April 13, 1954 A. R. SOBEK ET AL 2,675,303

METHOD AND APPARATUS FOR GROWING SINGLE CRYSTALS OF QUARTZ

Filed April 11, 1950 3 Sheets-Sheet 1

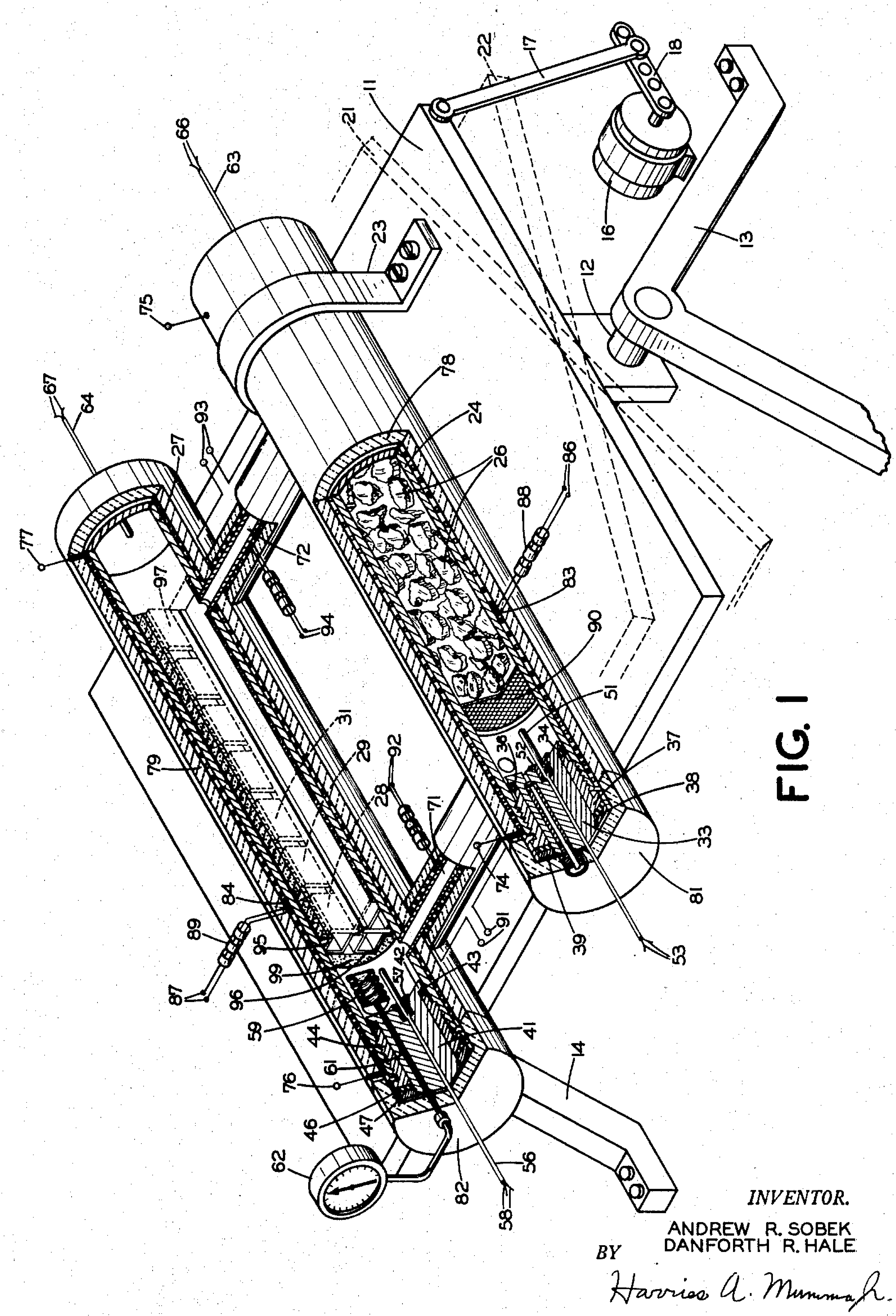

FIG. 1

INVENTOR.
ANDREW R. SOBEK
DANFORTH R. HALE

BY Harris A. Mummah Jr.

ATTORNEY

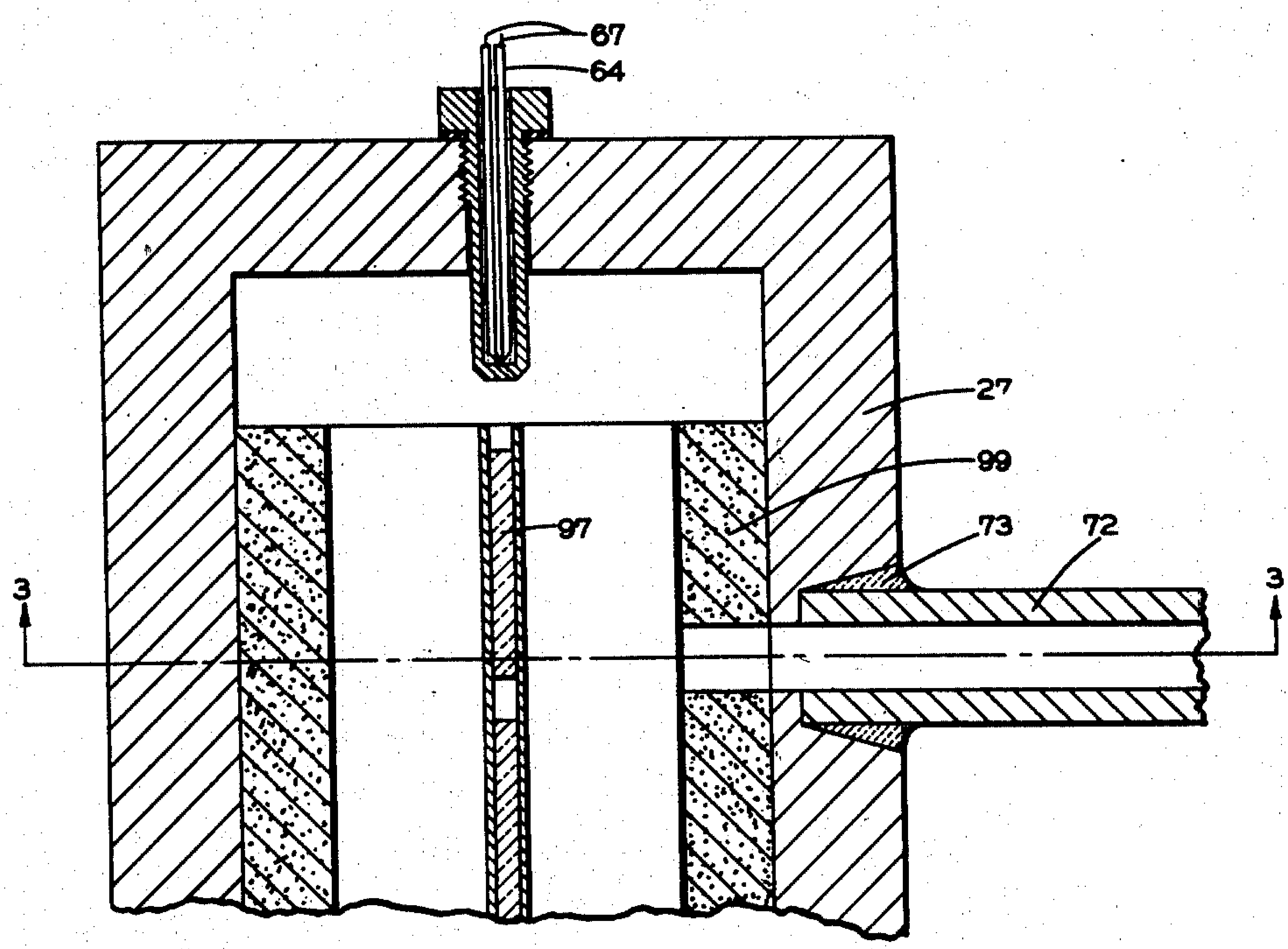

FIG. 2

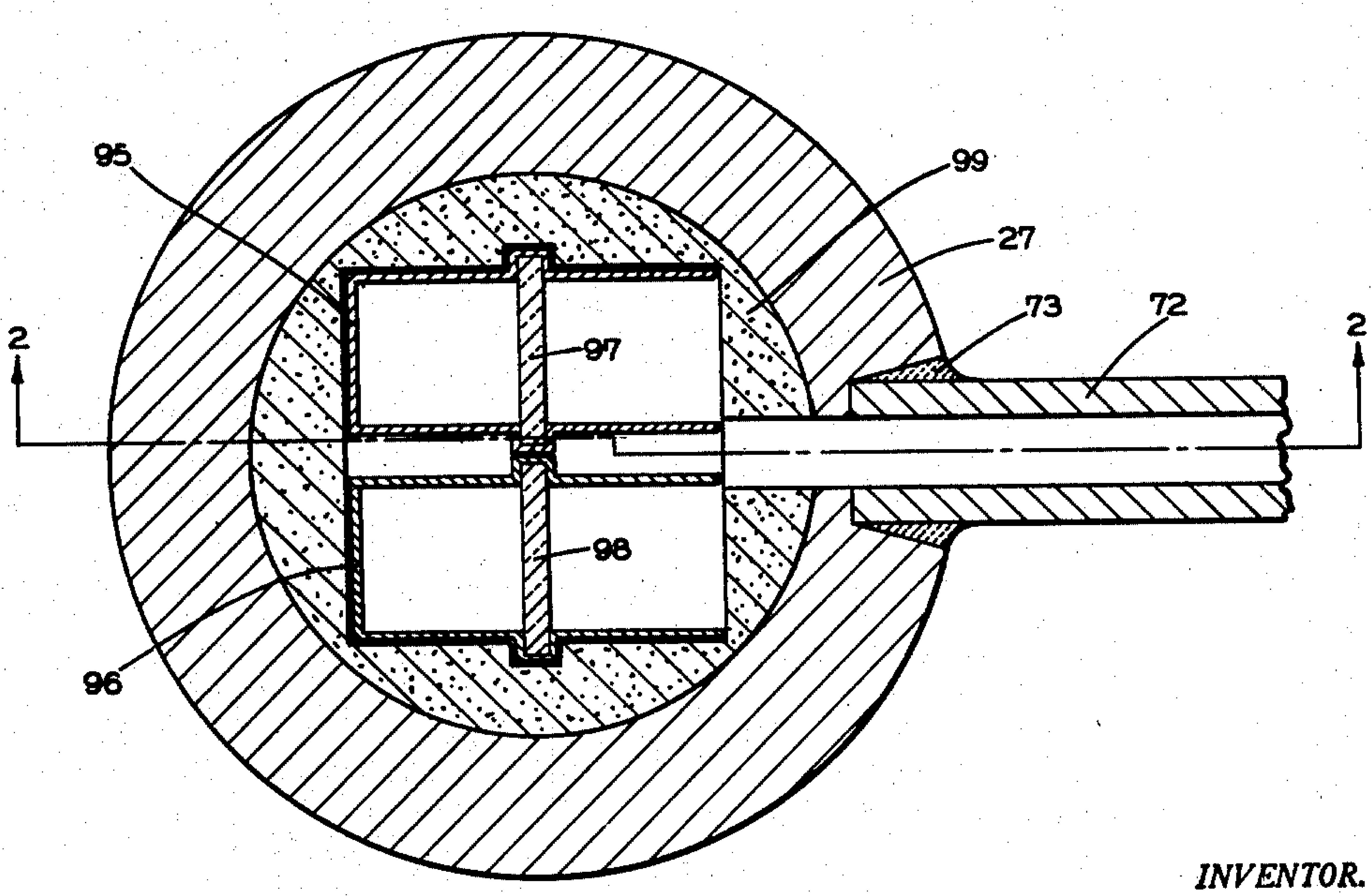

FIG. 3

INVENTOR.
ANDREW R. SOBEK
DANFORTH R. HALE
BY Harries A. Mumma Jr.
ATTORNEY

METHOD AND APPARATUS FOR GROWING SINGLE CRYSTALS OF QUARTZ

Filed April 11, 1950 3 Sheets-Sheet 3

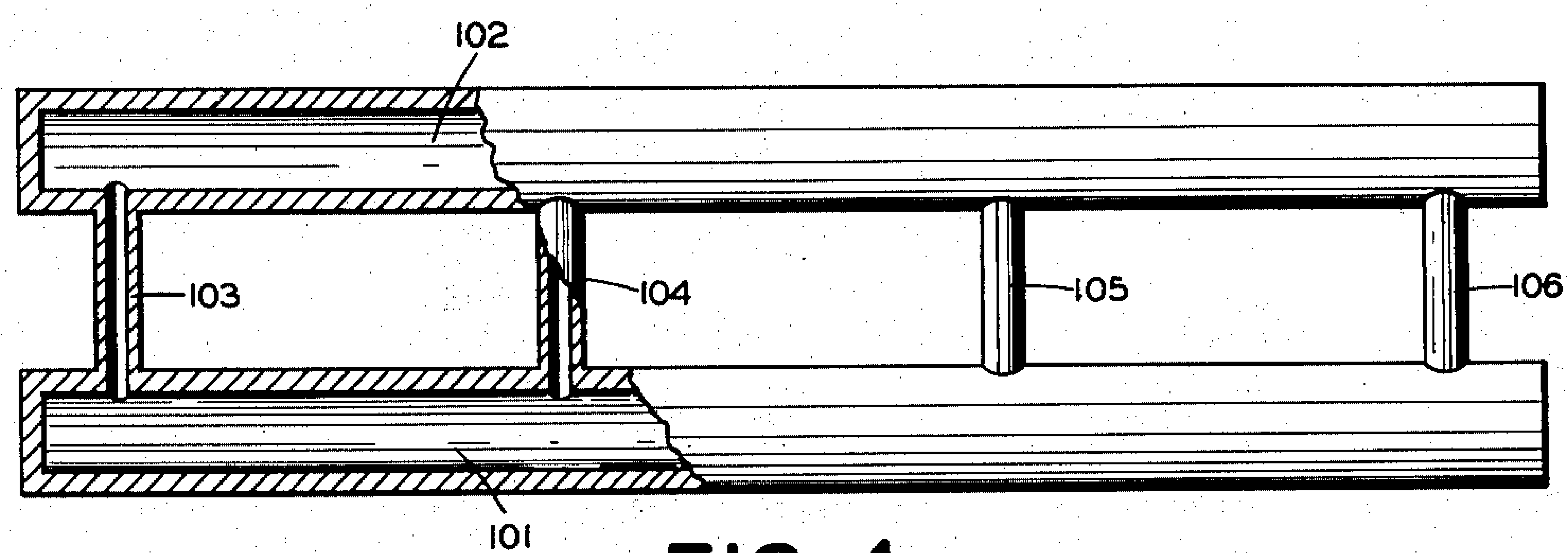

FIG. 4

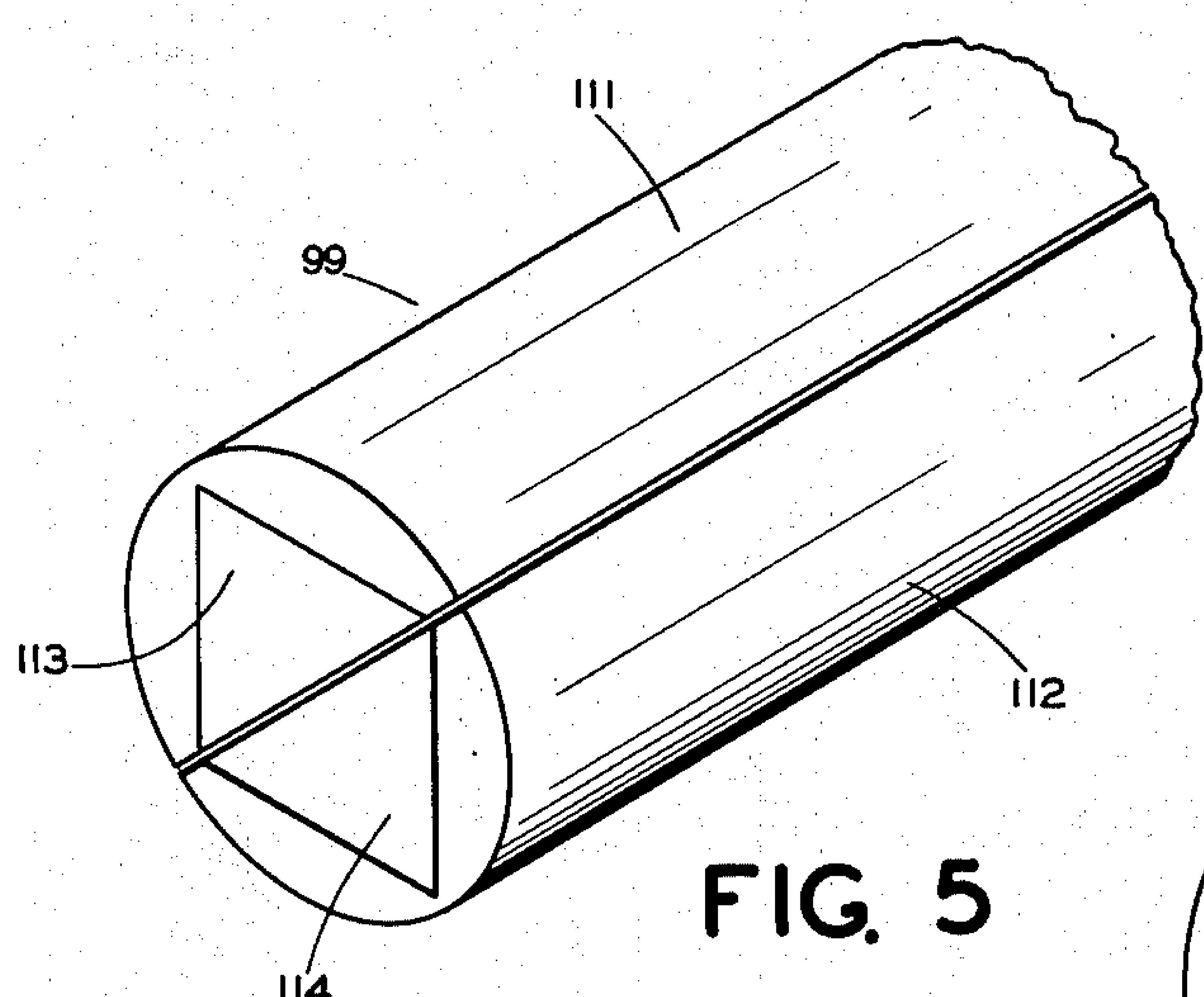

FIG. 5

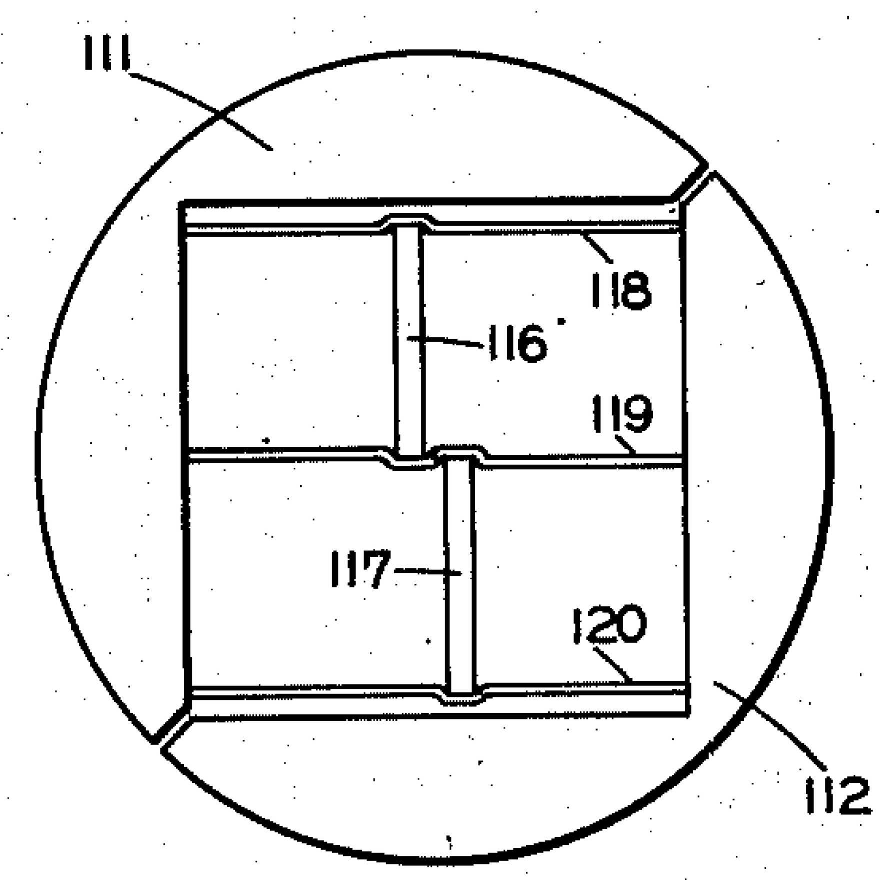

FIG. 6

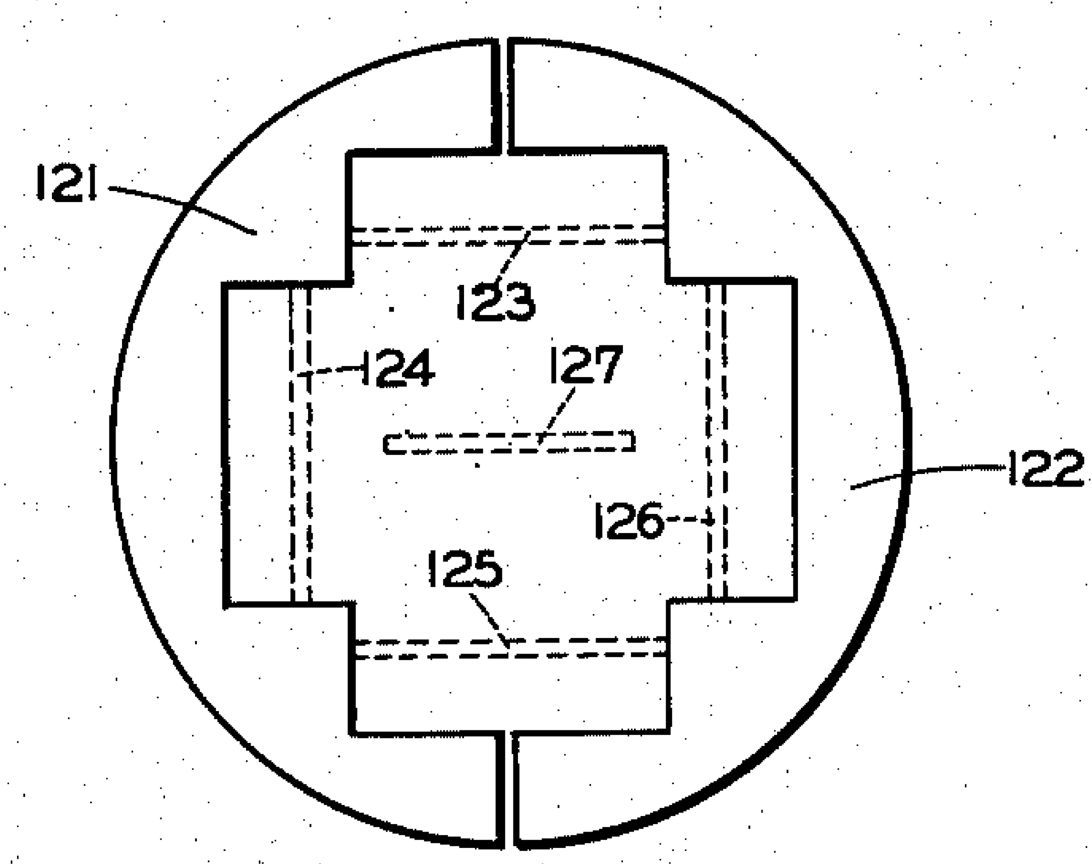

FIG. 7

INVENTOR.
ANDREW R. SOBEK
DANFORTH R. HALE

BY Harris A. Munn Jr.

ATTORNEY

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UNITED STATES PATENT OFFICE

2,675,303

METHOD AND APPARATUS FOR GROWING SINGLE CRYSTALS OF QUARTZ

Andrew R. Sobek, Cleveland, and Danforth R. Hale, Geauga Lake, Ohio, assignors, by mesne assignments, to Clevite Corporation, Cleveland, Ohio, a corporation of Ohio

Application April 11, 1950, Serial No. 155,221

19 Claims. (Cl. 23—301)

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This invention relates to improved apparatus for growing single crystals of quartz.

The synthesis of single crystals of quartz has been the subject of laboratory investigation for about 50 years. During the past 15 years there has been an enormous increase in demand for quartz crystals having substantial volumes of the flawless crystalline substance for electrical uses, for example, in the frequency-determining circuits of radio frequency oscillators and in filter circuits. This great demand, coupled with the remoteness and unreliability of the sources of natural quartz and the poor average quality of the natural mineral, has increased the importance of finding a commercially practical method of synthesis.

Nevertheless, it was only recently that processes for growing single crystals of quartz in commercially significant quantities have been devised. Such a process for growing a single crystal of quartz is described and claimed in application Ser. No. 94,682 for Letters Patent of the United States, filed May 21, 1949, in the names of Danforth R. Hale and Andrew R. Sobek and assigned to the same assignee as the present invention. In accordance with this process quartz is grown by exposing a quartz crystal seed under elevated temperature and pressure conditions to an aqueous medium including substantial quantities of an alkali metal carbonate material such as sodium carbonate or sodium bicarbonate. This material may be sodium carbonate having an initial molar concentration at room temperature of approximately one to two. This aqueous medium is maintained in contact with a supply material of crystalline quartz under still higher temperature conditions for effecting transfer of silica from the supply material to the quartz seed.

In another application, Ser. No. 94,683, for Letters Patent of the United States, filed in the names of Danforth R. Hale and Andrew R. Sobek on May 21, 1949, and assigned to the same assignee as the present invention, there is disclosed and claimed the process for growing a single crystal of quartz which comprises placing within a pressure vessel a quartz seed and a supply material of crystalline quartz, filling with an alkaline aqueous medium at least one third and preferably at least about one half of the remaining free volume in the vessel as measured at room temperature, and sealing the vessel and heating the contents thereof to a minimum temperature between 375° to 575° C. The application of heat is continued for a protracted period of time so as to maintain the contents of the vessel near the supply material appreciably hotter than the contents near the seed, the vessel and its contents being arranged to effect circulation of the aqueous medium by convection, whereby the supply material is dissolved in the medium with growth of the quartz seed.

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Apparatus for use in attempting a synthesis of quartz usually has taken the form of a bomb or autoclave. As illustrated in the drawings of the aforementioned copending applications, Ser. Nos. 94,682 and 94,683, of which the present application is a continuation-in-part, the autoclave is a thick-walled metal cylinder capable of withstanding elevated temperatures and internal pressures and disposed with its axis vertical. Giorgio Spezia, working in Italy some 40 years ago, used a bomb of the same general type with the supply material disposed in a basket near the top of the internal chamber and with a quartz seed affixed in the chamber beneath the supply material. The upper portion of the bomb was arranged to be heated. A warm silicate solution surrounding the supply material dissolved silica, which apparently diffused slowly downward until it reached the seed. The lower temperature in the neighborhood of the seed caused the aqueous medium to become supersaturated with respect to silica, which then deposited in an orderly manner on the quartz seed. This arrangement resulted in a slow increase in weight of the crystal. The seed crystal had to be placed in a region where the temperature of the solution was just enough lower than the temperature in the upper portion of the chamber to provide the desired growing conditions.

In the apparatus illustrated in the aforementioned copending applications, the silica supply material is placed near the bottom of the cylindrical chamber, while the seed is suspended near the top of the chamber. When the lower portion of the autoclave is heated, convection currents are established tending to transport silica dissolved from the supply material upward to the neighborhood of the seed for deposition thereon and tending to return the cooler solution to the lower part of the chamber for dissolving additional silica. While apparatus of this type has been used to grow quartz in commercially significant quantities within reasonable periods of time, considerable care must be exercised to adjust the temperature conditions within the autoclave, not only for the purpose of obtaining a desirable amount of supersaturation with respect to silica of the aqueous medium in the neighborhood of the quartz seed, but also to achieve a substantial thermal circulation of the fluid in the autoclave without causing excessive turbulence or destroying the temperature differential between the upper and lower portions of the chamber. It also will appear that the distribution of convection currents within the vertical chamber, when maintained hotter near the bottom, will be somewhat fortuitous and may depend largely on the precise location of the solid objects in the chamber and on rather small differences of temperature in the walls of the chamber. As a consequence the tendency for a quartz seed to grow may depend to an appreciable extent upon its exact position and orientation within the chamber, and only a rather small portion of the entire chamber may provide suitable locations for the quartz seed or seeds.

Accordingly it is an object of the present invention to provide new and improved apparatus for growing single crystals of quartz which substantially avoids one or more of the limitations and disadvantages of prior apparatus of the type described.

It is another object of the invention to provide new and improved apparatus for growing single crystals of quartz which permits easy adjustment of the conditions suitable for the synthesis of quartz.

It is a further object of the invention to provide new and improved apparatus for growing quartz crystals which provides extensive regions for receiving siliceous supply material and in which quartz seeds may be disposed.

It is also an object of the invention to provide new and improved apparatus for growing single crystals of quartz in large quantities and with commercially attractive control techniques.

In accordance with one feature of the invention, apparatus for growing single crystals of quartz comprises a pressure vessel including a silica-dissolving region for receiving a supply material of crystalline quartz and including a quartz-growing region arranged to hold at least one quartz crystal seed so that there may be disposed in the vessel a fluid for dissolving therein silica from the supply material and for depositing therefrom quartz on the seed. This apparatus also comprises constricted channel means in the pressure vessel communicating between the silica-dissolving region and the quartz-growing region. The apparatus further comprises means for maintaining the fluid under elevated temperature and pressure conditions in the quartz-growing region and under still higher temperature conditions in the silica-dissolving region and for effecting transfer of the fluid from each of these regions to the other thereof through the channel means.

In accordance with another feature of the invention, the above-mentioned pressure vessel includes a silica-dissolving region in the form of a chamber for receiving a siliceous supply material such as the aforementioned crystalline quartz and includes a quartz-growing region in the form of a chamber arranged to hold the seed; in this case the constricted channel means communicating between the silica-dissolving chamber and the quartz-growing chamber is a plurality of pipes forming part of the pressure vessel. In accordance with a further aspect of the invention, the means which functions to effect transfer of the fluid from each of the regions or chambers to the other thereof comprises a mechanical means which also functions for effecting dispersal within the quartz-growing region or chamber of the fluid so transferred thereto.

For a better understanding of the present invention, together with other and further objects thereof, reference is had to the following description taken in connection with the accompanying drawings, and its scope will be pointed out in the appended claims.

In the drawings,

Fig. 1 is a perspective view, partially cut away in several places, of an apparatus for growing a single crystal of quartz embodying the present invention, the apparatus being shown disposed in a roughly horizontal plane;

Fig. 2 is a central section taken horizontally through the upper right-hand portion of the apparatus as viewed in Fig. 1;

Fig. 3 is a sectional elevation taken in the direction indicated **3, 3** in Fig. 2;

Fig. 4 is a simplified plan view of another apparatus for growing a single crystal of quartz embodying the present invention, the view being sectionalized at the left hand side along a central horizontal plane to illustrate the internal arrangement of the several chambers and cross pipes in the apparatus;

Fig. 5 is a perspective view of one end portion of an internal liner used in the apparatus shown in Fig. 1;

Fig. 6 is an end elevation of the liner of Fig. 5 showing an alternative arrangement of the interior of the apparatus; and

Fig. 7 is an end view, taken similarly to the view of Fig. 6, of an alternative inner liner arrangement.

Referring now to Fig. 1, there is shown in perspective a complete apparatus for growing single crystals of quartz. The quartz-growing equipment is mounted on a table **11** which is centrally pivoted as at **12** for rocking about one of the axes of the table. The pivoting arrangement is supported on stationary brackets **13** and **14**. A slow speed motor **16** is arranged to rock the table **11** by means of a rocker arm **17** and an eccentric arm **18** having an adjustable radius. With this arrangement the table **11** may be rocked about a horizontal position to extreme positions such as **21** and **22**, shown in dashed lines, which may have an angular relationship with the horizontal position of from several degrees to as much as 45° or more, depending on the effective length of the eccentric arm **18**.

The quartz-growing apparatus proper may be secured to the table **11** by any suitable means such as one or more brackets **23**. It comprises a pressure vessel including an elongated silica-dissolving chamber **24** for receiving a siliceous supply material **26** and including an elongated quartz-growing chamber **27** arranged to hold at least one quartz crystal seed **28** and preferably a plurality of such seeds **28, 29, 31**, etc.

Each of the chambers **24** and **27** is provided with a removable end closure. The closure for the chamber **24** includes a central plug **33** having an internal shoulder **34** bearing against a gasket **36**. The end of the chamber **24** is threaded and receives an externally threaded collar **37**, the inner end of which also bears against the gasket **36**. The protruding end of the plug **33** receives a washer **38**, which bears against the outer end of the collar **37**. The outer end of the plug **33** also is threaded to receive a nut **39** over the washer **38**. When the nut **39** is tightened, plug **33** is drawn up to compress the gasket **36**, thus effecting a pressure seal. The chamber **27** similarly is provided with a plug 41 having an internal shoulder 42, an inner gasket 43, a threaded collar 44, an outer washer 46, and a nut 47.

A thermocouple well 51 extends centrally through the plug 33 and is sealed thereto by a nut and gasket arrangement 52 shown schematically on the inside end of the plug. The thermocouple leads extend from the inner end of the well 51 through the well to external leads 53 for connection to a conventional external temperature-measuring circuit, not shown. The chamber 27 similarly is provided with a thermocouple well 56 having an internal seal 57 and external leads 58. The chamber 27 also has a pressure-sensitive device 59 of the aneroid type with a connecting tube 61 extending through and sealed to the plug 41 and connecting with a pressure gauge 62 mounted externally of the pressure vessel. Additional thermocouple wells 63 and 64 extend through and are sealed to the other ends of the chambers 24 and 27 respectively, the respective thermocouples being located within the respective chambers and being provided with leads 66 and 67 respectively for connection to external temperature - measuring circuits, not shown. Thus the thermocouple leads 53, 58, 66, and 67 permit the continuous measurement of temperatures at each end of each chamber, and the gauge 62 permits the continuous measurement of the internal pressure in the apparatus.

The two chambers 24 and 27 are interconnected in a manner described hereinbelow so as to form a single vessel adapted to withstand high pressures. This vessel includes a silica-dissolving region, specifically the major interior portions of the chamber 24, and a quartz-growing region, specifically the major internal portions of the chamber 27. Channel means, also a part of the pressure vessel, communicate between the silica-dissolving region and the quartz-growing region. More specifically, the channel means may take the form of a plurality of pipes, for example two pipes 71 and 72, forming part of the pressure vessel. One of these pipes 72 may be seen in greater detail in Figs. 2 and 3 at the region where it joins the chamber 27. The chamber has a counterbored and tapered hole to receive the end of the pipe. This end of the pipe 72 seats against the counterbored portion of the hole in the chamber, and the taper is used to obtain a welded fillet 73, making the junction tight at high pressures.

The pressure vessel including the chambers 24 and 27 thus is arranged so that a solvent fluid may be disposed in the pressure vessel for dissolving in that fluid silica from the supply material 26 and for depositing from that fluid quartz on the seed 28 and on the other seeds as well. This silica-transporting fluid medium which is placed in the vessel may or may not include under operating conditions a liquid phase which fills the interior spaces in the pressure vessel, and for simplicity of illustration no attempt has been made in the drawings to indicate the presence of the fluid.

Means are provided for maintaining the fluid under elevated temperature and pressure conditions in the quartz-growing chamber and under still higher temperature conditions in the silica-dissolving chamber. For convenience of illustration this means is not shown in the sectional views of Figs. 2 and 3. This means includes resistance wire, having terminals 74, 75 and wound around the chamber 24, and also includes a similar winding around the chamber 27 having terminals 76, 77. These windings, as shown, are made up of turns which are spaced nearer together near the ends of the chambers to compensate for the greater rate of heat loss encountered there due to heat transfer through the end surfaces. The chambers 24 and 27 are lagged with heat-insulating coverings 78 and 79 respectively, including respective end coverings 81 and 82 which are placed over the closures. To facilitate temperature control thermocouples 83 and 84 are placed in contact with the outer surfaces of the respective chambers. These thermocouples have respective leads 86 and 87 which pass through ceramic insulating beads 88 and 89 as they leave the regions of the hot chamber walls.

The temperature of the fluid in the pipes 71 and 72 also must be maintained high enough to prevent nucleation and quartz deposits in these pipes. For this purpose resistance wire having terminals 91 is coiled around the pipe 71. A thermocouple having leads 92 is placed at the surface of this pipe to aid in adjusting the heating current which is caused to flow past the terminals 91 from a source of electric power, not shown. Similarly the pipe 72 is wound with a coil of resistance wire having terminals 93 and also is provided with a thermocouple having leads 94. Both pipes are lagged similarly to the other outer surfaces of the pressure vessel. If the pipes 71 and 72 are long enough, adjustment of heating currents through the windings 91 and 93 can be made to control the temperature of the pipe walls in spite of conduction of heat between these walls and the walls of the two chambers. In any case the pipes 71 and 72 should have sufficiently great lengths and sufficiently small wall thicknesses to permit substantial temperature differences between the walls of the two chambers without rapid conduction of heat therebetween through the walls of the connecting pipes.

The supply material 26 placed in the chamber 24 preferably is of crystalline quartz. A microcrystalline form of quartz may be used, but fairly large lumps of scrap quartz are preferred. With such lumps a rather coarse screen 90 near the entrance to pipe 71 and a similar screen, not shown, across the entrance to pipe 72 serve to prevent the supply material from leaving the silica-dissolving region.

The seeds are held in the chamber 27 by an upper seed holder 95 and a lower seed holder 96. As seen in Fig. 3, showing the rearmost seeds, the holder 95 carries a seed 97 and the holder 96 carries a seed 98. The seeds in the holder 95 and portions of this holder are shown for clarity by dotted lines in Fig. 1, although they would not be visible in this view because they occupy portions of the chamber 27 which have been cut away to show the internal arrangement.

Quartz seed arrangements, including seed holders similar to the holders 95 and 96 and including the crystal seeds themselves, are described and claimed in an application Ser. No. 155,222 for Letters Patent of the United States, filed concurrently herewith in the name of Andrew R. Sobek and assigned to the same assignee as the present invention.

At the close of a quartz-growing operation a large fraction of the space in the seed holders 95 and 96 is occupied by the quartz crystals into which the quartz seeds grow. However, it is difficult to arrange the seed holders and seeds to utilize the peripheral spaces between the seed holders and the inner wall of the chamber 27. If these spaces are left open they will be filled by large quantities of fluid, which then cannot aid materially in the quartz-growing process. Accordingly these spaces preferably are filled with a material of high heat conductivity which may be formed easily into the desired shape. Suitable liners for this purpose may be made of graphite. Such a liner 99 is illustrated in Figs. 1–3 and, as shown, has a hole to connect the interior of the pipe 72 with the interior of the chamber 27. Liners of this and related types will be described in greater detail hereinbelow.

Apparatus of the type described in connection with Figs. 1–3 advantageously may be used, in accordance with one feature of the invention, in carrying out the process for growing single crystals of quartz which comprises disposing at least one quartz crystal seed in one region of a pressure vessel, such as the chamber 27 in the vessel shown in Fig. 1, and disposing a siliceous supply material in another region of the vessel, such as the chamber 24, communicating through constricted channels, as provided by the pipes 71 and 72, with the one region or chamber 27. The process further comprises placing an alkaline aqueous solvent fluid in the vessel, applying heat to maintain the fluid under elevated temperature and pressure conditions in the one region or chamber 27 and under still higher temperature conditions in the other region or chamber 24 and at pressures above the critical pressure of water, and moving the pressure vessel to effect transfer of the fluid from each of the regions to the other thereof through the constricted channels, whereby silica is dissolved from the supply material by the fluid and quartz is deposited therefrom on the seed.

In accordance with another aspect of this process of the invention, a solvent fluid, such as the above-mentioned alkaline aqueous fluid, is placed in the vessel and heat is applied to maintain the fluid under elevated temperature conditions in the one region of the vessel holding the seed and under still higher temperature conditions in the other region in which the siliceous supply material is disposed. The vessel then is moved not only to effect transfer of the fluid between the two regions but also to effect dispersal within the first-mentioned one region of the fluid so transferred thereto.

In utilizing the apparatus of Figs. 1–3 in accordance with these procedures of the present invention, the supply material 26 is placed in the chamber 24 and the screen 90 slid into place, the liner 99 is slid into the chamber 27, and the holders 95 and 96 holding the quartz seeds are slid into the liners. An alkaline liquid, for example a one to two molar aqueous sodium carbonate solution or other solution having a composition formulated as discussed in the aforementioned application Serial No. 94,682, is poured into the vessel until the liquid occupies some 60% to 70% of the free space available in the vessel at room temperature. Then the plug, gasket, and collar assemblies 33, 36, 37 and 41, 43, 44 are slid and turned into their respective chambers 24 and 27. The washers 38 and 46 are slipped over the exposed ends of the collars and the nuts 39 and 47 tightened until the closures are well sealed. The heat-insulating caps 81 and 82 are put in place, and the motor 16 is started so as to provide, for example, a total angular excursion between the extreme positions 21 and 22 of the table 11 of 20° to 40° with a rocking period about 1/3 minute. In order to apply heat to the solvent fluid in the vessel and maintain the desired elevated temperatures of the fluid with the resulting elevated pressures, electric power is supplied from sources not shown to the four resistance windings. The current to the terminals 74, 75 is adjusted to be larger than the current to the terminals 76, 77 to provide higher temperature conditions in the silica-dissolving chamber 24 than in the chamber 27. Suitable degrees of filling of the liquid solvent medium, suitable compositions of the liquid, and suitable temperature and pressure conditions are discussed in the aforementioned copending applications Ser. Nos. 94,682 and 94,683.

As further examples, the liquid may fill 65% of the free space in the vessel at room temperature and the heating windings may be adjusted to provide readings of 387° C. from the thermocouple leads 53 and 66 in the silica-dissolving chamber and readings of 378° C. from the thermocouple leads 58 and 67 in the quartz-growing chamber. The pressure in the vessel then will be about 4900 p. s. i. A good yield of large, clear quartz crystals has been obtained under these conditions over a period of several weeks. Excellent results also may be obtained with a 70% charge at room temperature, for example, if the chamber 27 is maintained at a temperature within the range of about 350 to 370° C. while the temperature in the chamber 24 is maintained 6 or 8 degrees higher, giving a gauge pressure of about 6000 p. s. i.

The effect of the rocking depends to some extent on the physical condition of the fluid in the chamber under the growing conditions. Assuming the fluid to have the properties of pure water, only a single phase can be present in the vessel when the temperature is everywhere higher than the critical temperature of 374° C. Satisfactory operation often can be obtained, however, under lower temperature conditions, although the higher temperatures frequently are preferable. Moreover, if the pressure is maintained above the critical pressure by filling the vessel with enough liquid and then heating to a sufficiently high temperature, only one phase can be present in the vessel. The critical pressure of pure water is 3206 p. s. i. absolute, or 3191 p. s. i. gauge. These pressure or temperature conditions, or both, easily may be exceeded as the vessel is heated, the liquid placed in the vessel in sufficient quantity at room temperature having then expanded to fill the entire vessel with a fluid having no phase boundaries or liquid-vapor interfaces. It is noted that the critical temperature and the critical pressure may be somewhat different, and probably several percent or even more higher, for the system actually present in the pressure vessel, which has physical properties differing somewhat from those of pure water. However, if the fluid in the vessel is maintained at pressures above the critical pressure of pure water and under elevated temperature conditions, it is very unlikely that a vapor bubble of appreciable size will be present in the vessel in equilibrium with liquid solvent medium. In any event, it has been established that pressures above the critical pressure of water are conducive to rapid growth of quartz of high quality.

If one of the cross pipes 71 or 72 is maintained elevated always higher than the other cross pipe, and higher temperature conditions are maintained in the chamber 24 than in the chamber 27 a convection flow of the fluid in the vessel is established with warmer fluid moving from chamber 24 to chamber 27 through the higher cross pipe and with cooler fluid moving from chamber 27 to chamber 24 through the lower cross pipe. In such a case the provisions for heating the two chambers constitute means not only for maintaining the fluid under the specified elevated temperature and pressure conditions but also for effecting transfer of the fluid from each of the chambers to the other thereof through the interconnecting channels or pipes. Operation of the apparatus in this manner, however, has the disadvantage that substantial temperature gradients tend to appear lengthwise of the two chambers, and the continuous flow of the fluid in one direction carries so much heat that it becomes difficult to maintain a predetermined temperature difference between the two chambers.

The rocking motion of the table 11, described hereinabove, about an axis parallel to the cross pipes 61 and 62, so that one of the cross pipes is alternately higher and lower than the other, causes convection currents first in one direction and then in the other direction through each of the cross pipes. When the cross pipe 71 is higher during the rocking cycle, a small amount of the warmer, saturated fluid from the silica-dissolving chamber passes through this pipe into the chamber 27 and distributes itself around a rather limited region near the left end of the chamber 27, as seen in Fig. 1. Later in the rocking cycle, when the pipe 71 is lower than the pipe 72, the direction of flow tends to reverse. However, at the same time the warmer fluid which has just entered the chamber 27 tends to rise in this chamber toward the other end, which is now the higher end. Thus the second half of the rocking cycle tends to move the warmer fluid, which entered the chamber 27 during the first half of the cycle, away from the pipe 71, causing dispersal of the warmer fluid throughout the chamber 27 and mixing of the contents of the chamber. Likewise, cooler fluid from the chamber 27, which enters the chamber 24 through pipe 71 when the pipe 71 is lower, tends to flow along the chamber 24 and to be mixed with the warmer fluid in that chamber later in the rocking cycle when the pipe 71 is higher. If the rocking of the table 11 is limited to reasonable angular excursions, the dispersal or mixing action just described is sufficient to maintain substantially uniform temperatures throughout the lengths of the individual chambers 24 and 27 without causing more fluid to pass through the pipes 71 and 72 than can be assimilated by the convection mixing within each chamber. Nevertheless, the extent of the rocking should be sufficient to cause an appreciable transfer of fluid by convection currents between the two chambers in spite of the obstructing action of the solid contents of the two chambers and of the constricted openings in the connecting pipes. At the least, the temperature differences encountered at various points along either one of the chambers should be kept substantially smaller than the difference between the mean temperatures of the two chambers. Accordingly the rocking arrangement constitutes mechanical means, operating by moving and more specially by rocking the pressure vessels, for effecting transfer of the fluid from each of the chambers to the other thereof alternately in opopsite directions through the interconnecting channels or pipes and also for effecting dispersal within the quartz-growing region or chamber of the fluid so transferred thereto.

In accordance with another feature of the invention the composition and quantity of the fluid in the vessel are such as to provide, under the elevated temperature and pressure conditions used, a vapor-liquid phase boundary in the vessel with a substantial volume of the vapor phase. When this is the case the rocking causes not only convection movements of the fluid but also causes vapor bubbles to move from the lower to the higher ends of the chamber or chambers. This flowing motion of vapor bubbles may aid the flow of fluid between the silica-dissolving and quartz-growing regions and promotes desirable mixing of the liquid present in each of these regions. The two-phase condition may be obtained, for example, with temperatures in the neighborhood of 300 to 350° C. and an initial charge occupying some 50% of the free volume at room temperature. A substantial volume of the vapor phase under quartz-growing conditions of only 5% to 10% of the internal volume causes good fluid transfer and mixing conditions in apparatus of the type illustrated.

As was pointed out hereinabove, convection currents are set up in any quart-growing apparatus, when some portions of the fluid medium in an upper part of the presure vessel are maintained substantially cooler than other portions of the medium in a lower part of the vessel, which tend to move in fixed patterns of flow. In other words, the maintenance of these differences in temperature in the fluid medium causes thermal convection flow of the medium in a generally fixed pattern at any predetermined position of the vessel. These patterns of convection flow may be quite unpredictable and may eliminate all but a small part of the pressure vessel as suitable regions for growing quartz or for dissolving silica. A means for moving the vessel to provide varying relative elevations between the warmer and the cooler portions of the fluid medium, such as the rocking arrangement shown in the Fig. 1 apparatus, has the effect of varying the patterns of convection flow of the medium in the vicinity of the seed or seeds, thus increasing the size of the regions useful for growing quartz and also improving growing conditions by causing flow over the growing surfaces. This effect may be obtained in numerous types and arrangements of apparatus for growing quartz crystals.

Thus it will be understood that, in accordance with another feature of the invention, the process for growing single crystals of quartz comprises supporting at least one quartz crystal seed in a pressure vessel, placing in the vessel a siliceous supply material, such as lumps of crystalline quartz, and a silica-transporting fluid medium, such as an aqueous sodium carbonate solution, and sealing the vessel and maintaining the fluid medium therein under elevated temperature and pressure conditions to permit solution of the supply material in the fluid medium and deposition from the medium of quartz on the seed, some portions of the fluid medium in the vessel being maintained substantially cooler than other portions thereof so that the difference in temperature causes thermal convection flow of the medium at predetermined positions of the vessel. This process additionally comprises moving the pressure vessel, for example by rocking the vessel about a roughly horizontal axis, to provide varying relative elevations between the aforementioned several portions of the medium therein to effect varying patterns of the convection flow in the vicinity of the seed.

Fig. 4 is a simplified plan view illustrating a modified quartz-growing apparatus of the same general type as the Fig. 1 apparatus. It is assumed that the apparatus is in a generally horizontal position, and the left-hand portion of Fig. 4 is sectionalized along a central horizontal plane to show the interior portions of the chambers and interconnecting pipes. The Fig. 4 apparatus may be very similar to that illustrated in Fig. 1. Consequently all details of the contents of the chambers, the heating and heat-insulating arrangements, the supporting and rocking mechanism, and the temperature- and pressure-measuring devices are omitted from Fig. 4.

The Fig. 4 apparatus comprises an elongated silica-dissolving chamber **101** and a similar elongated quartz-growing chamber **102**. The channel means communicating between these two chambers comprises at least four substantially laterally separated cross pipes **103**, **104**, **105**, and **106**. The cross pipe construction may be as illustrated in Figs. 2 and 3 for the apparatus shown in Fig. 1. As an example of practical dimensions for the Fig. 4 apparatus, the elongated chambers may have an over-all length as great as 10½ feet with an internal diameter of 6 inches and a wall thickness of stainless steel of about 1½ inches. The relative dimensions of the other parts may be estimated from Fig. 4, the cross pipes being separated laterally by some 3 feet from each other. Seeds having major surfaces with both width and length dimensions more than 2 inches may be used, although a greater number of smaller seeds might prove preferable.

Apparatus constructed very similarly to that illustrated in Fig. 1 may have dimensions of the same order of magnitude; successful apparatus of this description has been used with the two elongated chambers about 3 feet long and about 3 inches in internal diameter. Using 19 seeds, each about 1 x 1½ inches in width and length, more than 2 pounds of quartz of good quality has been grown in less than 40 days. The high quality of the quartz grown makes the product 10 to 20 times as valuable in terms of usuable volume of oscillator grade quartz than the average raw electrical quartz of commerce.

The Fig. 4 apparatus is preferably rocked about an axis parallel to the cross pipes **103—106**, the axis conveniently being located centrally with respect to the four cross pipes. Accordingly, just as with the Fig. 1 apparatus, at one extreme position in the rocking cycle the pipes **103** and **104** will carry convection currents in one direction and the pipes **105** and **106** will carry convection currents in the other direction. If desired, the pipes **104** and **105** may have somewhat larger internal diameters, or the pipes **103** and **106** may be somewhat restricted at their entrances in order to equalize the convection currents through the four pipes, since the hydraulic pressure heads due to the differences in density between warmer and cooler fluid tend to be greater for the two end pipes **103** and **106**.

As noted hereinabove, the temperature distribution within the elongated chambers is determined by heat conduction through the walls of the cross pipes, by the rate of fluid transfer therethrough, and by the dispersal and mixing of the fluid transferred within the individual chambers. It is preferable that this dispersal be extensive enough so that not only does the temperature in an individual elongated chamber show little variation from one end of the chamber to the other, but also the concentration of all the fluid within either one of the chambers is substantially the same except in small regions adjacent to the openings of the cross pipes. It is convenient to use an even number of cross pipes so that a symmetrical arrangement will not involve a centrally located cross pipe, which would remain at a constant relative elevation during the rocking cycle and thus would tend to carry fluid in only one direction, if at all. When at least four cross pipes are used, for example the four pipes shown in Fig. 4, any local temperature variations in the chambers due to conduction of heat through the walls of the cross pipes to or from the walls of the chambers is minimized, since the pipes connect to the chambers at more closely spaced and more numerous points. Likewise the fluid moving back and forth through the pipes is removed from and injected into the chambers so that the fluid so transferred is more evenly distributed along the lengths of the elongated chambers. When the chambers are of rather great length the use of at least four cross pipes therefore adds materially to ease of control and uniformity of operation.

Apparatus for growing single crystals of quartz comprises, as illustrated and described hereinabove, a vessel adapted to withstand elevated temperatures and internal pressures and having an internal chamber with rounded wall portions, such as the chamber **27** of the apparatus of Figs. 1–3 or the chamber **102** of the Fig. 4 apparatus. In accordance with another feature of the present invention liner means is provided in contact with at least some of the rounded wall portions of the internal chamber and having a central opening with substantially plane bounding surfaces and square corners to provide channels adapted for disposition therein of quartz seeds. The liner **99** shown in Figs. 1–3 constitutes such liner means. This apparatus further includes means in the aforementioned channels in contact with the liner means for supporting quartz crystal seeds in portions of the chamber not occupied by the liner means. The supporting means just mentioned may take the form of the seed supports or holders **95** and **96** shown in Figs. 1–3.

The liner **99** of the Fig. 1 arrangement is shown in perspective in Fig. 5. It appears in the drawing to be fashioned from two hemicylindrical bars **111** and **112** with a large triangular notch **113** in the section **111** and a similar large triangular notch **114** in the section **112**. The two sections are placed together so that the two triangular notches meet in alignment and outline a square central opening inside the liner. When the pressure vessel and the internal seed-holding chamber therewithin are elongated, as in the embodiments illustrated in the drawings, this liner arrangement will be seen to provide an essentially four-sided elongated working portion within the chamber. The liner assembly also may be seen in the end view of Fig. 6, showing the two sections **111** and **112** outlining a square central opening. Within the opening two sets of seeds, an upper set including a seed **116** and a lower set including a seed **117**, are supported by an upper support **118**, a central support **119**, and a lower support **120**. The supports **118**, **119**, and **120** constitute an alternative form of the seed supports **95** and **96** shown in Figs. 1 and 3. The supports **118**, **119**, and **120** are notched, as shown in Fig. 6, so that the upper edge of the upper seed **116** is held in the support **118**, the lower edge of the upper seed **116** and the upper edge of the lower seed **117** are held in laterally spaced notches in the support **119**, and the lower edge of the lower seed **117** is held in a notch in the lower support 120. The left and right edges of the supports are held in contact with the plane bounding surfaces of the central opening in the liner 99.

An alternative form of liner is shown in end view in Fig. 7. This liner has two sections 121 and 122 with hemicylindrical surfaces, and the sections 121 and 122 fit together to form a cylindrical liner for sliding into the quartz-growing chamber. The interior of this composite liner means has an opening, as seen in Fig. 7, with plane bounding surfaces and square corners to provide channels adapted for disposition therein of quartz seeds. Means similar to the seed holders mentioned and illustrated hereinabove, and of conventional mechanical construction, are provided in the channel within the liner means and in contact with the liner means to support quartz seeds such as seeds 123—126 shown in Fig. 7. An additional seed 127 may be disposed in the central part of the opening in the liner. It will be apparent to one skilled in the art who is familiar with the shapes in which quartz naturally grows that other seeds may be placed behind the seeds 123—127 seen in Fig. 7, and that such seeds may be staggered length-wise of the central opening in the liner for the most efficient use of the space available.

To facilitate heating by conduction through the walls of the chamber containing the liner, it is advisable to use a heat-conducting liner. A suitable material is graphite, and graphite liners of the types shown in Figs. 5–7 may be formed from circular or square rods of preformed graphite by simple and inexpensive machining operations. The use of graphite has the added advantage that the material is frangible. Occasionally difficulty is experienced in removing the seed holders from the chambers, although ordinarily the graphite liner means of the type illustrated serve very conveniently for insertion and removal of the seed holders. If necessary, however, the frangible graphite liner may be broken up and the crystals removed from the chamber without damage to the crystals or to the pressure vessel.

While there have been described what at present are considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention. It is aimed, therefore, in the appended claims to cover all such changes and modifications which fall within the true spirit and scope of the invention.

What is claimed is:

1. Apparatus for growing single crystals of quartz comprising: an elongated vessel adapted to withstand elevated temperatures and internal pressures and having an elongated internal chamber with rounded wall portions, heat-conducting liner means in contact with at least some of said rounded wall portions and having a central opening providing an essentially four-sided elongated working portion within said chamber, and means in contact with said heat-conducting liner means for supporting quartz crystal seeds in portions of said chamber not occupied by said liner means.

2. Apparatus for growing single crystals of quartz comprising: a vessel adapted to withstand elevated temperatures and internal pressures and having an internal chamber with rounded wall portions, a graphite liner in contact with at least some of said rounded wall portions and having

a central opening with substantially plane bounding surfaces, and means in contact with said liner for supporting quartz crystal seeds in portions of said chamber not occupied by said liner.

3. Apparatus for growing single crystals of quartz comprising: a vessel adapted to withstand elevated temperatures and internal pressures and having an internal chamber with rounded wall portions, liner means in contact with at least some of said rounded wall portions and having a central opening with plane bounding surfaces and square corners to provide channels adapted for disposition therein of quartz seeds, and means in said channels in contact with said liner means for supporting such quartz seeds in portions of said chamber not occupied by said liner means.

4. Apparatus for growing single crystals of quartz comprising: a vessel adapted to withstand elevated temperatures and internal pressures and having an internal chamber with rounded wall portions, liner means in contact with at least some of said rounded wall portions and having a substantially square central opening, and means in contact with said liner means for supporting quartz crystal seeds in portions of said chamber not occupied by said liner means.

5. The process for growing single crystals of quartz, comprising: disposing at least one quartz crystal seed in one region of a pressure vessel and a siliceous supply material in another region of said vessel communicating through constricted channels with said one region and placing a solvent fluid in said vessel; applying heat to maintain said fluid under elevated temperature and pressure conditions in said one region and under still higher temperature conditions in said other region; and moving said vessel to effect transfer of said fluid from each of said regions to the other thereof through said channels and to effect dispersal within said first-mentioned one region of the fluid so transferred thereto, whereby silica is dissolved from said supply material by said fluid and quartz is deposited therefrom on said seed.

6. The process for growing single crystals of quartz, comprising: disposing at least one quartz crystal seed in one region of a pressure vessel and a siliceous supply material in another region of said vessel communicating through constricted channels with said one region and placing a solvent fluid in said vessel; applying heat to maintain said fluid under elevated temperature and pressure conditions in said one region and under still higher temperature conditions in said other region; and moving said vessel to effect transfer of said fluid from each of said regions to the other thereof alternatively in opposite directions through said channels and to effect dispersal within said first-mentioned one region of the fluid so transferred thereto, whereby silica is dissolved from said supply material by said fluid and quartz is deposited therefrom on said seed.

7. The process for growing single crystals of quartz, comprising: disposing at least one quartz crystal seed in one region of a pressure vessel and a siliceous supply material in another region of said vessel communicating through constricted channels with said one region and placing an alkaline aqueous solvent fluid in said vessel; applying heat to maintain said fluid under elevated temperature and pressure conditions in said one region and under still higher temperature conditions in said other region and at pressures above the critical pressure of water; and moving said vessel to effect transfer of said fluid from each of

said regions to the other thereof through said channels, whereby silica is dissolved from said supply material by said fluid and quartz is deposited therefrom on said seed.

8. The process for growing single crystals of quartz, comprising: disposing at least one quartz crystal seed in one region of a pressure vessel and a siliceous supply material in another region of said vessel communicating through constricted channels with said one region and placing an aqueous solvent fluid in said vessel; applying heat to maintain said fluid under predetermined elevated temperature and pressure conditions in said one region and under still higher temperature conditions in said other region, the composition and quantity of said aqueous fluid being such as to provide under said temperature and pressure conditions a vapor-liquid phase boundary in said vessel with a substantial volume of the vapor phase; and moving said vessel to effect transfer of said fluid from each of said regions to the other thereof through said channels, whereby silica is dissolved from said supply material by said fluid and quartz is deposited therefrom on said seed.

9. The process for growing single crystals of quartz, comprising: disposing at least one quartz crystal seed in one region of a pressure vessel and a siliceous supply material in another region of said vessel communicating through constricted channels with said one region and placing a solvent fluid in said vessel; applying heat to maintain said fluid under elevated temperature and pressure conditions in said one region and under still higher temperature conditions in said other region; and rocking said vessel to effect transfer of said fluid by convection currents from each of said regions to the other thereof through said channels and to effect dispersal within said one region by convection movements of the fluid so transferred thereto, whereby silica is dissolved from said supply material by said fluid and quartz is deposited therefrom on said seed.

10. The process for growing single crystals of quartz, comprising: disposing at least one quartz crystal seed in one region of a pressure vessel and a siliceous supply material in another region of said vessel communicating through constricted channels with said one region and placing a solvent fluid in said vessel; applying heat to maintain said fluid under elevated temperature and pressure conditions in said one region and under still higher temperature conditions in said other region; and rocking said vessel so that one of said channels is alternately higher and lower than another of said channels to effect transfer of said fluid by convection currents from each of said regions to the other thereof through said channels and to effect dispersal within said one region by convection movements of the fluid so transferred thereto, whereby silica is dissolved from said supply material by said fluid and quartz is deposited therefrom on said seed.

11. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including a silica-dissolving chamber for receiving a siliceous supply material and including a quartz-growing chamber arranged to hold at least one quartz crystal seed so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seed; a plurality of pipes forming part of said pressure vessel and communicating between said silica-dissolving chamber and said quartz-growing chamber; means for maintaining said fluid under elevated temperature and pressure conditions in said quartz-growing chamber and under still higher temperature conditions in said silica-dissolving chamber; and mechanical means for effecting transfer of said fluid from each of said chambers to the other thereof through said pipes and for effecting dispersal within said quartz-growing chamber of the fluid so transferred thereto.

12. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including a silica-dissolving chamber for receiving a siliceous supply material and including a quartz-growing chamber arranged to hold at least one quartz crystal seed so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seed; two pipes forming part of said pressure vessel and communicating between said silica-dissolving chamber and said quartz-growing chamber; means for maintaining said fluid under elevated temperature and pressure conditions in said quartz-growing chamber and under still higher temperature conditions in said silica dissolving chamber; and mechanical means for effecting transfer of said fluid from each of said chambers to the other thereof through said pipes and for effecting dispersal within said quartz-growing chamber of the fluid so transferred thereto.

13. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including an elongated silica-dissolving chamber for receiving a siliceous supply material and including an elongated quartz-growing chamber arranged to hold at least one quartz crystal seed so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seed; two pipes forming part of said pressure vessel, communicating between said silica-dissolving chamber and said quartz-growing chamber, and joined to each one of said elongated chambers at points spaced substantially apart therealong; means for maintaining said fluid under elevated temperature and pressure conditions in said quartz-growing chamber and under still higher temperature conditions in said silica-dissolving chamber; and mechanical means for effecting transfer of said fluid from each of said chambers to the other thereof through said pipes and for effecting dispersal within said quartz-growing chamber of the fluid so transferred thereto.

14. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including a silica-dissolving region for receiving a supply material of crystalline quartz and including a quartz-growing region arranged to hold at least one quartz crystal seed so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seed; constricted channel means in said vessel communicating between said silica-dissolving region and said quartz-growing region; and means for maintaining said fluid under elevated temperature and pressure conditions in said quartz-growing region and under still higher temperature conditions in said silica-dissolving region and for effecting transfer of said fluid from each of said regions to the other therof through said channel means.

15. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including a silica-dissolving chamber for receiving a supply material of crystalline quartz and including a

quartz-growing chamber arranged to hold at least one quartz crystal seed so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seed; a plurality of pipes forming part of said pressure vessel and communicating between said silica-dissolving chamber and said quartz-growing chamber; and means for maintaining said fluid under elevated temperature and pressure conditions in said quartz-growing chamber and under still higher temperature conditions in said silica-dissolving chamber and for effecting transfer of said fluid from each of said chambers to the other thereof through said pipes.

16. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including an elongated silica-dissolving chamber for receiving a siliceous supply material and including an elongated quartz-growing chamber arranged to hold a plurality of quartz crystal seeds so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seeds; two generally parallel pipes forming part of said pressure vessel, communicating between said silica-dissolving chamber and said quartz-growing chamber, and joined to each one of said elongated chambers at points spaced substantially apart therealong, said pipes having sufficiently great lengths and sufficiently small wall thicknesses to permit substantial temperature differences between the walls of said two chambers without rapid conduction of heat therebetween; means for heating said two chambers and said pipes to maintain said fluid in said vessel under elevated temperature and pressure conditions and substantially warmer in said silica-dissolving chamber than in said quartz-growing chamber; and mechanical means for rocking said pressure vessel about an axis generally parallel to said pipes, with said two chambers and said pipes disposed in a roughly horizontal plane at the mean position of said vessel, to effect transfer of said fluid from each of said chambers to the other thereof by convection currents alternately in opposite directions through said pipes and to effect dispersal of fluid so transferred by convection currents in lengthwise directions within the respective elongated chamber to which such fluid is transferred to keep any temperature differences in the fluid in each one of said two elongated chambers small compared with the difference between the mean temperatures of the fluid in said two chambers.

17. Apparatus for growing single crystals of quartz, comprising: a pressure vessel including an elongated silica-dissolving chamber for receiving a siliceous supply material and including an elongated quartz-growing chamber arranged to hold at least one quartz crystal seed so that there may be disposed in said vessel a fluid for dissolving therein silica from said supply material and for depositing therefrom quartz on said seed; a plurality of pipes forming part of said pressure vessel and communicating between said silica-dissolving chamber and said quartz-growing chamber; means for maintaining said fluid under elevated temperature and pressure conditions in said quartz-growing chamber and under still higher temperature conditions in said silica-dissolving chamber; and mechanical means for rocking said vessel about an axis roughly parallel to the axes of said pipes to effect transfer of said fluid by convection currents from each of said chambers to the other thereof through said pipes and to effect dispersal within said quartz-growing chamber by convection movements of the fluid so transferred thereto.

18. The process for growing single crystals of quartz, comprising: supporting at least one quartz crystal seed in a pressure vessel; placing a siliceous supply material and a silica-transporting fluid medium in said vessel; sealing said vessel and maintaining said fluid medium therein under elevated temperature and pressure conditions to permit solution of said supply material in said fluid medium and deposition from said medium of quartz on said seed, some portions of said fluid medium in said vessel being maintained substantially cooler than other portions thereof so that the difference in temperature causes thermal convection flow of said medium at predetermined positions of said vessel; and moving said vessel to provide varying relative elevations between said several portions of said medium therein to effect varying patterns of said convection flow in the vicinity of said seed.

19. The process for growing single crystals of quartz, comprising: supporting at least one quartz crystal seed in a pressure vessel; placing a siliceous supply material and a silica-transporting fluid medium in said vessel; sealing said vessel and maintaining said fluid medium therein under elevated temperature and pressure conditions to permit solution of said supply material in said fluid medium and deposition from said medium of quartz on said seed, some portions of said fluid medium in said vessel being maintained substantially cooler than other portions thereof so that the difference in temperature causes thermal convection flow of said medium at predetermined positions of said vessel; and rocking said vessel about a roughly horizontal axis to provide varying relative elevations between said several portions of said medium therein to effect varying patterns of said convection flow in the vicinity of said seed.

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