

Hydrothermal Synthesis of Quartz Crystals

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Research at the Bell Telephone Laboratories on the problem of growing large single crystals of quartz has now progressed to a point where it is possible to grow crystals weighing more than 1 lb. each in a period of 60 days or less. Equipment now in use includes autoclaves 4 inches in inside diameter and 4 ft. long, weighing about 1150 lb. each. In developing the hydrothermal process used to grow these quartz crystals it has been necessary to solve many problems in the little-known field of high pressure. The results point to the possibility of growing other types of crystals, and the field of usefulness of this process now appears to be much more extensive than was the case at the beginning of the investigation in 1946. Of prime importance is the fact that crystals grown from solution are likely to be better formed and of more perfect quality than those grown from the melt or by other methods. Many of the difficulties inherent in this work have been due to corrosion of steel in alkaline solution. This was a rather unexpected problem, since in high-pressure steam boilers alkali is added in small amounts to prevent corrosion of the boiler tubes. Such corrosion has been shown to be responsible for the appearance of electrical twinning on the growing faces of the quartz crystals. Other causes of such twinning have also been found in the course of this work.

I. Introduction

FOR many years the Bell System has been interested in the growing of piezoelectric crystals. A. M. Nicolson, in the Engineering Department of the Western Electric Company,* grew Rochelle salt crystals during World War I, and for some years thereafter, and adapted them to many electrical uses.¹ During World War II the Western Electric Company grew ammonium dihydrogen phosphate for use in submarine detecting devices.² This work was done in collaboration with the Brush Development Company, who had worked out a commercial process for producing am-

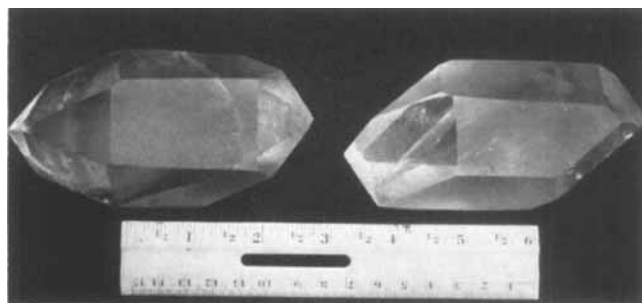


Fig. 1. Two quartz crystals grown in 42 days to weights of 540 gm.

monium dihydrogen phosphate crystals. At this time the Bell Telephone Laboratories developed a new type of rotary crystallizer.³ After World War II, ethylenediamine tartrate crystals were grown for use in telephone filter circuits as a substitute for quartz.⁴ In 1946 a project was initiated in these Laboratories for the purpose of growing quartz, based on information obtained from Germany. The experience gained in growing ammonium dihydrogen phosphate and ethylenediamine tartrate crystals was extremely helpful in the work on quartz.

Large single quartz crystals, free from twinning and suitable for piezoelectric purposes, have now been grown. Papers have been published on some aspects of this work.⁵ Recent progress has been such that quartz crystals weighing more than 1 lb. each have been grown in periods of less than 2 months (see Fig. 1).

II. Hydrothermal Process of Growing Quartz Crystals

Two methods using the hydrothermal process of growing quartz at high temperatures and pressures have been studied extensively at these Laboratories. They are (1) the constant-temperature method—amorphous silica nutrient and (2) the temperature-difference method—quartz nutrient.

III. The Constant-Temperature Method

This method, proposed by Nacken,⁶ and the Woosters,⁷ was used to grow quartz in dilute alkaline solutions at tempera-

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* Reorganized in 1925 as the Bell Telephone Laboratories, Incorporated.

¹(a) A. M. Nicolson, "Piezoelectric Effect in the Composite Rochelle Salt Crystal," *Trans. Am. Inst. Elec. Engrs.*, **38**, 1467 (1919).

(b) A. M. Nicolson, "Piezophony," U. S. Pat. 1,495,429, May 27, 1924.

(c) A. M. Nicolson, "Piezoelectrical Transmitter," U. S. Pat. 1,525,823, February 10, 1925.

(d) A. M. Nicolson, "Piezoelectric Device," U. S. Pat. 1,655,625, January 10, 1928.

(e) A. M. Nicolson, "Piezoelectric Oscillating and Stress Measuring Means," U. S. Pat. 2,137,852, November 22, 1938.

(f) A. M. Nicolson, "Generating and Transmitting Electric Currents," U. S. Pat. 2,212,845, August 27, 1940.

²A. C. Walker, "Piezoelectric Crystal Culture," *Bell Labs. Record*, **25** [10] 357-62 (1947).

³(a) A. N. Holden, "Growing Single Crystals from Solution," *Discussions Faraday Soc.*, **1949**, No. 5, 312-15; also "Rotary Gyrator Crystallizer for Growing Piezoelectric Ammonium Dihydrogen Phosphate Crystals," U. S. Pat. 2,484,829, October 18, 1949.

(b) C. J. Christensen and A. C. Walker, "Crystal Growing Apparatus," U. S. Pat. 2,459,869, January 25, 1949.

⁴A. C. Walker, "Growing Piezoelectric Crystals," *J. Franklin Inst.*, **250** [6] 481-524 (1950).

⁵(a) E. Buehler and A. C. Walker, "Growing Quartz Crystals," *Sci. Monthly*, **69**, 148-55 (1949).

(b) A. C. Walker and E. Buehler, "Growing Large Quartz Crystals," *Ind. Eng. Chem.*, **42** [7] 1369-75 (1950); *Ceram. Abstr.*, **1951**, August, p. 146d.

⁶R. Nacken, "Report on Research Contract for Synthesis of Oscillator Crystals," Captured German Report RDRDC/13/18, February 28, 1946; also Office of Technical Services Reports PB-6498, "Artificial Quartz Crystals, 1945"; PB-18,748; and PB-28,897, "Report of Investigations in European Theater, January 1946, with Special Reference to German Ersatz Quartz Program," Department of Commerce, Washington, D. C.

⁷Nora Wooster and W. A. Wooster, "Preparation of Synthetic Quartz," *Nature*, **157**, 297 (1946).

tures and pressures near the critical point of water. They used amorphous silica as nutrient because, according to Nacken, this form of silica is ten times as soluble as quartz, in water. This difference in solubility results in a very high degree of supersaturation of the solution with respect to quartz. Presumably the same order of difference in solubility of these two forms of silica holds in alkaline solutions as well as in water.*

Nacken tried solutions of the sodium salts of the following acids: carbonic, boric, phosphoric, acetic, halogenic, and the fatty acids, oleic and stearic. Best results were reported with sodium oleate, stearate, and bicarbonate, in that order. A maximum was observed in the growth-rate curve vs. solution concentration of the bicarbonate, at about 0.03 *N*. Nacken grew quartz more rapidly than it had ever been grown before in a laboratory, but the process worked well for only a few hours and stopped altogether after about 1 day.

(1) Inconsistencies in the Nacken Method

In the work in these Laboratories with amorphous nutrient, better results were obtained with carbonate or oleate solutions than with bicarbonate, whereas Nacken had concluded that bicarbonate was better than the carbonate. He also reported a maximum in the growth rate at 0.03 *N* carbonate concentration, but the present author could find no significant indications that this was the case. From experience in growing other crystals it seemed logical to expect that more rapid growth could be obtained the more concentrated the alkaline solution used, owing to the greater content of dissolved silica. Failure to obtain results consistent with those reported by Nacken, or to confirm experience with other crystals, may be partially explained by reference to Figs. 2 and 3.

Figure 2 shows the change in growth rate of a quartz seed during the first 24 hours of a run. Figure 3 is an estimate of the thickness of the porous quartz layer that forms rapidly with time on the surface of the clear fused silica nutrient (pieces cut from transparent rods about $\frac{5}{8}$ inch in diameter). These results are based on a series of tests, each 2 hours longer than the previous one, in a 0.03 *N* sodium oleate solution at 360°C., and 48% fill.†

The maximum rate of growth for any 2-hour interval was found to be of the order of 0.0035 in./hr.‡ It is difficult to fix points quantitatively on Fig. 2, or the thickness of the porous quartz layer on the nutrient as shown in Fig. 3, at definite time intervals, because of the time required to heat and cool the autoclave during runs of but a few hours. Some growth may take place even before the autoclave reaches the operating temperature, designated as zero on Fig. 2.

It is believed that the layer of porous quartz needles becomes effective in preventing more dissolved silica from getting into the growing solution, about the time the growth rate reaches the maximum. Thereafter, the solution as a whole loses its supersaturation with respect to quartz at a rate determined by the speed of growth on the seed crystal. Although growth soon stops on the seed plate, conversion of the amorphous material under the porous layer continues at a very rapid rate, as is evident from the amount transformed after 24 hours in Fig. 3.

Despite the limitations of the data on which are based Figs. 2 and 3, they show that the growth rate rises to a sharp

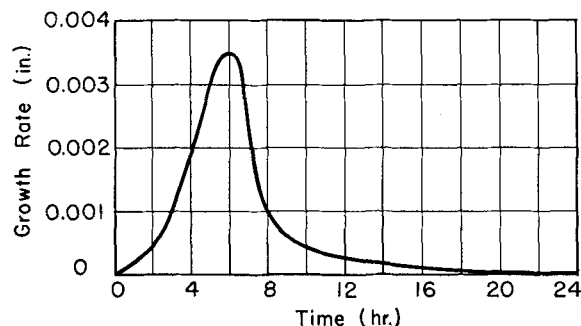


Fig. 2. Rate of growth of quartz from amorphous silica.

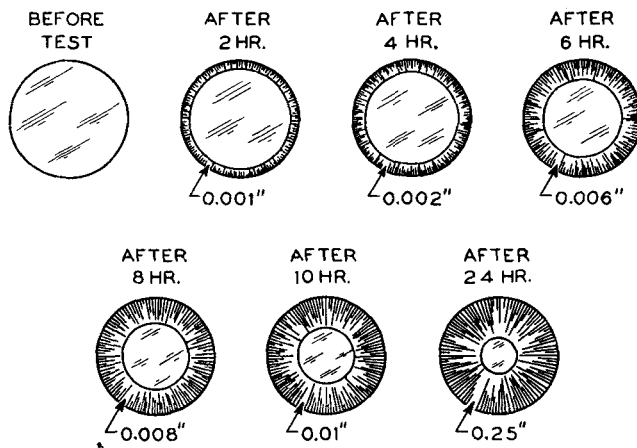


Fig. 3. Devitrification of amorphous silica.

maximum soon after the beginning of a run, and growth practically ceases long before the end of the first 24 hours, as the nutrient becomes covered with a layer of porous quartz. Some such conversion of fused silica to quartz may take place more slowly at lower temperatures in nature, to produce agate, a form of polycrystalline quartz.

It is doubtful if the effects of deliberately varied conditions, such as those involving kind, concentration, and pH of solution, or of mineralizers, to name but a few factors, can be evaluated in the presence of amorphous nutrient. The influence of such factors may be masked by changes in the growth rate caused by increasing amounts of silica diverted to spurious seeds, and the rate of conversion of the nutrient surface.

Neither Nacken nor the Woosters found a way to prevent the progressive decline in growth rate. Because the effective degree of supersaturation persists for but a few hours, the method has little to recommend it and was abandoned by this Laboratory in 1947 in favor of the temperature-difference method. Others who have used the temperature-difference method to obtain good results are Hale,⁸ of the Brush Development Company, and Thomas and his associates at the British General Electric Company.^{9,§}

* A. C. Swinnerton and associates at Antioch College have been working on this problem under a Signal Corps contract and are making contributions toward a better understanding of the solution and transport of silica under hydrothermal conditions.

† The percentage fill is the fraction of the free space in the growing chamber that contains solution, after deducting the space occupied by the nutrient material and seed.

‡ Growth is here measured as the total thickness of deposited quartz on the growing faces. In most of this work, seed plates were cut with the principal faces parallel to a minor rhombohedral face, found to be the one which grows most rapidly.

⁸ D. R. Hale, "Laboratory Growing of Quartz," *Science*, **107**, 393-94 (1948).

⁹ C. S. Brown, R. C. Kell, L. A. Thomas, Nora Wooster, and W. A. Wooster, "Growth of Large Quartz Crystals," *Nature*, **167**, 940-41 (June 9, 1951).

§ G. Spezia's use of this method has been referred to in a previous publication (footnote 5(a)). The reference is *Accad. Scienze di Torino*, **44**, 95-107 (1908).

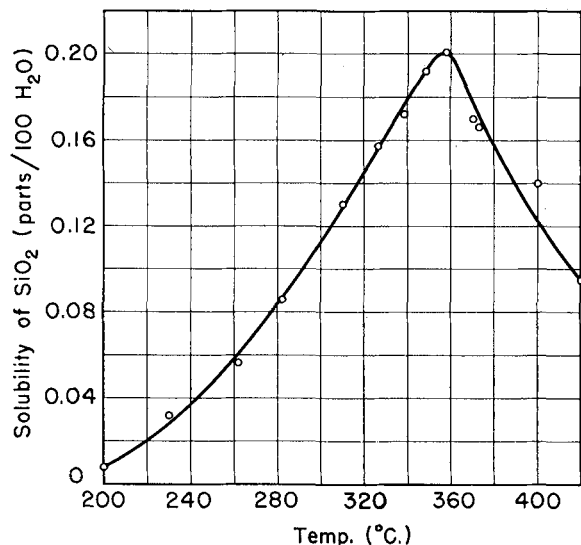


Fig. 4. Solubility of silica glass in water at 300 atmospheres.

IV. The Temperature-Difference Method

In searching for a way to grow quartz, some experiments were made in an autoclave longer than that described by Nacken in PB-28897.⁶ Using 0.03 *N* sodium oleate and amorphous silica nutrient, seed plates were suspended at different levels above the nutrient layer. It was found that all these seeds continued to grow at slow rates for 10 days. The seeds farthest from the nutrient layer in the bottom grew more than those closer to the nutrient.

Investigation showed that the long autoclave, standing vertically in the furnace, had a lower temperature at the top than at the bottom. This suggested that the method might work continuously if there was a substantial difference in temperature along the length of the tube. There appeared to be no advantage in using amorphous nutrient because it became covered with quartz so rapidly. Quartz also was preferable as nutrient because it minimized the formation of spurious seeds.

(1) Solubility of Silica

Recent investigators were unable to verify the large difference reported by Nacken in the solubilities of the two forms of silica.¹⁰ Morey and Hesselgesser^{10(a)} reported the ratio as about 7:1 at 135 atmospheres and 335°C. At higher pressures and temperatures they found the ratio to be of the order of 2:1. Kennedy^{10(b)} measured the solubilities of silica glass. At 300° and 360° his values were about twice those of Morey and Hesselgesser for quartz at the same temperatures.

It is difficult to establish this ratio accurately because of the rapid change in surface of the amorphous silica during test. Even a 2:1 difference in solubility provides a very high supersaturation with respect to quartz, and could explain the rapid growth for short intervals.

No information is available on the relative solubilities of amorphous silica and quartz in alkaline solution. The rapid conversion in dilute solution indicates that the difference in solubility is substantial here as well as in water. In more concentrated solutions the amounts of spurious seeds are

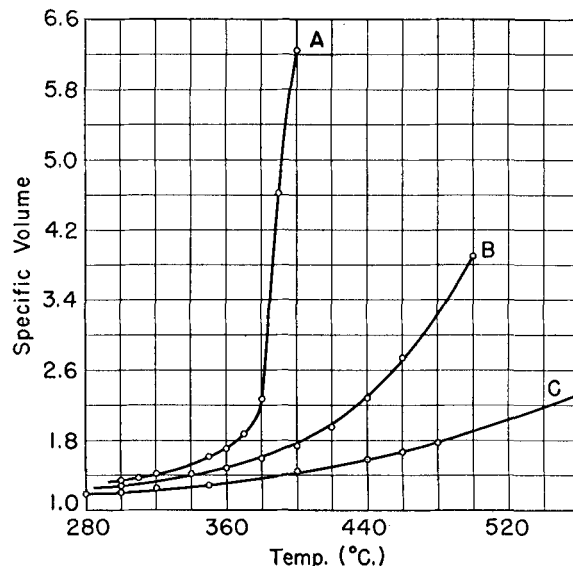


Fig. 5. Pressure-volume-temperature relations in water. Curve (A) 300 atmospheres; (B) 500 atmospheres; (C) 1000 atmospheres.

greater than in dilute solutions, and the amorphous material is converted to the crystalline form more readily.

Kennedy^{10(b)} found, in his study of the solubility of silica glass in water, that there is a maximum in the curve at 360°C., at a constant pressure of 300 atmospheres (see Fig. 4). This change from increasing to retrograde solubility above 360°C. he explained as being due to a sharp change in specific volume of water in this region of temperature and pressure (see Fig. 5). Thus the important factor, according to Kennedy, "determining solubility in the vapor or gas phase is the density of that phase, i.e., the closeness of packing of molecules; the closer this packing approaches that of a liquid, the more like a liquid solvent the gas behaves."

(2) Solubility of Quartz and Pressure-Volume-Temperature Relations

Two recent papers, one by Kennedy¹¹ and one by Nacken,¹² are important contributions to a better knowledge of the solubility of quartz in water and the pressure-volume-temperature relations. Figure 6, reproduced from Kennedy's data, with sufficient accuracy to show the general relations, contains two series of curves. One series consists of isobaric curves of the solubility of quartz in water vs. temperature. The other series of curves represents solubilities at constant specific volume, the reciprocal of density.

The curve for 300 atmospheres* has a maximum at about 360°C. and, except for the amount of silica dissolved, is of much the same form as that for amorphous silica in Fig. 4. A maximum is observed also in the 500-atmosphere curve, at about 380°C. These curves verify, in a more quantitative way, Kennedy's earlier conclusions. He stated that at 1000 atmospheres "the properties of a gas and a liquid are probably so nearly similar from the standpoint of their density and ability to act as a solvent that little is gained by advocating

¹¹ G. C. Kennedy, "Portion of the System Silica-Water," *Econ. Geol.*, **45** [7] 629-53 (1950); *Ceram. Abstr.*, 1951, April, p. 75c.

¹² R. Nacken, "Hydrothermal Mineralsynthese als Grundlage für Züchtung von Quarzkristallen," *Chem.-Ztg.*, **74** [50] 745-49 (1950).

* Kennedy reported pressures in bars in one paper (footnote 11) and in atmospheres in a previous paper (footnote 10(b)). To be consistent here, atmospheres will be used (1 bar = 0.987 atmosphere).

¹⁰ (a) G. W. Morey and J. M. Hesselgesser, "Solubility of Quartz and Some Other Substances in Superheated Steam at High Pressures," *Trans. Am. Soc. Mech. Engrs.*, **73** [7] 865-75 (1951); *Ceram. Abstr.*, 1952, Sept., p. 171d.

(b) G. C. Kennedy, "Hydrothermal Solubility of Silica," *Econ. Geol.*, **39** [1] 25-36 (1944); *Ceram. Abstr.*, **23** [7] 129 (1944).

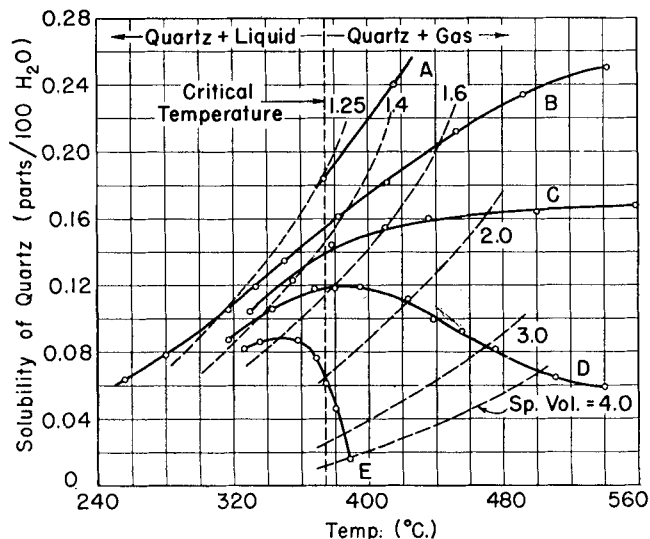


Fig. 6. Solubility of quartz in water. Curve (A) 1500 atmospheres; (B) 1000 atmospheres; (C) 750 atmospheres; (D) 500 atmospheres; (E) 300 atmospheres. Solid curves, isobaric curves of the solubility of quartz in water vs. temperature. Dashed curves, solubilities at constant specific volume, the reciprocal of density.

the existence of one phase in preference to the existence of another."

In addition, the curves for constant specific volume in Fig. 6 show that the solubility of silica increases with temperature so long as the density remains constant. Thus there is no reversal in solubility, such as is found in the low isobaric curves.

With quartz as nutrient, and using a temperature-difference method, two avenues of investigation were evident from these considerations. One was to take advantage of the change in density of the solvent in the vicinity of the critical point, at constant pressure, and grow quartz by a retrograde solubility method. The other avenue was to go to much higher pressures, and higher alkaline concentrations, to gain greatly increased solubility of silica. This second avenue takes advantage of the normal increase in solubility of silica with temperature, with the seed at a somewhat lower temperature than the dissolving nutrient.

(3) Retrograde Solubility

This method was tested in a two-chamber system. The nutrient was in one chamber at a lower temperature, the growing seed in a second chamber at a higher temperature. Figure 7 shows the results of one of these tests.

The seed plate, 1 cm. sq. by 0.06 in. thick, cut parallel to a minor rhombohedral face, grew slightly on these two faces along one edge, where the plate was in contact with the heated wall of the growing chamber. Heat conducted to the seed from the hot wall, and to the solution adjacent to the wall, lowered the solution density in this narrow zone near the wall and induced sufficient supersaturation to cause some growth. Despite efforts made to prevent spurious seeds, they always occurred at some point in the circulating system. Because of this, and also because growth was in such a narrow zone, the method was not considered promising.

(4) Growing Quartz Crystals at High Pressures

(A) *Operations at 80% Fill:* To test the other avenue of investigation, i.e., growing quartz at pressures much higher than those near the critical point, experiments were made at about 1000 atmospheres, where the isobaric curve shows a progressive increase in solubility of silica with temperature. Pressures of this order, estimated from the properties of water,

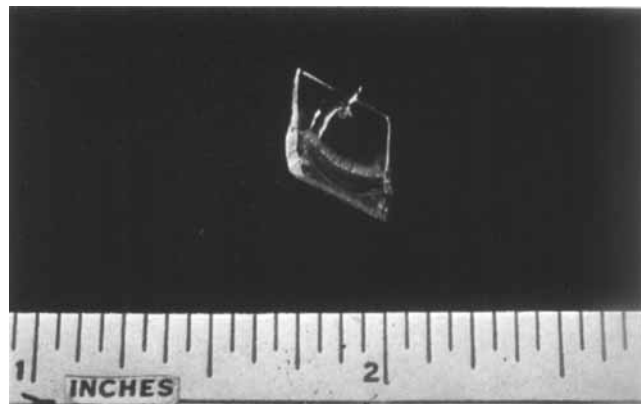


Fig. 7. Quartz plate with growth in zone of density change.

were obtained by filling the autoclave to 80% of its free space with solution and heating to 400°C.

The fastest rate of growth obtained under these conditions has been 0.1 in. per day, using 1 *N* sodium carbonate solution. At this growth rate there are always large numbers of spurious seeds. With temperatures up to 425°C., and solution concentrations up to 4 *N*, no further growth increase was obtained, only greater numbers of spurious seeds. Rates of growth of the order of 0.05 to 0.08 in. per day have been obtained with little or no spurious seeding in sodium carbonate solutions. Such rates of growth are of the same order of magnitude as those obtained with ammonium dihydrogen phosphate and ethylenediamine tartrate crystals at room temperature.

It may be that there is some reason, as yet unexplained, why quartz and other crystals may not grow more rapidly than this and still retain relative freedom from imperfections. Perhaps the mechanism of crystallization from solution is a limiting factor. The investigation has not been extended to higher temperatures and pressures to test the possibility of further increases in growth. To do so requires steel of greater strength and better creep properties than those readily available.

(B) *Autoclave Design:* Figure 8 shows the autoclave design now in use. Two important improvements have been made since this design was first published.^{5(b)} One is a baffle just above the top of the nutrient layer; the other is the welded closure of the liner.

The baffle maintains the nutrient at a higher average temperature relative to the growing zone than is possible without it. This gives a higher degree of supersaturation in the growing zone. The baffle contains a central hole having an area equal to a given small percentage of the cross-sectional area of the liner tube. An equal area of opening is distributed among eight semicircular holes located on the periphery of the plate. The clearance between the baffle and the wall of the tube is a minimum.

There are two sectional views of the welded closure. This closure is a round plate with a small shoulder on the edge of one face. When this plate is fitted into the open end of the tube, the shoulder rests on the lip of the tube. Welding consists of joining this shoulder and the lip of the tube, as may be seen in the first sectional view. The second section is a view after machining the outside of the welded tube to a taper to fit the recess in the retainer. When adequately supported, this assembly is capable of withstanding conditions well above those used in these experiments.

Autoclaves 1, 2, 3, and 4 inches in inside diameter have been used. The largest ones now in use are 4 inches in diameter and 48 inches long. The retainers are of Ketos steel, the threaded autoclave caps of a manganese steel, and the autoclave bodies of an alloy steel such as is used in gun barrels. Several runs have been made in units 4 inches in diameter, and thus far there have been no leaks in the welds.

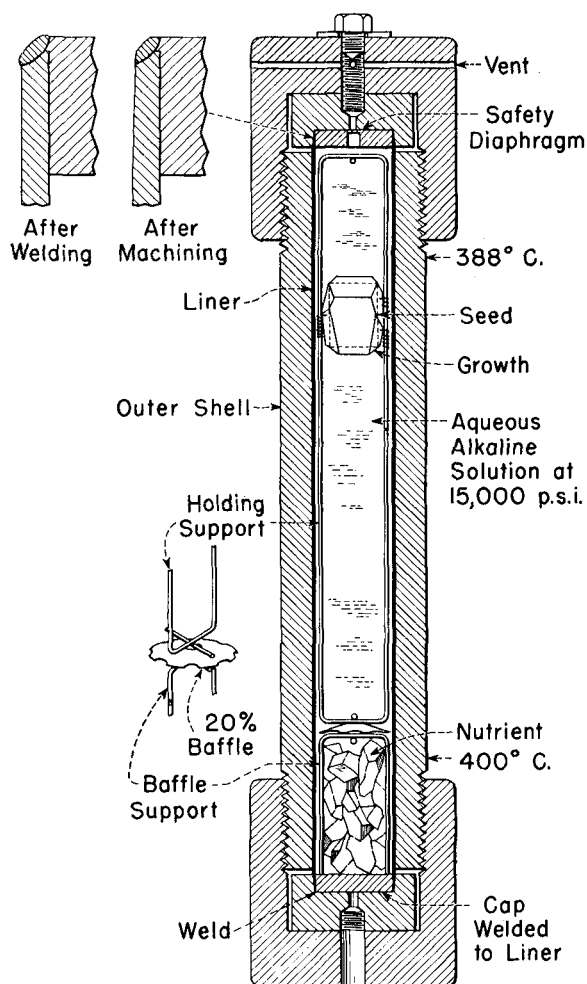


Fig. 8. Section through autoclave used to grow quartz.

Removal of the crystals after a run is performed as follows: The cool autoclave is subjected to a longitudinal pressure of between 50 and 150 tons, depending on the autoclave size, to crack loose the threads of the caps. These caps are then readily unscrewed by hand. After sawing off the welded ends of the liner protruding above the autoclave body, the frame containing the crystals may be easily lifted out. A slot is then sawed longitudinally in the wall of the open-ended liner with a horizontal power saw, and when thus loosened, the liner is easily removed. The autoclave is then ready for the next run.

(C) *Temperature Measurement:* Rate of growth of a crystal from a supersaturated solution is largely a function of the degree of supersaturation. To measure this, thermocouples are strapped to the outside of the autoclave at the two points where temperatures are shown in Fig. 8. To measure the true temperature at any point within the solution is extremely difficult. Some information has been obtained in two ways on which to estimate temperatures at different points.

The rate of cooling of a large autoclave in a well-insulated furnace gives some information on the temperature drop through the steel wall. In a 4-in.-diameter autoclave, with walls $2\frac{1}{2}$ in. thick, the drop was found to be less than 0.6°C . Thus the temperature registered by an outside thermocouple is within a degree of the inner wall at this point. The drop is no doubt less than this in 1-in.-diameter autoclaves, with $\frac{1}{2}$ -in. walls.

To obtain information on the solution temperatures, use was made of the melting points of CdI_2 and PbBr_2 . The actual samples of these salts which were used had melting points of 383° and 368°C ., respectively, although the litera-

ture values are 388° and 373°C . It did not seem necessary for this purpose to purify these salts to increase their melting points.

Small amounts of each salt were sealed in glass, and these in turn were placed inside welded steel capsules. The capsule containing PbBr_2 , the lower-melting salt, was placed just below the top cap of the filled autoclave, 1 inch in diameter and 8 inches long. The CdI_2 capsule was located just below the baffle, above the nutrient layer. At operation conditions, the top thermocouple registered 369°C ., one degree above the observed melting point of the bromide. On inspection, after opening the unit, the bromide was found to have been melted.

The bottom couple registered a temperature of 382°C ., one degree below the observed melting point of the CdI_2 . This salt was not melted in the test. In a second run, the top temperature was the same, and again the PbBr_2 was melted. In this case the iodide was in a capsule just above the baffle, and the temperature registered by the thermocouple at this point was between 384° and 385°C . (1° to 2° above the iodide melting point). The iodide showed signs of incipient melting. Another experiment should be made with the top temperature just below the melting point of the bromide, but the results thus far obtained indicate that the external thermocouple temperature is within a degree or so of the temperature at a corresponding point in the solution.

(D) *Degree of Supersaturation:* From the previous discussion it is evident that little is known of the true solution temperatures, upon which to determine the degree of supersaturation. Perhaps a reasonable estimate of supersaturation may be derived as follows: In an experiment with an autoclave 1 inch in diameter and 8 inches long, filled to 80% of its free volume with 1 *N* NaOH solution, the temperatures at the points designated in Fig. 8 were 400° and 388°C . It might be inferred that the saturation temperature was 400°C ., the growing temperature 388° , and the degree of supersaturation 12° . The inference is questionable as shown by the following observations:

There is a drop of 25° between the hot plate and upper layer of nutrient, because the hot-plate temperature is 425°C . The drop of 25° is through about 1 in. of steel, including cap, retainer, and welded liner closure, and through an additional 2-in. depth of nutrient. Tests made on an empty autoclave showed that the drop through 1 in. of steel is of the order of 5° . Thus the drop through the nutrient layer is of the order of 20° .

Some growth is always observed on the top pieces of nutrient. From this it may be concluded that not all the supersaturation set up by the higher temperature in the bottom layer of nutrient persists as the solution escapes through the baffle into the growing zone. Thus the saturation temperature is at some point between 420° and 400°C . As a first approximation it is assumed to be 410°C ., the mean of these two temperatures.

With a baffle such as that in Fig. 8, the difference in temperature between the point just above the baffle and the point level with the upper thermocouple is of the order of 6°C . From this information it is estimated that the degree of supersaturation is about 22° ($410^{\circ} - 388^{\circ}$) at the top seed to 16° ($410^{\circ} - 394^{\circ}$) opposite the bottom seed, just above the baffle. This is reasonably consistent with observations on growth, for the top seed usually grows about 25% more than one located just above the baffle.

(E) *Growth Rates in Short and Long Autoclaves:* In 1-in.-diameter autoclaves, repeated tests have shown that the longer the tube, the higher the growth rate. Of more importance is the fact that this appears to be true even for the same total temperature difference between the thermocouple points in Fig. 8. This information was of particular value when sodium hydroxide was used in place of sodium carbonate in the growing solution.

(F) *Sodium Carbonate vs. Sodium Hydroxide as Solvent:* Although the highest growth rates have been obtained with carbonate solution, growth is always accompanied by many

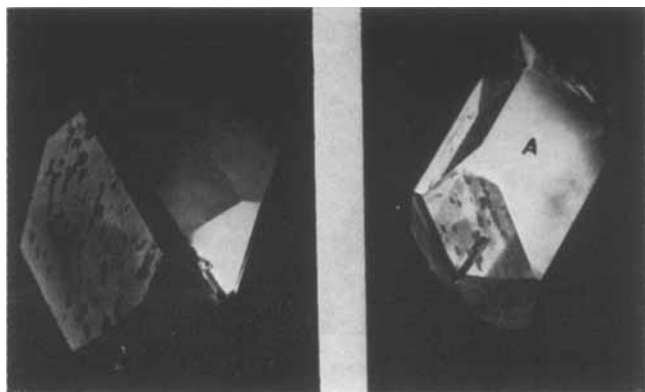


Fig. 9. (Left) twinned upper minor rhombohedral growing face of quartz crystal; (right) A, untwinned lower minor rhombohedral growing face of quartz crystal.

spurious seeds. Nacken reported that silica would not crystallize from a supersaturated solution in sodium hydroxide, even when the solution was cooled to room temperature from the hydrothermal conditions. Friedman,¹³ however, reported some growth of quartz, of the order of a few tenths of a gram, on cooling a hydroxide solution, saturated with silica at 325°C., to room temperature.

Early in this work with the temperature-difference method, small amounts of the hydroxide were added to carbonate solutions to minimize spurious seeds. It was found, however, that the higher the hydroxide concentration the lower the growth rate, with the same temperature difference, but there were fewer spurious seeds.

With sodium hydroxide alone, growth did occur, but at very low rates. The crystals that grew were extremely clear and brilliant, just as Friedman reported. They looked much like the Herkimer "diamonds," quartz crystals of exceptional clarity found near Herkimer, New York. No spurious seeds were observed, even with a temperature difference of 16°C.

These experiments were repeated in 1-in.-diameter tubes at a temperature difference of 50°C. To secure a difference of 50°C. it was necessary to use a longer autoclave. Growth rates of 0.05 to 0.06 in. per day were obtained in one 16 in. long. The crystals were of excellent clarity and form, and no spurious seeds were present even with this high temperature difference. In one run, an electrical storm caused a power failure and the temperature fell to 200°C. When this autoclave was opened several days later there were some spurious seeds, but not an excessive number.

Temperature control is not a critical factor with the hydroxide solution, as it is with the carbonate solution. Several minor temperature failures have occurred in hydroxide runs with no appearance of spurious seeds, nor effect on the growing crystals.

(G) *Corrosion of Steel:* It had been more or less taken for granted that alkali in the water would be effective in preventing attack of steel under these hydrothermal conditions. The cold-rolled steel tubing used as liners in 1-in.-diameter autoclaves tended to confirm this. At times, however, it was difficult to obtain reproducible results from run to run because of minor variations in the amount of attack of the liner by the alkali solution. In liners 2 and 3 inches in diameter the steel was of somewhat different quality and was less resistant to attack. The longer runs in these larger units also produced greater amounts of corrosion products than were usual in the small tubes.



Fig. 10. Evidence of twinning: (A) minor rhombohedral faces of quartz crystal; (B) major rhombohedral faces of quartz crystal.

In some runs the corrosion product was a sodium iron silicate known as aegirite. It crystallized as masses of small greenish crystals on the upper walls of the autoclave, as if the solution were supersaturated with this salt, as well as with quartz. In other runs the corrosion products were amorphous or colloidal aggregates of greenish color. The use of sodium oleate in small amounts appeared to minimize corrosion in 1-in. tubes, but increased it in the larger tubes.

(i) *Copper-Plated Liners:* To overcome corrosion, the steel liners were copper plated on the inside. Copper, however, dissolved in the alkaline solution in the bottom of the chamber, and recrystallized on the upper plated walls, and on the under side of the copper-plated closure. This would appear to be a form of syncrystallization much like that observed in the deposition of aegirite.

Sodium oleate had been used in some temperature-difference experiments because it appeared to improve the "join" of the added growth to the original seed, and to give clearer crystals in carbonate solution. When traces of it were added to this solution in copper-plated liners, the copper crystallized as microscopic clumps of crystals in the upper growing face of a 38° angle-mounted plate. This well-dispersed crystalline impurity imparted a pink tint to the quartz, making it look very much like rose quartz. It also induced the same kind of twinning as that resulting from iron corrosion products.

Figure 9 (left view) shows the upper face of such a crystal after grinding and etching with HF. This treatment brings out clearly the twinning pattern. This surface looked much like that in Fig. 10 before grinding. The right half of Fig. 9 shows the lower rhombohedral growing face, marked A. There is no evidence of twinning on this perfectly blank, etched face, although the twinning on the other face shows through the transparent major rhombohedral faces adjacent to this one. Whether twinning occurs on the top face or on both growing faces, under these conditions, appears to depend upon how much oleate is present initially. In the absence of sodium oleate, the copper crystallized only on the copper-plated walls of the tube, and not in the quartz crystal.

(ii) *Silver-Plated Liners:* Corrosion and twinning defects were overcome by the use of silver-plated liners and closures. This metal is quite inert in the alkaline solution under these

¹³ I. I. Friedman, "Laboratory Growth of Quartz," *Am. Mineral.*, **34** [7/8] 583-88 (1949); *Ceram. Abstr.*, 1950, April, p. 85h.

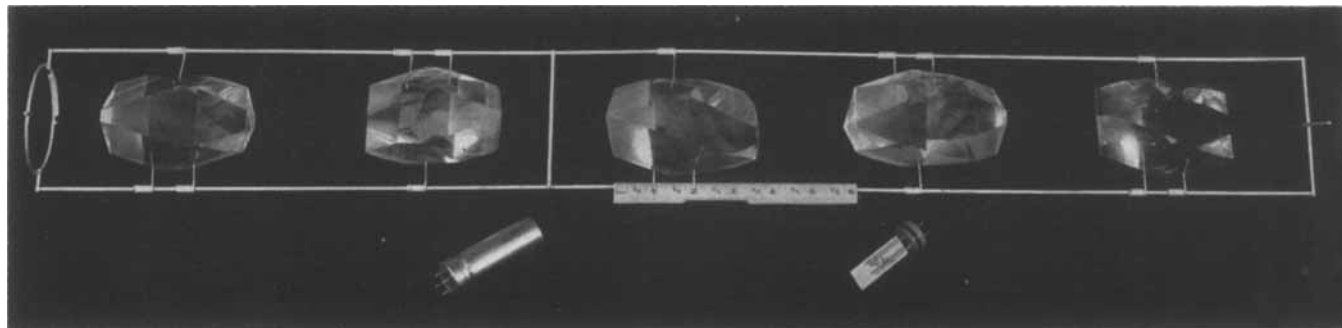


Fig. 11. Five quartz crystals grown at one time in 70 days. The three on the left weigh more than 1 lb. each.

hydrothermal conditions, and it is easily applied to the inside of the open-ended tubes before assembly. When this finish is used, it is possible to reproduce quartz in successive runs without the interference of corrosion.

(H) *Mounting of Seed Plates:* In 1-in. autoclaves the main object was to study effects of different factors on growth. The seeds were simply hooked to a suitable frame and hung vertically in the solution. The principal faces of the seeds were cut parallel to a minor rhombohedral face of the quartz crystal, because these faces grow most rapidly. The resulting maximum lengthwise extension of the crystal along its *c*-axis is, however, at a 38° angle to these cut faces. Crystals grown from hook-mounted plates therefore could eventually grow into the walls of the tube. The runs in 1-in. autoclaves were of short duration so this was no problem.

In the larger autoclaves the main purpose was to grow crystals as large as possible. The plates were rigidly mounted so that the cut faces were at a 38° angle to the vertical axis of the tube. Thus the resulting maximum lengthwise extension of the crystal was parallel to the long axis of the tube. Observations on the character of growth of crystals mounted in these two different ways led to one solution of the problem of twinning and emphasized the effectiveness of vertical circulation in the system.

(I) *Twinning and Its Effect on Growth Rate:* The action of the alkaline solution on the iron liner may give solid corrosion products that adhere readily to the growing faces of plates mounted at an angle of 38° to the vertical axis of the tube. Such adhesions interfere with the normal growing conditions, resulting in both optical and electrical twinning (see Fig. 10). Such twinning usually occurs on the top growing face of the angle-mounted seed plate only, but sometimes if corrosion is excessive, twinning occurs on the bottom growing face as well. It rarely occurs on hook-mounted seed plates, apparently because circulation of the solution over vertical growing faces is sufficient to prevent such adherence.

The rate of growth on the minor rhombohedral faces of the crystal in Fig. 10 was of the order of 0.015 in. per day. Normally a much higher growth rate is obtained. It thus appears that the twinning induced by corrosion products may influence growth rate. Examination of the surface in Fig. 10, after etching it with HF, showed that the recessed areas (B) were major rhombohedral faces and the raised areas (A) were

minor rhombohedral faces. This is known as electrical twinning. Optical twinning was also present in this growing surface, as shown by etch patterns. It is known from other experimental work that the growth rate on a minor rhombohedral face is several times that on a major rhombohedral face. The relatively poor rate on the extensively twinned surface in Fig. 10 suggests that large areas of a major rhombohedral face, when present in a minor rhombohedral growing face, reduce the over-all growth.

It is believed that some of the depositing silica molecules are prevented, by clumps of corrosion products, from growing in a normal fashion. Thus they may form nuclei whose exposed faces are the major rhombohedron rather than the minor rhombohedron. A section through such a crystal shows that these nuclei spread wedgelike up through the deposited quartz, eventually causing the irregular depressions.

(J) *Results with Large Autoclaves:* A number of long-term experiments have been made with two autoclaves, each 4 inches in inside diameter, 48 inches long, and weighing 1150 lb. It is possible to maintain a 50° temperature difference in these tubes, whereas the 2- and 3-in.-diameter autoclaves were too short to do this effectively. Figure 11 shows a group of crystals grown in 70 days from 1 *N* sodium hydroxide solution in one of these units. The growth rate was of the order of 0.04 in. per day, and no spurious seeds were present. Three of these crystals weighed more than 1 lb. each; the other two were slightly less than this. It should be possible to increase this growth rate by using greater temperature differences between the nutrient and the growing zone.

(K) *Hydrothermal Growth of Other Crystals:* Preliminary tests indicate that other substances may be crystallized effectively by this hydrothermal method, in much the same way that copper and aegirite are formed. For example, crystals of zinc oxide have been grown as large as $1/16$ in. in cross section. These crystals were slightly green in color owing to iron contamination. They were grown in an unplated steel liner.

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