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MECHANISM OF SOLID STATE REACTION BETWEEN $SrCO_3$ AND SiO_2

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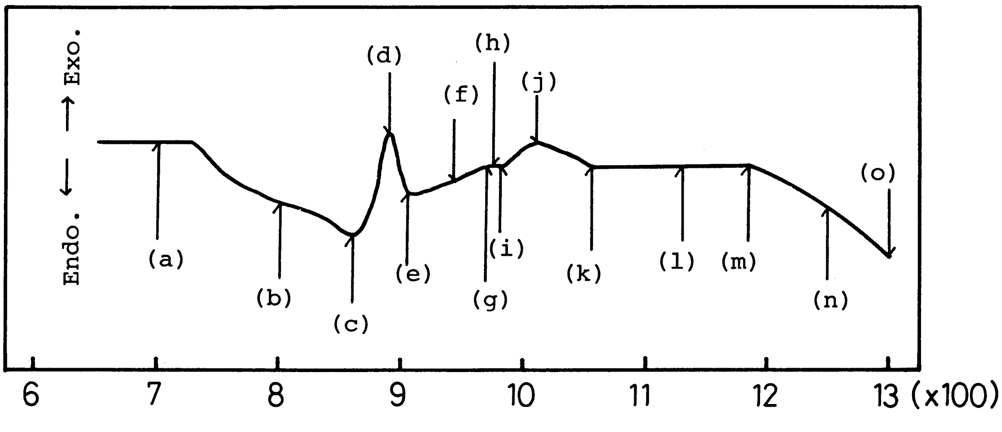
Metastable $SrSiO_3$ was formed during the course of the solid state reaction of $SrCO_3$ and SiO_2. The reaction mechanism was investigated by means of DTA and X-ray diffraction analysis. It was found that stable $SrSiO_3$ is formed via two processes: (a) transformation of metastable into stable $SrSiO_3$; (b) solid state reaction between Sr_2SiO_4 and SiO_2.

Though $SrSiO_3$ has been known only in the pseudo-wollastonite modification,$^{1)}$ Takahashi and Roy$^{2)}$ suggested that a new modification is obtained by heating the $SrSiO_3$ glass prepared by the splat-cooled method. Yamaguchi and Shimizu$^{3)}$ reported that this compound, apparently metastable, is formed at 850-910 °C from the mixed powder prepared by the alkoxy-method. In the present study, it was found that metastable $SrSiO_3$ is formed during the course of the solid state reaction between an equimolar mixture of $SrCO_3$ and SiO_2. A reaction mechanism was investigated by means of DTA and X-ray diffraction analysis using Cu $K\alpha$ radiation.

Reagent-grade chemicals were used as starting materials. Strontium carbonate and amorphous silica were pre-heated for 3 h at temperatures of 500 and 600 °C, respectively. The equimolar mixture was weighed, and then ball-milled in a polyethylene pot containing agate balls for 20 h. No liquid medium was used. The average particle size of the mixed powder is ca. 1.7 μm.

The DTA of the mixed powder was carried out in air from room temperature to 1300 °C(Fig. 1). Four reactions were observed at 730-970 °C, 860-910 °C, 980-1055 °C, and 1180-1300 °C. The X-ray diffraction analysis confirmed that the first endothermic peak(730-970 °C) is due to the formation of Sr_2SiO_4 and the second(1180-1300 °C) is due to that of stable $SrSiO_3$ by the solid state reaction between Sr_2SiO_4 and SiO_2. On the other hand, two exothermic reactions at 860-910 °C and 980-1055 °C were found to be the formation of metastable $SrSiO_3$ and the transformation of metastable into stable $SrSiO_3$, respectively.

Table 1 shows the results identified by X-ray diffraction analysis for specimens obtained by rapid quenching to room temperature after heating up to a definite temperature at the rate of 10 °c/min. No significant changes of the mixed powder were observed up to 700 °C. The X-ray diffraction peaks corresponding to Sr_2SiO_4 appeared after heating at 730 °C for 5 min, and the intensity increased up to 970 °C. According to Jander and Wuhrer,[4] Sr_2SiO_4 is always the first product formed from the mixture at any Sr/Si ratio. The present result is consistent with that of Jander et al. The peaks of $SrCO_3$ as a starting material disappeared at 970 °C. Irrespective of the formation of Sr_2SiO_4, metastable $SrSiO_3$[2,3] was formed in the temperature range



Temperature(°C)

Fig. 1 DTA curve for the equimolar mixture of $SrCO_3$ and SiO_2. Sample weight: 80 mg, Heating rate: 10 °C/min. Arrows show the temperatures at which the starting material was heated in order to obtain several specimens for X-ray diffraction analysis.

Table 1 Results identified by X-ray diffraction analysis for specimens heated at various temperatures.

Temperature(°C)	Phase
730-860	$SrCO_3$, Sr_2SiO_4
860-970	$SrCO_3$, Sr_2SiO_4, metastable $SrSiO_3$
970-980	Sr_2SiO_4, metastable $SrSiO_3$
980-1055	Sr_2SiO_4, metastable $SrSiO_3$, stable $SrSiO_3$
1055-1300	Sr_2SiO_4, stable $SrSiO_3$

The single phase of stable $SrSiO_3$ was obtained by heating at 1300 °C for 5 h.

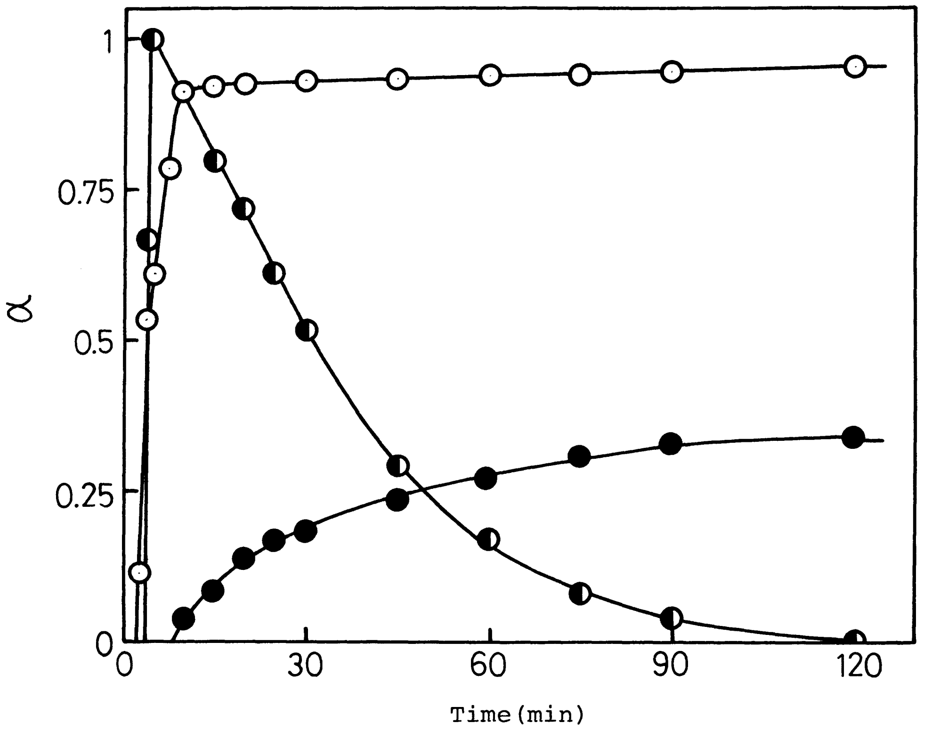


Fig. 2 Results of X-ray diffraction analysis during the reaction at 950 °C.

○:Sr_2SiO_4, ●:stable $SrSiO_3$, ◐:metastable $SrSiO_3$.

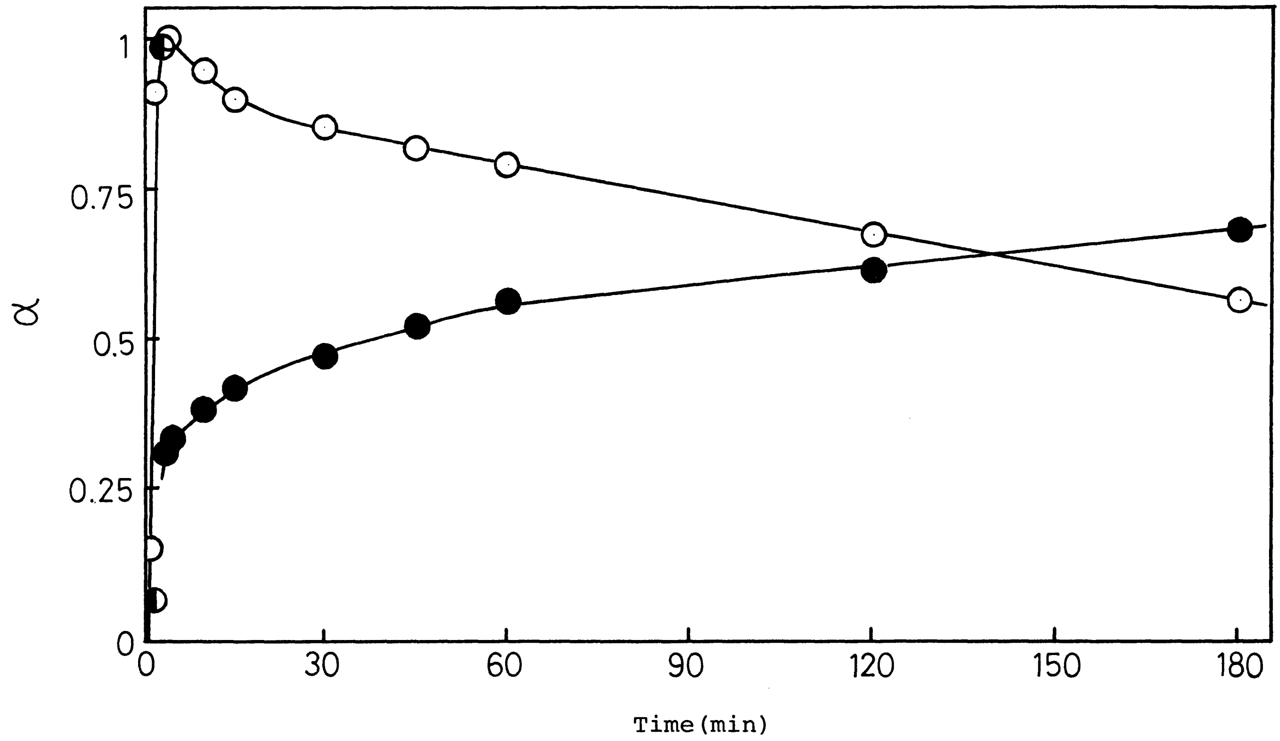


Fig. 3 Results of X-ray diffraction analysis during the reaction at 1200 °C.

○:Sr_2SiO_4, ●:stable $SrSiO_3$, ◐:metastable $SrSiO_3$.

of 860 to 910 °C, and transformed to stable $SrSiO_3$ between 980 and 1055 °C. The intensity of stable $SrSiO_3$ above 1180 °C increased gradually in inverse proportion to that of Sr_2SiO_4, and the specimen heated at 1300 °C for 5 h showed an X-ray diffraction pattern of only stable $SrSiO_3$.

It is important to consider two processes for the formation of stable $SrSiO_3$: (a) transformation of metastable into stable $SrSiO_3$; (b) solid state reaction between Sr_2SiO_4 and SiO_2. Figure 2 shows the results of X-ray diffraction analysis of the specimens heated at various reaction times at 950 °C. The fractions of Sr_2SiO_4, metastable $SrSiO_3$, and stable $SrSiO_3$ were determined from the heights of d=2.86 Å, d=2.68 Å, and d=3.57 Å, respectively, in comparison with those of the well-formed specimens, which were obtained by heating the mixed powder at 1000 °C 1 h for Sr_2SiO_4, 910 °C 1 h for metastable $SrSiO_3$, and 1300 °C 5 h for stable $SrSiO_3$. The fraction of Sr_2SiO_4 increased with the lapse of time regardless of the formation of $SrSiO_3$. This result suggests that Sr_2SiO_4 was directly formed by the reaction between $SrCO_3$ and SiO_2, not from $SrSiO_3$ and $SrCO_3$. The transformation of metastable into stable $SrSiO_3$ was observed from 5 to 120 min, and finally the fraction of stable $SrSiO_3$ was found to be 33.3±0.2%. Reaction isotherms above 1180 °C showed that the residual fraction, 66.7 ±0.2 %, is formed by the solid state reaction between Sr_2SiO_4 and SiO_2(Fig. 3). From the above mentioned results and the DTA data shown in Fig. 1, the reaction mechanism can be proposed as follows.

$$2SrCO_3 + SiO_2 \xrightarrow[730\text{-}970\ ^\circ C]{} Sr_2SiO_4 + 2CO_2 \qquad (1)$$

$$SrCO_3 + SiO_2 \xrightarrow[860\text{-}910\ ^\circ C]{} SrSiO_3(\text{metastable}) + CO_2 \qquad (2)$$

$$SrSiO_3(\text{metastable}) \xrightarrow[980\text{-}1055\ ^\circ C]{\text{transformation}} SrSiO_3(\text{stable}) \qquad (3)$$

$$Sr_2SiO_4 + SiO_2 \xrightarrow[1180\text{-}1300\ ^\circ C]{\text{solid state reaction}} 2SrSiO_3(\text{stable}) \qquad (4)$$

Effects of ball-milling and atmosphere on the reaction and the kinetics on the formation of Sr_2SiO_4 and $SrSiO_3$ are now under investigation and will be reported soon.

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