Thermodynamic properties of $Bi_{0.8}Dy_xEr_{1-x}FeO_3$

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The thermodynamic properties of the $Bi_{0.2}Dy_xEr_{1-x}FeO_3$ multiferroic have been studied in the temperature range of $120-800$ K. It is shown that when bismuth ferrite is doped with two rare-earth elements erbium and dysprosium, a two-phase rhombohedral $R3c$ and orthorhombic $Pnma$ structure is realized and leads to an additional contribution to the heat capacity in a wide temperature range, a shift in the temperature of the antiferromagnetic phase transition to the low temperature region and an increase in magnetization with an increase in the concentration of dysprosium. Additional information found on temperature dependencies anomaly of heat capacity and dielectric constant for compositions with $x = 0.05$ and 0.15 at $T \approx 542$ and 577 K, respectively, indicate that it may be due to a structural phase transition between rhombohedral and orthorhombic structures.

Keywords: multiferroic, heat capacity, magnetization, phase transition, Schottky anomaly.

1. Introduction

Much attention has been paid recently to the study of the crystal structure and physical properties of multiferroics. The interest in multiferroics is attributable to the broad prospects for their application in modern technology (creation of magnetic field sensors, information recording/reading devices, spintronics devices, microwave, etc.). Bismuth ferrite $BiFeO_3$ is one of such compounds, in which ferroelectric (at $T_c \sim 1083$ K) and antiferromagnetic (at $T_N \sim 643$ K) phase transitions occur above room temperatures [1–3]. The crystal structure of bismuth ferrite at room temperature is characterized by a rhombohedrically distorted perovskite unit cell (etc. gr. $R3c$). Spontaneous electric polarization is oriented along the direction of the [111] pseudocubic perovskite cell, and the antiferromagnetic ordering of the G-type occurs so that the magnetic moments of iron ions rotate in a spiral oriented along [101]. The bismuth ferrite has a complex spatially modulated magnetic structure of the cycloidal type with a period of 62 nm [4] in the temperature range below the Neel point T_N, which does not allow the presence of ferromagnetic properties. The destruction of the spatially modulated spin structure is a necessary condition for the occurrence of the magnetoelectric effect in $BiFeO_3$, which can be achieved by doping bismuth ferrite with rare earth elements, creating nanostructured and thin-film systems under the impact of high magnetic fields and pressures. The partial isovalent substitution of bismuth cations with cations of rare earth elements (as well as a change in the concentration of rare earth ions) results in changes of the phase composition of the synthesized compounds.

The analysis of numerous publications with the results of independent studies of the structure and physical properties of ceramic compounds of substituted bismuth ferrite cation, indicates that there is no consensus on the sequence of structural phase transitions and temperature ranges of the existence of various phases depending on the concentration and type of substituting cations. Despite the large number of experimental studies on bismuth ferrite doped with rare earth elements, there are relatively few works devoted to the study of the impact of Bi substitution by two REE simultaneously [5,6].

The results of studies of the structure, heat capacity, magnetization and permittivity of synthesized compounds $Bi_{0.8}Er_{0.2-x}Dy_xFeO_3$ (where $x = 0, 0.05, 0.15$) in the range temperatures $300-800$ K are presented in this paper.

2. Samples and experiment

Polycrystalline samples of $Bi_{0.8}Er_{0.2-x}Dy_xFeO_3$ ($x = 0, 0.15, 0.20$) were synthesized by solid-phase reactions using cold pressing at high pressure of $P = 4$ GPa. The initial oxides are Dy_2O_3, Er_2O_3 Bi_2O_3 and Fe_2O_3 (chemical purity 99.99). The type and parameters of the crystal lattice were determined on the basis of a full-profile analysis of diffractograms obtained using the diffractometer DRON-3M with $CuK_\alpha (\lambda = 1.54114$ Å) radiation at room temperature. The analysis and refinement of X-ray data was

Lattice parameters (a, b, c), values of volumes (V) of lattice cells and parameters of Rietveld analysis of compositions $Bi_{0.80}Dy_{0.20-x}Er_xFeO_3$ $(x = 0, 0.05, 0.10, 0.15, 0.20)$

Composition (Space group)	Lattice parameters, (Å)			Lattice cell volume., (Å^3)	Analysis parameters
	a	b	c	V	
$Bi_{0.80}Er_{0.20}FeO_3$ (*Pnma*)	5.7666	7.9306	5.5871	255.5	$\chi^2 = 1.32$; Rp $= 13.14$; Rwp $= 17.78$
$Bi_{0.80}Dy_{0.05}Er_{0.15}FeO_3$ (*Pnma*)	5.7715	7.9401	5.6125	257.2	$\chi^2 = 0.98$; Rp $= 12.05$; Rwp $= 16.12$
$Bi_{0.80}Dy_{0.10}Er_{0.10}FeO_3$ (*Pnma*)	5.7175	7.9154	5.5908	253.0	$\chi^2 = 0.92$; Rp $= 11.89$; Rwp $= 18.13$
$Bi_{0.80}Dy_{0.15}Er_{0.05}FeO_3$ (*Pnma*)	5.4186	7.9379	5.6026	241.0	$\chi^2 = 0.92$; Rp $= 11.67$; Rwp $= 15.39$
$Bi_{0.80}Dy_{0.20}FeO_3$ (*Pnma*)	5.4196	7.8977	5.6216	240.6	$\chi^2 = 1.19$; Rp $= 12.64$; Rwp $= 16.96$

performed in the JANA2006 software using the Rietveld method.

Heat capacity was measured using a differential scanning calorimeter NETZSCH DSC 204 F1 Phoenix®. A disk with a diameter of 4 and a thickness of 1 mm was used as a sample for measuring the heat capacity. The rate of temperature change was 5 K/min. The relative error of measurement f the heat capacity did not exceed 3%.

The LCR-78110G meter was used to determine the dielectric constant. The samples were made in a form of flat capacitors with silver paste electrodes.

The temperature dependences of the magnetization of samples placed in vacuum quartz ampoules were measured using the Faraday method [7] in the temperature range of $T = 300-1000$ K in the magnetic field $H = 0.86$ T.

3. Results and discussion

The results of the full-profile analysis of X-ray diffraction pattern of samples of $Bi_{0.8}Er_{0.2-x}Dy_xFeO_3$ performed using the Rietveld method are listed in the table. Co-doping of $BiFeO_3$ with cations Dy^{3+} and Er^{3+} results in the stabilization of crystal lattices and obtaining samples with a predominant content of *Pnma* phases. The amount of impurity $Bi_2Fe_4O_9$, which does not exhibit ferro- or ferrimagnetic and ferroelectric properties at temperatures greater than 250 K [8], is significantly lower in case of co-doping, than in bismuth ferrite. No traces of the initial oxides were found, which indicates their complete polymorphic transformation.

The chemical composition of the samples and their stoichiometric ratio of 1:1:3 are confirmed by data from the analysis of the energy spectrum measured using energy dispersive X-ray spectroscopy.

The results of the data analysis indicate that the values of the constant elementary cells of crystal lattices of $Bi_{0.2}Dy_xEr_{1-x}FeO_3$ compositions systematically change because of the effect of $4f$-compression, however, structural factors are weakly sensitive to small changes of composition. The diffraction peaks shift to the region of higher angle values with the increase of the degree of substitution, which is attributable to the smaller radii of the cations Dy^{3+} (1.05 Å) and Er^{3+} (1.03 Å) compared with the radius of

the cation Bi^{3+}. However, since the radii of the cations Dy^{3+} and Er^{3+} are close, the values of the parameters of the crystal lattices of the samples slightly vary depending on the degree of substitution. This circumstance gives reason to assume that changes of the magnetic properties of $Bi_{0.2}Dy_xEr_{1-x}FeO_3$ compounds will be more determined by the magnetic characteristics of the substituting cations than by changes of the parameters of their crystal lattices. The absolute value of the intrinsic magnetic moment of the cation Dy^{3+} ($10.7\mu_B$) is greater than that of Er^{3+} ($9.5\mu_B$), therefore it is logical to expect the observation of higher values of specific magnetizations with an increase of the degree of substitution at least, at low temperatures.

Figure 1 shows the results of studies of the heat capacity C_p of solid solutions of $BiFeO_3$, $Bi_{0.2}Dy_{0.05}Er_{0.15}FeO_3$ and $Bi_{0.2}Dy_{0.15}Er_{0.05}FeO_3$ in the temperature range of $300-800$ K. As can be seen from the figures, the temperature dependences of the heat capacity of all compositions show maximum anomalies in the region of antiferromagnetic phase transition temperature range $T_N \approx 645$ K, $T_N \approx 640$ K and $T_N \approx 637$ K, respectively. An additional pronounced anomaly characteristic of the structural phase transition is observed for the $Bi_{0.2}Dy_{0.05}Er_{0.15}FeO_3$ composition at a temperature of $T_1 \approx 542$ K. Doping of bismuth ferrite with

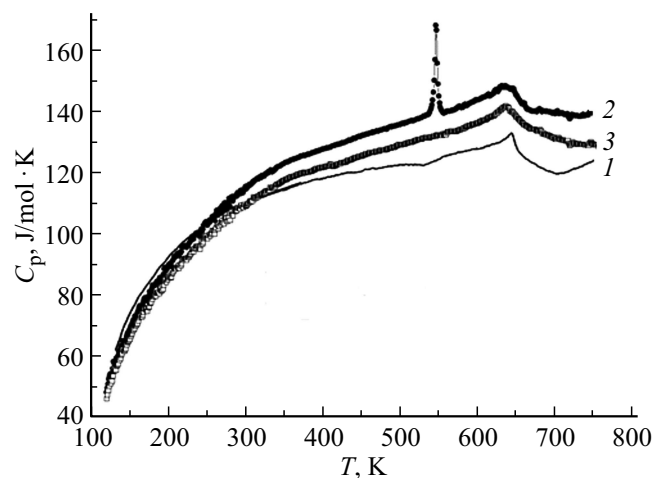**Figure 1.** Temperature dependence of the heat capacity of $BiFeO_3$ (*1*) and $Dy_xEr_{0.2-x}Bi_{0.8}FeO_3$ at $x = 0.05$ (*2*), $x = 0.15$ (*3*).
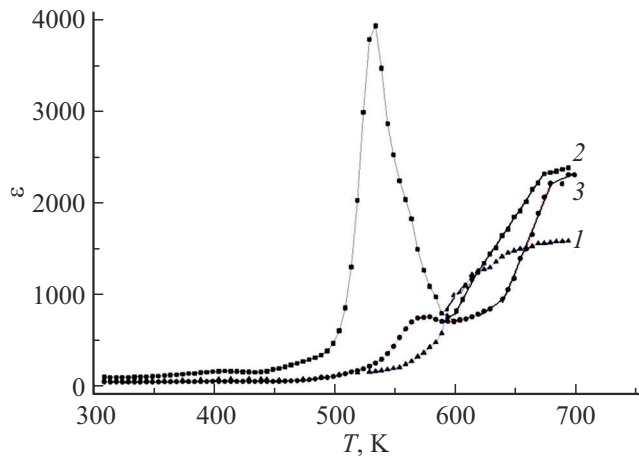
Figure 2. Temperature dependence of the dielectric constant of BiFeO$_3$ (*1*) and Dy$_x$Er$_{0.2-x}$Bi$_{0.8}$FeO$_3$ at $x = 0.05$ (*2*), 0.15 (*3*). The concentration dependence of the dielectric permittivity at room temperature is shown in the insert.

erbium and dysprosium results in an increase of the heat capacity in a wide temperature range above $T \geq 300$ K and a shift of the transition T_N to the low temperature region by 4.0 and 8.0 K, respectively, for compositions with concentrations of $x = 0.05$ and 0.15 (Figure 1). It was previously shown that the additional contribution of bismuth ferrite in the region of high temperatures $T \geq 300$ K to the heat capacity in case of REE doping can be interpreted as a Schottky anomaly for three-level states occurring from distortion of lattice parameters in case of substitution of bismuth with rare earth elements [9,10]. The temperature dependences of the dielectric constant ε of the compound Bi$_{0.8}$Dy$_x$Er$_{1-xc}$FeO$_3$ (where $x = 0.05$ and 0.15) in the temperature range of 300−750 K measured at a frequency of 1 kHz are shown in Figure 2. Two anomalies are observed based on the temperature dependences of the actual components of the dielectric constant ε (Figure 2) in Bi$_{0.8}$Dy$_{0.05}$Er$_{0.15}$FeO$_3$ and Bi$_{0.8}$Dy$_{0.15}$Er$_{0.05}$FeO$_3$ compositions: in the region of antiferromagnetic phase transition temperature T_N and characteristic of the structural phase transition at temperature of $T_1 \approx 538$ and $T_1 \approx 577$ K (below T_N), respectively, for compositions with $x = 0.05$ and 0.15. For the composition with $x = 0.05$ on the dependencies $C_p(T)$ and $\varepsilon(T)$, areas of abnormal behavior are observed at the same temperature T_1. The anomaly on the dependence $\varepsilon(T)$ erodes with an increase of the concentration of dysprosium (for composition c $x = 0.15$) and shifts to the high temperature region ($T_1 \approx 577$ K). There were no specific features in the behavior of the dependence $C_p(T)$ at this temperature. This behavior of heat capacity is usually typical for ferroelaxor materials in which a blurred phase transition is realized with the formation of a nanopolar structure [11,12].

The X-ray diffraction studies (table) at room temperature show that two phases are realized in Bi$_{0.8}$Dy$_x$Er$_{1-x}$FeO$_3$

compositions (where $x = 0.05$ and 0.15): rhombohedral $R3c$ and orthorhombic $Pnma$.

Therefore, it can be assumed based on a comparison of X-ray diffraction, calorimetric and dielectric studies, that the anomaly of heat capacity and dielectric constant at T_1 (in Figures 1 and 2) for the composition Bi$_{0.8}$Dy$_x$Er$_{1-x}$FeO$_3$ (where $x = 0.05$ and 0.15) may be attributable to a structural phase transition between rhombohedral and orthorhombic structures. It should be noted that rhombohedral $R3c$ and orthorhombic $Pnma$ phases were found at room temperature for $x = 0$ (i.e. for Bi$_{0.8}$Er$_{0.2}$FeO$_3$) and in paper [13] based on X-ray diffraction studies Bi$_{0.8}$Er$_{0.2}$FeO$_3$.

Figure 3 shows the temperature dependences of the magnetization of solid solutions of Bi$_{0.2}$Dy$_x$Er$_{1-x}$FeO$_3$. As can be seen from the figure, an increase of the concentration of dysprosium Dy$_x$ results in an increase of magnetic properties and the magnetization becomes maximum at $x \geq 0.15$. It can be seen from the figure that there are probably impurity phases with nonzero magnetization above the magnetic transition in the paramagnetic phase. In particular, this may be the rare-earth orthoferrites DyFeO$_3$ or ErFeO$_3$, in which a weak ferromagnetic moment persists at high temperatures (above 700K) [14,15].

Therefore, the results of studies of Bi$_{0.2}$Dy$_x$Er$_{1-x}$FeO$_3$ show that a two-phase rhombohedral $R3c$ and orthorhombic $Pnma$ structure is realized in case of doping of bismuth ferrite with two rare earth elements such as erbium and dysprosium which results in an additional contribution to the heat capacity in a wide temperature range, a shift in the temperature of the antiferromagnetic phase transition to the low temperature region and an increase of magnetization with an increase of the concentration of dysprosium. The additional anomaly of heat capacity and dielectric constant detected on temperature dependences for compositions with $x = 0.05$ and 0.15 at $T \approx 542$ and 577 K, respectively,
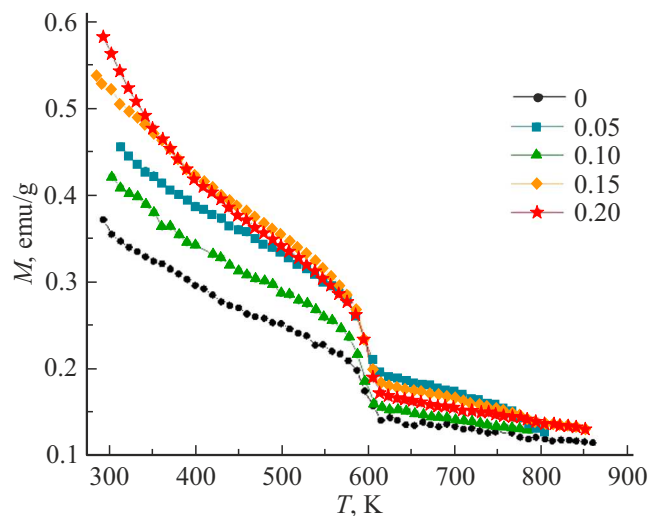

Figure 3. Temperature magnetization of heat capacity Dy$_x$Er$_{0.2-x}$Bi$_{0.8}$FeO$_3$ at different concentrations of Dy.

indicate that it may be due to a structural phase transition between rhombohedral and orthorhombic structures.

Conflict of interest

The authors declare that they have no conflict of interest.

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