
History

The first reports of the growth of quartz crystals by Schafhäült in 1845 and by de Sénarmont in 1851 produced microscopic crystals. G. Spezia, from 1898 to 1908, published reports on the growth of macroscopic crystals. He used solutions of sodium silicate, natural crystals as seeds and supply, and a silver-lined vessel. By heating the supply end of his vessel to 320-350°C, and the other end to 165-180°C, he obtained about 15 mm of new growth over a 200 day period. Unlike modern practice, the hotter part of the vessel was at the top.

In the period before and during World War II, Richard Nacken led an extensive German effort to grow quartz crystals, especially once the supply of natural crystals

from Brazil was blocked. They used an isothermal growth process that relied on the higher solubility of the vitreous silica supply to supersaturate the solution.

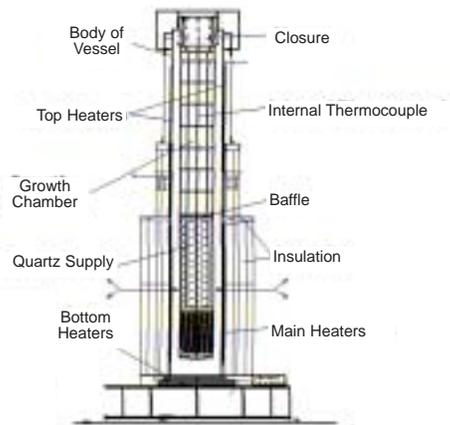
Following the war, researchers, working with the U.S. Army Signal Corps, studied the German work and developed it into a commercially viable process. C.B. Sawyer, D.R. Hale, Hans Jaffe and others at Brush Development, and then Sawyer Research Products, Inc., developed the low-pressure sodium carbonate process. R. Laudise, N.C. Lias, and others at Bell Laboratories and Western Electric developed the high-pressure sodium hydroxide process. Today, these processes are used world-wide.

Crystal Growth

With a melting point of 1670°C and high chemical resistance, quartz crystals would be very difficult to form by either melt or flux techniques. Since cooling through the Curie point at 573°C usually produces twins, any technique for production of single crystals must be done below the Curie temperature. The process used is a solution growth technique called hydrothermal growth. This technique is very similar to the processes by which natural quartz crystals are formed.

Hydrothermal growth is conducted in steel pressure vessels called autoclaves (see figure). A supply of

nutrient material, usually natural clear or milky quartz, is placed in the bottom half of the autoclave. In the top half, seed crystals, cut from either cultured (synthetic) or natural crystals are hung. The baffle, a metal plate with one or more holes cut in it to provide a constant and controlled opening, is placed between the upper and lower halves. An aqueous solution, usually an alkali metal hydroxide or carbonate solution, is added to the autoclave so that the solution occupies a set percentage of the total free volume of the vessel. The alkali metal compound acts as a mineralizer, increasing the solubility of the quartz in the solution, through the formation of soluble silicate complexes.



After sealing the vessel, the autoclave is heated to operating conditions with the use of external, resistance heaters. Typical operating conditions are between 300 and 400°C. The internal pressure developed is controlled by the temperature and the amount of solution added to the autoclave.

At operating conditions, the temperature is controlled such that a temperature difference is established between the internal temperature in the lower half of the autoclave, called the dissolving chamber, and the upper half, called the growing chamber. A temperature gradient in a closed cylinder of fluid in a gravitational field establishes a natural convection pattern called a closed thermosyphon. In the warmer dissolving chamber, quartz dissolves in the solution. The warm, less dense fluid rises. In the growing chamber, the cooler temperature leads to supersaturation of the solution for quartz and the quartz precipitates on the seed crystals. The cool, dense fluid sinks into the dissolving chamber and the cycle continues.

The temperature difference between the growing and the dissolving chamber is the chief process control of the growth rate. The temperature difference controls not only the supersaturation in the growth chamber, but together with the baffle, controls the rate of fluid and heat transfer between the two chambers. Growing temperature also has a strong effect, with growth rate increasing with increasing temperature. Other factors which influence the growth rate are pressure, mineralizer type and concentration, other chemical additives (particularly lithium), and seed orientation.

The mineralizer is a compound added to the solution to increase the solubility of the compound of interest, in this case, quartz. Typically, alkali metal salts, particularly sodium hydroxide or sodium carbonate, are used. In natural systems, sodium chloride is believed to be the most common mineralizer. The mineralizer increases the solubility by complexing with the solute to form more soluble species. While the exact form of the dissolved species is unknown, it is believed that soluble silicates of forms such as $\text{Si}_3\text{O}_7^{2-}$ and SiO_3^{2-} are formed in the presence of hydroxides and carbonates, respectively.

Lithium is added at low concentration (typically 0.01 to 0.10 moles/liter) to favorably improve the relationship between proton uptake and growth rate. The mechanism of this improvement is not completely understood.

Under these conditions, complex alkali metal-iron-silicates form on the steel surfaces of the autoclave. These silicates act as a passivation layer, preventing further corrosion. They are also the compounds which form inclusions.

Two similar processes are the most widely used in the cultured quartz industry. They are known as the low pressure and high pressure processes.

The high pressure process typically uses 1.0M sodium hydroxide solution, a growing temperature of 360°C, a temperature difference of 25°C, and a pressure of 1000-1500 bars. While the capital costs for such equipment are much greater, growth rates of up to 1.0 mm/day (Z) can be achieved at these conditions.

The low pressure process used at Sawyer Research Products, typically uses a 0.6 to 0.8M sodium carbonate solution, a growing chamber temperature of 345°C, a temperature difference of 10°C, and a pressure of 700-1000 bars. Typical growth rates are 0.4 mm/day in the Z - direction. The chief advantage is the lower capital expense of autoclaves which operate at this pressure.

The anisotropic structure of quartz results in large differences in growth rate in different crystallographic directions. Growth rate in the Z-direction can be up to three times the growth rate in the X- direction. The orientation of the seeds used can affect not only the growth rate of the crystals but the uptake of impurities.

References

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