

Chemical composition	Structure type	Packing consequence	C, nm
BaO \times 6Fe ₂ O ₃	<i>M</i>	<i>R S R</i> ζ <i>S</i> ζ	2.32
BaO \times 2MeO \times 8Fe ₂ O ₃	<i>W (MS)</i>	<i>R S S R</i> ζ <i>S</i> ζ <i>S</i> ζ	3.28
2BaO \times 2MeO \times 6Fe ₂ O ₃	<i>Y</i>	<i>T S T</i> ζ <i>S</i> ζ <i>T</i> ζ <i>S</i> ζ	4.35
3BaO \times 2MeO \times 12Fe ₂ O ₃	<i>Z (MY)</i>	<i>R S T S R</i> ζ <i>S</i> ζ <i>T</i> ζ <i>S</i> ζ	5.23
2BaO \times 2MeO \times 14Fe ₂ O ₃	<i>X (MMS)</i>	<i>R S R</i> ζ <i>S</i> ζ <i>S</i> ζ <i>R S R</i> ζ <i>S</i> ζ <i>S</i> ζ <i>R S R</i> ζ <i>S</i> ζ <i>S</i> ζ	8.43
4BaO \times 2MeO \times 18Fe ₂ O ₃	<i>U (MMY)</i>	(<i>R S R</i> ζ <i>S</i> ζ <i>T</i> ζ <i>S</i> ζ ∇_3)	11.43

The main problems, arising in the synthesis of similar materials, by the conventional method of chemical technology, are connected with the difficulties in obtaining of single-phase materials, which is due to the close neighborhood of compounds of various structural types on the triple diagram, as well as the necessity of synthesis at rather high temperatures (higher than 1300 °C for *W* type structure, and not less than 1400 °C for *X* type structure) [4, 5].

It is known that the dispersion of the initial charge for the preparation of oxide ferromagnetic and final product in high power mills can substantially influence optimal synthesis conditions, as well as magnetic characteristics of the final product. It should be noted that up to present investigations in this direction are not numerous for this class of ferromagnetic compounds, in the majority of works the effect of mechanical activation (MA) on the structure and magnetic properties of hexaferrites of the samples *M* structural type is considered [6, 7].

This investigation pursued two main goals:

1. The comparison of hexaferrite phase composition diagrams of *W* structural type, manufactured according to the traditional ceramic technology, and those obtained using materials activated at different synthesis – activation stages of the initial ferrite charge and activation of products obtained after preliminary agglomeration.
2. The investigation of the effect of mechanical activation on main magnetic characteristics: saturation magnetization and field anisotropy of hexaferrites.

EXPERIMENTAL

Mechanical activation was conducted in high power planetary mill (MPH) at the balls to sample mass ratios of 10 : 1 and 20 : 1, dispersion time varied from 1 to 120 min. X-ray phase analysis was used to determine phase composition of synthesized ferromagnetics (diffractometer of ADP-1 type, FeK_α radiation). Magnetic properties were investigated with automatic complex for measurement of characteristics of hard magnetic materials in pulse magnetic fields (field strength varying from 0.01 to 10 T, operating temperature interval was 80–600 K.

RESULTS AND DISCUSSION

In activation of ferrite charge during comminution at $t_{\text{MA}} \approx 2$ min, starting oxides became amorphous; besides, the mechanochemical reaction of spinel phase formation proceeded and some ultradispersed clusters with characteristic correlation radius of 8.2 and 5.5 Å were formed.

The growth of the spinel phase grains is observed with the increase of activation time. Figure 1 shows the fragment of X-ray pattern for the charge, being activated during 30 min.

Subsequent annealing of the activated charge at temperature from 1100 up to 1350 °C results in decrease of the intensity of diffusive reflections, but, together with *W* hexagonal phase being formed, the *M* type phase is present in substantial amounts, large amount of spinel phase is preserved. In all cases, the content of *W* phase doesn't exceed 50 % mol. Sufficiently large grains of *M* and *W* type hexagonal phases are formed as a result of presintering at $T = 1100$ °C for 6 h; besides, not less than 20 % mol of spinel phase and barium ferrite BaFe_2O_4 (*B* phase), is contained in samples.

Hexaferrite activation after preliminary annealing allows one to obtain the samples with *W* phase content of more than 90 mol. %, in this case the content of spinel phase slightly increases in comparison with traditional chemical technology and traces of above-mentioned ultradispersed clusters are observed. Optimal synthesis temperature decreases by 80–100 °C in comparison with ceramic technology. Fig-

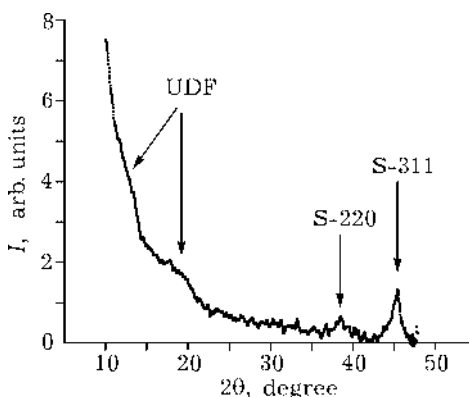


Fig. 1. X-ray pattern of ferrite mixture $\text{BaO} \times 1.3\text{ZnO} \times 0.7\text{CoO} \times 8\text{Fe}_2\text{O}_3$ after mechanical activation for $t_{\text{MA}} = 30$ min.

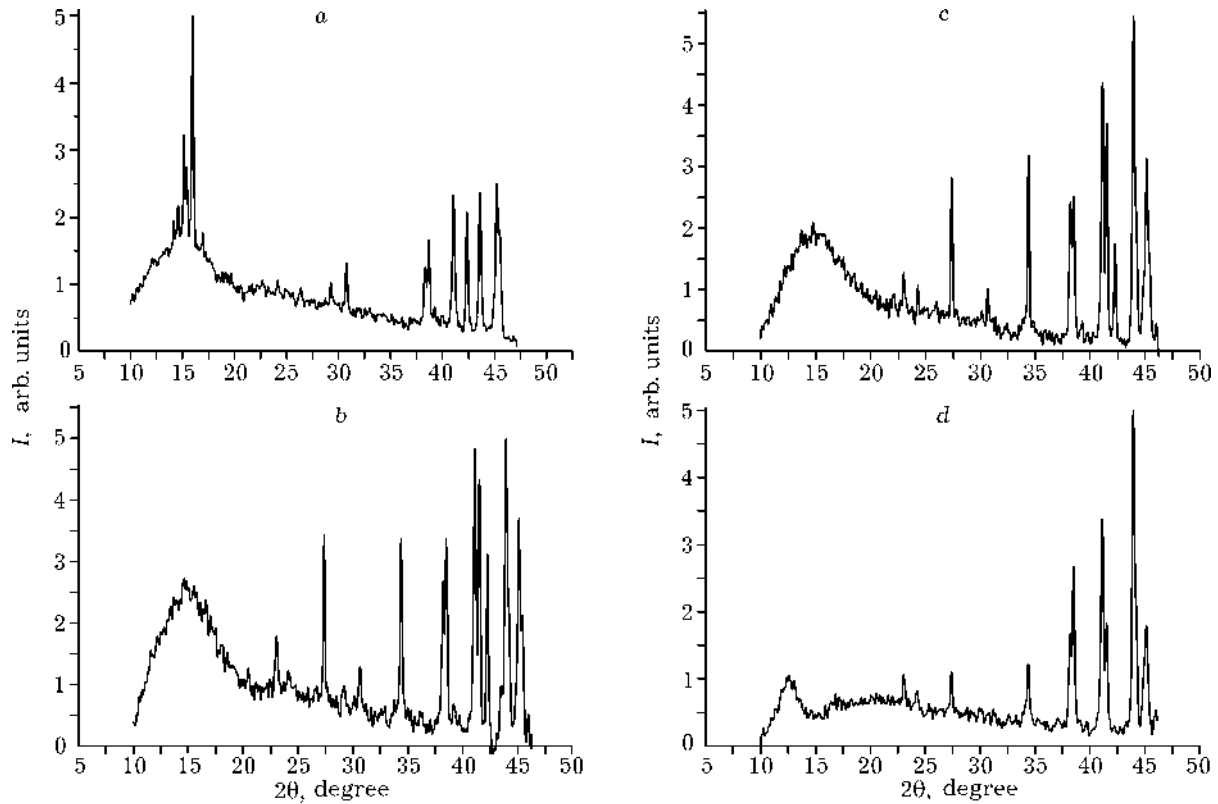


Fig. 2. X-ray patterns of sample, activated after preliminary annealing and agglomerated for 8 h at temperatures, °C: 1100 (a), 1150 (b), 1200 (c), and 1280 (d).

re 2 shows X-ray patterns of the samples, being subjected to activation by comminuting after preliminary annealing.

The analysis of intensities of more pronounced reflections of the observed phases allowed us to plot dependencies of phase composition of samples *versus* the sintering conditions. The comparison of diagrams given above shows the

difference between solid phase reactions for ceramic and activated samples (Fig. 3).

In the first case, the reaction proceeds in two stages: the formation of low temperature hexagonal phases of *M* and *Y* type and their decomposition with temperature increase with *W* type phase formation. In the second case, the phase with *W* type structure is mainly

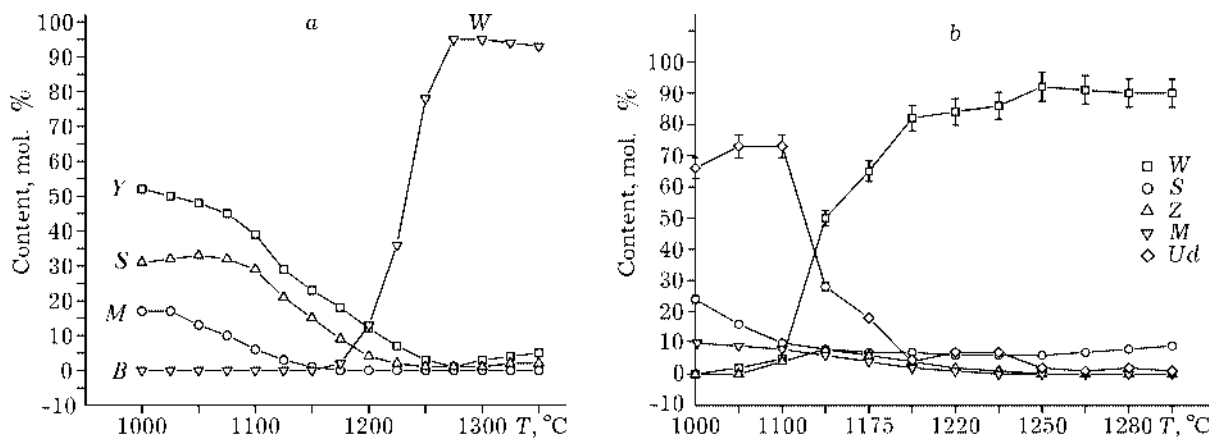


Fig. 3. The dependencies of hexaferrite $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ phase composition on agglomeration temperature: a – ceramic technology; b – mechanical activation after preliminary annealing.

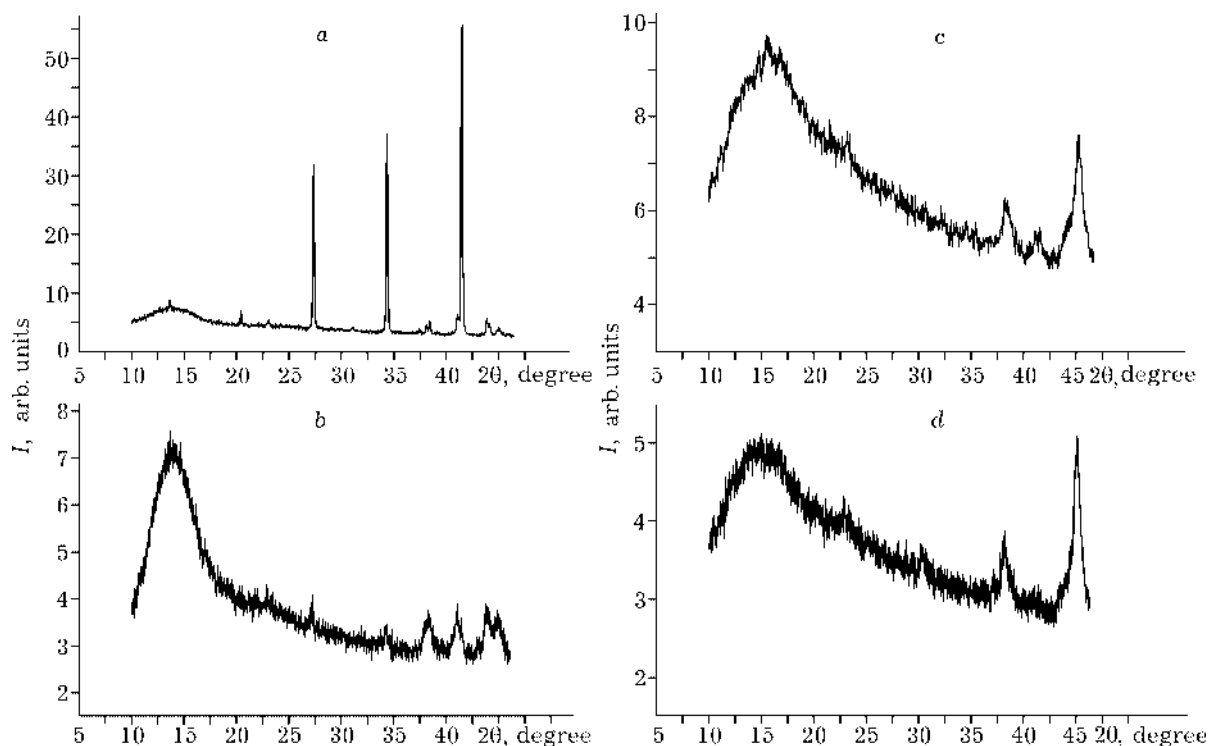


Fig. 4. X-ray patterns of hexaferrite $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ vs. time of mechanochemical treatment in vibratory mill for 1 h (a), 2 min (b), 10 min (c), and 20 min (d).

formed as a result of formation and connection of structure forming block in necessary consequence owing to ultradispersed phase. In this case the synthesis temperature decreases substantially.

Further we shall consider the effect of mechanical activation on the structure and magnetic properties of the final polycrystalline hexaferrite samples belonging to the system, mentioned above. Powder samples of polycrystalline hexaferrites with different concentration of zinc ions, prepared according to ceramic method, were subjected to mechanical activation during 1–30 min. Figure 4 shows fragments of X-ray patterns of samples for various treatment duration.

The W phase reflections, although substantially broadened, are still observed in X-ray patterns after treatment for 2 min. The evaluation of grains sizes of this phase, according to Scherrer formula, gives the value $D \approx 40\text{--}50\text{ nm}$, thus, the sizes of hexaferrite crystallites at $t_{\text{MA}} \approx 1\text{ min}$ satisfy the criterion of the single-domain state. Considerably intense diffusion maximum, pointing to the presence of ultradispersed fraction in the powder sample, appears

in the region of angles of $12\text{--}22^\circ$. At large treatment times, one can observe only traces of hexagonal phase reflections, at the same time, intensities of the diffusion peak and the spinel phase are increasing, the half-width of spinel reflections decreases beginning from $t_{\text{MA}} \approx 10\text{ min}$, pointing to the growth of grains of this phase. These data were directly confirmed during the analysis of microphotographs of powders, obtained on rastre electron microscope.

Not only structural characteristics, but magnetic properties of ferromagnetic change substantially during mechanical activation. Figure 5 shows curves of magnetization of $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$ hexaferrite powder samples for the material prepared according to ceramic method and a number of samples, being subjected to activation by comminuting during different time periods. It is seen that at $t_{\text{MA}} \approx 5\text{ min}$ in the region of large magnetizing fields the increase in magnetic susceptibility is observed, which points to the appearance of fraction with superparamagnetic properties in composition of samples.

Figure 6 shows the dependence of spontaneous magnetization of one and the same sample

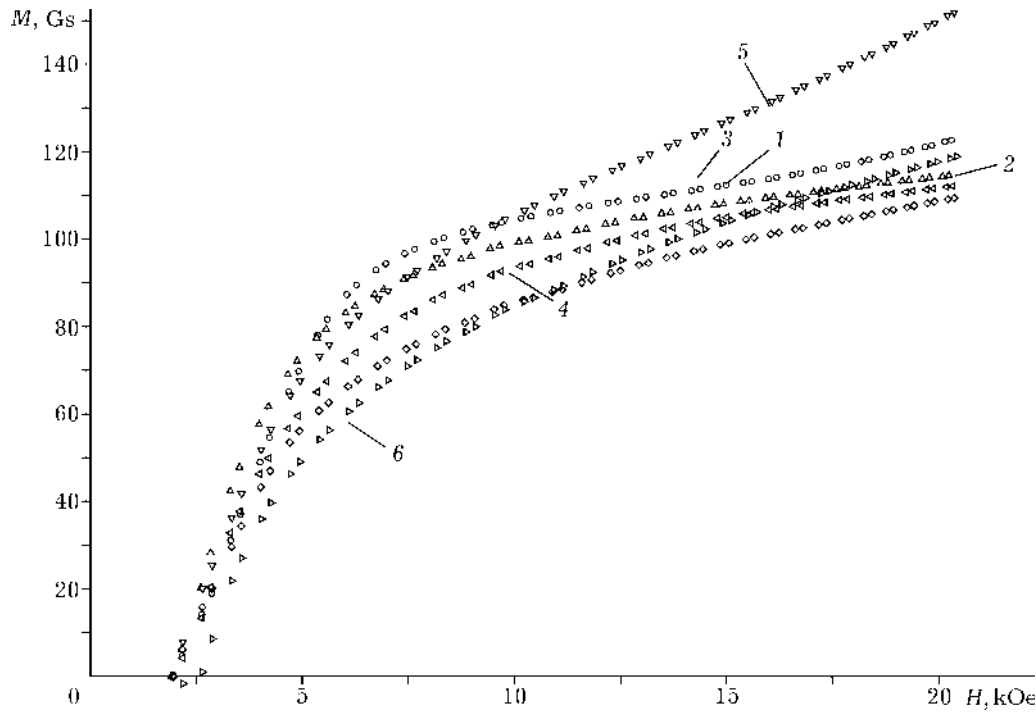


Fig. 5. The dependencies of magnetization curves of hexaferrite $\text{BaCo}_{0.7}\text{Zn}_{1.3}\text{Fe}_{16}\text{O}_{27}$: 1 - ceramic sample; 2-6 - after mechanical activation for 2 min (2), 3 (3), 5 (4), 10 (5), and 20 min (6).

on activation period ($M_S = M_{H \rightarrow 0}$), being obtained from these data.

Saturation magnetization value linearly decreases with the increase of activation time.

To obtain the information about anisotropy of dispersed powder samples, the processing of magnetization curves according to the approximation law to saturation was used, the similar method was proposed in [8] to describe the magnetic anisotropy of nanodimensional

crystallites of barium ferroxdure. Figure 7 shows activation time dependencies of values of effective constant of magnetic crystallographic anisotropy (MCA), obtained in such a way, for two samples of the system, under consideration, with zinc content of $x = 1.1$ and 1.3 . For the first of them, the state with the plane of light magnetization is realized at the room temperature, and for the second one - the axis of light magnetization.

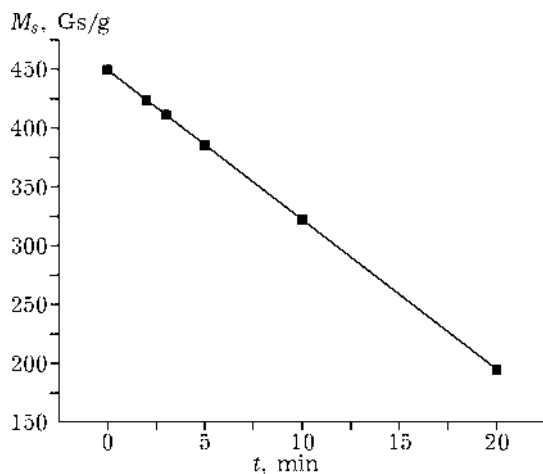


Fig. 6. The dependencies of spontaneous magnetization on activation time for hexaferrites $\text{BaCo}_{1-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{27}$.

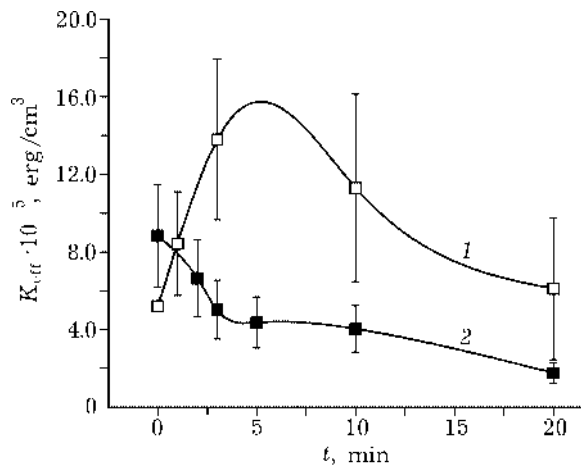


Fig. 7. The dependencies of effective anisotropy constants on activation time for hexaferrites $\text{BaCo}_{1-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{27}$. Value of x : 1.1 (1), and 1.3 (2).

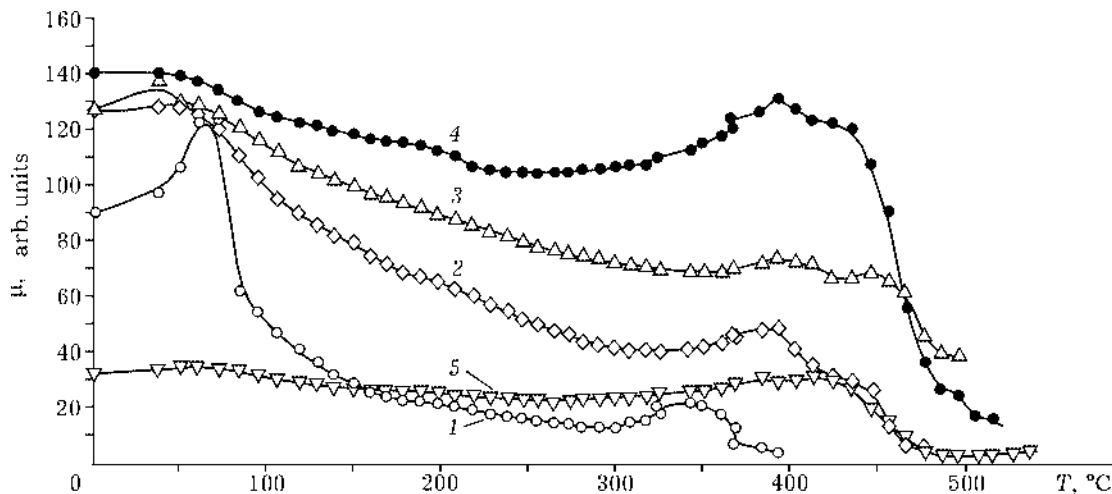


Fig. 8. The temperature dependencies of magnetic permeability of hexaferrite $\text{BaCo}_{0.9}\text{Zn}_{1.1}\text{Fe}_{16}\text{O}_{27}$ on activation time: 1 – ceramical sample, 2–5 – after activation for 2 min (2), 5 (3), 10 (4), and 20 min (5).

The effective constant of magnetic system anisotropy of single-domain particles can be written as: $K_{\text{eff}} = -K_{\text{MCA}} - K_f + K_s V_s/V$, where K_{MCA} is the constant of magnetic crystallographic anisotropy; K_f is the constants, determined by the availability of anisotropy of particles form; K_s is the constant of “surface” anisotropy, defined by the presence of structural-defect open surface, V_s/V is the ratio of volume of near-surface layer to the crystallite volume.

The dependencies shown in Fig. 7, allowed us to evaluate the value and the sign of “surface” anisotropy constant $(-1.5 \pm 0.5) 10^6 \text{ erg/cm}^3$, which is in good correlation with conclusions of [8].

Observed changes on magnetic anisotropy of hexaferrites, being investigated in mechanochemical treatment, are proved by results of investigation of temperature dependencies of the initial magnetic permeability of ceramic samples and the samples, being activated during various time periods (Fig. 8).

CONCLUSIONS

1. The mechanical activation of hexaferrites, conducted after preliminary annealing, allows

to substantially decrease the synthesis temperature by 80–100 °C, retaining the phase composition of polycrystalline material and its main magnetic characteristics.

2. Mechanochemical treatment of polycrystalline ferrimagnetics leads to the decrease of anisotropy effective constant due to the increase of the role of surface anisotropy during the dispersion and thus, is the effective method of control over fundamental magnetic properties of these compounds.

REFERENCES

- 1 M. Sugimoto, *Ferromagnetic Materials*, North-Holland Publ. Co., 1982, vol. 3, ch. 6.
- 2 S. M. Zhilyakov, E. P. Naiden, *FTT*, 37, 9 (1995) 2713.
- 3 E. P. Naiden, V. Yu. Kreslin, A. G. Chesnokov, *Izv. vuzov. Fizika*, 43, 2 (2000) 85.
- 4 E. N. Neckenburger, J. K. Severin, C. Vogal, G. Wikler, *Z. Angew. Phys.*, 18 (1964) 65.
- 5 Du Ben-xi, Lu Huai-xian, Du You-wei, *JMMM*, 31–34 (1983) 803.
- 6 S. J. Campbell, W. A. Kaczmarek, G.-M. Wang, *Nanostruct. Mater.*, 6 (1995) 687.
- 7 E. Estevez Rams, M. I. Montero, *J. Phys. D: Appl. Phys.*, 33 (2000) 2708.
- 8 Z. V. Golubenko, A. A. Kamzin, L. P. Ol'khovik, *FTT*, 40, 10 (1998) 1894.