Crystallization and Transformation of Amorphous GeO_2 derived from Hydrolysis of Germanium Isopropoxide

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The cristobalite and α-quartz forms of GeO_2 crystallize on prolonged heating at 675—770 °C of amorphous GeO_2 prepared by hydrolysis of $Ge(OC_3H_7)_4$. The cristobalite is transformed into α-quartz in the later stages of heating. On heating at a rate of 10 °C min^{-1}, only the α-quartz crystallizes above 810 °C. The kinetics of crystallization of α-quartz from an amorphous phase has been studied by means of *X*-ray diffraction. The crystallization isotherms are described by the Avrami equation $\ln(1-f) = -kt^n$ with $n = 4$, the activation energy being 276 kJ mol^{-1}. A mixture of the cristobalite and α-quartz forms has been ground in air. The cristobalite is transformed into rutile. The transformation mechanism is discussed. On grinding, α-quartz is converted into the amorphous form. The rutile form, prepared by grinding, is transformed into α-quartz at 1 010—1 050 °C on heating at 10 °C min^{-1}.

The relative stability of the three modifications of GeO_2 was considered by Laubengayer and Morton[1] to be as follows: hexagonal $\rightleftharpoons$ tetragonal $\rightleftharpoons$ glass. Later, Sarver and Hummel[2] studied this subject in detail and published a phase diagram. Kotera and Yonemura[3,4] reported that the transformation of pure GeO_2 from the hexagonal (α-quartz) into the tetragonal (rutile) form could not be detected by *X*-ray diffractometry and that in the presence of a catalyst the kinetic data can be interpreted in terms of a first-order equation, the activation energy being *ca.* 418 kJ mol^{-1}. Similar results were obtained by Albers *et al.*[5] in a study of the kinetics of transformation of GeO_2 thin films. Böhm[6] showed that a third crystalline form, isostructural with cristobalite (tetragonal), can be obtained by prolonged heating of GeO_2 glass at *ca.* 600 °C. It was not possible, however, to prepare this modification in pure form, additional crystallization of the α-quartz form always being observed. The crystal structure of the cristobalite form has been determined in greater detail by Seifert *et al.*[7]

In the present study, it was found that when amorphous GeO_2 prepared by hydrolysis of germanium isopropoxide was heated for long times at 675—770 °C both the cristobalite and α-quartz forms crystallize in the early stages and the cristobalite form is transformed into α-quartz in the later stages. On the other hand, only the α-quartz form crystallized above 810 °C on heating at a rate of 10 °C min^{-1}. On the basis of this result, a kinetic study was made on the crystallization of the α-quartz form. The effect of dry grinding on the transformation of GeO_2 was also examined.

Experimental

Materials and Procedure.—Germanium isopropoxide, $Ge(OC_3H_7)_4$, was a pure grade. An alcoholic solution containing 6 wt.% alkoxide was refluxed for 3 h at 82 °C. Hydrolysis was carried out as follows. A three-necked flask equipped with a stirring rod, a dropping funnel, and a thermometer was used. The alkoxide solution (300 cm^3) was introduced into the flask and maintained at 25 °C. An aqueous ammonia solution (100 cm^3) was then added dropwise from the dropping funnel. The resulting suspension was stirred for 30 min at 20—25 °C. The hydrolysis product was separated from the suspension by centrifugation and dried at 60 °C under reduced pressure. The powder obtained is termed 'starting powder.' Its average particle size, as determined by electron microscopy, was *ca.* 400 Å.

Measurements.—Thermal analyses (t.g.a., d.t.a.) were carried out in air at a heating rate of 10 °C min^{-1}. α-Alumina was used as a standard material in d.t.a. The heated specimens were examined by high-temperature *X*-ray diffraction using nickel-filtered Cu-K_α radiation. The kinetics of crystallization of the α-quartz form were followed by *X*-ray measurements. The starting powder was pre-heated as described below. The specimens were placed in an electric furnace equipped with a temperature regulator, heated for the desired time, and then cooled rapidly to room temperature. The fractional crystallization was determined from the intensity ratio of the α-quartz peak (101) † to the α-quartz + CaF_2 peak (220) as an internal standard, using a calibration curve prepared with known compositions. The α-quartz powder for electron microscopic observation was dispersed in propan-2-ol by an ultrasonic treatment for 3 min. The dispersed drops were dried on carbon film, and observed under a 80-keV (*ca.* 1.28 × 10^{-15} J) beam. Dry grinding was achieved in a mortar of super-hard alloy (WC–Co). Specimens (0.5 g) were taken out at intervals and examined by *X*-ray diffraction.

Results and Discussion

Thermal Analysis.—Thermogravimetric examination of the starting powder showed a weight loss of 12.7% up to 230 °C, attributed to loss of ammonia, absorbed water, and surface-absorbed propan-2-ol. On the other hand, an exothermic peak in d.t.a. was observed at 810—915 °C. High-temperature *X*-ray analysis confirmed that this peak is due to the crystallization of the α-quartz form from an amorphous phase.

X-*Ray Analysis.*—The starting powder was amorphous, no significant change being recognized up to the temperature of the exothermic peak (810—915 °C) in d.t.a. The peaks corresponding to the α-quartz form appeared after heating at 810 °C, and increased rapidly in intensity up to 915 °C. A specimen heated at 915 °C showed the characteristic *X*-ray diffraction pattern of the α-quartz form. No other modifications were identified up to the melting temperature at *ca.* 1 100 °C.

As described above, only α-quartz crystallized when the starting powder was heated at a rate of 10 °C min^{-1}. However, prolonged heat treatments at 675—770 °C resulted in the crystallization of the cristobalite and α-quartz forms in the

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† Quantitative *X*-ray measurements, except for the (101) peak, are not possible due to the weakness in intensities.

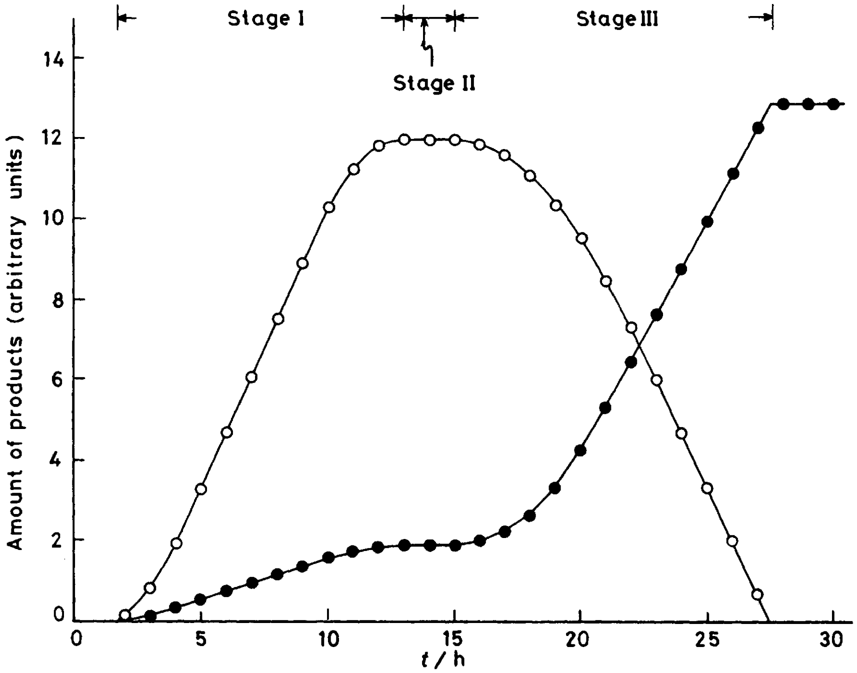

Figure 1. Results of X-ray diffraction analysis during the reaction at 690 °C. Phases: ○, cristobalite form; ●, α-quartz form

early stages and the transformation of the cristobalite form into α-quartz in the later stages. Figure 1 shows the results of X-ray diffraction analysis of the specimens quenched after heating for various times at 690 °C. The amounts of the two modifications in each specimen were determined by measuring the heights, $d = 4.08$ Å(011)[6] for the cristobalite form and $d = 3.43$ Å(101)[8] for the α-quartz form, of the strongest peaks in the spectra. Three stages were observed with lapse of time: simultaneous crystallization of the two modifications; completion of crystallization of both modifications, and transformation of the cristobalite into the α-quartz form. The amount of the cristobalite form crystallized in stage I decreased with increasing temperature and above 780 °C only the α-quartz form crystallized.

Kinetics of Crystallization of the α-Quartz Form.—The fraction of crystallization was determined as a function of time at different temperatures. The starting powder was preheated to 770 °C at a rate of 10 °C min^{-1}. A well crystallized specimen was obtained by heating the starting powder for 3 h at 1 000 °C. Crystallization isotherms were characterized by a sigmoidal shape, the kinetics being described by the Avrami equation (1) (Figure 2),[9] where f, t, k, and n are the fractional

$$\ln(1-f) = -kt^n \quad (n = 3.9\text{—}4.1) \qquad (1)$$

crystallization, time, rate constant, and a constant related to the reaction mechanism, respectively. Electron microscope observations showed that the α-quartz powder consists of nearly spherical particles. In view of this fact and also that the Avrami equation with $n = 4$ fitted the whole range of crystallization curves, three-dimensional nucleation of the α-quartz form is probably the rate-determining step. The activation energy calculated from the Arrhenius plot is 276 kJ mol^{-1}.

Dry Grinding.—Three specimens were used: (*a*) a mixture of cristobalite and α-quartz forms, (*b*) α-quartz, and (*c*) amorphous GeO_2. They were prepared by heating the starting powder for 21.5 h at 690 °C, for 3 h at 1 000 °C, and up to 770 °C at a rate of 10 °C min^{-1}, respectively. The variation of the observed intensities of the characteristic peaks of the modifications with the grinding time for specimen (*a*) is shown in Figure 3. The peak intensities of the cristobalite and α-quartz forms decreased rapidly with the initial grinding, and then

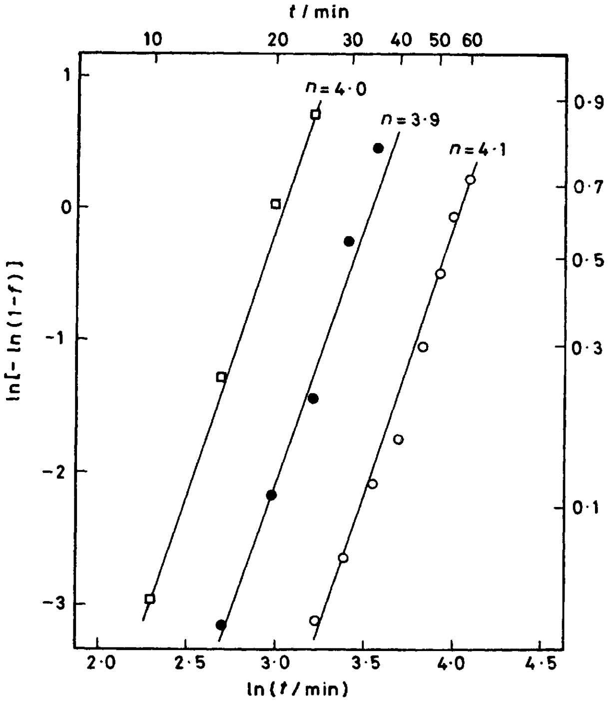

Figure 2. Avrami plots of the crystallization data of the α-quartz form. Temperature: ○, 800; ●, 820; □, 840 °C. f = Fraction of the α-quartz crystallized in time t

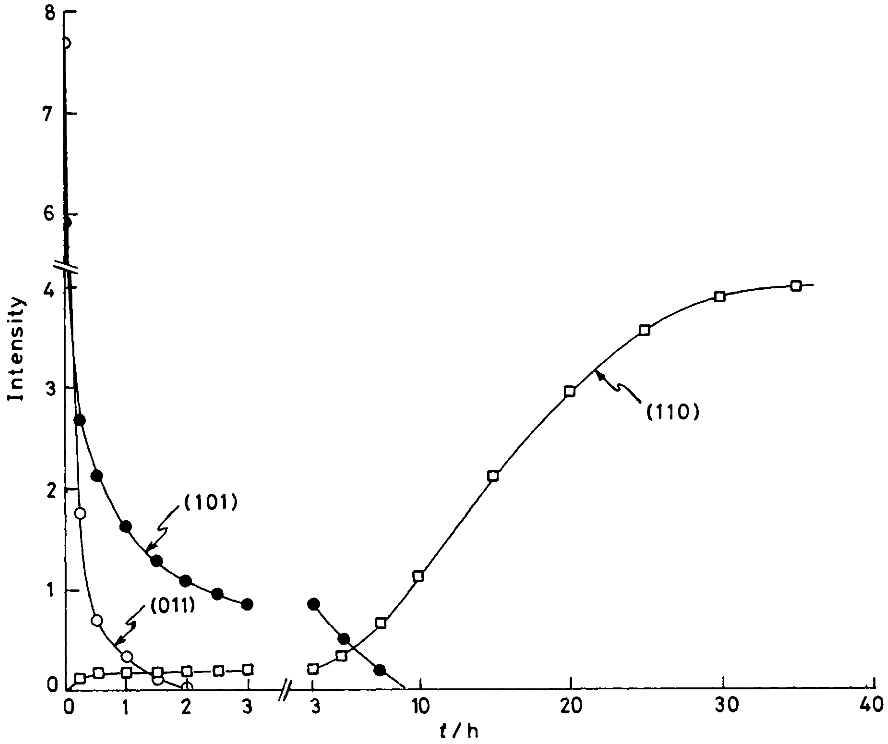

Figure 3. Phase conversion of the GeO_2 modifications with grinding time. Phases: ○, cristobalite form; ●, α-quartz form; □, rutile form. Grinding was carried out on a sample of weight 0.5 g

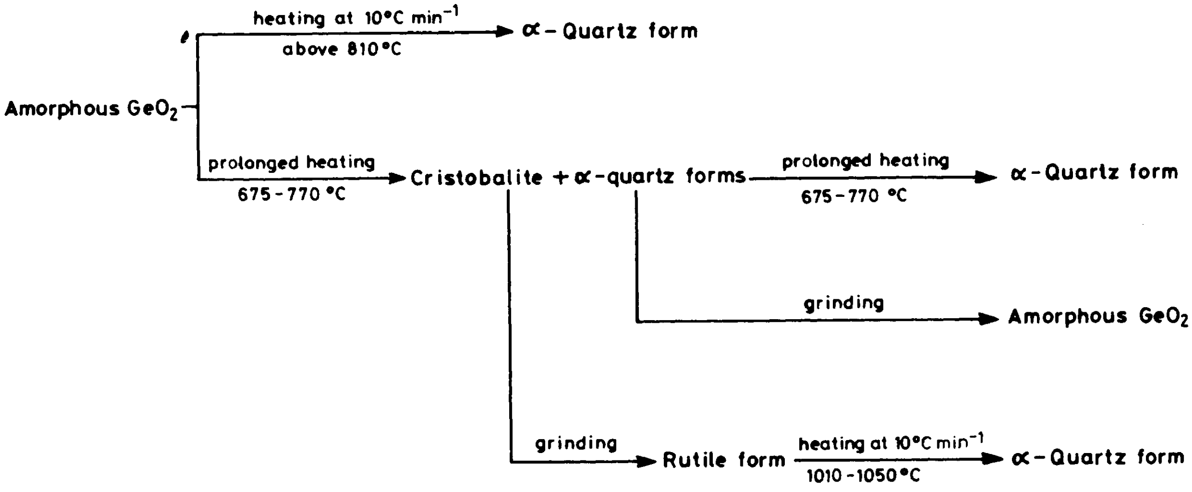

Figure 4. Crystallization and transformation of GeO_2 by heating and grinding

decreased gradually. Finally the peaks of both modifications disappeared, although there is a difference in the grinding time. No line broadening for both modifications was observed during the course of grinding. From the continuous decrease in peak intensities of the α-quartz form it is considered that the cristobalite form is not transformed into α-quartz. Peaks of the rutile form appeared from the beginning of griding and, although little change was observed initially, the intensities eventually increased with time. The formation of the rutile form can be ascribed to a transformation from cristobalite, since no transformation and crystallization were observed during grinding of specimens (*b*) and (*c*), respectively.

As shown in Figure 3, the transformation curve is sigmoidal. The initial short deceleratory period is followed, after an induction period, by an acceleratory period. It is reasonable to consider the transformation to start at the surface of the particles which are nucleated within a very short time (deceleratory period). During the induction period little transformation occurred. In the acceleratory period the bulk of the particles is transformed. The transformation is more complex than a simple cristobalite ⟶ rutile transformation, since the cristobalite was converted into the amorphous form after 2 h as shown in Figure 3. Therefore, perhaps the nuclei of the rutile form appear from the cristobalite in the initial period and thereby act as a catalyst for the crystallization of the remaining GeO_2 in the subsequent grinding. The fractional transformation of the rutile form was determined by the method described in the Experimental section, using the (110) peak. A well transformed specimen was obtained by grinding for 45 h. As a result, the acceleratory period can be represented by the Avrami equation[9] with $n = 2$. Considering that the rutile form prepared in this process comprises plate-like particles, the third stage probably represents two-dimensional growth of nuclei.

The crystallite sizes of the rutile form were calculated from the (110) peak using the Scherrer equation.[10] They had a constant value, *ca.* 120 Å, regardless of the grinding time. The rutile form was transformed into α-quartz at 1 010—1 050 °C on heating at a rate of 10 °C min^{-1}.

Conclusion

From the present thermal and *X*-ray data, the crystallization and transformation of GeO_2 can be summarized by Figure 4.

References

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