COURSE REPORT
Thermodynamik und Kinetik von Phasenübergängen

Phase Transition of Quartz and its Application in Industrial Fields

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❖ 1.1 WHAT IS QUARTZ

1.1.1 Introduction to Quartz

The technical formula is SiO_2 and it's composed of two elements, silicon and oxygen, also named by silica. Quartz is a quite important rock-forming mineral, which is also commonly used in our daily life. The crystalline form of SiO_2 or quartz is relatively abundant in nature, but in the highly pure form required for the manufacture of quartz crystal units, the supply tends to be small.

The pure quartz is a colorless, transparent and glass-like crystalline material along with very high hardness. While in the present of different impurities, quartz appears a lot of different colors like violet amethyst, milky quartz, yellow citrine, rose quartz, gray smoky quartz and etc. Besides, in its dense forms, it appears invisible crystals like agate and gray flint.
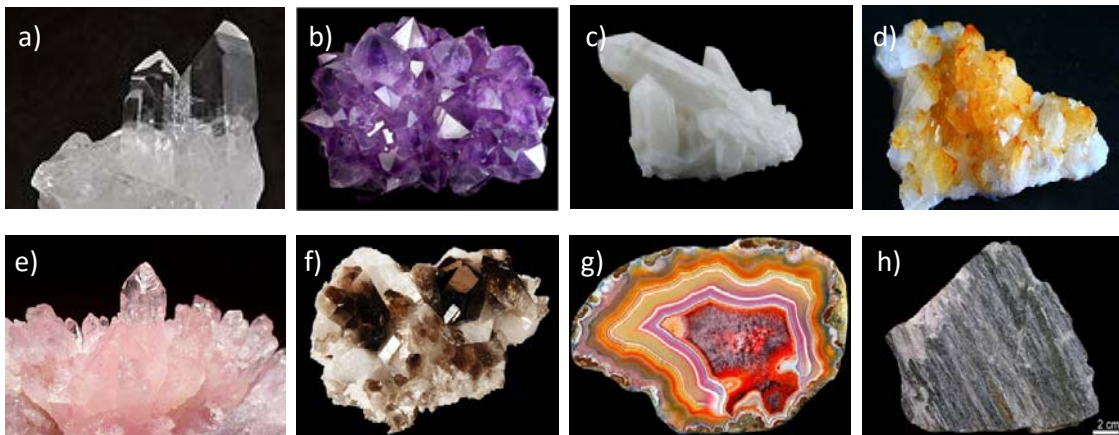
Figure 1-1: Morphorloy of quartz with color varities and different dense forms.

a) Clear rock crystal; b) Amethyst; c) Milky quartz; d) Citrine; e) Rose quartz; f) Smoky quartz; g) Agate; h) Flint.

The great number of varieties have been given their own names depending on its form and color. They are usually classified in two main groups.

❖ **Macrocrystalline** varieties are those that form crystals, like amethyst, or have a macroscopical crystalline structure [A. C. Akhavan, 2013].

Rock Crystal	Citrine	Prase	Rose Quartz
Smoky Quartz	Pink Quartz	Ametrine	Ferruginous Quartz
Amethyst	Prasiolite	Milky Quartz	Tiger's Eye
Aventurine	Cat's Eye	Blue Quartz	Hawk's Eye

❖ **Cryptocrystalline** varieties that do not show any visible crystals and have a dense structure, like agate. Cryptocrystalline varieties are sometimes grouped together under the term chalcedony [A. C. Akhavan, 2013].

Chalcedony	Agate	Carnelian	Heliotrope
Flint	Plasma	Chrysoprase	Chert
Jasper	Sard	Onyx	

1.1.2 Mineralogy of Quartz

a) Classification of Quartz

The classification of quartz can be slightly different according to different way. The below table gives the summary of different classification for quartz.

Name	Classification
IMA Status	Valid - first described prior to 1959 (pre-IMA) - "Grandfathered"
Strunz 8th ed.	4/D.01-10
Nickel-Strunz 10th (Pending) ed.	4.DA.05 4 : OXIDES (Hydroxides, V[5,6] vanadates, arsenites, antimonites, bismuthites, sulfites, selenites, tellurites, iodates) D : Metal: Oxygen = 1:2 and similar A : With small cations: Silica family
Dana 8th ed.:	75.1.3.1 75 : TECTOSILICATES Si Tetrahedral Frameworks 1 : Si Tetrahedral Frameworks - SiO_2 with [4] coordinated Si
Hey's Chemical Index of Minerals Ref.:	7.8.1 7: Oxides and Hydroxides 8: Oxides of Si

Table 1-1: Classifications of quartz according to different classify groups
[Retrieved from http://www.mindat.org/min-3337.html].

b) Crystallography of Quartz

Name	Crystallographic Properties
Crystal System	Hexagonal / Trigonal
Class (H-M)	3 2 - Trapezohedral
Space Group	$P3_1$ 2 1
Cell Parameters	a = 4.9133Å, c = 5.4053Å
Ratio	a:c = 1 : 1.1
Unit Cell Volume	113.00 Å³ (Calculated from Unit Cell)
Z	3

Table 1-2: Crystallographic Properties of quartz according to mindat.org.
[Retrieved from http://www.mindat.org/min-3337.html].

c) Optical Properties of Quartz

Name	Optical Properties
Color	colorless if pure, otherwise any color
Streak	none / white if pure
Luster	vitreous Cryptocrystalline: waxy to dull, vitreous if polished
Diapheny	transparent if pure, otherwise transparent to opaque
Fluorescence	none
Refractive Indices for Na D-Line (589nm)	n_o=1.54422 n_e=1.55332 Dispersion=0.0091 Cryptocrystalline: n = 1.53-1.54
Birefringence	uniaxial positive: n_e-n_o = +0.00910 lower in cryptocrystalline quartz
Pleochroism / Dichroism	none if pure, weak dichroism is observed in smoky quartz, amethyst, and certain citrines
Optical Activity [γ]= degrees / mm	γ = 21.73° for Na D-Line (589nm)

Table 1-3: Optic Properties of quartz according to mindat.org. [Retrieved from http://www.quartzpage.de/gen_min.html].

1.1.3 Polymorphs of Silica

As the compound silica, SiO_2 has 11 crystalline and 2 non-crystalline polymorphs, the quartz is just one of them. Most of these polymorphs can be found in nature and on earth. Here is the list of SiO_2 polymorphs in terms of silica polymorphs, non-silica polymorphs, non-crystalline mineraloids and related compounds.

SiO₂	Polymorphs
Silica Polymorphs	(Network Silicates)
	Quartz, Low-Quartz, α-Quartz, Alpha-Quartz
	High Quartz, β-Quartz, Beta-Quartz
	α-Tridymite, Low-Tridymite
	α-Tridymite, Low-Tridymite
	β-Tridymite, High-Tridymite
	α-Cristobalite, Low-Cristobalite
	β-Cristobalite, High-Cristobalite
	Moganite (Lutecite, Lutecine)
	Coesite
	Keatite
Non-Silica	Polymorphs
	Stishovite

	Seifertite
Non-Crystalline	**Mineraloids**
	Opal (contains water), with 2 microcrystalline and 2 non-crystalline variants
	Lechatelierite, Silica Glass
Related	**Compounds**
	Melanophlogite (not pure SiO_2)
	Chibaite, IMA2008-067 (not pure SiO_2)
	Silhydrite (not pure SiO_2, contains crystal water)

Table 1-4: SiO_2 polymorphs in terms of silica polymorphs, non-silica polymorphs, non-crystalline mineraloids and related compounds. [Retrieved from http:// http://www.quartzpage.de/gen_mod.html].

SiO_4 tetrahedron is the basic construction structure of silica while quartz is interconnected by SiO_4 tetrahedron in a rigid 3D network way. The diversity in silica polymorphs is mainly because of the possibilities of different connecting way between SiO_4 tetrahedra.

❖ **1.2 History of Quartz Usages**

The limited supply and the high cost of natural quartz have resulted in the development of a synthetic quartz manufacturing industry. Synthetic quartz crystals are produced in vertical autoclaves. The autoclave works on the principle of hydrothermal gradients with temperatures in excess of 400 °C and pressures exceeding 1,000 atmospheres. Seed quartz crystals are placed in the upper chamber of the autoclave with natural quartz (lascas) being placed in the lower chamber. An alkaline solution is then introduced which when heated increases the pressure within the chamber. The autoclave heaters produce a lower temperature at the top chamber in comparison to the bottom. This temperature gradient produces convection of the alkaline solution which dissolves the natural quartz at the bottom of the chamber and deposits it on the seed crystals at the top. Alpha crystals produced by this method can have masses of several hundred grams and can be grown in a few weeks (J. Brice, 1985).

The technological prominence of α-quartz stems largely from the presence of piezoelectricity, combined with extremely low acoustic loss. Pierre and Jacques Curie first discovered piezoelectricity in quartz in 1880. In the early 1920s, the quartz resonator was first used for frequency stabilization. Temperature-compensated orientations (the AT and BT shear cuts) were introduced in the 1930s, and assured the technology's success. By the late 1950s, growth of cultured bars became commercially viable, and in the early 1970s, cultured quartz use for electronic applications first exceeded that of the natural variety. The discovery of cuts that addressed compensation of stress and temperature transient

effects occurred in the 1970s, and led to the introduction of compound cuts such as the SC, which has both a zero temperature coefficient of frequency, and is simultaneously stress-compensated. (McGraw-Hill, 1946; E. EerNisse, 1975; J. Kusters et al. 1977; A. Ballato 1977; S. Stein et al. 1992). Between 10^9 and 10^{10} quartz units per year were produced by 2000 at frequencies from below 1 kHz to above 10 GHz. Categories of application include resonators, filters, delay lines, transducers, sensors, signal processors, and actuators.

Quartz is a well-known piezoelectric material. α-Quartz belongs to the triclinic crystal system with point group 32 and has a phase transition at 537°C to the β-type that is not piezoelectric. Quartz has a cut with a zero temperature coefficient of the resonance frequency change. For instance, quartz oscillators using the thickness shear mode of the AT-cut are extensively used as clock sources in computers and as frequency stabilized oscillators in TVs and video cassette recorder (VCRs). On the other hand, an ST-cut quartz substrate that has X-propagation has a zero temperature coefficient for SAWs and so is used for SAW devices that have highly stabilized frequencies. Another distinguishing characteristic of quartz is its extremely high mechanical quality factor Qm > 105 (M. Schwartz, 2008). Quartz crystals are an indispensable component of modern electronic technology. They are used to generate frequencies to control and manage virtually all communication systems. They provide the isochronous element in most clocks, watches, computers and microprocessors
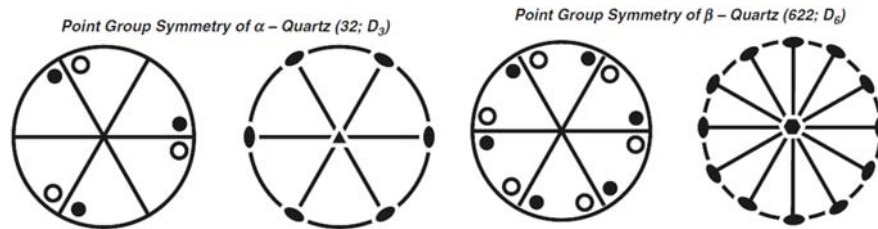
II. PHASE TRANSITION OF QUARTZ

❖ 2.1 SiO₂ Phase Diagram

Silica (SiO_2) is the second most abundant molecule on earth, after H_2O. The phase diagram of the silica system is sketched in Figure 2-1 (A. Ballato 2008). "Quartz" refers to crystalline α-SiO_2, arranged in point group symmetry 32 (Hermann-Mauguin)/D_3 (Schonflies). Figure 2-2 (A. Ballato, 2008) indicates its symmetry elements; z (x_3) is the axis of threefold symmetry. Three equivalent secondary axes x (x_1) are parallel to the twofold axes, and perpendicular to the x_3 axis; three equivalent y (x_2) axes are normal to x3 and to the respective x_1 axes. The trigonal axis is denoted "optical" (x_3 a screw axis, rotating polarized light), the digonal (x_1) axes are denoted "electrical" and are piezoelectrically active; the x_2 axes are "mechanical" axes. Axial and sign conventions are given in various IEEE Standards and related papers.
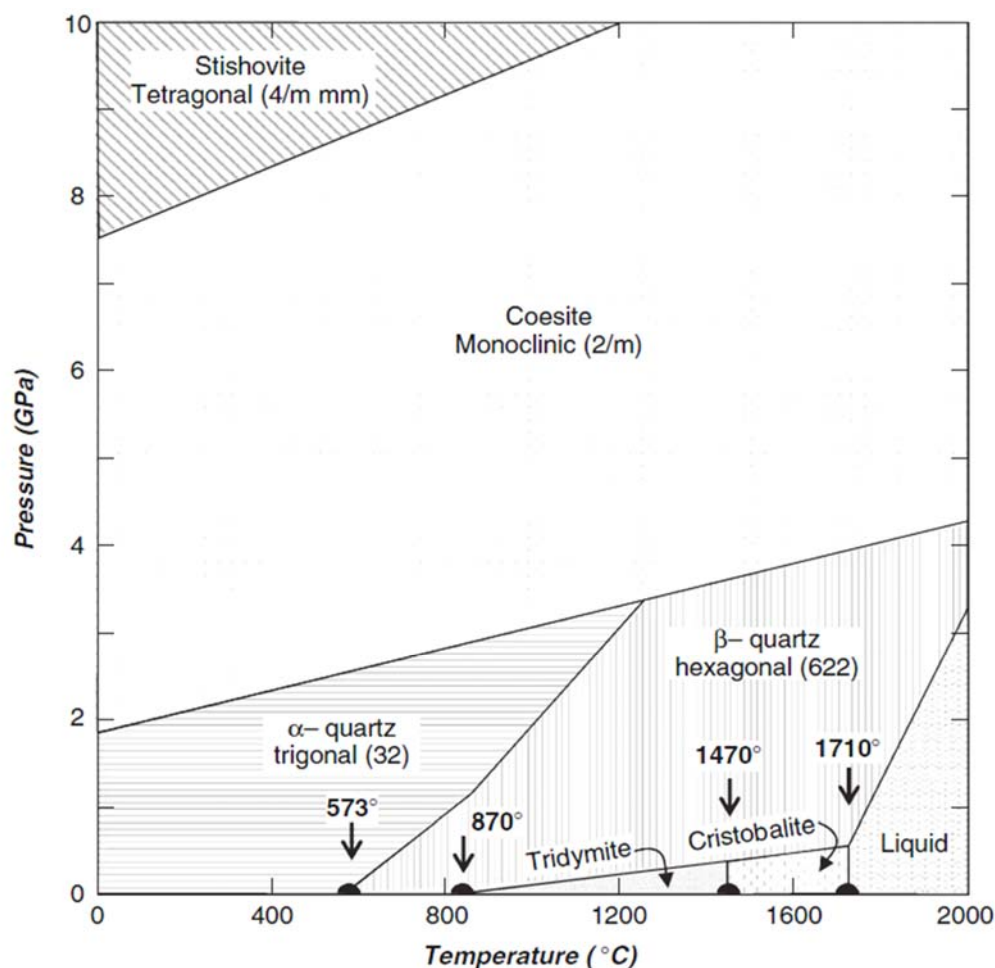
**Figure 2-1:** Phase diagram of silica polymorphs. [A. Ballato 2008]

Figure 2-2: Symmetry elements for α-quartz and β-quartz. [A. Ballato, 2008]
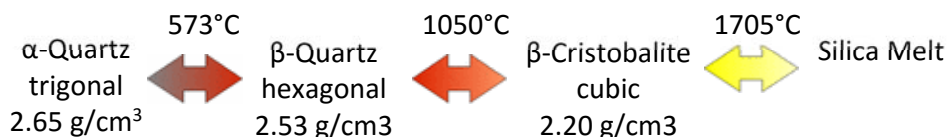
❖ 2.2 Normal Pressure Phase Transition

a) Equilibrium Phase Transition

In theory, upon heating, α-SiO$_2$ ("low quartz") undergoes a phase transition at 573.3 °C at normal pressure, becoming β-SiO$_2$ ("high quartz"); in the transition, the silicon atoms move only 0.03 nm, changing the trigonal axis to hexagonal, and the point group symmetry to 622/D$_6$. Beta quartz is also enantiomorphic, composed of space groups P6$_2$22/D$_6^4$ and P6$_4$22/D$_6^5$; handedness is preserved in the transition. Enantiomorphism implies the presence of piezoelectricity. Beta quartz is not stable below 573 °C. At 600 °C, unit cell dimensions are a$_0$ = 0.501 and c$_0$ = 0.547 nm, and density ρ = 2.533.
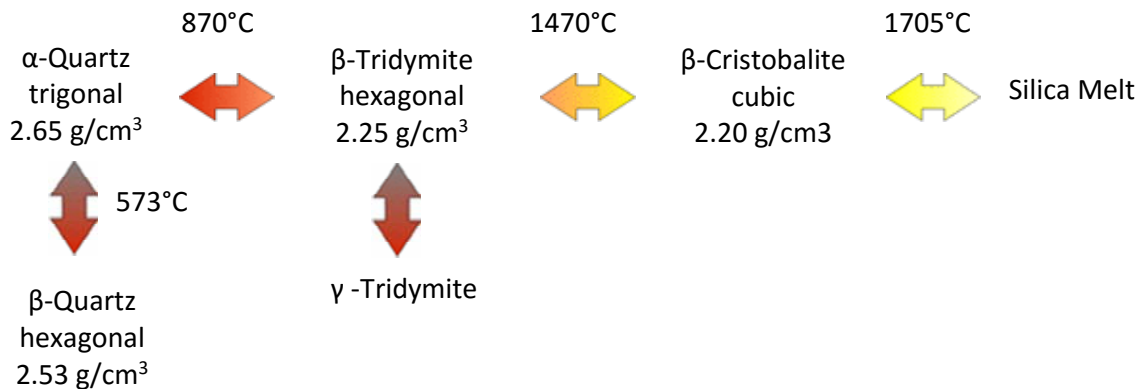
Figure 2-3: Phase transition of silica polymorphs under normal pressure.

Considering that in the usual case tridymite does not form from pure beta-quartz, thus trace amounts of certain compounds need to be added in to achieve this [P.J. Heaney, 1994]. Then this transition process becomes like with the skipping of β-quartz-tridymite transition:

Figure 2-4: Phase transition of silica polymorphs without the formation of tridymite under normal pressure.

The above we are talking quartz phase transition under nearly equilibrium situation by slow heating and cooling, thus the whole process is fully reversible. When the heating and cooling rates get faster, the non-equilibrium phase transition can be very different.

b) Non-equilibrium Phase Transition

When the heating up of quartz crystal is very fast, the β-quartz will then "skip" the transition to beta-cristobalite and directly melt at a much lower temperature at 1550°C compared with the case under equilibrium.
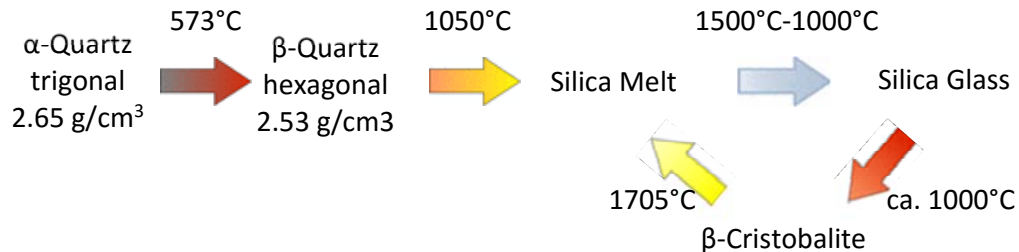
Figure 2-5: Phase transition of alpha-quartz under fast heating and cooling condition.

The beta-quartz has a lower melting point because it is less stable than beta-cristobalite at that temperature, thus its crystal lattice has more potentials to be broken up. If the silica melt is quickly cooled, the liquid morphology will be preserved and becomes amorphous silica glass, which doesn't have a certain defined melting point. And the whole process shows in figure 2-4 is not reversible.

But if you heat up the silica glass again, then it will just turn into β-Cristobalite and then goes to silica melt at 1705°C. This is vital for industrial manufacturing of silica glass due to the formation of cristobalite crystals within the silica glass, which could reduce the quality of silica glass products.

❖ **2.3 Low Pressure Phase Transition**

α-quartz, β-quartz, β-tridymite, and β-cristobalite have already been introduced as low pressure polymorphs, while coesite and stishovite are called high pressure polymorphs and are not stable at normal pressures. Coesite and stishovite have a higher density than the low pressure polymorphs.

Generally, there are three groups of silica polymorphs at low pressures. One low-temperature will be given an α-prefix (or low-prefix), and one high-temperature member of the same name, but with a β-prefix (or high-prefix). Here is the list of low pressure silica polymorphs.

Low Pressure Silica Polymorphs			
high- or β-polymorph	**β-Quartz**	**β-Tridymite**	**β-Cristobalite**
stable at	573°C - 870°C	870°C - 1470°C	> 1470°C
metastable at	-	117°C - 870°C	270°C - 1470°C
crystal system	hexagonal	hexagonal	cubic
Si-O-Si angle	153°	180°	151°
low- or α-polymorph	**α-Quartz**	**α-Tridymite**	**α-Cristobalite**
stable at	< 573°C	-	-
metastable at	-	< 117°C	< 270°C
crystal system	trigonal	triclinic	tetragonal
Si-O-Si angle	144°	140°	147°

Table: 2-1: High- or β-polymorph and low- or α-polymorph silica polymorphs at low pressure. [Retrieved from http://www.quartzpage.de/gen_mod.html]

Between these polymorphs there are basically two kind of transitions. One is displacive and the other one is reconstructive phase transition. The difference is the broken up of chemical bonds. As an example of a α- to a β-variant transition the atoms only get slightly displaced relative to each other, while in other transitions like from beta-quartz to beta-tridymite, the chemical bonds need to be broken up and reconstructed to modify the crystal structure. In addition, the reconstructive transition takes much more time than displacive transition, thus if the temperature changes quickly, it subjects to kinematic constraints and doesn't allow the rebuilding of new crystal structure.

For these two kinds of transition, all of them has volume changes during the phase transition. There is a table list of the theoretical calculation of volume changes during the polymorphs transition of SiO_2.

Reconstructive Phase Transition	Calculation Temp. (°C)	Volume Effect (%)	Displacive Phase Transition	Calculation Temp. (°C)	Volume Effect (%)
α-quartz→α-tridymite	1000	+ 16.0	β-quartz→α-quartz	573	+ 0.82
α-quartz→α-cristobalite	1000	+ 15.4	γ- tridymite →β-tridymite	117	+ 0.2
α-quartz→quartz glass	1000	+ 15.5	β- tridymite →α-tridymite	163	+ 0.2
quartz glass→α-cristobalite	1000	- 0.9	β- cristobalite →α - cristobalite	150	+ 2.8

Table 2-2: theoretical calculation of volume changes during the polymorphs transition of SiO_2.

III. APPLICATIONS OF QUARTZ PHASE TRANSITION

As is known that SiO_2 has very wide applications in industrial manufacture and quartz sand is the basic raw materials for glass, ceramics and refractories industries, especially used widely in producing glass and silica refractories. Besides, quartz glass can be employed in very precise optical instruments and also can be used as quartz crucible with its good chemical stability at high temperature. In electronic industry, β -quartz plays a very important role as Piezoelectric Crystal and it can be used in a variety of transducers. While the transparent crystal can be used in ultraviolet spectrometer prism, color complementary device and etc. Thus the study of SiO_2 phase transition and phase diagram is vital for the preparation and application of quartz.

In this chapter we mainly introduce two very wide and important applications for the quartz and its phase transition.
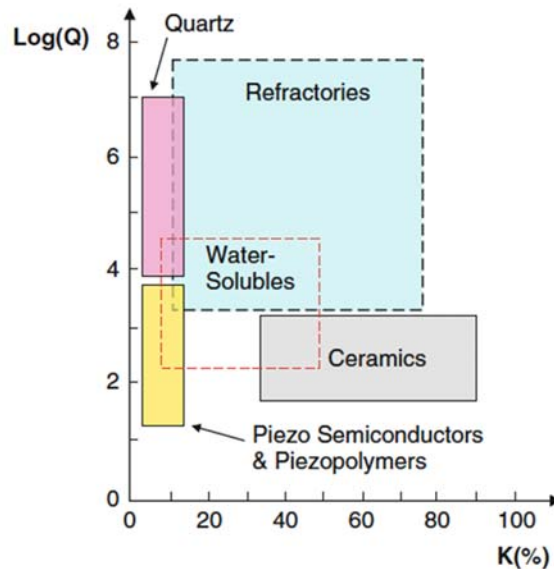
❖ **3.1 Synthesis of Piezoelectric Materials.**

3.1.1 Introduction to Piezoelectric Materials

Piezoelectricity is the electric charge that accumulates in certain solid materials (such as crystals, certain ceramics, and biological matter such as bone, DNA and various proteins) (F. Holler, 2007) in response to applied mechanical stress. The nature of the piezoelectric effect is closely linked to the occurrence of electric dipole moments in solids, which may either be induced for ions on crystal lattice sites with asymmetric charge surroundings (as in $BaTiO_3$ and PZTs) or may directly be carried by molecular groups (as in cane sugar) with electrical properties. A dipole is a vector named P, which has a direction and a value in accordance with the electrical charges around. These dipoles tend to have the same direction when next to each other, and they altogether form regions called Weiss domains. The domains are generally randomly oriented but they can be aligned using the process of poling, which is a process by which a strong electric field is applied across the material. However not every piezoelectric material can be poled. The reason why piezoelectric material creates a voltage is that when a mechanical stress is applied, the crystalline structure is disturbed and it changes the direction of the polarization P of the electric dipoles. Depending on the nature of the dipole (if it is induced by ion or molecular groups), this change in the polarization might either be caused by a re-configuration of the ions within the crystalline structure or by a re-orientation of molecular groups (A. Safari et al. 2008). As a result, the bigger the mechanical stress, the bigger the change in polarization and the more electricity is produced. Piezoelectricity may manifest in a

variation of the polarization strength, its direction or both, with the details depending on 1. the orientation of P within the crystal, 2. crystal symmetry and 3. the applied mechanical stress.

The phenomenon of piezoelectricity has a very distinguished history. The name "piezoelectricity" was given by Hankel; Lippmann predicted the converse effect in 1881, and it was verified by the Curies the same year. Kelvin provided an atomic model in 1893 (M. Trainer, 2003), and theories were advanced by Duhem and Pockels. In 1894, Voigt introduced the term "tensor" describing the phenomenological treatment of this and other effects in crystals. Langevin used Rochelle salt for sonar in the early 1910s, and Born theoretically calculated the piezoconstant of β-ZnS. Cady invented the quartz oscillator in the early 1920s. Tartrates and other water-soluble crystals with large piezoelectric values were investigated in the 1940s and 1950s (R. Bechmann et al. 1957), as were piezoceramics such as barium titanate and similar alloys (D. Berlincourt, 1981). Highly piezoelectric refractory oxides such as lithium niobate were introduced in the mid-1960s (T. Yamada et al. 1967; A. Warner et al. 1967; R. Smith et al. 1971), followed by piezopolymers in the late 1960s (G.M. Sessler 1981), and isomorphs of quartz in the late 1990s (R. Smythe, 1998). Piezoelectric materials can be natural or man-made.

The most common natural piezoelectric material is quartz, but man-made piezoelectric materials are more efficient and mostly ceramics. Figure 1 (A. Ballato, 2008) portrays the nominal ranges of coupling factor (which describes the ability of a piezoelectric material to convert electrical energy into mechanical energy and vice versa) and quality factor (Higher Q indicates a lower rate of energy loss relative to the stored energy of the oscillator) for the various classes of piezoelectrics mentioned. The material properties of quartz crystal are both extremely stable and highly repeatable. The acoustic loss or internal fraction of quartz is particularly low, which results in a quartz resonator having an extremely high Q-factor.

Figure 3-1: Acoustic quality factor (Q) vs. piezoelectric coupling factor (k) for various types of piezoelectric materials

As an example for α- cristobalite, it has point group of $O_h=m3m$, thus there is a symmetric center, which means non piezoelectric property. While for β-quartz, it has D_3 point group with no symmetric center, thus it appears piezoelectric property.

3.1.2 Growth of SiO₂ Single Crystal

a) Czochralski Method

The Czochralski method is pulling out with a seed crystal from the SiO_2 melt at 1713°C. According to the SiO_2 phase diagram, what we should get is α- cristobalite, which is not desirable for piezoelectric property. If we cool it down at a normal cooling rate, the product is β – cristobalite, which should have piezoelectric property due to its point group $D_2=222$ symmetry. But during the transition from α-cristobalite to β – cristobalite, the crystal is quite easy to be broken because of the accompanied big volume change in the α- β cristobalite phase transition. Also from the thermodynamic perspective, the β-cristobalite is kind of metastable phase at room temperature, which will finally turn into β-quartz. Thus in a conclusion, normally method for industry is directly synthesis of β-quartz by hydrothermal method.

b) Hydrothermal method

The schematic of hydrothermal synthesis of beta-quartz is like the following figure. The seed quartz crystal is hanged on the top of the autoclave and the temperature

keeps at 300 °C. At the bottom there are some quartz fragments and the temperature keeps at 400°C. The pressure inside the autoclave is 40530kPa and filled up with low concentration of $NaHCO_3$ solution. Because of the temperature difference between the top and bottom, the dissolved SiO_2 will follow the convection inside and come to the top. Thus the single crystal grows around the seed crystal on the top due to the saturated solution at low temperature. The temperature of the whole system is under 573°C, thus it gives the product of single beta-quartz, which has pretty good piezoelectric property and is stable at room temperature in terms of thermodynamic.

Figure 3-2: Schematic of hydrothermal method for synthesis of beta-quartz.

❖ **3.2 Preparation of Silica Refractories**

The aim of the preparation of silica refractories is to get more tridymite and less cristobalite. According to the phase diagram and the volume changes table, the biggest volume change is between alpha- and beta- cristobalite while the weakest is between alpha- and beta- tridymite. This is why we want to eliminate cristobalite to have more densified product.

In order to avoid the explosion of products, we should have precise controlling of heating and cooling rate in the temperature range of alpha- and beta-quartz transition (573°C). Also for eliminating the stress of volume effect during the alpha- and beta- cristobalite transition, normally we add some impurities like oxides of Fe, Mn, Ca and etc., which will turn it to be liquid at around 1000°C and accelerate the process of alpha-quartz and beta- tridymite transition.