SOME OBSERVATIONS ON THE CRYSTALLIZATION OF SILICIC ACID

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ABSTRACT

In the presence of calcium, added as $CaCO_3$ or $CaSiO_3$, the crystallization of amorphous silicic acid by heating at 1150° C. produces a mixture of quartz and cristobalite. Heating of the pure silicic acid at this temperature results in cristobalite only. The generation of quartz some 300° C. above the quartz-tridymite transition temperature, in the presence of calcium, is noteworthy. Investigation of the effects of other additives and of other firing temperatures is being carried out.

In a recent paper on the preparation of luminescent wollastonite (1) by the reaction of calcium carbonate and amorphous silicic acid, it was reported that quartz was found in the product when an excess of $SiO_2 \cdot xH_2O$ was used. This observation was surprising for two reasons: first, because it was at variance with statements in the literature that the crystallization of amorphous silica results only in cristobalite (2, 3); and second, because the firing temperatures employed in the above-mentioned work were some 300° C. above the quartz-tridymite transition temperature (4). It was, therefore, considered of interest to repeat these experiments, particularly since the preparation of the luminescent $CaSiO_3$ was complicated by the necessity of adding manganous carbonate and lead fluoride as "activators" for the luminescence.

The silicic acid employed in these experiments was Mallinckrodt "Special Bulky" silicic acid commonly used for the preparation of luminescent silicates. It appears that this silicic acid is made by precipitation of a sodium silicate solution with acid, followed by intensive washing to remove the soluble salts. Spectrographic analysis showed that the material contained 0.003% Na and 0.008% K by weight. The only other impurities detected were Mg, Fe, and Al, all of which were of the order of 0.002–0.003% by weight, and about one part per million of Cu. The water content of the silicic acid is variable, and averages about 10–15%. This finely-divided, high-purity silicic acid is made on a large scale for use in the synthesis of commercial fluorescent lamp and cathode ray tube phosphors and is readily available. The other reagents used in the present work were Baker's C. P. calcium carbonate and Baker's C. P. zinc oxide.

$CaCO_3$–$SiO_2 \cdot xH_2O$ mixtures in the proportions 1:1, 1:2, 1:5, 1:7.5, 1:10, 1:50, and 1:100 were made by milling the components with distilled water for two hours in pint porcelain ball mills equipped with flint pebbles. The mixtures were then filtered, dried for two to three hours at 110° C., and fired in Vitreosil or Amersil fused silica trays at 1150° C.

TABLE 1

Phases present in $CaCO_3-SiO_2 \cdot xH_2O$ mixtures heated three hours at 1150° C.

CaO/SiO_2 Ratio	Phases Identified from Powder Photograph
1:1	Wollastonite predominant; possibly quartz (one weak line, $d=4.3$)
1:2	Wollastonite; quartz; cristobalite
1:5	Quartz predominant; some wollastonite; cristobalite
1:7.5	Quartz predominant; some wollastonite; cristobalite
1:10	Quartz predominant; trace of wollastonite; cristobalite
1:50	Quartz predominant; trace of wollastonite; cristobalite (one line, $d=4.04$) (poor pattern)
1:100	Amorphous pattern

for three hours. The samples were loaded into a furnace which was already at temperature, the furnace recovering its 1150° C. temperature within 15 minutes after the samples were placed inside. At the conclusion of the firing the samples were removed from the hot furnace, and reached room temperature in about 15 minutes.

Powder patterns of the various samples were taken with filtered CuK radiation, and compared with patterns of natural quartz (source unknown), cristobalite from Cerro Montosa, New Mexico, and wollastonite from Inyo County, California, as well as with data from the *A.S.T.M.* tables. The results are given in Table 1 and Fig. 1.

The 1:100 CaO/SiO_2 sample was replaced in the furnace at 1150° C. and refired for 3½days. A powder photograph (cf. Fig. 1) then gave a very good quartz pattern. The presence of cristobalite was also established in this sample from the single line, $d=4.04$ Å. Microscopic examination by O. F. Tuttle of the Geophysical Laboratory confirmed the presence of both the quartz and the cristobalite in this sample. The microscopic examination showed that cristobalite was the major component of the mixture, and that it was of very low particle size; the quartz, although present in smaller amounts, occurred as considerably larger crystals. The predominance of quartz lines in the diffraction pattern is apparently due to this situation.

A fired sample of the 1:1 CaO/SiO_2 composition was mixed with four more moles of amorphous $SiO_2 \cdot xH_2O$, and refired overnight at 1150° C. The powder photograph of this preparation showed the quartz pattern predominant, and was indistinguishable from the diffraction pattern given by the 1:5 CaO/SiO_2 sample made directly from $CaCO_3$ and silicic acid.

In order to insure that the fused silica firing vessels were not affecting

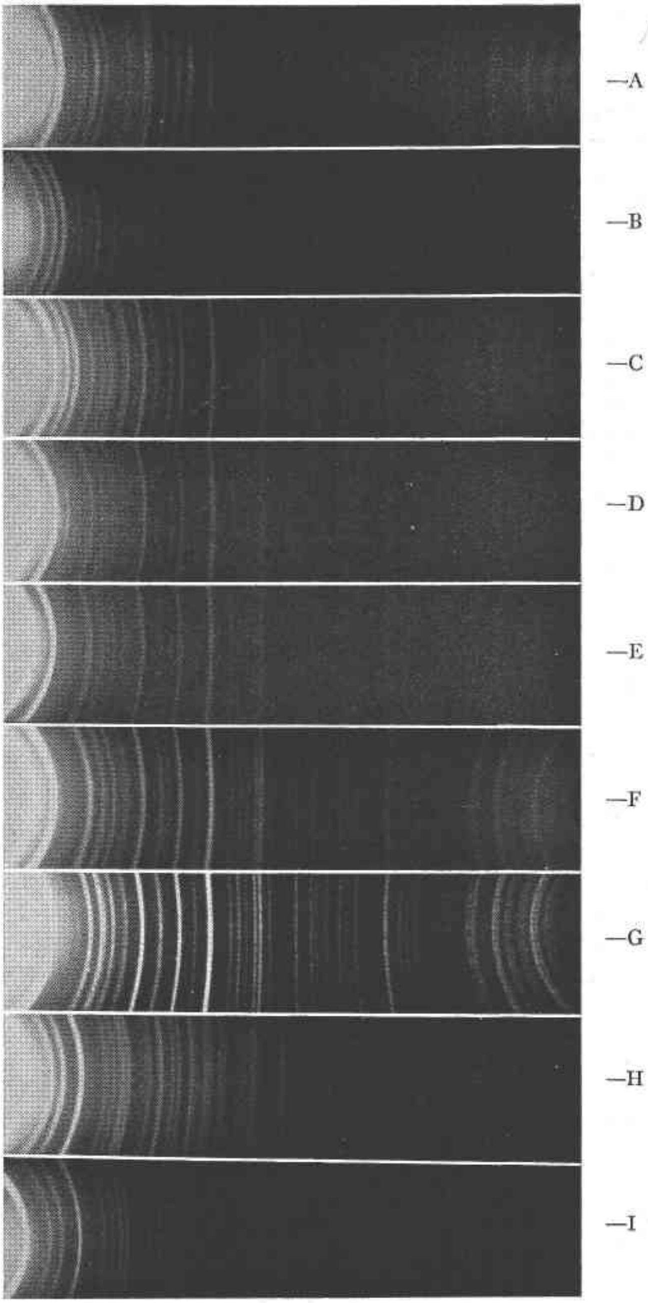

FIG. 1. X-RAY POWDER DIFFRACTION PATTERNS Cu K-radiation, Ni filter.

the results, mixtures with 1:5 and 1:50 $CaCO_3/SiO_2 \cdot xH_2O$ were made up by pebble milling as above and fired in platinum crucibles for three hours at 1150° C. The diffraction patterns were identical with those obtained when the firings were made in silica trays.

The original silicic acid was amorphous to *x*-rays, and remained so after successive firings of three and sixteen hours. After 4½ days of uninterrupted firing at 1150° C. a powder photograph of the product checked that of cristobalite line for line.

It was thought that perhaps the abrasion of the flint pebbles during the milling of the calcium carbonate-silicic acid mixtures might have had some effect on the subsequent crystallization of the latter, hence the following experiments were performed to check this point. Two samples of silicic acid were milled in the usual way, the first with distilled water and the second with redistilled acetone as the liquid medium. After filtration and drying, these samples were fired at 1150° C. along with a sample of unmilled silicic acid. The charges were removed from the furnace daily in order to take samples for powder photographs, and then replaced. Amorphous patterns were obtained from all three samples for the first ten days. After eleven days the unmilled silicic acid gave a good cristobalite pattern, while the two milled samples remained amorphous. After thirteen days a good cristobalite pattern was obtained from the acetone-milled silicic acid, and a very poor cristobalite pattern was obtained from the water-milled material. It was somewhat unexpected, although not unreasonable, that the interruption of the firing for about an hour every day should slow down the crystallization rate of the unmilled silicic acid by a factor of two or three. The further slowing down of the crystallization rate due to the water milling may be due to the removal of some of the residual alkali from the silicic acid by this treatment, acetone being presumably much less effective in this regard. In any event, these experiments showed that the generation of quartz is not ascribable to the effect of impurities ground off the flint pebbles or the porcelain mill during the mixing procedure.

A—natural wollastonite
B—1:1 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
C—1:2 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
D—1:5 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
E—1:10 $CaCO_3$—SiO_2, heated 3 hrs., 1150° C.
F—1:100$CaCO_3$—SiO_2, heated 3½ days, 1150° C.
G—Natural quartz
H—H_2SiO_3, heated 4½ days, 1150° C.
I—natural cristobalite

As a final check on this point, slurries of $CaCO_3$ and $SiO_2 \cdot xH_2O$ in the mole ratios of 1:5 and 1:50 were made up by adding distilled water to the powders in bakelite-capped glass bottles and gently agitating the suspensions for two hours. In this case no grinding pebbles were used. The slurries were filtered, dried, and fired in platinum crucibles at 1150° C. for three hours. The 1:5 CaO/SiO_2 sample gave a powder photograph which checked earlier preparations of this composition, while the 1:50 CaO/SiO_2 sample gave a practically amorphous pattern. After the samples were reheated at 1150° C. for about 55 hours, the 1:5 CaO/SiO_2 preparation showed no change in its pattern, while the 1:50 CaO/SiO_2 sample gave a powder pattern similar to that of the 1:5 CaO/SiO_2 preparation. The failure of the 1:50 CaO/SiO_2 mixture to crystallize in three hours in this experiment seems readily understandable in view of the poorer dispersion of the $CaCO_3$ by the less vigorous mixing technique employed here.

The possibility is not excluded that the initial formation of quartz nuclei may occur below the quartz-tridymite transition temperature even in the short time involved in heating up the $CaCO_3$–$SiO_2 \cdot xH_2O$ mixture. We have attempted to minimize this heating-up time by using small charges and furnaces of large heat capacity. In the experiments with the $CaCO_3$–$SiO_2 \cdot xH_2O$ slurries, for example, 30 ml. platinum crucibles were used as firing vessels. When two of these were placed in a furnace with a hot chamber 7″×10″×18″, the thermocouple temperature dropped to 1110° C. during the loading, and recovered its 1150° C. temperature within three minutes. We are, therefore, inclined to discount this possibility as an explanation of our results.

If this explanation is ruled out, and if the data of Fenner (4) placing the quartz-tridymite transition temperature at 870 ± 10° C. are correct, it would appear that we have here a case of the generation and persistence of a low temperature polymorphic form above its stability region. The anomalous generation and continued existence of high temperature polymorphic forms below their stability range is a very common phenomenon in mineralogy and chemistry. The inverse situation—although a priori equally possible—seems to have been seldom observed, the only other example known to us being the generation of arsenolite, the low temperature form of As_2O_3 (arsenolite-claudetite transition temperature $= -13°$ C.) (5) which readily precipitates from solutions of arsenious oxide at room temperature, and even at a few hundred degrees above room temperature from the vapor.

Experiments with the addition of ZnO, analogous to those performed with the calcium carbonate additions, were carried out, mixing of the components being carried out entirely by pebble milling, and the firings being conducted in fused silica trays at 1150° C. Willemite and cristobalite were the only phases found in these runs.

It is planned to continue these studies using different sources of amorphous silica, with other additives, and at other temperatures.

REFERENCES

(1) MERRILL, J. B., AND SCHULMAN, J. H., The $CaSiO_3$:(Pb+Mn) phosphor: *J. Opt. Soc. Amer.*, In press.

(2) COHN, G., AND KOLTHOFF, I. M., The thermal aging of silica: Abstracts of papers 108th meeting: *Am. Chem. Soc.*, Sept. 1944, page 14P–15P.

(3) SOSMAN, R. B., The Properties of Silica, pp. 171–172, Reinhold Pub. Co. (1927).

(4) FENNER, C. N., The stability relations of the silica minerals: *Am. Jour. Sci.*, **36,** 331 (1913).

(5) SCHULMAN, J. H., AND SCHUMB, W. C., The polymorphism of arsenious oxide: *J. Am. Chem. Soc.*, **65,** 878 (1943).