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Kinetics of the Formation of Alkoxy-derived Barium Metasilicate

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Amorphous $BaSiO_3$ or a mixture of this and $BaSiO_3 \cdot H_2O$ was formed by the simultaneous hydrolysis of barium and silicon alkoxides. The temperature of hydrolysis and the time of aging influence the crystallization of amorphous $BaSiO_3$ into $BaSiO_3 \cdot H_2O$. The decomposition of $BaSiO_3 \cdot H_2O$ into crystalline $BaSiO_3$ was analyzed by isothermal thermogravimetry. Decomposition isotherms were constructed by the equation $-\ln(1-\alpha)=kt$ and the activation energy was determined as 143.5 kJ/mol. The kinetics of crystallization of amorphous into crystalline $BaSiO_3$ was interpreted by the equation $1-(1-\alpha)^{1/3}=kt$. Activation energies were 276 kJ/mol and 204 kJ/mol for the initial and final stages, respectively.

Barium metasilicate ($BaSiO_3$) can be prepared by two methods: (a) solid state reaction of an equimolar mixture of barium carbonate and silica;[1-4] (b) decomposition of barium metasilicate hydrates. Barium metasilicate hydrates, such as $BaSiO_3 \cdot H_2O$, $BaSiO_3 \cdot 1.5H_2O$, and $BaSiO_3 \cdot 6H_2O$, are formed by the reaction of sodium silicate solutions and either barium chloride or barium hydroxide solutions.[5,6] Krüger and Wieker[6] reported that amorphous barium silicates are precipitated by addition of barium chloride solutions to sodium silicate solutions, and their crystallization into various barium silicate hydrates is dependent on the Na : Si ratio, the concentration of sodium silicate solutions, the Ba : Si ratio and the temperature during precipitation. The hydrothermal reaction using barium silicate hydrates of various compositions was studied.[5] However, no kinetic study on the formation of crystalline $BaSiO_3$ from amorphous $BaSiO_3$ and barium metasilicate hydrates has been carried out.

In the present study, it was found that amorphous $BaSiO_3$ or mixtures of this amorphous compound and $BaSiO_3 \cdot H_2O$ are formed by the simultaneous hydrolysis of barium and silicon alkoxides. Conditions for the crystallization of amorphous $BaSiO_3$ into $BaSiO_3 \cdot H_2O$ during hydrolysis were examined, and kinetic studies made on the decomposition of $BaSiO_3 \cdot H_2O$ and the crystallization of amorphous into crystalline $BaSiO_3$. The kinetic data were analyzed with use of available solid state models.

Experimental

Materials and Procedure. Silicon ethoxide of guaranteed purity was used. Barium isopropoxide was synthesized by heating barium metal (purity 99.9%) in an excess amount of dehydrated 2-propanol at 82 °C for 5 h in a nitrogen atmosphere. An alcoholic solution containing 12 wt% mixed alkoxides prepared in the mole ratio, Ba^{2+}/Si^{4+} 1 : 1, was refluxed under the same conditions. Hydrolysis was carried out as follows. A five-necked flask equipped with a refluxed condenser, a dropping funnel, a strirring rod, a thermometer and a thermo-controller was used. 400 ml of water was introduced into the flask, and then heated to the desired temperature. 100 ml of the mixed alkoxide solution was added dropwise from the dropping funnel to the stirred water in the flask. The resulting suspension was stirred. The product was separated from the suspension by filtration and dried at 60 °C under reduced pressure.

Measurement. Differential thermal analysis (DTA) was performed in the air at a 10 °C/min rate. Alpha-alumina of high purity was used as a reference substance. The products and the heated specimens were identified by means of DTA data and X-ray diffraction using nickel filtered copper K_α. The weight change was recorded as function of time with a thermobalance.

Results and Discussion

Hydrolysis Product. Results obtained under various conditions are given in Table 1. The products at 30 °C were amorphous. Barium silicates other than $BaSiO_3$ and free species were not observed during the course of heating. Thus, the products might be considered to be a compound corresponding to amorphous $BaSiO_3$. The peaks of $BaSiO_3 \cdot H_2O$[7] were recognized when subjected to hydrolysis at 45 °C for 30 min. Their intensity increased gradually with increase in hydrolysis temperature and time. Judging from this and the amount of crystalline $BaSiO_3$ formed by the decomposition of $BaSiO_3 \cdot H_2O$, the temperatures of hydrolysis and the aging time were found to be impor-

TABLE 1. HYDROLYSIS PRODUCT AND THE AMOUNT OF $BaSiO_3$ FORMED BY THE DECOMPOSITION OF $BaSiO_3 \cdot H_2O$ AND BY THE CRYSTALIZATION OF AMORPHOUS $BaSiO_3$

Run	Temp/°C	Time/min	Identified phase	Fraction/% A[a)]	Fraction/% B[b)]
1	30	15	Amorphous	0	100
2	30	30	Amorphous	0	100
3	30	60	Amorphous	0	100
4	45	15	Amorphous	0	100
5	45	30	$BaSiO_3 \cdot H_2O$	5.6	94.4
6	45	60	$BaSiO_3 \cdot H_2O$	7.2	92.8
7	60	15	$BaSiO_3 \cdot H_2O$	18.7	81.3
8	60	30	$BaSiO_3 \cdot H_2O$	21.6	78.4
9	60	60	$BaSiO_3 \cdot H_2O$	23.5	76.5
10	70	15	$BaSiO_3 \cdot H_2O$	26.5	73.5
11	70	30	$BaSiO_3 \cdot H_2O$	28.8	71.2
12	70	60	$BaSiO_3 \cdot H_2O$	30.2	69.8
13	80	15	$BaSiO_3 \cdot H_2O$	36.3	63.7
14	80	30	$BaSiO_3 \cdot H_2O$	38.8	61.2
15	80	60	$BaSiO_3 \cdot H_2O$	40.4	59.6

a) Amount of $BaSiO_3$ formed by decomposition of $BaSiO_3 \cdot H_2O$. b) Amount of $BaSiO_3$ formed by crystallization of amorphous $BaSiO_3$.

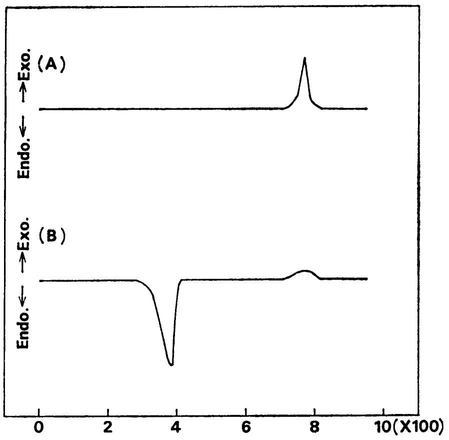

Fig. 1. DTA curves of the products hydrolyzed for 15 min at 30 °C (A) and for 1 h at 80 °C (B).
Sample weight: 60 mg.

tant factors for the crystallization of amorphous $BaSiO_3$ into $BaSiO_3\cdot H_2O$.

Formation Process of Crystalline $BaSiO_3$. The DTA curves of the products (Table 1, runs 1 and 15) are shown in Fig. 1. An exothermic reaction (run 1) was observed at 700—820 °C. X-Ray diffraction analysis confirmed that the reaction is due to the crystallization of amorphous $BaSiO_3$. On the other hand, a large endothermic peak (run 15) corresponding to the decomposition of $BaSiO_3\cdot H_2O$ was observed at 280—410 °C. The compound $BaSiO_3\cdot H_2O$ turned into crystalline $BaSiO_3$ after the completion of decomposition. The small exothermic peak (700—820 °C) is due to the crystallization of amorphous $BaSiO_3$ as in the case of run 1. This suggests that $BaSiO_3$ is formed *via* two stages: (a) decomposition of $BaSiO_3\cdot H_2O$, (b) crystallization of amorphous $BaSiO_3$.

All the products were heated at 450 °C and 900 °C for 1 h, respectively, and the amount of crystalline $BaSiO_3$ formed at each stage was determined from the height of the peak of d=3.43 Å which is the strongest of the $BaSiO_3$ spectrum.[8] The fractions of crystalline $BaSiO_3$ formed by the decomposition of $BaSiO_3\cdot H_2O$ and the crystallization of amorphous $BaSiO_3$ are dependent on the starting products which is strongly affected by hydrolysis temperature (Table 1).

Kinetics of the Decomposition of $BaSiO_3\cdot H_2O$. The decomposition of $BaSiO_3\cdot H_2O$ (run 15) was analyzed by isothermal thermogravimetric measurement. The product (average particle size *ca.* 800 Å) was heated at 200 °C for 30 min. Figure 2 shows α-t curves obtained at various temperatures, where α is the fractional decomposition and t time. Attempts were made to fit the results to kinetic laws. As shown in Fig. 3, decomposition isotherms are represented by the following equation over the whole range of fraction:

$$-\ln(1-\alpha) = kt. \qquad (1)$$

The rate constants were determined from the slopes of the straight lines. The activation energy calculated from the Arrhenius plot is 143.5 kJ/mol. This might represent the activation energy consumed for establishing

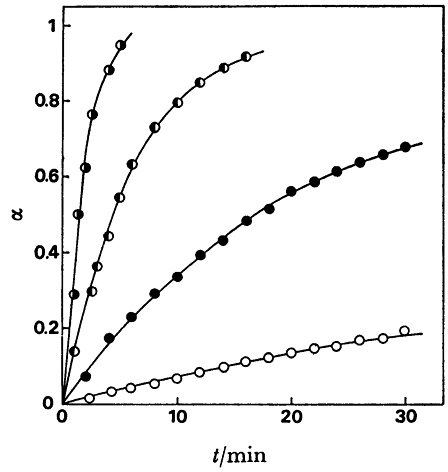

Fig. 2. Decomposition of $BaSiO_3\cdot H_2O$ as a function of time at different temperatures.
○: 290 °C, ●: 320 °C, ◐: 250 °C, ◑: 380 °C.

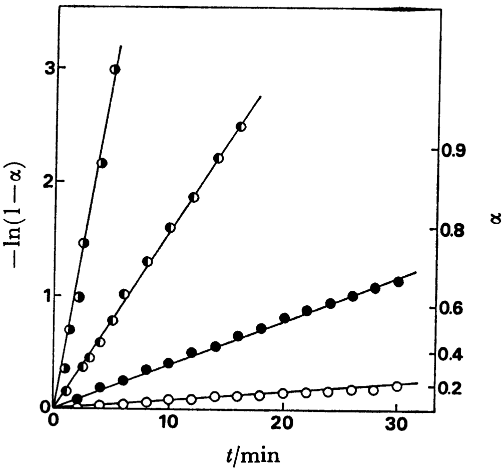

Fig. 3. Plots of $-\ln(1-\alpha)$ *vs.* time t of the data shown in Fig. 2.
○: 290 °C, ●: 320 °C, ◐: 350 °C, ◑: 380 °C.

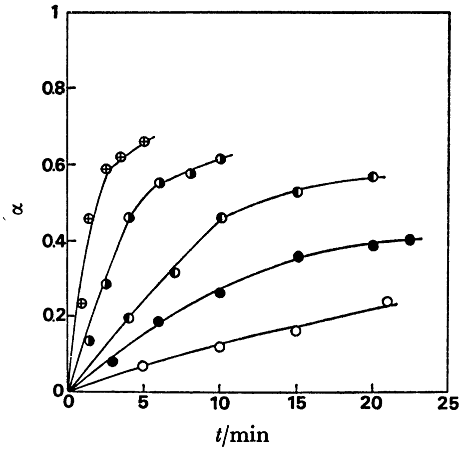

Fig. 4. Crystallization of amorphous $BaSiO_3$ as a function of time at different temperatures.
○: 680 °C, ●: 700 °C, ◐: 720 °C, ◑: 750 °C, ⊕: 780 °C.

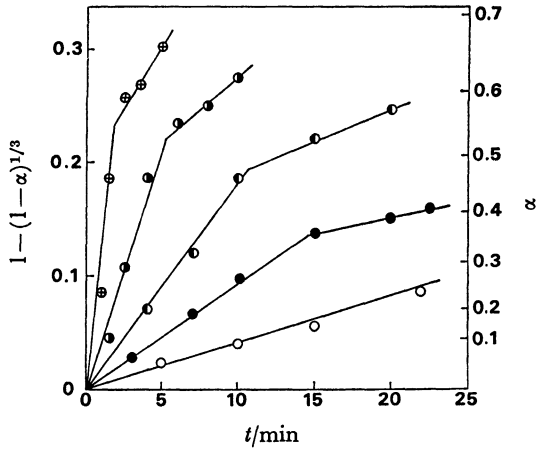

Fig. 5. Plots of $1-(1-\alpha)^{1/3}$ *vs.* time t of the data shown in Fig. 4.
○: 680 °C, ●: 700 °C, ◐: 720 °C, ◑: 750 °C, ⊕: 780 °C.

active nucleation centers.[9]

Kinetics of the Crystallization of Amorphous $BaSiO_3$. Figure 4 shows the fraction of the crystallized $BaSiO_3$ at different temperatures. The product of run 1 was heated at 550 °C for 1 h. The fractional crystallization of each specimen was determined from the height of the main characteristic peak (d=3.43 Å). A well-crystallized specimen was obtained by heating the starting product at 900 °C for 1 h. Magnesium oxide was used as an internal standard. The data can be interpreted by means of the equation

$$1-(1-\alpha)^{1/3}=kt, \tag{2}$$

where α is the fractional crystallization and t time (Fig. 5).[10] This indicates that crystallization is controlled by the rate of advance of the reaction interface. Two different linear portions, except at 680 °C, can be recognized in each of the plots. The rate constants were determined from the slopes of the straight lines. Activation energies were 276 kJ/mol and 204 kJ/mol for the initial and final stages, respectively.

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