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Formation of Sr_2SiO_4 and $SrSiO_3$ from Strontium Silicate Hydrate Prepared by the Alkoxy Method

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Synopsis. Sr_2SiO_4 and metastable $SrSiO_3$ were formed directly at low temperatures from $3SrO \cdot 2SiO_2 \cdot 3H_2O$ prepared by the alkoxy method. The transformation of metastable into stable $SrSiO_3$ was observed at 900—980 °C. A kinetic study was made on the formation of Sr_2SiO_4.

Strontium silicon oxide exists in three forms, $SrSiO_3$ (monoclinic), Sr_2SiO_4(monoclinic), and Sr_3SiO_5(tetragonal). Though $SrSiO_3$ has been known only in the pseudo-wollastonite modification,[1] Takamori and Roy[2] obtained a compound of new modification by heating $SrSiO_3$ glass. Yamaguchi *et al.*[3] found that the metastable compound is formed from an amorphous substance prepared by the alkoxy method, and carried out kinetic studies on the formation of metastable $SrSiO_3$ and the transformation of metastable into stable $SrSiO_3$. Their studies on the solid state reaction of an equimolar mixture between strontium carbonate and amorphous silica showed that stable $SrSiO_3$ is formed *via* two processes: (a) transformation of metastable into stable $SrSiO_3$; (b) solid state reaction between Sr_2SiO_4 and SiO_2.[4] This study was undertaken to elucidate the reaction mechanism in the heating process of the alkoxy-derived $3SrO \cdot 2SiO_2 \cdot 3H_2O$ and the kinetics of formation of Sr_2SiO_4.

Experimental

Silicon ethoxide of guaranteed purity was used. Strontium methoxide was synthesized by heating strontium metal, purity 99.9%, in an excessive amount of dehydrated methanol at 65 °C for 5 h. A mixture of these alkoxides with mole ratio $Sr^{2+}/Si^{4+}=3:2$ was prepared, and then poured into aqueous ammonia solution at 30 °C. The temperature was slowly raised up to 85 °C with stirring. The resulting mixed powder was washed repeatedly with hot water and dried at 65 °C under reduced pressure. The product was identified as $3SrO \cdot 2SiO_2 \cdot 3H_2O$[1] by X-ray diffraction analysis using nickel filtered copper $K\alpha$.

Results and Discussion

DTA was carried out at a heating rate of 10 °C/min. A large endothermic peak corresponding to dehydration was observed at 270—410 °C. The specimen turned amorphous after the completion of dehydration. Three exothermic reactions were observed at 700—815 °C, 815—860 °C, and 900—980 °C. X-Ray diffraction analysis confirmed that the first exothermic peak (700—815 °C) is due to the formation of Sr_2SiO_4, the second (815—860 °C) to that of metastable $SrSiO_3$, and the third (900—980 °C) to the transformation of metastable into stable $SrSiO_3$. The result is in line with that reported, *viz.*, Sr_2SiO_4 is always the first product obtained in solid state reaction,[4—7] regardless of the Sr/Si ratio.

Figure 1 shows the results of X-ray diffraction analysis of the specimens heated at 870 °C with various reaction times. The specimen was pre-heated at 450 °C for 30 min. The fractions of Sr_2SiO_4, metastable $SrSiO_3$, and stable $SrSiO_3$ were determined from heights $d=2.80$ Å, $d=2.68$ Å, and $d=3.57$ Å, respectively, in comparison with those of the well-formed products obtained by heating the specimens at 900 °C 1 h for Sr_2SiO_4, 860 °C 30 min for metastable $SrSiO_3$, and 1000 °C 1 h for stable $SrSiO_3$. The fractions of Sr_2SiO_4 and metastable $SrSiO_3$ attained a constant value in a short time. This suggests that both products are formed directly from the starting substance. No change was observed in the fraction of Sr_2SiO_4. On the other hand, the transformation of metastable into stable $SrSiO_3$ was observed with lapse of time. From the results as well as DTA data, the reaction mechanism can be postulated as shown in Fig. 2. More than one compound were observed during the course of solid state reaction in silicate systems; the final product can be predicted from the initial composition by referring to the equilibrium phase diagram. Results of the solid state reaction between strontium carbonate

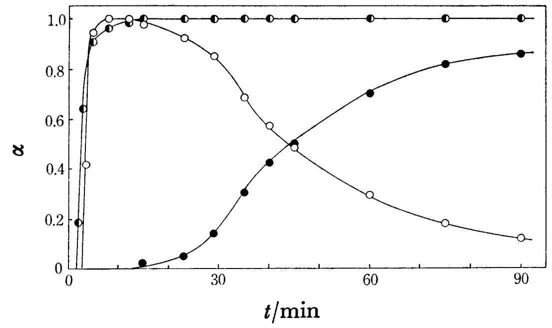

Fig. 1. Results of X-ray diffraction analysis during the reaction at 870 °C.
○: Metastable $SrSiO_3$, ●: stable $SrSiO_3$, ◐: Sr_2SiO_4.

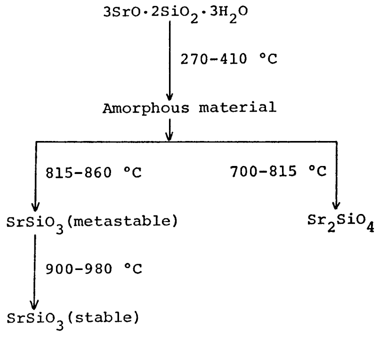

Fig. 2. Reaction scheme to the formation of $SrSiO_3$ and Sr_2SiO_4 from $3SrO \cdot 2SiO_2 \cdot 3H_2O$ as a raw material.

and amorphous silica (Sr/Si=3:2), mixed by ball-milling for 20 h, showed that metastable and stable $SrSiO_3$, Sr_2SiO_4, Sr_3SiO_5, and free SrO are formed during the course of heating. The discrepancy in the two results should be attributed to the difference in the contact between reactant between particles.

The fraction of Sr_2SiO_4 formation was determined by the lapse of time, since it is a function of time at different temperatures. The starting powder was preheated under the same conditions as mentioned above. The fraction of formation of each specimen was determined from the height $d=2.80$ Å ($2\theta=31.9°$), the strongest line of the Sr_2SiO_4 spectrum as observed by X-ray diffraction. Alpha-crystobalite was used as an internal standard. Short induction periods were observed, attempts being made to fit the results to kinetic laws by considering the induction periods. As shown in Fig. 3, formation isotherms are best described by the first-order equation $-\ln(1-\alpha)=k(t-t_0)$, where α is the fraction of formation, t time and t_0 induction period. The rate constants were determined from the slopes of the straight lines. Activation energies calculated from the Arrhenius plot were 142 kJ/mol and 113 kJ/mol for initial and final stages, respectively. They might represent activation energies employed for establishing a nucleation process and a propagation process, respectively.[8)]

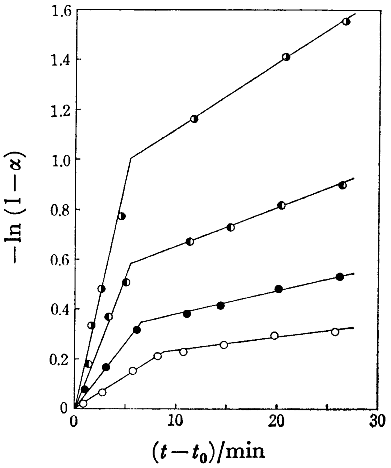

Fig. 3. Plots of $-\ln(1-\alpha)$ *vs.* time $t-t_0$.
○: 680 °C, ●: 720 °C, ◐: 760 °C, ◑: 800 °C.

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