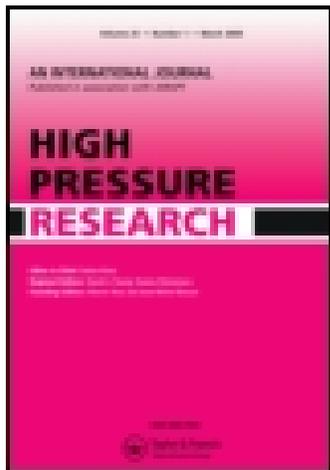


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### Hydrothermal synthesis of barium hexaferrite

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## HYDROTHERMAL SYNTHESIS OF BARIUM HEXAFERRITE

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The authors of the report carried out synthesis of barium hexaferrite (BHF) both in water vapor atmosphere and in liquid medium in the temperature range 200–400°C at pressures  $P_{H_2O}$  of 9–26 MPa in laboratory autoclaves. The results of research have shown that BHF with the best performances can be obtained by thermovaporous treatment of dry mixtures of precursors ( $\gamma$ - $Fe_2O_3$  with barium hydroxide or nitrate). As Fe – containing precursor,  $\alpha$ - $FeOOH$  can be also used. The formation of BHF begins at the temperature of about 200°C. The BHF crystals are hexagonal platelets with diameter  $\leq 1 \mu m$  and thickness 0,1–0,2  $\mu m$ . The magnetic properties of synthesized BHF can be improved by increasing the temperature of thermovapor treatment. The coercive forces of the BHF samples synthesized at about 400°C vary from 1.7–2.0 kOe and specific saturation magnetization of nonoriented samples from 40–50 emu/g. BHF crystals with low coercive force (0.6–0.7) kOe were obtained by introduction of doping micro-additives at the stage of their formation in water vapor atmosphere.

**Keywords:** Barium hexaferrite; Hydrothermal synthesis; Specific saturation magnetization; Coercive force

### INTRODUCTION

Pure and doped fine crystalline barium hexaferrite (BHF) can be effectively used as a magnetic medium for vertical high density magnetic entry and storage of information. BHF crystals have the form of hexagonal platelets and the direction of magnetization is

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perpendicular to planes of platelets that meets the requirements for materials used for the manufacture of magnetic disks. Various methods of BHF synthesis are known: chemical coprecipitation [1], molten salt [2], sol-gel technique [3], hydrothermal synthesis [4], and glass crystallization [5–7]. The principal aim of the developed method of synthesis of BHF is the control of not only the properties, but also the habitus and size of crystals with preservation of monophase product. The experiments have shown that the method of thermovapor treatment (TVT) [8] of precursors has good prospects for the synthesis of BHF with distinct properties. This method is ecological pure. The technological scheme of such process is rather simple and allows using various kinds of raw material.

## EXPERIMENTAL

As raw material for the production of fine-crystalline BHF, iron oxides ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) or iron oxihydroxide ( $\text{FeOOH}$ ) and oxide or hydroxide or nitrate or nitrite of barium were used. The preassigned amounts of precursors were mixed up dry or as water suspension. Beforehand each of the precursors was grinded in ball mill or in the mortar and was sifted through the sieve (0.25 mm). Then the reactants were intermixed and were sifted 2–3 times. The obtained mixture was loaded into the container of the autoclave, and then the container was located in the autoclave. For the creation of necessary water vapor pressure, the bottom of the autoclave outside of the container was filled up with water. For merging water suspension of reactants two procedures were used: (1) reactants mixed in water were dried at the temperature of 50–70°C, then the dry mixture was grinded in mortar and sifted; (2) humid mixture of suspensions of reactants was loaded into the container of autoclave. The autoclave was sealed hermetically and located in the furnace, which has before been heated up to temperature in the interval 200–400°C. The synthesis was proceeded in laboratory autoclaves with a volume of 16 cm<sup>3</sup>, and also in half-industrial autoclaves (volume 50 l). With the aim of optimization of the process the following parameters were varied: content of the initial mixture and ratio of reactants in respect of  $\text{Fe}_2\text{O}_3/\text{BaO}$ , temperature TVT in the range 200–400°C, pressure of water vapor in the range 10–30 MPa

and time of synthesis. The samples of BHF have been studied by X-ray diffraction. Besides, the magnetometric measurements were executed: specific saturation magnetization of nonoriented samples and their coercive force. The form and size of particles have also been studied by an electron-microscopic method.

## RESULTS AND DISCUSSION

The results of the interaction of  $\gamma\text{-Fe}_2\text{O}_3$  with barium hydroxide have shown that the structure and the properties of the product of synthesis depend on the method of preparation of the reacting mixture. The formed BHF appears as powder of dark brown color consisting of separate thin hexagonal plates. The size of plates can vary from 0.5 up to several microns under various conditions of synthesis. Plate-like crystals of BHF can be synthesized already at 200–250°C. Here the obtained product has a small degree of ordering with low magnetic characteristics. The magnetic properties of synthesized ferrite are improved upon the rise of TVT temperature, but the temperature dependence has complicated character (Fig. 1). Electronic microscopy studies of synthesis products has shown that at temperatures higher

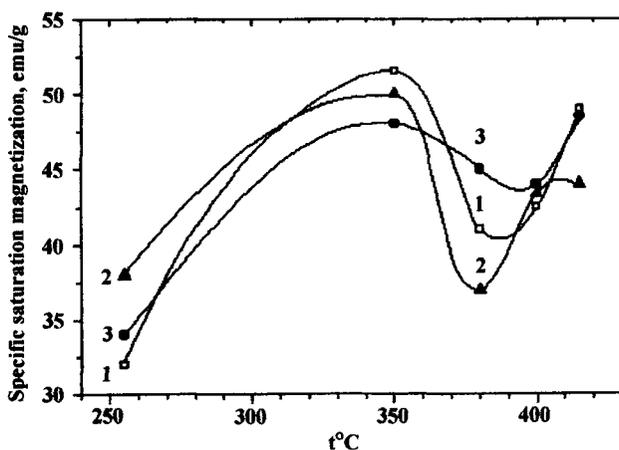


FIGURE 1 The dependence of specific saturation magnetization of BHF on temperature of TVT. Starting material: mixture of  $\gamma\text{-Fe}_2\text{O}_3$  with  $\text{Ba}(\text{OH})_2$  at mol. ratio  $\text{Fe}_2\text{O}_3/\text{BaO} = 3.40$  (curve 1); 3.42 (curve 2); 3.5 (curve 3).

than 405–410°C the process of thickening of plates (with preservation of their diameter) begins. Thus, the optimum temperature of BHF synthesis is 400°C. The study of dependence of structure and properties of a product of synthesis on mole ratio  $\text{Fe}_2\text{O}_3/\text{BaO}$  in starting mixture  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Ba}(\text{OH})_2$  has shown, that mono-phase barium hexaferrite is formed in a range of ratio 3.2–4.0. The enrichment of the mixture of precursors by iron oxide ( $\text{Fe}_2\text{O}_3/\text{BaO} > 4$ ) leads to the formation of  $\alpha\text{-Fe}_2\text{O}_3$  as impurity in the products of synthesis. In the case of a molar ratio  $\text{Fe}_2\text{O}_3/\text{BaO} < 3.2$ , barium biferrite is present as impurity in products. The magnetometry has allowed updating optimum of the composition of a dry initial mixture. In Figure 2 the dependence of specific magnetization of BHF on composition of initial mixture in the interval of ratio 3.2–4.0 is represented. It is visible, that the maxima of the magnetization correspond to composition with the ratio of oxides 3.42. The position of a maximum practically does not depend on temperature. The study of the dependence of the crystal morphology of synthesized BHF on duration of TVT has shown, that optimum time of synthesis at 400°C is 6–12 hours. In this range of time the crystal size is about 1 micron and the ratio of diameter to thickness more than 10. When the duration of TVT of reactants mixture is smaller than 6 hours, the formed like-plates crystals have no precise edges. Furthermore, when the synthesis duration is more than 12 hours, the thickness of plates

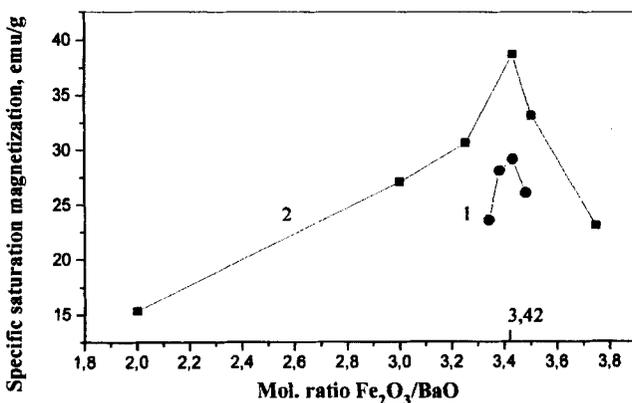


FIGURE 2 The dependence of specific saturation magnetization of BHF on mol. ratio  $\text{Fe}_2\text{O}_3/\text{BaO}$  of starting dry mixture  $\gamma\text{-Fe}_2\text{O}_3$  with  $\text{Ba}(\text{OH})_2$ . The conditions of TVT are:  $t = 300^\circ\text{C}$ , and  $P_{\text{H}_2\text{O}} = 8.6 \text{ MPa}$  (curve 1);  $t = 400^\circ\text{C}$ , and  $P_{\text{H}_2\text{O}} = 22 \text{ MPa}$  (curve 2).

TABLE I Performances of samples of barium hexaferrite synthesized from  $\gamma\text{-Fe}_2\text{O}_3$  at the temperature of TVT of 400°C and  $P_{\text{H}_2\text{O}}$  of 20–26 MPa

The second component	The doping component	Performance		
		Size, $\mu\text{m}$	$\sigma_s$ , emu/g	$H_c$ , kOe
Ba(OH) <sub>2</sub>	—	1–2	37	1.7
Ba(OH) <sub>2</sub>	KOH	1–2	41.4	2.05
Ba(OH) <sub>2</sub>	LiOH	1–2	25.9	1.05
Ba(NO <sub>3</sub> ) <sub>2</sub>	—	0.5–1	43	1.95
Ba(NO <sub>3</sub> ) <sub>2</sub>	—	0.5–1	43.3	1.95
Ba(NO <sub>3</sub> ) <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	1–2	40.2	1.4
Ba(NO <sub>3</sub> ) <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> + LiOH	1–2	41.9	0.7

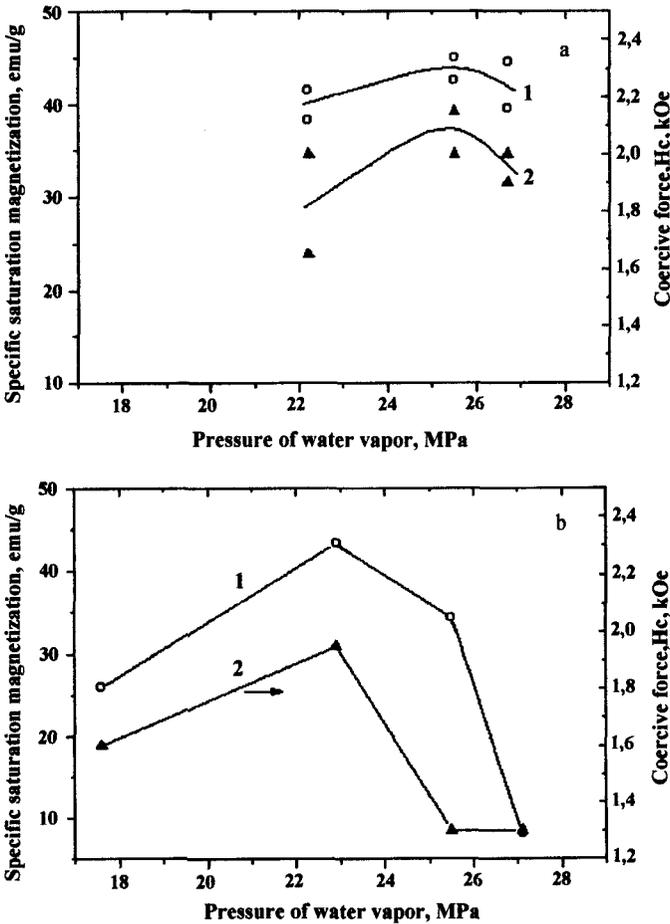


FIGURE 3 The dependence of specific saturation magnetization of BHF (curve 1) and coercive force (curve 2) on pressure during synthesis at 400°C. Starting material: mixture of  $\gamma\text{-Fe}_2\text{O}_3$  with Ba(OH)<sub>2</sub> at mol. ratio  $\text{Fe}_2\text{O}_3/\text{BaO} = 3.42$  (a); mixture of  $\gamma\text{-Fe}_2\text{O}_3$  with Ba(NO<sub>3</sub>)<sub>2</sub> at mol. ratio  $\text{Fe}_2\text{O}_3/\text{BaO} = 3.42$  (b).

of BHF increases. The product of TVT of the mixture of water suspension of reactants consists of a mixture of magnetite,  $\alpha$ - $\text{Fe}_2\text{O}_3$ , and barium biferrite with impurity of BHF. By using a dried mixture of reactants suspension we obtained similar results as with the mixture of dry reactants.

It is possible to use barium nitrate or nitrite instead of barium hydroxide. The interaction of barium nitrate (or nitrite) with  $\gamma$ - $\text{Fe}_2\text{O}_3$  under TVT in the presence of ammonia results in the formation of mono-phase BHF. The addition of ammonia enables nitrate and nitrite anions to be reduced up to nitrogen. In this case crystals of barium hexaferrite had the habitus of thin hexagonal plates with 0.5–1 micron in size (Tab. I). The barium hexaferrite can be obtained also by the interaction the barium nitrite with  $\alpha$ - $\text{FeOOH}$ . The magnetic properties of BHF synthesized by using as raw material the mixture barium nitrate or nitrite with  $\gamma$ - $\text{Fe}_2\text{O}_3$  depend on pressure of water vapor as in case of the mixture  $\gamma$ - $\text{Fe}_2\text{O}_3 + \text{Ba}(\text{OH})_2$  (Fig. 3).

The synthesis of barium hexaferrite in presence of doping elements allows changing its magnetic properties. Table demonstrates, that the decrease of coercive force is much stronger in BHF doped  $\text{Co}^{2+}$  together with  $\text{Li}^+$ .

## CONCLUSION

The synthesis of fine-crystalline barium hexaferrite was performed under hydrothermal conditions and water vapor atmosphere, in the temperature range from 200 to 400°C and pressure  $P_{\text{H}_2\text{O}}$  from 9 to 26 MPa. The synthesized barium hexaferrite is a fine powder, which consists of plate-like crystals with  $\leq 1 \mu\text{m}$  in size and 0.1–0.2  $\mu\text{m}$  in thickness. The most favorable magnetic properties of BHF were obtained by using as starting material a dry mixture of  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\text{Ba}(\text{NO}_3)_2$  or  $\text{Ba}(\text{NO}_2)_2$  with a ratio  $\text{Fe}_2\text{O}_3/\text{BaO} = 3.42$ , and under the following conditions of synthesis: thermovapor treatment of the dry mixture at 400°C and pressure of water vapor of 240 MPa. In this case the magnetic properties of barium hexaferrite were: coercive force, 1.8–2.0 kOe, and specific saturation magnetization, 45–50 emu/g. Barium hexaferrite crystals with low coercive force (0.6–0.7) kOe were obtained by using doping by ions of cobalt together with lithium.

### ***Acknowledgement***

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### ***References***

- [1] Haneda, K., Miyakawa, Ch. and Kojima, H. (1974). Preparation of high-coercivity barium iron oxide ( $\text{BaFe}_{12}\text{O}_{19}$ ), *J. Am. Ceram. Soc.*, **57**(8), 354.
- [2] Marcello, E. Di., Grande, B., Joubert, J. C. and Mollard, P. (1988). Synthesis of Barium Hexaferrites pigments for magnetic recording, *J. de Physique*, **C8**, Part II, 933.
- [3] Suerig, C., Hempel, K. A. and Bonnenberg, D. (1993). Formation and microwave absorption of barium and strontium ferrite prepared by sol-gel technique, *Applied Phys. Lett.*, **63**, 20, 2836.
- [4] Kiyama, M. (1976). Condition for the formation of compounds consisting of barium oxide and iron (III) oxide from aqueous suspensions, *Bull. Chem. Soc. Japan*, **49**, 1855.
- [5] Shirk, B. T. and Buessem, W. R. (1970). Magnetic properties of barium ferrite formed by crystallization of Glass, *J. Am. Ceram. Soc.*, **53**(4), 192.
- [6] Kubo, O., Ido, T. and Yokoyama, H. (1982). Properties of barium ferrite particles for perpendicular recording medias, *IEEE Trans. Magn.*, **MAG18**, 1122.
- [7] Goernert, P., Sinn, E., Schueppel, W., Pfeifer, H., Roesler, M., Schubert, Th., Jurisch, M. and Sellger, R. (1990). Structural and magnetic properties of  $\text{BaFe}_{12-2x}\text{Co}_x\text{Ti}_x\text{O}_{19}$  powders prepared by the glass crystallization method, *IEEE Trans. Magn.*, **26**, 12.
- [8] Lazarev, V. B., Panasyuk, G. P., Voroshilov, I. L., Boudova, G. P., Danchevskaya, M. N., Torbin, S. N. and Ivakin, Yu. D. (1996). New Ecologically Pure Technologies of Fine-Crystalline Materials, *Ind. Eng. Chem. Res.*, **35**, 3721.