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Kinetics on the Formation and Transformation of Alkoxy-derived $SrSiO_3$

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Synopsis. A metastable modification of $SrSiO_3$ was formed at 850—910 °C from mixed powders prepared by the alkoxy-method. Crystallization isotherms were best described by the first-order equation and the activation energy was determined as 130 kcal/mol. The kinetics on the transformation of metastable to stable $SrSiO_3$ was also studied.

Though $SrSiO_3$ is known only in the pseudo-wollastonite modification,[1] Takahashi and Roy[2] reported that a new modification is obtained by heating the $SrSiO_3$ glass prepared by the splat-cooled method. It was found that this compound, apparently metastable, is formed during the course of heating of alkoxy-derived $SrSiO_3$. The present study is concerned with the kinetics on the formation of metastable $SrSiO_3$ and the transformation of metastable into stable $SrSiO_3$.

Experimental

Silicon ethoxide used was of guaranteed purity. Strontium methoxide was prepared by the reaction of strontium metal and dehydrated methyl alcohol. The purity of strontium metal used was 99%. A mixture of these alkoxides with the mole ratio $Sr^{2+}/Si^{4+}=1:1$ was prepared, and then poured into aqueous solution of ammonia at *ca.* 30 °C. The temperature was slowly raised up to 90 °C with stirring. The mixed powders hydrolyzed in this way were washed repeatedly with hot distilled water and dried at 40 °C under reduced pressure. The average particle size of the mixed powders is approximately 400—500 Å.

Results and Discussion

The TG of the mixed powders was carried out in the air from room temperature to 1000 °C(Fig. 1). The weight loss of 11% up to 650 °C is attributed to the loss of absorbed H_2O, $NH_3(aq)$, and organic residue from the parent alcohol. DTA of the mixed powders was also performed. Two exothermic reactions were observed at 850—910 °C and 950—1020 °C. From the results of X-ray diffraction, the reactions were found to be the crystallization of metastable $SrSiO_3$ from an amorphous phase and the transformation of metastable into stable $SrSiO_3$, respectively.

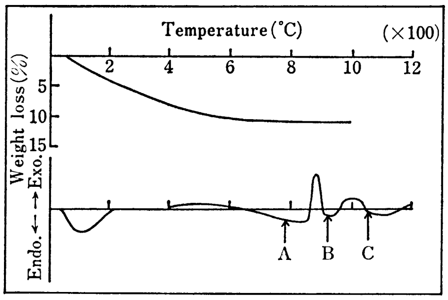

Fig. 1. TG and DTA curves of alkoxy-derived powder. Arrows show the temperatures at which the starting material was heated to obtain three specimens for X-ray diffraction.

Figure 2 shows the variation of X-ray diffraction patterns of $SrSiO_3$ with increasing temperature. The mixed powders as a raw material were amorphous, no significant changes being observed up to 820 °C. The peaks corresponding to metastable $SrSiO_3$[2] appeared after heat treatment at 850 °C for 20 min, and the intensity increased rapidly up to 900 °C. The specimen heated at 1050 °C showed an X-ray diffraction pattern of only stable $SrSiO_3$.[3]

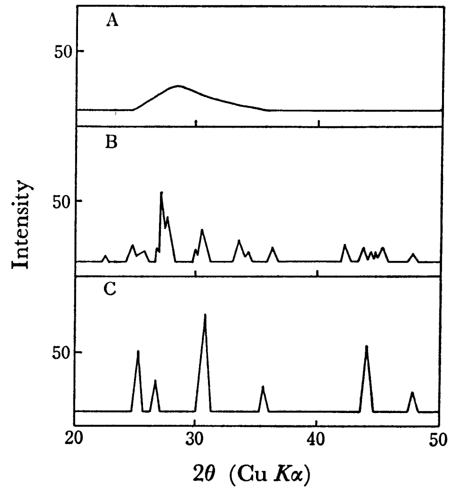

Fig. 2. X-Ray diffraction patterns for alkoxy-derived $SrSiO_3$ powder.
A: 780 °C, B: 920 °C, C: 1050 °C.
Heating rate: 600 °C/h.

Figure 3 shows the fraction of the metastable $SrSiO_3$

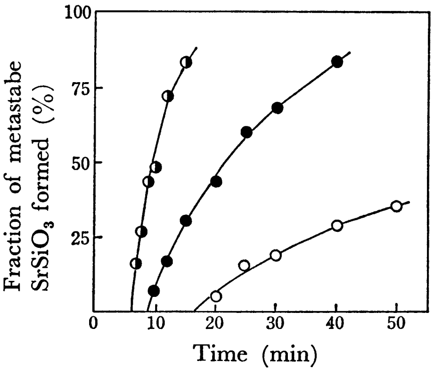

Fig. 3. Formation of metastable $SrSiO_3$ as a function of time at different temperatures.
○: 850 °C, ●: 870 °C, ◑: 890 °C.

crystallization determined for 850, 870, and 890 °C. The mixed powders were pre-heated at 400 °C for 15 min. The fraction of crystallization of each specimen was determined from the height of d=3.28 Å(2θ=27.2°) which is the strongest line of the metastable $SrSiO_3$ spectrum. A well-crystallized specimen was obtained by heating the alkoxy-derived mixed powders at 900 °C for 30 min. Calcium fluoride was used as a standard material. Induction periods were observed, attempts being made to fit the results to kinetic laws by considering the induction periods. The data can be interpreted in terms of the first-order equation. Figure 4 shows the first-order plots of $-\ln(1-\alpha)$ against t, where α is the fraction of crystallization and t time. The rate constants were determined from the slopes of straight lines. The value of activation energy calculated from the Arrhenius plot was *ca.* 130 kcal/mol. This represents the activation energy employed for establishing active nucleation centers.[4]

Figure 5 shows the fraction of the transformation of metastable into stable $SrSiO_3$ as a function of time at different temperatures. The specimens heated at 900 °C for 30 min were used as starting material. The fraction of transformation was established by determining the decrease of height of the strongest line(d=3.28 Å) in the metastable diffraction pattern. Transformation isotherms were described by the zero-order equation $\alpha=kt$, where α is the fraction of transformation, t time and k the rate constant of propagation.[4] The result suggests that the transformation, which might take place in two processes(Fig. 5, broken line), is due to only a rearrangement of atoms or ions within the crystal, no penetration of a new phase from the surface being required. The values of activation energy were *ca.* 143 kcal/mol and 44 kcal/mol for initial and final stages, respectively.

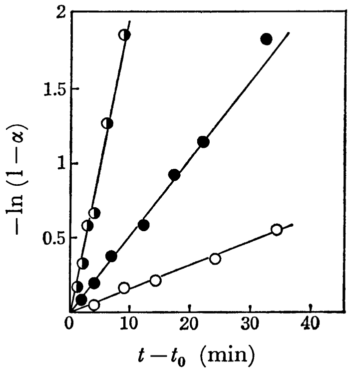

Fig. 4. First-order plots of the data of Fig. 3.
○: 850 °C, ●: 870 °C, ◑: 890 °C.

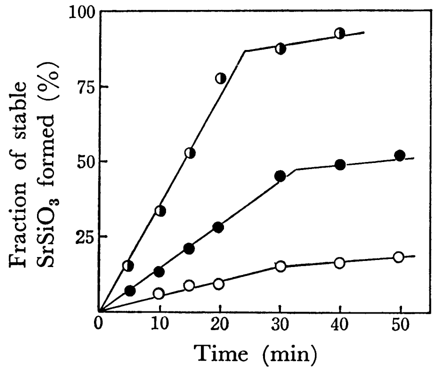

Fig. 5. Phase transformation from metastable to stable $SrSiO_3$ as a function of time at different temperatures.
○: 950 °C, ●: 970 °C, ◑: 990 °C.

References

1) E. T. Carson and L. S. Wells, *J. Res. Nat. Bur. Stand.*, **51**, 73 (1953).

2) T. Takahashi and R. Roy, *J. Am. Ceram. Soc.*, **58**, 348 (1975).

3) X-Ray powder data file (ASTM card 6-0415).

4) R. W. Grimshaw, J. Hargreaves, and A. L. Roberts, *Trans. Brit. Ceram. Soc.*, **55**, 36 (1956).