Magnetic anisotropy of an ensemble of Ca-substituted barium hexaferrite nanoparticles

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We studied the parameters of the effective magnetic anisotropy of system of hexaferrite nanocrystals of composition $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$ with an average size 35 nm at 300 K. The constant the field of effective magnetic anisotropy determined from the magnetization curves using five different methods. It was shown that the substitution of ions Ba^{2+} by ions Ca^{2+}, while maintaining the magnetic matrix, the constant K_a^{ef} reduced by more than half in comparison with unsubstituted composition powder of the same dispersion.

Keywords: barium hexaferrite, cations substation, nanocrystall, magnetic anisopropy.

Исследовались параметры эффективной магнитной анизотропии системы нанокристаллов гексаферрита $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$ со средним размером 35 нм при 300 K. Константа и поле эффективной магнитной анизотропии определены из кривых намагничивания с помощью пяти различных методов. Показано, что в результате замещения ионов Ba^{2+} ионами Ca^{2+}, при сохранении магнитной матрицы, константа K_a^{ef} уменьшается более чем вдвое в сравнении с порошком незамещенного состава той же дисперсности.

Кючевые слова: гексаферрит бария, катионное замещение, нанокристалл, магнитная анизотропия.

Досліджувалися параметри ефективної магнітної анізотропії системи нанокристалів гексафериту складу $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$ зі середнім розміром 35 нм при 300 K. Константа і поле ефективної магнітної анізотропії визначені з кривих намагнічування за допомогою п›яти різних методів. Показано, що в результаті заміщення іонів Ba^{2+} іонами Ca^{2+}, при збереженні магнітної матриці, константа K_a^{ef} зменшується більш ніж удвічі в порівнянні з порошком незаміщеного складу тієї ж дисперсності.

Ключові слова: гексаферит барію, катіонне заміщення, нанокристал, магнітна анізотропія.

Introduction

Barium hexaferrite $BaFe_{12}O_{19}$ is highly anisotropic ferrite. At room temperature, the constant of his magnetocrystalline anisotropy $K_1 = 3.3 \cdot 10^6$ erg·cm³, the anisotropy field $H_{ak} = 17 \cdot 10^3$ Oe [1].

Magnetic parameters of small particles and their ensembles markedly differ from the magnetic parameters of macroanalogue that due to the existence of structurally defective surface layer that is comparable with the volume of the particle volume and has a "canted" magnetic structure [2]. Subsurface region makes a certain volumetric contribution to the effective magnetic anisotropy of the particles in the form of so-called "surface" anisotropy [3].

In [4] have been investigated in the temperature range (4.2 - 700 K) the anisotropic parameters of the barium ferrite nanocrystals with an average particle size of $\langle d \rangle = 60$ nm and a thickness of $\langle h \rangle = 15$ nm. The volume fraction of the -surface layer of the particles having a thickness of $\delta \sim 3.5$ nm [5], was 45 %.

Effective magnetic anisotropy constant was determined using the law of approach to saturation magnetization [6]. At 300 K, it was to $2.5 \cdot 10^6$ erg·cm⁻³, that is its value is different from the value for macroanalogue by 25 % due to the negative contribution of the "surface" anisotropy. In the same paper, using the method developed in [7], was found the distribution of particles by fields of effective magnetic anisotropy, according to which the average effective magnetic anisotropy field of the particles at 300 K is also different from H_{ak} of macroanalogue, towards reduction by 20%.

It was of interest to investigate the effect of partial substitution of Ba^{2+} ions by Ca^{2+} ions with preservation of the magnetic matrix, on the anisotropic properties of the nanodispersive particles of barium ferrite. Substitutions of this type were made for the hexaferrite macrosamples [8]. It was found that the magnetocrystalline anisotropy energy of Ca-substituted ferrite is described not only by a constant K_1, but also by constants of higher orders. In this case, the order of magnitude of K_2 is comparable with the K_1.

Method of preparation and certification of powder sample of composition $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$

One of the primary conditions for obtaining particles of nanometer range is the creation of a high chemical homogeneity of the original ferrite mixture. This was accomplished by using the method that uses elements of the cryochemical technology.

Schematic block diagram of a method of producing ferrite particles is shown in Fig.1.
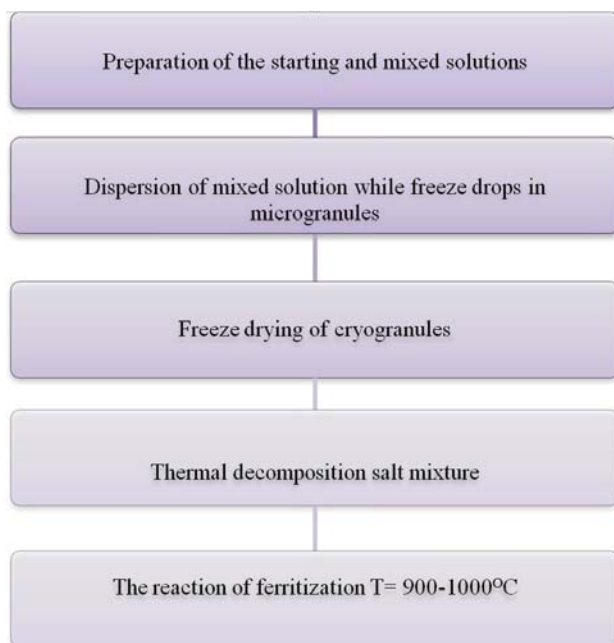

Fig.1. A block diagram of a method of obtaining nanodispersed ferrite powders using elements of cryochemical technology.

At the freezing step was conducted spraying of the solution which was a mixture of solutions of compatible salts of $Ca(CH_3COO)_2$, $Ba(NO_3)_2$, $Fe(CHOO)_3$ in a specified stoichiometric ratio, into an inert refrigerant. As refrigerant was used liquid nitrogen (~ 10 liters of nitrogen per 1 liter of solution). In the system was created a fixed pressure (0.12 - 0.2 atm), under the influence of which the working fluid is fed into the vortex chamber of injector. As a result, the jet of solution is divided into individual droplets of diameter 3-70 μm. Particles entering the liquid nitrogen are rapidly crystallized. As the inert gas injected to the installation under pressure, argon was used. Removal of the solvent from cryogranules was conducted by sublimation-drying – the process of transition of the solvent from the crystalline to the gaseous state, avoiding the liquid phase. This allowed minimizing the agglomeration of the formed particles of product on the freezing step by eliminating occurrence of the liquid phase in material.

A technological operation that preceding to the process of ferritization consists in the thermal decomposition of the salt components of the mixture. Value of thermolysis temperature of components mixture shouldn't be less than the decomposition temperature of each component. Of the above acetates the most high-temperature transition is $Ca(CH_3COO)_2 \rightarrow CaO$. In stages thermal decomposition of calcium acetate to oxide occurs in the form:

$$Ca(CH_3COO)_2 \xrightarrow{160^{\circ}C} Ca_2C_2O_4 \xrightarrow{200^{\circ}C}$$
$$CaCO_3 \xrightarrow{825^{\circ}C} CaO$$
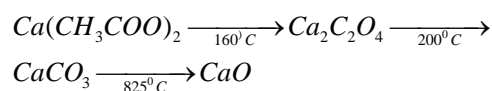
Considering the fact that for the macroscopic analogue of $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$ full ferritization provides the temperature 1270 °C [9], that is much greater than for $BaFe_{12}O_{19}$ hexaferrite (1150 °C), in the case of highly dispersive particles ferritization was held at 900 °C instead of 800 °C for the base composition. This extremely low annealing temperature provided full ferritization, and helped to keep the size of the particles within the nanometer range.

X-ray phase analysis of the obtained powder showed it's a single-phase. Non-magnetic impurity content of α-Fe_2O_3 phase is insignificant, and do not exceed 6%.

To determine the size of the particles used electron microscopy. Electron microscopic studies were performed on a transmission electron microscope Selmi TEM-125 K. Fig. 2 shows a fragment of an electron-microscope image of the powder particles.
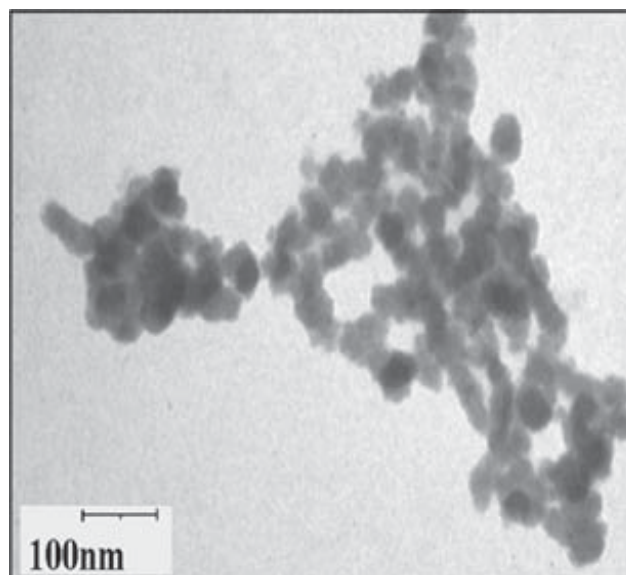

Fig.2. Electron microscopic picture of the powder particles of hexaferrite $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$.

It can be seen that the particle size corresponds to the nanometer range. The average particle size <d> = 35 nm.

Basic magnetic measurements
Results of the data processing

Magnetic measurements at T = 300 K were performed on a pendulum (the main magnetization curve) and induction (hysteresis loop) magnetometers. Fig. 3 shows the main magnetization curve and a part of the marginal hysteresis loop. The magnetization curve is observed
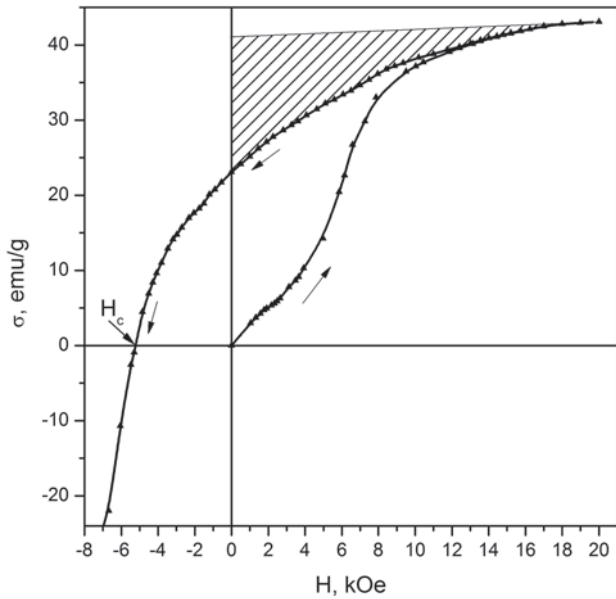
Fig.3. The dependence of the specific magnetization of the nanodispersed sample from the intensity of the magnetic field at 300 K.

typical for systems of small particles non-saturation of the magnetization in fields up to the anisotropy field of macroanalogue [10, 11]. Value of high-field magnetic susceptibility $\chi = 6 \cdot 10^{-4}$ emu·g^{-1}·Oe^{-1} is within values characteristic for fine ferrite systems (1-10 emu·g^{1}·Oe^{-1}) [12, 13].

The results of these measurements were the basis of determining the parameters of the effective magnetic anisotropy of the studied system of nanocrystals. For this purpose, five approaches was used: 1) a method based on the law of approach of magnetization to saturation (LAS) [6]; 2) the method of singular point on the magnetization curve (SPD) [14]; 3) "magnetization- area" method (MA) [15]; 4) a method based on the relationship between the magnetic anisotropy field and coercive force H$_c$ of the material [16] and 5) a method based on the field dependence of the remanence magnetization I$_r$ [7, 17].

The first two of these cases to determine the constant/ field of magnetic anisotropy is directly use the main magnetization curve.

According to LAS, the magnetization can be written as

$$I(H) = I_s \left(1 - \frac{a}{H} - \frac{b}{H^2} - \dots \right), \qquad (1)$$

where: I_s- saturation magnetization, a- parameter of heterogeneity [18], $b = \dfrac{4}{15}\dfrac{K^2}{I_s^2}$, where $K = K_a^{ef}$ - constant of effective magnetic anisotropy or, in terms of the specific magnetization $\sigma = I/\rho$ (ρ- density),

$$\sigma = \sigma_s \left(1 - \frac{a}{H} - \frac{4}{15}\frac{K^2}{\rho^2 \sigma_s^2}\frac{1}{H^2} - \dots \right). \qquad (2)$$
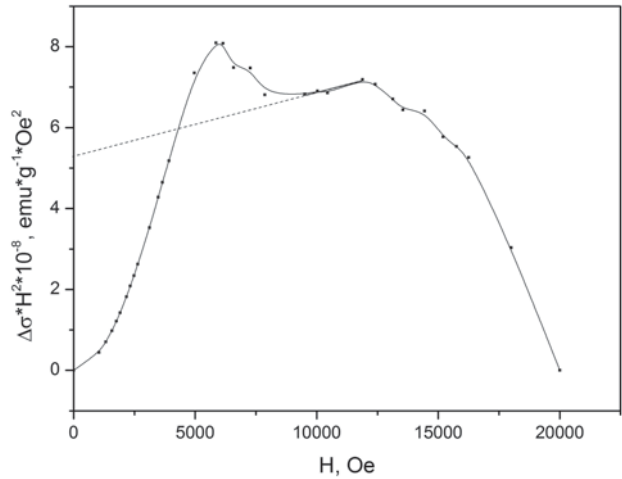

Fig.4. The magnetization curve constructed for calculationanisotropy constant with the law of approach to saturation using.

Dependence of $\sigma(H)$ presented in the coordinates $\left(\sigma_S - \sigma \right) H^2 = \Delta\sigma \cdot H^2 = f(H)$ (Fig.4). Intercept on the y-axis with linear part of the dependence extrapolated to zero field,

$$l = \frac{4}{15}\frac{K^2}{\rho^2 \sigma_S^2},$$

where

$$K = K_a^{ef} = 1.936\rho\sqrt{\sigma_S l} . \qquad (3)$$

Field of the effective magnetic anisotropy of the ensemble of randomly oriented magnetically uniaxial particles can be determined by the following:

$$H_a^{ef} = \frac{2K^{ef}}{I_S} = 3.872\sqrt{l/\sigma_S} \quad [16]. \qquad (4)$$

The method of singular point allows determining the anisotropy field of polycrystalline and powder samples by differentiating the magnetization curve. The position of the extremum on the curve of the second derivative of the magnetization on the field (Fig.5) corresponds to H_a^{ef}.

In [15] it is shown that for a system of randomly oriented magnetically uniaxial domains the area bounded by the demagnetization curve and by a straight line, that extrapolate the high-field part of the main curve to the field H=0 (Fig. 3, shaded area), that is,

$$\int_{I_r}^{I_S} H dI = \frac{2}{3}K \qquad (5)$$

Magnetization value obtained by extrapolation (I0) is the spontaneous magnetization. This creates the possibility to find a constant, and hence the effective magnetic anisotropy field of the studied system of single-domain magnetically uniaxial nanoparticles.

Anisotropy field of polycrystalline materials in the case of uniaxial anisotropy connected to the coercive force
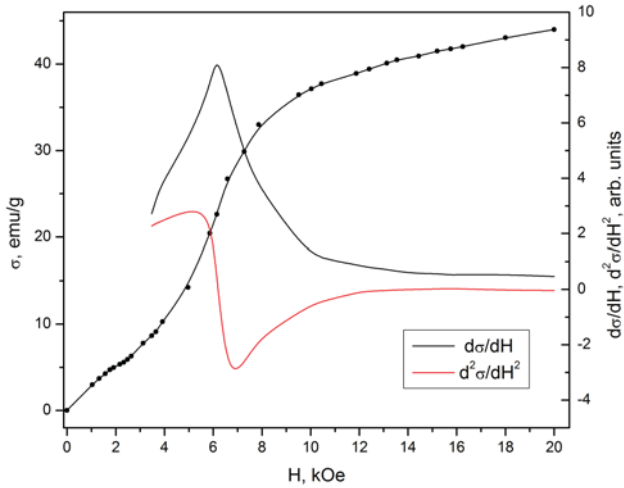
Fig.5. The field dependence of the specific magnetization and of its derivatives by field.
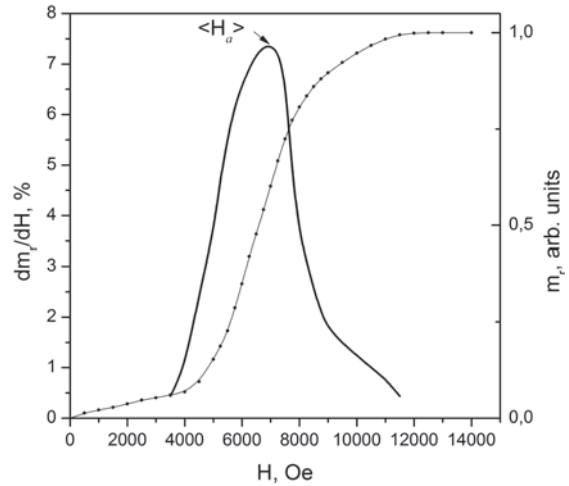

Fig.6. The dependence of the reduced remanence magnetization from the values of the field and the distribution of the powder particles by the fields of effective magnetic anisotropy.

by correlation

$$H_C = 0.48H_a \ [16]. \tag{6}$$

Applying this formula to the powder sample with randomly oriented magnetically uniaxial particles allows finding H_a^{ef} by experimentally measured H_C.

The method developed in [7, 17], allows to obtain the distribution of the powder particles by anisotropy fields $f(H_a)$ by differentiation of field dependence of the remanence magnetization σ_r:

$$f(H_a) = \frac{dm_r(H)}{dH}. \tag{7}$$

Here $m_r = \sigma_r(H)/\sigma_r(\infty)$.

In Fig.6 is shown the $m_r(H)$ dependence and dependence of its derivative by field from the values of the field in percentage. Position of the peak on the curve $dm_r(H)/dH = f(H)$, because of its symmetrical shape, corresponds to the mean value of the anisotropy field of the particles system and, thereby, the effective magnetic anisotropy field.

Calculation results of the magnetic anisotropy parameters obtained by these methods are listed in the table.

As seen from the table, the constant K_a^{ef} for test

sample of nanodispersive powder has the same order of magnitude as the magnetocrystalline anisotropy constant K_1 a of unsubstituted macroanalogue of barium ferrite [1] and a lower value, not only in comparison with macroanalogue, but also in comparison with a sample of the same degree of dispersion, for which $K_a^{ef} = 2.5 \cdot 10^6$ erg·cm^{-3} [4]. The received average value of K_a^{ef} is equal to $(1.0 \pm 0.2) \cdot 10^6$ erg·cm^{-3}. Closest to the average the value obtained by using the method of the "magnetization area" and value obtained from the experimentally measured value of the coercive force. Value $\langle H_a^{ef} \rangle = (9.4 \pm 2.0)$ kOe also less then for unsubstituted powder (16.3 kOe), due to the magnitude of the effective anisotropy constant.

The observed effects (at constant concentration of magnetic Fe^{3+} ions), apparently related to the structural distortions caused by difference of radius of Ca^{2+}(1.06Å) ions from Ba^{2+} ions (1.43Å) [19].

Table 1

The parameters of the effective magnetic anisotropy of the nanosized ferrite of powder $Ca_{0.5}Ba_{0.5}Fe_{12}O_{19}$ obtained by different methods dmr/dH

	Method dm_r/dH	$K^{ef} \cdot 10^{-6}$, erg*cm^{-3}	H_a^{ef}, kOe
1	LAS	1.5	13.8
2	SPD	0.8	7.0
3	MA	0.9	8.5
4	H_C	1.1	10.5
5		0.8	7.0

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