# Study of the magnetic anisotropy of the multiphase samples of the ferrimagnets with hexagonal crystal structure by the method of ferromagnetic resonance



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# Study of the magnetic anisotropy of the multiphase samples of the ferrimagnets with hexagonal crystal structure by the method of ferromagnetic resonance

**V A Zhuravlev[1], R M Minin[2], V I Itin[2], Y M Lopushnyak[1], A V Zhuravlev[1] and E P Lilenko[1]**

[1]National Research Tomsk State University, Lenina av., 36, Tomsk, 634050 Russia
[2] Tomsk Scientific Center SB RAS, pr. Academicheskii 10/4, Tomsk, 634021 Russia

E-mail: ptica@mail.tsu.ru

**Abstract.** The influence of machining conditions in a planetary ball mill on the phase composition, structural and magnetic parameters of hexaferrite powders composition $BaFe_{12}O_{19}$ was investigated. The properties of powders vary greatly depending on the power density and the time of machining. Magnetocrystalline anisotropy of multiphase powders was studied by the method of ferromagnetic resonance. The effective field of magnetic anisotropy is reduced by more than two times, with decreasing particle size of ~ 67 nm to ~ 10 nm when the processing time equal to 10 minutes. The flow of mechanochemical reactions during grinding leads to the disintegration of the hexagonal crystal phase and the formation of the magnetite phase with a small value of the magnetocrystalline anisotropy field.

## 1. Introduction

Currently, there is a marked increase in the number of publications devoted to the study of the physical properties and different aspects of the application of oxide ferrimagnets with hexagonal crystal structure (hexaferrites) [1]. The unique properties of hexaferrite are due to the large values of magnetocrystalline anisotropy fields and the rather large values saturation magnetization [2]. The surge of interest in this class of materials in recent years is due to the fact that a number of them are the multiferroics at room temperatures [1, 3, 4].

The traditional method of changing the properties of ferrimagnets is the chemical substitution of the iron ions by the other metal ions. However, there is an alternative way - by reducing its particle size to the submicron and nanoscale dimensions. This significantly increases the influence of a defective surface layer on the magnetic characteristics of the ferrimagnetic particles [5]. One of the methods to produce the nanostructured powders is machining in high energy ball mills [6 – 8]. Thus there is not only grinding but also takes place the mechanical activation (MA) of processed materials. According to [7, 8], the MA has little effect on the value of the effective anisotropy field of ultrafine powder of hexaferrite $Zn_2Y$ with magnetic ordering of type the easy magnetization plane (EMP) [8], while the anisotropy field of powders of hexaferrite $BaFe_{12}O_{19}$ (Ba-M) with magnetic ordering of type the easy magnetization axis ( EMA) significantly reduced [5, 6]. This decrease is due to the influence of the contribution of the anisotropy of the defective surface layer, which has in hexaferrites EMP type and, accordingly, reduces the effective anisotropy constant nanoparticles with EMA.

In this paper we investigated the phase composition, the structural parameters and the magnetic anisotropy of ultrafine powders of hexaferrite Ba-M. They were obtained by grinding in a high-energy planetary ball mill of the powders of industrial permanent magnets 19BA260 brand.

## 2. Preparation of samples and methods of research

The starting powder hexaferrite Ba-M was obtained from the ferrite permanent magnet 19BA260 brand. Magnet demagnetized by heating above the Curie temperature. It was annealed at a temperature 600 °C for 2 hours and cooled off with the oven. Then it was grinding in a ball mill. For the experiments the fraction of agglomerates of particles with a size less than 60 microns was used.

After preliminary grinding in a ball mill, powders were subjected to treatment in a high-energy planetary mill of the MVP type. Two regime were used, namely, a "soft" one with an energy intensity of 15 *g* and a "hard" one with an energy intensity of 60 *g*. The ratios of the ball mass to the powder mass were 5:1 and 20:1, respectively. Where *g* is the acceleration of free fall. The maximum processing time was 10 minutes for both modes.

The phase composition and the crystal lattice parameters of the powders thus prepared were studied by X-ray diffraction (SHIMADZU XRD-6000 polycrystalline diffractometer in the Bragg-Brentano geometry with a focusing pyrographite crystal monochromator inserted into the secondary gamma-quantum beam., *CuKa* radiation). The computer database of x-ray powder diffractometry PDF4+ of the International Center for Diffraction Data (ICDD, Denver, USA) was used for a qualitative analysis of the phase composition. Quantitative analysis of the phase composition, refinement of structural parameters of the detected phases and identification of coherent scattering regions (CSR) carried out by the program full-profile analysis Powder Cell 2.4. CSR data were used to estimate the average size of nanoparticles.

The magnetic anisotropy of multiphase hexaferrite powders was investigated by the ferromagnetic resonance (FMR) methods. The FMR spectrum was measured with using the passing through technique with standard waveguide in the frequency range 36 ÷ 53 GHz. To investigate the FMR, powders of the examined samples were put in the thin-walled quartz tubes with inner diameter of 0.7 mm and length of ~ 10 mm. The densities of powder samples were approximately identical. The tubes were arranged into a rectangular waveguide parallel to the wide wall of the waveguide in order that the alternating magnetic field was directed along the sample axis. A permanent magnetizing field was directed perpendicularly to the wide wall of the waveguide. Method of treatment of experimental data to determine magnetocrystalline anisotropy fields from FMR measurements is described in details in [9 - 11].

## 3. The results of X-ray diffraction analysis

Results of the study changes of the phase composition of the powders by mechanical activation time are shown in Figure 1 - "soft", in Figure 2 - "hard" mode. Curve 1 is initial phase content of hexaferrite $BaFe_{12}O_{19}$, curve 2 is the content of phase magnetite $Fe_3O_4$ and curve 3 is the content of phase hematite $Fe_2O_3$. The starting powder consists of 99.1 % of the hexagonal phase of Ba-M and 0.9 % $Fe_3O_4$ phase.

According to Figure 1, with the "soft" machining mode, a monotonic decrease of the initial phase Ba-M and an increase in the content of magnetite and hematite phases with increasing time of MA over 2 minutes are observed. Treated for 10 minutes, the powder contains 52.7 % $BaFe_{12}O_{19}$, 33.8 % $Fe_2O_3$ and 13.5 % $Fe_3O_4$.

A more complex pattern is observed in "hard" MA mode. The Ba-M phase content decreases more rapidly and at $t$ = 10 min is only 8.4%. The content of the magnetite phase increased up to 91.3% at $t$ = 10 min. The content of hematite changes not monotonically with increasing time of MA. First, it increases to about 4 minutes and then decreases to almost 0 % for 10 minutes dispersion time.

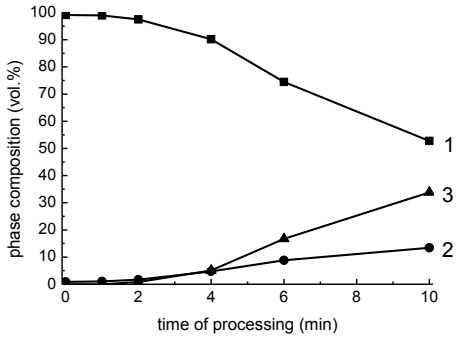


**Figure 1.** The dependence of the phase composition of the powders BaM on the activation time. "Soft" mode. 1 is $BaFe_{12}O_{19}$ phase, 2 is $Fe_3O_4$ phase, 3 is $Fe_2O_3$ phase.

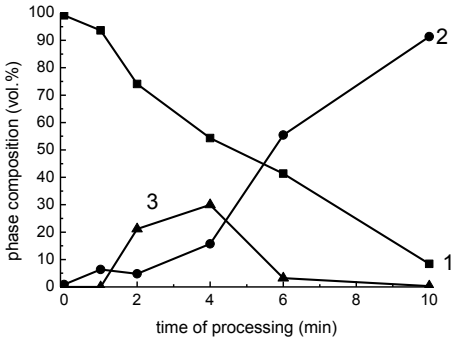


**Figure 2.** The dependence of the phase composition of the powders BaM on the activation time. "Hard" mode. 1 is $BaFe_{12}O_{19}$ phase, 2 is $Fe_3O_4$ phase, 3 is $Fe_2O_3$ phase.

Determined from X-ray analysis values of the lattice constants of the phase are close to known from the literature and are not presented here. The CSR values are shown in Table 1. The initial powder of a permanent magnet 19BA260 mark consists of nanostructured agglomerates less than 60 microns in size, consisting of particles with CSR ≈ 67 nm. Increasing the machining time leads to a substantial reduction of the initial particle size of the hexagonal phase in both processing modes to ~ 10 nm. The particle sizes of magnetite phase do not exceed ≈ 20 nm. At the "soft" mode the increase in the average size of the hematite particles with increasing time of MA to 32 nm at $t$ = 10 min is observed.

**Table 1.** Dimensions of coherent scattering regions of investigated powders

| Time, min | CSR, "soft" mode | | | CSR, "hard" mode | | |
|---|---|---|---|---|---|---|
| | Ba-M, nm | $Fe_3O_4$, nm | $Fe_2O_3$, nm | Ba-M, nm | $Fe_3O_4$, nm | $Fe_2O_3$, nm |
| 0 | 67 | ~16 | - | 67 | ~16 | - |
| 1 | 47 | 13 | - | 15 | 22 | - |
| 2 | 22 | 10 | 9 | 18 | 10 | 9 |
| 4 | 15 | 21 | 15 | 13 | 12 | 9 |
| 6 | 16 | 14 | 20 | 11 | 13 | 9 |
| 10 | 10 | 18 | 32 | ~10 | 17 | - |

## 4. The study of the magnetic anisotropy by the FMR method

A non-oriented polycrystalline ferrimagnets are the ***macroscopically*** isotropic medium. However, the shape of FMR line of polycrystals differs significantly from the FMR curves of isotropic media and of FMR curves of single-crystal samples. The FMR curves of polycrystals have substantially greater line width. At the resonance curves there are additional features: the maximums and (or) the steps. The main reasons for this are as follows: i) the magnetocrystalline anisotropy (MCA); ii) a different form of grains; iii) the dispersion of the values of MCA fields in various grains [12].

Investigations of the FMR spectra of the multi-phase samples of powders and polycrystalline ferrimagnets with a hexagonal crystal structure is the only ways to determine from the experiment important for practical applications the parameters of these materials [9 - 11]. These are: a) the values and sign of the magnetocrystalline anisotropy fields ($H_{ai}$); b) the value of the effective gyromagnetic ratio $\gamma = ge/2mc$, here $g$ is effective $g$-factor, $e$ is charge, m is mass of electrons, $c$ is speed of light. The calculations of the FMR resonance curves [10] and a component of the permeability tensor [11] of uniaxial single-domain polycrystalline and powder materials have shown that on the form of the resonance curves one can determine what type of anisotropy: EMP or EMA has the material. Features on FMR curves (the maximums and (or) the steps) are observed near the magnetizing field's values

$H_{\parallel}$ and $H_{\perp}$ corresponding to the stationary directions on the angular dependence of the resonant field. The values of these resonance fields (or frequencies) are determined by the formulas [10]:

$$\omega_{\parallel} = \gamma_{\parallel}\left[H_{\parallel} + (\gamma_{\perp}/\gamma_{\parallel})H'_{a1}\right], \quad \omega_{\perp} = \gamma_{\perp}\left[H_{\perp}\left(H_{\perp} - H_{\theta}\right)\right]^{1/2}. \tag{1}$$

Here $\omega_{\parallel}$, $\gamma_{\parallel}$ and $\omega_{\perp}$, $\gamma_{\perp}$ are the resonant frequencies and gyromagnetic ratio's to the directions along the hexagonal axis *c* and in the basal plane, respectively; $H'_{a1}$, $H_{\theta}$ are the fields of magnetic anisotropy. These fields include the contributions from the magnetocrystalline anisotropy and shape anisotropy of the crystallites:

$$H_{\theta} = H'_{a1} + H_{a2} + H_{a3}, \; H'_{a1} = H_{a1} + 4\pi M_S(N_{\perp} - (\gamma_{\perp}/\gamma_{\parallel})^2 N_{\parallel}). \tag{2}$$

In the formula (2) $H_{ai} = 2ik_i / M_S$ is the fields of magnetocrystalline anisotropy, $N_{\perp}$, $N_{\parallel}$ is the transverse and the longitudinal demagnetization factor of a particle having the shape of an ellipsoid of revolution, and $2N_{\perp} + N_{\parallel} = 1$. Here $M_S$ is the saturation magnetization per unit volume. Thus, the study of the frequency dependence of the maximums and steps on FMR curves can estimate the values of $\gamma_{\parallel}$, $\gamma_{\perp}$, and obtain estimates for the anisotropy fields $H'_{a1}$ and $H_{\theta}$. Further, by a detailed comparison of the form of calculated and experimental resonance curves, you can clarify the values of the anisotropy fields $H'_{a1}$ and $H_{\theta}$.

The calculated imaginary part of the diagonal component of the permeability tensor (line) and experimental (points) curve of FMR of initial powder Ba-M at a frequency of 50 GHz is shown in Figure 5. The experimental curves in Fig. 5, 6 and 7 were normalized to the theoretical. The calculated FMR curve is estimated for the following parameters: $M_S$ = 0.38 kGs; $H_{a1}$ = 16.7 kOe; $\gamma/2\pi$ = 2.80 GHz/kOe and $\alpha$ = 0.1 is decay constants in the Landau-Lifshitz-Gilbert equation for a monocrystalline grain. Note that the value of $H_{a1}$ is close to the value known from the literature (17 kOe) [2].

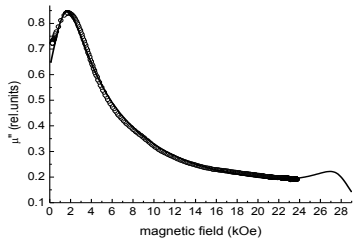


**Figure 5**. Experimental (points) and calculated (line) FMR curves Ba-M of initial powder. The frequency of 50 GHz.

The resonance curve in Figure 5 is a typical for the uniaxial polycrystalline and powder materials with the EMA and the large value of the anisotropy field. The low-field maximum corresponds to the resonance field for the crystallites in which the direction of the magnetic field closes to the direction of easy magnetization. The high-field feature corresponds to a resonant field of crystallites in which the field is oriented near the direction of hard magnetization. Because in the range of the magnetizing fields available for us on experimental curves FMR hexaferrite Ba-M was observed only one maximum in a field close to $H_{\parallel}$, the only experimentally determined values for us were the $\gamma_{\parallel} = \gamma$ and the $H'_{a1}$. Transformation of the form of powders FMR curves over time of MA is shown in Figure 6 ("soft") and Figure 7 ("hard") treatment regimes. The measurements frequency equals to 50 GHz.

It is evident that with increasing the time of MA the intensity of the peaks corresponding highly anisotropic phase Ba-M decreases and the line widths increases substantially for both processing modes. It is noteworthy that in the fields greater then 3 kOe, on the slopes of the curves there are additional features that can be interpreted as the disintegration of the initial phase of Ba-M into several fractions with different particle sizes and values of the anisotropy fields. Along with this process, the additional FMR peak corresponding to the phase with the low value of the anisotropy field appears and becomes more intense. This phase is the magnetite with the anisotropy field $H_a \approx 0.55$ kOe [2] in accordance with the data of X-ray analysis. It is evident that these processes occur more intensively

with "hard" processing mode. From a comparison of the data in Figures 6 and 7 with the results of X-ray diffraction analysis (Figure 1, 2) it is seen that they are correlated. The content in the samples of highly anisotropic phase Ba-M with increasing $t$ is decreases and the content of small anisotropic phase $Fe_3O_4$ is increases.

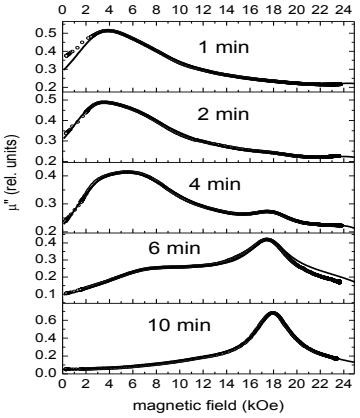


**Figure 6.** Experimental (points) and calculated (lines) FMR curves. "Soft" mode. MA time is shown in the figures.

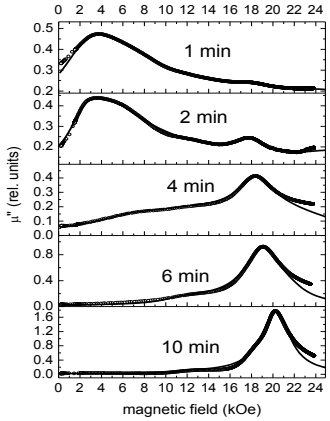


**Figure 7.** Experimental (points) and calculated (lines) FMR curves. "Hard" mode. MA time is shown in the figures.

The comparison of the FMR curves of the samples treated at 10 minutes of "soft" and "hard" mode shows that the main contribution to the total absorption gives the phase of $Fe_3O_4$, and the contribution of the phase Ba-M in both cases is much less. According to the data of X-ray analysis, the phase content of the Ba-M and $Fe_3O_4$ to $t$ = 10 min is as follows: 52.7% and 13.5% of "soft" and 8.4% and 91.3% of "hard" modes, respectively. Thus 52.7% of the phase Ba-M for "soft" mode gives approximately the same contribution to the resonance curve as 8.4% phase Ba-M for "hard" mode. Since the common absorbance at FMR is proportional to the saturation magnetization, this fact can be explained by a significant decrease in the saturation magnetization of Ba-M phase during milling.

The theoretical interpretation of the experimental data was based on the results of X-ray diffraction (Figure 1, 2). The resonance curve of the sample was calculated as the sum of the contributions from the phase Ba-M and the magnetite phases with relevant content. The contribution from antiferromagnetic phase of hematite is not taken into account. We used data on the saturation magnetization of unit volume from [2] when calculate the imaginary parts of the diagonal components of the permeability tensor at the first stage. For Ba-M $M_S$ = 0.38 kGs and for $Fe_3O_4$ $M_S$ = 0.48 kGs. Further refinement of the $M_S$ values was carried out by a detailed comparison of the shapes of calculated and experimental curves. The appearance of additional features on the resonance curves was seen as the result of the disintegration of the initial phase of Ba-M into fractions with different values of the anisotropy fields. To describe the resonance curves for a "soft" mode was sufficient to take into account only two fractions. In "hard" mode for processing times 1 and 2 minutes it must take into account the presence of the three fractions. The total content of Ba-M phase of the powder in such approach redistributed between the groups of fractions with appropriate relative volumes. The calculation results are represented by lines in Figure 6 and 7 and the parameters of calculated curves are summarized in Table 2. It is evident that at dispersing the particles of Ba-M there is a significant decrease in the magneto-crystalline anisotropy fields. According to modern concepts, such behavior is due to the increasing influence of the anisotropy of defective surface layer with decreasing particle size [5, 6, 8]. Effective anisotropy constant uniaxial magnetic nanoparticles can be written as: $k_{eff} = k_1 + k_f + k_S(V_S / V)$. Where $k_1 + k_f$ is the sum of the contributions from the magnetocrystalline anisotropy and shape anisotropy of the particles. These terms are written in the formula (2) as $H'_{a1}$. The value of $k_S = -1.9$ Erg/cm$^3$ is estimated in [5] contribution of the surface anisotropy, $V_S$ is the volume of the defective surface layer, $V$ is the volume of the particle. According to table 2, the reduction of particles size and the values of anisotropy fields $H_a$ are going no monotonically because there are at least two fractions of Ba-M phase with markedly different values of $H_a$.

**Table 2.** Parameters of the calculated curves

| Time of MA, min | $BaFe_{12}O_{19}$ | | | | | | | | | $Fe_3O_4$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | fraction 1 | | | fraction 2 | | | fraction 3 | | | | |
| | $H_a$, kOe | α | rel. volume | $H_a$, kOe | α | rel. volume | $H_a$, kOe | α | rel. volume | α | γ/2π, GHz/kOe |
| "soft" mode | | | | | | | | | | | |
| 0 | 16.7 | 0.1 | 1 | - | - | - | - | - | - | - | - |
| 1 | 15.2 | 0.15 | 0.94 | 12.0 | 0.11 | 0.06 | - | - | - | 0.25 | 2.80 |
| 2 | 15.6 | 0.15 | 0.85 | 12.2 | 0.10 | 0.15 | - | - | - | 0.25 | 2.80 |
| 4 | 15.5 | 0.15 | 0.67 | 12.2 | 0.13 | 0.33 | - | - | - | 0.14 | 2.80 |
| 6 | 12.2 | 0.20 | 0.79 | 7.0 | 0.20 | 0.21 | - | - | - | 0.12 | 2.80 |
| 10 | 7.0 | 0.30 | 1 | - | - | - | - | - | - | 0.10 | 2.78 |
| "hard" mode | | | | | | | | | | | |
| 1 | 15.4 | 0.15 | 0.88 | 12.2 | 0.10 | 0.10 | 6 | 0.1 | 0.02 | 0.15 | 2.78 |
| 2 | 15.6 | 0.10 | 0.69 | 13.0 | 0.10 | 0.28 | 6 | 0.1 | 0.03 | 0.08 | 2.80 |
| 4 | 12.0 | 0.19 | 0.65 | 6.8 | 0.17 | 0.35 | - | - | - | 0.11 | 2.72 |
| 6 | 7.5 | 0.09 | 1 | - | - | - | - | - | - | 0.11 | 2.62 |
| 10 | 6.5 | 0.02 | 1 | - | - | - | - | - | - | 0.08 | 2.46 |

There is also a noticeable difference in the gyromagnetic ratios of magnetite phases with low anisotropy at various MA modes.

## 5. Conclusion

Thus, by dispersing in a high-energy planetary ball mill of the powders of industrial permanent magnets 19BA260 brand the values of the anisotropy field of Ba-M phase is decreased more than doubled and content of magnetite phase with low value of the anisotropy field is increased. Changing the properties of hexagonal phase is not monotonic and comes through fractions with markedly different values of the anisotropy fields.

## Acknowledgments

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