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SYNTHETIC QUARTZ GROWTH USING LITHIUM IONS IN THE NUTRIENT SOLUTION

Original Filed Dec. 20, 1961 2 Sheets-Sheet 1

FIG. 1

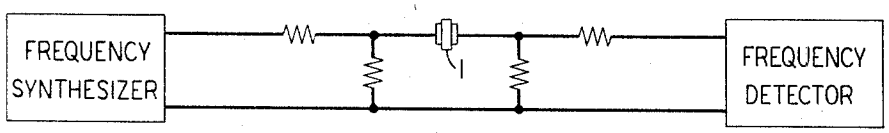


FIG. 2

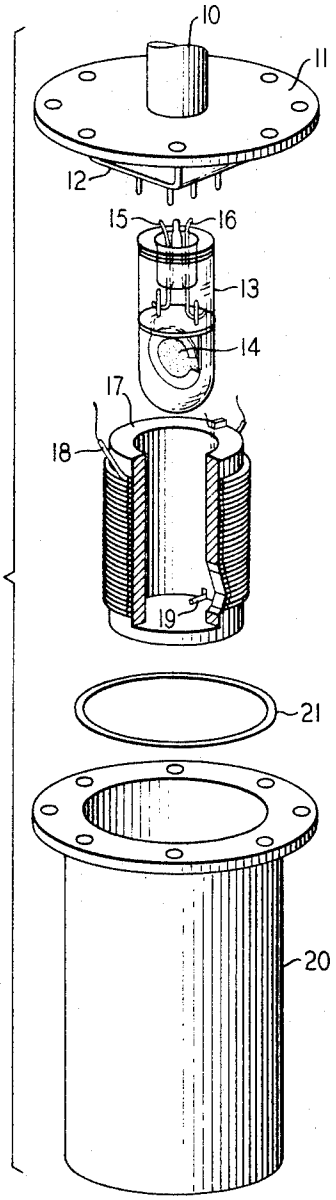
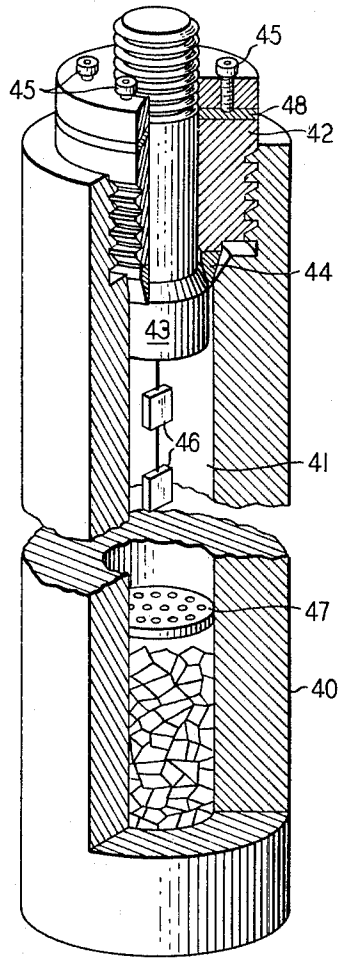


FIG. 4



INVENTORS A. A. BALLMAN
J. C. KING
R. A. LAUDISE

BY

ATTORNEY

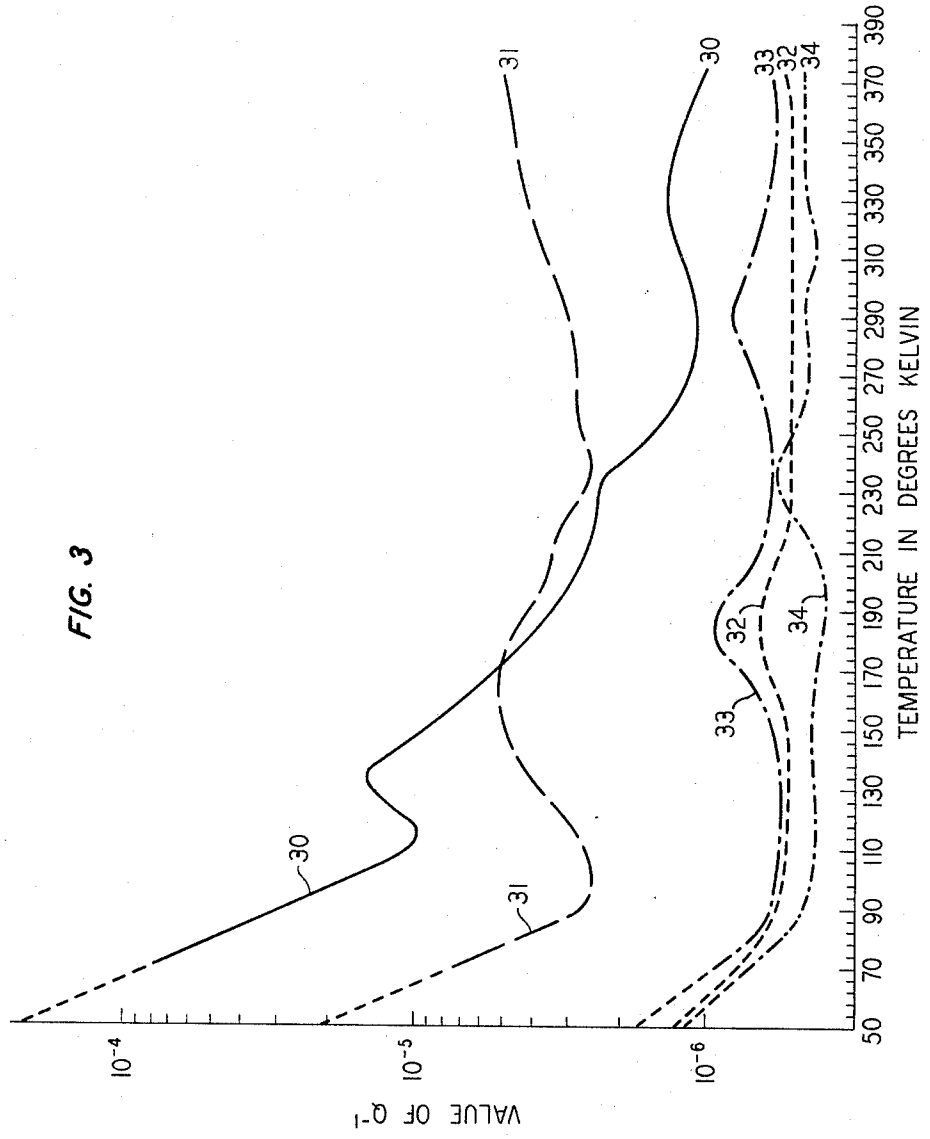

VALUE OF Q⁻¹
10⁻⁴
10⁻⁵
10⁻⁶
TEMPERATURE IN DEGREES KELVIN
50 70 90 110 130 150 170 190 210 230 250 270 290 310 330 350 370 390
30
31
32
33
34

FIG. 3

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SYNTHETIC QUARTZ GROWTH USING LITHIUM IONS IN THE NUTRIENT SOLUTION

Albert A. Ballman, Woodbridge, N.J., James C. King, Albuquerque, N. Mex., and Robert A. Laudise, Berkeley Heights, N.J., assignors to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

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3 Claims. (Cl. 252—62.9)

ABSTRACT OF THE DISCLOSURE

The specification describes hydrothermal methods for synthesizing quartz crystals having low acoustic absorption even when grown at high rates. The essential feature of the process is the incorporation of lithium ions into the sodium hydroxide- or sodium carbonate-containing hydrothermal solution.

This is a continuation of our copending application, Ser. No. 160,719, filed Dec. 20, 1961, now abandoned, and relates to improved synthetic quartz crystals and to methods for their preparation. More particularly, it concerns a novel additive which has been found to improve significantly 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 is now possible to synthesize quartz crystals which perform electrical functions with essentially the same efficiency and dependability as is obtained with natural quartz. One particular growth technique which has met with outstanding commercial success is described in U.S. Patent 2,785,058 granted Mar. 12, 1957.

These 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 generally obtained 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 now been found that synthetic quartz crystals can be significantly improved by the incorporation into the crystal of significant amounts of lithium. This lithium dopant acts to compensate for crystal imperfections introduced as the crystal is grown.

The specific amounts of lithium which have been found effective in achieving the improved electrical properties are of the order of 10–1000 parts per million and preferably 100–500 p.p.m.

The improved electrical characteristics and the following specific growth techniques will be appreciated through reference to the drawing in which:

FIG. 1 is a block diagram of a transmission circuit test set used to measure resonator characteristics of quartz crystal samples;

FIG. 2 is a perspective view of a holder (disassembled for clarity) for crystal samples used for making the electrical measurements described herein;

FIG. 3 is a plot of the acoustic absorption, Q^{-1}, versus temperature for five samples of quartz, two control curves obtained with synthetic quartz samples grown according to conventional prior art techniques, two curves for samples doped with lithium in accordance with this invention and a fifth curve showing the usual low acoustic loss of natural quartz; and

FIG. 4 is a perspective view partly in section of an apparatus suitable for growing the quartz crystals according to this invention.

The acoustic absorption, a measure of the rate of dissipation of vibrational energy, for certain quartz crystal samples was measured to illustrate the unexpected effects of incorporating lithium into the crystal. A block diagram of the essential components of the circuit used to measure the absorption is shown in FIG. 1. The resonant frequency of the crystal unit **1** at minimum impedance is the frequency of the variable oscillator (frequency synthesizer) adjusted to obtain a peak reading at the detector. For this condition, the equivalent resistance of the crystal unit is the value of a resistor which, when substituted for the crystal, gives the same detector reading.

The resistance of the crystal at resonance, which in these runs was the fifth overtone of a 1 mc. fundamental resonant crystal, is directly proportional to the acoustic absorption. The specific relationship is:

$$Q^{-1}=\frac{R_s}{L\omega}$$

where R_S is the electrical resistance of the crystal at series resonance, L is its equivalent inductance and ω is the angular frequency of vibration. For the measurements described herein the crystals were AT-cut, plano convex. The inductance was 9 henries and $\omega=2\pi f$ where the frequency, f, was 5 mc.

Since the Q for natural quartz thickness shear overtone vibrators is consistently as high as several million, therefore Q^{-1} for such resonators is taken to be a measure of the acoustic loss of the quartz itself, i.e., it is independent of the mounting structure.

The crystal and resistance network shown in FIG. 1 are located in the holder assembly of FIG. 2 which is suspended in a Dewar containing liquid nitrogen.

FIG. 2 shows a thin-wall tube **10** welded to the cover flange **11** for housing a series of electrical leads which protrude through the cover flange. The under surface of the cover supports a terminal bridge **12** for connection to the electrical components within the holder.

A sealed-glass envelope **13** contains the quartz crystal sample **14** with exposed leads **15** and **16** connected across the crystal. The glass envelope is filled with helium gas to a pressure of 1 mm. Hg at room temperature before it is sealed off. The heating unit consists of a copper liner **17** wound with constantan resistance heating wire **18**. The temperature of the crystal sample **14** within the liner **17** is indicated by a copper-constantan thermocouple **19**. The leads from the thermocouple are attached to the terminal bridge **12**. The heater unit is sealed within a stainless steel holder **20** with the aid of a gold-O-ring seal **21**. For each incremental increase in heater current, the oven will equilibrate at some higher temperature. The equivalent crystal resistance and frequency at resonance is recorded for increasing temperature.

The frequency of the crystal unit is used to indicate whether the quartz sample is at temperature equilibrium with its surroundings. This technique is quite sensitive, because of the large temperature coefficient of frequency above 15° K. for the type of crystals investigated.

The results of these measurements are shown by the five curves of FIG. 3. Each curve is a plot of the acoustic absorption, plotted as Q^{-1}, versus temperature. Curves **30**

and **31** were measurements taken from synthetic quartz crystals grown by conventional prior art techniques. Curve **30** was obtained with a sample grown from a z-minor seed and curve **31** was obtained with a sample grown on a Z-cut, i.e., basal cut seed. Curves **32** and **33** were obtained with synthetic quartz samples doped with lithium in accordance with an essential feature of this invention. Curve **32** represents data obtained from a quartz sample cut from a crystal grown from a z-minor cut seed. Curve **33** was obtained from a sample cut from a crystal grown from a Z-cut seed.

Curve **34** is a representation of the acoustic absorption of a natural Brazillian quartz crystal which is generally considered to be high quality piezoelectric material.

These curves illustrate at least two significant points. Various thoretical considerations (see J. C. King, The Anelasticity of Natural and Synthetic Quartz at Low Temperatures, Bell System Technical Journal, vol. 38, pp. 573–602) indicate that the frequency/temperature characteristics of quartz crystals near room temperature can be predicted from a study of their acoustic absorption at low temperatures. More specifically, it has been found that as the 50° K. crystal defect, which characteristically occurs to varying extents in synthetic quartz, is reduced, the frequency/temperature response of resonators operating above 50° K. more nearly approaches that of natural quartz. The advantage of obtaining synthetic quartz crystals which essentially match the frequency/temperature characteristics of natural quartz resonators is to permit the continued use of existing crystal cuts based upon known data. The burden of converting existing data based upon a low 50° K. absorption value, to specifications relying on various magnitudes of the 50° K. absorption and even the difficulty in making the absorption measurement itself, establishes the present invention as a significant contribution to the art. As is seen in FIG. 3, the curves have been extrapolated (dotted portion) to 50° K. to show the relative magnitudes of this defect in conventional synthetic quartz and in quartz doped with lithium. This extrapolation is based upon the slope of the approach to the defect which was obtained experimentally and which, according to previous experience with such curves, provides a valid estimate of the 50° K. peak. Note that the samples produced according to this invention (curves **32** and **33**) approximate the 50° K. absorption value of natural quartz and are significantly improved in this regard over the prior art material represented by curves **30** and **31**.

Another factor significant to this invention is the value of the acoustic absorption at room temperature, i.e., temperatures normally contemplated for device applications. Note that the absorption in the samples of this invention is substantially lower than that of the prior art material and is comparable with the acoustic absorption levels of natural quartz.

The measure of Q is the accepted figure of merit for piezoelectric materials. It is not only a representation of the acoustic efficiency of a material but is also directly proportional to the frequency stability with time.

The above factors indicate that synthetically growing quartz crystals so as to include lithium in accordance with this invention make feasible the construction of precision frequency resonators with quartz grown synthetically by existing fast growth techniques and equipment.

The synthetic quartz samples used for obtaining the electrical measurements of curves **30** and **31** were grown according to a hydrothermal growth technique described and claimed in U.S. Patent 2,785,058 issued Mar. 12, 1957.

The sample used in obtaining the measurements of curve **30** was grown in an 0.5 molar NaOH hydrothermal solvents at 80 percent fill, with a temperature differential of 20° C. and a crystallization temperature of 380° C. The growth rate for this crystal was 26 mils/day.

The sample used for the measurements illustrated in curve **31** was grown by the same general procedure except that the temperature differential between the nutrient and seed was 33° C., the crystallization temperature was 347° C. and the resulting growth rate was 39 mils/day.

The samples doped with lithium were grown by a variation of the technique disclosed in the aforementioned patent so as to obtain the desired quantity of lithium in the final quartz crystal. The general procedure followed in growing the samples is as follows.

The growing of the crystals was carried out in a pressure bomb adapted for hydrothermal crystal growth techniques. Various types of apparatus are appropriate for such procedures. One such apparatus is described in detail in the aforementioned patent. The particular bomb used in these experiments was a modified Bridgeman closure as shown in FIG. 4. In FIG. 4 the main body of the closure **40** contains a chamber **41** having approximate dimensions of 2 inches by eighteen inches. A main nut **42** is threaded into the upper portion of the chamber. A plunger **43** is fitted into the bore **41** and is free to rise under the influence of pressure within the chamber. As the plunger rises it contacts a steel seal ring **44** and is finally stopped by bearing against the main nut **42** through the seal ring. This action provides an effective seal for the growth chamber. The chamber is initially temporarily sealed by means of the sets screws **45** which compress a resilient washer **48** against the shank of the plunger.

For the growth procedure the chamber **41** is charged with nutrient quartz crystals in an amount and size as hereinafter specified. An aqueous medium of a sodium salt containing a 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 **46** are suspended as shown. For the growth of the samples described herein a baffle **47** 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 opening. The design and operation of this type of baffle is fully treated in U.S. Patent 2,895,812 issued 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 to permit the quartz to be dissolved sufficiently rapidly 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 **41**. The amount of nutrient should be at least the weight desired in the final crystals.

The seeds **46** 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 crystall 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 silicate. 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 solution 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 and since clearer, more perfect crystals are formed.

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. Mixtures of sodium hydroxide and sodium carbonate or of sodium silicate and sodium carbonate or of all three compounds may be used.

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 0.5 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.

To obtain the desired concentration of lithium ions in the grown crystal, i.e., 10–1000 p.p.m. and preferably 100–500 p.p.m. a soluble lithium salt is added to the solution. Specific salts found suitable are lithium hydroxide, lithium nitrate, lithium borate, lithium carbonate, lithium formate, lithium oxalate, lithium phosphate, lithium silicate, lithium sulfate, lithium fluoride, lithium iodide, lithium chloride and lithium bromide. Concentrations of these salts in the aqueous medium necessary to provide the above-prescribed lithium concentrations are .01–1 molar and preferably .02–.5 molar.

The growing of the quartz crystals by the process of the present invention is carried out with the aqueous solution at pressures preferably above the critical pressure of the aqueous solution. The critical pressure is approximately the same as the critical pressure of water.

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 somewhat 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, 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 volumes.

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 better 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 critical point 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 critical point 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 about 30°–40° C. have been found suitable. 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 differenials. With smaller particle sizes, smaller temperature differentials give the best results.

The following specific example will illustrate the manner in which the present invention may be practiced.

The chamber **41** is charged with approximately 500 grams of nutrient quartz crystals of a size such as to pass a No. 4 sieve but not a No. 6 sieve. An aqueous medium of 1.25 molar NaOH containing 0.14 molar LiF was added in an amount sufficient to fill 85 percent of the chamber at room temperature (excluding volume of nutrient, seeds and supporting means). The seed crystals, including both *z*-minor and basal-cutseeds, were in the form of plates approximately 0.05 inch in thickness. The temperature of the crystallization portion of the chamber was 371° C. while the temperature of the nutrient seeds was 403° C. The growth rate on the *z*-minor cut seed was 24 mils/day. The growth rate on the basal-cut seed was 44 mils/day. The amount of lithium found in the synthetic crystal was approximately 100 parts per million.

Various additional modifications of this process will become apparent to those skilled in the art. All such variations and deviations, which basically rely on the fundamental teachings through which this invention has advanced the art, are properly considered within the scope of this invention.

What is claimed is:

1. The method of synthetically growing quartz crystals which comprises the steps of suspending a quartz seed above a nutrient mass of crystalline, quartz particles within an essentially cylindrical pressure bomb, said quartz particles having a diameter not substantially exceeding one-third of the diameter of the pressure bomb, said bomb containing an amount of an aqueous solution consisting of sodium ions and lithium ions in concentrations of 0.5 molar to 4.0 molar and 0.02 molar to 0.5 molar respectively the said aqueous solution filling at least 60 percent of the free space of the bomb at room temperature, sealing the bomb, heating the aqueous solution to a temperature in the range of 300° C. to 550° C. while under a pressure exceeding its critical pressure and main-

taining a temperature difference between said seed and said nutrient mass of between 15° C. and 70° C., the said concentrations, pressure, solution temperature and temperature difference being adjusted such that the growth rate of the crystal exceeds 15 mils per day and the room temperature acoustic absorption of the crystal so produced is lower than the value obtained in the absence of the lithium ion in the aqueous solution.

2. The method of claim **1** wherein the said sodium ions are derived from sodium hydroxide.

3. The method of claim **1** wherein the said sodium ions are derived from sodium carbonate.

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TOBIAS E. LEVOW, *Primary Examiner.*

ROBERT D. EDMONDS, *Assistant Examiner.*