Structure and Properties of the $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ Multiferroics Solid Solutions

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Abstract The $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ ferrites solid solutions were synthesized and their crystal structure, magnetic susceptibility, thermal expansion, electrical conductivity, thermo-EMF and dielectric properties were studied. It was found that $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ had rhombohedral structure (space group $R3c$), but $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ one had orthorhombic structure (space group $Pnma$) and all the complex oxides studied were the antiferromagnetic semiconductors of p -type, which electrical conductivity values were larger than for unsubstituted bismuth ferrite BiFeO_3 , Neel temperature and thermo-EMF coefficient sharply decreased at partial substitution of iron by manganese and linear thermal expansion coefficient values varied within $(10.0\text{--}13.4)\cdot 10^{-6}\text{K}^{-1}$. The values of charge carriers transfer parameters in $(\text{Bi,Nd})(\text{Fe,Mn})\text{O}_3$ phases were calculated.

Keywords Bismuth Ferrite, Multiferroics, Magnetic Susceptibility, Thermal Expansion, Electrical Conductivity, Thermo-EMF, Dielectric Susceptibility, Dielectric Losses

ferrite or its derivatives, as well as by partial substitution of bismuth ions in BiFeO_3 by ions of rare earth elements(REE) [4,5] or of iron ions by 3d-metal ions [6, 7].

One can effectively regulate the physico-chemical properties of perovskite oxides (ABO_3) by means of joint substitution of cations located in the A- and B-sublattices of their crystal structure with maintaining (ABO_3) or violation their oxygen stoichiometry ($\text{ABO}_{3-\delta}$). Similar approach was used by different authors [8–10], which have studied magnetic and dielectric properties of $\text{Bi}_{1-x}\text{Dy}_x\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ ($0.03 \leq x \leq 0.30$) solid solutions [8], thermal expansion and electrical properties of $\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{CoO}_3$ ($0.0 \leq x \leq 1.0$) bismuth–praseodymium ferrites–cobaltites [9], as well as the magnetic properties of $\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-x}\text{CoO}_3$ ($1.0 \geq x \geq 0.7$) solid solutions [10].

In analysis of properties of double-substituted solid solutions it is difficult to isolate the impact of individual replacing ion. Therefore the aim of this work was to study the effect of separate and joint replacement of bismuth ions by neodymium ions and of iron ions by manganese ions on the crystal structure and physico-chemical properties of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ solid solutions.

1. Introduction

As a base for development of multiferroics of new generation which able to find use in a variety of devices of electronics, spintronics, etc., bismuth ferrite with perovskite structure BiFeO_3 is considered [1], since this double oxide possesses high values of temperatures of antiferromagnetic (near 640K) and ferroelectric ordering (near 1100K) [1, 2]. The disadvantage of BiFeO_3 is the presence in it of an incommensurate spatially modulated structure of cycloid type, and therefore it does not have a linear magnetoelectric effect, and possesses only considerably less intense quadratic one [1]. The suppression of the spatially modulated structure, giving the possibility to obtain multiferroics with large linear magnetoelectric effect based on BiFeO_3 , can be achieved by the application of large magnetic fields, by production thin films based on the bismuth

2. Materials and Methods

The $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ и $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ ceramic samples were synthesized by means of solid-state reaction method from Bi_2O_3 (chemically pure grade), Nd_2O_3 (super pure grade), Fe_2O_3 (super pure grade) и Mn_2O_3 (super pure grade) in air within 1073–1113 K during 8–40 h [9]. X-ray diffraction analysis (XRD) of the powder samples using Bruker D8 XRD diffractometer ($\text{CuK}\alpha$ -radiation, Ni-filter) was performed; unit cell parameters of the solid solutions prepared by means of XRD table processor RTP and data filing of International Center for Diffraction Data (ICDD JCPDS) were determined [10]. IR-absorption spectra of the powder samples were recorded in tablet powder mixtures with KBr (chemically

pure grade) for the Nexus Thermo Nicolet Fourier spectrometer in the frequency range 300–1500 cm^{-1} ($\Delta\nu \leq \pm 2 \text{ cm}^{-1}$). The apparent density of the samples (ρ) was determined using their mass and geometrical dimensions.

The specific magnetization (σ) of the samples in a magnetic field of 0.86 T in the temperature range 80–1000 K by Faraday method was measured at the Scientific and Practical Materials Research Centre of the NAS of Belarus.

Thermal expansion, DC and AC (1 kHz frequency) electrical conductivity, thermo-EMF, dielectric susceptibility and dielectric losses (1 kHz frequency) of the sintered samples were studied in air within 300–1100 K (for thermal expansion within 300–760 K) using methodologies described in [9, 11, 12]. Values of the linear thermal expansion coefficient (LTEC, α) of the samples were calculated from the linear parts of $\Delta l/l_0 = f(T)$ dependences. Activation energy of electrical conductivity (E_A) and thermo-EMF (E_S) of ceramic samples were calculated from the linear parts of $\ln(\sigma T) = f(1/T)$ and $S = f(1/T)$ dependences respectively.

3. Results and Their Discussion

On the powder diffractograms of the samples after final stage of the synthesis in addition to the reflexes of main phase (BiFeO_3 -type perovskite) the reflexes of impurity phases – $\text{Bi}_{25}\text{FeO}_{39}$ (syllenite) and $\text{Bi}_2\text{Fe}_4\text{O}_9$ (mullite) were detected (Figure 1). Our results are in a good accordance to the literature data [13, 14], which claim that using solid-state reactions method the monophasic samples of perovskite bismuth ferrite cannot be obtained practically, because due to the difficulties of transfer of bismuth oxide through the layer of product – BiFeO_3 – the reaction

cannot be completed: along with the reaction product – BiFeO_3 perovskite – in the reaction mixture remains some amount of semiproducts – enriched by bismuth oxide $\text{Bi}_{25}\text{FeO}_{39}$ syllenite and enriched by iron oxide $\text{Bi}_2\text{Fe}_4\text{O}_9$ mullite [14]. This problem cannot be solved by increasing of annealing time or temperature, because will lead either to the depletion of mixture by Bi_2O_3 due to its sublimation into gas phase or to the peritectic melting of BiFeO_3 – in both cases the ceramics formed will be enriched by mullite ($\text{Bi}_2\text{Fe}_4\text{O}_9$) [13].

The $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ samples had rhombohedrally distorted perovskite structure (space group $R3c$) like BiFeO_3 , but $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ had the orthorhombically distorted perovskite structure (space group $Pnma$) (Figure 1, Table 1). This structural change at transition from $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ to $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ is due, probably, to the increasing concentration of cations-substituents in the latter (from 7.5 mol.% to 15 mol.%). So, it was found in [15], that in the BiFeO_3 – NdMnO_3 quasi-binary system the $\text{Bi}_{1-x}\text{Nd}_x\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$ solid solutions at $x < 0.12$ (concentration of substituting cations is less than 12 mol.%) had rhombohedrally distorted perovskite structure, but at $x > 0.12$ (concentration of substituting cations is more than 12 mol.%) had orthorhombically distorted perovskite structure.

According to the literature data, the a and b unit cell parameters of BiFeO_3 are equal to 0.56207(3) and 1.3692(13) nm [4], 0.55786 and 1.38667 nm [5], 0.5576 and 1.386 nm [9], and 0.558760 and 1.38670 nm [16] respectively.

Figure 1. X-ray powder diffractograms ($\text{CuK}\alpha$ -radiation) (1–3) and IR-absorption spectra (4–6) of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ (1, 4), $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (2, 5), and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (3, 6) samples. Symbols * and # depict the reflexes of impurity phases $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{39}$ respectively

Table 1. Syngony, space group, parameters (a , b , c) and volume (V) of the unit cell, volume of perovskite unit cell (V_p) of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ ferrites solid solutions

Sample	Syngony	Space group	a , nm	b , nm	c , nm	V , nm^3	V_p , nm^3
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$	R	$R3c$	0.5575(3)	–	1.382(1)	0.3772(6)	0.0629(1)
$\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$	R	$R3c$	0.5573(4)	–	1.381(1)	0.3716(8)	0.0619(2)
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$	O	$Pnma$	0.5579(11)	0.7847(12)	0.5582(15)	0.2444(15)	0.0611(4)

Figure 2. Temperature dependences of specific magnetization of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ (A), $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (B), and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (C) powders

Partial substitution of bismuth ions by neodymium ions and of iron ions by manganese ions led to the expected decreasing of the unit cell parameters of solid solutions formed (according to [17], ionic radii of Bi^{3+} , Nd^{3+} , Fe^{3+} and Mn^{3+} for C.N. = 6 are equal to 0.102 nm, 0.0995 nm, 0.0645 nm and 0.065 nm respectively [17]) which was most pronounced for double-substituted $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ solid solution (Table 1).

On the IR-absorption spectra of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ solid solutions having rhombohedrally distorted perovskite structure four absorption bands with

maxima at 357–363 cm^{-1} (ν_1), 390 cm^{-1} (ν_2), 436–445 cm^{-1} (ν_3) and 550–553 cm^{-1} (ν_4) were observed (Figure 1). On the IR-absorption spectrum of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ having orthorhombically distorted perovskite structure only two absorption bands with maxima at 388 cm^{-1} (ν_2) and 561 cm^{-1} (ν_4) were found (Figure 1). According to [18], these absorption bands correspond to the stretching (ν_4) and bending (ν_3) vibrations of the (Fe,Mn)–O bonds and vibrations of (Bi,Nd)–O bonds (ν_1 , ν_2) in the crystal structure of these complex oxides. We have previously found that for BiFeO_3 values of ν_1 , ν_2 , ν_3 , and ν_4 absorption bands on the IR-absorption spectrum are equal to 350 cm^{-1} , 384 cm^{-1} , 430 cm^{-1} , and 540 cm^{-1} respectively [9]. Comparing results of this work with the data for BiFeO_3 we can conclude that partial substitution of bismuth ions by neodymium ions and of iron ions by manganese ions in bismuth ferrite with perovskite structure leads to the increasing of energy of metal–oxygen interactions in the structure of (Bi,Nd)(Fe,Mn) O_3 solid solutions. It should be noted that IR-absorption spectroscopy results are in a good accordance with the XRD data which show that unit cell parameters for (Bi,Nd)(Fe,Mn) O_3 oxides are less than for unsubstituted bismuth ferrite BiFeO_3 (Table 1).

On the temperature dependences of specific magnetization of bismuth–neodymium ferrites–manganites during heating and cooling at temperatures below Neel temperature hysteresis was observed: values of specific magnetization of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ powders in the antiferromagnetic region during cooling were larger (Figure 2A, 2C), but for $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ sample were smaller than during heating (Figure 2B).

The reason of hysteresis observed is probably presence in the samples of small amounts of impurity phases – $\text{Bi}_{25}\text{FeO}_{39}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ (Figure 1). Syllenite ($\text{Bi}_{25}\text{FeO}_{39}$) is paramagnetic within 5–950 K [19] and for mullite ($\text{Bi}_2\text{Fe}_4\text{O}_9$) magnetic phase transition from antiferromagnetic into paramagnetic state take place at 260 K [20]. Taking this into account, the hysteresis on the $\sigma = f(T)$ dependences for the (Bi,Nd)(Fe,Mn) O_3 oxides (Figure 2) can be associated with partial ordering having ferromagnetic nature of microdomains of impurity phases (syllenite and mullite) and microdomains of the main phase (solid solution on the base of perovskite bismuth ferrite) while cooling the samples in magnetic field.

The value of Neel temperature (T_N) for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ solid solution was 624 K, is close to the Neel temperature of BiFeO_3 (640 K [2]), but for the $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ solid solutions T_N values were equal to 470 K and 473 K respectively (Table 2).

Thus, the intensity of the magnetic interactions of iron ions in bismuth ferrite BiFeO_3 at partial substitution of Fe^{3+} ions by Mn^{3+} ions decreases stronger than at the partial substitution of Bi^{3+} ions by Nd^{3+} ions in its structure.

Table 2. Magnetic properties of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ (BNFO), $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (BFMO), and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (BNFMO) ferrites

Sample	T_N , K	Θ , K	C , $\text{cm}^3\cdot\text{K}/\text{mol}$	$10^3\cdot\Delta\chi$, cm^3/mol	$10^3\cdot\chi_{T_N}$, cm^3/mol	$10^3\cdot\chi_{T=0}$, cm^3/mol	P_{eff}^{exp} , μ_B	P_{eff}^{theor} , μ_B
BNFO	624	-1054	4.090	1.37	3.81	2.61	5.72	6.01
BFMO	470	-938	3.564	0.89	3.42	1.98	5.34	5.76
BNFMO	473	-764	3.932	2.96	6.14	2.57	5.61	5.86

The values of jump of molar magnetic susceptibility ($\Delta\chi$) of $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ ferrites–manganites at their transition from antiferromagnetic into paramagnetic state was $\approx(0.9\text{--}3.0)\cdot 10^{-3} \text{ cm}^3/\text{mol}$ and was greatest for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (Table 2). Value of molar magnetic susceptibility of ceramics studied at Neel temperature varied within $(3.4\text{--}6.1)\cdot 10^{-3} \text{ cm}^3/\text{mol}$ and was maximal for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ – $6.14\cdot 10^{-3} \text{ cm}^3/\text{mol}$ (Table 2). Extrapolation of linear parts of $\chi_{\text{mol}} = f(T)$ dependences at $T < T_N$ to the $T = 0 \text{ K}$ for the samples studied gave us their $\chi_{T=0}$ values (Table 2). It is known that for uniaxial antiferromagnetics having two sublattices the theoretical value of $\chi_{T=0}/\chi_{T_N}$ is $2/3 = 0.667$ [21]. For $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ this ratio (0.69) was close to the theoretical value, but for $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ it was equal to 0.58 and 0.43 respectively, which is significantly smaller.

In the paramagnetic region the temperature dependences of molar magnetic susceptibility of the samples obeyed Curie–Weiss law

$$\chi_{\text{mol}} = \frac{C}{T - \Theta}, \quad (1)$$

where C is a molar Curie constant and Θ is a Weiss constant (paramagnetic Curie temperature).

Table 2 lists the values of constant of Curie–Weiss law (C and Θ), and the effective magnetic moment (P_{eff}^{exp}) per formula unit evaluated from the Curie constant (C) as

$$P_{eff}^{exp} = \frac{\sqrt{3RC}}{N_A \mu_B}, \quad (2)$$

where R is gas constant, N_A is Avogadro's number, and μ_B is the Bohr magneton. Also given in Table 2 are (P_{eff}^{theor}) theoretical values obtained as

$$P_{eff}^{theor} = \sqrt{\sum_{i=1} \mu_i^2}. \quad (3)$$

Here μ_i is the magnetic moment per cation in the i th magnetic subsystem,

$$\mu_i = \sqrt{n(n+2)} \mu_B \quad (4)$$

where n is the average number of unpaired electrons per magnetic cation ($n = 3, 4$, and 5 for Nd^{3+} , Mn^{3+} , and Fe^{3+} ions respectively).

As can be seen from the data given in the Table 2, for all

samples studied C values are close each other and paramagnetic Curie temperatures are negative, which points to a negative sign of exchange interactions between the magnetic ions in the structure, that is, to antiferromagnetic order of the magnetic moments of $3d$ transition metals cations (Fe^{3+} and Mn^{3+}) and Nd^{3+} cations in the $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ perovskites.

Ratio $|\Theta|/T_N$ for the $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ ferrites is equal to 1.69, 2.00, and 1.62 respectively.

Values of P_{eff}^{exp} for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ were $0.29 \mu_B$ (4.8%), $0.42 \mu_B$ (7.3%), and $0.25 \mu_B$ (4.3%) respectively smaller than P_{eff}^{theor} ones (Table 2) which is may be due to the high covalence of metal–oxygen bonds in the crystal structure of these oxides or due to the fact that part of iron or manganese ions present in the crystal lattice of these phases in the low-spin state.

Comparing values of apparent density of the $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ samples (Table 3) with ρ values of BiFeO_3 ceramics, sintered at the same conditions (4.87 g/cm^3 [9]) one can conclude that sinterability of BiFeO_3 derivatives deteriorates at partial substitution of bismuth ions by neodymium ions and improves at partial substitution of iron ions by manganese ions in these compounds.

Temperature dependences of the relative elongation of the samples were linear practically. So, within 300–750 K temperature region these complex oxides do not undergo the structural phase transitions. Value of LTEC (Table 3) for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ solid solutions was larger but for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ was smaller than for BiFeO_3 ($11.9\cdot 10^{-6} \text{ K}^{-1}$ [9]).

The dielectric susceptibility and dielectric losses of the samples studied, in the whole, increased at temperature increasing, passing through a number of extrema (minima for $\epsilon = f(T)$ dependences and maxima for $\text{tg}\delta = f(T)$ ones) (Figure 3), associated with the transition samples from antiferromagnetic into paramagnetic phase ($T \approx T_N$) as well with processes of dipoles disordering which occurs in oxides $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ at elevated temperatures.

Values of ϵ_{300} and $\text{tg}\delta_{300}$ for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ were equal to 450 and 0.75, 190 and 4.57, 240 and 2.21 respectively. Thus, highest dielectric susceptibility and lowest dielectric losses at room temperature possesses the Nd-substituted $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ solid solution.

Figure 3. Temperature dependences of dielectric susceptibility (1) and dielectric loss tangent (2) of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ (A), $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (B), and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (C) ceramic samples.

Table 3. Values of apparent density (ρ), linear thermal expansion coefficient (α) and charge carriers transfer parameters (E_A , E_S , E_m) for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ sintered ceramics

Sample	ρ , g/cm ³	$\alpha \cdot 10^6$, K ⁻¹	E_A^{DC} , eV	E_A^{AC} , eV	E_S , eV	E_m , eV
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$	4.80	12.9	0.540	0.487	0.212	0.328
$\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$	5.40	13.4	0.454	0.454	0.073	0.381
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$	3.70	10.0	0.547	0.499	0.080	0.467

As can be seen from the Figure 4, all the $(\text{Bi,Nd})(\text{Fe,Mn})\text{O}_3$ ceramic samples studied were semiconductors ($\partial\sigma/\partial T > 0$) of p -type (for $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{FeO}_3$ ceramics within 930–1030 K temperature interval the values of Seebeck coefficient were negative ($S < 0$)).

Values of DC electrical conductivity of bismuth–neodymium ferrites–manganites studied within 300–1100 K temperature interval varied within $1.9 \cdot 10^{-7}$ – 0.062 S/cm, $1.9 \cdot 10^{-6}$ – 0.218 S/cm, and $8.6 \cdot 10^{-7}$ – 0.221 S/cm for $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ respectively and at elevated temperatures were significantly larger than for unsubstituted bismuth ferrite (according to [9], σ values for BiFeO_3 increased from $1.3 \cdot 10^{-6}$ to 0.026 S/cm at temperature increasing from 300 to 1100 K). Comparing results, obtained for $(\text{Bi,Nd})(\text{Fe,Mn})\text{O}_3$ oxides, one can conclude that partial substitution of iron ions by manganese ions in BiFeO_3 results in higher increasing of σ values of ceramics forming than partial substitution of bismuth ions by neodymium ions.

Values of DC and AC electrical conductivity of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ compound for all temperature interval studied were close each other (Figure 4A), but for $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ samples DC electrical conductivity values were larger than AC ones (Figure 4B, C). The last is probably due to the fact that the electrical conductivity of these samples are making a significant contribution impurity phases ($\text{Bi}_{25}\text{FeO}_{39}$, $\text{Bi}_2\text{Fe}_4\text{O}_9$ and their solid solutions), located at the grain boundaries of ceramics and having a higher conductivity than the main phase ($\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ perovskite solid solutions).

The values of activation energy of electrical conductivity (E_A) of the $(\text{Bi,Nd})(\text{Fe,Mn})\text{O}_3$ samples ranged within 0.454–0.547 eV (DC), 0.454–0.499 eV (AC) (Table 3) and were significantly lower than for BiFeO_3 (0.632 eV [9], 0.628 eV [22]). Thus, partial substitution of Bi^{3+} by Nd^{3+} and of Fe^{3+} by Mn^{3+} in BiFeO_3 leads to decreasing of activation energy of electrical conductivity of solid solutions forming, herewith the minimal values of E_A possesses the Mn-substituted compound and for Nd- and Nd,Mn-substituted samples the E_A values are close each other.

Figure 4. Temperature dependences of DC (1) and AC (2) electrical conductivity and thermo-EMF (3) of $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ (A), $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (B), and $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ (C) sintered ceramics

Values of thermo-EMF coefficient for $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ ceramics were lower than for unsubstituted bismuth ferrite (according to [9], Seebeck coefficient of BiFeO_3 within 623–1073 K varies from 595 to 1000 $\mu\text{V/K}$) (Figure 4), and for Mn-containing solid solutions, taking into account the values of their electrical conductivity, were abnormally low (so, for example, within 600–800 K temperature region $\sigma(\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3) \approx \sigma(\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3)$, but $S(\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3) \gg S(\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3)$), and

for $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ the temperature coefficient of thermo-EMF at 980 K changed sign from negative ($\partial S/\partial T < 0$) to positive ($\partial S/\partial T > 0$) (Figure 4B). Similar anomalies of thermo-EMF are not typical for semiconductors, but may occur in the strongly correlated systems, which include many perovskites and layered cobaltites of REE and barium, layered sodium or calcium cobaltites as well as perovskite bismuth ferrite.

So, in the work [23] at describing of thermo-EMF of sodium cobaltite Na_xCoO_2 was used modified Heikes's equation

$$S = \frac{k}{e} \ln \left(\frac{g_4[\text{Co}^{3+}]}{g_3[\text{Co}^{4+}]} \right), \quad (5)$$

where k is Boltzmann's constant, e is charge of electron, g_4 and g_3 are degeneracy of Co^{4+} and Co^{3+} cations respectively, and $[\text{Co}^{3+}]$ and $[\text{Co}^{4+}]$ are their concentrations in the Na_xCoO_2 structure.

It was shown by authors of [22] that depending on spin states (low-spin state, intermediate-spin state, high-spin state) of Co^{4+} and Co^{3+} cobalt cations in the Na_xCoO_2 structure the value of thermo-EMF coefficient of this phase can vary from –84 to 214 $\mu\text{V/K}$. Taking it into account we can assume that partial substitution of iron ions by manganese ions in BiFeO_3 leads to the change of spin state of iron ions in the structure of the Mn-substituted solid solutions which stipulates observed anomalies of thermo-EMF of the $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ phases.

Temperature dependences of electrical conductivity and thermo-EMF of strongly correlated systems are described with the formulae

$$\sigma = \frac{A}{T} \exp \left(-\frac{E_A}{kT} \right), \quad (6)$$

$$S = \frac{k}{e} \exp \left(-\frac{E_S}{kT} + B \right), \quad (7)$$

where $E_A = E_S + E_m$ and E_S are the activation energies of electrical conductivity and thermo-EMF, herewith the E_S characterizes the excitation energy of charge carriers and E_m does energy of their transfer [24].

In [9] was found that for BiFeO_3 E_S and E_m values were equal to 0.422 and 0.210 eV respectively. As it follows from the data given in the Table 3, the partial substitution $\text{Nd}^{3+} \rightarrow \text{Bi}^{3+}$, $\text{Mn}^{3+} \rightarrow \text{Fe}^{3+}$ in BiFeO_3 significantly reduces excitation energy of charge carriers but increases the energy of their transfer, herewith electrical transport is the most difficult for the double-substituted $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ solid solution which is characterized by highest concentration of ions substituents.

3. Conclusions

By means of solid state reactions method the $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$, $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$, and

$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ bismuth–neodymium ferrites–manganites solid solutions were synthesized and their crystal structure, magnetic susceptibility, thermal expansion, electrical conductivity, thermo-EMF, dielectric susceptibility and dielectric losses were studied and the effect of partial substitution of Bi^{3+} by Nd^{3+} and of Fe^{3+} by Mn^{3+} on the crystal structure and physicochemical properties of the $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ solid solutions was discussed.

It was found that $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$ and $\text{BiFe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ compounds had rhombohedrally distorted perovskite structure (space group $R3c$), but $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_3$ one had orthorhombically distorted perovskite structure (space group $Pnma$) and all the complex oxides studied were the antiferromagnetic p -type semiconductors, which electrical conductivity values were large than for based bismuth ferrite BiFeO_3 , Neel temperature and thermo-EMF coefficient sharply decreased at partial substitution of iron by manganese and linear thermal expansion coefficient values varied within $(10.0\text{--}13.4)\cdot 10^{-6} \text{ K}^{-1}$. It was established that partial substitution $\text{Nd}^{3+} \rightarrow \text{Bi}^{3+}$, $\text{Mn}^{3+} \rightarrow \text{Fe}^{3+}$ in BiFeO_3 reduces excitation energy of charge carriers but increases the energy of their transfer in the $(\text{Bi},\text{Nd})(\text{Fe},\text{Mn})\text{O}_3$ solid solutions.

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