Kirk-Othmer Encyclopedia of Chemical Technology.

SILICA, SYNTHETIC QUARTZ CRYSTALS

Silicon dioxide [7631-86-9], SiO_2, exists in both crystalline and glassy forms. In the former, the most common polymorph is α-quartz (low quartz). All commercial applications of crystalline quartz use α-quartz, which is stable only below ca 573°C at atmospheric pressure. Some of the properties of α-quartz are listed in Table 1.

Quartz is mainly used in electronic applications, for which it must be free of electrical and optical twinning, voids, foreign minerals, and liquids. Moreover, it must be large enough for convenient processing. The principal source of electronic-grade natural quartz is Brazil, but manufacturers generally use synthetic quartz for electronic devices. Until the discovery of economic processes for quartz synthesis in the 1950s, natural quartz was used for commercial applications. The size, perfection, and properties of natural quartz vary. In addition, because natural crystals are generally irregular in shape, automated cutting is cumbersome and the yield is lower.

In an attempt to stimulate onshore production of synthetic quartz and piezoelectric devices in the 1970s, Brazil imposed an embargo on exports and ultimately raised the price several-fold for small quartz crystals used as the starting material for quartz growth. However, sources of suitable pure quartz were located in the United States and Canada, including vein and pegmatic deposits (1). Synthetic processes compatible with the natural U.S. quartz starting material from a variety of sources were developed, and U.S. production became relatively independent of imports (1).

As of 1996, synthetic quartz was produced in the United Kingdom, France, CIS, Venezuela, Canada, China, Japan, Brazil, Poland, as well as the United States. The principal nondomestic source is Japan. Some producers in the United States are Eastlake, in Ohio; Motorola, in Carlisle, Pennsylvania; and Thermo Dynamics, in Shawnee Mission, Kansas.

1. Synthesis

α-Quartz cannot be crystallized from its pure melt because viscous SiO_2 melts almost always form silica glass upon cooling. When crystals are formed, these are high temperature polymorphs of SiO_2, eg, cristobalite [14464-46-1] and tridymite [15468-32-3], that do not easily transform to untwinned α-quartz. α-Quartz is soluble in a variety of molten salts but the melts are viscous and crystallization below the α-transition temperature is not practical. Silicon dioxide is insoluble in most aqueous solvents at ambient conditions, except in HF solutions, and α-quartz is not the stable solid phase in equilibrium with such solutions. No successful practical vapor transport reaction for α-quartz growth has been discovered. However, α-quartz is stable and soluble in water at elevated temperatures and pressures, ie, under hydrothermal conditions. The solubility at a convenient temperature (400°C) and pressure (ca 17 MPa (25,000 psi)) is only a few tenths of a wt % and is not large enough for crystal growth. However, reactions of the following type take place in basic solutions under hydrothermal conditions.

$$2\,OH^- + SiO_2 \rightleftharpoons SiO_3^{2-} + H_2O$$

Table 1. Properties of α-Quartz[a]

Property	Value
Structural	
crystal class, space group	32[b]
lattice constant, nm	
a	0.491
b	0.540[c]
Optical	
indexes of refraction, Na D line	
n_0	1.5442
n_E	1.5533[d]
optically active, Na D line	
α, °/mm	27.71
transmission range, nm	150–3000
Electrical	
resistivity, Ω·cm	10^{15}
dielectric constant	
ϵ_1^T	4.58
ϵ_3	4.70
piezoelectric coupling coefficient, %	10
piezoelectric constant, FC/N[e]	
d_{11}	−23.12
d_{14}	727
Mechanical	
hardness, Mohs'	7
thermal conductivity, W/(m·K)	6.69–12.13
acoustic Q	$(0.1 - 3) \times 10^6$

[a] Many properties are directionally dependent, therefore values listed are indicative only.

[b] Trigonal trapezohedral class of the rhombohedral subsystem.

[c] Variable, depending on purity.

[d] Birefringent; $n_E - n_o = 0.0091$.

[e] To convert FC/N to stat C/dyn, divide by 333×10^8.

The result is that the weight solubility of quartz is increased to several percent. α-Quartz is the stable solid phase in equilibrium with such solutions and large crystals can be grown. This is the basis of the processes used for commercial quartz growth (see Hydrothermal processing).

The first known successful attempt to grow quartz crystals hydrothermally was in 1905 (2). Small crystals were formed in a thermal gradient from a sodium silicate solution. In Germany during World War II, quartz crystals were grown in an isothermal system using α-quartz seeds and vitreous silica nutrient (3). After that war, research programs aimed at practical quartz production began (4–7). It soon became apparent that processes depending on the supersaturation caused by the presence of silica glass were impractical. Metastable phases have a higher solubility than stable phases, but the supersaturation caused by their presence persists only as long as they are present. In the case of silica glass, its surface devitrifies rather quickly under hydrothermal conditions and growth on α-quartz seeds ceases. All successful quartz growth processes depend on the supersaturation produced by dissolving small particles of quartz nutrient in a hot region of the high pressure system and crystallizing it onto α-quartz seeds in a cooler part of the system. Thus, it is necessary to employ a solvent in which quartz is the stable solid phase having reasonable solubility and in which the dependence of solubility upon temperature produces an appropriate supersaturation, ΔS, and an appropriate temperature differential, ΔT, between the dissolving and growth zones.

All commercial processes (8–10) use either NaOH (4) or Na_2CO_3 (5) as solvent systems. The dissolving mechanism is similar in both solvents because $CO^{2-}{}_3$ hydrolyzes to OH^-. Sodium salts are required because insoluble sodium iron silicates form on the steel walls of the high pressure vessels when Na^+ and silicates are present (see Silicon compounds). These compounds are relatively insoluble under hydrothermal conditions and form a protective coat on the walls, allowing the use on unlined, relatively inexpensive vessels. The slope of the solubility–temperature curve is greater in $CO^{2-}{}_3$ than it is in OH^-. Thus loss of control in $CO^{2-}{}_3$ with poor quality growth and spontaneous nucleation is more likely than it is in OH^-. The practical solution to this problem in $CO^{2-}{}_3$ is to use a lower ΔT, which produces a ΔS safely below the poor quality region. Thus in $CO^{2-}{}_3$ processes the growth rates are usually lower. Indeed, in OH^- the temperature control required is generally less than that in $CO^{2-}{}_3$.

The hydroxide process developed by Bell Telephone Laboratories (8, 9) is used by most producers (11). It is usually operated at higher pressures than the carbonate process and quartz is grown at faster rates. Less precise temperature controls are needed.

1.1. Equipment

A typical commercial quartz-growing autoclave is illustrated in Figure 1. The material of construction for use at 17 MPa (25,000 psi) and 400°C can be a low carbon steel, such as 4140, or various types of low alloy steel. The closure, a modified Bridgeman closure, is based on the unsupported area principle (12). That is, the pressure in the vessel is transmitted through the plunger to the steel surfaces which initially are nearly line contacts. Thus, the pressure in the seal surface greatly exceeds the pressure in the vessel because most of the area of the plunger is unsupported. Hydrothermal equipment has been further discussed (10).

After long periods of time at operating temperature, the brittle–ductile transition temperature in autoclave steels increases (13). At temperatures much above 200°C for the solutions and fills used in ordinary hydrothermal processes, pressures and hence stresses in autoclaves can cause failure of metal in the brittle state. Ordinarily, the brittle region is well below these temperatures but careful monitoring of the brittle–ductile transition of the steel is necessary for safe autoclave use over many years.

The baffle is a perforated metal disk that restricts convective circulation within the vessel and thus creates two isothermal regions, the dissolving and growth zones. As a result, all seed crystals experience the same ΔT and ΔS and grow uniformly. No growth takes place on the nutrient. The autoclave is heated by appropriately placed external resistance heaters. The temperature is measured and controlled from externally placed thermocouples; the pressure is measured by strain and Bourdon gauges. In order to increase the yield and hence increase the efficiency and cost effectiveness of the synthesis, the size of the autoclave has been increasing. Originally, autoclaves of 15.24 and 25.4 cm dia were used. More recently, autoclaves up to a meter in diameter have been used to produce over 450 kg of synthetic crystal in a single run.

Modern process facilities are computer controlled. Temperature and ΔT are programmed upward during the start of a growth cycle, pressure and temperature are monitored and controlled, and pressure and temperature overshoot alarms and overrides are provided. Such systems also store data from previous runs for correlations with properties or for identical replication of past conditions.

1.2. Typical Run

In a typical run, small particle size α-quartz nutrient is added to a large autoclave, a 5% open area baffle is inserted, and a frame holding many seed plates, the principal surface of which is (0001) or an orientation close to that, is placed within the autoclave. The autoclave is filled to 83% of its free volume with 1.0 M NaOH and then closed. The vessel is heated so that the nutrient zone is at a temperature of about 400°C and the growth

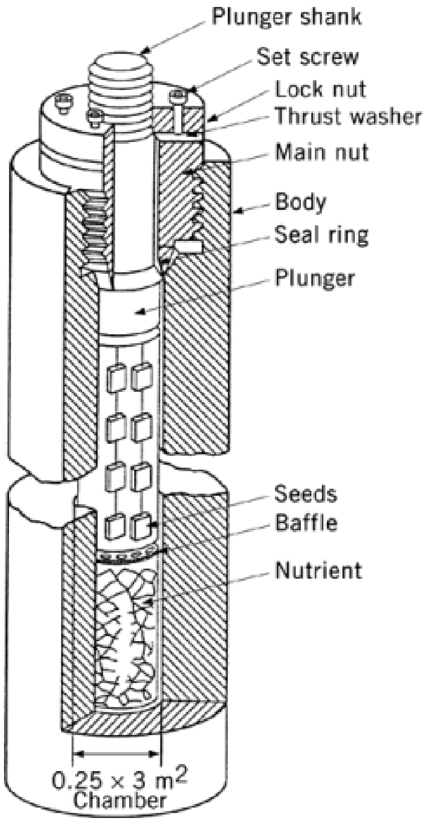

Fig. 1. Hydrothermal quartz autoclave.

zone at a temperature of about 350°C. Under these conditions, the pressure is ca 16.5 MPa (24,000 psi). The vessel is held at these conditions for several weeks and then cooled. Once removed and rinsed with distilled water, the grown crystals are ready for processing. A typical growth rate under such conditions would be ca 1.27 mm/d for growth on the basal (0001) planes. Depending on the particular piezoelectric application, the seed orientation is adjusted to produce a grown crystal that can most efficiently be cut into piezoelectric plates of the orientation dictated by the application. The three seed orientations generally used are basal, $+5^{\circ}x$ (rotated $+5$ from the basal seed), and seed plates rotated 3° off the minor rhombohedral face, which are sometimes called *r*- or *z*-face (14). This last orientation, in spite of the fact that its growth rate is about half of basal growth, gives a grown crystal particularly useful for AT-cut ($\sim 35^{\circ}$ off the *z*-axis) piezoelectric resonators (15) and is often used (14).

1.3. Effects of Rate Conditions

It is essential for commercial α-quartz crystals to have usable perfection growth at a high rate and at pressure and temperature conditions that allow economical equipment design. The dependence of rate on the process parameters has been studied (8, 14) and may be summarized as follows. Growth rate depends on crystallographic direction; the (0001) is one of the fastest directions. Because ΔS is approximately linear with ΔT, the growth rate is linear with ΔT. Growth rate has an Arrhenius equation dependence on the temperature in the

Table 2. Acoustic *Q* of Synthetic Quartz

Synthetic quartz growth solution	Q
1 M NaOH	1×10^5
1 M NaOH + 0.2 M LiOH	$(2 - 3) \times 10^5$
1 M NaOH + 0.2 M $LiNO_2$	$(0.5 - 1) \times 10^6$
1 M NaOH + 0.2 M $LiNO_2$[a]	2×10^6

[a] Crystallization in silver-lined tube.

crystallization zone:

$$k = e^{-\Delta E/RT}$$

where k is the rate in a particular crystallographic direction, E the energy of activation, T the absolute temperature, and R the gas constant. Growth rate is increased by an increase in fill, ie, percentage of free volume filled with solvent at room temperature.

Piezoelectrical quartz must be free of twins, bubbles, and particulate inclusions. If the seeds used in quartz synthesis are untwinned and the growth takes place at an appropriate rate and pressure–temperature conditions, synthetic quartz is relatively free of the imperfections. If the rate is too high for the pressure–temperature conditions, the growth becomes limited by the rapidity with which silica can diffuse across a locally depleted zone close to the growing seed. The result is imperfect or crevice-flawed growth. Such growth, which contains many voids and liquid inclusions and is not usable for piezoelectric applications, is caused by conditions analogous to those causing dendritic growth in the preparation of metal crystals. Thus the success of commercial processes depends on careful mapping of the pressure, temperature, and temperature differential conditions in order to find regions where crevice flawing does not occur at commercially useful rates.

Particular difficulty with cracking occurs in z-face-grown quartz. High strain in seeds leads to a strain buildup in the grown quartz that exceeds the elastic limit. This can produce cracks in the as-grown material or lead to cracking during subsequent processing. Severe losses in yield can result (14). Careful inspection of seeds between crossed polarizers in an immersion oil of matching index of refraction reveals strain and allows high quality seeds to be selected so that a high yield of unstrained material is possible (14). Strains result from dislocations generated at particulate inclusions of Na–Fe silicates (16). Growth in the absence of iron in silver cans contained in hydrothermal autoclaves greatly reduces inclusions and strain and produces strain-free seeds for subsequent use under normal conditions (16). The pressure in the can is balanced by filling the space between the can and the autoclave with H_2O to a height slightly above that of the NaOH solution used in the can. The higher fill is required to ensure that the can is under compression, a situation less prone to rupture. Careful choice of seeds and conditions using a silver-lined vessel has even resulted in the growth of low dislocation quartz in the laboratory (16).

An additional requirement for piezoelectrical quartz is a high acoustic quality factor, Q (13, 17–19). The acoustic Q of a piezoelectric material is equal to the Q of the resistance–capacitance–inductance circuit, which is electrically equivalent to the piezoelectric resonator circuit. The higher the Q of a piezoelectric material, the more efficiently it converts mechanical to electrical energy. In low Q materials, much energy is lost by thermal processes in this conversion. The acoustic Q of ordinary materials may be thought of as being higher the longer they ring when struck mechanically. Lead, for instance, is not used to make bells because it has a low Q.

The acoustic Qs of quartz prepared under a variety of conditions are given in Table 2. The acoustic Q of natural quartz is $(1 - 2) \times 10^6$.

Infrared absorption studies have shown that Q correlates with an absorption at 3 μm associated with an OH-stretching frequency (20). Indeed, infrared absorption provides a useful tool for Q evaluation in rapid production quality control. Infrared and other studies show that Q degradation is caused by proton inclusion in the grown quartz.

The distribution constant for OH or a proton depends on the presence of other ions. The proton enters the quartz lattice interstitially and is compensated by +3 or +2 ions such as Fe^{2+}, Fe^{3+}, and Al^{3+} substituted at Si^{4+} lattice sites. Iron originates in the autoclave and Al^{3+} is an impurity in the natural quartz starting material. Other +1 ions such as Na^+ or Li^+ can also compensate interstitially for non $_{+4}$ ions at the Si^{4+} site. Thus, Li^+ doping can be used to improve Q as well as quartz growth in a silver liner, or it can be used to exclude iron (21). Furthermore, the distribution constant for impurities depends on the quartz growth rate in a predictable manner, and slower growth excludes protons (22). Systematic studies of distribution constants have been used to identify the commercial conditions used for high Q and high optical transmission quartz growth (22–24). Thus, high Q quartz can be grown at such rates that large crystals (>5 cm grown material) can be produced in 65–90 d.

2. Health and Safety Factors

The principal consideration in quartz synthesis is the safe management of the high pressures required for growth (see High pressure technology). The autoclave must be designed on the basis of proper stress analysis and materials selection. Autoclaves are shielded either by armor plate or by placement in cement-lined pits in the ground. Rupture disks that release pressures of ca 35 MPa (5000 psi) above the operating conditions as well as pressure and temperature overrides and alarms are standard practice. Autoclave embrittlement over long service life must be monitored and those in danger of operating at pressures much above ambient in the brittle range should be removed from service. The hydroxide solutions used in growth should be handled with standard safety measures, including eye shields for operators and safety showers. Activities in high pressure areas should be limited to essential maintenance. The disposal of spent solutions presents no special pollution problems because, at the conclusion of growth, runs are not strongly basic and can be easily neutralized.

3. Uses

The principal uses of α-quartz are mostly related to the piezoelectric effect (see Ferroelectrics). Crystals are used in electrical filters and oscillators for frequency and timing and frequency-division multiplexing and demultiplexing. They have also been used as electromechanical transducers in ultrasonic generators and electronic weighing microbalances. Crystal quartz is generally the material used wherever precise timing control is required. Thus, it is widely used in computers, portable as well as stationary telephones, citizen band (CB) radios, and watches. The use of quartz surface-acousic wave devices in cellular phones is an expanding market. The piezoelectric properties and design of filters and resonators have been discussed (15, 25). It is estimated that the production of crystal quartz is about 450 metric tons annually (26), but production fluctuates rapidly owing to demand.

The advent of satellites for timing and communication requires the use of quartz that is not only radiation resistant but of greater mechanical strength and accuracy than material used for other purposes. Whereas the amount of quartz required for these, as well as some military uses, is small, exceedingly careful preparation of devices is essential. The global positioning satellites operate in the range of the radioactive Van Allen belt. Because aluminum substituted for quartz has been shown to be detrimental to radiation resistance (20), the concentration of aluminum must be reduced to a few parts per billion in the crystals. This is done by using slow growth and special starting materials low in aluminum, such as previously grown crystals or crystals grown from high purity fused quartz. The resonator is not fabricated using the AT, but from a doubly rotated stress-compensated (SC) crystal (27), which has been shown to be less temperature sensitive. Use of computerized fabrication equipment has made device preparation possible. Because these devices are subject to large stresses during liftoff into space, they must be free of etch channels which can reduce the mechanical strength of the device. In addition, during the chemical part of the device fabrication, hydrofluoric acid (HF) is used. The HF tends to etch into dislocations and cause etch channels, which not only weaken the device but can affect the frequency stability.

Etch channels can be reduced or essentially eliminated in a number of ways. Use of different orientation of the seed, the so-called x-seed, can produce a crystal having almost no dislocations (28). The grown crystal, however, is not the usual size, making resonator fabrication difficult and expensive. Another, more accepted technique involves applying solid-state electrolysis (sweeping). In this procedure (29), blocks are cut from the crystal above and below the seed, leaving the seed to be reused. A voltage of 1000–2000 V/cm is then passed across the block in the c direction, which causes lithium and hydrogen (or hydroxide) to migrate out of the crystal. This technique is exceedingly effective in reducing etch channels (30).

Quartz also has modest but important uses in optical applications, primarily as prisms. Its dispersion makes it useful in monochromators for spectrophotometers in the region of 0.16–3.5 m. Specially prepared optical-quality synthetic quartz is required because ordinary synthetic quartz is usually not of good enough quality for such uses, mainly owing to scattering and absorption at 2.6 μm associated with hydroxide in the lattice.

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