

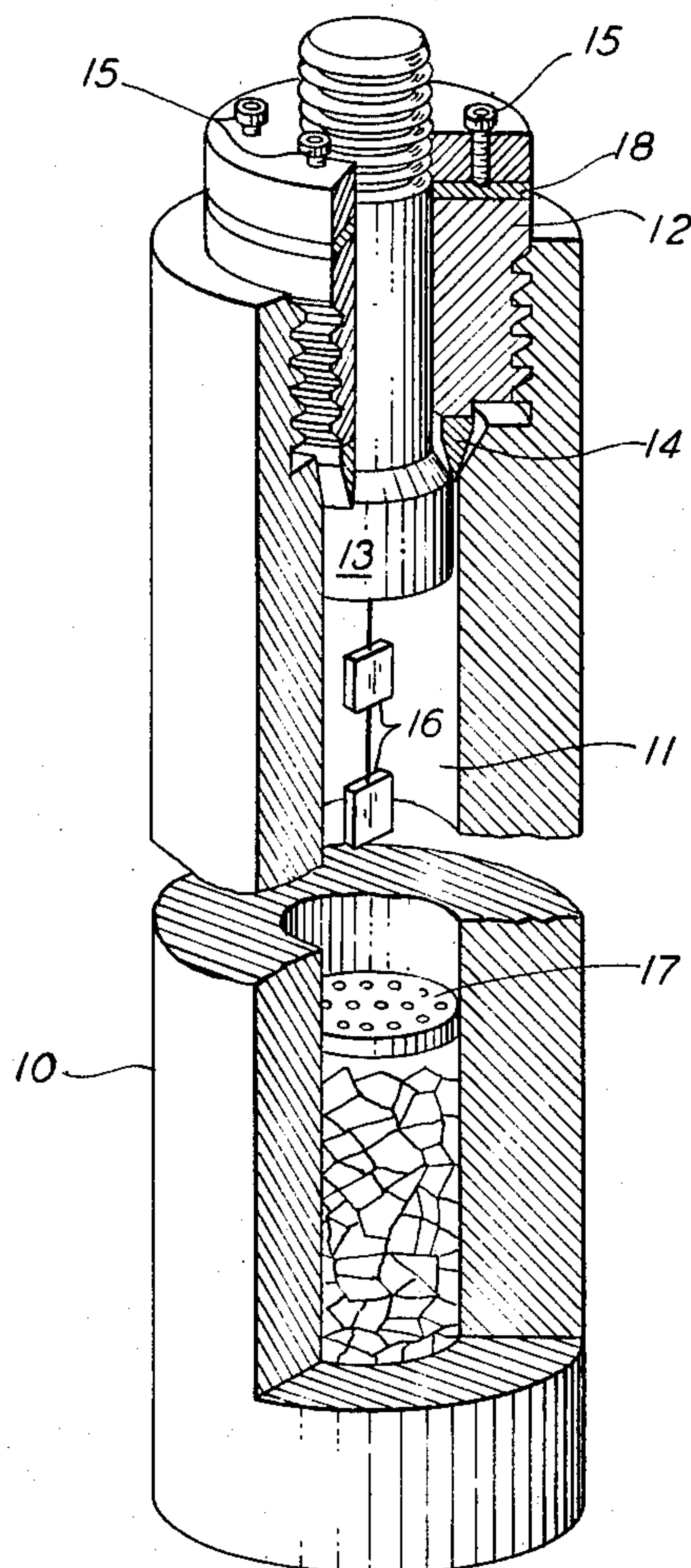
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SYNTHETIC QUARTZ GROWTH

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1

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SYNTHETIC QUARTZ GROWTH

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This invention relates to improved synthetic quartz crystals and to methods for their preparation. More particularly, it concerns a novel additive which has been found to significantly improve the resonator efficiency of synthetic quartz crystal bodies.

To satisfy the need for increasing quantities of quartz crystals for use in electrical devices such as piezoelectric resonators and transducers and to provide a dependable supply, various synthesis procedures have been extensively investigated and significant improvements in growth techniques have been developed. Thus, it has been possible over the past several years to synthesize quartz crystals which adequately perform the electrical functions which previously could be achieved only with natural quartz. One particular growth technique which has met with outstanding commercial success is described in United States Patent 2,785,058, granted to E. Buehler, Mar. 12, 1957.

Recent advances in synthetic growth procedures have made possible extremely fast growth rates which may be as high as one-half inch per day. Commercial considerations often require rates in excess of 0.015 inch/day and faster rates are economically desirable. However, it is characteristic of crystals grown at these high rates that crystal imperfections tend to interfere with the high acoustic efficiency characteristic of natural quartz and obtainable in slow-grown synthetic quartz. Thus, it becomes highly desirable to find a synthetic growth mechanism which permits fast growth and still provides crystals of high resonator quality.

It has been found that a significant improvement in the acoustic quality of synthetically grown quartz crystals can be realized by growing the quartz crystal in a hydrothermal solution containing lithium ions. While the mechanism is not fully understood this expedient produces crystals which characteristically exhibit twice the Q value of quartz grown in the conventional manner. This improved process for synthesizing quartz is described and claimed in application Ser. No. 160,719, filed Dec. 20, 1961.

It has been believed that the anion accompanying the desired lithium ion is inconsequential to the process. Hydrothermal solutions employing lithium carbonate are currently used in commercial production. However, all soluble lithium salts would be expected to be more or less equivalent in terms of their affect on the ultimate acoustical properties of the crystal.

It has now been found that the anion in solution can be extremely significant. Specifically, it has been discovered that the use of lithium nitrite, and to a lesser extent lithium nitrate, in the hydrothermal growth solution profoundly improves the acoustic performance of the final crystal product. The useful lithium nitrate and lithium nitrite concentrations are from 0.02 molar to 0.5 molar. The preferred range is 0.04 molar to 0.15 molar.

The basic hydrothermal solution may have a conventional composition, i.e., at least 0.2 molar and preferably 1.0 molar soluble sodium salt such as sodium hydroxide, sodium carbonate, sodium silicate or mixtures thereof.

These and other aspects of the invention will become

2

more apparent with the following detailed description. In the drawing:

The figure is a perspective view, partly in section, of an autoclave used for the growth of quartz crystals.

Various crystal samples were prepared according to the standard commercial growth technique except that in each case a lithium salt was added to the hydrothermal growth solution. The acoustic absorption of the individual samples was measured according to the infrared absorption technique described and claimed in application Ser. No. 433,676, filed Feb. 18, 1965. In this manner a survey was performed to evaluate the effect of the presence of various anions in the hydrothermal solution on the acoustic behavior of the crystals formed. The basic growth procedure used is that described and claimed in United States Patent 2,785,058, issued to E. Buehler, Mar. 12, 1957.

The growing of the crystals was carried out in a pressure bomb adapted for hydrothermal crystal growth. Various types of apparatus are appropriate for such procedures. One such apparatus is described in detail in the aforementioned patent. The particular autoclave used in these experiments was a modified Bridgman closure as shown in the figure. In the figure the main body of the autoclave 10 contains a chamber 11 having approximate dimensions of 6 inches x 132 inches. A main nut 12 is threaded into the upper portion of the chamber. A plunger 13 is fitted into the bore 11 and is free to rise under the influence of pressure within the chamber. As the plunger rises it contacts a steel seal ring 14 and is finally stopped by bearing against the main nut 12 through the seal ring. This action provides an effective seal for the growth chamber. The chamber is initially temporarily sealed by means of the set screws 15 which compress a resilient washer 48 against the shank of the plunger.

For the growth procedure the chamber 11 is charged with nutrient quartz crystals in an amount and size as hereinafter specified. An aqueous medium of a sodium salt and the aforementioned lithium salt is added in an amount sufficient to fill at least 60 percent of the chamber at room temperature (excluding the volume of the nutrient, seeds and supporting means). The seed crystals 16 are suspended as shown. For the growth of the samples described herein a baffle 17 was interposed between the nutrient mass and the seed crystals so as to divide the chamber into essentially two thermal zones. This baffle maintains a reliable temperature differential between the nutrient crystals and the crystallization zone. This particular baffle had 4 percent open area. The design and operation of this type of baffle is fully treated in United States Patent 2,895,812 issued to G. T. Kohman, July 21, 1959.

The quartz used as the nutrient should possess a particle size such as to present a sufficient surface area to the solvent thereby permitting the quartz to be dissolved to an extent adequate to sustain the desired rapid growth of the seed crystal. It has been found that with proper control of the other conditions, sustained rapid growth may be obtained with a nutrient consisting of quartz particles of such size that the average particle diameter is as large as about one-third the diameter of the growing chamber 11. The amount of nutrient is not important as long as it is at least the weight desired in the final crystals.

The seeds 16 may consist of any whole crystal, fragment or cut of natural or synthetic quartz. The seed should be free of twinning if it is desired to produce an untwinned crystal.

Growth on the seed crystal has been obtained by the process of the present invention when the aqueous medium used for transporting the silica from the nutrient to the seed has contained sodium ions. Suitable compounds for supplying the sodium ions have been found to be sodium hydroxide, sodium carbonate and sodium sili-

cate. Since sodium silicate is the reaction product of silica and sodium hydroxide, it is apparent that whether sodium hydroxide or sodium silicate is added initially, the solute will include sodium silicate during the operation of the process.

Sodium carbonate is a desirable compound for use since it permits the rapid growth of quartz with a small temperature differential between nutrient and seed. However, in a reaction chamber in which a higher temperature differential can be readily maintained, it may be more advantageous to use sodium hydroxide (or sodium silicate) since the system is more stable with this compound so that there is a lesser tendency toward spurious seeding.

Growth can be obtained with other sodium salts, particularly salts of weak acids. Salts of sodium with organic acids which are stable against substantial decomposition at the temperatures and concentrations used may also be employed.

For reasonably rapid growth, the concentration of sodium ions in the aqueous solution should be at least about 0.2 molar and preferably at least 1.0 molar. In general, as the concentration is increased, the rate of growth increases somewhat until concentrations of about 4 molar or 5 molar are reached. Further increase in concentration appears to produce only a slight increase in growing rate, but obviously higher concentrations may be used, if desired, provided quartz remains as the stable phase.

The growing of the quartz crystals by the process of the present invention is carried out with the aqueous solution at pressures above the pressure at which the liquid phase completely fills the autoclave.

The temperature in the growth part of the chamber should not fall below 300° C. and should preferably be at least 350° C.

The rate of growth of the crystal appears to increase as the average temperature in the chamber is increased but the temperature of the growing crystal should be maintained safely below 573° C., the inversion temperature for quartz, and safely within the mechanical limitations of the bomb in which the growing takes place. It is preferable that the temperature in the vicinity of the crystal, or more preferably in the hottest part of the chamber, not exceed about 550° C. More practical operating temperatures are below 500° C., and preferably below 450° C.

The density of the aqueous medium in which the quartz crystal is grown, and therefore the pressure existing in the bomb during the growing operation, exert a considerable influence upon the rate at which the quartz crystal is grown. The density, or inversely the specific volume, of the aqueous medium is controlled by the degree to which the free space in the growing chamber is filled with the aqueous solution prior to the sealing of the chamber. Filling about 33 percent of the free space in the chamber with liquid at room temperature will result in a specific volume, at the critical temperature of pure water, which is equal to the critical volume. Practical rates of growth can be achieved by the present process only by using considerably higher degrees of fill, with correspondingly lower specific volume.

To obtain a practical rate of growth, it is necessary to fill the free space of the chamber, excluding the space occupied by nutrient, seed and supporting means, to at least 60 percent with the liquid aqueous growing medium at room temperature. As the degree of fill is increased, the growing rate increases markedly. The upper limit to the degree of fill to be used is set only by the ability of the bomb to withstand the pressure which is generated. A fill of about 80 percent has been found very satisfactory but a fill of 90 percent will give faster results in a bomb designed to withstand the pressure.

With a liquid fill of about 60 percent of the free space at room temperature, the specific volume of the aqueous solution above the point where the vessel fills completely is about 1.67 times the specific volume of the liquid at

room temperature. With fills of 80 percent and 90 percent, the specific volumes above the point where the vessel fills completely are 1.25 and 1.11 times those at room temperature, respectively.

It is important to the rate of growth of the crystal that the proper temperature differential be maintained throughout the process, between the aqueous solvent leaving the mass of quartz nutrient and the aqueous solvent in the vicinity of the quartz seed crystal. With a very small temperature differential, the rate of growth is slow. As the differential increases, the rate of growth increases but, if it becomes excessive, a degree of spurious seeding occurs on the walls of the bomb. In avoiding the possibility of spurious seeding, it is necessary to avoid an excessive temperature differential not only between the nutrient mass and the seed crystal but also between the nutrient mass and any portion of the bomb. As indicated above, the temperature differential can be controlled with the apparatus shown in the drawing by varying the amount of insulation placed around the bombs in the furnace. Temperature differentials between the crystallization portion of the chamber and the nutrient mass of approximately 55° C. are typical in commercial operations. Differentials as low as about 15° C. and as high as 70° C. can be used satisfactorily.

The optimum temperature differential within the ranges set forth above may also be dependent upon other operating conditions, such as the particle size of the quartz nutrient. With the larger particle sizes, the best results are obtained with the greater temperature differentials. With smaller particle sizes, smaller temperature differentials give the best results.

The following description illustrates the specific manner in which the crystal samples were prepared.

The chamber 11 of the autoclave was charged with approximately 31,780 grams of nutrient quartz crystals of a size approximately one to two inches cubed. An aqueous medium of 1.0 molar NaOH containing the addition as indicated in Table I was added in an amount sufficient to fill 82 percent of the chamber at room temperature (excluding volume of nutrient, seeds and supporting means). The seed crystals were in the form of basal plates approximately 0.05 inch in thickness. The temperature of the crystallization portion of the chamber was 345° C. while the temperature of the nutrient seeds was 400° C. The autoclave pressure under these conditions is approximately 22,000 p.s.i. The growth rate was approximately 70 mils/day, total growth on each side of the seed plane.

All of the samples were prepared in an essentially identical manner. The measurements of "Q" on each sample were made as previously indicated and the results are reported in the following table. The "Q" value is the reciprocal of the acoustic absorption at 5 mc., the standard figure of merit for acoustic materials.

TABLE I

Additive	Concentration (molar)	Q Value
None		100, 000-150, 000
LiOH	0.1	200, 000-300, 000
Li ₂ CO ₃	0.1	
LiBO ₂	0.1	
LiCl	0.1	
LiF	0.1	
Li ₂ SO ₄	0.1	
Li ₃ PO ₄	0.1	350, 000-500, 000
LiNO ₂	0.1	
LiNO ₃	0.04	
LiNO ₂	0.10	
	0.15	620, 000-760, 000

The ranges indicate that several crystals in each category were measured giving different values. The differing concentration of lithium nitrite suggest a wide range of concentration which give useful results and other experience indicates that these concentration effects are applicable to nitrate ions as well. Thus, a concentration

5

range of 0.02 to 0.15 molar nitrate or nitrite can be prescribed for the scope of this invention although no particular advantage is seen in extending the concentration appreciably beyond 0.1 molar.

The following specific embodiment illustrates the unusual crystal quality obtainable through the use of the invention. This run was made using a lower temperature differential between the seed and nutrient and a slightly smaller fill percentage both of which contribute to a slower growth rate and thus a higher quality product.

The hydrothermal solution was 0.1 M NaOH and 0.1 M LiNO₂ and the degree of fill was 79 percent. This produces a pressure of the order of 15,500 p.s.i. The temperature of the growth region was 355° C. and the nutrient zone temperature was 380° C. The seeds were z-cut as before. The growth rate was about 40 mils/day. The measured "Q" value for crystals produced according to this procedure ranged from 1,200,000 to over 2,000,000.

Various additions, modifications and extensions of this invention will become apparent to those skilled in the art. For instance, it is obvious that the nitrate or nitrite ion does not necessarily have to be added in association with lithium. Thus, sodium hydroxide, sodium nitrite and lithium carbonate can be dissolved in water to achieve an identical solution for the purposes of the invention. All variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. A method for synthesizing quartz crystals which comprises disposing a quartz crystal seed and a mass of nutrient SiO₂ in an aqueous medium comprising sodi-

6

um ions at least .2 molar has been inserted, lithium ions at least .02 molar and an anion selected from the group consisting of nitrate and nitrite, heating said medium to a temperature of at least 300° C. while under a pressure exceeding the pressure present when the vessel is filled to at least 60 percent of its volume with said aqueous medium at room temperature and then heated to 300° C. and maintaining a temperature difference between said seed and said nutrient mass of at least 15° C. until a substantial increase in the size of said seed is obtained.

2 The method of claim 1 wherein the aqueous medium comprises NaOH.

3. The method of claim 1 wherein the aqueous medium comprises Na₂CO₃.

4. The method of claim 1 wherein the anion is nitrate.

5. The method of claim 1 wherein the anion is nitrite.

6. The method of claim 1 wherein the aqueous medium is heated to a temperature in the range 350° C.-573° C.

7. The method of claim 1 wherein the temperature difference is in the range 15-70° C.

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