Notes

Crystallization of Amorphous Silica into Quartz

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Crystallized quartz has been obtained from amorphous silica prepared by the hydrolysis of silicon alkoxide containing calcium or magnesium alkoxide (10 mol %). The crystallization of $CaSiO_3$ and $MgSiO_3$ is observed prior to that of quartz. Crystallization isotherms are described by the contracting cube equation $1 - (1 - f)^{\frac{1}{3}} = k(t - t_0)$ and activation energies have been determined as 435 and 498 kJ mol^{-1} in the presence of Ca^{2+} and Mg^{2+} respectively.

THE phase transformations of silica shown by Fenner[1] are shown below. Although there is no doubt that

$$\text{quartz} \xrightleftharpoons{870\ ^\circ\text{C}} \text{tridymite} \xrightleftharpoons{1\,470\ ^\circ\text{C}} \text{cristobalite} \xrightleftharpoons{1\,720\ ^\circ\text{C}} \text{liquid}$$

quartz and cristobalite are true polymorphs of silica, uncertainty[2-6] surrounds the exact position and chemical nature of the tridymite phase. Consequently, transformations in pure silica are mainly restricted to quartz and cristobalite under conditions of normal pressure. However, it is generally accepted that amorphous silica, as a metastable phase, crystallizes directly into cristobalite when heated at temperatures ranging from 900 to *ca.* 1 500 °C.[7] It has also been reported that in the presence of an impurity, such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, or Li^+, amorphous silica temporarily crystallizes into quartz,[8-11] although good quartz crystals have not been obtained. Metastable solid solutions of quartz in glass ceramics are also well known.[12]

In the present study it was found that crystals of quartz can be obtained from amorphous silica prepared by hydrolysis of silicon alkoxide containing calcium or magnesium alkoxide (10 mol %). On the basis of this result, kinetic studies were undertaken on the crystallization of quartz, the data being analyzed with the aid of available solid-state models.

EXPERIMENTAL

Materials and Procedure.—The silicon ethoxide used was of pure grade. Calcium and magnesium methoxides were synthesized by heating the metal in an excess of dehydrated methanol with a small amount of iodine as catalyst for 5 h at 64 °C. The purity of both metals was 99.9%. The mixed alkoxides prepared in mole ratios $Si^{4+} : M^{2+}$ (M = Ca or Mg) 9 : 1 were refluxed for 20 h also at 64 °C and then hydrolyzed by adding aqueous ammonia solution at 25 °C. The temperature was slowly raised to 80 °C with stirring. The resulting mixed powders (A, $Si^{4+} : Ca^{2+} = 9 : 1$ and B, $Si^{4+} : Mg^{2+} = 9 : 1$) were washed repeatedly with hot water and dried under reduced pressure. The average particle size of both reagents is 400 Å.

Measurements.—Thermal analyses (t.g.a. = thermogravimetric and d.t.a. = differential thermal analysis) were carried out in air at a heating rate of 10 °C min^{-1}. The compound α-alumina was used as the standard in d.t.a. The species obtained in the heating and cooling processes at the rate of 10 °C min^{-1} were identified by means of high-temperature *X*-ray diffractometry using nickel-filtered Cu-K_α radiation. Kinetic studies of quartz crystallization were made by *X*-ray measurement. Both starting powders were pre-heated as described in the Results and Discussion section. Samples were placed in an electric furnace equipped with a temperature regulator, heated for the desired time, and then cooled rapidly to room temperature. The fraction of crystallization was determined from the intensity ratio of the α-quartz (101) peak † to the α-quartz + CaF_2 (220) internal standard peak, using a calibration curve prepared with known compositions. Quartz powder for electron microscopic observation was dispersed in ethanol by an ultrasonic treatment for 3 min. The dispersed drops were dried on carbon film and observed under a 35 keV ‡ beam.

RESULTS AND DISCUSSION

Crystallization of Pure Silica.—Amorphous–quartz crystallization was not observed in the pure silica obtained from alkoxide, in agreement with the results reported previously.[7] Heating above 1 200 °C caused crystallization of cristobalite.

Thermal Analysis.—Thermogravimetric investigation showed a weight loss of 21.6% up to 405 °C in the starting powder A and of 22.8% up to 420 °C in the starting powder B. This can be attributed to the loss of ammonia, organic residues from the parent alcohol, absorbed water, and hydrated water. Figure 1 shows the d.t.a. curves of both starting powders. Two exothermic peaks were observed at 845—900 and 970—1 055 °C for A and at 865—915 and 1 030—1 115 °C for B. High-temperature *X*-ray diffraction analysis confirmed that the first peaks in A and B were due to the crystallization of calcium metasilicate (wollastonite, $CaSiO_3$) and magnesium metasilicate (clinoenstatite, $MgSiO_3$) respectively and the second peaks to amorphous silica-β-quartz crystallization. In the cooling process, small exothermic peaks were detected in both cases at *ca.* 575 °C; these were found to be due to the transformation of β(high)- into α(low)-quartz.

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† Quantitative *X*-ray measurement, except for the (101) peak, is impossible to carry out due to the weakness in intensities.

‡ Throughout this note: 1 eV ≈ 1.60×10^{-19} J.

High-temperature X-Ray Analysis.—Both starting powders, A and B, were amorphous, no significant change in structure being detected up to the temperatures of the first exothermic peaks in the d.t.a. Calcium metasilicate ($CaSiO_3$) and $MgSiO_3$ crystallized at 845—900 and 865—915 °C respectively and remained above the crystallization temperature of quartz. The peaks due to β-quartz began to appear when A was heated at 970 °C and B at 1 030 °C, the intensity of the peaks increasing rapidly up to 1 055 and 1 115 °C in A and B respectively. This result suggests that amorphous silica is crystallized directly into β-quartz, in the high-temperature form. The transformation of quartz into cristobalite was observed above 1 320 °C. Therefore, $CaSiO_3$ and $MgSiO_3$ confer metastability on quartz.

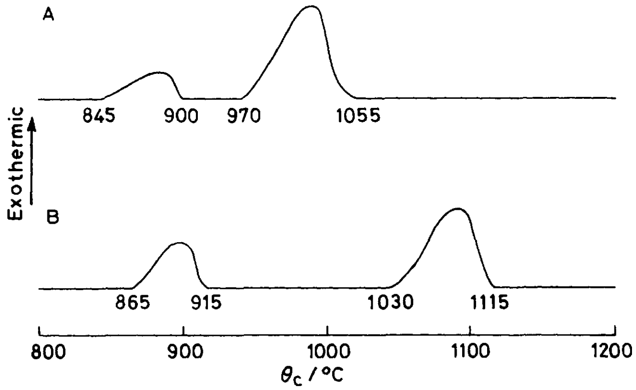

FIGURE 1 D.t.a. curves of the starting powders A and B. Sample weight = 115 mg

Kinetics of Quartz Crystallization.—Starting powders A and B, prepared from amorphous silica containing $CaSiO_3$ and $MgSiO_3$, were heated for 1 h at 900 and 915 °C respectively. Figure 2 shows the fraction of crystallized quartz at different temperatures. A rapid transformation of β- into α-quartz takes place at *ca.* 575 °C and since the β form cannot be quenched, we are dealing with the α form. Crystallized samples were prepared by heating the starting powders A and B for 1 h at 1 250 °C. The quartz powder thus obtained consists of nearly spherical particles (Figure 3). Attempts were made to fit the results to kinetic laws by considering the induction periods (see Figure 2). The data can be interpreted in

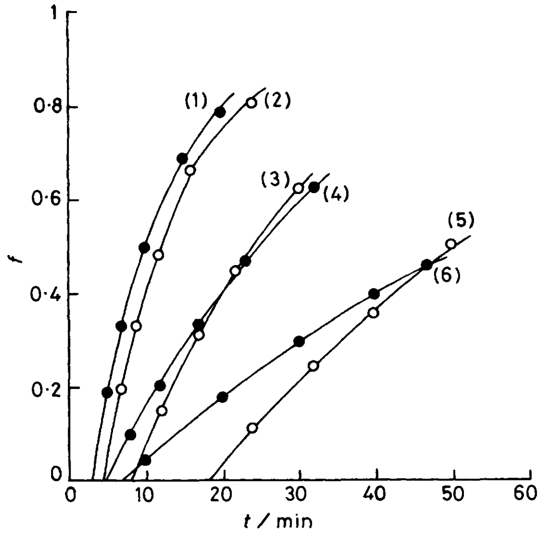

FIGURE 2 Crystallization of quartz as a function of time at different temperatures, 1 070 (1), 980 (2), 960 (3), 1 040 (4), 940 (5), and 1 020 °C (6); from amorphous SiO_2 containing $CaSiO_3$ (○) and from amorphous SiO_2 containing $MgSiO_3$ (●)

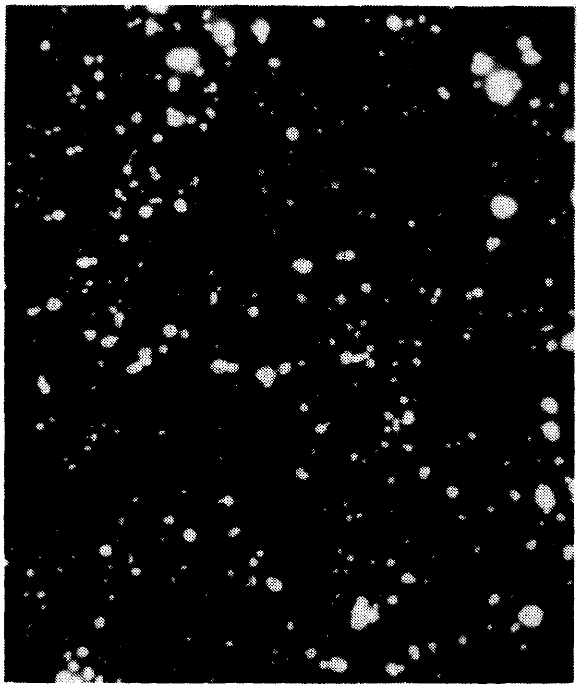

FIGURE 3 Electron micrograph of the quartz powder containing $CaSiO_3$ obtained by heating starting powder A for 1 h at 1 250 °C

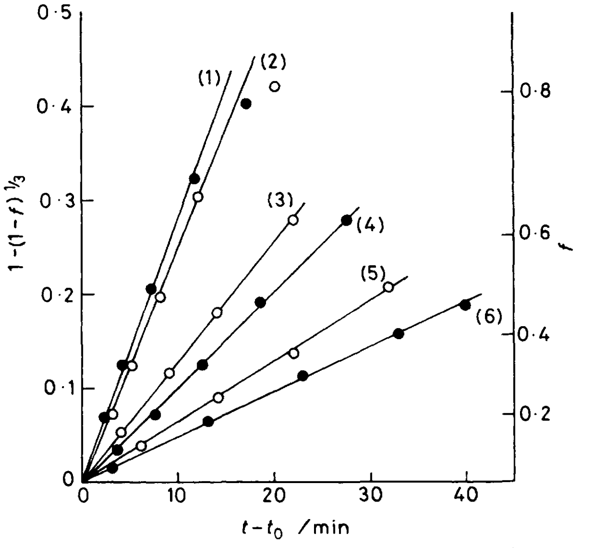

FIGURE 4 Plots of $1-(1-f)^{\frac{1}{3}}$ *vs.* time, $t - t_0$, of the data shown in Figure 2. See Figure 2 for key. f = Fraction of quartz crystallized in time $t - t_0$

terms of the contracting cube equation (1) (Figure 4),[13]

$$1 - (1 - f)^{\frac{1}{3}} = k(t - t_0) \qquad (1)$$

where f is the fraction of crystallization, t is the time in minutes, and t_0 the induction period. Equation (**1**), which has been employed to explain the kinetics of thermal decomposition of solids, is equivalent to one of the limiting forms of the Mampel equation.[14] Here, $k = v/r$, where v is the rate of advance of the interface and r is the radius of the particle. By considering the powder to be composed of a large number of isotropic spheres of uniform radius, Mampel derived a general expression for the fraction decomposed, from probability considerations, taking into account the possibility of the overlapping of the zones of decomposition radiating from neighbouring nuclei. The general expression reduces to simpler forms for three special cases: (i) for small values of t, f is proportional to t^4; (ii) at intermediate periods, equation (1) gives a close approximation; and (iii) for the final stages (t large), the reaction tends towards a unimolecular rate law. In the present case, equation (1) has been used to explain the kinetics, which indicates that crystallization is controlled by the rate of advance of interfacial growth. Activation energies are 435 and 498 kJ mol^{-1} in the presence of Ca^{2+} and Mg^{2+} respectively.

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