron analytical microscope suggest that the sequence of bone-bonding starts with the secretion and adsorption of bone matrix proteins onto biomaterials. Because many bone matrix proteins have affinity with hydroxyapatite and, particularly, poorly crystallized carbonate-containing hydroxyapatite, a bond can form between hydroxyapatite and bone. The major proteins adsorbed are osteopontin and bone sialoprotein (see Section 16.8). Mineralization of these matrix proteins occurs by nucleation of nanocrystalline calcium phosphate. The earliest detectable crystallites in this organic matrix are 1–2 nm in size, which corresponds to one or two unit cells of hydroxyapatite. These crystals grow in the organic matrix. At this early stage in the bone-bonding process, no collagen is observed in the organic matrix. Later, an initial collagen fiber assembly is formed on the mineralized organic matrix. Then the collagen is mineralized, producing morphologically identifiable bone matrix.

### 16.3.2 Calcification of biomaterials used in contact with blood

Apatite formation is an undesirable property for biomaterials or artificial organs used in contact with blood, such as bioprosthetic heart valves, aortic homografts, artificial blood pumps, assist devices, and a total artificial heart. Apatite formation on blood-contacting biomaterials results in thrombosis and/or the loss of flexibility of the biomaterials, thereby causing their mechanical failure and degradation [44–48]. For example, glutaraldehyde-preserved porcine aortic heart valves (bioprosthetic valves), which have been widely used for heart valve replacement, suffered from apatite deposition occurring in 10–20% of the adult recipients within 10 years [49].

A bioprosthetic valve is a collagen-based material. The collagen fibers must be cross-linked to diminish antigenicity and enhance material stability and thus to reduce degradation. The most widely applied cross-linking agent is glutaraldehyde, because it introduces thermally and chemically more stable cross-links into collagen fibers than other aldehydes such as formaldehyde. Many factors are involved in the calcification of glutaraldehyde-treated bioprosthetic valves. First, residual, noncovalently bonded glutaraldehyde encourages calcification, which is demonstrated by the reduction in hydroxyapatite formation by careful removal of nonco-

valently bonded or labile-associated glutaraldehyde by rinsing and neutralization before implantation [50]. Second, glutaraldehyde treatment and other pretreatments cause loss of endothelial cells, loss of interstitial cell viability, loss of inhibitors to calcification, fragmentation of cell membranes, and disruption of the cytoplasm. The cytoplasm, which is an essential part of the cell and is surrounded by a cell membrane, contains a liquid that differs in chemical composition from extra cellular fluid. The cytoplasmic fluid is primarily a phosphate buffer solution containing a very small amount of calcium: normal cells have an approximately ten thousand-fold gradient of calcium from outside to inside ( $10^{-3}$  vs.  $10^{-7}$ ). Non-viable cells and disrupted cell membranes are unable to maintain such a low intracellular calcium level. Moreover, cell membranes are rich in phospholipids that are known to act as nucleation sites for calcium phosphates. Consequently, nucleation of calcium phosphate occurs at the fragmented cell membranes. Third, alteration of collagen by cross-linking induces calcification although the mechanism is still poorly understood [51]. Fourth, a series of proteins induces calcification. Proteins containing gamma-carboxyglutamic acid (GLA), a calcium-binding amino acid, have been identified in calcified bioprosthetic valves [52]. GLA-containing proteins such as osteocalcin, one of the bone matrix proteins (see Section 16.8), might play a role in the calcification process. Although the source of GLA-containing proteins is unclear, they might be transported by circulating macrophages which are cells involved in the immune system. Fifth, it is known that mechanical stress also stimulates calcification [53,54] although the mechanism is poorly understood. Calcification has been shown to occur in regions of highest stress-strain levels in bioprosthetic valves. In general, all moving parts of the leaflets calcified more than static areas, indicating the importance of stress in the calcification process [55].

Recent evidence suggests that the calcification of bioprosthetic valves is regulated by functional protein molecules similar to those of the bone matrix. The presence and absence of osteopontin have been demonstrated at calcified and non-calcified areas, respectively, on implanted porcine aortic heart valves [56,57]. Osteopontin is a sulfated calcium-binding phosphoprotein rich in sialic acid groups, and is a prominent constituent of the bone matrix and dental cementum. Osteopontin is also associated with diffuse calcification in human coronary atherosclerosis, suggesting an implication of this protein in the onset and progression of calcified atheroma. Although osteopontin is a potent inhibitor of hydroxyapatite formation, osteopontin is considered to be an adhesion molecule between hydroxyapatite crystals and many substrates including valve surfaces, bioactive materials, ligaments, tendons, and dental cementum [58].

The prevention of bioprosthetic valve calcification has been actively attempted although there is still no satisfactory clinical means for preventing the calcification (Table 16.2) [52,59]. The approaches to prevent calcification include extensive extraction of noncovalently bonded glutaraldehyde, extraction of phospholipids, extraction of noncollagenous proteins, nonaldehyde treatments, treatment with inhibitors of calcification, and incorporation of metallic salts.

**Table 16.2.** Strategies to Prevent Calcification of Bioprosthetic Valves

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Removal of glutaraldehyde
Enzymatic removal of noncollagenous proteins
Alternative crosslinking methods
Diphosphonate
Trivalent metal ions
Amino oleic acid
Surfactants
Ethanol

---

Fresh soft tissue rich in collagen was treated with pepsin, an enzyme that decomposes certain kinds of proteins. Pepsin treatment was carried out under conditions of high ionic strength, which allowed the collagen fibrillar structure to remain intact, while noncollagenous interfibrillar materials, cytoplasmic components, and the antigenic telepeptides of collagen were mostly removed. This pepsin-treated material, subsequently cross-linked with glutaraldehyde using standard procedures, was found to elicit a much reduced calcification response compared to cross-linked pericardium that was not treated by pepsin [50].

Epoxy-cross-linked collagen showed a large reduction in calcification compared with glutaraldehyde-cross-linked materials [60,61]. Dermal sheep collagen was cross-linked by glutaraldehyde, 1,4-butanediol diglycidyl ether (BD), or a combination of 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS). These cross-linked dermal collagens were implanted subcutaneously in rats up to six weeks. The dermal sheep collagen cross-linked by glutaraldehyde resulted in intensive calcification while that cross-linked by EDC and NHS resulted in moderate calcification at six weeks. No calcification occurred for the collagen cross-linked by BD at 6 weeks. A photooxidative preservation method was also effective to inhibit calcification [62].

Diphosphonate is known to inhibit calcification in bone and pathologic mineral deposition by binding hydroxyapatite and preventing further crystal growth [63]. Diphosphonate compounds are characterized by a P-C-P bond instead of P-O-P bond of pyrophosphate. Local controlled release of ethane hydroxy diphosphonate (EHDP:  $\text{PO}(\text{OH})_2\text{-CCH}_3\text{OH-PO}(\text{OH})_2$ ) in the vicinity of bioprosthetic valves implanted subcutaneously in rats prevented the calcification of bioprosthetic valves for up to 84 days [64]. Amino propane hydroxy diphosphonate (APDP:  $\text{PO}(\text{OH})_2\text{-C(CH}_2\text{CH}_2\text{NH}_3\text{)}\text{OH-PO}(\text{OH})_2$ ) inhibited the calcification of bioprosthetic valves when covalently incorporated in cuspal tissue [65].

Trivalent iron and aluminum ions prevented the calcification of glutaraldehyde-pretreated bioprosthetic valves. These trivalent ions are known to inhibit the activity of alkaline phosphatase, an enzyme that catalyzes the hydrolysis of phosphoesters, thus producing phosphate ions. The presence of alkaline phosphatase has been demonstrated in fresh porcine aortic valves and glutaraldehyde-treated bioprosthetic valves implanted in rats. The alkaline phosphatase in the implanted valves came from the recipient and was found to be adsorbed rapidly following

implantation with maximum enzyme activity at 72 h. Simultaneously with the maximum activity of alkaline phosphatase, bulk calcification was initiated in the bioprosthetic valve. Preincubation of bioprosthetic valves in either  $\text{FeCl}_3$  or  $\text{AlCl}_3$  solution inhibited calcification and reduced alkaline phosphatase activity significantly [66].

Treatment of glutaraldehyde-treated bioprosthetic valves with 2-amino oleic acid was effective in preventing the calcification of glutaraldehyde cross-linked cusps of aortic valves, but not aortic walls. The mechanism of prevention is considered to be the retardation of the diffusion of calcium ions into the aortic cusps of bioprosthetic valves [67].

Incubation of glutaraldehyde-treated bioprosthetic valves in sodium dodecyl sulfate inhibits calcification. Sodium dodecyl sulfate is an anionic detergent that can hypothetically modify the bioprosthetic tissue in a variety of ways including the extraction of lipids or proteins, protein denaturation, or charge modification. Sodium dodecyl sulfate prevents calcification in the presence of acidic phospholipids and calcium phosphate complexed lipids *in vitro* [68]. The principal effect of sodium dodecyl sulfate is reported to be phospholipid extraction from glutaraldehyde-treated bioprosthetic valves [69].

Pretreatment of glutaraldehyde-cross-linked bioprosthetic valves with 80% ethanol prevented calcification [70,71]. The pretreatment extracts phospholipids, cholesterol, noncovalently bonded glutaraldehyde, and water from the valve and changes the conformation of collagen. Ethanol pretreatment greatly reduces the uptake of cholesterol *in vitro*.

## 16.4 Apatite Deposition on Biomaterials as Surface Modification

Apatite layers are formed on various substrates in metastable supersaturated solutions to improve biocompatibility of biomaterials. A calcium phosphate layer with a thickness of 7.9 nm was found to be formed on titanium immersed in Hanks' balanced solution (Table 16.3) for 30 days [72]. The Ca/P molar ratio of the calcium phosphate layer was 1.63, indicating the formation of calcium-deficient hydroxyapatite. The apatite layer was formed on a titanium oxide layer on the surface of metallic titanium. A similar calcium phosphate layer is also formed on the surface of titanium implanted in human bone tissue [73]. These calcium phosphate layers are considered to be important for the superior biocompatibility of titanium metal.

It is suggested that Ti-OH groups on the surface of titanium or titanium alloys act as sites for the primary nucleation of calcium titanate in calcium-containing solutions, which subsequently act as secondary nucleation sites for apatite formation [74]. Ti-OH groups can be introduced on the titanium surface by immersing in a NaOH solution at 60°C for 24 hours, followed by heating in air at 600°C for one hour. The titanium thus treated induces apatite formation on its surface in a simulated body fluid (SBF, Table 16.3) or in bone tissue [75]. However, the alkali

**Table 16.3.** The Ion Concentrations of Supersaturated Fluids (mM)

	Na	Ca	K	Mg	Cl	$\text{HPO}_4^{2-}$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	pH	Temp. [°C]	Refs.
Hanks	142	1.26	5.81	0.81	145	0.78	0.81	4.17	7.40	37	72
SBF	142	2.5	5.0	1.5	148	1.0	0.50	4.2	7.25– 7.40	37	74
Blood plasma	142	2.5	5.0	1.5	103	1.0	1.0	27.0	7.40	37	

and heat treatment method is ineffective for inducing apatite formation on stainless steel and Co-Cr-Mo alloy. Calcium titanate and/or calcium hydroxyde that act as the nucleation site of apatite formation has been directly formed by immersing titanium in a  $\text{Ca}(\text{OH})_2$  solution at room temperature, followed by heating at 600°C for 30 minutes at a reduced pressure of 10 MPa [76].

An apatite layer is also known to form on hydrated silica-gel layers on the surface of some silicate-containing glasses and glass ceramics. An amorphous calcium phosphate layer is formed on the silica-gel layer on the surface of Bioglass® with a composition 24.5 $\text{Na}_2\text{O}$ -24.5 $\text{CaO}$ -45 $\text{SiO}_2$ -6 $\text{P}_2\text{O}_5$  followed by crystallization of the amorphous calcium phosphate into apatite by the incorporation of  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ , or  $\text{F}^-$  anions from the surrounding solution [77]. Glasses in the system  $\text{CaO}$ - $\text{SiO}_2$ , free from  $\text{P}_2\text{O}_5$ , form the apatite layer in SBF, although a glass in the system  $\text{CaO}$ - $\text{P}_2\text{O}_5$  does not [78,79]. The former glasses form a silica hydrogel layer prior to the nucleation of apatite. Pure silica gel, prepared by the sol-gel method, forms an apatite layer on its surface when soaked in SBF, although neither silica glasses nor crystalline quartz form the apatite layer [80]. The apatite-forming ability of silica gel depends on the heat-treatment temperature. Silica gel prepared from the hydrolysis of tetraethoxysilane followed by heating at a temperature of 800°C or lower formed an apatite layer on its surface, although that heated at 900°C or higher did not [81]. Therefore, hydrated silica gel, or more specifically, silanol groups on the silica gel surface could be responsible for the nucleation and formation of the apatite layer.

It has been suggested that silica dissolved in solution also contributes to apatite formation [82]. Polyether sulfones treated with  $\text{O}_2$  plasma were placed in SBF parallel to plates of silica gel and silica glass with various silica solubilities at a distance of 0.5 mm. After four days soaking, the polyether sulfone plates were removed from the SBF and soaked in 1.5SBF that has ionic concentration 1.5 times that of SBF. All of the silica gel plates released silicate ions in the SBF at the first soaking, although the silica glass plates did not. The dissolved silicate ions adsorbed to the polyether sulfone plates. Only polyether sulfone plates with adsorbed silicate formed an apatite layer on their surface during the second soaking. Therefore, silicate ions dissolved from the silica gel and adsorbed to the substrates have apatite-forming ability.

Apatite can also deposit on polymer surfaces with appropriate functional groups. Poly(ethylene oxide) (PEO)/poly(butylene terephthalate) (PBT) copolymer

induces apatite deposition because of the presence of the hydrophilic PEO component [83]. Polar groups such as carboxylic and carbonyl groups introduced on polyether sulfone by glow discharge treatment in O<sub>2</sub> gas effectively induced apatite nucleation on the surface of polyether sulfone in SBF [84]. Methacryloyloxyethylene phosphate (MOEP) with the chemical structure CH<sub>2</sub> = C(CH<sub>3</sub>) - CO - OCH<sub>2</sub>CH<sub>2</sub>O - PO - (OH)<sub>2</sub> was graft-polymerized onto the surface of poly(ethylene terephthalate) (PET). Apatite was rapidly deposited on this polymer substrate with phosphate graft chains in a supersaturated solution. It is considered that the graft chains produced some interfacial bonds with the deposited hydroxyapatite layer [85]. Phosphorylated polymer surfaces also induce hydroxyapatite deposition [86]. Hydroxyapatite was formed on self-assembled monolayers (SAMs) of alkanethiols with CH<sub>3</sub>, PO<sub>4</sub>H<sub>2</sub>, COOH, CONH<sub>2</sub>, OH, and NH<sub>2</sub> terminal groups in SBF [87]. The most potent inducer of apatite nucleation was the SAM with PO<sub>4</sub>H<sub>2</sub> groups. The SAMs with CONH<sub>2</sub>, OH, and NH<sub>2</sub> groups possess much weaker inducing ability, and that with CH<sub>3</sub> possesses the least ability. The growth rate of hydroxyapatite on these SAMs shows a tendency similar to their nucleation ability: the growth rate decreased in the order PO<sub>4</sub>H<sub>2</sub> > COOH >> CONH<sub>2</sub> ≡ OH > NH<sub>2</sub> >> CH ≡ 0. Negatively charged groups strongly induced apatite formation although positively charged groups did not.

Hydroxyapatite crystals were precipitated on compressed Langmuir monolayers [88]. Langmuir monolayers of surfactant molecules can be used as molecular templates for the oriented nucleation of either organic or inorganic crystals. The compressed Langmuir monolayer of stearic acids was effective for the nucleation of hydroxyapatite from a subphase solution prepared by mixing a calcium hydrogen-carbonate solution (Ca: 5.0 mM), an ammonium hydrogen phosphate dibasic solution (P: 3.0 mM), and CO<sub>2</sub> gas. As CO<sub>2</sub> gas was liberated from the solution, hydroxyapatite crystals precipitated because of the increase in pH. The nucleation of hydroxyapatite occurred mainly at the air/water interface. The (00l) planes of hydroxyapatite were parallel to the interface. It was considered that the hydroxyapatite was nucleated epitaxially because the arrangement of calcium in the hydroxyapatite (00l) plane is very similar to that of the stearic acid head groups in the monolayer.

Heterogeneous nucleation of apatite is also affected by the surface charge of substrates. Negatively charged substrates accelerated the nucleation and growth of apatite in 1.5SBF compared with uncharged and positively charged substrates [89]. Hydroxyapatite ceramics (1 mm thick) sintered at 1200°C with a flow of steam were electrically polarized at 120 V/mm for one hour in a dc field at 300°C followed by immersion in 1.5SBF. Apatite was formed within 6 to 12 hours on the negatively charged surface of the hydroxyapatite disk, although no growth occurred on the positively charged surface even after immersion for three days. The growth rate on the negatively charged surface was six times higher than that on the uncharged surface.

A study for comprehensive understanding of the factors that control the heterogeneous nucleation of calcium phosphates has been carried out by analyzing the surface tension components for silicone rubber, poly(methyl methacrylate), poly(tetrafluoroethylene-co-hexafluoropropylene), anatase, and rutile [90]. Al-

though the Lifshitz-van der Waals surface tension components are approximately the same for all these materials, the Lewis acid-base surface tension components vary greatly. Effective nucleation of calcium phosphates was observed only on surfaces with relatively high values of the Lewis acid-base surface tension component. Comparison of the induction time for the heterogeneous nucleation of hydroxyapatite on rutile and anatase surfaces revealed that the induction time on the anatase surface was much shorter than that on the rutile surface under the same supersaturation. The calculated surface tension components showed a very high value of the Lewis base surface tension parameter associated with the anatase surface,  $48 \text{ mJm}^{-2}$ , in comparison with that associated with the rutile surface,  $16 \text{ mJm}^{-2}$  [91].

Hydroxyapatite was formed on collagen in the presence of poly-L-aspartate (MW 13700) by mixing a calcium-containing collagen solution and a neutral phosphate solution [92]. It is known that bone mineralization is controlled by so-called noncollagenous proteins containing unusual amounts of anionic amino acids such as aspartate and glutamate (see Section 16.8). For this reason, polyaspartate and polyglutamate have been used as model compounds for the noncollagenous proteins. Indeed, polyaspartate and polyglutamate strongly affect the kinetics of calcium phosphate formation by interacting with calcium. The calcium-containing collagen solution was prepared by adding a calcium chloride solution to a collagen solution. The calcium-containing collagen solution was mixed with a potassium phosphate solution buffered at pH 7.4 containing poly-L-aspartate. The reaction is a combination of collagen fibril formation and calcium phosphate formation. In this way, a homogeneously mineralized collagen gel was obtained with a three-dimensional network of collagen fibrils covered by calcium phosphate, which is probably an intermediate phase between octacalcium phosphate and hydroxyapatite. In the absence of poly-L-aspartate, calcium phosphate microcrystals aggregated spherically and loosely bound to the fibrils. However, in the presence of poly-L-aspartate, the microcrystals located separately on or inside the collagen fibrils. The adsorption of two polyelectrolytes, poly-L-glutamate (25.2 KD) and poly-L-aspartate (28.8 KD), on hydroxyapatite crystals was studied both experimentally and theoretically [93]. Langmuir adsorption isotherms were obtained for both polyelectrolytes, with binding constants of  $K = 6 \times 10^6$  and  $3 \times 10^6 \text{ M}^{-1}$ , respectively, at  $37^\circ\text{C}$ , at pH 7.4 and at an ionic strength of 0.15 M. Theoretical analysis indicated the presence of a “train-loop” type of adsorption of the molecules on the surface of hydroxyapatite, where a 42% portion of the molecular chain is attached to hydroxyapatite.

Hydroxyapatite was formed using alkaline phosphatase and calcium  $\beta$ -glycerophosphate solutions at pH 9.0 and  $37^\circ\text{C}$ . Alkaline phosphatase is an enzyme that catalyzes the hydrolysis of phosphate monoesters to form inorganic orthophosphate ions. The optimal pH for alkaline phosphatase activity is 10. Alkaline phosphatase is present on the cell membrane of osteoblasts and plays important roles in bone formation. It was demonstrated that apatite grew on a modified collagen tape in solutions containing alkaline phosphatase, calcium  $\beta$ -glycerophosphate, and phosvitin (a phosphoprotein), through the decomposition of

calcium  $\beta$ -glycerophosphate by alkaline phosphatase [94]. The collagen tape functioned as a template for inducing apatite deposition. Although the mechanism associated with collagen templating remains unknown, this method was applied in the production of apatite-collagen complexes for bone substitutes [95]. Reconstituted type I collagen as well as sheet collagen was cross linked in the presence of alkaline phosphatase and egg-yolk phosvitin. The cross linked collagens were immersed in daily-renewed calcium  $\beta$ -glycerophosphate solutions for two or four weeks to induce the deposition of apatite on the collagen fibers. The complex showed visible elastic deformation without detachment of apatite crystals, which is never shown by sintered hydroxyapatite ceramics. The complex material resembles bone more closely than any other currently available material.

Supersaturated bicontinuous microemulsions were used to synthesize polycrystalline hydroxyapatite with an organized microstructure. In a typical experiment, freshly prepared supersaturated calcium phosphate solution was added dropwise to a stirred mixture of didodecyldimethylammonium bromide and alkane oils. The mixtures were stored at various temperatures from  $-25$  to  $+46^\circ\text{C}$  for 3 to 90 days. Nucleation of apatite occurred within the nanometer-size water conduits of the oil/water microemulsions. After extraction of the oils, the polycrystalline hydroxyapatite material exhibited a microskeletal or “reticulated” architecture composed of micron-sized crystals [96,97].

## 16.5 Calcium Phosphate Cements

Hardening of calcium phosphate cements for dental and orthopedic uses involves hydroxyapatite growth. Calcium phosphate cements are of considerable interest in medicine and dentistry owing to their biocompatibility, bioactivity, ability to form *in situ*, and ability to harden *in vivo*. Calcium phosphate cement paste is used to fill the spaces between prosthetic implants and bone tissue, to fill the defects in dental enamel and dentin, and to fill dental pulp cavities.

Calcium phosphate cements consist of combinations of aqueous solutions and powders of calcium phosphates, except hydroxyapatite. The calcium phosphate powders convert into calcium-deficient hydroxyapatite or octacalcium phosphate in aqueous solutions by hydrolysis because hydroxyapatite is the most stable phase in water at neutral pH. Interwinding and heterogeneous nucleation of micro crystals of calcium-deficient hydroxyapatite cause the hardening of calcium phosphate cements. The hardening of calcium phosphate powder was first reported by Monma for  $\alpha$ -tricalcium phosphate in water [98]. However, this cement required two hours at  $80^\circ\text{C}$  to harden and was far from satisfying clinical requirements. Many  $\alpha$ -tricalcium phosphate cements using organic acid solutions were developed in the 1980s with satisfactory reduction in the hardening time and improved mechanical strength. However, the organic acid solution was less biocompatible, evoking an adverse tissue reaction because of its low pH. To overcome this problem, two  $\alpha$ -tricalcium phosphate cements without using organic acids were developed which harden at neutral pH [99]. They are the mixtures of 95–90%  $\alpha$ -

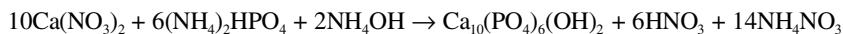
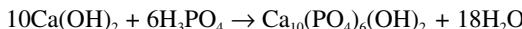
tricalcium phosphate and 5–10% dicalcium phosphate dihydrate heated at 1250°C with a Ca/P ratio of 1.47, accompanied by a solvent containing 10% sodium chondroitin sulfate, 12% sodium succinate, and 78% water.

Another class of calcium phosphate cement uses tetracalcium phosphate and dicalcium phosphate dihydrate or dicalcium phosphate anhydrous as cement powders which harden at or near neutral pH [100,101]. Calcium-deficient hydroxyapatite with a Ca/P molar ratio of 1.5 is formed initially in the hardening of an equimolar mixture of tetracalcium phosphate and dicalcium phosphate anhydrous. The calcium-deficient hydroxyapatite exhibits a gradual increase in Ca/P molar ratio, a process of so-called maturation. An excess amount of dicalcium phosphate anhydrous in the mixture delays the increase in Ca/P molar ratio during hardening. The highest mechanical strength of the set cement is associated with an equimolar mixture of tetracalcium phosphate and dicalcium phosphate anhydrous. The setting reaction and the properties of the set cement are highly dependent on the molar ratio of tetracalcium phosphate to dicalcium phosphate anhydrous [102].

A paste consisting of monocalcium phosphate monohydrate,  $\alpha$ -tricalcium phosphate, calcium carbonate, and a sodium phosphate solution has useful rheological characteristics before hardening, and thus can be implanted into fractured sites in bone by the minimally invasive means of injection through the skin to repair the fracture [103]. The paste hardens in minutes, concurrent with the formation of carbonate-containing hydroxyapatite under physiological conditions, with an ultimate compressive strength of 55 MPa.

## 16.6 Hydroxyapatite Ceramics

The manufacture of hydroxyapatite ceramics involves processes related to crystal growth. Hydroxyapatite ceramics are used as artificial bone to repair bony defects, to augment alveolar ridges, to enhance guided tissue regeneration, and to reconstruct the middle ear in either porous sintered bodies or dense sintered bodies. The preparation of hydroxyapatite ceramics consists of three steps: (1) preparing the apatite powder, (2) compacting it into a desired shape, and (3) sintering it in the temperature range of 900 to 1200°C. For preparing apatite powders, the following two reactions are widely utilized:



A typical example of the former reaction is the drop wise addition of a 1.8 mol/L solution of  $\text{H}_3\text{PO}_4$  into a 3 mol/L suspension of  $\text{Ca}(\text{OH})_2$  in water with vigorous stirring [104,105]. After the addition of  $\text{H}_3\text{PO}_4$ , the reaction mixture is aged for 3 to 48 hours to complete the reaction. Because the solubility of  $\text{Ca}(\text{OH})_2$  is as low as 0.02 mol/L at the saturation point in water, the mechanism of apatite formation is not likely to be a simple ionic reaction; this remains to be clarified. The reaction product is poorly crystallized apatite with a crystallite size of 30 to 50 nm, as de-

terminated by the Debye-Scherrer method, or that of approximately 15 to 50 nm, as determined by transmission electron microscopy. The poorly crystallized apatite is heated over the temperature range of 700 to 850°C before compaction. During this heat treatment, the apatite particles grow to a size of 50 to 100 nm. By sintering the compacted apatite powder, the particles grow further to a size of 600 nm to 3 µm.

## 16.7 Hydrothermal Growth of Hydroxyapatite

The most successful method to grow hydroxyapatite single crystals is hydrothermal synthesis (Table 16.4). Using hydrothermal methods, crystals with sizes larger than one millimeter have been grown in the temperature range of 200 to 700°C. A review of earlier works was published by Skinner (1974) [106] and Elliott (1994) [107]. Phase diagrams in the system CaO-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O were reported in the temperature range of 300 to 600°C at 200 MPa and in the temperature range of 700 to 950°C at 100 MPa [106,108]. Because hydroxyapatite exhibits retrograde solubility, a gradual increase in temperature is an effective way to grow large crystals [109]. Flux-grown single crystals of hydroxyapatite or carbonated apatite were prepared in the temperature range of 745 to 1400°C.

Hydrolysis reactions employed in the hydrothermal growth of hydroxyapatite single crystals lead to the production of phosphoric acid that decreases the pH. For example:



Hydroxyapatite crystals tend to grow larger in acidic hydrothermal solutions than in neutral or alkaline solutions. However, the excess H<sup>+</sup> ions in the solution are readily incorporated into the hydroxyapatite lattice, resulting finally in the formation of calcium-deficient hydroxyapatite crystals with a Ca/P molar ratio lower than the stoichiometric value of 1.67.

Hydrothermal techniques are used to stabilize plasma-sprayed apatite coated on metallic implants. The plasma-sprayed apatite layer contains amorphous calcium phosphate, α-tricalcium phosphate, calcium oxides, and/or tetracalcium phosphate phases, all of which are the decomposition products of hydroxyapatite formed at a high temperature of ~10,000°C associated with the plasma-spraying process. To convert the decomposition products into hydroxyapatite, the coated implants are treated hydrothermally or heated in water vapor after plasma spraying.

Hydroxyapatite whiskers have been prepared by the hydrothermal method to develop new asbestos-substituting materials. Hydroxyapatite whiskers could be the most biocompatible material among the currently available inorganic fibrous materials such as glass, carbon, asbestos, SiC, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>. Moreover, stoichiometric hydroxyapatite has better heat resistance than chrysotile, the main component of asbestos: it has a decomposition temperature of 1200°C which is 600°C higher than that of chrysotile [117]. Although hydrothermally synthetic

**Table 16.4.** Hydrothermal Growth of Hydroxyapatite

Starting Material	Method	Temp. °C	Pressure MPa	Product	Size mm	Ref.
DCPA	hydrolysis	300	8.6	HAP		110
HAP	recrystallization	430–500	200	HAP	3.5	111
TCP-Ca(OH) <sub>2</sub>	flux growth	900–775	103	HAP	4	112
TCP-Ca(OH) <sub>2</sub> -H <sub>2</sub> O	flux growth	900–745	103	HAP	4	112
DCPA, CO <sub>2</sub>	hydrolysis	180–290		A-CHAP*	12.5×0.2	109
DCPA	hydrolysis	170–230		HAP	8.3	113
HAP	recrystallization	390–470	310–412	HAP	7×7×0.2	114
TCP, CaCO <sub>3</sub>	hydrolysis	850	15	A-CHAP		115
TCP, Ca(OH) <sub>2</sub> , CaCO <sub>3</sub>	hydrolysis	750–900	103	B-CHAP <sup>†</sup>		115
αTCP-CaCO <sub>3</sub>	flux growth	1400	54	AB-CHAP <sup>‡</sup>	0.7	116

\*A-CHAP: A-site (OH site) carbonated hydroxyapatite

<sup>†</sup>B-CHAP: B-site (PO<sub>4</sub> site) carbonated hydroxyapatite

<sup>‡</sup>AB-CHAP: Both A and B-site carbonated hydroxyapatite

whiskers are calcium-deficient hydroxyapatite with lower heat resistance, their Ca/P molar ratio is improved to the stoichiometric value of 1.67 after heating with calcium carbonate at 600°C [118]. The hydrothermally synthetic hydroxyapatite whiskers have diameter, length, and aspect ratio in the range of 1 to 10 μm, 30 to 50 μm, and 5 to 20, respectively. The mechanical properties of hydroxyapatite whiskers were measured by three-point bending and tensile tests. The three-point bending strength is 500 ± 184 MPa in air and 454 ± 204 MPa in water [119]. The tensile strength is 410 ± 13 MPa in air [113].

A porous hydroxyapatite body for use as an implant material is prepared from coral skeletal calcium carbonate by hydrothermal conversion, in addition to the conventional ceramic manufacturing processes [120]. The open pore structure of porous hydroxyapatite bodies is clinically important because vascular formation in the pores promotes bone ingrowth and regeneration. However, it is difficult to manufacture a porous body, by the conventional ceramic processes, with sufficiently open and interconnected pores and with mechanical strength at a level that satisfies clinical requirements. Coral skeletal calcium carbonate has an open and interconnected pore structure and is hydrothermally converted into hydroxyapatite according to the following reaction:



The reaction takes place in a temperature range of 180 to 250°C while maintaining the porous structure of the coral skeleton. A topotactic reaction of aragonite with phosphate would take place in the hydrothermal conversion into hydroxyapatite [121].

## 16.8 Factors Influencing Apatite Formation in Hard Tissues

Apatite is formed in bone, dentin, and dental enamel in vertebrates. Bone and dentin belong biologically to the same class of tissue originating from the mesoderm, although dental enamel originates from the ectoderm; this means that dental enamel is a completely different tissue from bone and dentin, and is rather close to skin. Therefore, in the mechanism of formation, cells and proteins involved are somewhat similar between bone and dentin, but very different between dental enamel and these two calcified tissues. Bone and dentin consist of cells, matrix protein (approx. 30 wt%), and apatite (approx. 70 wt%). The most important cells in bone are osteoblasts and osteoclasts. Osteoblasts form apatite and matrix proteins, although osteoclasts dissolve them by decreasing the local pH and using various enzymes. Cells involved in the formation of dentin are called odontoblasts. In dentin, there are no cells corresponding to the osteoclasts in bone. Dental enamel consists of 2 to 6 wt% protein and 94 to 98 wt% apatite with no cells. Dental enamel is formed by ameloblasts.

Various factors influence apatite formation in bone, dentin, and dental enamel (Table 16.5). The *in vivo* formation and dissolution of apatite are controlled not only by physicochemical factors such as inhibitors, promoters, and supersaturation but also by other cell-biological factors. The cell-biological factors, which regulate various cells, include matrix proteins, growth factors, growth hormones, and essential trace elements. Several factors show the opposite effect on apatite formation under different conditions.

The matrix proteins of bone and dentin consist of a large amount of collagen (50–90%) and a small amount of noncollagenous proteins [122]. Collagen in bone and dentin are mainly Type I collagen. Noncollagenous proteins include osteopontin, osteocalcin (bone Gla protein), bone sialoprotein, and osteonectin for bone, and dentin phosphophoryn and osteocalcin for dentin (Table 16.5). Many of these noncollagenous proteins show inhibitory effects on hydroxyapatite formation when they are present in solution as free molecules, although some of them show promotive effects when they are immobilized on substrates such as agarose and collagen. These opposite effects are considered to result from the conformational differences in these proteins when they are present as free molecules and as immobilized ones. Moreover, many of the noncollagenous proteins show concentration-dependent promoting and inhibiting effects on hydroxyapatite formation, promoting at low concentrations and inhibiting at high concentrations [123,124].

Type I collagen is the most abundant protein among bone matrix proteins. Type I collagen in bone is produced from the same gene as that in noncalcified tissue. Therefore, Type I collagen in bone is essentially the same molecule as that in noncalcified tissue. The differences between bone Type I collagen and that in noncalcified tissue arise from the so-called posttranslational modification. This modification includes hydroxylation of lysine residues, glycosylation of hydroxylysine, and phosphorylation, and is believed to play an integral role in collagen mineralization [125]. From the viewpoint of hydroxylation, for example, the extent of hy-

droxylation of lysine residues is much higher in bone collagen than in noncalcified tissue. The extent and site of the hydroxylation governs cross-linking patterns, hence, packing of collagen molecules. It is noteworthy that the average gap between collagen molecules in tendons (0.3 nm) is smaller than the diameter of phosphate ion, although that in bone (0.6 nm) is larger than that of phosphate ion which enables the phosphate ions migrate into collagen fibrils [126].

Apatite crystals grow preferentially lengthwise in the direction of the long axis of collagen and in width along channels or grooves that are formed by adjacent hole zones of collagen [127]. However, numerous studies indicate that collagen is not a direct nucleator of apatite deposition. Rather, collagen provides a template for mineral deposition which may be initiated by associated noncollagenous proteins [128].

Osteocalcin is the most abundant protein among the noncollagenous proteins in bone, and is produced by osteoblasts [122,128]. Osteocalcin contains  $\gamma$ -carboxyglutamic acid (Gla) and has affinity with calcium and hydroxyapatite. However, a number of studies have demonstrated the inhibitory effects of osteocalcin on hydroxyapatite formation. In dentin, osteocalcin is a very minor constituent. Osteocalcin appears to be more involved in the regulation of bone turnover, particularly in the inhibition of hypercalcification.

Osteopontin and bone sialoprotein have many similarities in their structures, that is, they contain many sugar chains with sialic acid [122,128]. They both have the Arg-Gly-Asp sequences for cell attachment. However, osteopontin inhibits hydroxyapatite formation whereas bone sialoprotein promotes it. The promotional effects of bone sialoprotein on hydroxyapatite formation are due to the poly(glutamic acid) sequences that are present in bone sialoprotein and absent in osteopontin. Osteopontin is a prominent constituent of bone matrix and dental cementum.

Dentin phosphophoryn is dentin-specific and is also the most abundant noncollagenous protein in dentin [129]. Dentin phosphophoryn contains approximately 40% aspartic acid and 50% serine. Most serine residues are phosphorylated, resulting in a very high negative charge density.

Osteonectin is a glycoprotein that is present in high concentrations in bone. The role of osteonectin in apatite formation is less clear [122,128].

Zinc and magnesium are typical inorganic inhibitors of hydroxyapatite formation [130–132]. The former is 100 to 1000 times more effective in inhibiting hydroxyapatite growth than the latter. The inhibitory effect arises partly from the mismatch of the ionic radius between these elements (Mg: 0.072 nm and Zn: 0.075 nm) and calcium (0.100 nm). These ions are adsorbed on the surface of hydroxyapatite and inhibit the growth. However, trizinc phosphate octahydrate (hopeite) formation on the surface is also involved in the inhibitory mechanism. In contrast, a small amount of zinc stimulates osteoblast activity and suppresses osteoclast activity, resulting in enhancement of bone formation [133–136]. The mechanism of the stimulatory effect of zinc on bone formation is not sufficiently clear because of the presence of many zinc-containing proteins and enzymes in the cells.

**Table 16.5.** Matrix Proteins and Ions Influencing Hydroxyapatite Growth

	Hydroxyapatite formation	Remarks
Type I collagen	—	serves as a template for mineral deposition
OPN	inhibits formation [137–139]	promotes cell attachment [58] an acidic protein
OC(f)	inhibits formation [140,141]	inhibits hyperactivity of osteoblasts [142]
OC(i)	inhibits seeded growth [143,144] promotes or no effect [145,146]	binds to HAP, but not to ACP [140] affinity for HAP (100) face [147] affinity for collagen [148] an acidic protein
ON(f)	inhibits formation [141] inhibits seeded growth [143,149,150]	binds to HAP and Type I collagen [149]
ON(i)	no effect (on agarose) [145] inhibits and promotes formation (on collagen) [151,152]	affinity for HAP (100) face [147] an acidic protein
DPP(f)	inhibits formation [141] inhibits growth [154] promotes formation at low conc. [123]	affinity for collagen [153] affinity for Ca and PO <sub>4</sub> ions [155] affinity for HAP (100) face [147]
DPP(i)	promotes nucleation promotes formation [145,146,156,157]	an acidic protein
BSP(f)	promotes nucleation [158]	promotes cell attachment [159] affinity for collagen [148] promotes osteoblast differentiation [160] an acidic protein
EN(f)	inhibits formation [161]	an acidic protein
AM(f)	inhibits formation [161,162]	
Zinc	inhibits formation [163] inhibits seeded growth [130,132]	promotes osteoblast activity [133,164]
Magnesium	inhibits seeded growth [130,132]	
Fluorine	promotes formation	fluorosis in dental enamel at an elevated concentration

OPN: osteopontin; OC: osteocalcin; BSP: bone sialoprotein; ON: osteonectin; DDP: dentin phosphophoryn; EN: Enamelin; AM: Amelogenin. Symbols (f) and (i) indicate free and immobilized proteins, respectively.

## 16.9 Ectopic Calcifications

Hydroxyapatite growth is often associated with pathological and ectopic calcifications such as arteriosclerotic calcification, dental calculus, and urinary stones.

In human atherosclerotic lesions, cholesterol often coexists with calcium-containing deposits that are most likely hydroxyapatite [165]. Crystallographically, hydroxyapatite and cholesterol monohydrate usually develop (001) faces. A fit of the (001) planes shows close superposition of the hydrogen bonding groups from the two crystal structures [166]. The corresponding superlattice nets have  $a = 1.884$ ,  $b = 1.631$  nm,  $\gamma = 90^\circ$  for hydroxyapatite and  $a = 1.913$ ,  $b = 1.584$  nm, and  $\gamma = 90.1^\circ$  for cholesterol monohydrate. Each structure may serve as a nucleus for the growth of the other crystal, utilizing the intervention of a transition layer of hydrogen-bonded water molecules. It is therefore possible that cholesterol monohydrate is implicated in calcification often associated with the later stages in the development of atherosclerotic plaques. *In vitro* nucleation of cholesterol crystals on hydroxyapatite occurred when hydroxyapatite seeds were immersed in an ethanolic solution of cholesterol that was very slightly supersaturated with respect to cholesterol [167].

However, evidence is accumulating that vascular calcification is an active process that has many similarities with ossification. Messenger RNAs (mRNAs) for OP, ON, OC, and bone morphogenetic protein type 2 (BMP-2) were detected in calcified atherosclerotic plaques. This indicated that there were cells producing OP, ON, OC, and BMP-2 in the calcified plaques. All these proteins are commonly associated with normal calcification and remodeling of bone. In particular, OC and BMP-2 are bone-specific proteins produced by osteoblasts. The origins of bone-forming cells and osteoclast-like cells in the artery wall remain unknown. It is considered that calcification in coronary artery disease is not a passive process but an active process closely associated with plaque development, which is regulated in a fashion similar to bone mineralization [168–171].

Dental calculus is mineralized dental plaque formed both above (supragingival) and below (subgingival) the gumline dental enamel [172]. Mineral crystals found in human dental calculus are typically calcium phosphates including dicalcium phosphate dihydrate, octacalcium phosphate, hydroxyapatite, and magnesium-substituted whitlockite [173]. It has been suggested that calculus mineralization begins with the deposition of kinetically favored precursor phases such as dicalcium phosphate dihydrate and octacalcium phosphate, and is followed over time by maturation into hydroxyapatite and whitlockite phases.

The development of human dental calculus invariably involves plaque bacterial calcification. Dental plaque consists of approximately 80% water, 14% microorganisms, and 6% organic materials including a numbers of proteins. Dental plaque itself adsorbs calcium and phosphate from the surrounding fluids such as saliva for supragingival calculus and crevicular fluid for subgingival calculus, resulting in an increase in supersaturation. Areas adjacent to saliva ducts where fresh saliva is supplied tend to suffer more from calculus formation than any other areas [174]. Supersaturation can also increase by a local increase in pH, which is caused by bacterial ammonium formation [175]. Cell membranes of microorganisms containing phospholipids act as nucleation sites for calcium phosphates. Nonviable microorganisms are unable to maintain cytoplasmic fluid, a phosphate buffer solution inside the microorganisms, and are also unable to block calcium inflow into microorganism from the surrounding fluid. The contribution of the cell membrane

and nonviable microorganisms to calcification is quite similar to the case of the calcification of bioprosthetic valves (see Section 16.3.2). Other factors contributing to calculus mineralization may include salivary ion levels and dietary components such as silicon [176]. On the other hand, natural inhibitory factors may include salivary phosphoproteins and pyrophosphate. Clinical strategies to inhibit dental plaque mineralization include utilization of pyrophosphate, gantrez acid copolymer, and zinc citrate with antimicrobial ingredients as dentifrice components [172].

In urinary stones, hydroxyapatite is not necessarily the major component. However, 56.4 to 62% of urinary stones still contain hydroxyapatite as one of the crystalline components [177]. Other crystalline components include calcium oxalate, dicalcium phosphate dihydrate, magnesium ammonium phosphate, uric acid, and cystine. Most urinary stones are admixtures of two or more components, with the primary admixture being calcium oxalate and hydroxyapatite [177,178]. Hydroxyapatite-containing urinary stones often possess a periodically laminated central structure [177].

## 16.10 Kinetics of Hydroxyapatite Crystal Growth in Solution

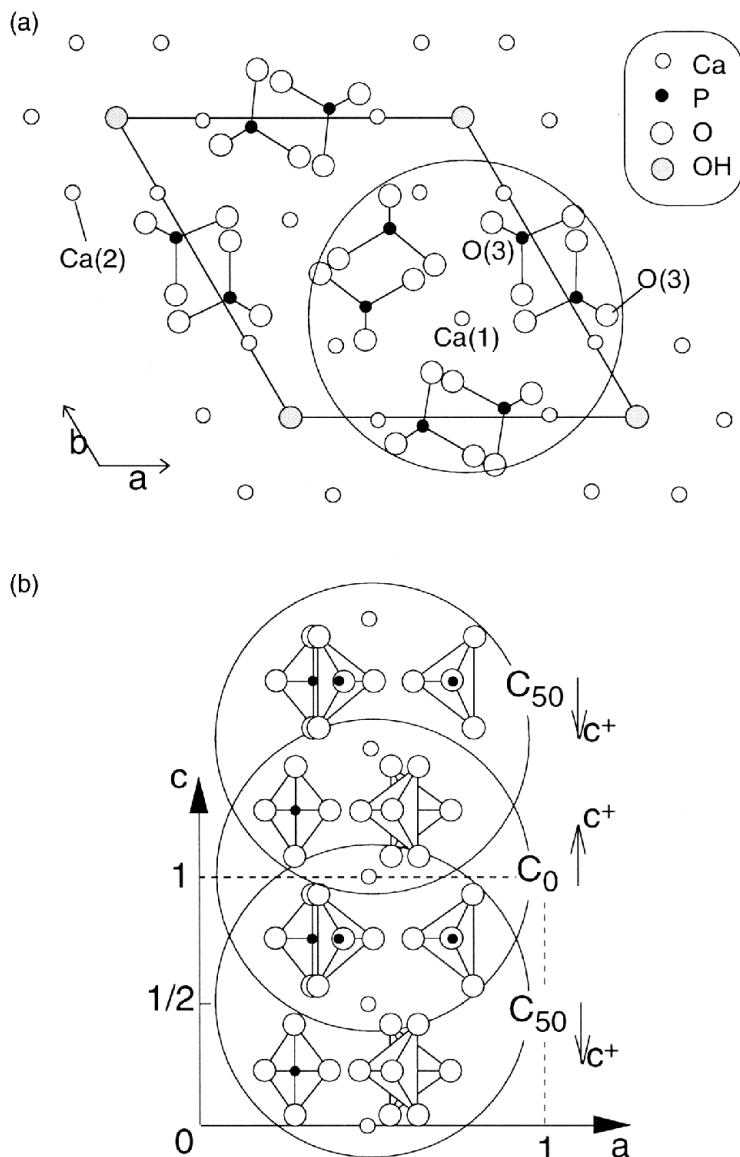
Most information about kinetics of hydroxyapatite crystal growth has been obtained from the constant pH method or the constant composition method [179,180]. Depending on supersaturation, precursors appear such as octacalcium phosphate, dicalcium phosphate dihydrate, or an amorphous phase with a Ca/P molar ratio of  $1.45 \pm 0.05$  [181–183]. In a less supersaturated solution, there is general agreement that the growth rates are too low to be transport-controlled. Many studies have shown the values of the effective reaction order,  $n$ , to range from 2.1 to 4.0 in the formula

$$R = k\sigma^n,$$

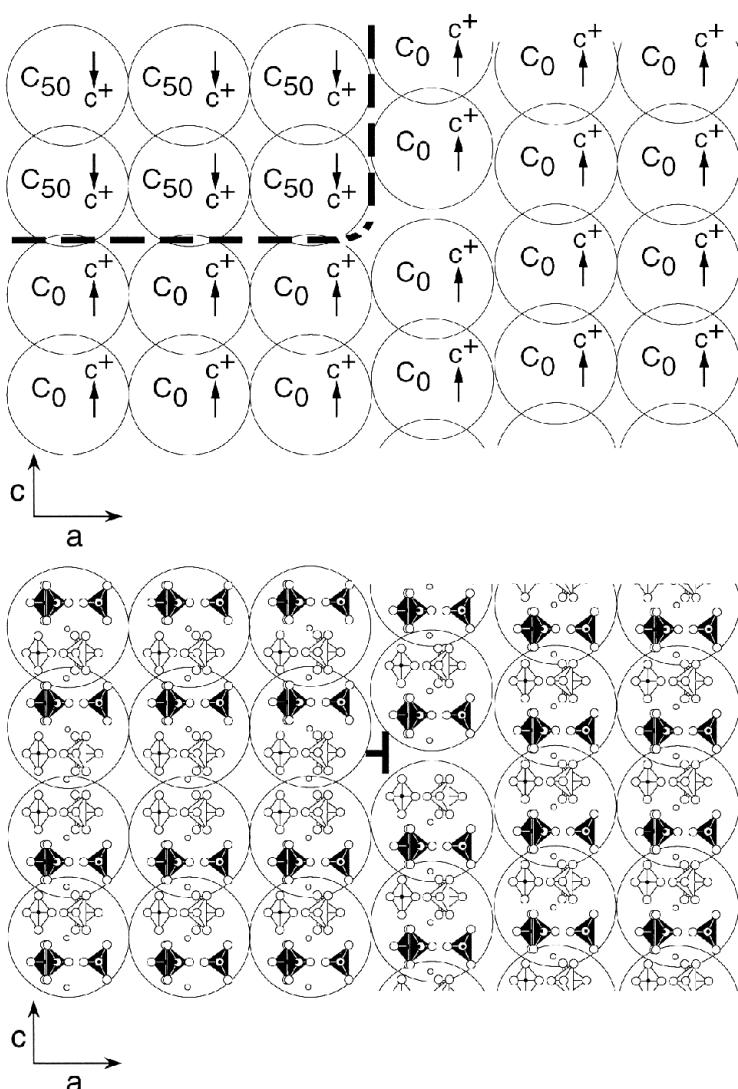
where  $R$ ,  $k$ , and  $\sigma$  are growth rate, effective rate constant, and thermodynamic driving force, respectively [184]. This indicates the involvement of a polynucleation mechanism. Values of interfacial tension between hydroxyapatite surfaces and the solution phases ranged from 10 to 120  $\text{mJm}^{-2}$  [184]. Values of interfacial tension obtained from growth data are greater than those obtained from dissolution kinetics. Growth rate measurement for hydroxyapatite at very low supersaturation demonstrated that the linear growth rate as a function of driving force in the pH range of 5.0 to 6.5 was different from that in the pH range of 7.0 to 8.5 [185]. As a result, the growth rate of hydroxyapatite is approximately 2.5 times larger in the pH range of 5.0 to 6.5 than in the pH range of 7.0 to 8.5 even under the same supersaturation. Between these pH ranges, there is the point of zero charge of hydroxyapatite at about pH 7.0, which were verified experimentally [186,187]. An understanding of the apparent change in the kinetics of hydroxyapatite growth at pH above and below this value may require elucidation of the role of surface

charge on crystallization. A similar pH dependence of the growth rate was reported for the growth of dicalcium phosphate dihydrate [185].

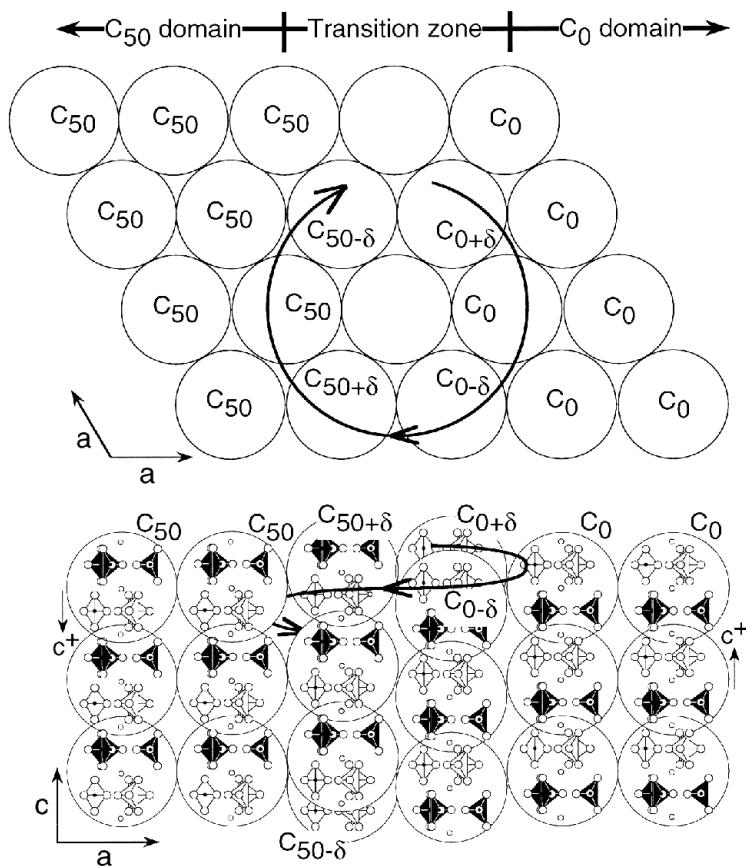
Using atomic force microscopy and large single crystals of hydroxyapatite as seeds, *in situ* growth observation was performed in a simulated body fluid [109,188,189]. Under this condition, growth on the *c*-face proceeded by a polynuclear mechanism and no spiral growth was observed. Growth on the *a*-face proceeded by step flow with step heights of 0.8 and 1.6 nm as well as by two-dimensional nucleation. Step velocity on the *a*-face as functions of the step height and interstep distances indicates that none of volume diffusion, surface diffusion, nor dehydration of growth units determines the growth rate. The step kinetic coefficient,  $\beta$ , which is the reciprocal of the relative resistance to incorporation of a growth unit into the bulk crystal, was calculated to be  $0.4 \times 10^{-4}$  cm/s. This value is 100 to 1000 times lower than those of other inorganic crystals, and is comparable to those of protein and virus crystals growing by the unit of a macromolecule which have extremely low probability of incorporation [190]. The value of edge free energy of hydroxyapatite also shows similarities to that of protein and virus crystals [191]. Therefore, it is possible that the growth units of hydroxyapatite are not simple spherical ions but calcium phosphate clusters. The presence of calcium phosphate clusters with a size of approximately 0.8 nm was demonstrated by dynamic light scattering measurements, in a magnesium-carbonate-free simulated body fluid, the simulated body fluid (SBF in Table 16.3), and other calcium phosphate solutions [192–194]. The calcium phosphate clusters were detected even when the solutions were undersaturated with respect to amorphous calcium and octacalcium phosphates and were supersaturated with respect only to hydroxyapatite. On the basis of these findings, a cluster growth model for hydroxyapatite is proposed in which hydroxyapatite grows by hexagonal packing of  $\text{Ca}_9(\text{PO}_4)_6$  clusters 0.8 nm in size [192]. Stacking faults of clusters can create a reflection twin crystal, edge dislocations with Burgers vector of  $C/2$ , and screw dislocations (Figs. 16.1, 16.2 and 16.3). Therefore, spiral dislocations can be introduced even when hydroxyapatite does not grow by the spiral growth mechanism. The same type of  $\text{Ca}_9(\text{PO}_4)_6$  cluster exists in the structure of amorphous calcium phosphate and octacalcium phosphate, both of which are the precursors of hydroxyapatite. Theoretically, clusters with a size smaller than that of the critical nucleus can exist stably in solutions when the size dependence of surface tension is taken into account in the theory of homogeneous nucleation [195]. *Ab-initio* calculation revealed a large stabilization energy associated with the clustering of  $\text{Ca}_3(\text{PO}_4)_2$  species with a  $D_{3h}$  symmetry in vacuum [196].



**Fig. 16.1.**  $\text{Ca}_9(\text{PO}_4)_6$  cluster unit,  $\text{C}_0$  and  $\text{C}_{50}$ , projected on the  $ab$  plane (a) and  $ac$  plane (b) of the hydroxyapatite. Because both cluster units have only  $\text{C}_3$  symmetry (noncentrosymmetric) and are related by mirror planes at  $z = 1/4$  and  $3/4$ , they are chiral. (Reprinted with permission from Onuma, K., Ito, A. *Chemistry of Materials*, 10:3346–3351 (1998). Copyright 1998 American Chemical Society.)



**Fig. 16.2.** A edge dislocation with Burgers vector of  $C_0$ /2 formed by stacking fault of  $C_0$  and  $C_{50}$  clusters. The interface between  $C_0$  domain and  $C_{50}$  domain is perpendicular to the  $c$ -axis, and the  $C^+$  direction of each domain is anti-parallel.



**Fig. 16.3.** A screw dislocation formed by a stacking fault of  $C_0$  and  $C_{50}$  clusters. The interface between the  $C_0$  domain and the  $C_{50}$  domain is parallel to the  $c$ -axis, and the  $C^+$  direction of each domain is anti-parallel. In the transition zone, clusters slightly shift upward or downward by  $\delta$  along the  $c$ -direction. The positional shift,  $\delta$ , is expressed as  $\delta = 100R/3T$ , where  $R$  and  $T$  are the cluster diameter in  $ab$  plane and the width of transition zone, respectively. The figure represents the minimum width of transition zone ( $T = 2R$ ), hence, the largest  $\delta$ . (Reprinted with permission from Onuma, K.; Ito, A. *Chemistry of Materials*, 10:3346–3351 (1998). Copyright 1998 American Chemical Society.)

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# 17 Crystal Growth of Gemstones

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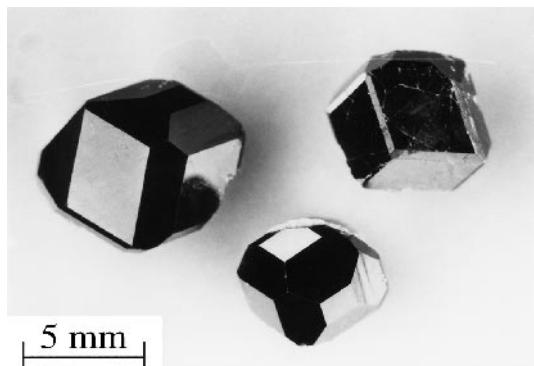
## 17.1 Introduction

Gemstones are usually used for human ornamentation. Diamond (C), ruby ( $\text{Al}_2\text{O}_3:\text{Cr}$ ), and emerald ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}$ ) are well-known gemstones. The gemstones are principally natural minerals that are highly valued for their beauty, durability, and rarity. Portability is also required for the use of gem materials. The majority of gemstones are single crystals of minerals. As an example of natural minerals, spessartine garnet crystals found at Wada-toge Pass, Nagano Prefecture, Japan, are shown in Fig. 17.1. The garnet crystals have a beautiful glassy luster, and are black and opaque. They can be used for ornamental purposes without cutting. Other gemstones are not single crystals. Opal is one of the best-known non-crystalline gemstones. Natural minerals of good quality are getting scarce with the passing of time.

The high value placed on gemstones for use in jewelry has led to many attempts to synthesize natural gemstones. The duplication of beautiful gemstones in the laboratory has been one of man's aims. Manmade and natural gemstones have the same chemical composition and crystal structure. Ruby crystals were grown by the flux method in 1837 by Gaudin [1]. He grew ruby crystals of up to 0.187 g from molten potassium alum and potassium chromate. Small emerald crystals were grown from lithium molybdate and lithium vanadate fluxes in 1888 by Hautefeuille and Perrey [2]. The method involving use of flame fusion was developed in 1902 by Verneuil [3]. The method of pulling from the melt was first developed in 1918 by Czochralski [4]. A lot of scientists tried to grow diamond crystals. A reproducible synthesis of diamond was first reported in 1955 by Bundy et al. [5]. Metallic solutions at high pressure and high temperature were used to grow diamond crystals. A listing of major single crystal gemstones used in jewelry, which have been successfully grown as synthetics is given in Table 17.1. Many other gemstones such as spinel ( $\text{MgAl}_2\text{O}_4$ ) and rutile ( $\text{TiO}_2$ ) crystals have also been grown. Crystal growth is progressing gradually from an art to a science. Now, synthetic gemstones are marketed on a large scale. Figure 17.2 shows synthetic ruby and sapphire (pure  $\text{Al}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  doped with transition elements) cut stones. Synthetic star ruby and sapphire stones are shown in Fig. 17.3. Synthetic gem-

stones are also used in electronics devices. Excellent books and reviews that deal with the crystal growth and characterization of gemstones have been published by Elwell and Scheel [6], Elwell [4], Nassau and Nassau [7], and O'Donoghue [8]. A comparison of natural gem materials with synthetic ones has been described by Sunagawa [9] earlier and also in Chapter 1 of this book.

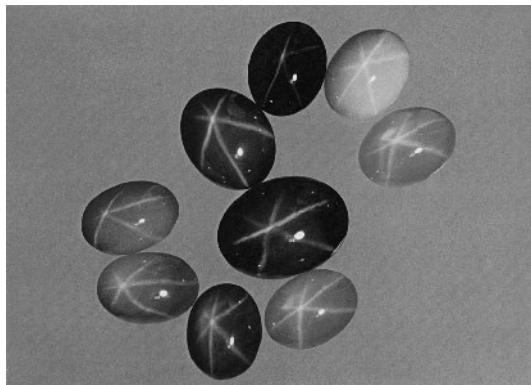
This chapter describes a simple method of growing crystal gemstones. An outline of the growth methods is given. The flux method is mentioned in some detail since the stones produced closely resemble the natural gems. The flux growth of emerald crystals as an example of gemstones is described. Growth of emerald crystals by the flux evaporation technique is introduced to make a collection of man-made gemstones. You can grow beautiful emerald crystals with a minimum of equipment and information.



**Fig. 17.1.** Natural garnet crystals found at Wada-toge Pass, Nagano Prefecture, Japan



**Fig. 17.2.** Synthetic ruby and sapphire cut stones



**Fig. 17.3.** Synthetic star ruby and sapphire stones

**Table 17.1.** Major Single Crystal Gemstones and the Growth Methods

Gemstone	Mineral	Chemical Formula	Growth Method
Diamond	Diamond	C	High Pressure
Emerald, Aquamarine	Beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	Hydrothermal, Flux
Quartz	Quartz	$\text{SiO}_2$	Hydrothermal
Ruby, Sapphire	Corundum	$\text{Al}_2\text{O}_3$	Verneuil, Czochralski, Hydrothermal, Flux

## 17.2 Growth Methods of Gemstones

Matter may exist in three states of aggregation — solid, liquid, or gas. Solids have rigidity, fixed shape, and mechanical strength. A crystalline solid is characterized by long-range order extending over many atom diameters. Crystals are by no means grown at equilibrium. Crystal growth of gemstones involves precise control of a phase change. The growth requires that the equilibrium is displaced very slightly in the direction of the intended solid. This is usually accomplished by careful control of the temperature. After a stable nucleus has been formed, it grows at a rate fixed by the conditions of temperature and the degree of supersaturation or supercooling.

Crystal growth processes may be divided into three main categories: (1) growth from the solid (solid → crystal), (2) growth from the liquid (liquid → crystal), and (3) growth from the vapor (vapor → crystal). Solid-state growth (1) requires atomic diffusion in the crystalline solid. Even at high temperatures, the rate of diffusion is usually very low. Therefore, the solid-state growth technique is seldom

employed to grow large crystals. Vapor growth (3) is often the technique by which whiskers or thin film crystals can be formed. Growth from the liquid (2) has been used to advantage in growing large crystals. It is convenient to divide growth from the liquid into two classes according to whether the liquid involved is composed only of the same components as the crystal (a melt) or components in addition to those contained in the crystal (a solution). The rate of growth from the melt is normally much higher than that from the solution. Melt growth can produce large crystals and is commercially the most important method of crystal growth. The principal advantage of growth from solution is that crystal growth occurs at a lower temperature than that required for melt growth. Another advantage of solution growth is that the crystal can grow with well-developed faces. The solubility data of solutes in fluxes are very important to grow crystals. The use of phase diagrams in crystal growth has been mentioned [10]. Excellent books and reviews on various growth methods have been published by Pamplin [11,12], Laudise [13], and Byrappa and Yoshimura [14].

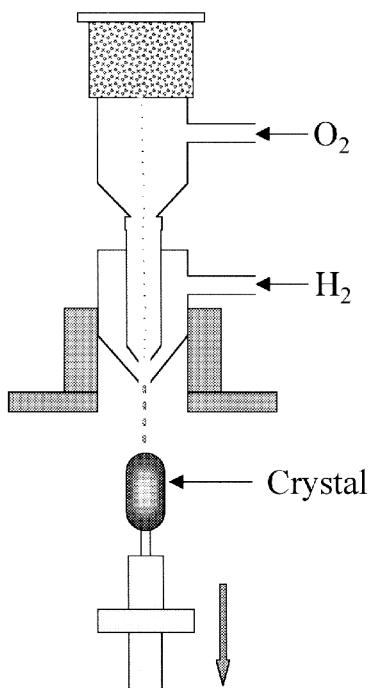
Major techniques for the crystal growth of gemstones from melts are the Verneuil and Czochralski methods. Typical growth techniques from solutions are the hydrothermal and flux methods. These methods are outlined below and a relatively detailed description of flux growth is given.

### 17.2.1 Verneuil method

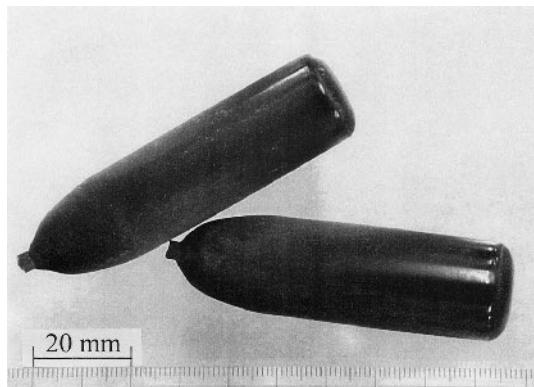
The Verneuil technique is a commercial method for growing gemstones. It was developed in 1902 by Verneuil [3]. The principle of the method is schematically shown in Fig. 17.4. The apparatus is basically an oxyhydrogen torch through which powders of the material to be grown are passed. The powders melt in the flame and form a small puddle on a seed crystal. The crystal is grown on the seed crystal, which is lowered as the crystal builds up. The form of the crystal grown by the Verneuil method is cylindrical.

The Verneuil method has the great advantage of being crucible less. In addition, it can grow larger crystals of gemstones at higher temperatures than any other technique. The upper temperature is limited by the oxyhydrogen flame temperature. By regulating the  $H_2/O_2$  ratio in the flame, one can sometimes grow oxide crystals that are difficult to prepare in other methods. Because the method is non-conservative, solid solutions of uniform composition can be grown. A disadvantage is that the growing crystal is exposed to a steep temperature gradient. Some of grown crystals have consequently been broken into pieces.

Shinkosha Co., Ltd., Japan, has produced ruby and sapphire crystals by the Verneuil method. Red and transparent ruby boules grown are shown in Fig. 17.5. The synthetic ruby, sapphire, star ruby, and star sapphire crystals shown in Figs. 17.2 and 17.3 were also grown by this method.



**Fig. 17.4.** Schematic diagram of Verneuil apparatus

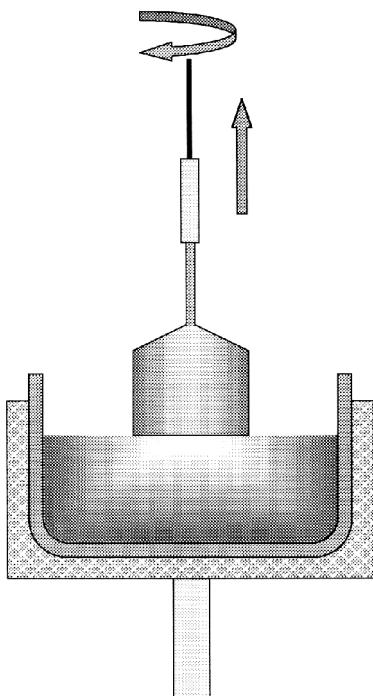


**Fig. 17.5.** Ruby boules grown by Verneuil method

### 17.2.2 Czochralski method

The Czochralski technique is a popular method of crystal growth because it can produce large and dislocation-free crystals in a relatively short time. The principle of the method is schematically shown in Fig. 17.6. The material to be grown is molten in a crucible. A seed crystal is then dipped into the melt and slowly withdrawn. The seed is rotated at the same time in order to attain thermal symmetry and also to stir the melt. The crystals grown by the Czochralski method have the form of a cylinder. With semiconductor silicon material, the Czochralski method is a very important process.

The opportunity to grow crystals of many orientations is one of the major advantages of the Czochralski method. Another advantage is that separation of the crystal from the melt is not necessary. Still another advantage is that by pulling small crystals from large melts one can minimize the compositional change in solid solution crystals. However, considerable operator skill is necessary for crystal pulling. The method requires a crucible, so contamination can be a problem, and atmosphere control is complicated. Furthermore, the equipment is usually expensive since it requires very well designed and constructed motors and mechanisms for rotation and withdrawal of the crystals.



**Fig. 17.6.** Schematic diagram of Czochralski apparatus

### 17.2.3 Hydrothermal method

Hydrothermal technique is a method of crystal growth from a solution in water at high temperatures and pressures [13,14,15]. Spezia made the first attempt to produce quartz ( $\text{SiO}_2$ ) crystals on the seed crystals in the system  $\text{SiO}_2\text{-H}_2\text{O}$  [14,15]. Since then hydrothermal systems involving quartz have been studied extensively because of the economic importance of piezoelectric quartz devices. The basic hydrothermal process is essentially a solution growth by temperature gradient transfer. Small quartz nutrient is placed in the bottom of the vessel (autoclave) and seed crystals of quartz are suspended in the upper growth region. The vessel is filled to some predetermined fraction of its free volume, typically 0.8 with a dilute basic solution such as 0.5 M NaOH. The vessel is placed in a furnace that has been designed to heat the lower dissolving section isothermally hotter than the upper growth region, which is also maintained isothermal. A typical example of quartz crystal hydrothermally grown on an industrial scale is shown in Fig. 17.7. The colorless and transparent crystal is surrounded by well-developed faces.

There are practical advantages to the technique. The modest temperature required and the large thermal mass of the autoclave permit the use of simple and inexpensive furnaces and controllers. Although autoclaves are expensive, they have a long life if handled carefully. A disadvantage of the method is the possibility of incorporating  $\text{H}_2\text{O}$  or  $\text{OH}^-$  in the crystals.



**Fig. 17.7.** Quartz crystal hydrothermally grown

### 17.2.4 Flux method

Flux growth is a method by which a wide range of gemstones may be obtained with less sophisticated equipment and information. Components of the gem material desired in the single crystal form are dissolved in a flux (solvent). A flux permits the growth to proceed at temperatures well below the melting point of the solute phase. This reduction in temperature is the principal advantage of flux

growth over growth from the pure melt. Excellent books and reviews have been published by Chase [16], Elwell and Scheel [6], Elwell [17,18], and Wanklyn [19].

A reduction in the temperature is desirable for the growth of a wide range of materials, in particular those in the following categories:

- a. Materials which are incongruently melting
- b. Materials which have a very high melting point
- c. Materials which undergo a phase transition
- d. Materials which have a very high vapor pressure at the melting point
- e. Materials which have a very volatile constituent

Other advantages of flux growth are based on the fact that the growing crystal is not exposed to steep temperature gradients and that the crystal can grow free from mechanical or thermal strain into the solution. Therefore, well-formed crystals are grown. The disadvantages of the method are substitutional or interstitial incorporation of flux ions into the crystal, inclusions of flux or impurities, and a slow growth rate.

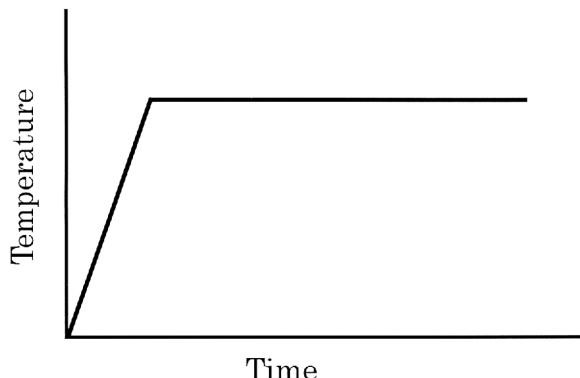
The choice of flux is difficult because very little work has been done to date concerning the solubility of the solute in flux at high temperatures. From the solubility point, a good flux should be chemically similar concerning the type of bonding to the solute. On the other hand, crystal-chemical differences should exist in order to prevent solid solubility between the solute and flux. There are no fixed rules for choosing a suitable flux. One of the easiest starting points for choosing a flux is to study information contained in phase diagrams [20]. Another useful practice is to survey the literature for fluxes that have been used for similar compounds. In many cases, this approach will yield a suitable flux. In this way, the flux has been normally chosen by trial and error procedures, taking into account previous experiences. On the other hand, a guide to the choice of suitable fluxes for the crystal growth of oxides was proposed [21]. In this guide, the criteria have been formulated using some fundamental information, such as ionic radius, melting point, ionicity of chemical bondings, Dietzel's parameter, and acidity and basicity.

In the flux growth, supersaturation can be obtained by a slow cooling, by flux evaporation or by the temperature gradient technique. The flux growth can be classified into three techniques.

1. *Slow Cooling Technique*: The most common technique for producing supersaturation in flux growth is by slow cooling of the solution. In general, a linear cooling rate of 1 to 10°C/h is applied. The slower the cooling rate is, the better and larger the crystals are. The slow cooling technique is relatively simple for the growth of known and also new crystals up to mm size. The technique is highly suitable for exploratory materials research.
2. *Flux Evaporation Technique*: Flux evaporation could be generally used to grow crystals, which show a low variation of solubility with temperature. Since flux evaporation may be carried out isothermally, this technique offers the advantages connected with growth at constant temperature. As shown in Fig. 17.8,

the temperature program is very simple. An approximately constant concentration of equilibrium defects and homogeneous incorporation of dopants can be expected.

3. *Temperature Gradient Technique*: This technique is suitable for the growth of large crystals. Growth experiments have been performed with the knowledge of the appropriate solubility data. The principle of the temperature gradient technique is similar to that of hydrothermal growth of quartz crystals. Nutrient is held at the bottom (hotter region) in a solution. By natural or forced convection, a flow of solution occurs towards a cooler region where a seed crystal is held, the solution becomes supersaturated and crystal grows on the seed crystal.



**Fig. 17.8.** Temperature program of flux evaporation experiment

## 17.3 Emerald

### 17.3.1 Growth of emerald crystals

Emerald ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}$ ) has been regarded as a beautiful and attractive gemstone from olden times. Emerald is a beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , beryllium aluminum silicate) doped with chromium. The chromium gives emerald its characteristic green color. The emerald crystals belong to the hexagonal system with space group  $P6/mcc$  [22].

Like diamond, emerald has been the object of many attempted syntheses. Synthetic emerald crystals have always been of considerable interest for gemstones. There has been a paper focused only on synthetic emerald crystals [23]. Emerald melts incongruently at high temperature [24]. In spite of this problem, Gentile and his colleagues have grown emerald crystals by the Verneuil method [25]. A boule several inches in length and 0.5 inch in diameter was grown in three to four hours. Crystal growth of emerald has been made by using a high-pressure temperature

technique [26,27]. Emerald crystals have also been produced by the hydrothermal method on a commercial basis [4,8]. By the flux method, the first successful synthesis of emerald crystals was reported in 1888 by Hautefeuille and Perrey [2]. The flux process for emerald crystals was developed by Espig, Zerfass, Nacken, Chatham, and Gilson [4,7,8,23]. The growth of emerald crystals from fluxes is particularly attractive because it readily allows the growth. There have been a number of investigations into the flux growth of emerald crystals. The following fluxes have been used:

- MoO<sub>3</sub> [28,29]
- Li<sub>2</sub>O-MoO<sub>3</sub> [2,29,30,31,32,33,34,35,36]
- K<sub>2</sub>O-MoO<sub>3</sub> [37,38]
- MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> [39]
- PbO-MoO<sub>3</sub> [4,40]
- Li<sub>2</sub>O-WO<sub>3</sub> [4,30]
- PbO-WO<sub>3</sub> [4,40]
- PbO-PbF<sub>2</sub> [29]
- V<sub>2</sub>O<sub>5</sub> [30,31,40,41,42,43,44]
- Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> [2,33]
- PbO-V<sub>2</sub>O<sub>5</sub> [31,45,46,47]
- B<sub>2</sub>O<sub>3</sub> [6,29]

In particular, Li<sub>2</sub>O-MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> fluxes have been successfully used by the slow cooling and temperature gradient techniques, respectively. We have grown emerald crystals from a PbO-V<sub>2</sub>O<sub>5</sub> flux by a slow cooling method [46]. Large emerald crystals weighing 150 ct have been grown on seeds from the PbO-V<sub>2</sub>O<sub>5</sub> flux by controlled crystallization [47]. However, the flux is too time-consuming to dissolve the solidified flux in hot nitric acid. In addition, Pb and V are toxic to human beings.

Little work has been reported on the growth of emerald crystals by the flux evaporation method. Because flux evaporation may be carried out isothermally, this technique offers the advantages connected with the growth at constant temperature; for example, the temperature control is very easy. Growth of emerald crystals from pure MoO<sub>3</sub> flux has been reported only very briefly with no description of the experimental conditions and results [29]. Pure MoO<sub>3</sub> has not been used as flux due to its volatility and generally speaking is not a suitable flux. However, we have easily grown emerald crystals from MoO<sub>3</sub> [28], Li<sub>2</sub>O-MoO<sub>3</sub> [36], K<sub>2</sub>O-MoO<sub>3</sub> [38], and MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> [39] fluxes by the flux evaporation method. A technique of easily growing emerald crystals from MoO<sub>3</sub>-based fluxes is described below.

### 17.3.2 A simple method of growing emerald crystals

Well-formed emerald crystals can be easily grown by the evaporation method of MoO<sub>3</sub>, Li<sub>2</sub>O-MoO<sub>3</sub>, K<sub>2</sub>O-MoO<sub>3</sub>, and MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> fluxes. The concentration of emerald constituents in the solution may be slowly increased by evaporation of the

fluxes. The evaporation technique is carried out isothermally. Since the temperature control is easy, a temperature controller is not always needed. Operating skill is not necessary. The basic requirements for the growth of emerald crystals are a crucible, furnace, thermocouple, and chemicals.

## **Experimental**

Reagent grade BeO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and B<sub>2</sub>O<sub>3</sub> were used for the flux growth of emerald crystals. The beryl mixture (3BeO + Al<sub>2</sub>O<sub>3</sub> + 6SiO<sub>2</sub>) was prepared from BeO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> powders and the oxide dopant (Cr<sub>2</sub>O<sub>3</sub>) added as 1.0 mass% of the beryl mixture. This mixture was used as a solute for flux growth runs. Pure MoO<sub>3</sub>, Li<sub>2</sub>O-MoO<sub>3</sub>, K<sub>2</sub>O-MoO<sub>3</sub>, and MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> were used as fluxes. BeO is toxic to humans. Care is required to handle it.

The solute and flux powders were weighed out and mixed together. The mixtures were put into platinum crucibles of 30 cm<sup>3</sup> capacity (36 mm in diameter and 40 mm high). In the case of K<sub>2</sub>O-MoO<sub>3</sub> flux, a 240 cm<sup>3</sup> crucible (60 mm in diameter and 80 mm high) was also used to grow large crystals. After closing the lids, the crucibles were placed in an electric furnace with silicon carbide heating elements. The furnace was heated at about 45°C/h to 1100°C and held at this temperature for 0–240 h. Then the crucible was removed and allowed to cool rapidly to room temperature. The crystal products were then separated from the flux in warm water.

The cost of the apparatus can be relatively low. The most readily available material of crucible is platinum. A 30 cm<sup>3</sup> crucible is enough to grow emerald crystals with a few mm in size. Furnaces able to reach 1300°C can be obtained commercially.

The crystals obtained were examined using an optical microscope and a scanning electron microscope (SEM). The crystal phases were identified by X-ray diffraction (XRD). The length, *L* (parallel to the *c*-axis), and width, *W* (perpendicular to the *c*-axis), of the emerald crystals grown were measured. The density of the crystals was pycnometrically determined. Infrared (IR) absorption spectra of the crystals were measured. The samples were prepared as KBr disks. An electron probe microanalyzer (EPMA) was used to study variations in the concentration of the major constituents of the grown crystals. The presence of impurities from the fluxes and Pt crucible was also checked. However, these processes of characterizing are not always necessary if you only enjoy yourself by making beautiful emerald crystals.

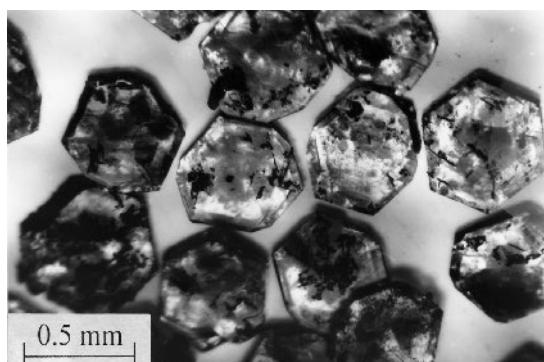
## **Flux growth of emerald crystals**

A lot of small emerald crystals were easily grown by the MoO<sub>3</sub> flux evaporation method [28]. The obtained emerald crystals were transparent and exhibited the typical emerald-green color. Their form was a twelve-sided prism bounded by well-developed faces. The oxide MoO<sub>3</sub> used as a flux was too volatile to grow large emerald crystals. The high volatility of MoO<sub>3</sub> flux is expected to be greatly lowered when the complex must be stable in the high-temperature solution by the

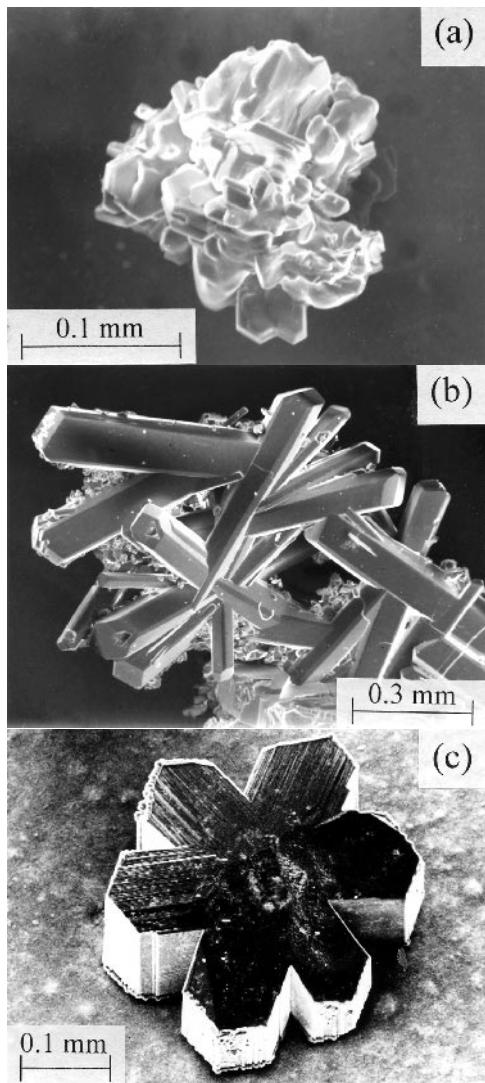
addition of basic oxide such as Li<sub>2</sub>O or K<sub>2</sub>O. Addition of Li<sub>2</sub>O to MoO<sub>3</sub> flux in fact made the high-temperature solution relatively nonvolatile. Similarly, K<sub>2</sub>O added to MoO<sub>3</sub> flux acted to control the amount of flux evaporation. Relatively large emerald crystals were grown from Li<sub>2</sub>O-MoO<sub>3</sub> and K<sub>2</sub>O-MoO<sub>3</sub> fluxes [36,38]. The form of the crystals grown from these fluxes was also a twelve-sided prism. As an example, typical emerald crystals grown from Li<sub>2</sub>O-MoO<sub>3</sub> flux are shown in Fig. 17.9. At first sight, the crystals look just like hexagonal prisms because of six well-developed prismatic faces. On the other hand, an attempt to improve flux properties was performed by adding B<sub>2</sub>O<sub>3</sub> to MoO<sub>3</sub> flux. Since B<sub>2</sub>O<sub>3</sub> has a high viscosity, it is expected that B<sub>2</sub>O<sub>3</sub> generally suppress flux evaporation. Addition of B<sub>2</sub>O<sub>3</sub> to MoO<sub>3</sub> actually suppressed evaporation of the flux. Hexagonal thin plate-like emerald crystals as shown in Fig. 17.10 were grown from MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> flux [39].



**Fig. 17.9.** Emerald crystals grown from Li<sub>2</sub>O-MoO<sub>3</sub> flux



**Fig. 17.10.** Emerald crystals grown from MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> flux



**Fig. 17.11.** By-product crystals of (a) cristobalite, (b) phenacite, and (c) chrysoberyl

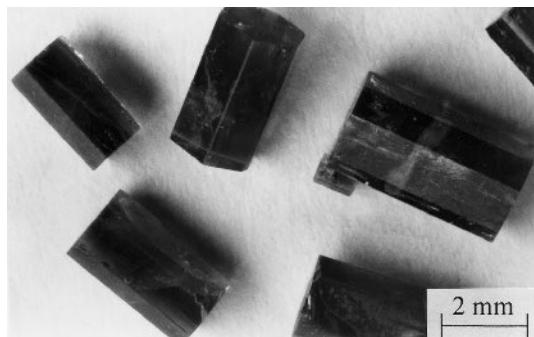
It was found that prismatic and plate-like emerald crystals can be grown by the simple operation of only evaporating  $\text{MoO}_3$ -based fluxes at constant temperature. The resulting crystals could be readily separated from the  $\text{MoO}_3$ -based fluxes in warm water. The platinum crucibles were found to be undamaged after use with no evidence of attack from the  $\text{MoO}_3$ -based fluxes. The fluxes were compatible with platinum at the intended temperature. A disadvantage of the isothermal flux evaporation technique was the difficulty of controlling the evaporation rate. By-

products such as cristobalite ( $\text{SiO}_2$ ) and phenacite ( $\text{Be}_2\text{SiO}_4$ ) crystals were formed from  $\text{MoO}_3$ ,  $\text{Li}_2\text{O}-\text{MoO}_3$ ,  $\text{K}_2\text{O}-\text{MoO}_3$ , and  $\text{MoO}_3-\text{B}_2\text{O}_3$  fluxes. The former crystals were colorless and transparent. Their form was a thin plate. The latter crystals were also colorless and transparent. Their form was a hexagonal rod. In the small number of the growth experiments, dark green chrysoberyl ( $\text{BeAl}_2\text{O}_4$ ) crystals were formed. The grown crystals were always twinned. The twin crystals had pseudo-hexagonal symmetry owing to cyclic twinning. By-product crystals of cristobalite, phenacite, and chrysoberyl are shown in Fig. 17.11. The secondary phases (insoluble in warm water) could be clearly distinguished from emerald crystals because of the differences in color and shape. Owing to the formation of 2 or 3 kinds of by-product crystals, the system used for growing emerald crystals cannot rigorously be reduced to a pseudo-binary system of solute and flux. The crystallization process of emerald crystals from the high-temperature solutions of the  $\text{MoO}_3$ -based fluxes is very complex.

*$\text{MoO}_3$  flux* [28]: The most suitable composition of the high-temperature solution was solute (9.06 g)- $\text{MoO}_3$ (30.0 g) when the holding time was 30 h. The evaporation loss of the  $\text{MoO}_3$  flux was about 99 mass%. The approximate rate of evaporation was calculated as  $8.8 \times 10^{-4}$  g/(h mm<sup>2</sup>). The crystal growth was promoted by the evaporation of flux, which increased with the holding time. A lot of small emerald crystals, up to 0.86 mm *L* and 0.64 mm *W*, were grown from the flux. The crystal sizes were dependent on the evaporation loss of flux. The numbers of obtained crystals were very large. The obtained crystals were twelve-sided prism-shaped and the crystal surfaces were very flat. The aspect ratios (*L/W*) were in the region of 1.2 to 1.5. It was found that  $\text{MoO}_3$  flux could produce emerald crystals. However,  $\text{MoO}_3$  was insufficient as a flux to grow large emerald crystals due to its very high volatility.

*$\text{Li}_2\text{O}-\text{MoO}_3$  flux* [36]: The most suitable composition of the high-temperature solution was solute (7.00 g)- $\text{Li}_2\text{O}$ (1.50 g)- $\text{MoO}_3$ (30.0 g) when the holding time was 40 h. Evaporation loss of the  $\text{Li}_2\text{O}(1.50 \text{ g})-\text{MoO}_3(30.0 \text{ g})$  flux was about 7 mass%. The rate of evaporation was calculated as approximately  $5.4 \times 10^{-5}$  g/(h mm<sup>2</sup>). The evaporation loss of flux decreased gradually with an increase in the amount of  $\text{Li}_2\text{O}$  added to  $\text{MoO}_3$ . Addition of  $\text{Li}_2\text{O}$  to  $\text{MoO}_3$  made the high-temperature solution relatively less volatile owing to the interaction between  $\text{Li}_2\text{O}$  and  $\text{MoO}_3$ . The  $\text{Li}_2\text{O}$  acted to control the amount of flux evaporation. It was considered that the evaporation loss from the  $\text{Li}_2\text{O}-\text{MoO}_3$  flux consisted mainly of  $\text{MoO}_3$ . The evidence for this view came from the precipitation of  $\text{MoO}_3$  on the crucible lid and furnace brick. Owing to the preferential evaporation of  $\text{MoO}_3$ , the flux composition changes with time. Emerald crystals of up to 3.4 mm *L* and 2.4 mm *W* were readily grown by the  $\text{Li}_2\text{O}-\text{MoO}_3$  flux evaporation method. The crystal sizes were evidently dependent on the amount of  $\text{Li}_2\text{O}$  present, that is, the evaporation loss of flux. The obtained emerald crystals were twelve-sided prisms bounded by well-developed faces with aspect ratios in the region of 1.2 to 1.9.

*$\text{K}_2\text{O}-\text{MoO}_3$  flux* [38]: The most suitable composition of the high-temperature solution was solute (3.80 g)- $\text{K}_2\text{O}$ (1.50 g)- $\text{MoO}_3$ (28.5 g) when the holding time was 24 h. About 34 mass% of the  $\text{K}_2\text{O}(1.50 \text{ g})-\text{MoO}_3(28.5 \text{ g})$  flux evaporated. The



**Fig. 17.12.** Large emerald crystals grown from  $\text{K}_2\text{O}$ - $\text{MoO}_3$  flux

approximate rate of evaporation was calculated to be  $4.2 \times 10^{-4} \text{ g}/(\text{h mm}^2)$ . The evaporation loss decreased gradually with an increase in the amount of  $\text{K}_2\text{O}$ , which acted to control the amount of flux evaporation in a similar manner as the case of  $\text{Li}_2\text{O}$ . The evaporation loss from  $\text{K}_2\text{O}$ - $\text{MoO}_3$  flux consisted mainly of  $\text{MoO}_3$ . Emerald crystals of up to 1.8 mm  $L$  and 1.3 mm  $W$  were readily grown by the  $\text{K}_2\text{O}$ - $\text{MoO}_3$  flux evaporation method. The form of the obtained crystals was similar to that of crystals grown from  $\text{MoO}_3$  and  $\text{Li}_2\text{O}$ - $\text{MoO}_3$  fluxes. The aspect ratios were in the region of 1.2 to 2.3.

An attempt to grow large crystals by scaling up the mass of the mixture by a factor of 6 was investigated. The composition of the mixture was solute (22.8 g)- $\text{K}_2\text{O}$ (9.00 g)- $\text{MoO}_3$ (171.0 g). The holding time was 240 h. The evaporation loss of the flux was about 58 mass%. Emerald crystals of up to 4.5 mm  $L$  and 2.9 mm  $W$  were grown. The mass of the largest crystal was about 0.04 g (0.2 carat). Large emerald crystals are shown in Fig. 17.12.

*$\text{MoO}_3$ - $\text{B}_2\text{O}_3$  flux* [39]: The suitable composition of the high-temperature solution was solute (9.00 g)- $\text{MoO}_3$ (30.0 g)- $\text{B}_2\text{O}_3$ (0.36 g) when the holding time was 30 h. Approximately 60 mass% of the  $\text{MoO}_3$ (30.0 g)- $\text{B}_2\text{O}_3$ (0.36 g) flux evaporated. The approximate evaporation rate was  $5.8 \times 10^{-4} \text{ g}/(\text{h mm}^2)$ . The evaporation of flux decreased gradually with an increase in the amount of  $\text{B}_2\text{O}_3$  added to  $\text{MoO}_3$  flux. The  $\text{B}_2\text{O}_3$  addition remarkably suppressed  $\text{MoO}_3$  flux evaporation. The evaporation loss from  $\text{MoO}_3$ - $\text{B}_2\text{O}_3$  flux consisted mainly of  $\text{MoO}_3$ . Hexagonal thin plate-like emerald crystals of up to 1 mm  $W$  were readily grown by the  $\text{MoO}_3$ - $\text{B}_2\text{O}_3$  flux evaporation method. The aspect ratios of the plate-like crystals were approximately 0.2. The flux is found to be a suitable flux for the growth of plate-like thin emerald crystals. The morphology of emerald crystals was controlled by the  $\text{B}_2\text{O}_3$  addition.

### **Characteristics of the emerald crystals**

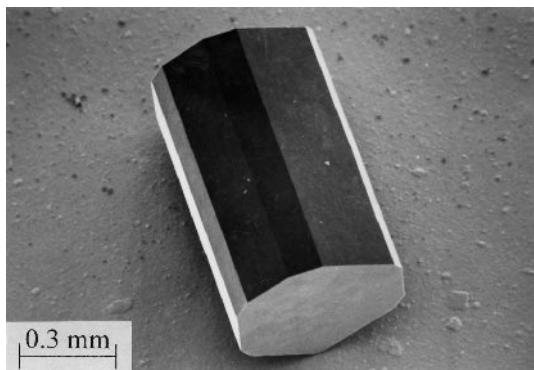
Some characteristics of emerald crystals grown from  $\text{MoO}_3$ ,  $\text{Li}_2\text{O}$ - $\text{MoO}_3$ ,  $\text{K}_2\text{O}$ - $\text{MoO}_3$ , and  $\text{MoO}_3$ - $\text{B}_2\text{O}_3$  fluxes were investigated [28,36,38,39]. The emerald crys-

tals obtained were transparent and with the typical emerald-green color as described above. The sizes of the prismatic emerald crystals were up to 4.5 mm *L* and 2.9 mm *W*. The widths of thin plate-like emerald crystals were up to 1 mm. They were identified as emeralds by their powder XRD patterns, using data given in the JCPDS card [48].

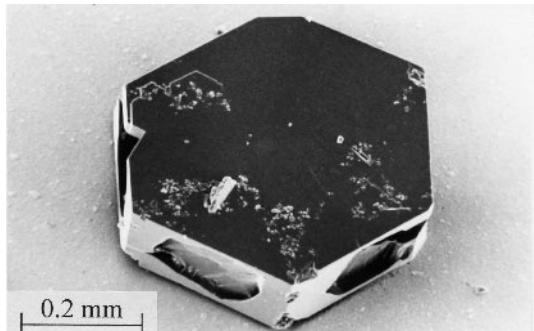
Emerald crystals obtained from  $\text{MoO}_3$ -based fluxes were classified into two distinct morphological types: prism and plate. The forms were dependent on the fluxes used. The form of the emerald crystals grown from  $\text{MoO}_3$ ,  $\text{Li}_2\text{O}-\text{MoO}_3$ , and  $\text{K}_2\text{O}-\text{MoO}_3$  fluxes was a twelve-sided prism. A typical prismatic crystal grown from  $\text{Li}_2\text{O}-\text{MoO}_3$  flux is shown in Fig. 17.13. On the basis of the XRD data and interfacial angle measurements, it was found that the crystals were bounded by the  $c\{0001\}$ ,  $m\{10\bar{1}0\}$ , and  $a\{11\bar{2}0\}$  faces. The *c* and *m* faces were always well-developed. Natural emerald crystals are also prismatic [49]. On the other hand,  $\text{MoO}_3-\text{B}_2\text{O}_3$  flux produced the hexagonal thin plate-like emerald crystals of up to 1 mm *W*. A typical plate-like crystal is shown in Fig. 17.14. The plate-like crystals were bounded mainly by the *c* and *m* faces. There were crystals in which some small *a* faces appeared. The *c* faces were smooth while *m* and *a* faces were rough, forming skeleton crystals in many cases. Only the addition of a slight amount of  $\text{B}_2\text{O}_3$  to  $\text{MoO}_3$  flux suppressed the growth of emerald crystals in the *c*-axis direction, and crystal habit changed from columnar to thin plate-like crystals as  $\text{B}_2\text{O}_3$  content increased. The probable causes are that boron atoms from  $\text{B}_2\text{O}_3$  are selectively adsorbed by the *c* faces of emerald crystals and crystal components are hardly supplied to the *c* faces, and that there is an effect of a change in supersaturation by regulating the evaporation rate of flux.

The variations in the concentration of the major constituents in the grown prismatic emerald crystals were investigated by the use of EPMA. Aluminum, silicon, and oxygen were distributed almost homogeneously in the crystals. The distribution of beryllium could not be determined due to the low atomic mass of the element. The EPMA data showed that chromium was incorporated preferentially in the central parts of the crystals. A small amount of chromium existed in the outer parts of the crystals. In addition, there was a preferential incorporation into the prismatic faces compared to the basal ones. The orientation-dependent chromium incorporation is probably due to the difference in adsorption on specific faces or in the crystallographic direction. Molybdenum from the fluxes and platinum from the crucible were not detected. Emerald crystals grown from  $\text{K}_2\text{O}-\text{MoO}_3$  flux were contaminated by a very small amount of potassium from the flux. The potassium was incorporated in the central parts of the crystals.

The density of the emerald crystals was pycnometrically determined to be 2.65–2.66 g/cm<sup>3</sup>, in good agreement with literature values (2.64 [48] and 2.69 [4] g/cm<sup>3</sup>). IR absorption spectra recorded in the range 450–4000/cm were obtained for the emerald crystals grown. Absorption bands at approximately 493, 523, 590, 650, 681, 740, 806, 961, 1020, and  $1204 \pm 3/\text{cm}$  were observed. These values were in good agreement with literature data for emerald crystals grown from  $\text{V}_2\text{O}_5$  flux [41]. The observed bands were independent of the crystal growth conditions. A broad band at 3450/cm was also observed, which is believed to be extraneous to



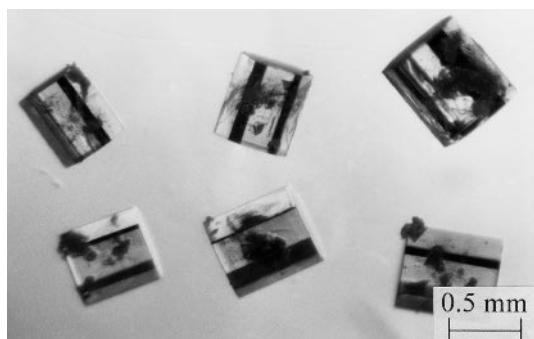
**Fig. 17.13.** A twelve-sided prismatic emerald crystal



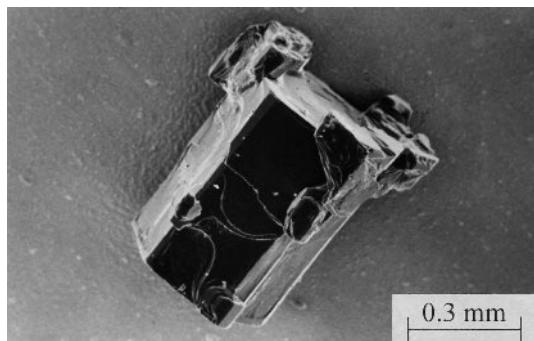
**Fig. 17.14.** A plate-like emerald crystal

the sample and related to water pick-up by KBr during sample preparation. Of course, sharp OH bands were not observed because the emerald crystals grown from flux contained no water. Natural and synthetic hydrothermal emerald crystals exhibited sharp OH bands [7,9,23,30,31].

Inclusions were rarely found in the emerald crystals grown from  $\text{Li}_2\text{O}-\text{MoO}_3$  and  $\text{K}_2\text{O}-\text{MoO}_3$  fluxes. The quality of these crystals was good. On the other hand, various kinds of imperfections were present in the crystals grown from  $\text{MoO}_3$  flux although good crystals were also obtained. The crystals generally had flux inclusions in the central parts but the peripheral portion was quite transparent, as shown in Fig. 17.15. It is considered that the growing crystal trapped flux. This is evidence of an internal defect suggesting that some considerable degree of supersaturation is first experienced and a rapid growth stage follows nucleation. Subsequently, higher quality growth occurs on the outer surfaces, but at a slower rate. In addition, emerald crystals having raised corners and edges were also grown and a



**Fig. 17.15.** Emerald crystals having inclusions in the central parts



**Fig. 17.16.** Emerald crystal having raised corners and edges

typical example is shown in Fig. 17.16. The proportion of terraced crystals grown tended to increase as flux evaporation losses increased. The higher supersaturation at the corners and edges of a crystal will lead to an onset of more rapid growth in these regions. A progressive increase in the supersaturation gradient leads first to the formation of raised corners and edges, then to the development of terraced crystals.

## 17.4 Summary

An outline of the crystal growth of gemstones was given. The flux growth of emerald crystals as an example of gemstones was described. Well-formed and transparent emerald crystals exhibiting emerald-green color could be easily grown by the evaporation of  $\text{MoO}_3$ ,  $\text{Li}_2\text{O}-\text{MoO}_3$ ,  $\text{K}_2\text{O}-\text{MoO}_3$ , and  $\text{MoO}_3-\text{B}_2\text{O}_3$  fluxes. The forms of the emerald crystals were prismatic and plate-like. Growing beautiful

emerald crystals is enjoyable and can be done with the minimum of equipment and information.

## Acknowledgments

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<u>Index Terms</u>	<u>Links</u>
% fill	351
15R SiC	224
2D nuclei	70
2D-nucleation growth mode	61
2D-nuclei	57
2D-SROES	125
II-VI compounds	498
III-V epitaxy	55
4H SiC	190
6H SiC	190
abrasive tool coating	98
absolute solubility	343
absorption	421
absorption coefficient	361
absorption measurements	361
absorption spectra	362
acetate	305
acetylene	118
Acheson method	186
acidity and basicity	568
activation energy	100 257 318
activity	246
adatom concentration	59
adsorption	576
AlGaAs	72
alkali	309
alkali metal hilides	445
alkali metals	423
alkaline	324
ammonia ( $\text{NH}_3$ )	325
amorphous carbon	103
anatase	318
angular acceptance bandwidth	438
anionic group	420
antiphase domain-free	84
apparent activation energies	318
aquamarine	563
Arrhenius equation	317
Arrhenius plot	344
Arrhenius-type	257
arsenic oxide	73
as-grown surfaces	355
associated melt	498
atomic force microscope	105
atomic hydrogen	94
autoclave	567

**Index Terms****Links**

automatic weight controller	404
back-reflection synchrotron white beam X-ray topography (BR-SWBXT)	213
back-reflection topography	205
basal plane dislocations	204 221
BaSnO <sub>3</sub>	301
(Ba,Sr)TiO <sub>3</sub>	301
(Ba,Sr)(Ti,Zr)O <sub>3</sub>	301
BaTiO <sub>3</sub>	301
Ba(Ti,Sn)O <sub>3</sub>	301
Ba(Ti,Zr)O <sub>3</sub>	301
BaZrO <sub>3</sub>	301
Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> :Cr	561
beauty	561
beryl	569
beryllium aluminum silicate	569
Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	483
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	483
Bi <sub>2</sub> Sr <sub>2</sub> CuO <sub>6</sub>	483
bias-enhanced nucleation	104
birefringence	389 419
bismuth germanate	387
bismuth vanadate	342
Bi-Sr-Ca-Cu-O superconductor	458
block structures	356
borate	420
bole	564
Bridgman technique	498
BR-SWBXT	213
Burgers vector	204
buffer layer	104
bulk diamond	98
bulk growth	193
buoyancy flow	238
buoyancy force	237
by-product	573
C/H ratio	118
carbide	95
carbon mole fraction	117
carbon phase	102
carbonate	308
carbon-containing species	95
catalyzer	93
CaTiO <sub>3</sub>	301
CaZrO <sub>3</sub>	301
CdTiO <sub>3</sub>	301
characteristics	575

**Index Terms****Links**

chemical reaction	239
chemical vapor deposition (CVD)	93 191
chemical vapor transport (CVT)	501
choice of flux	568
chromium	569
chrysoberyl	574
closed core screw dislocations	204
coil	236
cold THM (CTHM)	499
color centers	335
combustion flame CVD	97
complexation process	344
compositional homogeneity	389
computational domain	251
concentration	307
conduction and radiation	235
congruent melt	389
conoscopic interferrogram	402
container-free epitaxial growth	194
contamination	513 566
contrast formation mechanism	208
cooling	237
copper coil	236
coprecipitation	299
corundum	563
cristobalite	574
critical supersaturation	63
critical temperature	61
critical thickness	82
critical width	89
crucible	236
crucible assembly	392
crystal cross-section controller	403
crystal defects	395
crystal growth	185 347 561
crystal growth rate	403
crystal habit	576
crystal pulling	566
crystal surface	574
crystalline perfection	395
crystallization	300
CsB <sub>3</sub> O <sub>5</sub> (CBO)	420
CsLiB <sub>6</sub> O <sub>10</sub> (CLBO)	422
cubic	311
Curie temperature	300
current density	241
curvilinear grid	243
cutting tool coating	98
CVD	93

**Index Terms****Links**

CW characteristics	361
Czochralski (Cz) growth	422
Czochralski method	566
Czochralski (Cz) technique	340 389
damage threshold	433
dangling bond	107
DC arc plasma jet CVD	97
decomposing reaction	97
decomposition	300
defect	102
degradation	427
degree of supersaturation	351
dendritic	321
density	571
denuded zone	75
deposition	239
desorption	95
device structure	214
diamond	93 561
diamond film	93
diamond film quality	123
diamond growth	93
diamond ID cutter	401
diamond synthesis	93
diamond-like carbon	102
Dietzel's parameter	568
diffraction/rocking curves	397
diffusion	95 316
diffusion coefficient	239
diffusion length	59
diode-laser pumped	335 359
dipole	300
discrete exchange factor (DEF)	244
dislocation	204 263
dislocation free	86
dislocation image	209
dislocation nucleation	213
dislocation pair	217
displacement	264
dissolution	312
dissolution-precipitation	312
dopant	569
doping	200 428 513
double crystal X-ray diffractometer	395
DTA curves	399
durability	561

**Index Terms****Links**

Eddy currents	241
effective conductivity	236
effective heat capacity	243
effective heat transfer coefficient	243
effective nonlinear optical coefficient	419
eighth harmonic generation, $8\omega$	432
elastic material constant	264
electric furnace	571
electrical conductivity	236
electrochemical-hydrothermal	318
electromagnetic field	241
electron bombardment	106
electron cyclotron resonance	
microwave plasma-assisted CVD	97
electron paramagnetic resonance (EPR)	440
electron probe microanalyzer (EPMA)	571
electron temperature	128
electron trap	73
electronic	300
electronic device	97
emerald	569
emerald-green	571
emission cross-sections	336
emission intensity	124
emissivity	240
energy barrier for migration	75
energy transport	242
enviornmental	299
epilayer	214
epitaxial films	200
epitaxial growth	200
epitaxial relationship	109
equilibrium	563
equilibrium constant	245
equilibrium partial pressure	247
Er <sup>3+</sup> -doped fiber	432
etch pits	212
ethylene diamine tetra acetic acid (EDTA)	305
eutectic reaction	478
evaporation diffusion length	66
excimer laser	419
exothermic and endothermic	239
face centered cubic	300
feed back control system	403
ferroelectric domains	401
ferroelectric	299
field-electron emission	101

**Index Terms****Links**

fifth harmonic generation, $5\omega$	419
fine focus X-ray source	396
finite element	249
finite volume	249
five crystal X-ray diffractometer	397
flame fusion	561
flat-panel display	101
fluorescent lifetime	336
flux	561
flux agents	342
flux evaporation	568
flux growth	341
flux impurites	342
flux method	567
fourth harmonic generation, $4\omega$	433
Frank's theory	204
frequency conversion	419
 GaAs	58
garnet	561
gas phase reaction	131
gas temperature	114
gas-phase chemistry	120
gas-phase species	113
GdCa <sub>4</sub> O(BO <sub>3</sub> ) <sub>3</sub> (GdCOB)	420
Gd <sub>x</sub> Y <sub>1-x</sub> Ca <sub>4</sub> O(BO <sub>3</sub> ) <sub>3</sub> (GdYCOB)	420
gel	309
gem material	561
gemstone	561
Gibbs free energy	114
Gibbs function	114
Gibbs-function	245
graphite insulation	236
graphite susceptor	241
graphitization	203
Grashof number	238
gray-track	440
gray-track threshold	442
grazing incidence reflection topograph	215
green light emission	498
growth	181 235
growth atmosphere	442
growth kinetics	197 248
growth layers	356
growth mechanism	103 336
growth method	563
growth of vanadates	343
growth process	94 197
growth rate	93 197 257 351

**Index Terms****Links**

growth spirals	201	205	
growth system	195	235	
halide ions	445		
Hancock and Sharp	315		
heat power	235		
heat resistance	240		
heat sink	97		
Henry's law	246		
heteroepitaxy	103		
hexagonal voids	204	222	
HFCVD	94		
high melting point	362		
high pressure	561		
high pressure and high temperature	93		
high pressure Bridgman	503		
high resolution transmission electron microscopy	106		
high resolution X-ray diffractometry	404		
high resolution X-ray topography	404		
high temperature	561		
high temperature CVD	192		
high temperature growth technique	343		
high temperature optical microscopy	491		
high temperature solution growth	193	341	
highly-mismatched heteroepitaxy	84		
high-oriented diamond film	95		
high-T <sub>c</sub> crystal	467		
hollow core	204		
homoepitaxy	102		
homogeneity	310	422	
hot-filament CVD	94		
hot-wall CVD	192		
HPHT	93		
HRTEM	107		
HTCVD	192		
humidity	427		
hydrates	430		
hydrocarbon	103		
hydrogen	94		
hydrogen passivation	75		
hydrothermal	299		
hydrothermal autoclave	347		
hydrothermal conditions	335		
hydrothermal growth	343		
hydrothermal method	336	510	567
hydrothermal mineralizers	343		
hydrothermal process	343		
hydrous	309		

<u>Index Terms</u>	<u>Links</u>
hydroxyl	311
hygroscopic	427
image contrast	213
imperfection	577
impurities	513
impurity	217
inclusion	217 577
incongruent melt	569
incongruent vanadium oxide	
vaporization	342
incongruent vaporization	337
incorporation	576
incorporation diffusion length	66
incorporation lifetime	70
indigenous versatile crystal puller	392
induction heating	195
inert gas pressure	259
in situ diagnostic technique	116
in situ fabrication of the morphology	362
in situ observation	474
in situ transformation	312
integral equation for radiative heat transfer	244
integrated intensity	397
interface	105
interface demarcation	262
interface supersaturation	62
interfacial energy (IE)	319
interstitial	421
intersurface diffusion	68
ion bombardment	95
ion exchange	316
ionic compensation	443
ionic radius	568
ionicity	497 568
IR absorption	576
IR studies	358
iron doped LiNbO <sub>3</sub>	401
isobaric expansion coefficient	238
jewelry	561
Johnson-Mehl-Avrami (JMA)	314
K <sub>2</sub> Al <sub>2</sub> B <sub>2</sub> O <sub>7</sub> (KAB)	443
K <sub>2</sub> CO <sub>3</sub>	308
K <sub>2</sub> O-MoO <sub>3</sub>	570
KB <sub>5</sub> O <sub>8</sub> .4H <sub>2</sub> O (KB5)	420
KBe <sub>2</sub> BO <sub>3</sub> F <sub>2</sub> (KBBF)	420

**Index Terms****Links**

KBr	319
KDP ( $\text{KH}_2\text{PO}_4$ )	420
KF	446
kinetics	312
$\text{KNbO}_3$	420
Knudsen cell	56
Kronecker's delta	244
KTP ( $\text{KTiOPO}_4$ )	420
large area deposition	95
large effective absorption	336
laser ablation CVD	97
laser-induced damage threshold	419
laser-induced damages	433
laser-induced fluorescence (LIF)	120
laser spectroscopy	358
latent heat	239
lateral flow	70
lateral sticking probability	75
lattice	300
lattice constant	429
lattice mismatch	109
layer-by-layer growth	78
layered structure	443
Lely method	187
Lely plate	197
Lely seed	253
$\text{Li}_2\text{B}_4\text{O}_7$ (lithium tetraborate)	420
$\text{Li}_2\text{O}-\text{MoO}_3$	570
$\text{LiB}_3\text{O}_5$ (LBO)	420
LiCl	446
LIF	120
ligand	321
light emitting devices	513
$\text{LiIO}_3$	420
$\text{LiNbO}_3$	420
LiOH	309
liquid	561
liquid phase epitaxy (LPE)	193
lithium niobate ( $\text{LiNbO}_3$ )	387
low thermal gradient Czochralski (LTGCz)	393
low toxicity	75
LPE growth of low $T_c$ crystal	467
magnetic vector potential	251
man-made gemstone	561
Markov-Davydov technique	505
mass transfer	236

**Index Terms****Links**

mass transport	445
mass transport limited regime	78
MASTRAPP	249
Maxwell's equation	241
MBMS	123
mechanism	312
melt growth	498 564
melting point	568
metal organic chemical vapor deposition (MOCVD)	55
metastable	311
metastable condition	93
methane	118
methyl radical	118
microbalance	395
microchannel epitaxy	84
micropipes	201 204
microprocessor controls of crystal growth	403
microscope	571
micro steps	356
microwave plasma -assisted CVD	95
mild hydrothermal conditions	336
mineral	561
mineralizer	309 347
mineralizer solution	350
minimum reaction temperature	311
MOCVD	55
model	305
modeling and simulation	235
modified Lely method	189 235
MoK <sub>α</sub> 1 X-ray beam	397
molar ratio	307
molarity of the mineralizer	351
molecular beam epitaxy (MBE)	55
molecular beam mass spectroscopy (MBMS)	123
monodispersed	316
MoO <sub>3</sub>	570
MoO <sub>3</sub> -B <sub>2</sub> O <sub>3</sub>	570
morphology	319 351 575
morphology control	336
morphology of rare earth orthovanadates	351
morphology of rare earth vanadates	351
MPCVD	95
multigrid	249
NaF	446

**Index Terms****Links**

nano	327
NaOH	309
native defects	512
natural gemstone	561
Nd:GdVO <sub>4</sub>	336
Nd:RVO <sub>4</sub>	335
Nd:YAG	358
Nd:YAG laser	419
Nd:YVO <sub>4</sub>	336
Nd:YVO <sub>4</sub> laser	440
negative electron affinity (NEA)	101
network analysis	240
Nielsen's equation	317
nitrogen-containing radical	127
noncritical phase-matching (NCPM)	434
non-diamond substrate	103
non-equilibrium thermodynamical process	114
nonlinear optical (NLO) crystals	419
nonlinear optics	434
non-preferential etching	391
nonradiative center	73
normal stress	264
n-type doping	100
nucleation	103 217 314 447
nucleation density	104
nucleation process	103
nucleation site	104
nutrient	567
OES	123
opal	561
optical damages	440
optical emission spectroscopy (OES)	123
optical homogeneity	387
optical lense	99
optical transparency	96
optical window	99
optic-axis picture	402
optimization of growth parameters	400
opto-electronic material	387
order-of-magnitude analysis	236
ornamentation	561
Ostwald ripening	314
output power	360
oxidation	300
oxide crystal	564
oxide single crystals	387
oxyborate	434

**Index Terms****Links**

oxygen defects	335
oxygen deficiency	335 400
oxygen imperfections	335
oxygen impurity	73
oxygen partial pressure	339
oxygen stoichiometry	335
p/n junctions	513
paraelectric	300
partial pressure	245
Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	342
(Pb,La)(Zr,Ti)O <sub>3</sub>	301
Pb(Sc,Nb)O <sub>3</sub>	301
Pb(Zr,Ti)O <sub>3</sub>	301
Pb(Zr,Ti)O <sub>3</sub> – MnO	301
Pb(Zr,Ti)O <sub>3</sub> – Nb <sub>2</sub> O <sub>3</sub>	301
PbO	307
PbTiO <sub>3</sub>	301
PbZrO <sub>3</sub>	301
peak absorption cross-section	361
Péclet number	238
peritectic reaction	479
pH	307
pH of the growth medium	347
pH of the medium	351
pH of the mineralizer	351
phase	324
phase change	563
phase diagram	112 564
phase diagram – LiNbO <sub>3</sub>	389
phase diagram of high T <sub>c</sub> phase	483
phase equilibrium	114 336
phase purity	305
phase transformation	299
phase transition	497
phase-matching	434
phase-matching angle	436
phenacite	574
photorefractive	440
physical vapor deposition	94
physical vapor transport	235
physics-based mathematical model	239
piezoelectric	300
piezoelectric material	387
plane wave dynamical diffraction	
theory	405
plasma	124
plastic deformation	263
plate-like crystal	576

**Index Terms****Links**

platinum crucible	571
poling	389
poling by electric field	401
Polyacrylic acid	322
Polycrystalline diamond film	93
Polymorphism	497
Polynuclear controlled growth	317
Polytypism	202
Poly-vinyl-alcohol (PVA)	322
porosity	236
portability	561
post-growth cooling	392
Potassium hydroxide (KOH)	307
Potassium titanate	316
powder	305
powder charge	236
Prandtl number	238
precipitation	300 314
precursor	107 324
preheating	236
presence of mixed phases	342
pretreatment	104
primary crystallization field (PCF)	491
prismatic crystal	576
pseudo-binary phase diagram	478
p-type doping	99
purity	513
PVD	94
quantum dot	82
quantum well wire	80
quartz	567
quartz tube	236
R <sub>2</sub> O <sub>3</sub> +V <sub>2</sub> O <sub>5</sub> +Nd <sub>2</sub> O <sub>3</sub>	349
radiation	243
radiation from particle to particle	240
radiative heat flux	242
radical	107
radio-frequency current	236
radius	309 318
radius of curvature measurement	397
Raman spectroscope	103
rare earth orthovanadates	356
rare earth vanadates	335
rarity	561
rate	312
rate controlling	312
rate of evaporation	574

**Index Terms****Links**

rate-limiting	316
$\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$	478
reaction	311
reaction time	311
reconstruction	71
reflection high-energy electron diffraction (RHEED)	56
residual impurity	74
residual stress	82 388
resistance heating	392
resolved shear stress	264
Rf heating	392
RF induction	236
RHEED oscillation	57
rhombohedral structure	388
ring element	243
role of pH	336
ruby	561
ruby pull rod	395
rutile	318 561
$\text{RVO}_4$	338
$\text{RVO}_4 \bullet n\text{H}_2\text{O}$	344
 salts	300
sapphire	561
saturated vapor	247
scanning electron microscope (SEM)	571
scanning electron microscopy (SEM)	107
scanning tunneling microscopy (STM)	107
scintillator	387
screw dislocation	201 205 319
second harmonic generation (SHG), $2\omega$	419
section topography	205
seed crystal	564
seeded physical vapor transit	507
seeded sublimation	194
seeded vertical Bridgman	504
seed holding assembly	392
seeding	197
seed-melt interface	393
seed pulling assembly	392
seed rotation assembly	392
segregation of impurity defects	406
self-flux	445
self-sealing technique	502
self-seeding method	478
self-surfactant effect	78
SEM	107

**Index Terms****Links**

shape	324
shear stress	264
Shellmeier equation	435
short afterglow	387
Si- monochromator-collimator	396
SiC	181
SiC-based devices	181
silicon	566
silicon carbide	235
simulated contrast	212
single crystal	561
single domain crystals	389
sintered nutrient	351
sintering	309
size	324
skeleton crystal	576
skin depth	251
slip system	265
slope efficiency	358
slow cooling	568
small angle boundaries	204 221
soft ampoule method	499
sol-gel	299
solid	563
solid matrix	236
solid solution	564
solid-state growth	563
solid-state laser host crystals	335
solid-state recrystallization (SSR)	509
solid/gas interface	242
solubility	343 568
soluble mobile complexes	343
solute	564
solution growth	502 567
solvent	567
solvent-solute interaction	343
sp <sup>3</sup> bonding	105
spatial distribution	115
special crucible cover	395
spectra acceptance bandwidth	422
spinel	561
spiral growth	108 341
spontaneous nucleation	347 447
Sr <sub>2</sub> Be <sub>2</sub> BO <sub>7</sub> (SBBO)	420
SrTiO <sub>3</sub>	301
SrZrO <sub>3</sub>	301
Stefan flow	238
Stefan-Boltzmann constant	240
step bunching	80

**Index Terms****Links**

step flow	61
step flow mode	64
step-flow mode	78
steric	324
sticking coefficient	238
stirred solution technique	433
STM	107
stoichiometric composition	389
stoichiometric	422
strain field	207
Stranski-Krastanow growth mode	80
stress	427
stress-assisted epitaxy	85
stress-strain relation	263
striations	356
structural characterization	387
sublimation	238
sublimation sandwich method (SSM)	190
substitution	436
substrate surface	94
substrates	513
sum-frequency generation	419
supercooling	563
supersaturation	197 253 312 447 568
superscrew dislocation	205
surface chemical reaction	115
surface diffusion	59
surface diffusion coefficient	61 75
surface dissolution features	356
surface enrgy	322
surface free energy	103
surface morphology	94 355
surface reaction	315
susceptibility	421
SWBXT	204
synchrotron transmission topograph	214
synchrotron white beam X-ray	
topography (SWBXT)	204
synthesis	305
synthesis of vanadates	336
teflon liners	347
temperature	307
temperature acceptance bandwidth	422
temperature differential	189
temperature distribution	254
temperature gradient	197 253 569
temperature monitoring	395
template	324

<u>Index Terms</u>	<u>Links</u>
tensile stress	103
terraced crystal	578
tetragonal	311
tetramethylammonium hydroxide (TMAH)	309
textured diamond film	110
theoretical half-width of diffraction curve	395
thermal conductivity	96 240
thermal cycle treatment	85
thermal dephasing	422
thermal expansion coefficient	103
thermal stress	263
thermal-elastic anisotropic	263
thermodynamic	305
thermodynamics	113
thermoelastic	263
third harmonic generation (THG), $3\omega$	435
threading screw dislocations	215
three-zone furnace	395
threshold pump power	360
Ti:sapphire lasers	439
titania ( $\text{TiO}_2$ )	318
top-seeded Kyropoulos	422
top-seeded solution growth (TSSG)	342 422
transmission topography	205
transmittance spectra	360
transparency	419
transport model	241
transport rate	248
traveling heater method (THM)	499
traveling-solvent floating zone (TSFZ) method	493
traverse topographs	409
traversing mechanism	396
TSSG	342
tunable mid-infrared sources	514
twinning	497 574
two-dimensional nucleation	108
two-dimensional step	107
two-step growth	111
unsaturated bond	104
UV absorption edge	421
UV light	419
vacuum degassing	236
valency of vanadium	338
vanadium ions	338

**Index Terms****Links**

vapor growth	186	501	564
Verneuil method	564		
vertical circle goniometers (VCG)	397		
vertical gradient freeze technique	499		
very low angle grain boundaries	411		
Vickers hardness	428		
view factor	244		
viscosity	445	572	
Voigt notation	264		
volatility	445	570	
wafer	184		
walk-off angle	422		
wavelength	419		
weighing mechanism (WM)	393		
wet chemical	299		
white beam synchrotron X-ray			
topography	204		
white LEDs	514		
wide band gap	99		
X-ray diffraction (XRD)	204	571	
X-ray lithography	99		
X-ray topography	204		
XRD studies	358		
Y <sub>2</sub> O <sub>3</sub> -V <sub>2</sub> O <sub>3</sub> -Y <sub>2</sub> O <sub>5</sub> system	339		
Y <sub>2</sub> O <sub>3</sub> -V <sub>2</sub> O <sub>5</sub>	336		
Y <sub>2</sub> O <sub>3</sub> -V <sub>2</sub> O <sub>5</sub> -V <sub>2</sub> O <sub>3</sub>	337		
Y <sub>2</sub> O <sub>3</sub> -V <sub>2</sub> O <sub>5</sub>	336		
Y <sub>2</sub> O <sub>3</sub> -V <sub>2</sub> O <sub>5-y</sub>	337		
Y <sub>8</sub> V <sub>2</sub> O <sub>17</sub>	342		
YCa <sub>4</sub> O(BO <sub>3</sub> ) <sub>3</sub> (YCOB)	420		
yield diagram	307		
YVO <sub>4</sub>	336		
YVO <sub>4</sub> •nH <sub>2</sub> O	344		
YVO <sub>4-x</sub> (0<x=1) phases	342		
YVO <sub>4-x</sub> phases	337		
yield diagram	307		
zinc chalcogenides	497		
zirconia (ZrO <sub>2</sub> )	316		
ZnO	510		
ZnS	509		
ZnSe	502		
ZnTe	498		
zone melting	339		
β-BaB <sub>2</sub> O <sub>2</sub> (BBO)	420		