

Kinetics of the Formation and Transformation of Alkoxy-derived Strontium Metaborate

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A new metastable SrB_2O_4 was formed by heating amorphous material prepared by the simultaneous hydrolysis of strontium and boron alkoxides. Crystallization isotherms were obtained by means of the Avrami equation $\ln(1-\alpha) = -kt^n$ with $n=2$, the activation energy being determined to be 351 kJ/mol. The kinetics of transformation of metastable into stable SrB_2O_4 is interpreted by the first-order equation $-\ln(1-\alpha) = kt$. Activation energies are 498 kJ/mol and 343 kJ/mol for initial and final stages, respectively.

Crystalline strontium metaborate (SrB_2O_4) has been known only in orthorhombic modification.^{1,2)} In a previous paper³⁾ dealing with the heating process of mixed powder prepared by the simultaneous hydrolysis of strontium and boron alkoxides, it was reported that metastable SrB_2O_4 , similar in structure to low-temperature form of ZnB_2O_4 ,^{4,5)} is formed at 650–690 °C. The present study deals with the kinetics of the formation of metastable SrB_2O_4 and the transformation of metastable into stable SrB_2O_4 . The kinetic data were analyzed with use of available solid state models.

Experimental

Materials and Procedure. Boron triethoxide was of guaranteed purity. Strontium methoxide was synthesized by heating strontium metal (purity 99.9%) in an excess amount of dehydrated methanol at 64 °C for 5 h. A mixture of boron and strontium alkoxides in the mole ratio $\text{Sr}^{2+}/\text{B}^{3+}=1:2$ was poured into aqueous ammonia solution at 25 °C. The temperature was slowly raised up to 60 °C while being stirred. The resulting mixed powder (starting powder, average particle size *ca.* 550 Å) was washed repeatedly with hot water and dried at 60 °C under reduced pressure.

Measurement. Thermal analyses (TG, DTA) were carried out in the air at the heating rate 10 °C/min. Alpha-alumina was used as a standard material in DTA. On the basis of DTA data, the specimens heated at the rate 10 °C/min were examined by means of X-ray diffraction using nickel filtered copper K_α . The scanning speed 1/4°/min of the goniometer was selected to satisfy the accuracy of *d*-spacing. Kinetic studies of the formation of metastable SrB_2O_4 and its transformation into stable SrB_2O_4 have been made by means of X-ray diffraction. The starting powder was pre-heated; 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.

Results and Discussion

Thermal Analysis. TG analysis of the starting powder showed that the weight loss is 16.7% due to the loss of ammonia, absorbed water, hydrated water, and organic residue from the parent alcohol up to 560 °C. On the other hand, two exothermic reactions in DTA were observed at 650–690 °C and 715–780 °C. X-Ray diffraction analysis confirmed that the first exothermic peak (650–690 °C) is due to the crystallization of metastable SrB_2O_4 from an amorphous phase, the second (715–780 °C) to the transformation of metastable phase into stable SrB_2O_4 .

X-Ray Analysis. The starting powder was amorphous, no significant change being observed up to 600 °C. The peaks corresponding to metastable SrB_2O_4 ³⁾ appeared after heating at 620 °C for 5 min, and the intensity increased rapidly up to 670 °C. Table 1 gives the X-ray powder diffraction data of metastable SrB_2O_4 . The observed *d*-values of the compound were similar to those of ZnB_2O_4 of low-temperature form, the structure of which has not been determined. Both compounds disagree in relative intensities of main peaks.³⁾ The peaks of stable SrB_2O_4 (orthorhombic)^{1,2)} appear when heated at 710 °C, the specimen heated at 780 °C showing characteristic X-ray diffraction pattern of stable SrB_2O_4 .

Kinetics of the Formation of Metastable SrB_2O_4 . Figure 1 shows the fraction of the crystallized metastable SrB_2O_4 at 620, 640, and 660 °C. The starting powder was pre-heated at 580 °C. The fractional crystallization of each specimen was determined from

TABLE 1. X-RAY POWDER DIFFRACTION DATA OF METASTABLE SrB_2O_4

<i>d</i> /Å	<i>I</i> / <i>I</i> ₁	<i>d</i> /Å	<i>I</i> / <i>I</i> ₁
5.97	32	2.675	2
5.56	2	2.607	7
5.25	8	2.550	2
4.26	2	2.501	3
4.17	3	2.417	41
4.12	2	2.411	43
4.01	3	2.338	5
3.952	6	2.304	2
3.731	6	2.268	36
3.693	2	2.225	7
3.569	3	2.219	8
3.548	5	2.166	2
3.460	100	2.137	3
3.363	84	2.083	4
3.238	3	2.062	5
3.159	5	2.029	20
3.131	3	1.991	42
3.105	2	1.979	53
2.998	42	1.941	31
2.921	52	1.907	7
2.871	5	1.873	8
2.853	5	1.845	10
2.801	19		

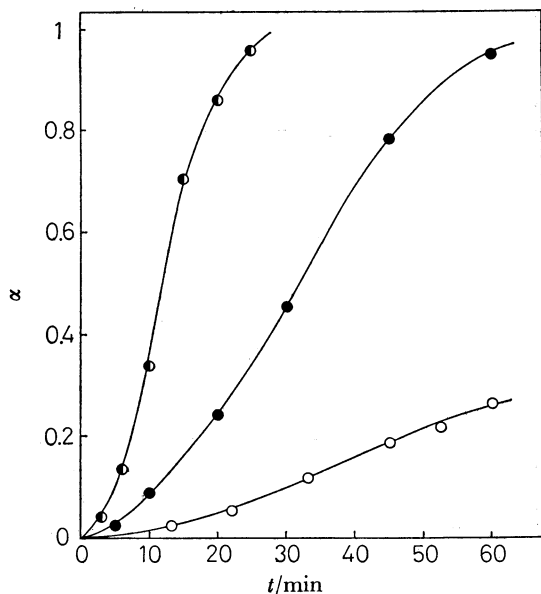


Fig. 1. Formation of metastable SrB_2O_4 as a function of time at different temperatures.

○: 620 °C, ●: 640 °C, ◐: 660 °C.

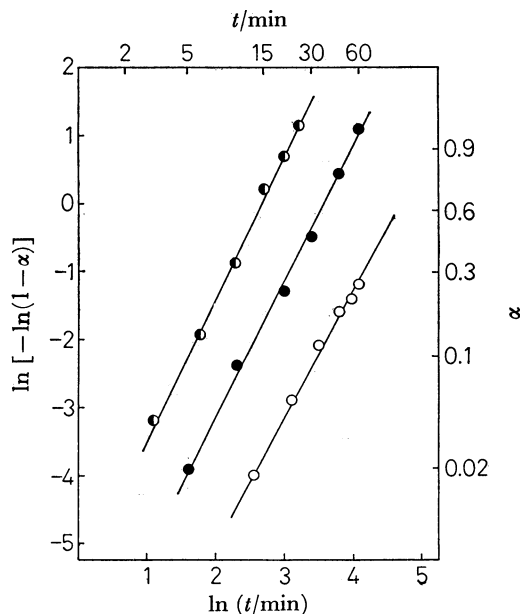


Fig. 2. Plots of $\ln(1-\alpha)$ vs. time t of the data shown in Fig. 1.

○: 620 °C, ●: 640 °C, ◐: 660 °C.

the height of $d=3.36 \text{ \AA}$, the main characteristic peak. A well-crystallized specimen was obtained by heating at 670 °C for 30 min. Magnesium oxide (MgO) was used as an internal standard. Crystallization isotherms were characterized by sigmoidal shape (Fig. 1), the kinetics being best described by the Avrami equation (Fig. 2),⁶⁾

$$\ln(1-\alpha) = -kt^n \quad (n=1.9-2 \div 2) \quad (1)$$

where α , t , k , and n are the fractional crystallization, time, rate constant, and a constant related to the reaction mechanism, respectively. The metastable SrB_2O_4 powder consists of plate-like particles. From the result and the fact that the Avrami equation with $n=2$

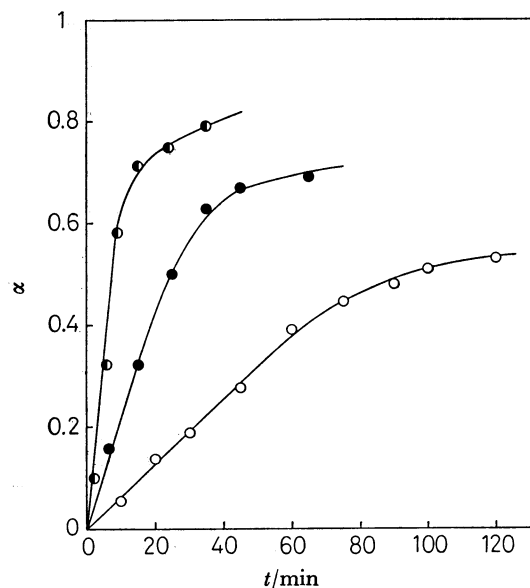


Fig. 3. Phase transformation from metastable into stable SrB_2O_4 as a function of time at different temperatures.

○: 710 °C, ●: 730 °C, ◐: 750 °C.

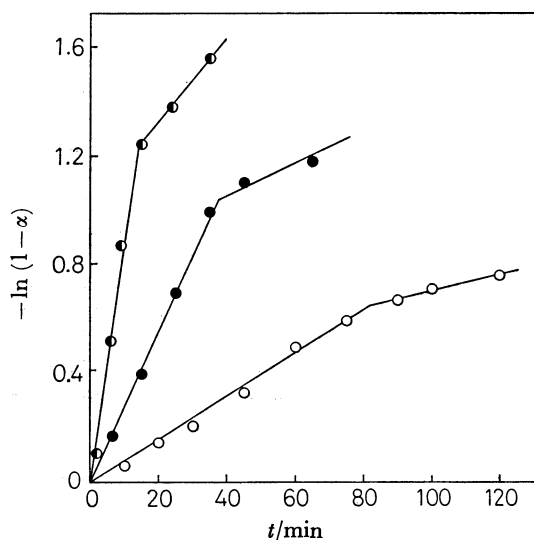


Fig. 4. First-order plots of the data shown in Fig. 3.

○: 710 °C, ●: 730 °C, ◐: 750 °C.

fits crystallization curves over the whole range, two dimensional growth of metastable SrB_2O_4 with site-saturation for nucleation seems to be the rate-determining step. The activation energy calculated from the Arrhenius plot is 351 kJ/mol.

Kinetics of the Transformation. The fractional transformation of metastable into stable SrB_2O_4 was determined as a function of time at different temperatures (Fig. 3). Metastable SrB_2O_4 obtained by heating the starting powder at 670 °C for 30 min was used as a starting material. The fractional transformation was determined from the heights of the main characteristic peaks of metastable ($d=3.36 \text{ \AA}$) and stable SrB_2O_4 ($d=2.69 \text{ \AA}$), using the calibration curve prepared with known compositions. No line broadening was observed during the course of transformation.

Attempts were made to fit the results to kinetic laws. As shown in Fig. 4, transformation isotherms are best described by the first-order equation,⁷⁾

$$-\ln(1-\alpha) = kt \quad (2)$$

where α is the fractional transformation and t time. There are linear portions in each of the plots. The rate constants were determined from the slopes of the straight lines. Activation energies are 498 kJ/mol and 343 kJ/mol for initial and final stages, respectively. They might represent activation energies for nucleation process and propagation process, respectively.⁸⁾

References

- 1) C. E. Weir and R. A. Schroeder, *J. Res. Nat. Bur. Stand.*, **68A**, 465 (1964).
 - 2) X-Ray powder data file (ASTM card 15—779).
 - 3) O. Yamaguchi, M. Kamata, and K. Shimizu, *Chem. Lett.*, **1979**, 1341.
 - 4) D. E. Harrison and F. A. Hummel, *J. Electrochem. Soc.*, **103**, 491 (1956).
 - 5) X-Ray powder data file (ASTM card 9—107).
 - 6) M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); **8**, 212 (1940).
 - 7) For example, R. W. Grimshaw, J. Hargreaves, and A. L. Roberts, *Trans. Brit. Ceram. Soc.*, **55**, 36 (1956).
 - 8) For example, Y. Kotera and Y. Yonemura, *Trans. Faraday Soc.*, **59**, 147 (1963).
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