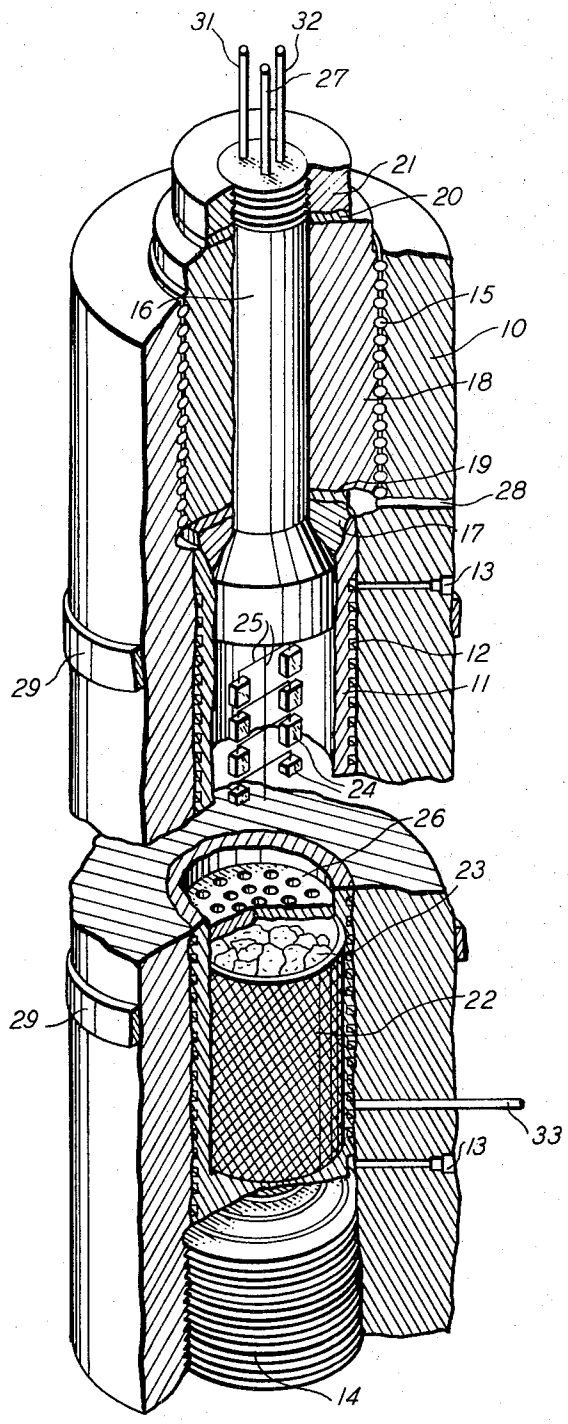
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HIGH PRESSURE HYDROTHERMAL GROWTH OF QUARTZ WITH HIGH "Q" VALUES

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HIGH PRESSURE HYDROTHERMAL GROWTH OF QUARTZ WITH HIGH "Q" VALUES

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ABSTRACT OF THE DISCLOSURE

Hydrothermal growth of high acoustic quartz (Q greater than 10^6) at fast rates of about 100 mils per day (2.5 mm./da.) is made possible by the utilization of pressures exceeding 30,000 p.s.i. (2,069 bars) and a growth temperature exceeding 350° C.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

Quartz piezoelectric plates cut from large single crystals of quartz are utilized in a variety of electric apparatus, such as filters, oscillators, etc. This invention relates to hydrothermal processes for artificially growing single crystals of quartz having suitable size to produce plates for use in such apparatus.

(2) Prior Art

One hydrothermal quartz growing process which has been commercially successful is described in U.S. Pat. No. 2,785,058 issued to E. Buehler on Mar. 12, 1957. Single crystals of quartz are grown on single crystal seeds or plates of quartz which are suspended in an upper or growing zone of a vertically elongated autoclave or high pressure vessel. The vessel contains a fluid, such as an aqueous alkaline solution, in which quartz becomes increasingly soluble with increasing temperatures and pressures. A baffle separates the upper zone of the vessel from a lower or dissolving zone, which contains particulate quartz or quartz nutrient. The design and operation of the baffle is described in U.S. Pat. No. 2,895,812 issued to G. T. Kohman on July 21, 1959. The fluid in the vessel is heated to elevated temperatures and pressures with the fluid in the lower zone maintained at a higher temperature than the fluid in the upper zone. The quartz nutrient dissolves and the dissolved quartz is conveyed by convection or diffusion to the upper zone of the vessel. The lower temperature in the upper zone results in supersaturation of the dissolved quartz and nucleation or crystallization onto the seeds producing larger single crystals of quartz.

The quality of quartz for use as piezoelectric devices in electrical apparatus is usually expressed in terms of Q. The Q of quartz refers to the reciprocal of the internal friction of the quartz in its natural or unmounted condition. There are at least three techniques for determining the Q of a section of quartz crystal. They are (1) the logarithmic decrement procedure, (2) the transmission procedure, and (3) the infared absorption procedure. In the logarithmic decrement procedure, the quartz section is vibrated and the number of cycles required for the amplitude of vibration to decay to ⅓ times the initial amplitude are counted to determine Q. In the transmission procedure, the quartz section is driven by an electric circuit with known resistance, inductance and capacitance characteristics. By varying the known characteristics and measuring voltage amplitude, the Q can be calculated. The infared

absorption procedure is based upon the recognition that the Q of quartz is directly related to the absorption of certain frequencies of infared radiation. The infared absorption procedure is described in U.S. Pat. No. 3,351,757 issued to D.B. Fraser and D. W. Rudd on Nov. 7, 1967.

Quartz crystals are presently grown in vessels at pressures from 10,000 p.s.i. to 25,000 p.s.i. (690 bars to 1725 bars) and temperatures from 350° C. to 400° C. at rates of 10 mils to 60 mils per day (0.25 mm. to 1.5 mm. per day) with temperature differentials between the growing and dissolving zones of the vessels maintained from 5° C. to 70° C. In order to produce quartz having a high Q, greater than 10^{+6}, it has been necessary to utilize a slow growth rate, less than 25 mils per day (0.63 mm. per day). Utilizing such slow growth rates necessitates a total growth period of approximately 60 days to produce quartz crystals of sufficient size to cut into quartz plates. Increasing demand for quartz and particularly for high Q quartz necessitates a substantial increase in quartz growing facilities or improved processes for growing high Q quartz at faster rates.

One improved process that has resulted in the faster growth of quartz is described in U.S. Pat. No. 3,356,463 issued to A. A. Ballman, R. A. Laudise, and D. W. Rudd on Dec. 5, 1967. In this process, lithium ions and nitrite or nitrate ions are added to the solvent to produce quartz with higher Q's resulting in higher production rates.

It is well known that increasing the pressure within the vessel and/or increasing the temperature differential between the growing and dissolving zones of the vessel increases the growth rate of quartz on the seeds. However, such as increase in growth rate in the past has produced quartz with reduced Q. Also, high growth rate heretofore has resulted in crystal flawing or imperfections believed due to spurious crystallization at the growth interface caused by an excessive supersaturation of quartz in the growing zone. The increase of pressures above 25,000 p.s.i. (1725 bars) has been believed only to result in an increased cost for vessels designed to withstand higher pressures without any substantial increase in the rate of high Q quartz growth thereby.

SUMMARY OF THE INVENTION

An object of the invention is a new and improved process for growing single crystals of quartz on seeds.

Another object of the invention is a new and improved process for growing single crystals of high Q quartz on seeds at faster rates than has heretofore been possible.

A further object of the invention is the growth of single crystals of quartz at rates which result in an improved economic utilization of the growing facilities.

In accordance with these and other objects of the invention, a new and improved process of growing single crystals of quartz contemplates the utilization of a pressure vessel wherein single crystal seeds of quartz are deposed in a first zone of the pressure vessel and a siliceous supply material is disposed within a second zone of the pressure vessel. An aqueous solvent is placed within the vessel and then heated to expand and produce a pressure exceeding 30,000 p.s.i. (2,069 bars) within the vessel. The temperature in the first zone is maintained at a lower magnitude than the temperature in the second zone to grow quartz on the seed. It has been discovered that at pressures exceeding 30,000 p.s.i. (2,069 bars) and preferably above 35,000 p.s.i. (2,414 bars), high quality quartz may be grown at substantially faster rates than has heretofore been possible.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is an isometric view of a pressure vessel suitable for high pressure growth of single crystals of quartz.

DETAILED DESCRIPTION

Referring to the drawing, there is shown a high pressure vessel which may be placed in an installation similar to that described in the U.S. Pat. No. 3,183,063 issued to J. K. Gilson, C. W. Higgins, W. O. Huff and L. V. Stonebraker on May 11, 1965. The vessel has an outer cylindrical body **10** with an inner cylindrical lining **11**. The outside of the inner lining **11** has a helical groove **12** communicating with vents **13—13** in the body **10** to safely discharge the pressure in event the inner lining **11** fails. The bottom of the liner **11** is supported by a suitable threaded base **14** in the body **10**. The open top of the liner **11** is closed by a cover **16**, a sealing ring **17**, a closer **18**, thrust washers **19** and **20**, and a locking nut **21**. Preferably, the body **10**, liner **11**, cover **16**, closer **18** and base **14** are made from high strength steel or other comparable metals or alloys. The interior surfaces of the vessel may be plated with silver or another highly corrosion resistant metal or alloy. A helically wound spring-like member **15** is disposed in helical grooves in the body **10** and closer **18** to retain the closer **18** in the body **10**. A safety valve member **27** communicating through the cover **16** into the vessel and a vent **28** in the body **10** to the top of the seal **17** are further safety features. Quartz nutrient **23** is disposed within a wire basket **22** in a lower zone of the vessel while quartz seed plates **24** are mounted in a spaced relationship on a wire rack **25** in the upper zone of the vessel. A baffle **26** separates the upper or growing zone from the lower or dissolving zone of the vessel to insure that a temperature gradient may be maintained between the fluid in the upper zone and the fluid in the lower zone. Suitable resistance heating bands **29—29** surround the cylindrical body **10** to heat the vessel. A suitable temperature sensing element **31** and a pressure sensing element **32** extend through the cover **16** into the upper portion of the vessel to respectively sense the temperature and pressure of the fluid therein. A temperature sensing element **33** extends through the body **10** against the liner **11** to sense the temperature of the fluid in the lower zone of the vessel. The temperature sensing elements **31** and **33** may operate suitable facilities (not shown) for automatically controlling the current to the heating bands **29—29** to maintain a first temperature in the upper zone and a higher second temperature in the lower zone.

High acoustic loss, or low Q, in quartz severely degrades its usefulness in piezoelectric devices, especially for high frequency applications. Acoustic loss is directly related to the quantity of interstitial hydrogen ions (H^{+1}) which enter the crystal lattice as $(OH)^{-1}$ from the basic growth solution to charge compensate nonplus four ions such as Fe^{+3}, Fe^{+2}, Cu^{+2} and Al^{+3} present in the lattice at Si^{+4} sites. The Fe^{+3}, Fe^{+2}, Cu^{+2} and Al^{+3} are believed to come mostly from the quartz nutrient. Some may come from the walls of the vessel. At slower growth rates, lesser amounts of the impurity ions are accepted into the crystal lattice. This is believed due to a preference of the crystal for Si^{+4} over the impurity ions. Such preference is probably the result of a lower energy state in the crystal when the crystal only contains SiO_2. At slower growth rates, the crystal is given a greater chance of accepting the preferred Si^{+4} rather than the nonpreferred impurity at the growth interface.

It has been discovered that at pressures exceeding 30,000 p.s.i. (2,069 bars) and preferably above 35,000 p.s.i. (2,414 bars), the hydrothermal growth rate of quartz may be substantially increased to grow quartz having a Q that is equal to quartz grown at substantially slower rates at pressures less than 30,000 p.s.i. Some additional improvement in Q has been noted by increasing the pressure up to 45,000 p.s.i. (3,103 bars). It is believed that at pressures exceeding a threshold of about 30,000 p.s.i., substantially more of the impurity ions are rejected from the crystal lattice. This may be due to the increased energy of the solvent passing a bonding energy level of the impurity. Thus, preferred Si^{+4} more readily replaces the impurity ions at the growth interface. This discovery makes possible the growth of quartz having a Q greater than 10^6 at rates exceeding 100 mils per day (2.5 mm./da.). Where a lesser quality quartz is acceptable, even faster rates of growth are possible. A substantial economic gain is realized even though the cost of the pressure vessel capable of withstanding the higher pressures is more than pressure vessels capable of withstanding relatively low pressures.

The temperatures in the respective upper and lower zones of the vessel are carefully controlled. The temperature in the upper or growth zone may be selected from the range of 340° C. to 450° C. It is preferable that the temperatures in the growth zone be above 350° C. It is believed that the solubility of H^+ in crystalline quartz decreases with increasing temperatures so that temperature increases tend to improve Q. Temperatures higher than 450° C. may be used, but the increased solubility of quartz at higher temperatures makes the process more difficult to control. The upper temperature will generally be set by the maximum temperature capability of the vessel. In no case should the temperatures in the vessel exceed the alpha-beta quartz transition temperature. The alpha-beta transition temperature is a function of pressure and is in the vicinity of 573° C. at moderate pressures. Preferably, the temperature in the growing zone with aqueous sodium hydroxide solution is maintained between 350° C. and 385° C. to produce the highest quality quartz. The temperature in the dissolving or lower zone is maintained from 5° C. to 70° C. higher than the temperature in the upper zone. For sodium carbonate solutions, the optimum temperature differential between the upper and lower zones is within the range from 8° C. and 20° C. For sodium hydroxide solutions, the acceptable temperature differentials range from 15° C. to 70° C. For growth in sodium hydroxide solutions at pressures exceeding 30,000 p.s.i. (2,069 bars), the temperature differential is preferably maintained between 30° C. and 70° C.

The pressure within the vessel is dependent upon the temperature, the expansion of the fluid, the expansion of the vessel and the percentage of volume to which the vessel is initially filled with fluid. With selected operating temperatures, the pressure within the vessel is controlled by selection of the proper percentage of initial fill. The percentage of fill is determined by initially adding the solvent fluid to the vessel with the nutrient and seeds in the vessel until the level of the fluid rises to a level corresponding to the selected percentage of the volume of the vessel. For operating temperatures ranging from 340° C. to 500° C., percentages of fill from 80% to 95% may be selected to produce pressures from 30,000 p.s.i. (2,069 bars) to 45,000 p.s.i. (3,103 bars).

A number of aqueous solutions are capable of dissolving the quartz nutrient and transporting the dissolved quartz to the growing zone. Most commercial production employs aqueous solutions containing sodium hydroxide or sodium carbonate. Other alkaline solutions such as a aqueous solutions of sodium silicate and rubidium hydroxide have also been used. The concentration of alkaline salt may be from 0.2 to 2.0 moler with 0.7 to 1.3 molar being the preferred range of concentration. Generally, fast rates of growth in sodium hydroxide have produced quartz which is superior to quartz grown in other solutions at the same rates.

The percentage of cross sectional horizontal area occupied by the baffle **26** within the vessel is carefully selected relative to the temperature differential between the upper and lower zones. The percentage of area occupied by the baffle **26** must be large enough to substantially restrict fluid convection to maintain the temperature differential between the upper and lower zones. Also, baffle **26** must allow some convection flow to transport dis-

solved quartz from the lower to the upper zone. For higher temperature differentials, the percentage of area occupied must be higher than that for lower temperature differentials. Generally, the baffle **26** is selected to occupy from 50% to 98% of the cross sectional area within the vessel. For temperature differentials from 15° C. to 70° C., the percentage of cross sectional area occupied by the baffle **26** preferably ranges from 90% to 98%.

Advantageously, lithium carbonate and sodium nitrite or sodium nitrate is added to the solution in the vessel in accordance with U.S. Pat. No. 3,356,463. The presence of lithium ions and nitrite or nitrate ions improves the growing process to produce a higher quality quartz.

As the seed plates **24** grow into larger crystals and the supply of nutrient **23** decreases, the rate of growth also decreases. This results in an undesirable difference in the Q of quartz near the seed plate from the Q of quartz further away from the seed plate. In U.S. patent application Ser. No. 131,916 filed on Apr. 7, 1971, by R. K. Bhattacharyya, A. F. Fiore, and D. W. Rudd, there are described procedures which may be utilized for controlling the temperatures and temperature differentials to maintain an even rate of growth throughout the growth period of a quartz crystal.

The following example illustrates the manner in which the present invention may be practiced. Particles of quartz or broken quartz crystals **23**, having an average size of about 1 cubic inch (16 $cm.^3$) are placed within the wire basket **22** in the lower zone of the pressure vessel shown in the drawing. A baffle **26** occupying about 96% of the horizontal cross section within the vessel is disposed above the basket **22**. A plurality of seed plates **24**, each cut from a single crystals of quartz with the plane of each plate parallel to the X axis and rotated +5° from the Y axis, are mounted on the wire rack **25** above the baffle **26** in the upper zone of the vessel. An aqueous solution of 1.0 molar sodium hydroxide, 0.025 molar lithium carbonate and 0.1 molar sodium nitrite is added to the vessel until the vessel is filled to about 88% of its closed volume. The vessel is closed and heated to produce a temperature of about 374° C. in the fluid in the upper zone and a temperature of about 397° C. in the lower zone. The pressure in the vessel is about 40,000 p.s.i. (2,760 bars). The temperatures in the upper and lower zones are maintained for 10 days. The vessel is then allowed to cool and is opened. About 1.03 inches (26.2 mm.) of quartz has grown on the seed plates for an average rate of about 103 mils (2.62 mm.) per day. The Q of the grown quartz is measured by the infared absorption technique and found to average about 1.4×10^6.

The above-described embodiment is only illustrative of the principles of the invention. Many embodiments may be devised by those skilled in the art without departing from the scope and spirit of the invention.

What is claimed is:

1. In a process of growing single crystals of high acoustic quartz having a Q greater than 10^6, which process comprises: disposing at least one single crystal seed of quartz in a first region of a pressure vessel and a siliceous supply material in a second region of the pressure vessel, placing in the pressure vessel an aqueous solvent, in which silica becomes increasingly dissolvable with increasing temperatures, and applying heat to maintain elevated temperature and pressure conditions in the pressure vessel with the temperature in the first region being lower than the temperature in the second region to grow quartz on the seed, the improvement comprising:

maintaining a pressure greater than 30,000 p.s.i. within the pressure vessel.

2. In a process as defined in claim **1** wherein the temperature in the first region is maintained between 350° C. and 385° C.

3. In a process as defined in claim **1** wherein the pressure within the pressure vessel is maintained at a pressure greater than 35,000 p.s.i.

4. A process of growing single crystals of high acoustic quartz, having a Q greater than 10^6, in a vertically elongated pressure vessel having a baffle for restricting fluid flow between an upper zone and a lower zone in the vessel, comprising:

placing a supply of particulate quartz in the lower zone;

placing a plurality of quartz plates in spaced relationship in the upper zone; each plate being a section cut from a single crystal;

partially filling the vessel to a predetermined level with an aqueous solvent in which quartz in increasingly, dissolvable with increasing temperatures; and

heating the vessel in a manner to produce a temperature between 340° C. and 450° C. in the upper zone and to produce a temperature in the lower zone which is from 5° C. to 70° C. higher than the temperature in the upper zone, said predetermined level of aqueous solvent selected to produce a pressure exceeding 30,000 p.s.i. in the vessel at said temperature to grow quartz on the quartz plates.

5. A process as defined in claim **4** wherein the predetermined level of aqueous solvent is selected to produce a pressure exceeding 35,000 p.s.i. in the vessel at said temperatures.

6. A process as defined in claim **4** wherein the aqueous solvent is sodium hydroxide, sodium carbonate, sodium silicate, or rubidium hydroxide.

7. A process as defined in claim **4** wherein:

the aqueous solvent is sodium hydroxide;

the temperature in the upper zone is between 350° C. and 385° C.; and

the temperature in the lower zone is between 15° C. and 70° C. higher than the temperature in the upper zone.

8. A process as defined in claim **7** wherein the predetermined level of aqueous solvent is selected to produce a pressure exceeding 35,000 p.s.i. in the vessel at said temperatures.

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