Crystallization of Quartz at High Temperatures

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It has generally been accepted that amorphous silica[1] and vitreous silica[2] crystallize into cristobalite when they are heated in the absence of a flux. It has also been reported that a mixture of quartz and cristobalite was obtained[3] when amorphous silica was heated at 1200—1300°C with addition of a mineralizer which did not contain alkali or strontium compounds, although at these temperatures quartz is unstable*. Crystallization of quartz as a single phase has been described by Wittels[4], who obtained it by annealing,at 930°C for 16 hours, metamict silica produced by fast neutron bombardment (2×10^{20}neutrons/cm).

It has become evident that the presence of a very small amount of alkali plays an important role in the crystallization of silica, whereas the previous workers do not seem to have paid attention on this point. Therefore, the author has reinvestigated the crystallization of silica at high temperatures using amorphous silica which is free from alkali. It was found that quartz was obtained as a single phase even at 1388±5°C.

Experimental

"Aerosil", amorphous silica, made by DEGUSSA was used as the starting material. Chemical analysis and physical constants of this material are shown in Table I. No trace of alkali was found by means of a chemical analysis. The specimen was held in a platinum boat, and was heated at a given temperature (±5°C) in an electric tube furnance, and was very rapidly cooled in air. No flux was added. The cooled

TABLE I
CHEMICAL ANALYSIS AND PHYSICAL CONSTANTS OF UNFIRED SILICA SPECIMEN

SiO_2	99.9%
Fe_2O_3	0.004%
CaO	None
MgO	None
Free moisture	1.72%
Ignition loss (=Total H_2O)	4.2%
Specific density	2.2
Bulk density	0.050

TABLE II
FIRED SILICA SPECIMEN

Heating Temperature (°C)	Heating hours (hr.)	Cristobalite (111) Intensity (Counts/sec)	Cristobalite (111) Diffraction angle (2θ) (°)	Cristobalite (111) Spacing (Å)	Quartz (101) Intensity (Counts/sec)	Quartz (101) Diffraction angle (2θ) (°)
ca. 1600	5	ca. 2000	22.06	4.029	0	—
1453	1/2	16	22.03	4.034	0	—
1413	1	26	21.96	4.047	0	—
1399	2	28	21.95	4.050	0	—
1392	2	35	21.92	4.054	0	—
1388	1	0	—	—	29	26.65
1374	1	0	—	—	16	26.65
1373	1	0	—	—	0	—
1362	1	0	—	—	0	—
1352	1	0	—	—	0	—

* According to Flörke[7] and Scairer and Yagi[8], quartz is unstable above ca. 1050°C, while according to Fenner[5] it is unstable above 870°C.

1) R. B. Sosman, "The Properties of Silica", The Chemical Catalog Co., Inc., New York, 1927, p. 171.
2) ibid., p. 97.
3) J. H. Schulman, E. W. Claffy and R. J. Ginter, *Am. Mineral.*, **34**, 68 (1949); D. A. Bailey, ibid. **34**, 601 (1949); L. S. Birks and J. H. Schulman, ibid. **35**, 1035 (1950); G. D. Rieck and J. M. Stevels, *J. Soc. Glass Technol.*, **35**, 284 (1951).
4) M. Wittels and F. A. Sherrill, *Phys. Rev.*, **93**, 1117 (1954).
5) C. N. Fenner, *Am. J. Sci.*, **36**, 331 (1913).
6) T. Tokuda, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **14** (1957) in press.
7) O. W. Flörke, *Naturwiss.*, **43**, 419 (1956).
8) J. F. Scairer and K. Yagi, *Am. J. Sci.*, Bowen Vol., 500 (1952).

specimens were analysed by the "Norelco" X-ray diffractometer. Filtered Cu—K_α was used with an X-ray tube running at 30 kV, 15 mA. Divergence and scatter slits were 1°, and the receiving slit was 0.006″ in width respectively.

Results

The reflection (111) for cristobalite was detected along with the amorphous band with specimens which were heated at 1392, 1399, 1413, or 1453°C for one hour (Fig. 1). The reflection (101) for quartz was detected along with the amorphous band with those which were heated at 1388 or 1374°C for one hour (Fig. 2). These are the highest temperatures at which quartz has been crystallized, reported in the literature. The diffraction angle for (101) of quartz of these products is, as is shown in Table II, equal to that of a large transparent Brazilian quartz within an experimental error (0.01°). On the other hand, it was found that, for crisiobalite, as the temperature of heating is lower, the products show larger spacing. Thus a specimen which was heated at 1392°C±5 for one hour showed a spacing for cristobalite 0.6% larger compared to that of the standard specimen which was obtained by heating amorphous silica at ca. 1600°C for five hours.

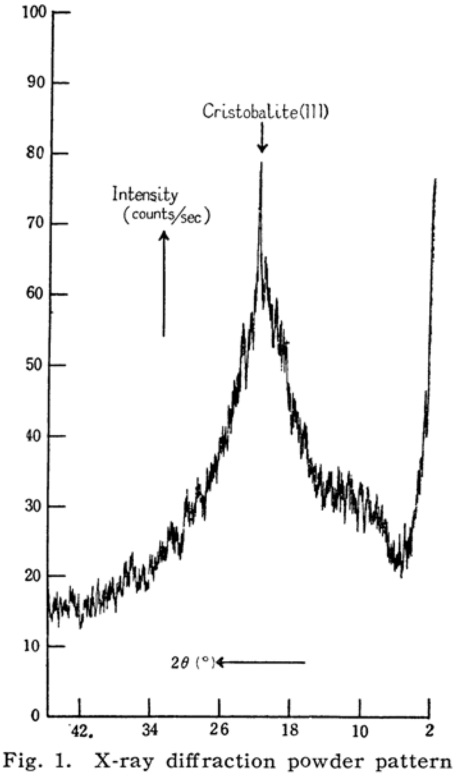

Fig. 1. X-ray diffraction powder pattern of amorphous silica heated at 1413±5°C for one hour in air, showing the appearance of cristobalite.

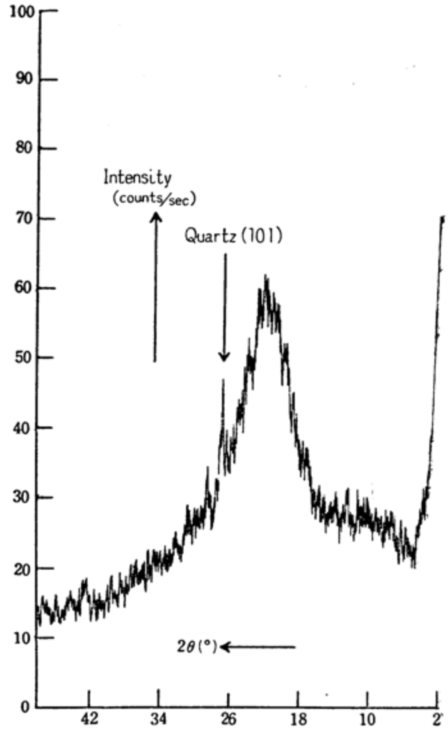

Fig. 2. X-ray diffraction powder pattern of amorphous silica heated at 1388±5°C for one hour in air, showing the appearance of quartz.

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