

THE LABORATORY GROWTH OF QUARTZ

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ABSTRACT

The lack of a supply of domestic quartz suitable for piezoelectric applications has stimulated interest in methods of synthesis.

The system $\text{H}_2\text{O-SiO}_2\text{-Na}_2\text{O}$ was chosen for investigation. Data are presented giving the solubility of quartz in sodium hydroxide solutions from 1% to 13% Na_2O at temperatures from 250° to 450° C. The solubility rate and rate of quartz growth from these solutions was determined. The large growth rate led to successful attempts at laboratory synthesis. A discussion is given of several growth techniques.

The use of quartz as a frequency controlling element in radio and radar circuits has increased to the extent that almost 10,000,000 units were used during the final year of the last war. The raw material for this purpose must be fairly free from optical twinning, as well as from electrical (dauphiné) twinning. Brazil is the main source of suitable material. The possibility of the loss of this source due to either enemy action or through depletion has initiated research for quartz substitutes as well as for methods of synthesis of quartz. The success which has been achieved in the synthesis of large single crystals of a great variety of materials, has prompted interest in the synthesis of quartz crystals suitable as raw material for piezoelectric use. Late in 1945 the author began a consideration of this problem.

Previous workers^{2,3,4} have grown quartz by what might be called "trick" methods, such as convection transport, differential "solubility" of the different forms of silica, etc. The writer, having had some experience in growing water soluble materials such as ammonium dihydrogen phosphate, lithium sulfate monohydrate, iodic acid, etc., reasoned that quartz could be grown by these proven methods.

The method which was decided upon was first to find a system where quartz would be the primary crystalline phase, and one in which quartz would be:

- (a) sufficiently soluble and
- (b) supersaturate sufficiently to make the method practical.

A suggestion of Morey and Ingerson led the author to investigate the $\text{H}_2\text{O-Na}_2\text{O-SiO}_2$ system. Temperatures from 250° to 450° C. were investigated.

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² Kerr, Paul F., and Armstrong, Elizabeth, *Bull. Geol. Soc. Am.*, **54**, Suppl. 1, 1-34 (1943).

³ Spezia, G., *Accad. Sci. Torino, Atti*, **44**, 95-107 (1908).

⁴ Nacken, R., "Report on the Research Contract for Synthesis of Oscillator Crystals," Captured German Report RDRDC/13/18.

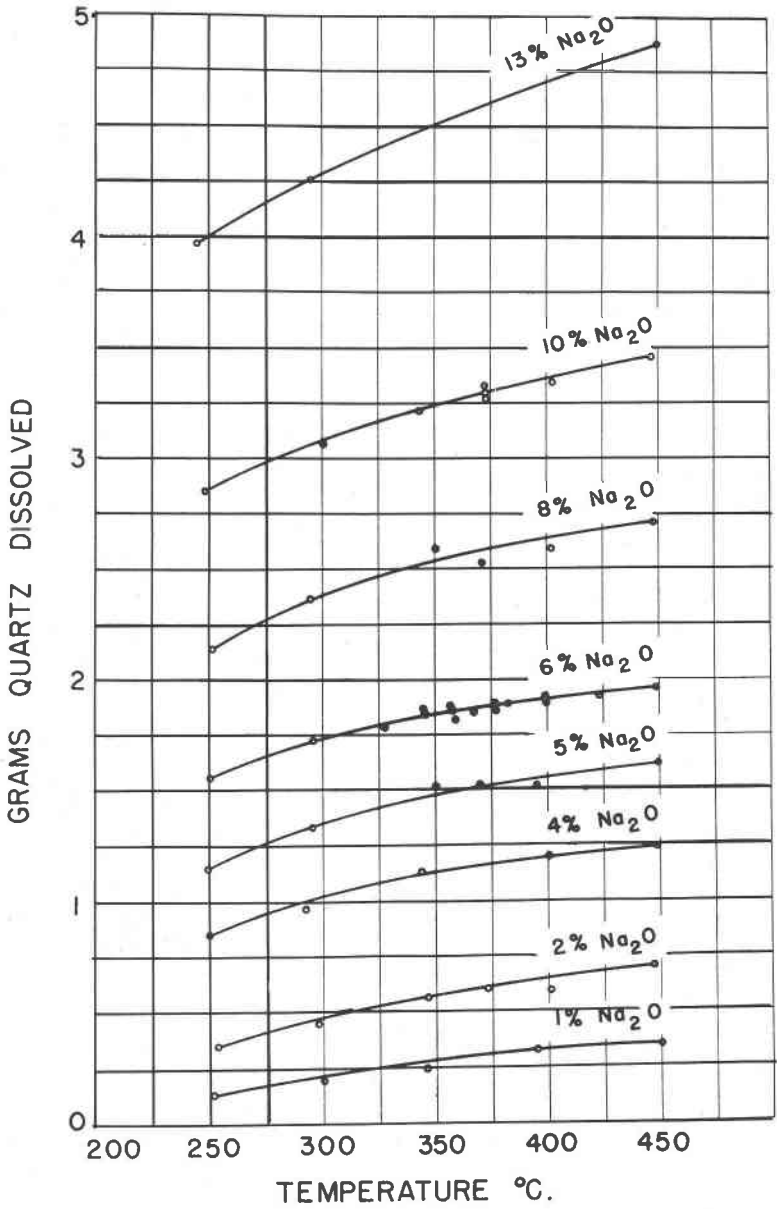


FIG. 1. Concentration in wt.%

After the work had progressed to the point where it could be evaluated, the reports of Nacken's work in Germany during the war⁴ became available. Several inaccuracies in this research, plus the conviction that the German method was impractical and basically unsound from a crystal growing standpoint, prompted me to continue. Subsequent attempts of several laboratories in this country to put the German method into practice, with generally negative results, have strengthened this viewpoint.

EXPERIMENTAL

The solubility of quartz was determined by observing the loss in weight of a quartz block in contact with NaOH solution for a given temperature and concentration. A weighed block of quartz was placed in an 18 ml. high pressure bomb, 10 ml. of sodium hydroxide solution of known concentration was pipetted into the bomb and the bomb sealed. It was then placed in an electric furnace and equilibrated at a definite temperature. The whole apparatus was slowly rocked to provide agitation. A description of the apparatus will be found described by Tuttle and Friedman.⁵ After heating for from 8 to 120 hours, the bombs were removed from the furnace and quickly quenched under a cold water tap. They were then opened and the remainder of the quartz block was washed, dried and weighed. The solubility of quartz in sodium hydroxide solutions is shown as a function of temperature in Fig. 1.

In order to determine whether the data represented equilibrium values, the rate of solution of quartz was also determined. For this purpose uniform quartz blocks cut parallel to the second order prism ($11\bar{2}0$) 2.5 cm. \times 1.5 cm. \times 0.25 cm. were used. The results for two sodium hydroxide concentrations are given in Fig. 2.

In any synthesis of quartz, the rate of growth will determine the practicability. To determine the approximate rate of growth, runs were begun as before, using the above "X" cut quartz blocks. However, instead of quenching when equilibrium was reached, the furnaces were slowly cooled at a known rate. After cooling through 25° C., the bombs were quenched as before. The rate of cooling was decreased until the maximum amount of quartz re-deposited, as determined from the solubility curves (Fig. 1). The results are given in Fig. 3. The tendency of quartz to supersaturate in sodium hydroxide solutions prevents spontaneous "snow storms" of small crystals when the rate of cooling is in excess of the maximum equilibrium rate.

The dropping off of the growth rate below 300° C. will fix the lower temperature limit of any commercial growth process using these com-

⁵ Tuttle, O. F., and Friedman, I. I., *J. Am. Chem. Soc.*, **70**, 919 (1948).

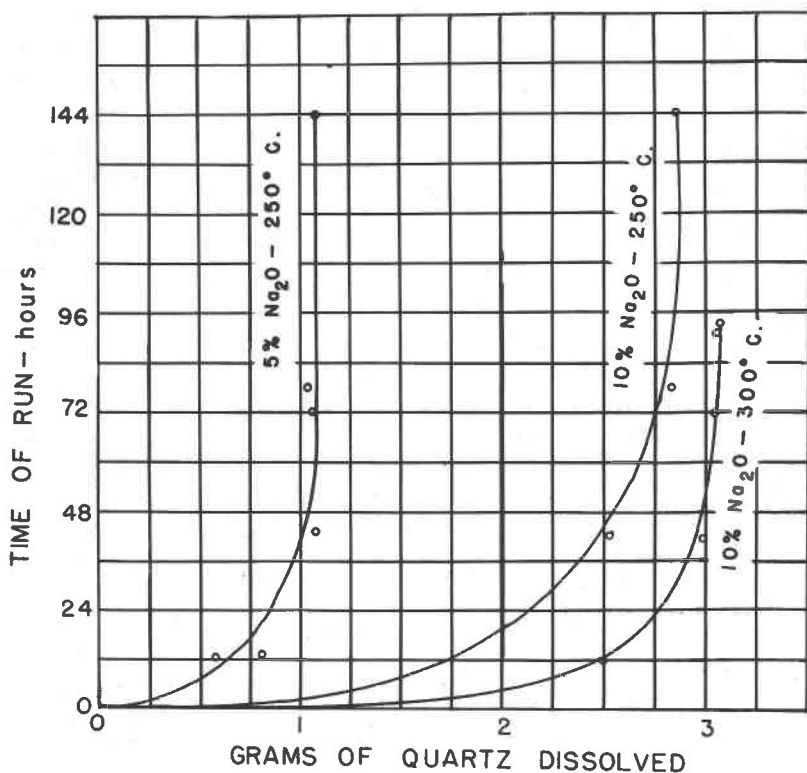


FIG. 2

positions. The upper limit is fixed by the α - β inversion at 573° C. Quartz cooled through the inversion will become electrically twinned, unless very special methods are employed of applying stress to the crystal as it passes through the inversion. Actually, a somewhat lower temperature than the inversion temperature may be desirable due to the temperature-pressure limitations of large scale equipment.

The greater the concentration of sodium hydroxide, the larger the quartz yield per run in a batch method. However, the viscosity of the high Na₂O-SiO₂ concentrations will slow down diffusion and cause growth difficulties.

The liquid immiscibility observed in this system⁵ introduces another factor which has a bearing on crystal growth. The author has observed that the growth on a quartz plate immersed in both phases is mainly upon the surface of the quartz plate which is in contact with the "heavy" (lower water content) phase. The rate of solution and redeposition will

probably differ in the two phases. There is some experimental evidence to show that solubility takes place more rapidly in the "lighter" phase, and deposition more rapidly from the "heavier" phase. It might, therefore, be possible to suspend quartz fragments in the light phase, and immerse quartz "seeds" in the heavy phase. Oscillating the temperature should then cause quartz to migrate from the fragments to the seed.

As a check on the practicability of quartz growth from the $H_2O-Na_2O-SiO_2$ system, a water glass containing 20% Na_2O , 64% SiO_2 , 16% water (Philadelphia Quartz Company—"G" brand sodium silicate) was used as a starting material. 5.0 grams of the "G" brand sodium silicate was placed in an 18 ml. bomb, 10 ml. of water pipetted in, a quartz seed added and the bomb sealed. The solution was saturated with respect to quartz at approximately 450° C. The bombs were then heated to 325° C. and allowed to equilibrate at that temperature for thirty hours while being continuously rocked. They were then rapidly cooled (100°/hour)

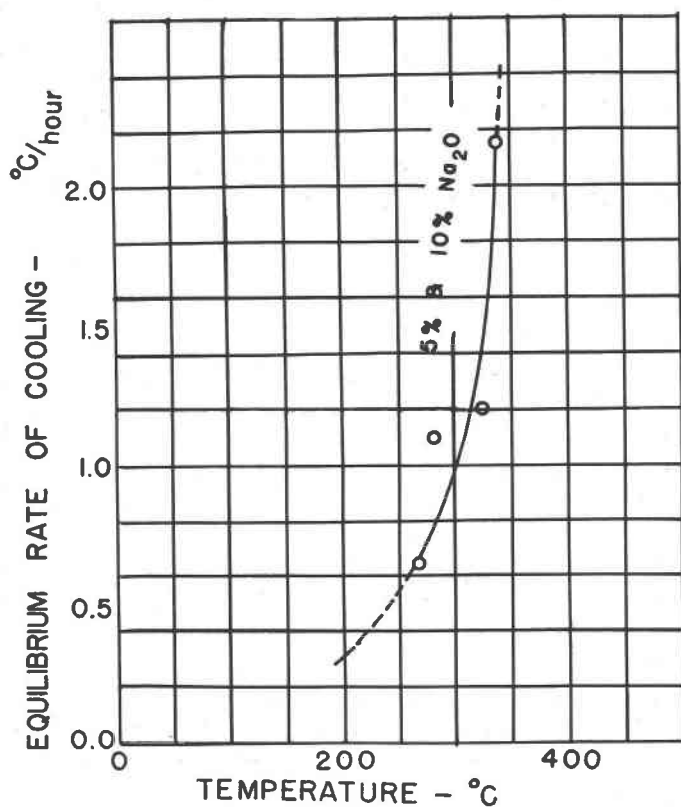


FIG. 3

to room temperature and opened. In every run the seed gained from 0.25 to 0.3 grams.

In a few cases five or six consecutive runs were made using the same seed. There is no veil or other line of demarkation to mark the boundaries of each run. The growth was remarkably good, even as compared to certain easily grown materials such as alum or Rochelle salt.

With the exception of two seed plates cut parallel to the major rhomb ($10\bar{1}1$), all the seed plates used were cut parallel to the second order prism ($11\bar{2}0$).

The ($11\bar{2}0$) plates developed rhomb ($10\bar{1}1$ and $01\bar{1}1$) and first order prism faces. Most of the growth was in a direction of the minor ($01\bar{1}1$) and major ($10\bar{1}1$) rhombs. The use of seeds cut parallel to the minor rhomb resulted in nearly all growth taking place on the large ($01\bar{1}1$) surface. The growth rate should be greater with seeds so oriented, since the direction of fastest growth in natural quartz is normal to the minor rhomb ($01\bar{1}1$) faces, closely followed by the rate normal to the major rhomb ($10\bar{1}1$) face.

The author wishes to acknowledge the aid given to him by Dr. O. F. Tuttle who helped initiate this research project and is responsible for many of the ideas embodied herein. A great debt is also owed to Mr. Charles Jackson for his assistance in carrying out the experimental work.