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Magnetocrystalline anisotropy of the multiphase samples of the hexaferrites $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$ studied by the ferromagnetic resonance method

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Abstract. This paper presents structural and magnetic investigation of the hexaferrites $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$ system in the Cu^{2+} concentration range $0 \leq x \leq 1.4$. Samples were synthesized according to traditional ceramic processing technology. The samples were multiphase, since the optimal conditions of synthesis were not specially worked out. According to the data of X-ray diffraction analysis, the samples contain both a target phase and impurity phases of magnetite and hematite, as well as hexagonal phase of Ba-M. The values of the saturation magnetization of the samples were a little more than the values in the literature. It could be explained by the contribution from impurity phases with large magnetization values. The values of the anisotropy fields of the separate phases, which are contained in the investigated samples, were determined by the method of ferromagnetic resonance. The anisotropy field decreases with an increase in the content of copper ion. It is show that the value of the anisotropy field of hexaferrite Ni_2Y is close to the literature value.

1. Introduction

Ferrimagnetic materials with hexagonal crystal structure (hexaferrites) are widely used in various areas of modern engineering. According to the review [1], nowadays an exponential increase of number of publications, which are devoted to investigations of the physical properties and various aspects of hexaferrites applications are observe. The uniqueness of the hexaferrite properties are the result of large values of the magnetocrystalline anisotropy (MCA) and saturation magnetization (M_0) [2].

Hexaferrites with a positive anisotropy constant have magnetic order of the easy magnetization axis (EMA) type. Such ferrites are one of the most commonly used materials for permanent magnets, magnetic recording media and radio-absorbing materials and coatings of millimeter and sub millimeter wavelength bandwidths. Hexaferrites with a negative anisotropy constant have magnetic order of the easy magnetization plane (EMP) type. They have a significantly higher value of the permeability in the microwave range than materials with the EMA. Their application areas are substrates for antennas and nonreciprocal devices of the microwave technology and broadband radar-absorbing materials and protective coatings. A recent raise of interest to the hexaferrites is determined by a fact that some of these possess multiferroic properties at room temperature [1, 3, 4].

It is necessary to know the values and signs of the MCA field (H_a) and the values of saturation magnetization for the targeted application of hexaferrites. If the single-crystal hexaferrites are available, the measurements of the anisotropy fields are easy to carry out. However, in the majority of cases samples in the form of polycrystalline or powder materials are used. Notwithstanding that the

such materials are macroscopically isotropic, there are three methods to determine the value of H_a via an experiment on the polycrystalline and powder hexaferrites:

i) the law of approach to saturation (LAS) [5 – 7];
ii) the singular point detection (SPD) technique [8, 9];
iii) the ferromagnetic resonance (FMR) method.

To satisfy the LAS requirement, it is necessary that the values of magnetizing fields (H_0) was higher than the values of anisotropy field $H_0 > H_a$. According to [7] the errors of the H_a value estimation can be significant. Our estimates have shown that the 10% error in the determination of the value of H_a of EMA type materials is occurred for more than 4 H_a magnetizing field values.

The second method is based on the investigation of the magnetization curves. The article [8] is shown that the second derivative of the magnetization curve has a singularity at the magnetizing field value equal to the magnetocrystalline anisotropy field value ($H_0 = H_a$) for the uniaxial magnets, which are have the positive constant of anisotropy. This method used to measure of H_a in the pulsed magnetic fields [9].

The FMR method is a sensitive and enough simple technique that determine accurate values of the magnetocrystalline anisotropy field and the effective magnetomechanical ratio $\gamma = ge/2mc$. Here g is the effective g-factor of the investigated material, e is the electron charge, m is the mass of the electron, and c is the velocity of light. For these reason, it is more preferable to estimate the H_a of materials with the high anisotropy field values, for example hexaferrites.

The FMR of the nanostructured samples of Ba-M and $Sr(Co_xTi_x)Fe_{12-2x}O_{19}$ ($0.0 \leq x \leq 1.0$) hexaferrites was tested in the EHF range (37 ÷ 53 GHz) in the articles [10] and [11], respectively. The resonance curve shapes analysis allows defining the anisotropy field values as well as the magneto-mechanical ratios.

It should be noted that another advantage of the FMR method in comparison with LAS and SPD is to the possibility of identifying the magnetocrystalline anisotropy fields of separate phases in multiphase samples. Thus, in [12, 13], the effect of the dispersion time in a high-energy ball mill on the phase composition and magnetocrystalline anisotropy fields of hexaferrites powders was studied by FMR method. It is demonstrated that mechanical treatment of initial single-phase hexaferrites leads to the emergent and the volume increase of the phase with low value of the anisotropy field. Moreover, the anisotropy field value of the Zn_2Y hexaferrite with the anisotropy EMP type does not depend on the processing time [12], whereas the anisotropy field value of the BaM hexaferrite with the anisotropy EMA type is substantially decreases [13].

We note that the ferromagnetic resonance method was also used to study the magnetic anisotropy in Ni (l - x) Pd (x) nanowires in [14].

It is known that the temperature regions for the synthesis of different phases of hexaferrites of M-, Y-, Z-, W-, and U-types overlap [1, 2]. Therefore, the synthesis of single-phase samples is not a trivial problem. To save time, it is interesting to analyze the MCA fields of the initial multiphase samples in order to select a material with the required value of the anisotropy field. Only then will it be possible to concentrate efforts to obtain the single-phase samples with the required value H_a. The present article aims to analyze the anisotropy fields of multiphase hexaferrite samples of the $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$ ($Ni_{2-x}Cu_x$–Y) system in the Cu concentration range $0 \leq x \leq 1.4$.

2. Preparation of samples and methods of research

The polycrystalline samples of the $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$ ($Ni_{2-x}Cu_x$–Y) system ($0 \leq x \leq 1.4$) were prepared using high temperature reactions in solid phase. The initial materials for the synthesis were the oxides Fe_2O_3, NiO, Cu_2O and $BaCO_3$. The powders were weighed according to the stoichiometric contents. The final firing was been carried out by the temperature of 1100 ℃ for 6 hours. Then initial samples were grinding in a ball mill. The fraction of the particles with a size less than 60 microns was be used for the experiments.

The phase composition and the crystal lattice parameters of the powders 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 carried out by the full-profile analysis Powder Cell 2.4 software.

The value of the specific saturation magnetization is determined from the study of the magnetization curves in pulsed magnetic fields up to 20 kOe according to the methodology that are described in [15].

Investigations of the FMR spectra of the multi-phase samples of powders and polycrystalline ferrimagnets with a hexagonal crystal structure is the unique ways to the experimental determine of the parameters of materials. These results are important for practical applications of these materials [10–13]. The MCA of multiphase $Ni_{2-x}Cu_x$–Y hexaferrite powders was determined by this method. The standard transmission technique in the frequency range 26–37 GHz in rectangular waveguide channel was used to measure the FMR spectrum. To investigate the FMR, powders of the studied samples were put in to the thin-walled quartz tubes with inner diameter of 0.7 mm and length of ~ 10 mm. The densities of powder samples were roughly identical. The tubes were arranged into a rectangular waveguide and were located parallel to the wide wall of the waveguide. Consequently, the alternating magnetic field was directed along the sample axis. The 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 [10 – 13]. All measurements were carried out at room temperature.

3. Results and Discussions

3.1. The results of X-ray diffraction analysis

Table 1 lists the phase composition of the synthesized materials. It can conclude that all samples were multiphase. The content of the target Y-phase does not exceed 85 %. All samples contain impurity spinel phases: magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and an appreciable amount of hexagonal M-phase.

Table 1. Phase composition of hexaferrites $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$.

Concentration, *x*	Y-phase, %	Fe_3O_4, %	α-Fe_2O_3, %	M-phase, %	σ, Gs*cm^3/g
0.0	63.5	12.4	3.0	21.1	28.7
0.2	72.7	9.3	4.0	14.0	30.9
0.4	83.0	8.9	1.5	6.6	30.6
1.0	83.0	11.0	3.0	3.0	34.9
1.2	85.0	8.1	2.2	4.7	32.3
1.4	52.5	9.2	38.3	0.0	30.5

3.2. Magnetization curve investigation

The last column of Table 1 represents the measured saturation magnetization values. The values of the specific magnetizations in our research are a little more than the values in the literature. According to [2], the hexaferrite Ni_2Y has the value σ = 24 Gs * cm^3 / g, and the hexaferrite Cu_2Y has the value σ = 27 Gs * cm^3 / g. This discrepancy is apparently due to the presence in our samples the impurity phases of magnetite (σ = 92 Gs * cm^3 / g) and Ba-M (σ = 72 Gs * cm^3 / g) with large values of the specific magnetization [2].

3.3. The study of the magnetic anisotropy by the FMR method

Both non-oriented polycrystalline sample and powder of the ferrimagnet are the ***macroscopically*** isotropic substances. However, the shape of the FMR curve of the polycrystals (powders) differs from FMR curves of the isotropic materials and of the single-crystal samples significantly. Namely, the

FMR linewidth of the polycrystals are much more than the FMR linewidth of the isotropic substances and the single-crystal samples. There are additional features at the resonance curves. It is the maximums and (or) the steps. The main reasons of these features are follows: i) the magnetocrystalline anisotropy (MCA); ii) a different form of grains; iii) the porosity of samples [16]. Without in-depth study on the technical detail for research the FMR spectra, we consider only its main stages.

Figures 1, 2 show the calculated FMR curves (field dependences of the imaginary part of the diagonal component of the permeability tensor of a polycrystals) for materials with the anisotropy of EMA type (Figure 1) and with the anisotropy EMP types (Figure 2). The calculation was carried out according to the procedure described in [17] for frequency 37 GHz.

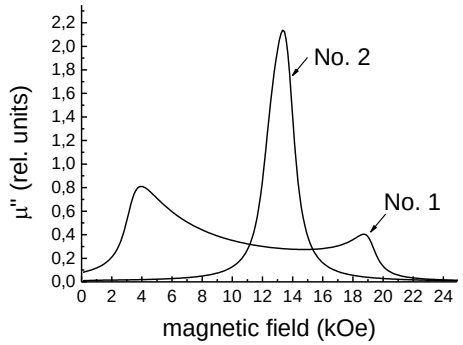

Figure 1. The calculated FMR curves of material with an anisotropy of the EMA type. Curve No. 1 – H_a = 10 kOe, curve No. 2 – H_a = 1 kOe. $\gamma/2\pi$ = 2.8 GHz/kOe. The damping constant α = 0.05.

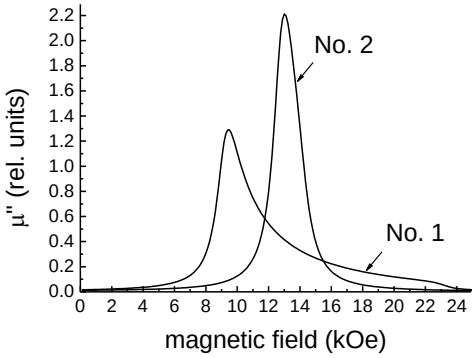

Figure 2. The calculated FMR curves of material with an anisotropy of the EMP type. Curve No. 1 – H_a = –10 kOe, curve No. 2 – H_a = 1 kOe. $\gamma/2\pi$ = 2.8 GHz/kOe. The damping constant α = 0.05.

The comparison of the shape of the FMR curves No. 1 ($H_a = \pm$ 10 kOe) in Figures 1 and 2 shows that the type of magnetic order (EMA or EMP) can be determined from the shape of the resonance curves. The shape of the resonance curves No. 2 ($H_a = \pm$ 1 kOe) of materials with a small value of the anisotropy field is close to a symmetric Lorentz curve in this frequency range. The magnitude of their resonance field is close to the resonance field of the isotropic material ω/γ = 13.2 kOe. Thus, analysis of the resonance curves shape makes it possible to share the contributions to the total absorption at FMR from the phases with large and small values of the anisotropy fields.

Figure 3 shows the results of the comparison of the shape of the experimental and calculated resonance curves. Curves 1 are contributions to the total absorption at FMR from $Ni_{2-x}Cu_x$–Y phase. Curves 2 are contributions from the spinel phase of magnetite with a small value of the anisotropy field. Curves 3 are the total resonance curves. The highly anisotropic Ba-M phase contributions were not considered, since the resonance absorption for this phase locates in substantially higher frequencies because this phase has the NFMR at the high frequency range.

Table 2 lists the parameters of the calculated curves for separate phases.

Table 2. Concentration dependences of the parameters of the calculated curves for different phases of hexaferrites $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$.

Concentration, x	0.0	0.2	0.4	1.0	1.2	1.4
			Y-phase			
H_a, kOe	–12.9	–12.6	–11	–11.3	–7.1	–7.5
$\gamma/2\pi$, GHz/kOe	2.87	2.88	2.92	2.8	2.89	2.86
α, dim-less val.	0.04	0.06	0.05	0.04	0.06	0.06
			Magnetite phase			
H_a, kOe	–0.5	–0.6	–0.6	–0.6	–0.6	–0.5
$\gamma/2\pi$, GHz/kOe	2.95	2.94	2.94	2.89	2.95	2.95
α, dim-less val.	0.05	0.06	0.04	0.04	0.08	0.09

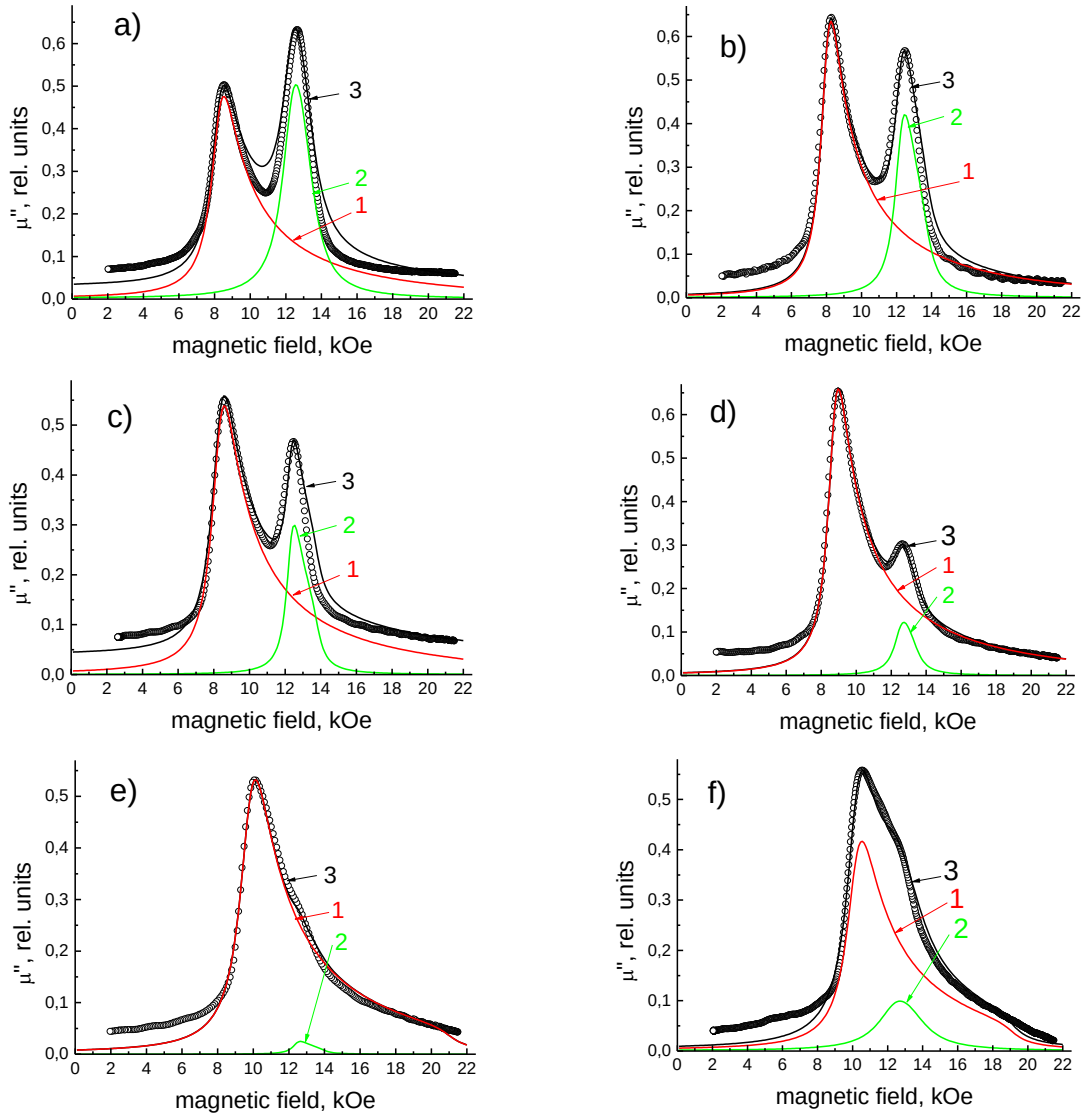

Figure 3. Experimental (points) and calculated (lines) FMR curves of hexaferrites $Ni_{2-x}Cu_x$–Y. Freguency 37 GHz. Fig 3a – x = 0.0, 3b – x = 0.2, 3c – x = 0.4, 3d – x= 1.0, 3e – x = 1.2, 3f – x = 1.4. Numeral 1 indicate the calculated curves of $Ni_{2-x}Cu_x$–Y phase, 2 – magnetite phase, curve 3 is the sum of curves 1 and 2.

Table 2 shows that the magnitude H_a of the Y-phase decreases as soon as the concentration x of copper ions increases. The value of the anisotropy field of the Ni_2Y hexaferrite is equal to 12.9 kOe, which is consistent with the literature value 14 kOe [1, 2].

Estimates of the H_a phase of magnetite are also close to the data [2]. Magnetomechanical ratios of both high-anisotropic and low-anisotropic phases are close to the magnetomechanical ratio for the spin of a free electron, $\gamma/2\pi$ =2.8 GHz/kOe.

4. Conclusions

Thus, the paper presents the results of an investigation of the structural and magnetic characteristics: saturation magnetization, anisotropy fields, and effective magnetomechanical ratios of hexaferrite samples of the $Ba_2Ni_{2-x}Cu_xFe_{12}O_{22}$ system in the Cu concentration range $0 \le x \le 1.4$. The experimental samples were synthesized from conventional ceramic technology. Since a special study of the synthesis regimes for obtaining single-phase samples was not carried out, the synthesized materials turned out to be multiphase. Along with the target phase $Ni_{2-x}Cu_x$–Y, they contain impurity spinel phases of magnetite and hematite, as well as hexagonal Ba-M phase. It shows that the study of FMR in multiphase hexaferrite samples makes it possible to determine the parameters of the separate phases, which are into samples. The value of the anisotropy field of hexaferrite Ni_2Y and magnetite phases are close to the literature values.

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