May 12, 1953 I. I. FRIEDMAN ET AL 2,638,408

METHOD OF SYNTHESIZING LARGE SINGLE CRYSTALS OF QUARTZ

Filed July 6, 1948 3 Sheets-Sheet 1

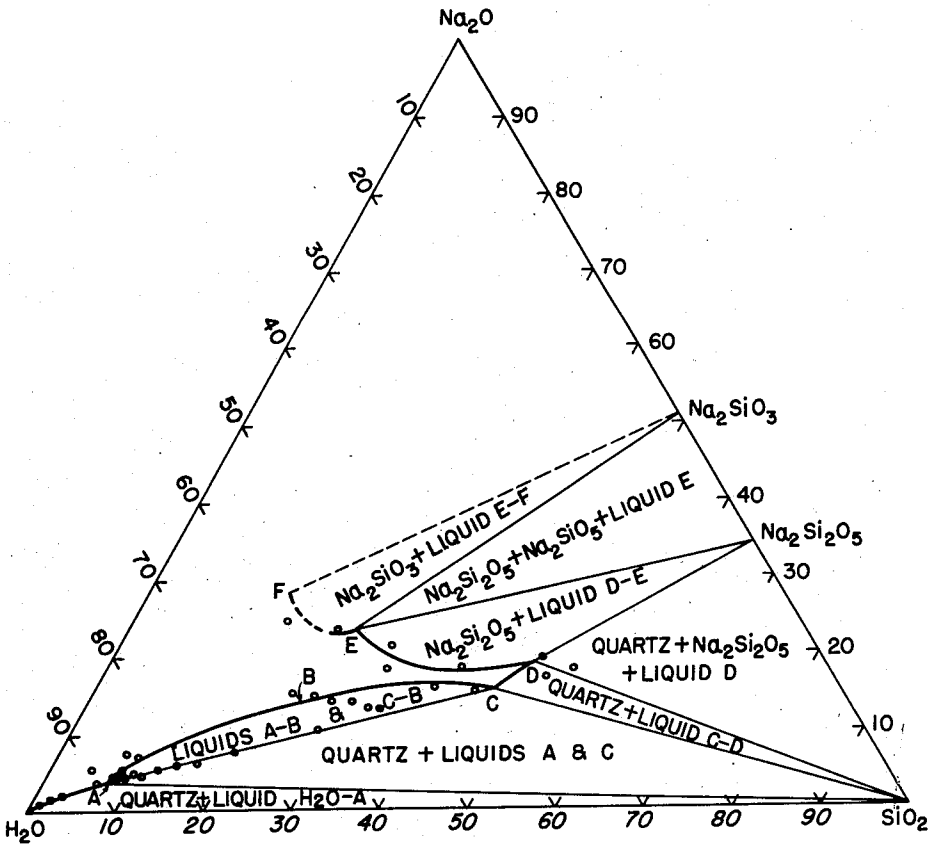


FIG. 1

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FIG. 2

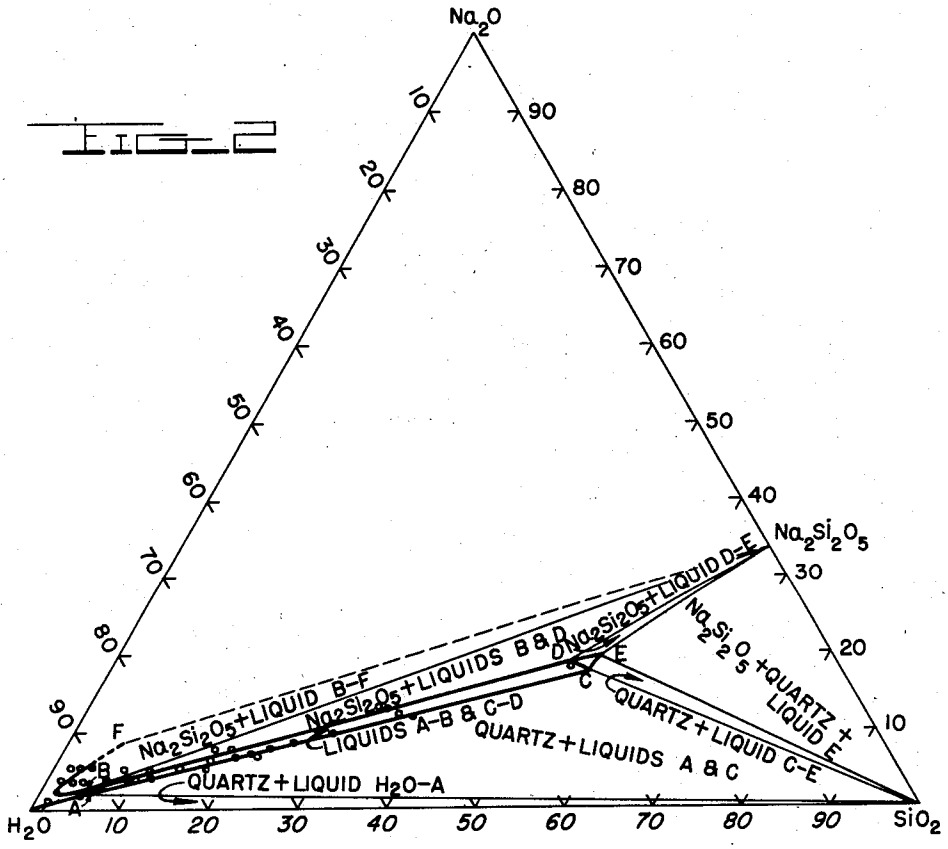
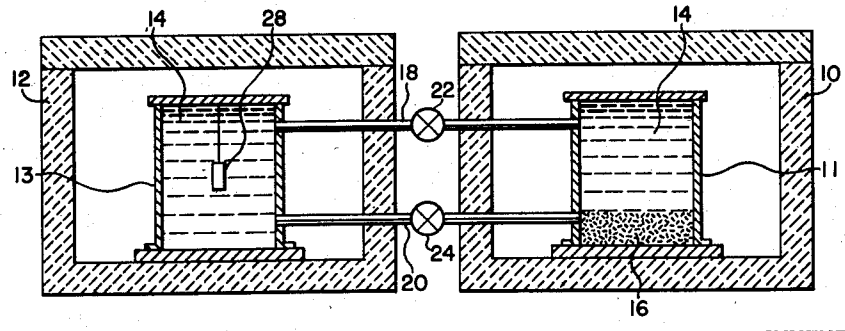


FIG. 4



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FIG. 3

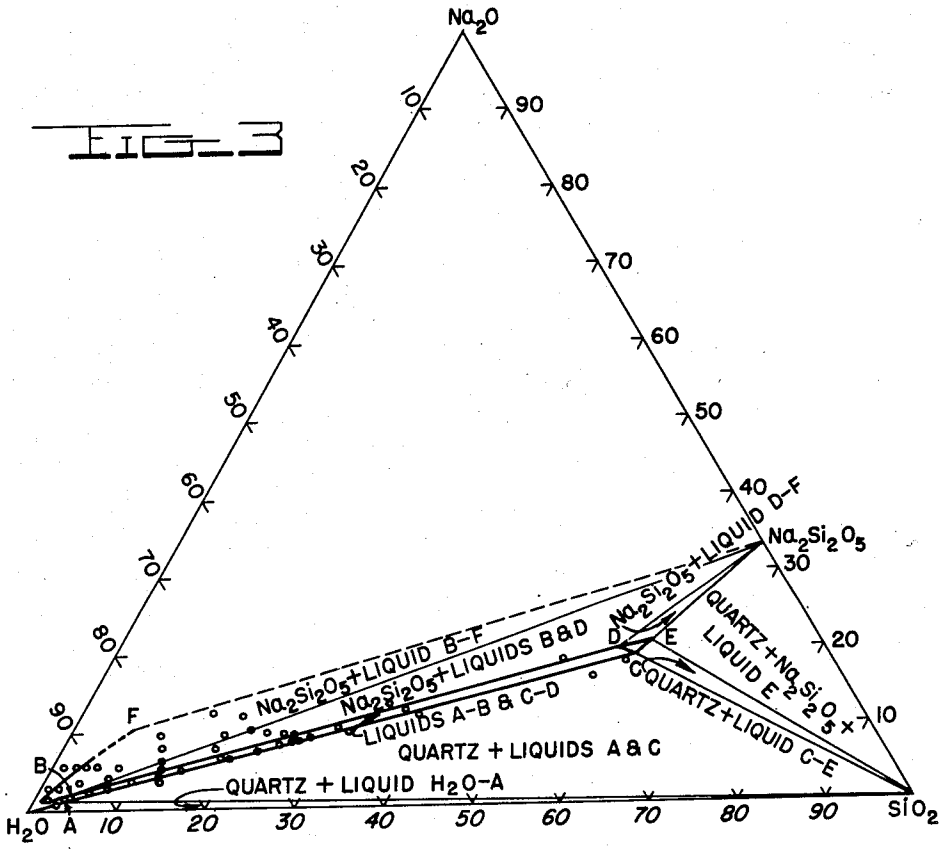
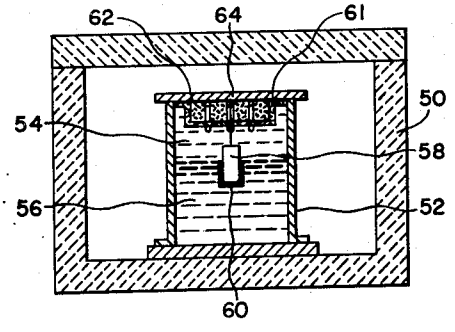


FIG. 5



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2,638,408

METHOD OF SYNTHESIZING LARGE SINGLE CRYSTALS OF QUARTZ

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2 Claims. (Cl. 23—301)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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This invention relates to a method of synthesizing large single crystals of quartz and in particular to the composition of the solution from which the quartz is crystallized.

The general object of the invention is to provide a solution saturated with respect to quartz at a given temperature.

It is also an object of the invention to provide a solution of silica which is of a viscosity sufficiently low to promote relatively rapid crystallization.

These and other objects of the invention will be apparent from the following description and from the drawings hereto appended which are merely illustrative of physical-chemical relationships found in the applicants' research or of conventional apparatus used and are not to be taken as limitative of the method herein described.

In these drawings,

Figure 1 represents a tri-axial diagram of the ternary system —Na_2O—H_2O—SiO_2 at a constant temperature of 250° C.

Figures 2 and 3 show the same at temperatures of 300° C. and 350° C. respectively.

Figure 4 shows in section an arrangement of apparatus for carrying the applicants' method into effect. The showing includes two interconnected tanks or bombs positioned one of each in two separate furnaces.

Figure 5 shows in section a single bomb arrangement for carrying the applicants' method into effect.

Referring to Figure 1 the practicable area of quartz concentration in solution is here shown. The area below the lines extending from the H_2O apex through A, C, D to the silica apex is the one which is definitive of the applicants' invention. Here the little circles represent concentrations tested. In all of the subdivided areas below the lines above indicated quartz is present in solution of one or more liquids. In the area D, $Na_2Si_2O_5$ to the SiO_2 apex quartz and sodium bisilicate are both present in solution of liquid D. Both of these compounds crystallize out together which from a quartz crystallization standpoint is undesirable. Furthermore, because of the relatively high concentration of silica within this area, the solution is very viscous and crystallization is very slow. Also concentrations in the vicinity of points C and D are too viscous for the same reason. Concentrations in the neighborhood of point A, while relatively low in silica are at the same time low in viscosity and the quartz in solution readily

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crystallizes out upon a predetermined drop in temperature or upon evaporation of solution. The applicants have found that concentrations intermediate of these extremes produce maximum crystallization, for normal amounts of agitation.

Figures 2 and 3 show the relationship of the same three components at temperatures of 300° C. and 350° C. respectively. These increased temperatures have caused the shifting of the points C, D and E to the right and toward the SiO_2 apex, thereby indicating a greater concentration of the SiO_2. Also at these higher temperatures points F and A have shifted toward the left and toward the H_2O apex. Within the area of the diagrams the various "Liquids" indicated at points A, B, C, D, E and F are concentrations of different sodium silicates in water. Thus it is apparent from the diagrams that whether one makes a solution of silica with sodium hydroxide alone or with a sodium silicate, within certain concentrations, the solid phase exists as quartz only; that within other concentrations the solid phases both exist as quartz and sodium bisilicate in equilibrium with the solution. Also, with the temperature increase shown, the liquids associated with the quartz and the silicates changed, in the analogous areas, from that shown in the diagram at 250° C. In the operation of the method the solutions of the different concentrations of the "Liquids," here described, separated as distinct phases. Their composition was determined by quantitative analysis. In general these liquids were various sodium silicates, and the relative proportions present depended upon the particular concentration, viz, its position on the diagram.

Figure 4 discloses a conventional arrangement of apparatus for carrying out the applicants' method of crystallization. In this figure, 10 and 12 represent two furnaces which are heated by electrical means (not shown). The temperature in these furnaces is thermostatically controlled. Saturator tank 11 and crystallizing tank 13 contain solution 14 which may consist of a solution of SiO_2 in from .5 to 20% by weight of sodium hydroxide, or a solution of Na_2O and silica of a concentration within the defined area derived from any sodium silicate source. Fragments of quartz are shown in the bottom of the saturator tank at 16. Conduits 18 and 20 connect tanks 11 and 13 as shown. These conduits are provided with valves 22 and 24 by means of which the rate of circulation of the solution is controlled. At least one seed crystal 28 is suspended in crystallizing tank 13 as indicated.

The applicants' method of crystallization is not necessarily limited to the arrangement of apparatus shown by Figure 4. This method may be also accomplished in a single tank or bomb apparatus as illustrated in Figure 5. In this figure furnace **50** is shown supporting tank **52** which contains quartz solutions **54** and **56**. At least one seed crystal **58** may be suspended as shown. Basket **61** containing quartz fragments **62** may be attached to cover plate **64**.

In performing the applicants' method by means of a single bomb or tank the latter is filled with the solution which as above indicated, may be sodium hydroxide in water, sodium silicate alone, in water. Cover **64** supporting seed crystals **58** and basket **61** containing quartz fragments **62** is then placed on the bomb. The furnace may then be heated by thermostatically controlled electrical means (not shown) to a temperature of approximately 375° C. and the solution allowed to reach equilibrium at this temperature. The temperature may then be gradually reduced to approximately 325° C. The solution of quartz is supersaturated and the quartz in excess of that which can be dissolved at this lower temperature crystallizes out on the seed crystals. In this single bomb operation the silica solution at equilibrium separates into two liquid phases shown at **54** and **56** in the drawing. The supernatent phase is of lower density, more aqueous and less silicious than the phase lying below. A seed crystal, suspended so as to extend across the interface of these two phases, grows at an uneven rate. The part extending into the lower phase will increase in weight more rapidly as shown at 60 than the part extending into the supernatant phase. This is due to the difference in silica content of the two phases. The crystal must therefore be suspended so that it will lie entirely within the lower phase.

The method of operation of the apparatus as shown by Figure 4 is believed to be obvious from the foregoing description. It consists of introducing sufficient solution of the desired concentration viz, .5 to 20% of sodium hydroxide in water, or a sodium silicate alone to fill both tanks. The covers are placed on the tanks and the furnaces may be heated to predetermined temperatures; furnace **10** to within the range of about 250° C. to about 450° C. and furnace **12** to a temperature of from about 5° to 50° C. less. After the solution reaches saturation equilibrium in tank **11** valves **22** and **24** are opened to permit circulation of the solution between the tanks. The solution becomes supersaturated in tank **13** and the excess silica crystallizes out as quartz on the seed crystals suspended in this tank. There is no formation of liquid phases in tanks **11** or **13** because of the flow of the solution. The growth of the seed crystals is therefore uniform and even.

The following specific examples are given in order to illustrate more clearly the applicants' invention

EXAMPLE #1

A solution of sodium hydroxide was prepared by diluting 5 cc. of a solution of sodium hydroxide (containing 732 gms. of NaOH per liter) by the addition thereto of 23 cc. of water. The dilute solution contained 3.91 gms. of NaOH. To this diluted solution were added 3.3 gms. of ground fused quartz. The solution was then placed in a single bomb containing a seed crystal and heated to 360° C. and equilibrated at 350°

C. for eight hours. The bomb and contained solution were then cooled at the rate of two degrees centigrade per hour to a temperature of 150° C. and were then quenched under tap water at a temperature of approximately 15° C. The results were as follows:

	Wt. in gms.	
Seed Crystal	0.8413	before test
	0.9289	after test
	0.0876	gain in weight

The seed crystal started to form faces on some of the corners. Also there were some separate seeds formed which were approximately 2 mm. in length.

EXAMPLE #2

500 gms. of a sodium silicate having the approximate formula of $Na_2Si_4O_9.3H_2O$ were added to 1 liter of water. This solution was heated to and equilibrated at 340° C. for about 12 hours in a bomb containing 21 seed crystals suspended on radial rods carried by a vertical axial shaft positioned within the bomb. The bomb and solution were cooled to 315° C. in forty-eight hours. The bomb and contents were then allowed to cool to room temperature in about four hours.

Results

Seed Crystal	#2	#3	#5	#10	#26
Weight Before (gms.)	3.290	3.040	5.450	2.980	3.240
Weight After	3.376	3.368	5.536	3.383	3.470
	0.086	0.328	0.086	0.403	0.230

In this test seeds positioned in the center and lower portion of the bomb gained in weight. From the foregoing it is apparent that the applicants have developed a method for the successful crystallization of quartz from silicate solution. While the description has been drawn to solutions of the alkali metal sodium compounds such as the hydroxide and silicate, it is not desired to be strictly limited thereto as the hydroxides and silicates of the other alkali metals such as potassium and lithium may be used in the same manner. Slight variations in the concentration of the solutions used could be made by those skilled in the art to obtain the equivalent crystallization effect without departing from the spirit or scope of the invention. Such variations are intended to be included within the scope of the invention to the extent as defined by the herewith appended claims.

The invention herein described may be made and used by or for the Government of the United States of America for governmental purposes without the payment of any royalty thereon or therefor.

What is claimed is:

1. A method of growing larger crystals of quartz by deposition of quartz from solution onto crystal seed quartz which comprises cooling in a closed system in the presence of crystal seed quartz a hot body of aqueous sodium silicate solution which is in equilibrium saturation with respect to quart, has a sodium oxide equivalent equal to a concentration of from about 0.5 to about 20% by weight of sodium hydroxide and

is at a temperature within the range of between about 250 and about 450° C., and conducting the cooling of said solution at a rate such that while quartz is deposited therefrom onto the crystal seed quartz, the resulting solution attains equilibrium saturation with respect to quartz at each succeeding lower temperature level.

2. A method of growing larger crystals of quartz by deposition of quartz from solution onto crystal seed quartz which comprises cooling to a lower temperature within the range of between about 250 and about 350° C. in a closed system in the presence of crystal seed quartz a hot body of aqueous sodium silicate solution which is in equilibrium saturation with respect to quartz, has a sodium oxide equivalent equal to a concentration of from about 0.5 to about 20% by weight of sodium hydroxide and is at a temperature within the range of between about 325 and about 450° C., and conducting the cooling of said solution at a rate such that while quartz is deposited therefrom onto the crystal seed quartz, the resulting solution attains equilibrium saturation with respect to quartz at each succeeding lower temperature level.

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