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Synthesis of BaFe₁₂O₁₉ Powders in Molten Alkali Metal Chlorides

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Very fine powders of barium ferrite BaFe₁₂O₁₉ were prepared by the reaction of iron(III) oxide and barium carbonate in the medium of molten alkali metal chlorides. The effect of the temperature and the time of the isothermal heating on the conversion degree and the size of the BaFe₁₂O₁₉ crystals was studied. BaFe₁₂O₁₉ originates already at the temperature of 800 °C, however it becomes to be the dominating reaction product above the temperature of 850 °C and the heating time of 1 h. It was found that at the temperature of 850 °C and the reaction time of 0.5–2 h the rate of the BaFe₁₂O₁₉ crystal growth is controlled by surface chemical reaction. The activation energy of the BaFe₁₂O₁₉ formation has the value $\Delta E = 300 \text{ kJ mol}^{-1}$ corresponding to the reaction in the liquid medium as the rate-limiting process.

Barium ferrite BaFe₁₂O₁₉ is a typical representative of the ferrites with high magnetic remanence, widely used in the production of the permanent magnets. It is produced from commercial iron(III) oxide and barium carbonate by the solid-state reaction at about 1100 °C [1].

Very fine powders of mixed oxides may be prepared with advantage by precipitation in molten salt medium [2]. In the present work the experimental conditions for the BaFe₁₂O₁₉ barium ferrite preparation by precipitation in the molten alkali metal chloride mixture were studied.

EXPERIMENTAL

Barium ferrite BaFe₁₂O₁₉ was prepared by the reaction of iron(III) oxide with barium carbonate in the medium of molten alkali metal chlorides according to the equation



The heating temperatures in the interval of 750–950 °C and the exposure times of 0.5–2 h were chosen for the preparation. The equimolar mixture NaCl + KCl in the three-fold mass surplus was used as a flux. After the isothermal heating at the desired temperature the samples were cooled and dissolved in boiling distilled water. The composition of insoluble remainder was determined by means of the X-ray powder diffraction analysis. The diffraction line at 0.277 nm was used for the semiquantitative analysis of BaFe₁₂O₁₉.

The crystal diameters in terms of the temperature and time of heating were measured. On the basis of the statistical analysis of the time dependence of the average crystal diameters the probable control mechanism of the isothermal crystal growth of BaFe₁₂O₁₉ as well as the activation energy of its formation was determined using the procedure described in [3].

The size of the crystals of the powdered products was studied using the scanning electron microprobe Jeol X5C. The average diameter of crystals was determined on the microphotographs by direct measurement of the individual crystal size in a set of minimum 100 crystals. The detailed description of the working procedure used is given in our previous work [3].

RESULTS AND DISCUSSION

The results of the semiquantitative X-ray phase analysis of samples heated for 2 h at the temperatures of 750–950 °C are given in Table 1. From the

Table 1. Content of BaFe₁₂O₁₉ in the Sample in Dependence on the Temperature at Constant Time of the Isothermal Heating of 2 h

θ °C	$w(\text{BaFe}_{12}\text{O}_{19})$ %
750	0
800	54
850	87
900	89
950	90

Table 2. Content of BaFe₁₂O₁₉ in the Sample in Dependence on the Time of the Isothermal Heating at Constant Temperature of 850 °C

t h	$w(\text{BaFe}_{12}\text{O}_{19})$ %
0.5	49
1.0	70
1.5	80
2.0	87

table it follows that in the presence of molten alkali metal chlorides the reaction of iron(III) oxide and barium carbonate to form BaFe₁₂O₁₉ takes place already at the temperature of 800 °C and with increasing temperature the content of BaFe₁₂O₁₉ in the samples increases. The presence of flux increases also the rate of the reaction. While in the solid-state reaction BaFe₁₂O₁₉ becomes to be the dominating product after heating at 1050 °C for 2 h [1], in the molten salts medium it happens already at 850 °C and after 1 h of isothermal heating. This finding is evident from the results given in Table 2, where the mass fractions of originating BaFe₁₂O₁₉ at the temperature of 850 °C at different heating times are summarized.

From the microphotographs of the powders synthesized at the temperature of 850 °C and the reaction times of 0.5–2 h the average diameters of the originating BaFe₁₂O₁₉ crystals were determined (Ta-

Table 3. Mean Diameters (d_{mean}) and the Standard Deviation $s(d)$ of BaFe₁₂O₁₉ Crystals in Dependence on Reaction Time at Constant Temperature of 850 °C

t h	$d_{\text{mean}} \cdot 10$ μm	$s(d) \cdot 10^2$ μm
0.5	4.95	4.36
1.0	6.41	6.55
1.5	7.61	5.88
2.0	8.82	5.97

ble 3). From these values it follows that the average diameter of the BaFe₁₂O₁₉ crystals increases with increasing time of the isothermal heating. This finding is evident also from Figs. 1 and 2, where the obtained BaFe₁₂O₁₉ crystals after heating at 850 °C for 0.5 and 2 h, respectively, are shown.

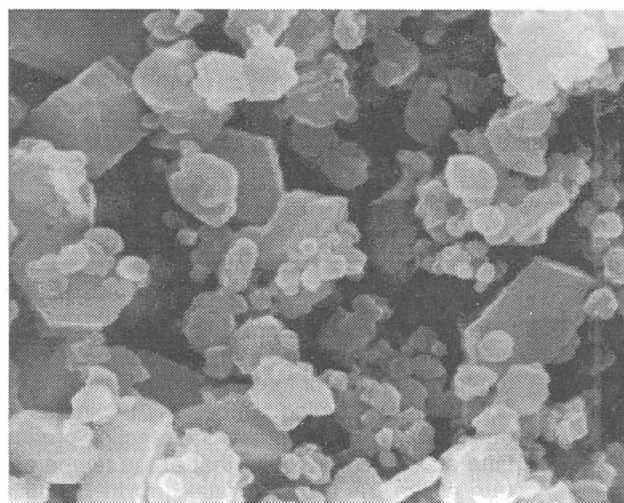


Fig. 1. Microphotograph of the BaFe₁₂O₁₉ powder prepared at 850 °C after isothermal heating of 0.5 h. Magnification 20 000 ×.

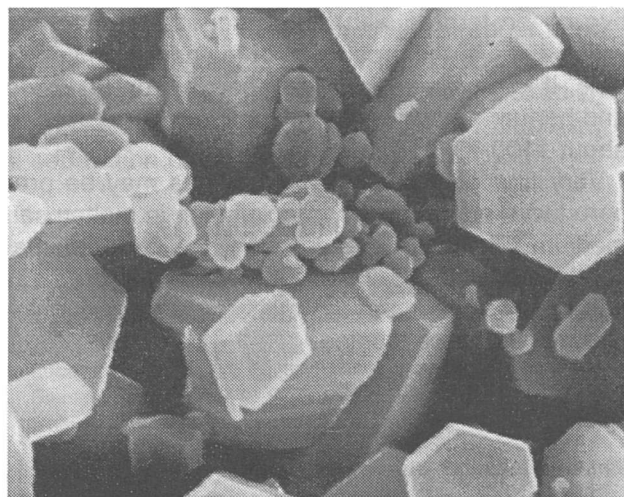


Fig. 2. Microphotograph of the BaFe₁₂O₁₉ powder prepared at 850 °C after isothermal heating of 2 h. Magnification 20 000 ×.

Table 4. Parameters of the Equation $\bar{d}^n = k_0 + k_1 t + k_2 t^2$ for the BaFe₁₂O₁₉ Isothermal Crystal Growth and the Standard Deviation of the Fit

n	k_0	k_1	k_2	$s(d)$
	μm	$\mu\text{m h}^{-1}$	$\mu\text{m h}^{-2}$	μm
2	7.8×10^{-4}	3.45×10^{-3}	—	8.3×10^{-5}
3	—	2.06×10^{-4}	6.36×10^{-5}	7.4×10^{-6}

To determine the control mechanism of the isothermal growth of the BaFe₁₂O₁₉ crystals the statistical regression analysis was done of the dependences

$$\bar{d}^n = k_0 t \quad (1)$$

where \bar{d} is the mean crystal diameter, t is the time, k_0 is the rate constant, and n depends on the nature of the rate-controlling mechanism, $n = 2$ for surface chemical reaction control and $n = 3$ for diffusion control. The result of the regression analysis is given in Table 4. From the table it follows that a linear plot was obtained for $n = 2$, it means the surface chemical reaction, e.g. dissolution and precipitation of BaFe₁₂O₁₉ is the most probable control mechanism at the isothermal crystal growth.

On the basis of the experimentally determined conversion degree (Tables 1 and 2) and using the procedure described in [3, 4] the activation energy of the BaFe₁₂O₁₉ formation was calculated according to the general kinetic equation [5, 6]

$$\alpha = \left\{ 1 - \exp \left[A' \exp \left(-\frac{\Delta E}{RT} \right) \right] \right\} \alpha_{\max} \quad (2)$$

where $A' = A t^m$, t is the time, m depends on the reaction mechanism, nucleation rate, and the geometric factors, A is the frequency factor in the Arrhenius equation, ΔE is the activation energy of the reaction, and α_{\max} is the calculated limiting conversion degree, which has been introduced to take into account some experimental hindrances preventing the completion of the reaction, e.g. the imperfect homogeneity of the starting mixture and/or the sedimentation of solid particles in the melt.

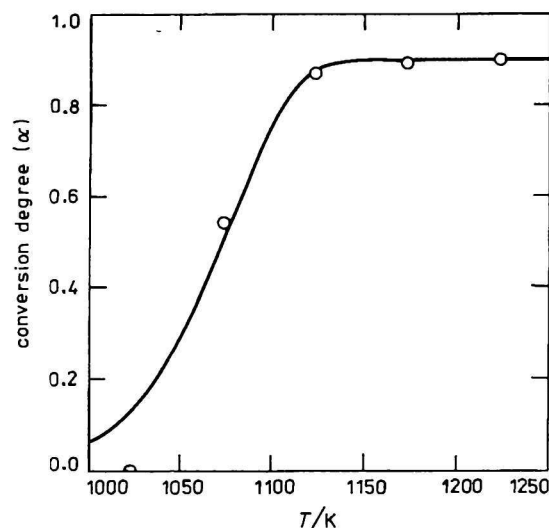


Fig. 3. Dependence of the conversion degree on temperature for the formation reaction of BaFe₁₂O₁₉ in molten alkali metal chlorides. ○ Experimental, — according to eqn (2).

Eqn (2) describes the experimentally determined course of the BaFe₁₂O₁₉ formation very well for $m = 1$ and for the value of the activation energy of the BaFe₁₂O₁₉ formation $\Delta E = 300 \text{ kJ mol}^{-1}$. The limiting conversion degree for the experimental conditions used is $\alpha_{\max} = 0.9$ and the Arrhenius frequency factor has the value $A = 4.5 \times 10^{10} \text{ s}^{-1}$. The measured and calculated dependences of the conversion degree on temperature for the exposition time of 2 h are shown in Fig. 3 for illustration.

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