Traditional Ceramics

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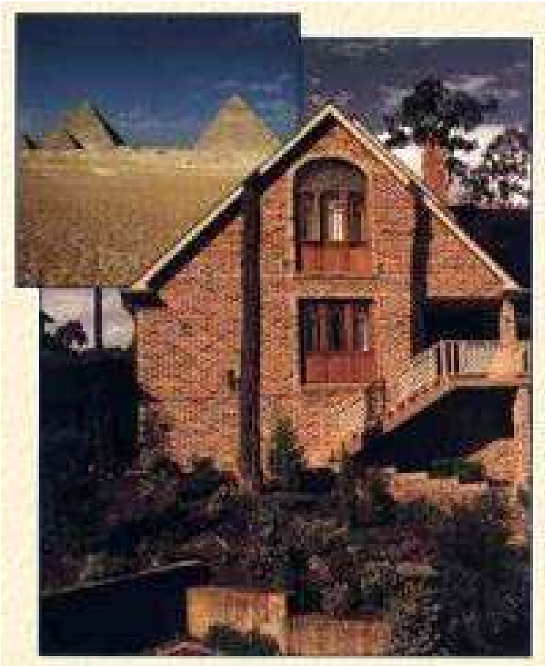


Ceramics – Objectives Part I

- Review the basics
  - Definition, general properties
- Historical overview
- Crystal structures
  - Ionic structures (simple, complex)
  - Covalent structures
  - Carbon based
  - Silicates (Clay)
- Amorphous ceramics (glasses)
  - Definition, general properties

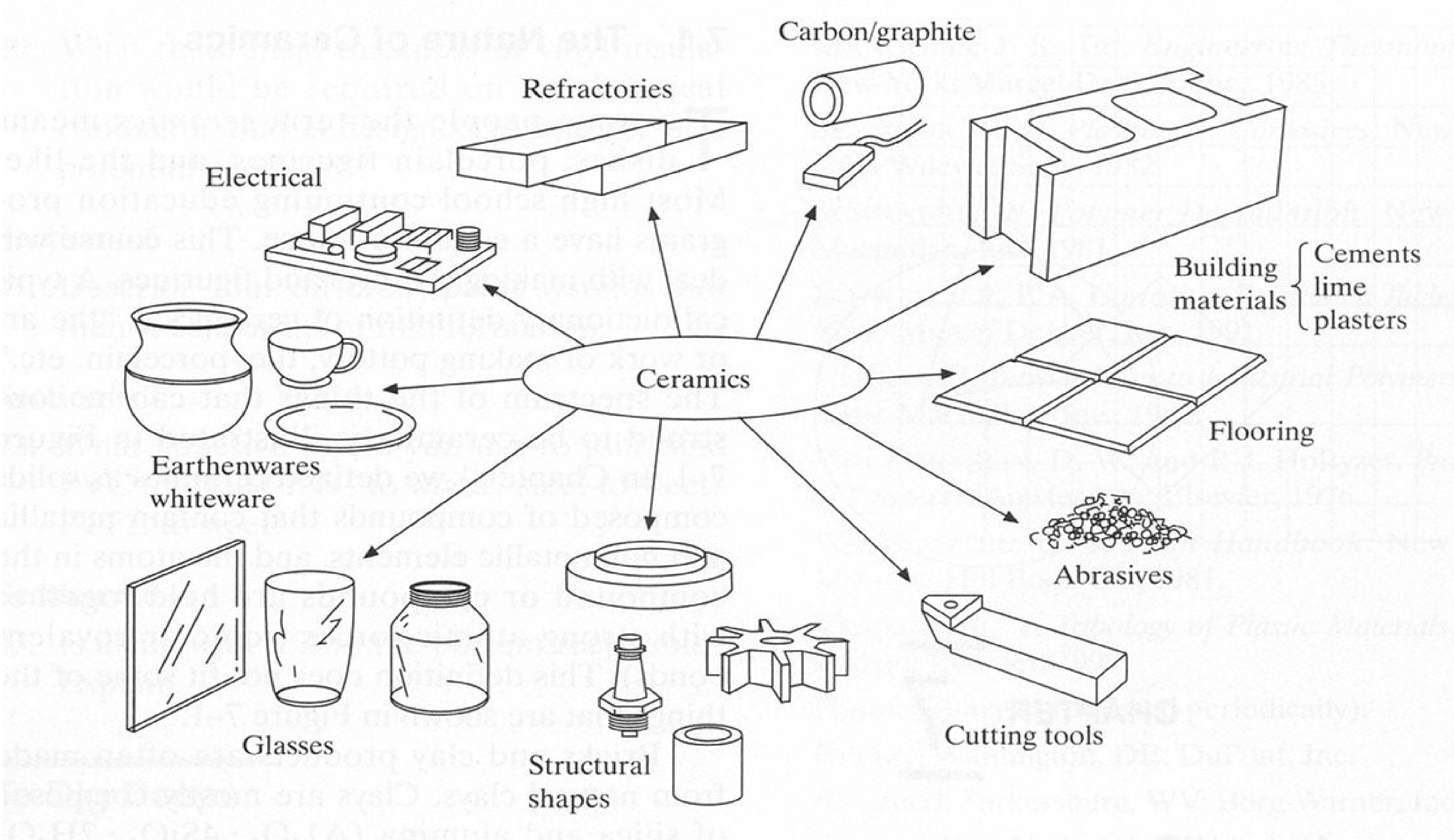
Ceramics – Objectives Part 2

- Microstructure defects
- Stages in solid state and liquid phase sintering
- Explain the driving forces for sintering
- Discuss parameters used to control the process
- Compare solid state and liquid phase sintering
- Describe and compare continuous and batch furnaces

What are ceramics

A ceramic material may be defined as any inorganic crystalline material, compounded of a metal and a non-metal. It is solid and inert. Ceramic materials are brittle, hard, strong in compression, weak in shearing and tension. They withstand chemical erosion that occurs in an acidic or caustic environment. In many cases withstanding erosion from the acid and bases applied to it. Ceramics generally can withstand very high temperatures such as temperatures that range from 1,000 ° C to 1,600 ° C (1,800 ° F to 3,000 ° F). Ceramic materials that do not have oxygen such as silicon carbide can withstand 2,730 ° C.

Ceramics



A ceramic is an inorganic, non-metallic, solid material comprising metal, non-metal or metalloid atoms primarily held in ionic and covalent bonds.

Ceramics

- worldwide market >$100 billion per year*
  - glass 55%
  - advanced ceramics 17%
  - whiteware 10%

*excluding concrete – hydraulic cement production is approx 3 billion tonnes p.a.

Ceramics and Human History

- fired clay pottery ca 10,000BC
  - well developed techniques by 6000BC
  - hand formed (slab, coil techniques)
- pottery wheel
  - probably Mesopotamia, ca 3500BC

Ceramics and Human History

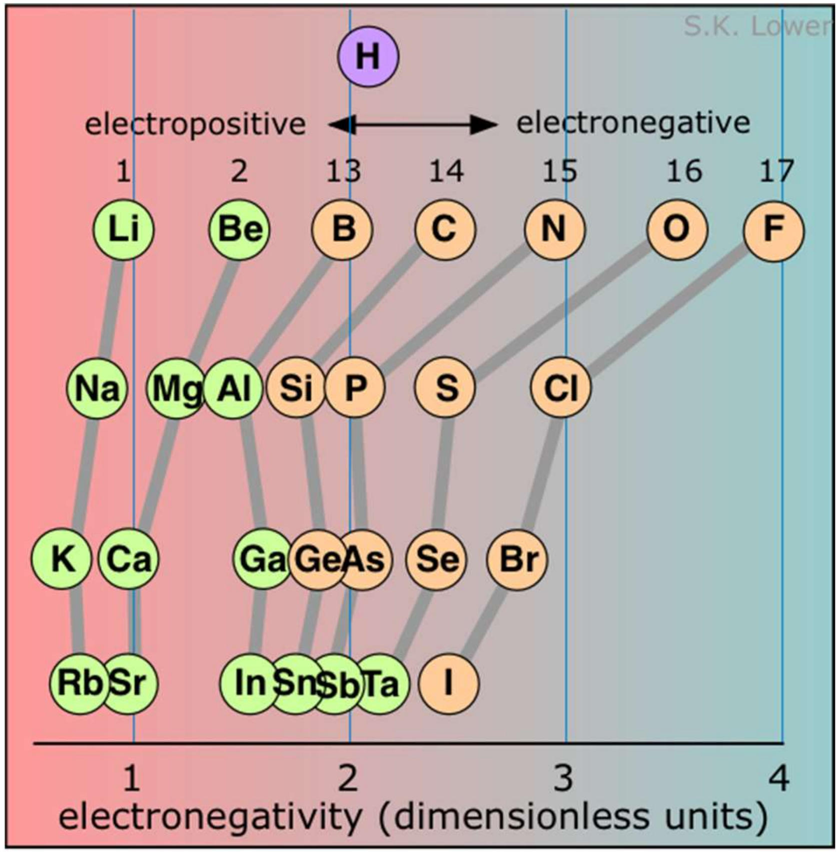
- glass, ca 3000BC , Egypt
- hydraulic cement, ca 200BC, Rome
- porcelain 200AD, China
- silicon nitride 1857
- MgO steelmaking refractories 1880

20^{th} Century

- 1940 $BaTiO_3$
- 1950 SiAlONs
- 1975 transformation toughening of ZrO_2
- 1986 high T superconductors

Crystal Structures

- Begin with ionically bonded structures
  - Most ceramics have mixed primary bonds
  - Greater difference in electronegativity gives greater ionic character

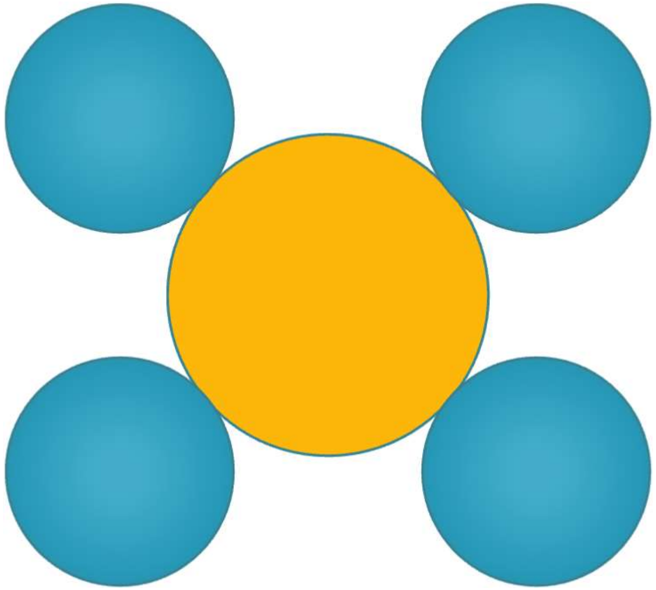


http://www.chem1.com/acad/webtext/atoms/atpt-6.html

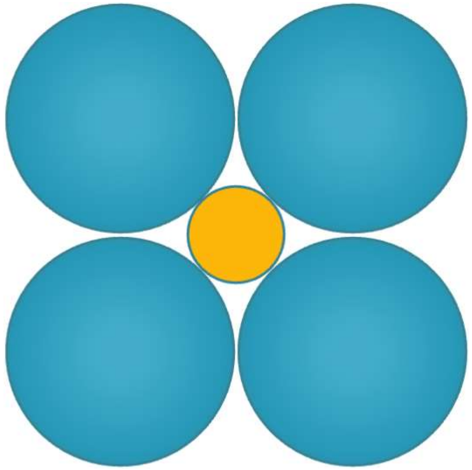
Pauling's Rules for Ionic Crystals

- Neighbouring ions must be touching for stable structure
  - Radius ratio of cation to anion determines geometry
- Local electroneutrality must be maintained
- Shared edges, faces reduce stability
- If several cations, small, high valency ones tend not to share edges, faces
- Number of types of ions tend to be small

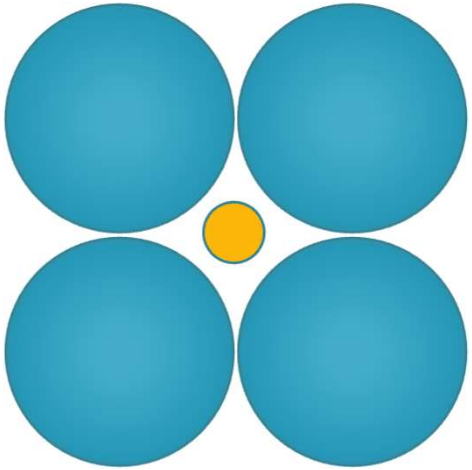
Ionic Crystals



stable



stability limit



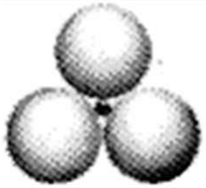
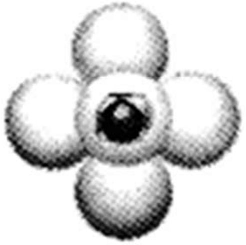
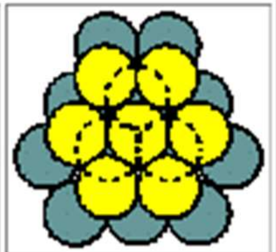
unstable

Critical Radius Ratios

Polyhedron	Co-ord Number	Minimum r_M/r_X
cube	8	0.732
octahedron	6	0.414
tetrahedron	4	0.225
triangle	3	0.155

- where r_M is the cation (metal) radius and r_X is the anion radius

Ionic Crystals

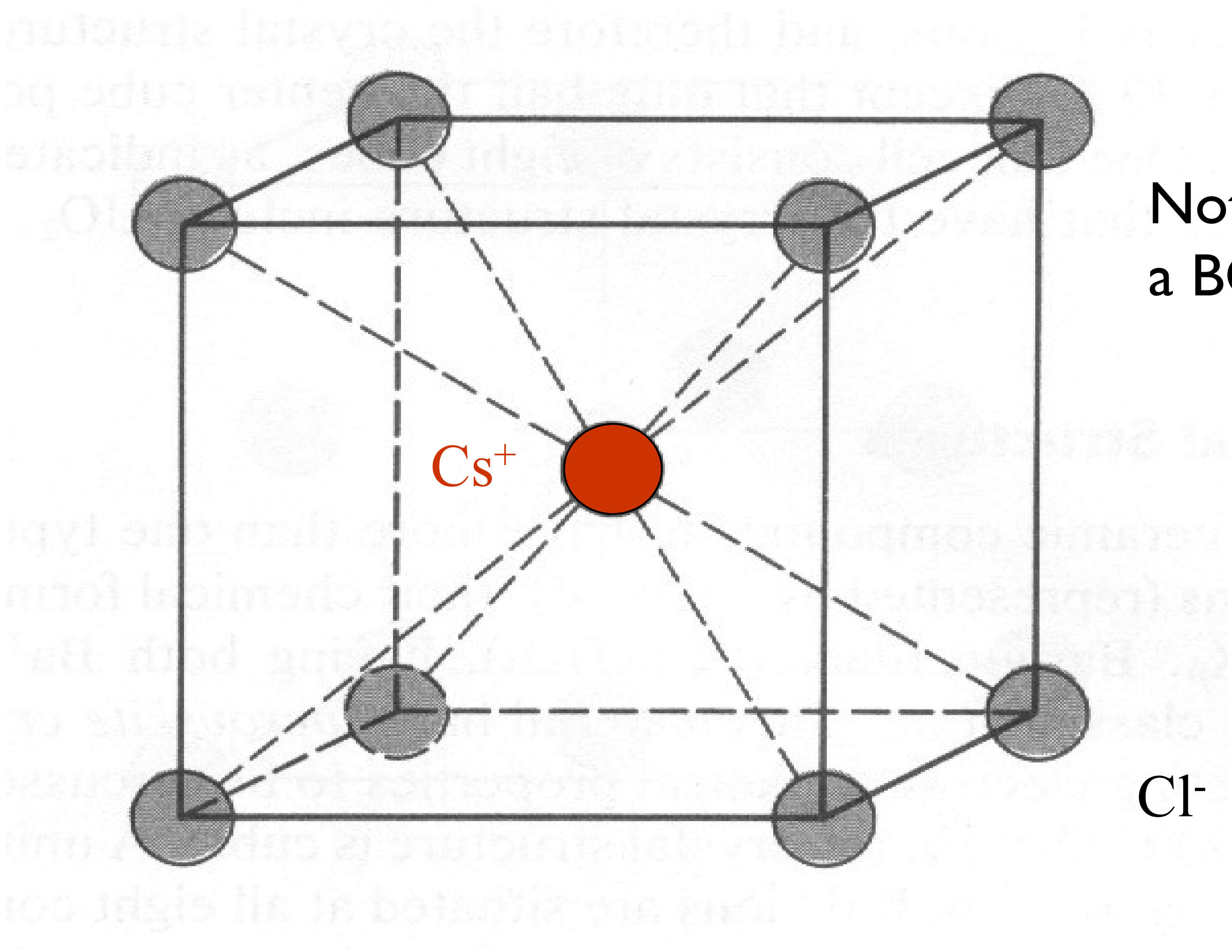
r/R	CN	Name	Geometry
0 - 0.155	2	Linear	
0.155 - 0.225	3	Triangular	
0.225 - 0.414	4	Tetrahedral	
0.414 - 0.732	6	Octahedral	
0.732 - 1.0	8	Cubic	
1.0	12	12-fold (not unique)	

- Geometry dependent on ratio of cation radius to anion radius (r/R)
- Greater ionic character tends to give closer packing

Simple Structures – AX

- one to one ratio of cation to anion
- many ceramic materials have these structures

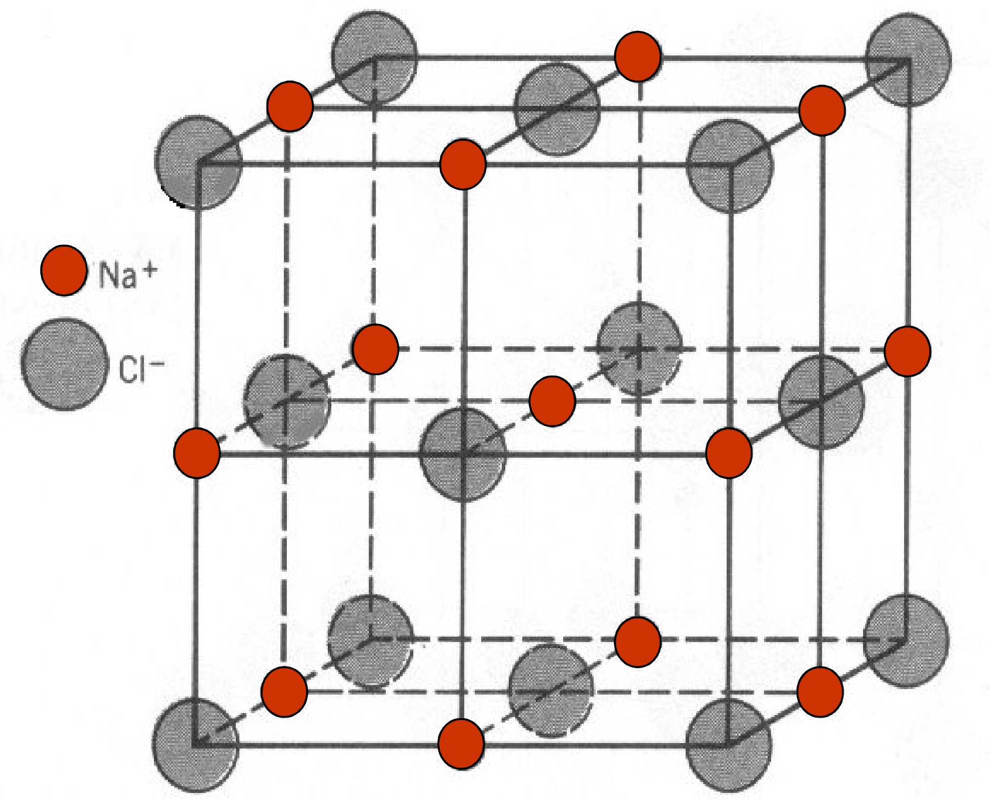
AX Structure - CsCl



Note: This is <u>not</u> a BCC structure.

Simple Cubic lattice – radius ratio=0.94

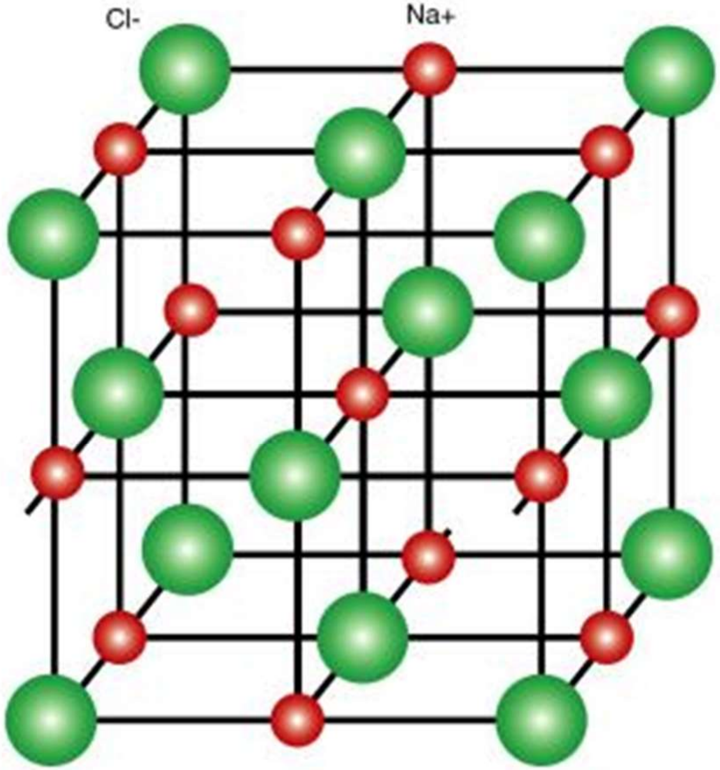
AX Structure - NaCl

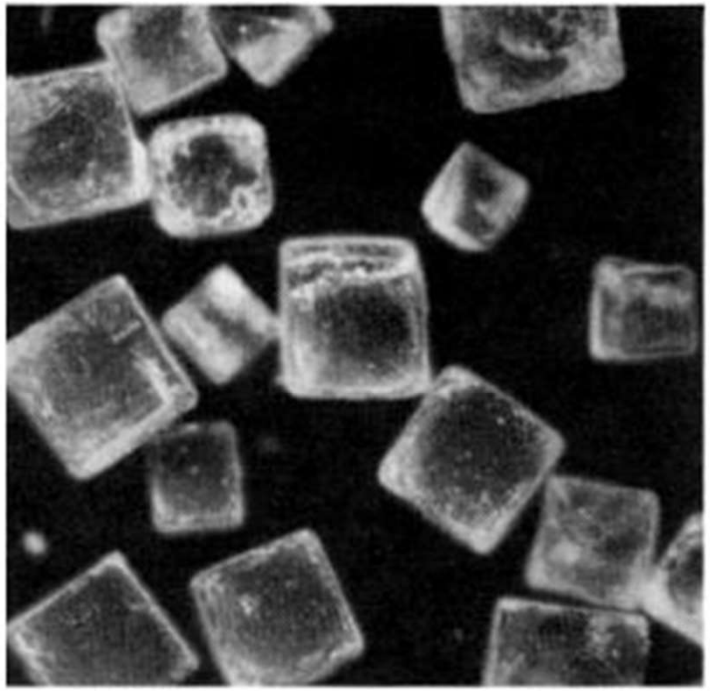


2- FCC interpenetrating lattices.

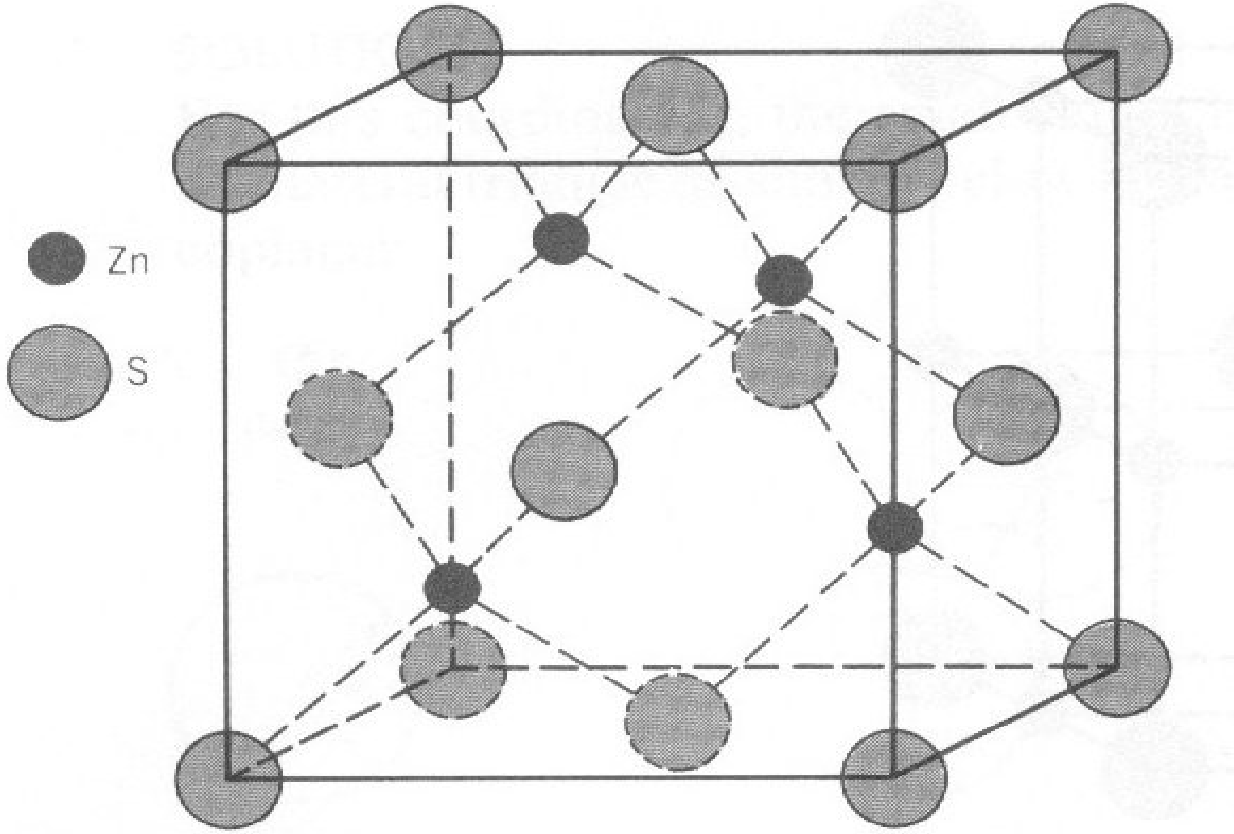
MgO, FeO, NiO, Some sulphides, & carbides

Sodium chloride structure



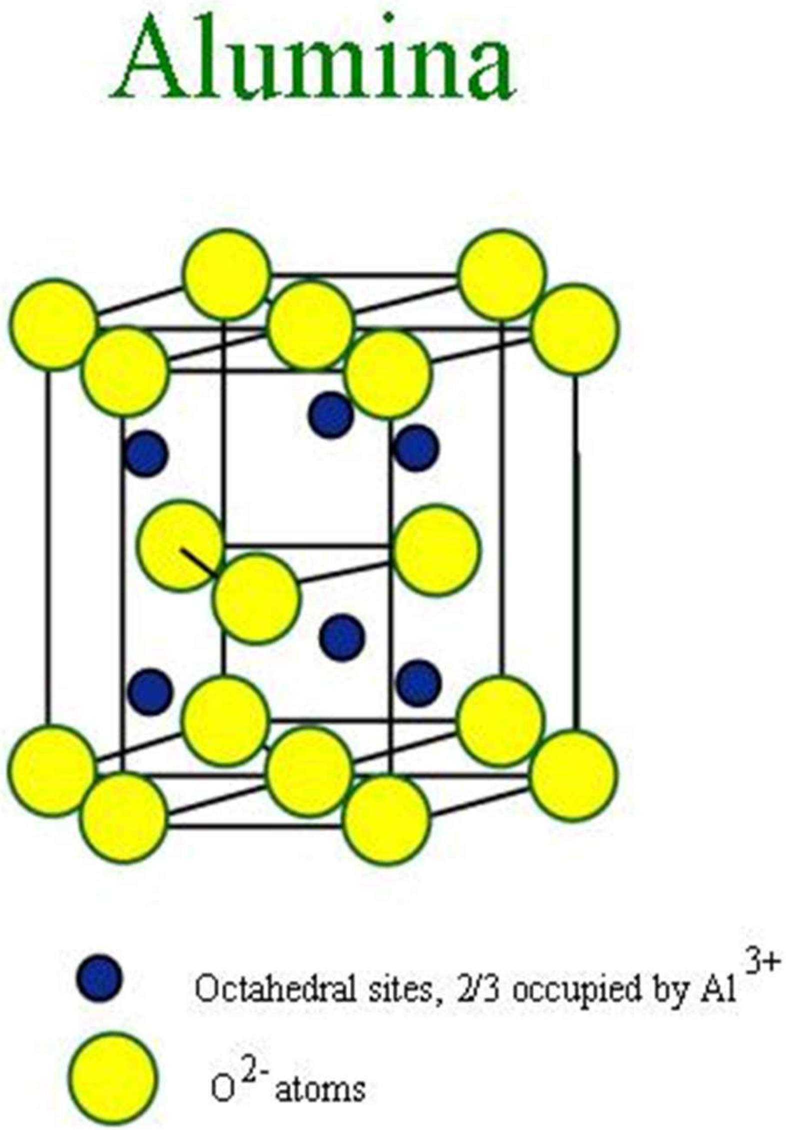


AX structure – ZnS



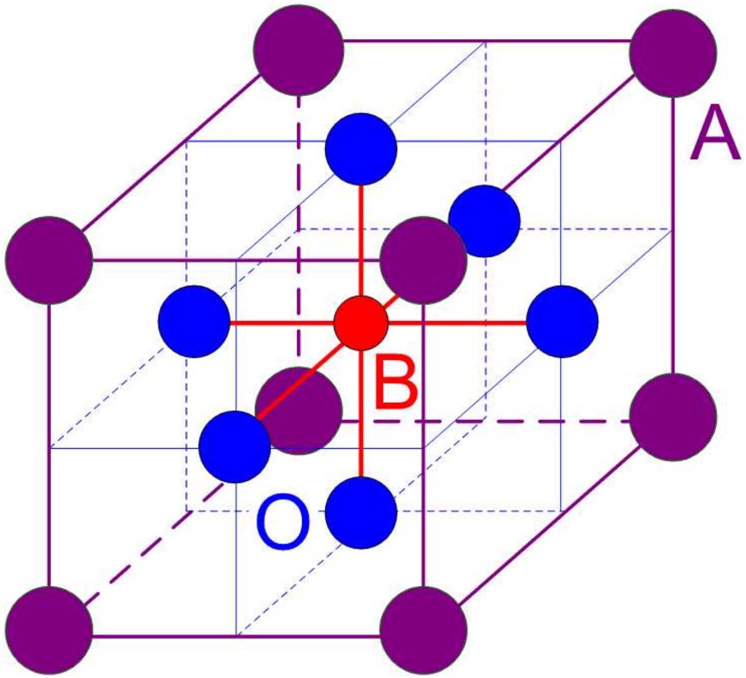
Fcc lattice, radius ratio = 0.34 for ZnS

GaAs, InP, cubic SiC



- Al_2O_3 has trigonal structure, but can be represented as hexagonal oxygen lattice with Al ions in octahedral interstices

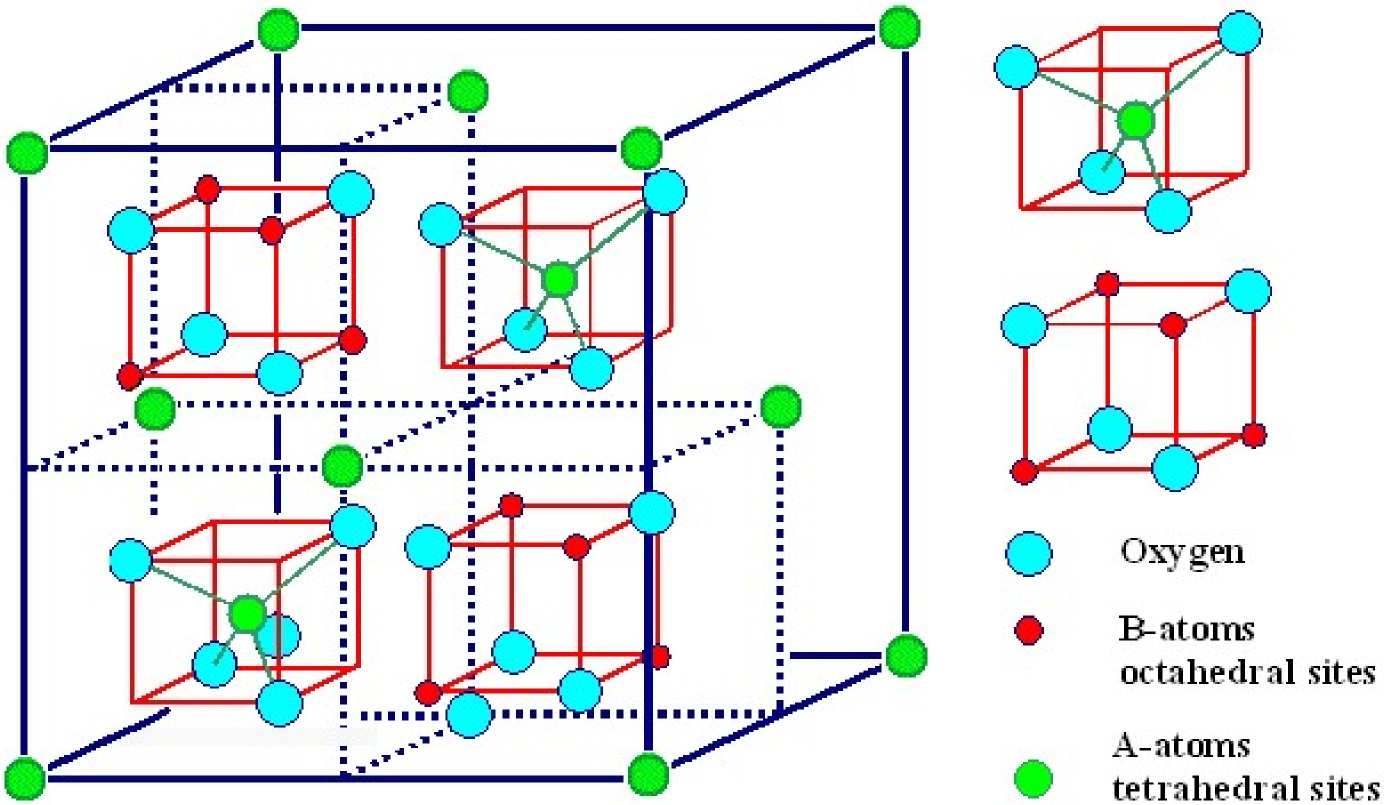
Perovskite (ABO_3) Structure



http://research.ncku.edu.tw/re/articles/e/20080411/images/080304092145kgEFTR.jpg

- $BaTiO_3$ is typical
- Below 120°C Ti^{4+} ion sits off-centre, creating dipole
- Common amongst ferroelectric, piezoelectric ceramics

Spinels (AB_2O_4 or $AO.B_2O_3$)



AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell

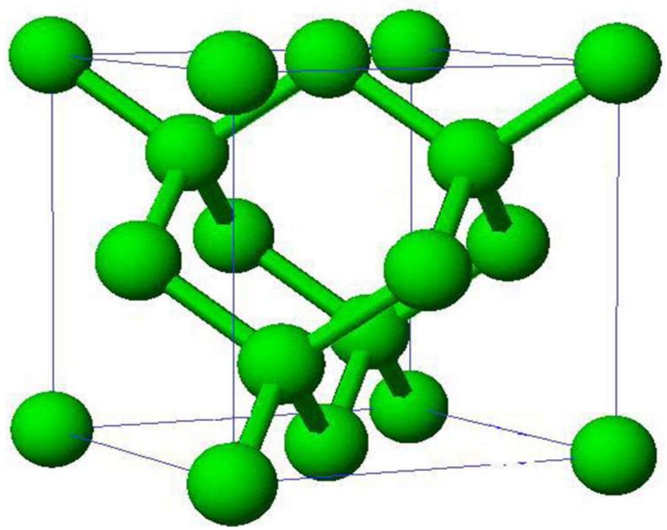
http://www.freewebs.com/diendanhoak26/hoahocvoco.htm

Summary of most common ceramic crystal structures

Structure Name	Structure Type	Anion Packing	Coordination Numbers: Cation	Coordination Numbers: Anion	Examples
Rock salt (sodium chloride)	AX	FCC	6	6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2, ThO_2
Perovskite	ABX_3	FCC	12(A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

Covalent Crystals

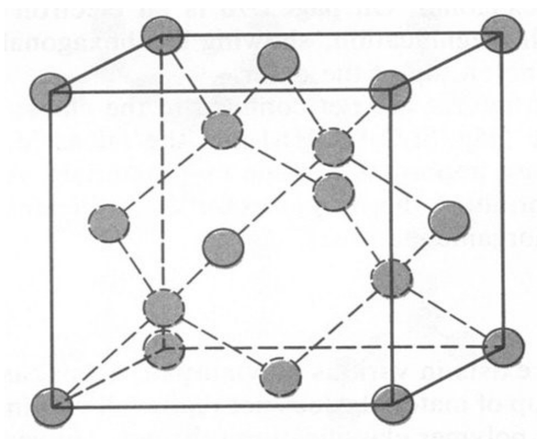
- more open structures
  - Not close packed
- e.g. diamond
  graphite
  "Bucky balls"



Carbon

- Pure carbon -many polymorphs also exists in the amorphous state.
  - Diamond, similar to ZnS in structure
  - Graphite is considered to be a crystalline ceramic
  - Fullerenes, $C_{60,}$ recently discovered polymorph - with interesting properties.

Diamond



- AX type crystal structure similar to ZnS.
- Each carbon atom covalently bonded to four other C atoms in a *diamond-cubic* crystal structure
- optically transparent and extremely hard (hardest natural material known)
- cruder or industrial forms used as abrasives, indentors and coatings (especially thin films)

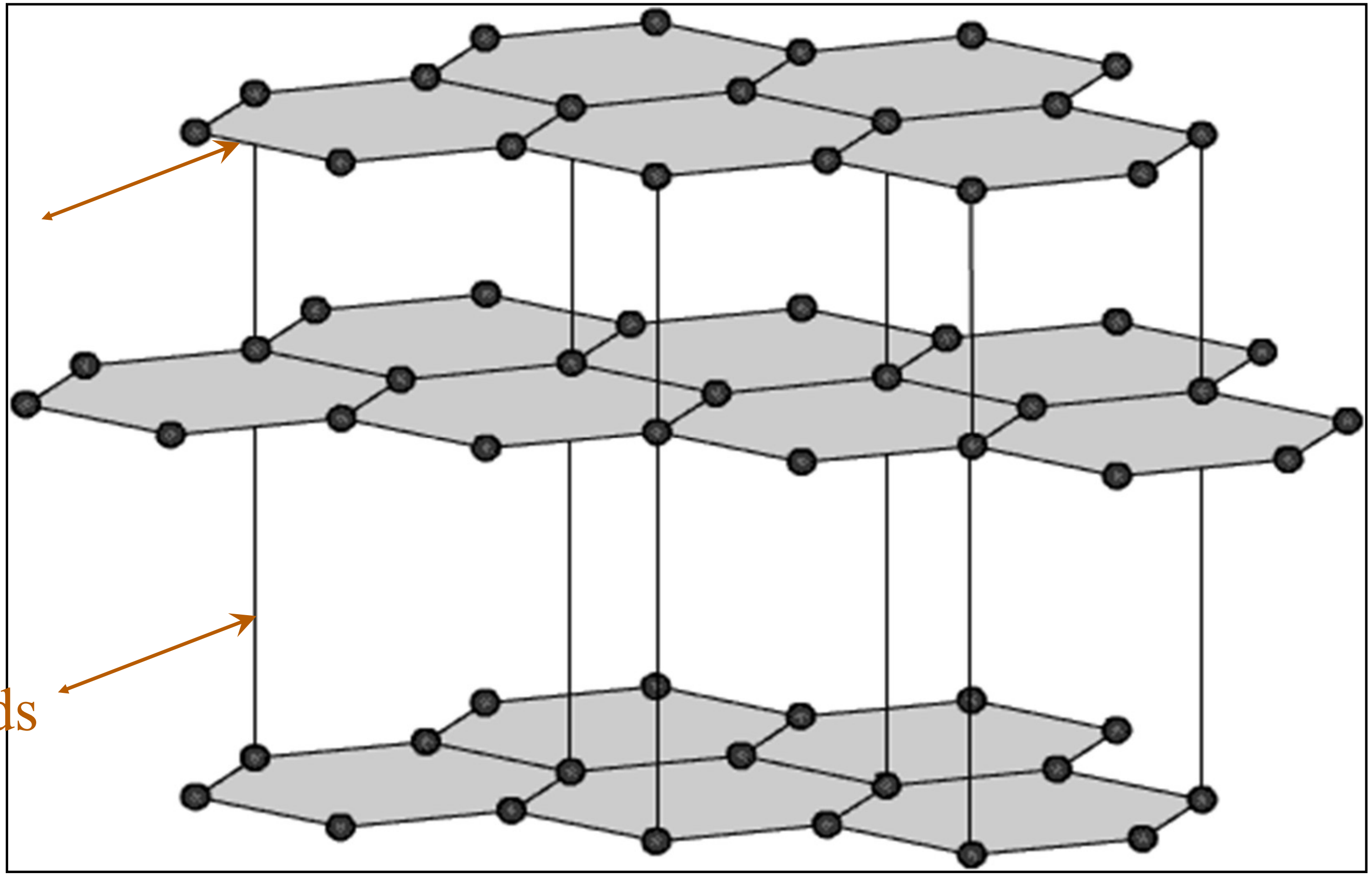
Graphite

- Layers of hexagonally arranged covalently bonded C atoms
- Layers bonded by weaker Van der Wals bonds giving easy slip
- Excellent as a dry lubricant, relatively high strength at elevated temperatures, high thermal and electrical conductivity, low thermal expansion, resistance to thermal shock, and good machinability.
- Usage: electrodes, heating elements, crucibles, casting molds, rocket nozzles, and other applications.

Graphite

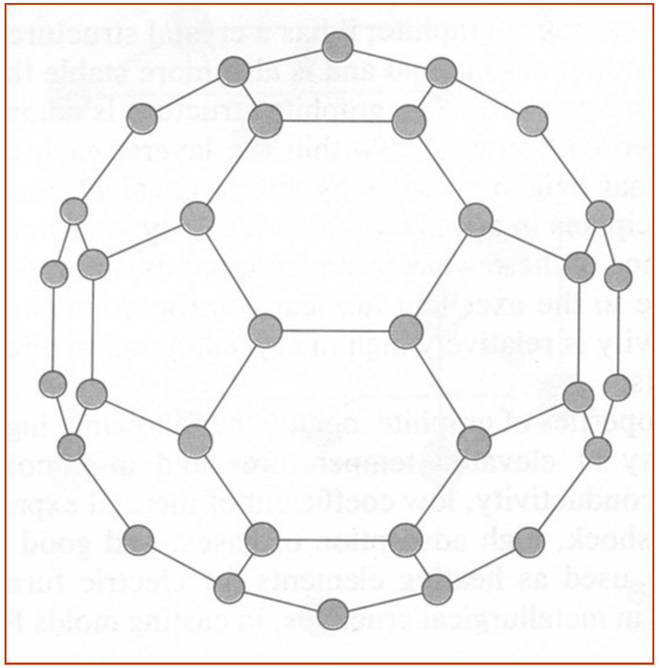
covalent bonds

secondary bonds



Fullerenes, C_{60}

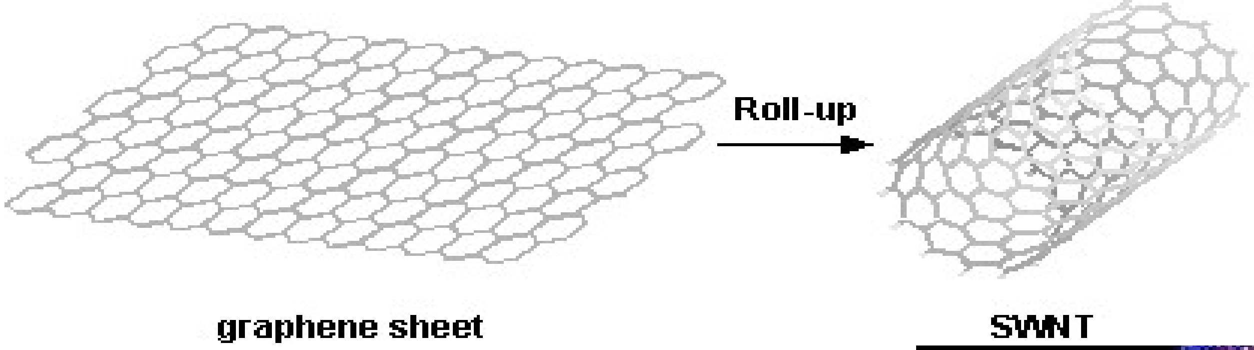
- **M**olecular form of carbon hollow spherical structure resembling a geodesic dome
- Discovered 1985, have since been found to occur naturally
- In solid crystalline state, C_{60} molecules pack together in a FCC unit cell arrangement, lattice parameter a =1.41nm.
- pure solid material density ~1.65 g/cm^3
- relatively soft
- non-conducting (no free electrons)

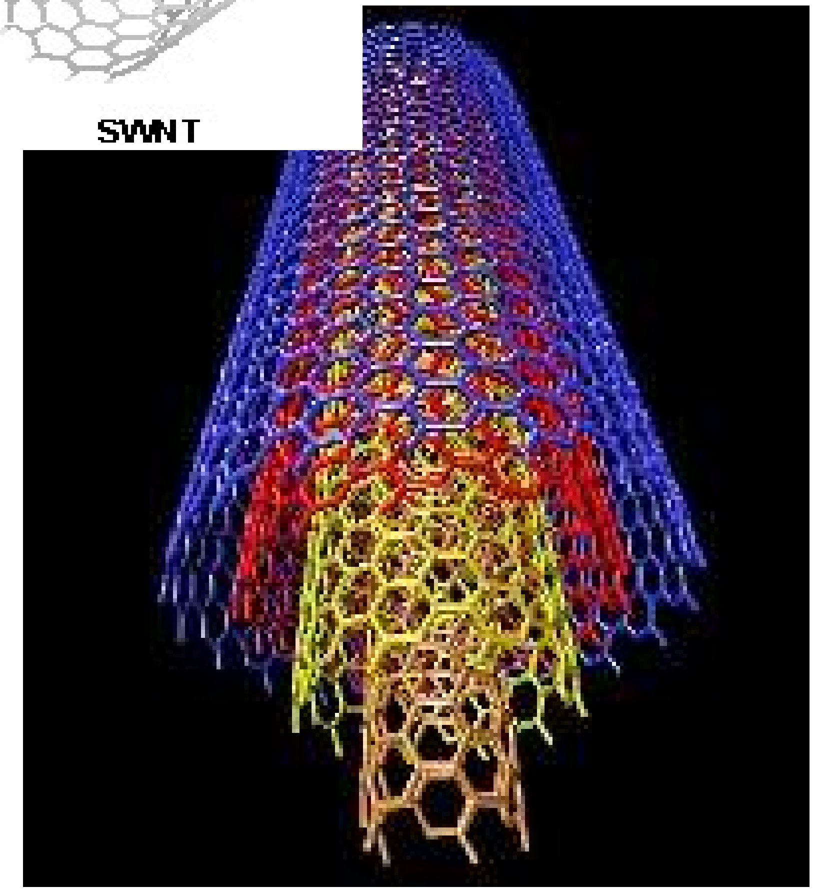


Properties of Buckyballs

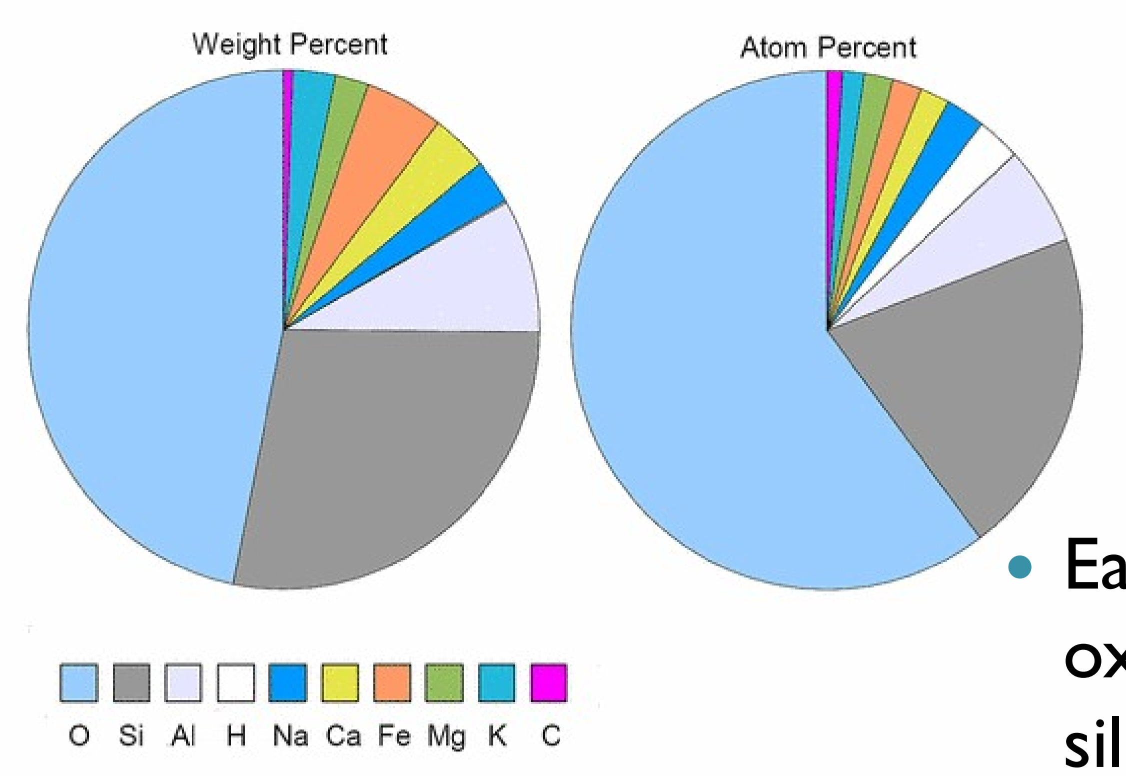
- If alkali metal anions, (e.g. K^+) present (usually 3 per C60 molecule), material (K_3C_{60}) displays characteristics of a metal.
  - In fact, K_3C_{60} is considered to be the first molecular metal
- K_3C_{60} buckyballs and similar molecular materials become super conducting at about 18K
- Applications in low-power consumption, low-pollution, magnetic-levitation and propulsion devices for mass transit systems.

Carbon Nanotubes





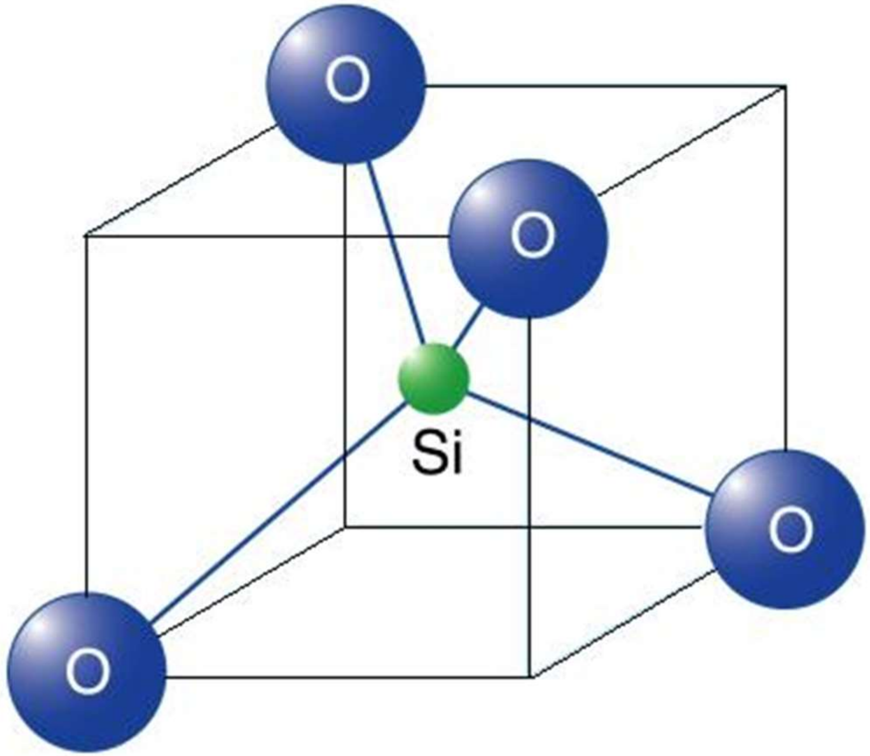
Silicates



http://www.quartzpage.de/gen_ori.html

- Earth's crust ~65% oxygen atoms, 25% silicon
- Silica and silicates are everywhere!

Tetrahedral Silica unit

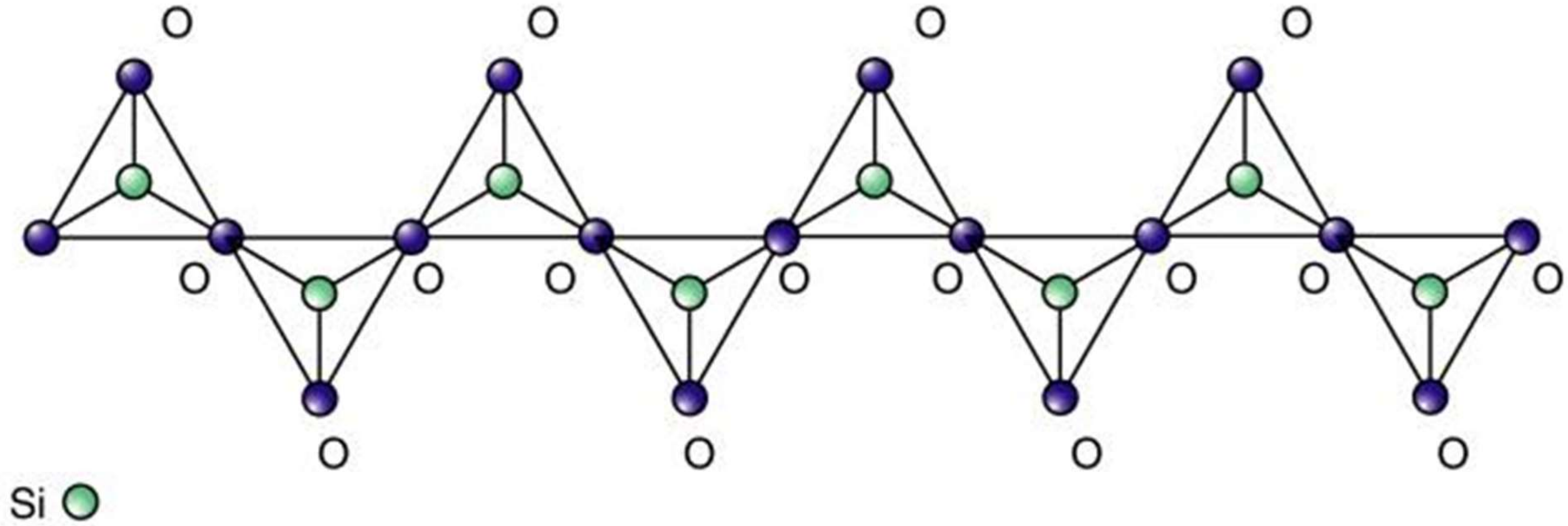


Radius ratio = 0.29, tetrahedral co-ordination

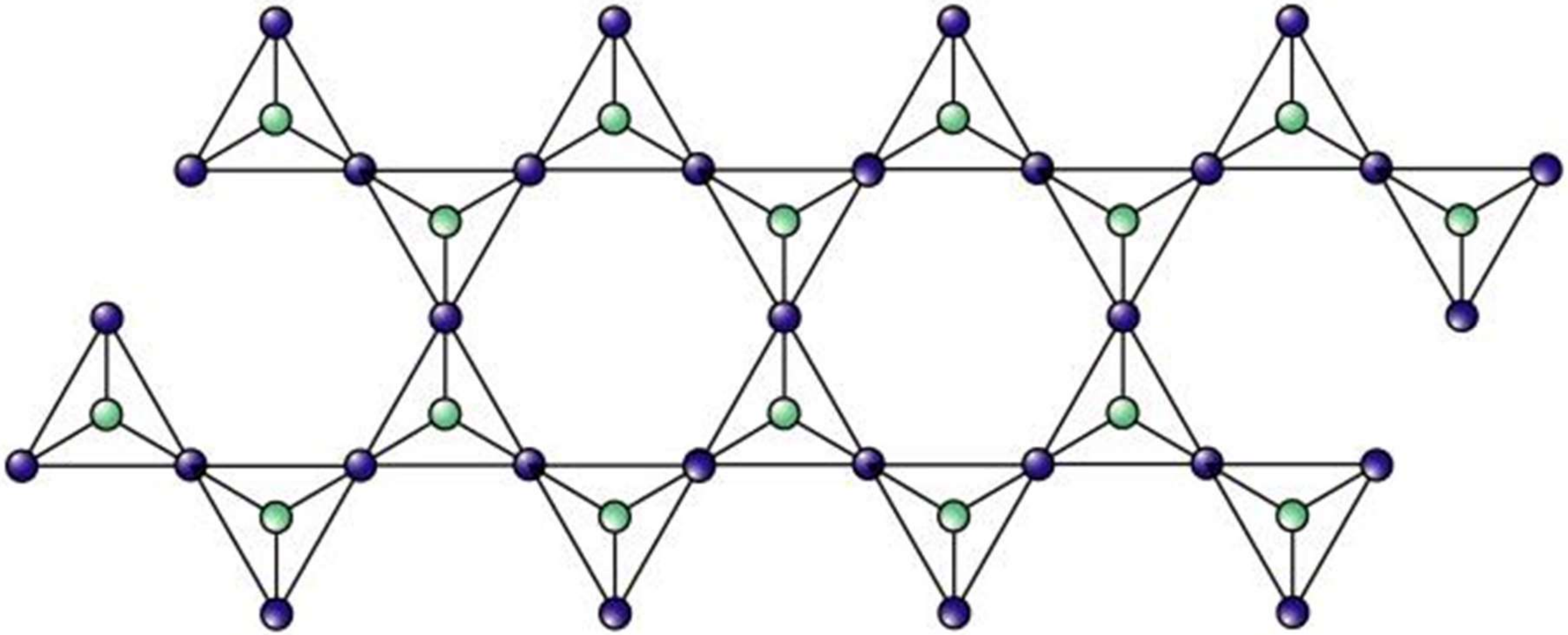
Silicates

- SiO_4^{4-} tetrahedra can be combined in many ways
- Joined at corners by oxygen = "bridging oxygen"
  - Number of bridging oxygens characterises structure
- Primary bond has significant covalent and ionic character

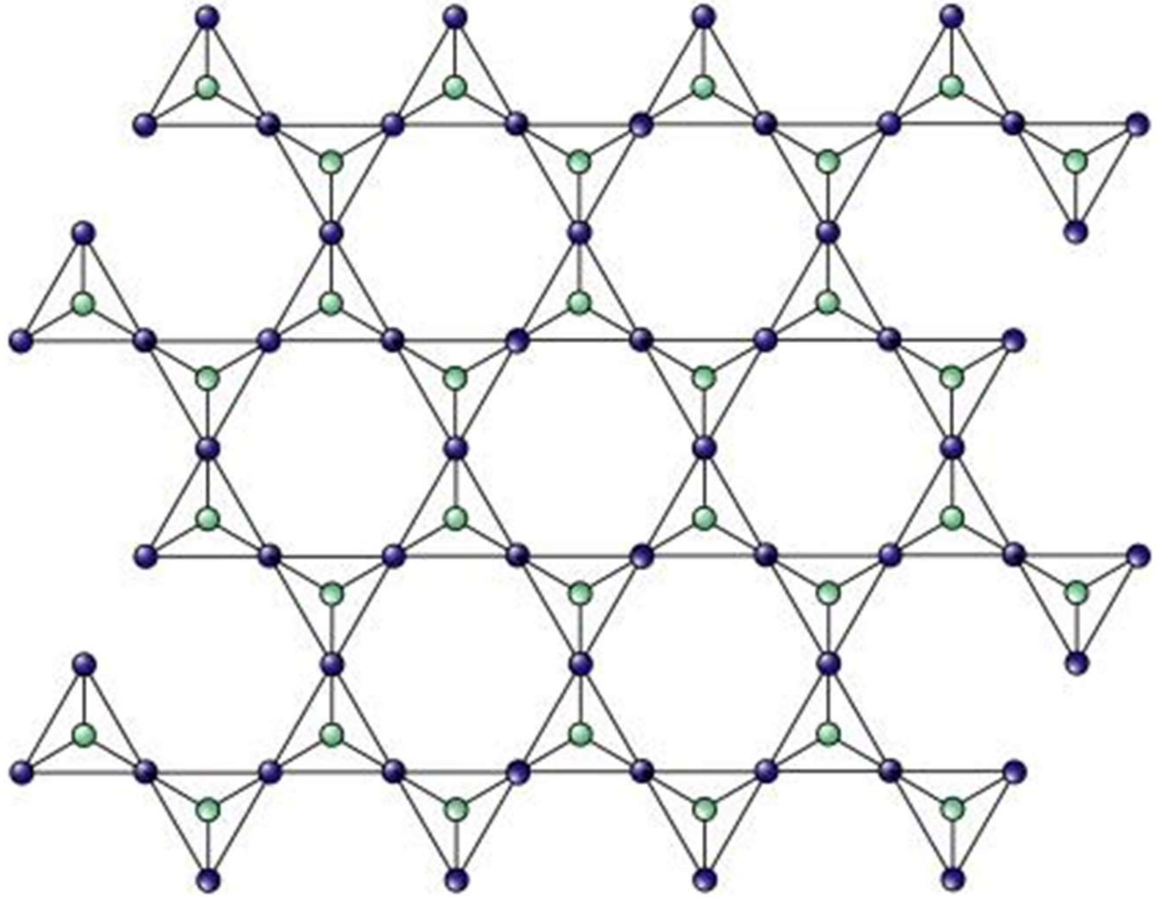
Single chain of SiO_4^{4-} units



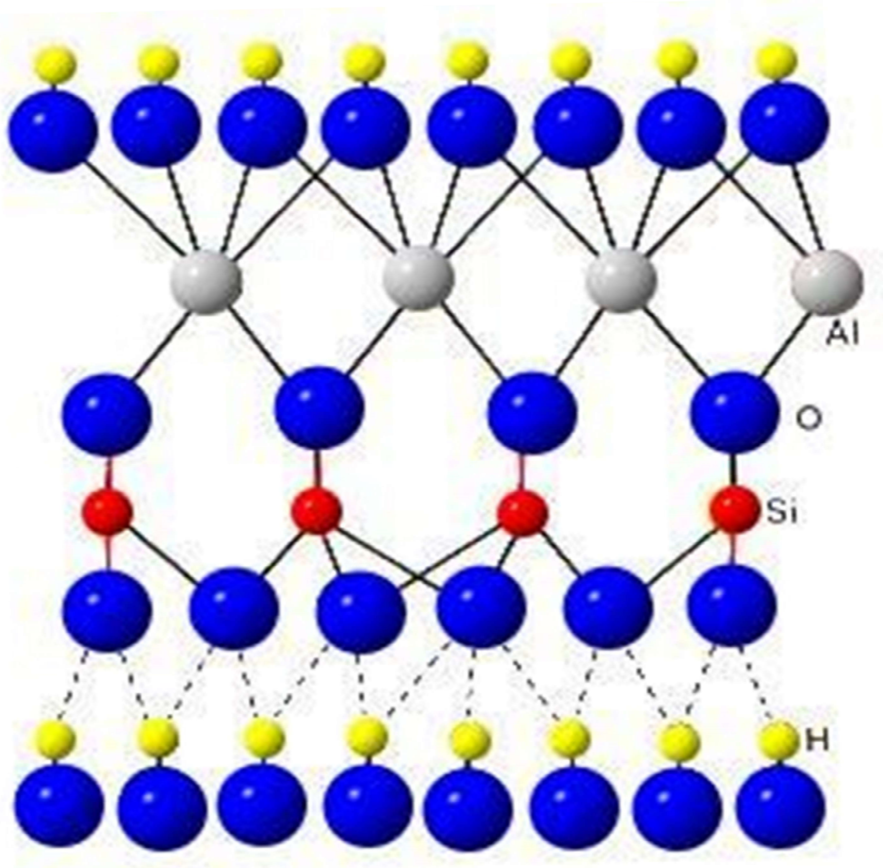
Double chain of SiO_4^{4-} units



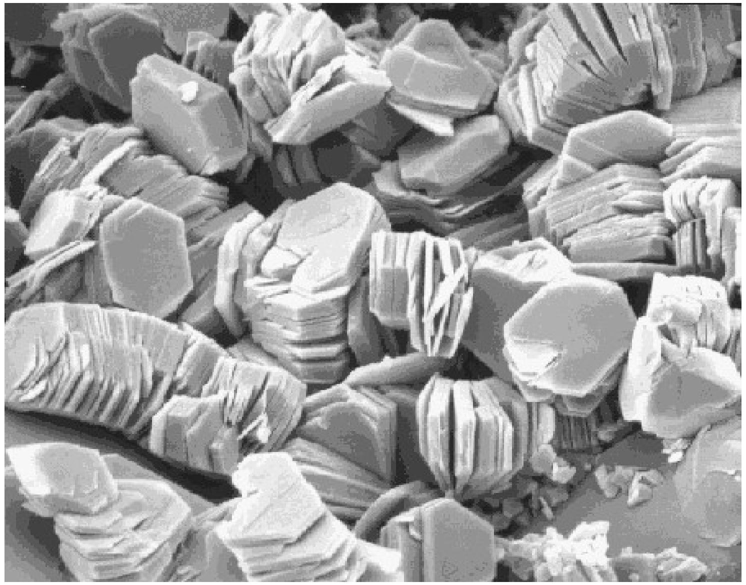
Silicate sheet



Kaolinite

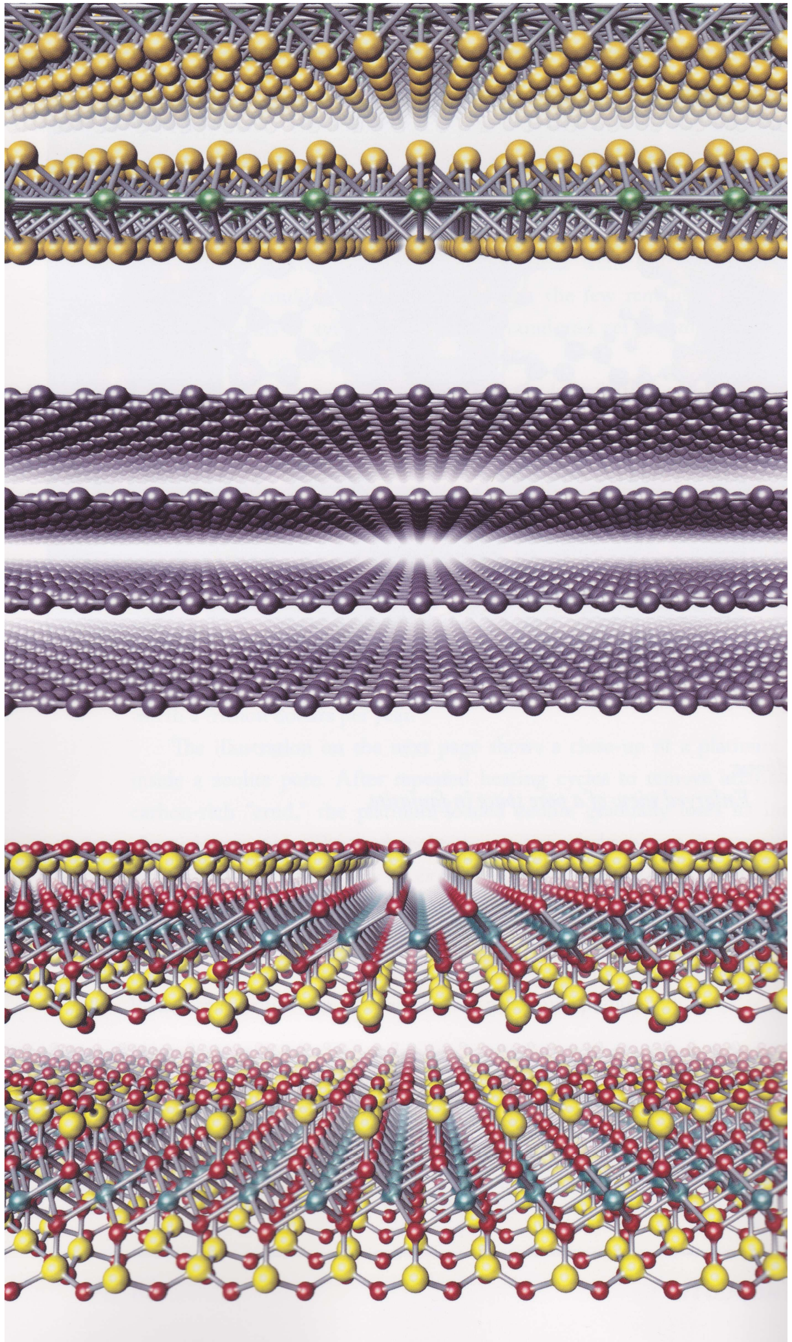


http://www.doctorspiller.com/ceramics_1.htm



http://originoflife.net/information/graphics/kaolinite.png

Sheet Structures



Molybdenite
MoS_2

Graphite
C

Talc
$Mg_3(Si_4O_{10})(OH)_2$

K.S. Deffeyes, S.E. Deffeyes, Nanoscale: Visualising an Invisible World, MIT Press, 2009

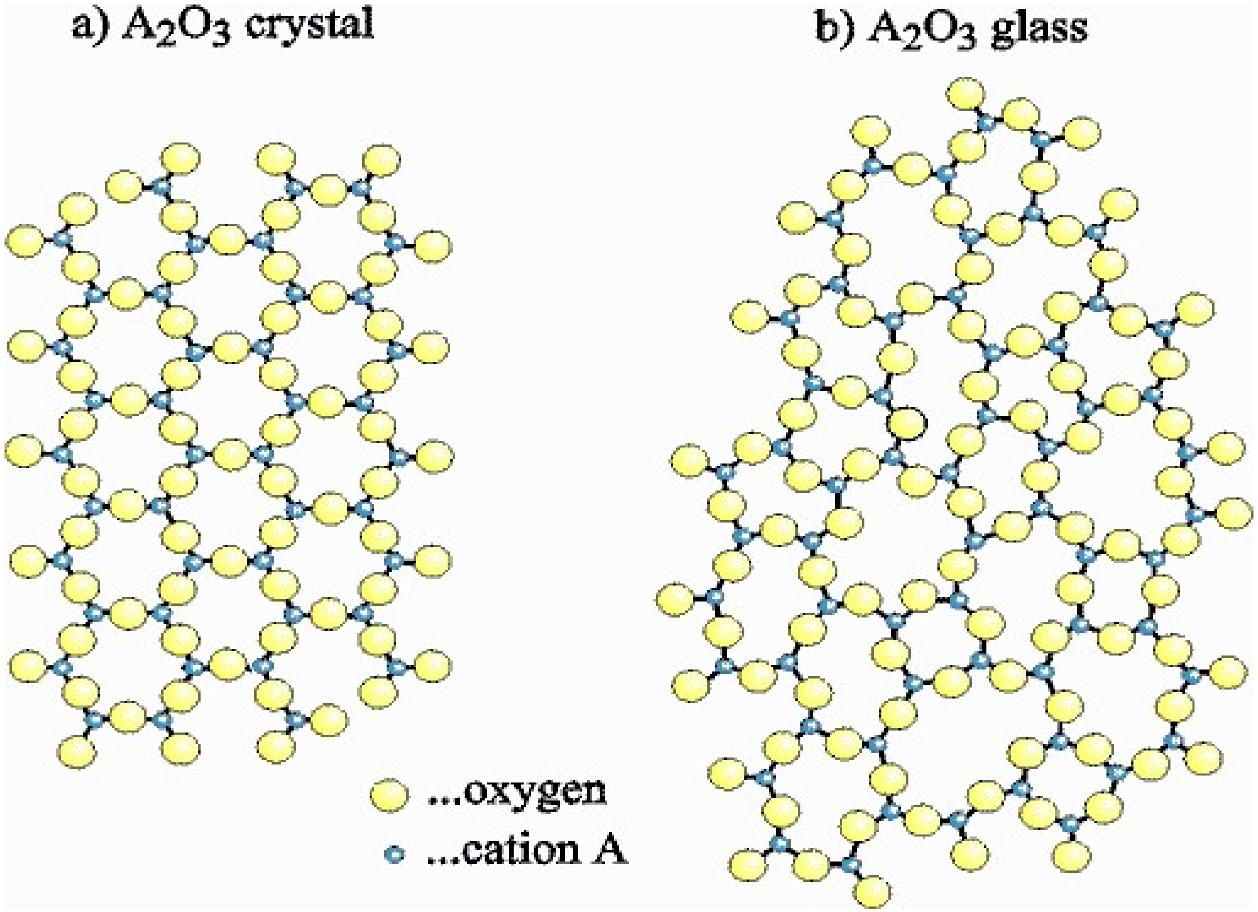
Non-Crystalline Ceramics

- commonly based on silicon dioxide ("silica")
- random structure, lacks long range order
- "glass" structure
  - Mainly ionic bonds

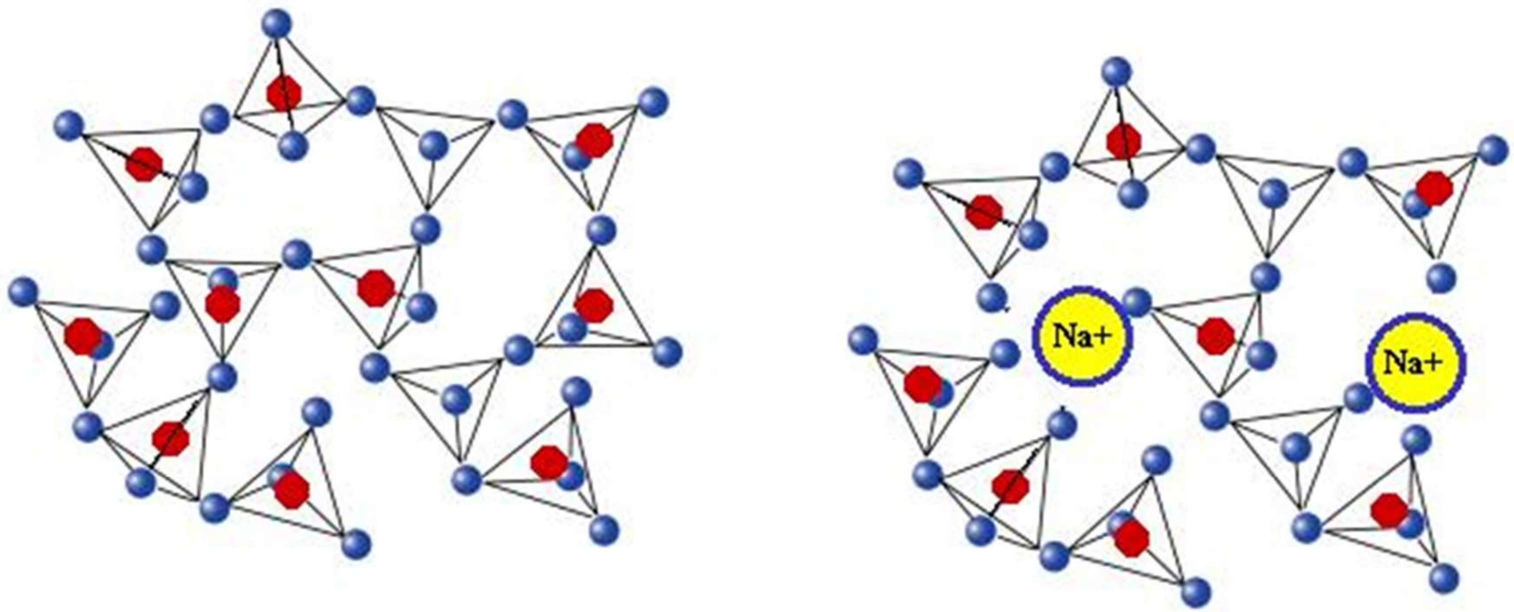
Amorphous Ceramics - Glasses (Na_20, $Ca0$, K_2O, etc)

- The viscosity of the material at ambient temperature is relatively high, but as the temperature increases there is a continuous decrease in viscosity.
- When the viscosity has decreased to the point that the ceramic is a fluid, it is considered to have melted.
- At ambient temperature while it is still solid, it is said to be in the "glassy" condition.
- There is no distinct melting temperature (T_m) for these materials as there is with the crystalline materials.
- The glass transition temperature, T_g, is used to define the temperature below which the material is a "solid" and defines a practical upper limit on service temperature.

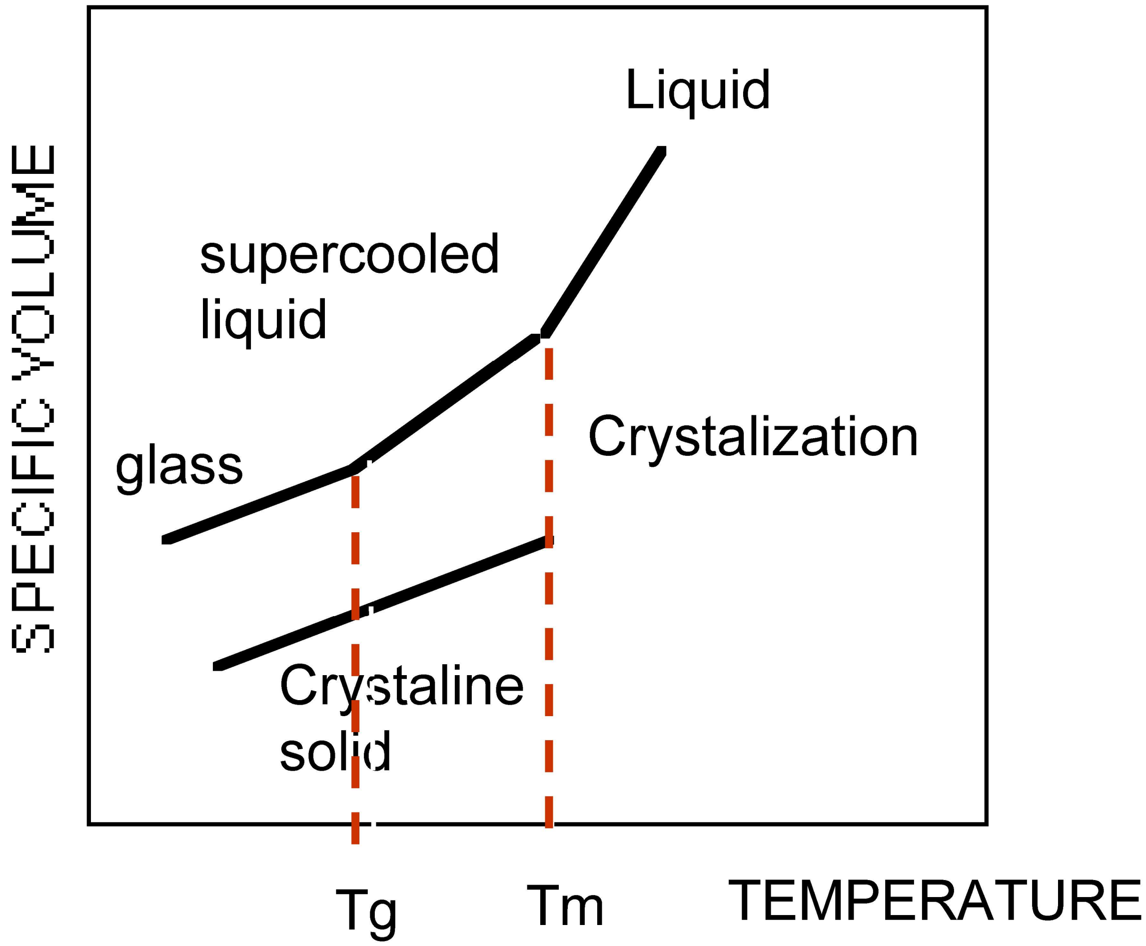
Crystalline vs Amorphous (Glass)



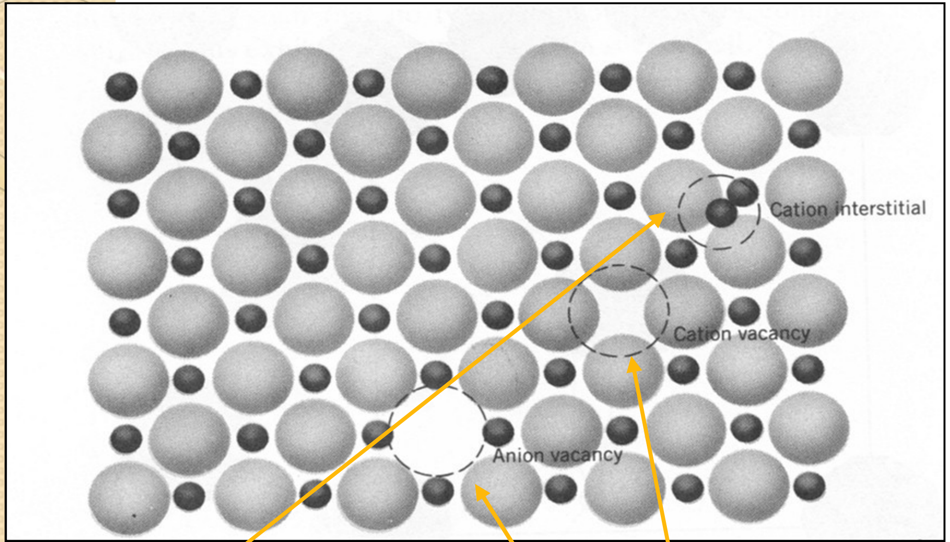
Formation of common glass



Specific volume of amorphous and crystalline ceramics.

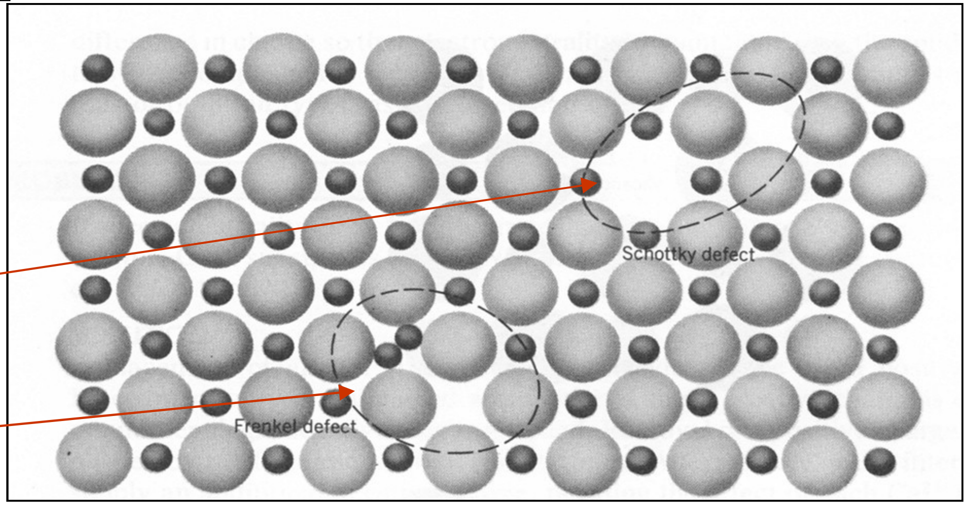


Defects in Crystalline Ceramics



- Vacancy
- Interstitial
- Dislocation
- Grain Boundary

Cation Interstitial
Anion Vacancy
Cation Vacancy

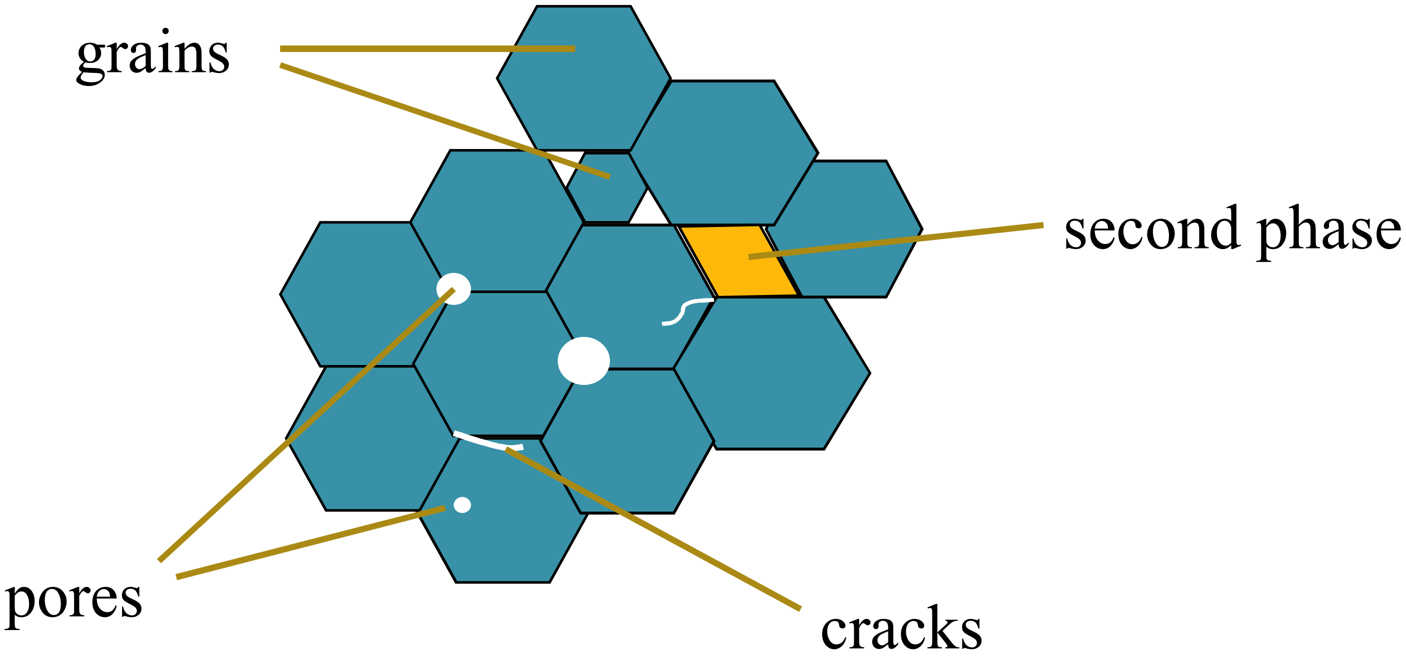


Schottky Defect
Frenkel Defect

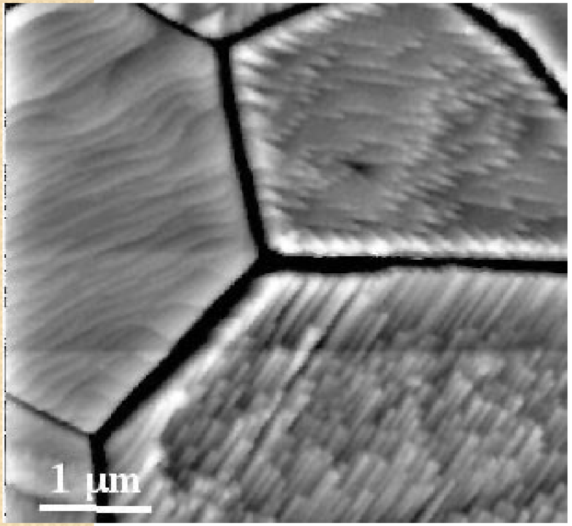
Electro-neutrality

Microstructure

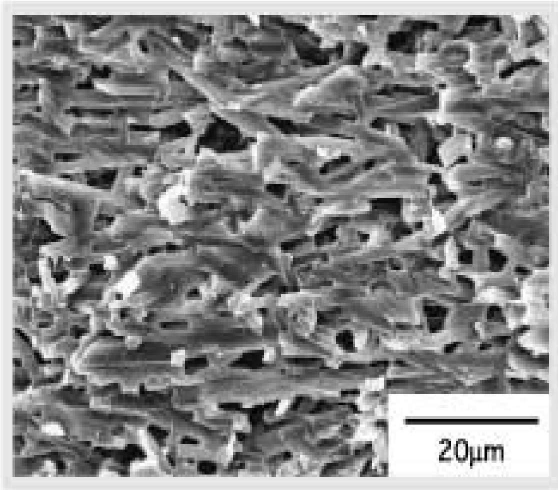
- Put a lot of atoms, unit cells together get "microstructure"



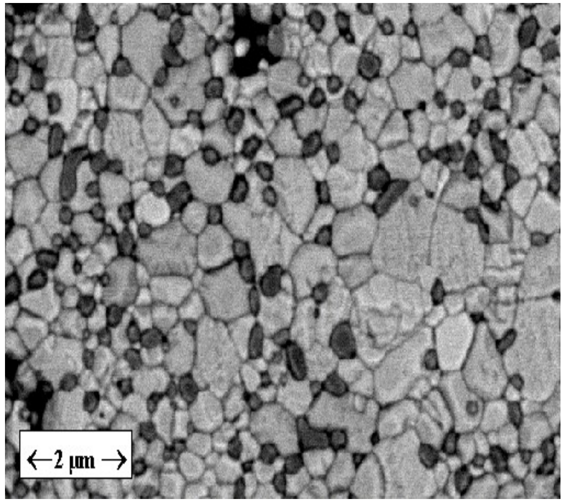
Ceramic Microstructures



Aluminium
Oxide

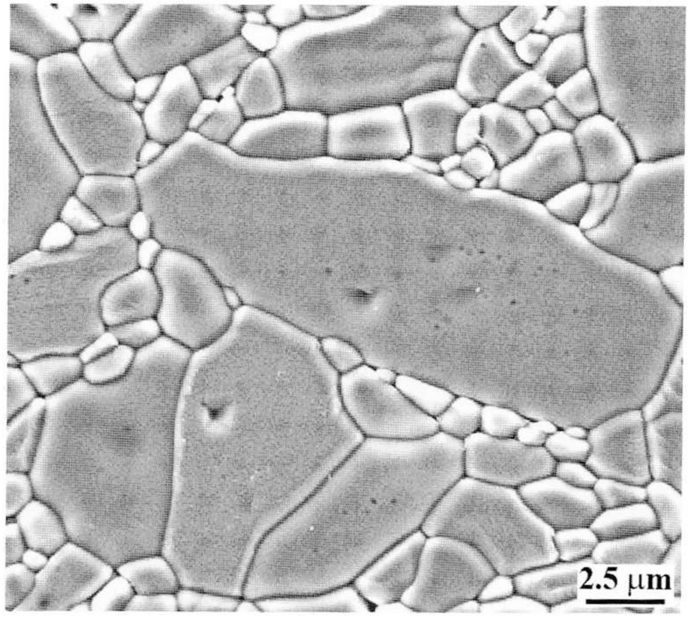


Silicon Nitride
(14% porosity)



Rare Earth Doped
Cerium Oxide

Firing and Sintering



Objectives

- Describe stages in solid state and liquid phase sintering
  - Clay based ceramics
- Explain the driving forces for sintering
- Discuss parameters used to control the process
- Compare solid state and liquid phase sintering
- Describe and compare continuous and batch furnaces

Sintering

- shaped green ceramic has particulate nature
  - porous
  - little strength
- increased strength and density achieved by “sintering”
  - solid state (diffusion)
  - liquid phase (flow, dissolution)

Sintering

- application of heat (>$0.5T_m$)
- driving force is the lowering of surface energy
  - surface area reduced
  - can lead to shrinkage
  - increased density

Stresses and Surfaces

- stresses associated with curved surface
  - higher surface area per unit vol
- effective surface stress on sphere

$$\sigma = \frac{4\gamma}{D}$$

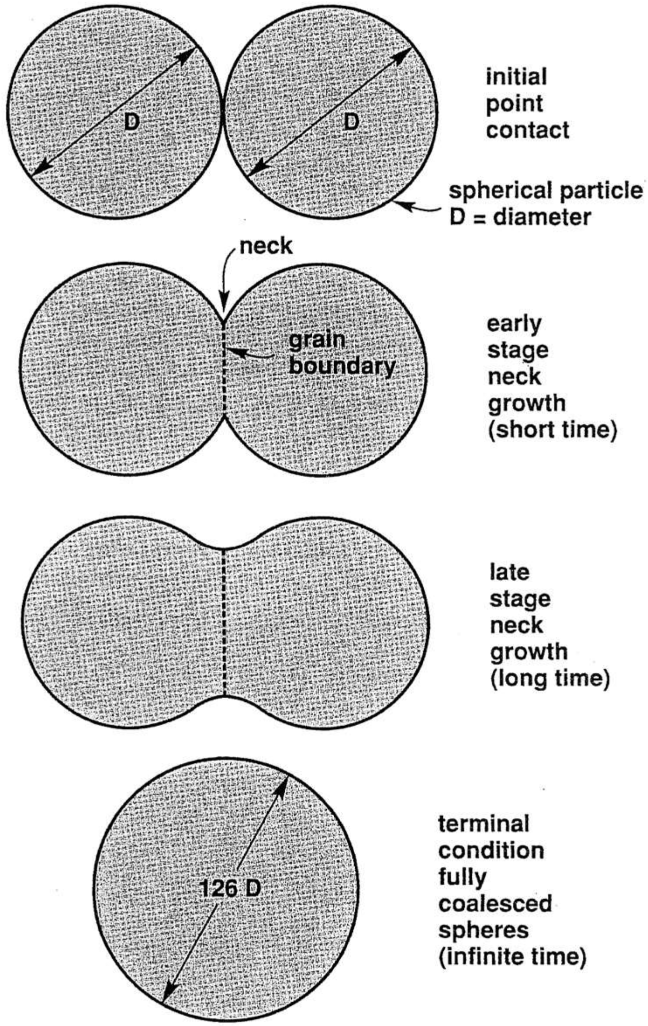
surface energy

diameter

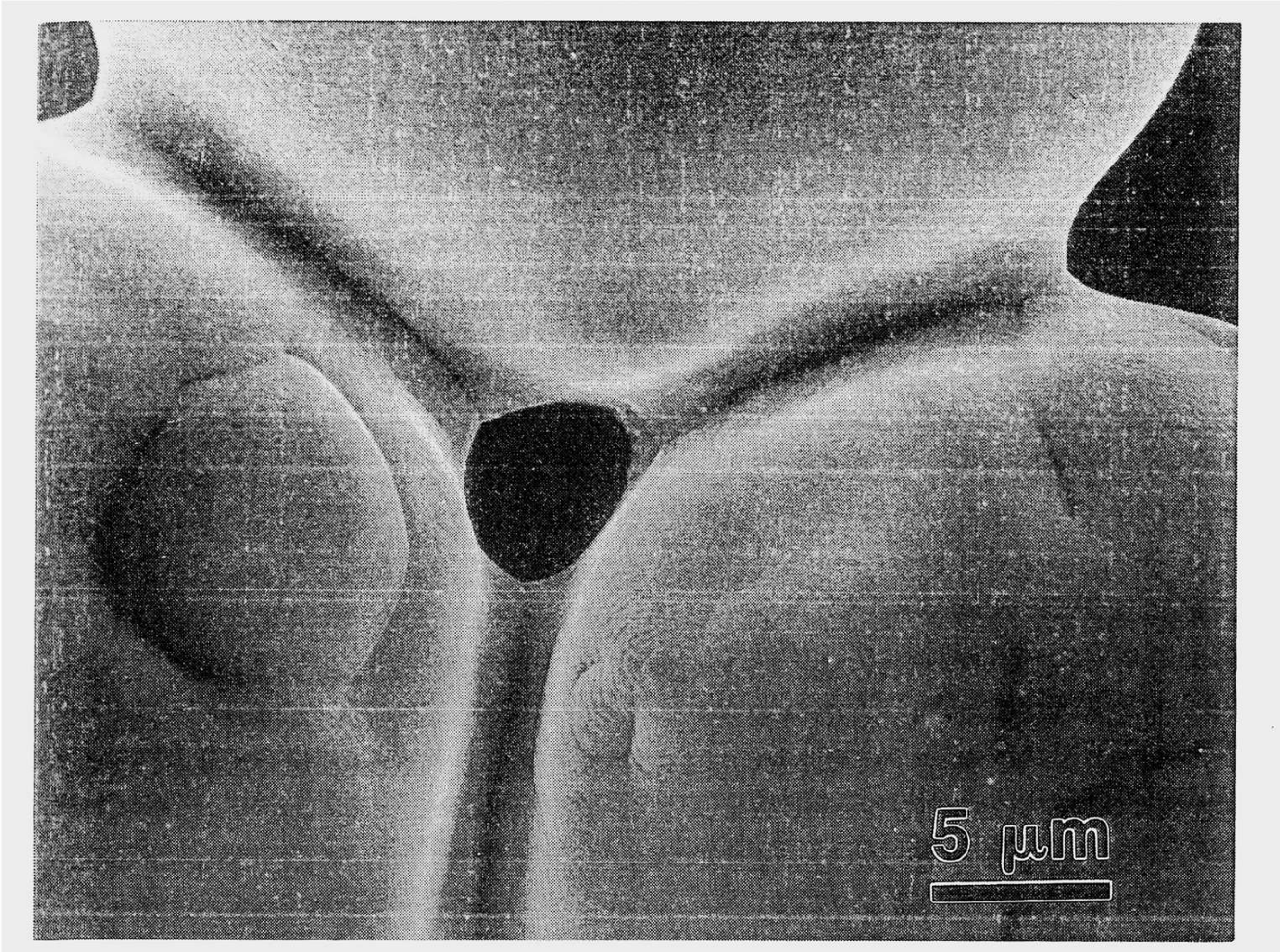
Particulates

- inherent driving force for mass flow
  - smaller particles, greater driving force
- heat allows for mass flow to occur
  - move to reduce stress
    - diffusion
    - plastic flow
    - viscous flow

Solid State - 2 Sphere Model



Neck Formation



Densification and Mass Transfer

E-C = evaporation-condensation
VD = volume diffusion
SD = surface diffusion
PF = plastic flow
GB = grain boundary diffusion

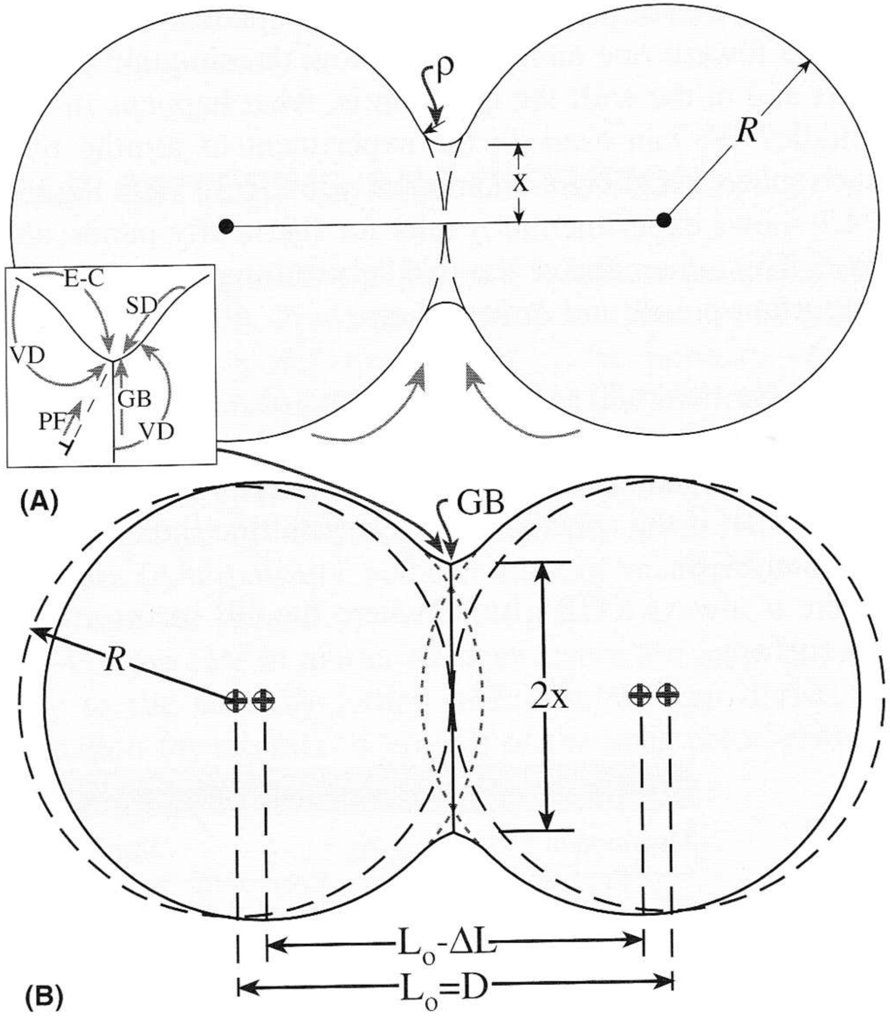
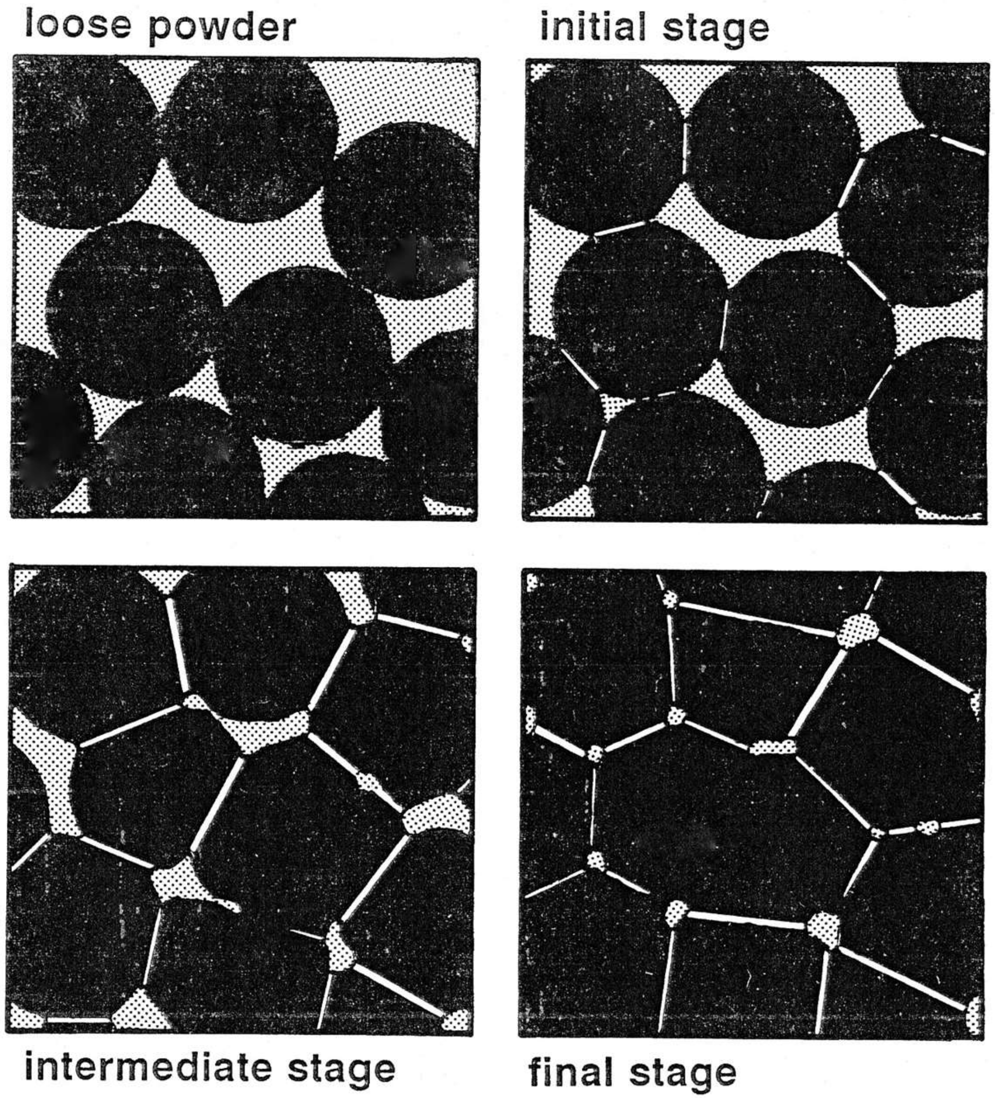


FIGURE 24.5 (a, b) Sintering and curvature. The two-sphere model showing the transport paths, the two curvatures (ρ and *x*), and the process leading to densification.

Densification and Transport

- surface transport can cause neck growth
  - evaporation-condensation
  - surface diffusion
  - volume (lattice) diffusion
- bulk transport gives neck growth and densification
  - grain boundary diffusion
  - volume (lattice) diffusion

Stages in Solid State Sintering



R.M. German, Sintering Theory and Practice,Wiley Interscience, 1996, Fig 1.7

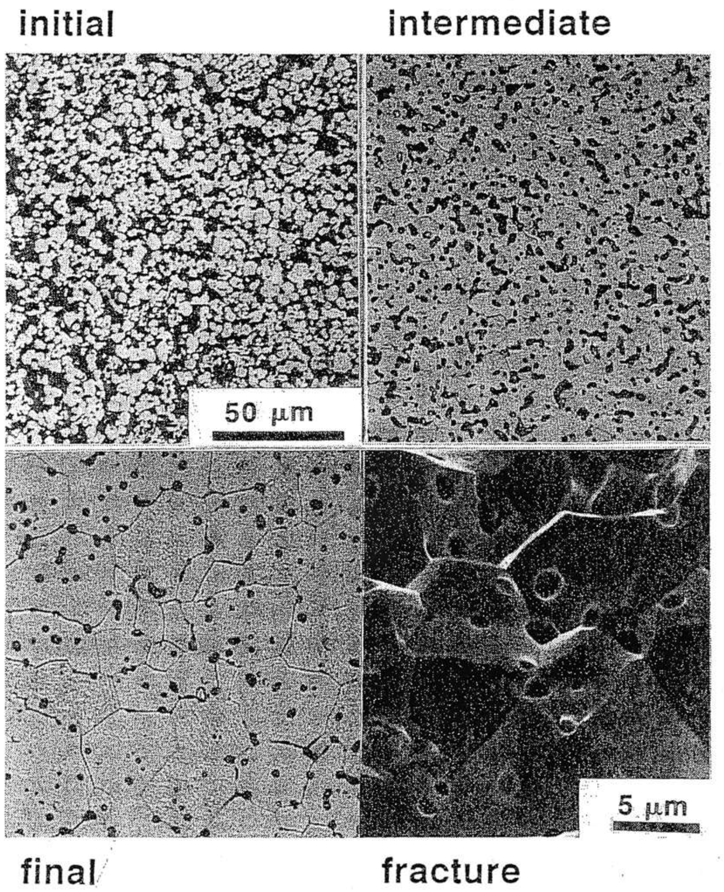
Stages of Sintering

- Adhesion
  - compacted particles
- Initial
  - neck growth, significant loss of surface area
  - some densification

Stages of Sintering

- Intermediate
  - pore rounding and elongation
  - most open pores gone
  - significant densification
  - some grain growth
- Final
  - pore closure
  - minimal densification
  - extensive grain growth

Stages in Solid State Sintering



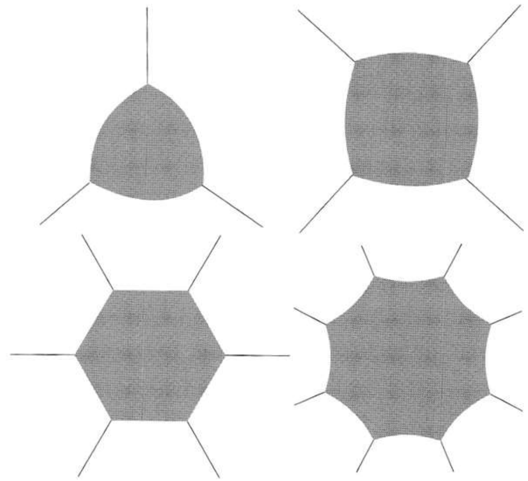
Stages of Sintering

Stage	Process	Surface Area Loss	Densification	Coarsening
Adhesion	contact formation	minimal (unless high P is used)	none	none
Initial	neck growth	large, up to 50% loss	small	minimal
Intermediate	pore rounding, elongation	loss of most open porosity	major	grain growth and larger pores
Final	pore closure, densification	very little	very little, slow	extensive grain growth and pore growth

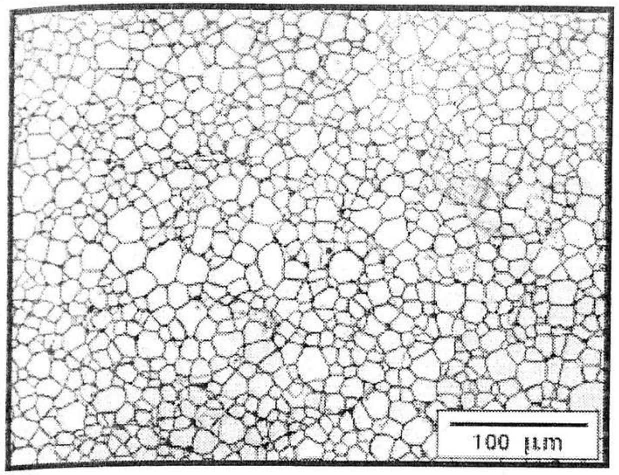
Grain Growth

- grain growth related to curvature of grain boundary

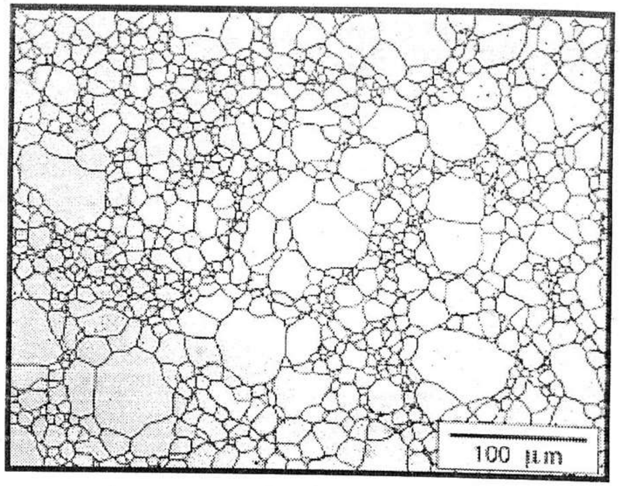
https://en.wikipedia.org/wiki/File:Grgr3d_small.gif



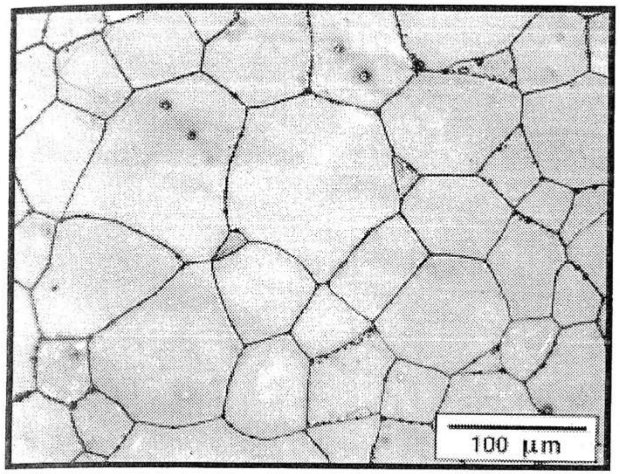
Grain Growth

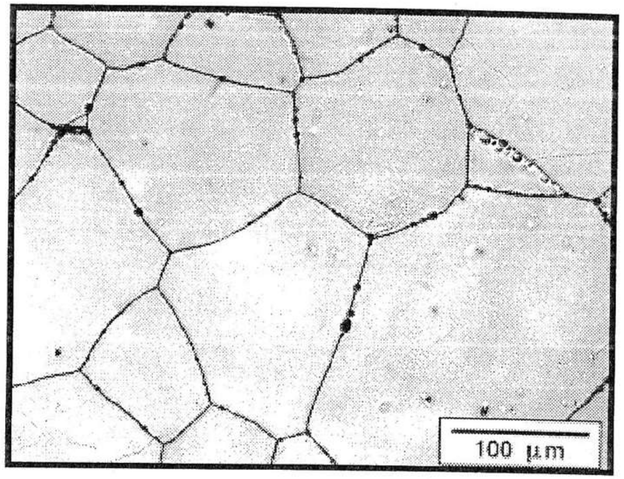


(a)



(b)

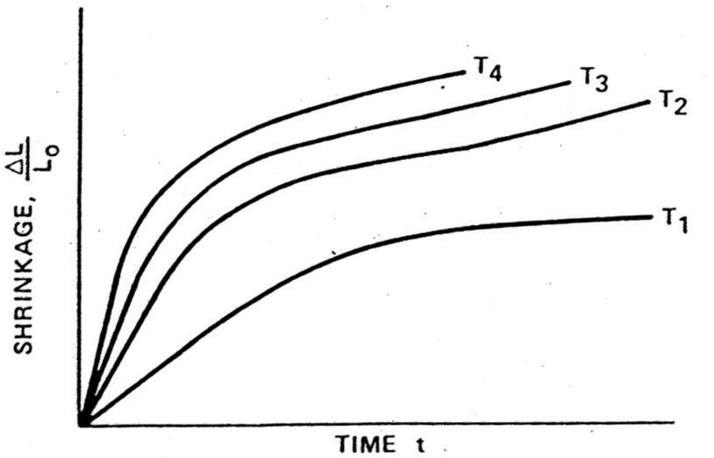




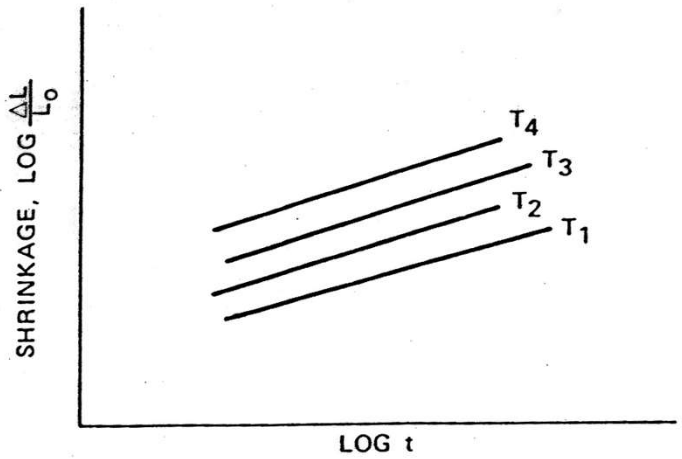
Factors Affecting Solid State Sintering

- temperature
  - diffusion is thermally activated
- green density
- uniformity of green density
- atmosphere
- impurities
  - sintering aids
- size distribution
- particle size

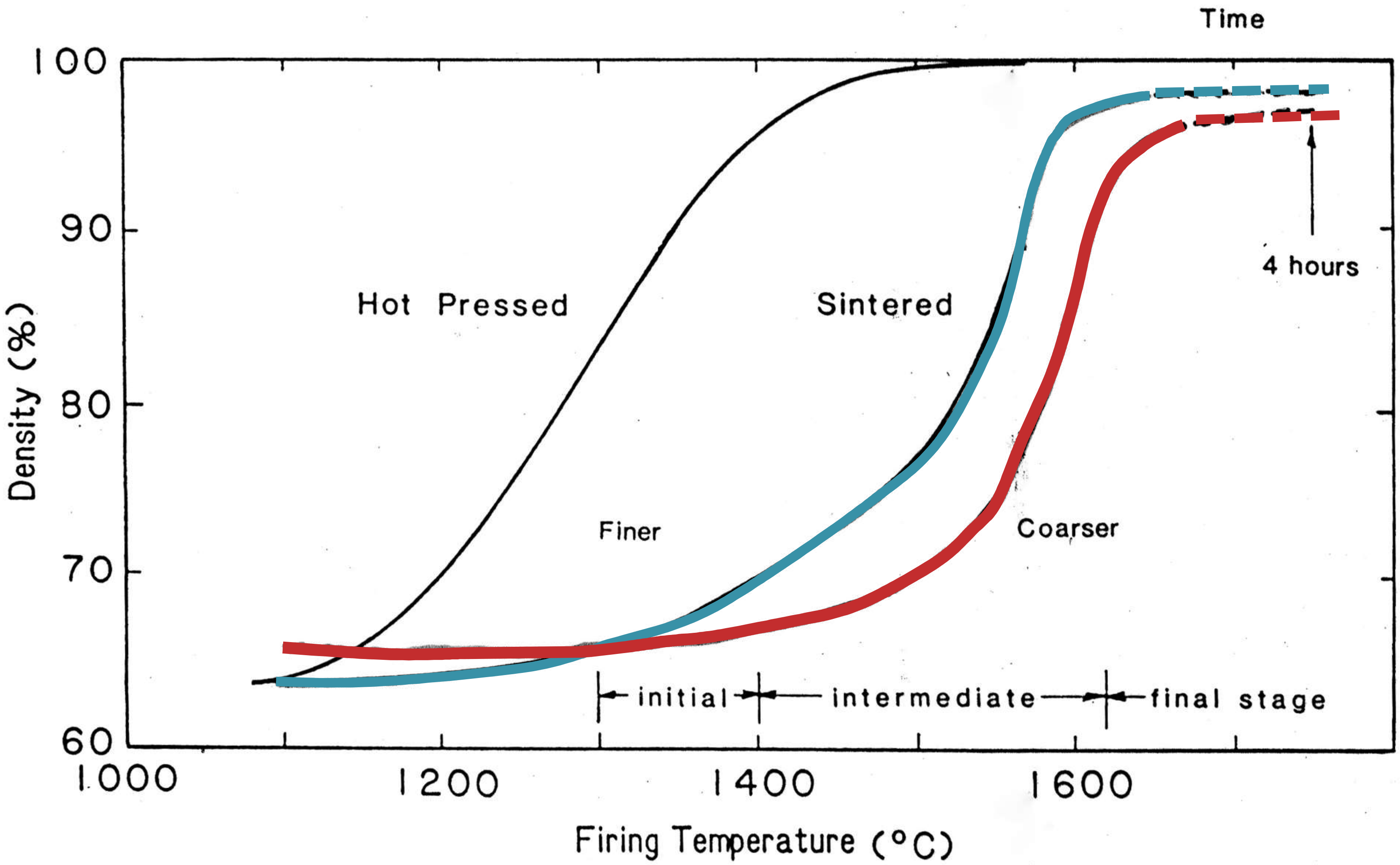
Effect of Temperature



$T_4>T_3>T_2>T_1$



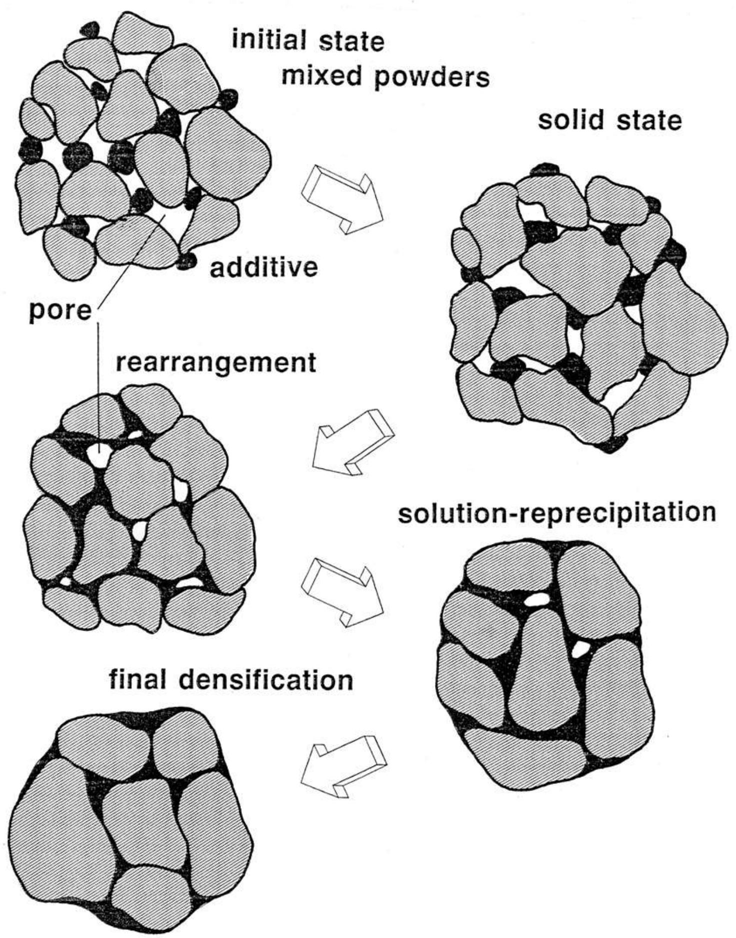
Effect of Grain Size and Pressure



Liquid Phase Sintering

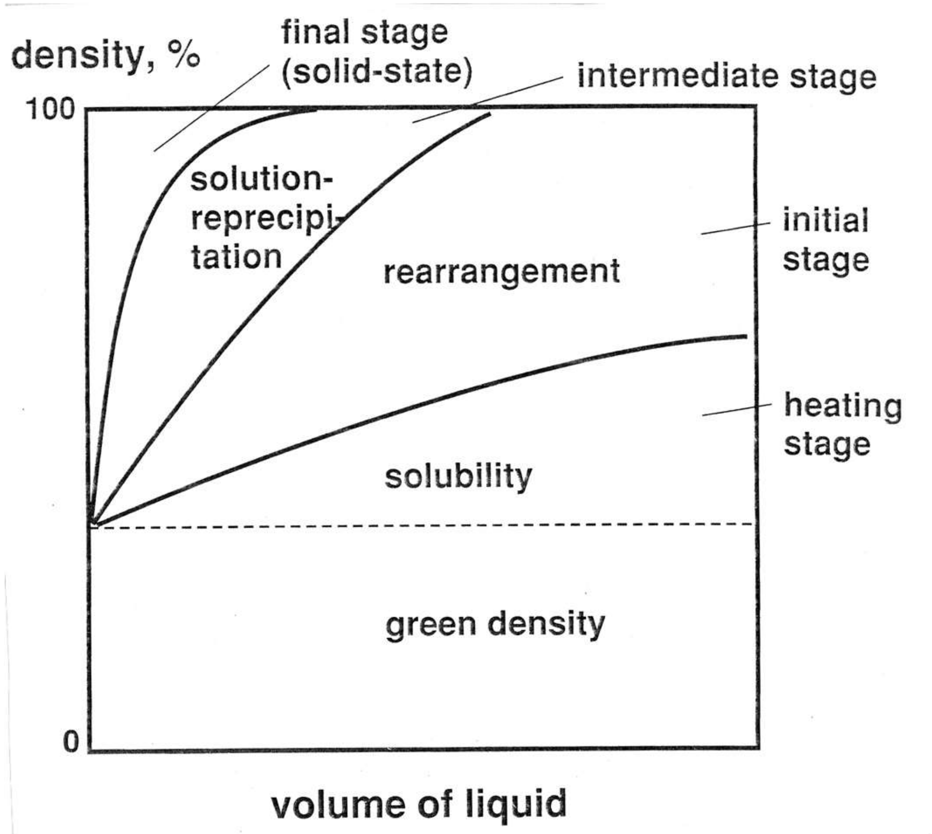
- mixed powders heated
  - solid state sintering during heating
- liquid forms
  - liquid wets solid
  - fills pores, reducing surface area
  - higher diffusion rates

Stages in Liquid Phase Sintering

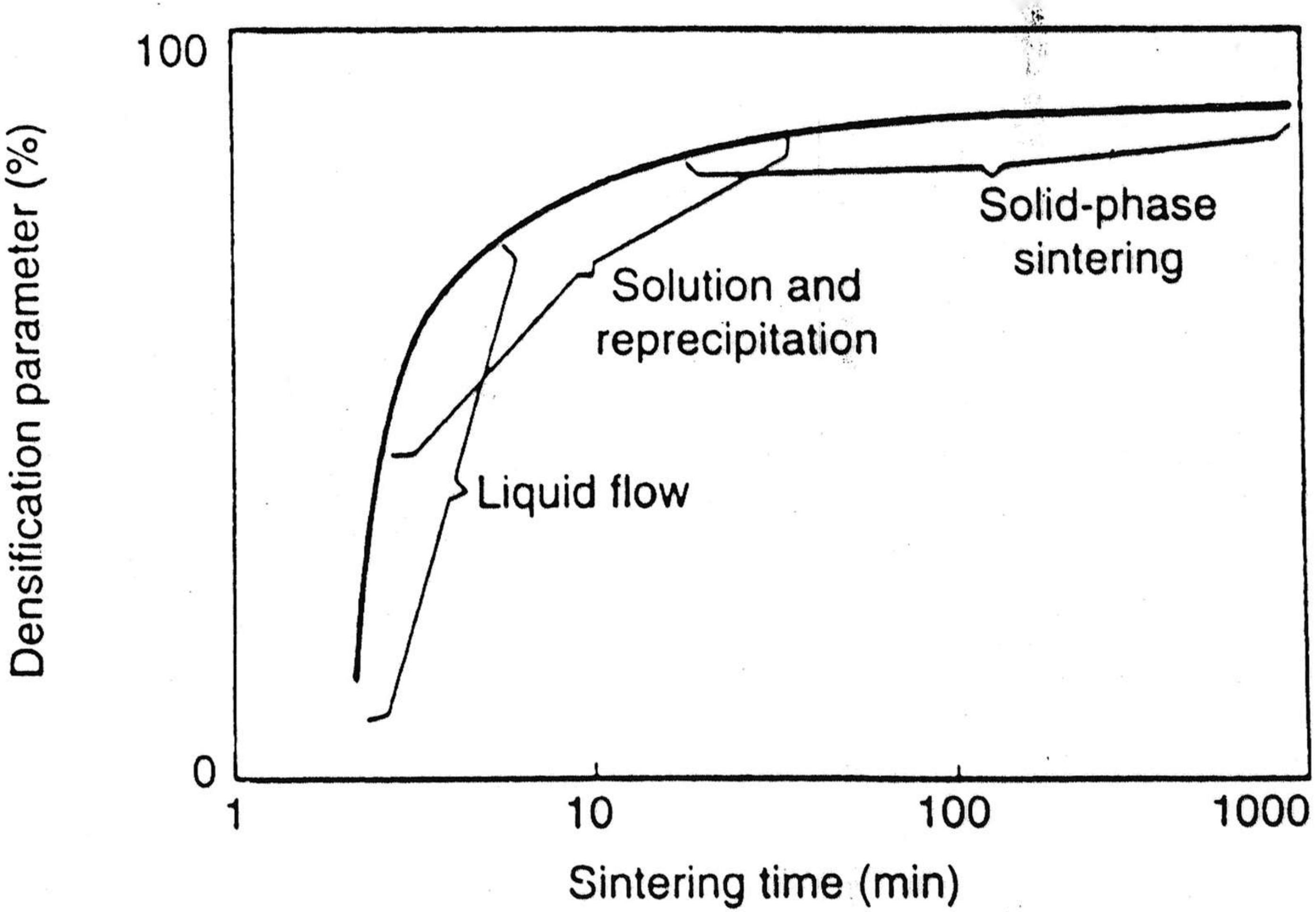


Stages in Liquid Phase Sintering

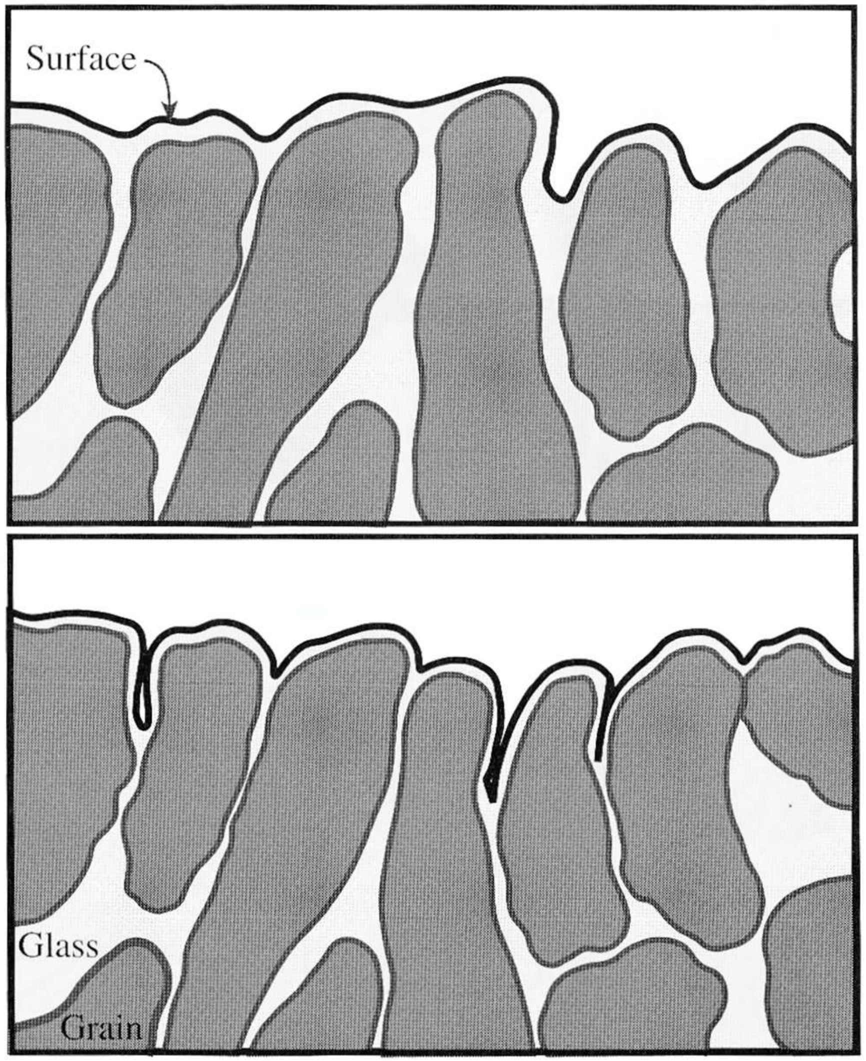
- rearrangement
- solution-reprecipitation
- final stage sintering



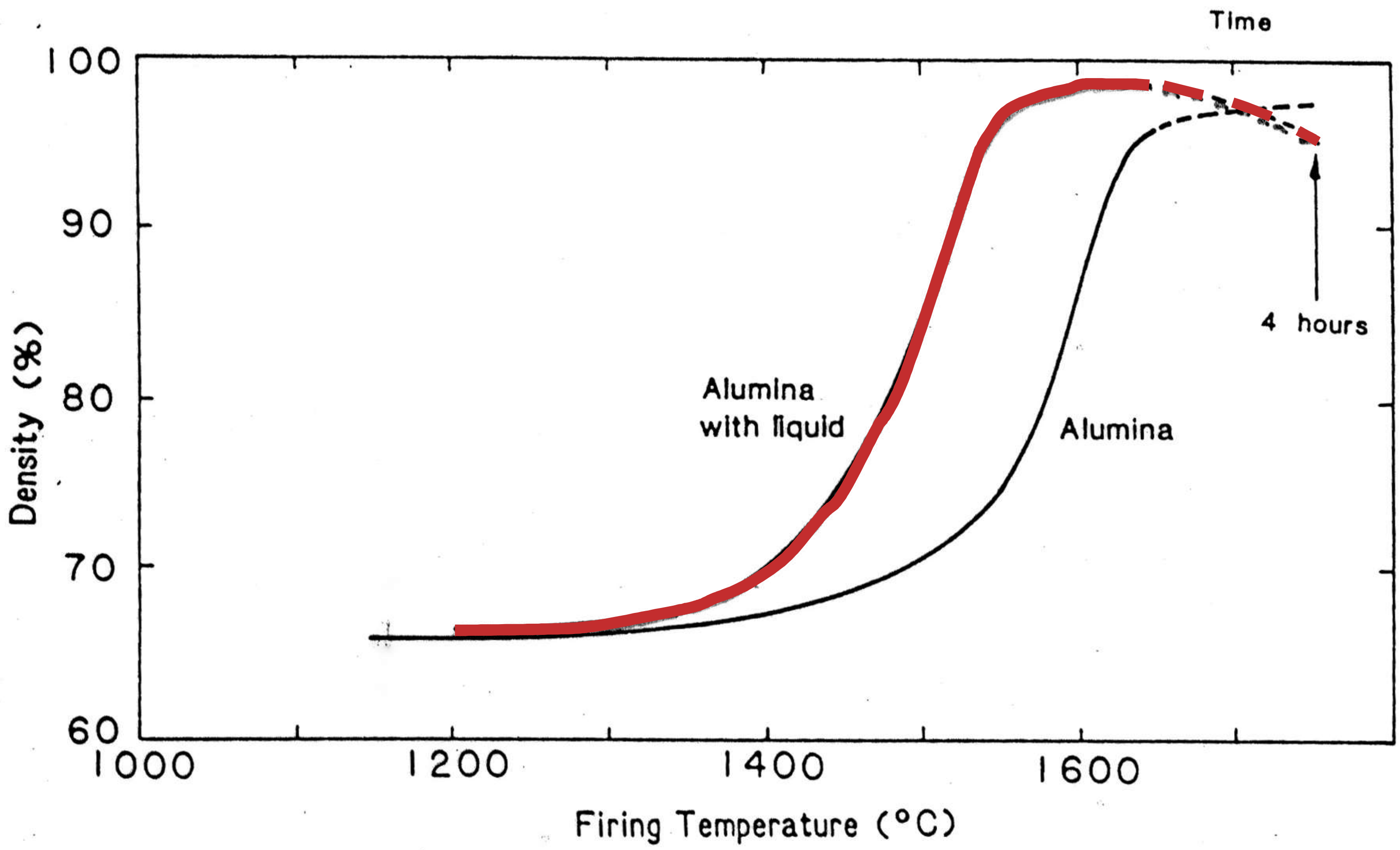
Densification with a Liquid Phase



Liquid Phase



Effect of Liquid Phase



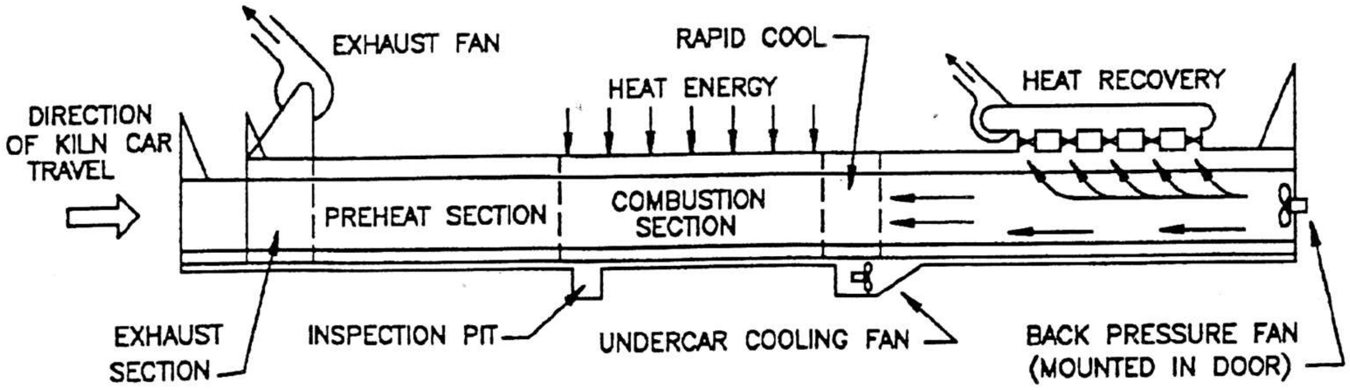
Liquid Phase Sintering

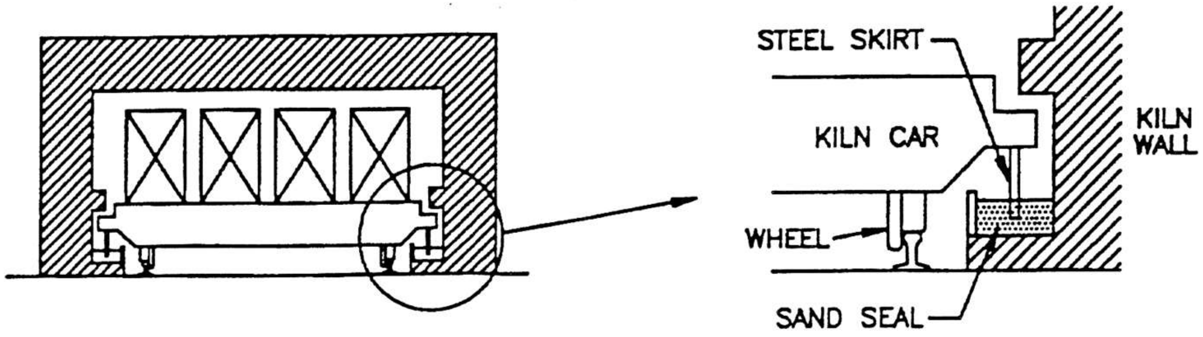
- small amount of liquid forms
  - lubricates grains, fills pores
- lower temperature required
- matrix phase bonds grains
- matrix phase often has inferior properties as compared to grains

Tunnel Kilns

- allow continuous processing
- most are gas heated
- arrangement of ware important for heat distribution
- typically 100 – 150m long

Tunnel Kilns





Tunnel Kilns

http://www.made-in-china.com