

Magnetic and Electrical Characteristics of Bismuth Ferrite, Depending on the Impurities, Method of Preparation and Size of the Nanoparticles

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The prospect of application of the multiferroics in devices and spintronics devices is shown. A comparative analysis of magnetic and dielectric properties of nanostructures based on bismuth ferrite which were synthesized by various ways was made. The results of studies of the structure and properties of the nanostructured bismuth ferrite powder, synthesized by combustion of nitrate - organic precursors, are presented.

Keywords: Bismuth ferrite nanoparticles, Dielectric properties, Curie temperature, X-ray, magnetic properties, The Neel temperature

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1. INTRODUCTION

Creating the substances - multiferroics, having both magnetic and electrical properties [1], opens up new opportunities and prospects for their use in spintronics - the science engaged in the processing problems, storage and transmission of information using the magnetic moment of the electron. The main task of spintronics - the transformation of the information provided in the form of the magnetization in the electric voltage and vice versa. The transformation of the magnetization in the electric voltage can naturally be at the expense of a linear magnetoelectric effect, which can be written as two relations $M = \alpha E$ and $P = \alpha H$, where M - magnetization, E - electric field, P - polarization, H - intensity of the magnetic field, α - coefficient characterizing the magneto-electric effect. For the first time the interaction of the electronic and magnetic subsystems was observed Astrov DN [2] in the compound Cr_2O_3 , and a little later in the GA Smolensky lab was created a whole class of multiferroics with magnetoelectric properties [3]. The value of α in of Cr_2O_3 , as defined in the system CGSM units, was 20 mV/(cm Oe). It should be noted that in the bismuth ferrite films thickness 50 nm at room temperature was opened giant magnetoelectric effect [4] with the α value equal to 3B/(cm Oe). It should be noted that the linear magnetoelectric effect in BiFeO_3 can only occur when the antiferromagnetic spin cycloid (with a period of 62 nm) is suppressed. One way to achieve this effect is production BiFeO_3 (BFO) in nanoscale form (film, nanopowders, nanostructured ceramics). Doping with ions of rare earths leads to structural transformation of BFO, whereby there is a change of magnetoelectric properties of the material. In [5] it is shown that the simultaneous doping BFO nanocrystalline yttrium and manganese increases the magnetic and electrical properties, as well as magnetoelectric coefficient compared to pure BFO. At the same time, the doping leads to increasing of conductivity even at room temperature, which reduces the effect of the spontaneous polarization and dielectric properties. Epitaxial thin films can, in principle, may be weak ferromagnetic, but epitaxial stresses can

influence on the crystal structure, polarization and magnetization.

2. METHODS FOR THE PREPARATION OF BISMUTH FERRITE NANOPOWDERS

High values of α , the temperature of the antiferromagnetic ($T_N = 370$ °C) and ferroelectric (the $T_C = 827$ °C) transitions in bismuth ferrite predetermined his prospects of wide application in spintronics, sensory and microwave technology, devices for converting, recording, reading and storing information [6] and other. Analysis of the literature shows a certain spread of values of the dielectric and magnetic properties, Curie and Neel temperatures in nanostructures based on bismuth ferrite, what may be due to size effects, different regimes of annealing (temperature - time, the surrounding atmosphere), the influence of impurities. Among the many ways to obtain bismuth ferrite nanopowders can be identified the following methods.

The sol-gel method [6] with using bismuth nitrate and iron nitrate, followed by annealing at a temperature of 600 °C for 30 minutes. The method does not provide a monophasic composition and requires additional procedures for the purification of the resulting material from $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ and Bi_2O_3 impurities. The authors reported about method of production the nanopowders bismuth ferrite with a particle size of 200 nm and the value of the real part of the permittivity at room temperature equal 15 at the frequency 10 kHz.

Single phase BiFeO_3 nanoparticles (nanoparticles size - 47 nm) have been prepared [8] by a combustion method using metal nitrates and citric acid without any solvent. Dielectric constant at room temperature at a frequency of 10 kHz equal $\epsilon' = 60$. The magnetization of nanoparticles is small, but the dependence not saturated at $H = 17,500$ Oe, Mössbauer effect indicates the presence only of ferric (Fe^{3+}).

Method of combustion of organic nitrate precursors with the addition of ethylene glycol and simultaneous doping In and Mn is given in [5]. Such doping reduces the average grain size of 15 nm, and thus affects on their magnetic and electrical properties. For example,

the saturation magnetization increased significantly from 0,20 emu / g for the BFO to 3,50 emu / g for In and Mn co-doped sample. The disadvantage of the method can be considered the use of toxic ethylene glycol.

Solid phase synthesis of samples $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ $x = 0,15; 0,25, 0,35$ it was used in [9]. Received a significant increase of the saturation magnetization of the samples $M = 6.0$ emu/g, the value of ϵ' is equal to 380 at 10 kHz at room temperature. For the first time, in the doped bismuth ferrite it was measured magnetic field effect on the value of ϵ' . The effect is to increase the ϵ' by 1.7 % in the field of 8 kOe.

In [10-12] is described the role of size effects, determining the effect of the size of the bismuth ferrite nanoparticles on the saturation magnetization and Neel temperature. In particular, in [14] reported the Neel temperature shift to 60° at changing nanoparticle size in the range 23-54 nm.

3. EXPERIMENTAL MEASUREMENTS OF MAGNETIC AND DIELECTRIC PROPERTIES OF BISMUTH FERRITE NANOPOWDERS

BiFeO_3 nanopowder was synthesized [13] by method of burning equimolar precursors from aqueous solutions of nitrates iron $\text{Fe}(\text{NO}_3)_3$ and bismuth $\text{Bi}(\text{NO}_3)_3$ with the addition of nitric acid and glycine. The resulting solution evaporated with stirring to the density 1,14-1,16 g/cm, the heating rate up to the flash point

was 10-30 K /min. On the X-ray source of nanopowder (diffractometer PANalytical Empyrean-2) are not observed crystals of other stoichiometry, except the BiFeO_3 (1a). The average particle size of the powder determined from the Debye-Scherrer formula was 50 nm. After heat treatment for 1 hour at 600, 700 and 800 °C (Fig. 1b, 1c, 1d) in the nanopowder appear and recrystallized sillenite $\text{Bi}_{25}\text{FeO}_{39}$ and mullite $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases.

The magnetization of nanopowders [14] was studied at room temperature under field 15 kOe. Already since 4 kOe dependence $M-H$ reaches saturation.

The maximum value of the initial powder magnetization at 15 kOe (6 emu /g) significantly exceeds the value of M , presented in [5,10], and after calcination, starting with the 700 °C, the magnetization approaches to characteristic for BiFeO_3 values. High values of the initial magnetization nanopowder may be associated with the presence there of amorphous incidental phase, such as, for example, maghemite ($\gamma\text{-Fe}_2\text{O}_3$). For maghemite above 400 °C is observed [15] transition $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ (hematite-antiferromagnetic), which completes at 600 °C [15]. The samples heat treated at 600 °C and above, practically not contained maghemite. The magnetization of nanopowders, after heat treatment at 700 °C and 800 °C corresponds to the values characteristic of the BiFeO_3 , as part of the nanopowder retains the dimensions below 62 nm.

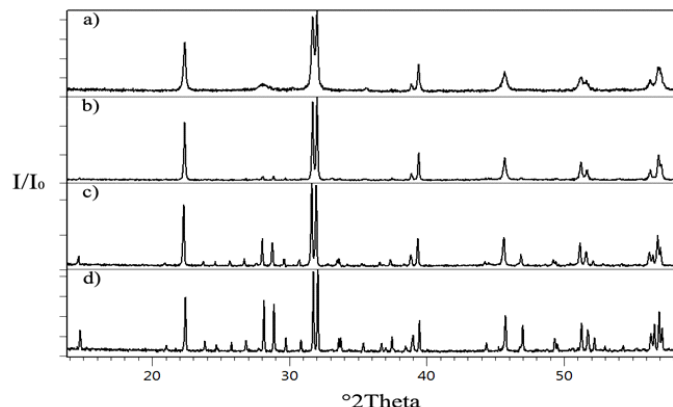


Fig. 1 – Diffraction patterns of the initial and the heat-treated nanopowders

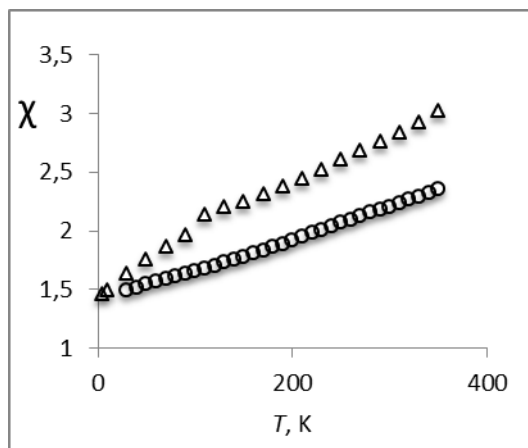


Fig. 2 – The dependence $\chi(T)$ of nanopowder bismuth ferrite: Δ – not heat-treated; O – after heat treatment at 600 °C

Measurements of the magnetic susceptibility χ performed using complex to study the physical properties of materials in a wide range of temperatures and magnetic fields of PPMS-9 + EverCool-II in the temperature range 4-350 K in the alternating magnetic field with frequencies from 10 Hz to 10 kHz and intensities of 0.01 Oe-10 Oe.

The dispersion of χ value in the specified frequency range is not detected, and nonlinear effects when changing the intensity of the alternating magnetic field H is not manifested, so we present the results of measurements χ obtained at a frequency of 1 kHz and in a field $H = 10$ Oe. Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi(T)$ of two samples of the nanocrystalline powder of bismuth ferrite: not heat treated and after heat treatment at 600 °C for 2 hours.

It should be noted the following. In – the first, at 350 K, the magnetic susceptibility of the calcined sample is at 30 % lower compare to the non-calcined sample [8]. The difference in the magnetic susceptibility of these samples decreases with decreasing temperature, and at 4K they are the same. It is known that the magnetic susceptibility (χ) of antiferromagnetics near 0 K is small, because the strong exchange interaction prevents the spin orientation by an external magnetic field. With increasing temperature, spin ordering is disturbed and magnetic susceptibility of AF, in contrast

to the paramagnetic materials, increases to the Neel temperature T_N .

Second, for the non heat-treated sample near the temperature 120 K there is a bend in the behavior of $\chi(T)$. This behavior $\chi(T)$ can be explained by the presence in the sample a small amount of magnetite, for which at this temperature is intense recharging of ferrous ions and ferric iron, and the corresponding change in the magnetization, which is confirmed by Mossbauer spectroscopy [16]. The technical capabilities of the experimental setup does not allow to reach the Neel temperature of the bismuth ferrite ($T_N = 643$ K), however, the linear extrapolation of the $\chi(T)$ dependence for the heat-treated sample to the value T_N shows that the value of χ at T_N nearly twice higher than χ at 4 K, which agrees well with earlier measurements by Smolenskiy and other [17] for polycrystalline bismuth ferrite samples.

Dielectric properties of cold pressed (pressure ~ 1 GPa) and the heat treated powders were measured using the dielectric NOVOCONTROL BDS spectrometer in the temperature range from 123 to 723 K in the frequency range from 10 Hz to 40 MHz. Contacts to the samples with a diameter of 4 mm, 2 mm thick were made using silver paste brand SP-40 + Water Based Silver Ink. Fig. 3 in a semi-logarithmic scale shows the

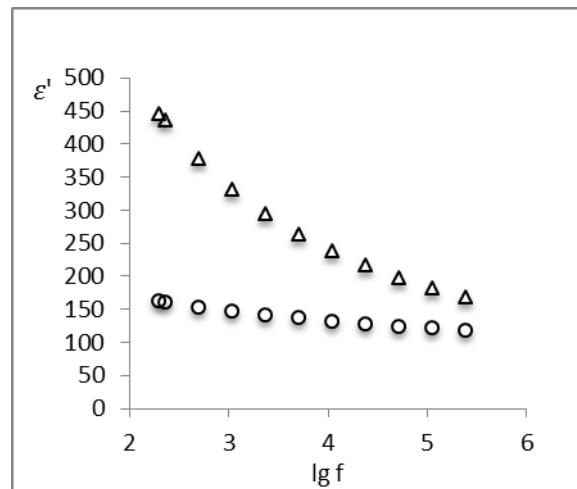


Fig. 3 – The dependence of $\varepsilon'(f)$ ($T = 30$ °C, Δ – not heat-treated; O – after heat treatment at 600 °C)

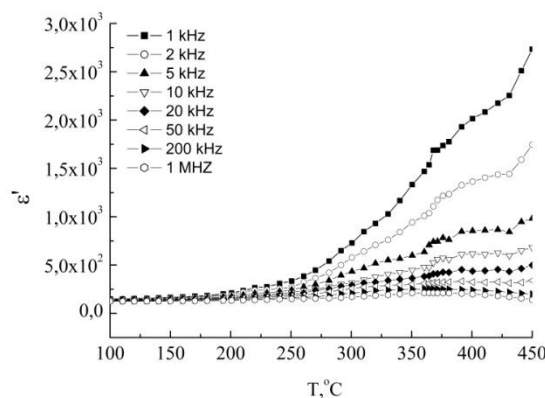


Fig. 4 – The $\varepsilon-T$ dependence at different frequencies (sample calcined at 600 °C)

dependence of the real part of the dielectric constant ϵ' on the frequency f at temperature $T = 300$ °C both for the unannealed sample and heat treated sample (annealing temperature of 600 °C).

The Figure 3 shows significant variance of ϵ' , especially for the initial sample and that as a result of annealing, character of dependence ϵ' changes considerably, especially at low frequencies.

Figure 4 shows the temperature-frequency dependence of ϵ at high temperatures (100-450 °C for a sample

annealed at 600 °C. Near Neel temperature (370 °C) on the $\epsilon'(T)$ curves is clearly observed anomalies associated with an antiferromagnetic phase transition.

The results of studies of the magnetic and dielectric properties of nanocrystalline bismuth ferrite obtained by different methods, are summarized in Table 1, which gives the values of ϵ' at 300 °C at the frequency of 10 kHz; the nanocrystals size d ; the magnitude of saturation magnetization M_s (emu/g) and values saturation fields H_s .

Table 1 – Results of studies of the magnetic and dielectric characteristics BiFeO₃ powder

Method	Annealing regime	d, nm	ϵ'	M_s	H_s
Sol-gel [7]	600 °C, N ₂	200	15	–	–
Citrate combustion method [8]	600 °C, 2 h	47	60	0,2	15 kOe
Citrate combustion method [5]	600 °C, 1 h	15 In +Mn	–	3,5	2 kOe
Solid phase synthesis doped with Ba [10]	–	–	380	6.0	15kOe
Combustion of precursor [11]	600 °C-800 °C	50	180-120	6.0-0,15	4 kOe

4. CONCLUSION

A review of the experimental measurements and own researches by the authors of this article clearly demonstrate the presence of magnetoelectric coupling and significant dependence of magnetic and dielectric properties of bismuth ferrite from the frequency of the alternating electric field, temperature, conditions for synthesis and heat treatment, the magnitude of the magnetic field, the nanocrystal size and the degree of

doping by impurity ions.

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REFERENCES

1. А.П. Пятаков, А.К. Звездин, *УФН* **186** No 2, 593 (2012) (A.P. Ryatakov, A.K. Zvezdin, *Phys.-Usp.* **55**, 557 (2012)).
2. Д.Н. Астров, *ЖЭТФ* **38**, 266 (1960) (D.N. Astrov, *ZhETF* **38**, 266 (1960)).
3. Г.А. Смоленский, И.Е. Чупис, *УФН* **137** No 3, 415 (1982) (G.A. Smolenskiy, I.Ye. Chupis, *Phys.-Usp.* **25**, 475 (1982)).
4. J.H. Lee, et al., *J. Adv. Mater.* **26** No 41 7078 (2014).
5. C.S. Aria, N.S. Negi, *J. Phys. D: Appl. Phys.* **46**, 095004 (2013).
6. A.N. Kalinkin, *J. Inorg. Mater.* **49** No 10, 1031 (2013).
7. Kong Kuk Kim, Sang Su Kim, Won-Jeong Kim, *Mater. Lett.* **59**, 4006 (2005).
8. Samar Layek, H.C. Verma, *Adv. Mater. Lett.* **3** No 6, 533 (2012).
9. D.H. Wang, W.C. Goh, M. Ning, C.K. Ong, *Appl. Phys. Lett.* **85**, 212907 (2006).
10. A. Manzoor, S.K. Hasanain, A. Mumtaz, M.F. Bertino, L. Franzel, *J. Nanopart. Res.* **14**, 1310 (2012).
11. J. Lu, A. Gunther, F. Schrettle, F. Mayr, S. Krohns, P. Lunkenheimer, A. Pimenov, V.D. Travkin, A.A. Muchin, A. Loidl, *Eur. Phys. J. B* **75**, 451 (2010).
12. S. Shetty, V.R. Palkar, R. Pinto, *Pramana J. Phys.* **58** No 5- 6, 1027.
13. М.Х. Рабаданов, Д.К. Палчаев, Ш.В. Ахмедов, М.П. Фараджева, Ж.Х. Мурлиева, С.Н. Каллаев, С.А. Садыков, Патент РФ № 2556181, 2015, Бюл. № 19 10.07.2015 (M.Kh. Rabadanov, D.K. Palchayev, Sh.V. Akhmedov, M.P. Faradzheva, Zh.Kh. Murliyeva, S.N. Kallayev, S.A. Sadykov, Patent RF № 2556181, 2015, Byul. No 19 10.07.2015.).
14. С.А. Садыков, Д.К. Палчаев, Ж.Х. Мурлиева и др., *ФТТ* **58** No 5, 929 (2016) (S.A. Sadykov, D.K. Palchayev, Zh.Kh. Murliyeva, *Phys. Solid State* **58** No 5, 929 (2016)).
15. V.N. Nikiforov, A.E. Goldt, E.A. Goodilin, V.G. Sredin, V.Y. Irkhin, *Bull. Russian Academy of Sciences: Phys.* **78** (10), 1076 (2014).
16. V.M. Sarnatsky, V.G. Semenov, E.V. Charnaya, S. Chien, *Poverkhnost* **1**, 26 (2006).
17. G. Smolenskii, V. Isupov, A. Agranovskaya, et al., *Sov. Phys. Solid State* **S2** (1961).