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CRYSTAL STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF THE $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ MULTIFERROICS SOLID SOLUTIONS

The ceramic samples of the $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ ($0.0 < x \leq 0.21$) ferrites solid solutions using solid-state reactions method were prepared and their crystal structure, thermal expansion, electrical conductivity and thermo-EMF were studied. It was shown that in the samples with $0.06 \leq x \leq 0.21$ the coexistence of rhombohedrally and orthorhombically distorted perovskite phases were observed. It was found, that $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ oxides were the *p*-type semiconductors which electrical conductivity values increased but thermo-EMF coefficient ones slightly changed at *x* increasing.

Introduction. A promising basis for the development of a new generation of multiferroics able to find wide application in various fields – from spintronics and photonics to medicine [1] – is a perovskite bismuth ferrite $BiFeO_3$, which possesses high temperatures of antiferromagnetic (T_N = 643 K) and ferroelectric ordering (T_C = 1083 K) [1]. However, the intensity of magnetoelectric interactions in bulk samples of bismuth ferrite is small, as antiferromagnetic structure $BiFeO_3$ is cycloidal modulated and is incommensurate to its crystal structure. In such phases, there is no linear magnetoelectric effect, and there is only quadratic one, the value of which is much less than for linear. Destruction of incommensurate magnetic structure of bismuth ferrite can be achieved by means of high pressure [1] or by the partial substitution of Fe^{3+} [2] or Bi^{3+} cations [3] in its structure.

The aim of this work is the study of effect of simultaneous substitution of bismuth ions by neodymium ions and iron ions by manganese ions in the structure of perovskite-like bismuth ferrite on its crystal structure, thermal expansion, electrical conductivity and thermo-EMF.

Experimental technique. Ceramic samples of the $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ ($0.0 < x \leq 0.21$) ferrites solid solutions from Bi_2O_3 (pure grade), Nd_2O_3 (super pure grade), Mn_2O_3 (super pure grade) and Fe_2O_3 (pure for analysis) oxides using solid-state reactions method in air during 8 hours at 1073 K were obtained.

Identification of the samples and determination of their lattice constants by means of X-ray diffraction analysis (XRD) (X-ray diffractometer D8 Advance Bruker AXS (Germany), CuK_α-radiation) and IR-absorption spectroscopy (Furier spectrometer Nexus) was performed.

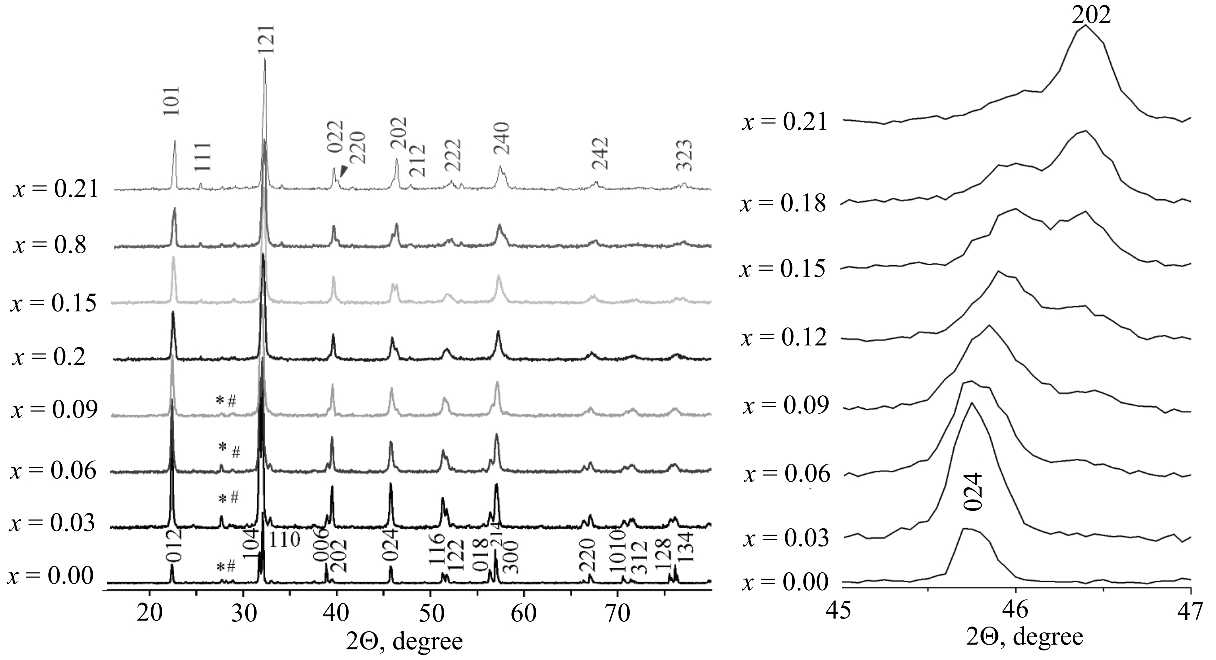
The apparent density of the samples (ρ_{app}) was determined using their mass and geometrical dimensions. Thermal expansion, electrical conductivity (σ) and thermo-EMF (S) of ceramics were studied in air within 300–1100 K (for thermal expansion within 300–760 K) using methods described in [4–6]. Values of the linear thermal expansion coefficient (LTEC, α) and activation energies of electrical conductivity (E_A) and thermo-EMF (E_S) of the samples were calculated from linear parts of $\Delta l/l_0 = f(T)$, $\ln(\sigma \cdot T) = f(1/T)$ and $S = f(1/T)$ dependences respectively.

Results and their discussion. On the diffractograms of $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ samples the reflexes of impurity phases – $Bi_{25}FeO_{39}$ (syllenite) and $Bi_2Fe_4O_9$ (mullite) were detected, which amounts were maximal for the compositions of $0.03 \leq x \leq 0.09$ (Fig. 1, *a*). Our results are in a good accordance to the literature data [7, 8], which claim that using solid-state reactions method the monophase 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

$$Bi_2O_{3,s} + Fe_2O_{3,s} = 2BiFeO_{3,s}$$

cannot be completed: along with the reaction product – $BiFeO_3$ perovskite – in the reaction mixture remains some amount of semiproducts – enriched by bismuth oxide $Bi_{25}FeO_{39}$ syllenite and enriched by iron oxide $Bi_2Fe_4O_9$ mullite [8]. 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 ($Bi_2Fe_4O_9$) [7]. As can be seen from Fig 1, *b*, the solid solution with $x = 0.03$ possessed rhombohedrally distorted perovskite structure ($BiFeO_3$ structure), but in the samples with $0.06 \leq x \leq 0.21$, according to the XRD data, the coexistence of rhombohedral (space group *R*3*c*) and orthorhombic (space group *Pnma*) phases of $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ perovskites was found and with the *x* increasing the amount of orthorhombic phase is also increased. Such morphotropic transition in the system $BiFeO_3$–$PrCoO_3$ was detected [9].

As it seen from Fig. 1, with increasing of substitution degree of bismuth by neodymium and of iron by manganese the diffraction peaks of $Bi_{1–x}Nd_xFe_{1–x}Mn_xO_3$ powders shifted to higher angles, indicating that unit cell dimensions of these solid solutions decreased at *x* increasing (Table 1).



a *b*

*– $Bi_{25}FeO_{39}$; # – $Bi_2Fe_4O_9$

Fig. 1. X-ray diffractograms of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ powders

On the IR-absorption spectra of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ solid solutions with $0.0 < x \leq 0.09$ (Fig. 2), similar to the spectrum of $BiFeO_3$, four absorption bands at maxima at 540–553 cm^{-1} (ν_1), 438–440 cm^{-1} (ν_2), 384–389 cm^{-1} (ν_3), 358–359 cm^{-1} (ν_4) are observed, which indicate that in these samples prevail the rhombohedrally distorted perovskite phase. ν_1 and ν_2 absorption bands, according to [10], correspond to the Fe – O bonds vibrations. On the IR-spectra of the samples with $0.15 \leq x \leq 0.21$ only two absorption bands with maxima at 559–561 and 388–401 cm^{-1} were found, so, in these solid solutions the orthorhombically distorted perovskite phase prevail. As can be seen from Fig. 2, absorption bands shift to higher wave numbers at x increasing, indicating that partial substitution of bismuth by neodymium and of iron by manganese leads to increasing of energy of metal – oxygen interaction in the structure of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ solid solutions. IR-absorption spectroscopy results are in a good accordance with the XRD data which show that lattice constants of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ oxides decrease at x increasing (Table 1).

Table 1

Values of lattice constants (*a*, *b*, *c*, *V*), perovskite unit cell (a_p) as well as apparent density (ρ_{app}) of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ solid solutions

x	Structure (space group)	*Z*	*a*, nm	*b*, nm	*c*, nm	*V*, nm^3	a_p, nm	ρ_{app}, g/cm^3
0.0	*R* (*R*3*c*)	6	0.5576	–	1.386	0.3733	0.3962	4.87
0.03	*R* (*R*3*c*)	6	0.5580	–	1.385	0.3734	0.3963	4.60
0.06	*R* (*R*3*c*)	6	0.5577	–	1.383	0.3727	0.3961	4.67
	O (*Pnma*)	4	0.5601	0.7881	0.5588	0.2467	0.3951	
0.09	*R* (*R*3*c*)	6	0.5574	–	1.379	0.3713	0.3956	4.23
	O (*Pnma*)	4	0.5597	0.7893	0.5589	0.2469	0.3952	
0.12	*R* (*R*3*c*)	6	0.5571	–	1.367	0.3677	0.3924	3.97
	O (*Pnma*)	4	0.5570	0.7889	0.5570	0.2448	0.3941	
0.15	*R* (*R*3*c*)	6	0.5558	–	1.377	0.3684	0.3945	3.70
	O (*Pnma*)	4	0.5578	0.7846	0.5582	0.2443	0.3938	
0.18	*R* (*R*3*c*)	6	0.5538	–	1.362	0.3616	0.3921	3.49
	O (*Pnma*)	4	0.5559	0.7871	0.5529	0.2419	0.3925	
0.21	*R* (*R*3*c*)	6	0.5531	–	1,360	0.3603	0.3916	3.37
	O (*Pnma*)	4	0.5556	0.7872	0.5517	0.2413	0.3922	

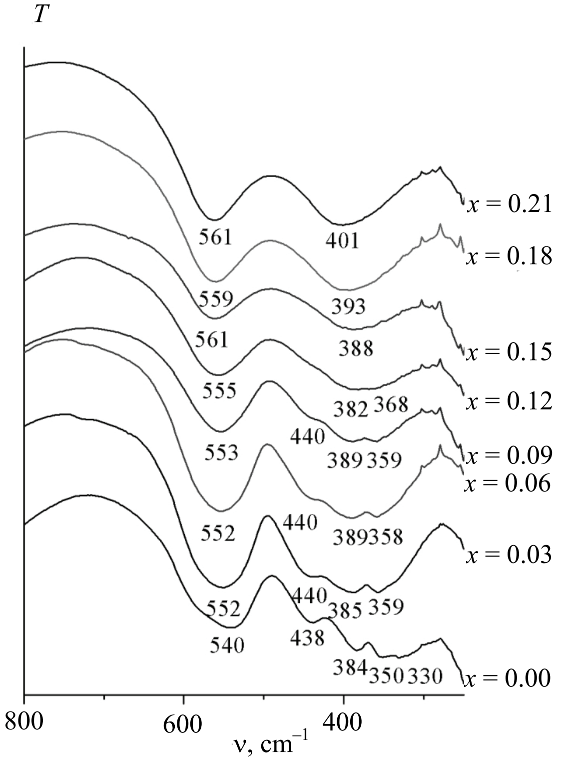


Fig. 2. IR- absorption spectra of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$

Linear thermal expansion coefficient (LTEC) was $\approx 13 \cdot 10^{-6}\ K^{-1}$ for the samples with predominance of rhombohedral phase and $(10–11) \cdot 10^{-6}\ K^{-1}$ for the samples in which the orthorhombic phase is prevailed (Table 2). For the $Bi_{0.88}Nd_{0.12}Fe_{0.88}Mn_{0.12}O_3$ sample LTEC had intermediate value of $12.2 \cdot 10^{-6}\ K^{-1}$.

Table 2

Linear thermal expansion coefficient (α) and activation energies of electrical transport (E_A, E_S, $E_m = E_A - E_S$) of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$

x	$\alpha \cdot 10^6$, K^{-1}	E_A, eV	E_S, eV	E_m, eV
0.03	12.8	0.948	0.076	0.872
0.06	13.0	0.696	0.081	0.615
0.09	13.3	0.655	0.071	0.584
0.12	12.2	0.563	0.078	0.485
0.15	10.0	0.547	0.080	0.467
0.18	10.0	0.504	0.088	0.416
0.21	11.7	0.512	0.074	0.438

The $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ materials were semiconductors ($\partial\sigma/\partial T > 0$) of p-type ($S > 0$), which electrical conductivity increased (Fig. 3), but thermo-EMF coefficient slightly changed at x increasing and for the solid solutions studied was significantly smaller than for nonsubsituted bismuth ferrite $BiFeO_3$. On the temperature dependence of thermo-EMF coefficient of $Bi_{0.97}Nd_{0.03}Fe_{0.97}Mn_{0.03}O_3$ sample similar to the base phase the maximum near 900 K was observed and for the samples with $0.06 \le x \le 0.12$ on the $S = f(T)$ dependences the minimum within temperature interval of 800–900 K was found. For other samples investigated thermo-EMF coefficient monotonously decreased at temperature increasing.

Electrical conductivity of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ samples at temperature increasing from 300 to 1100 K increased by about 6 orders from $\sigma_{300} = 9.8 \cdot 10^{-8}\ S \cdot cm^{-1}$ to $\sigma_{1100} = 8.6 \cdot 10^{-2}\ S \cdot cm^{-1}$ for $Bi_{0.94}Nd_{0.06}Fe_{0.94}Mn_{0.06}O_3$.

For the substances with polaronic character of charge transfer which include the studied in this paper $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ oxides, temperature dependences of electrical conductivity and thermo-EMF with relations $\sigma = (A/T) \cdot \exp(-E_A/kT)$, $S = (k/e) \cdot [(-E_S/kT) + B]$ are described, where $E_A = (E_S + E_m)$ and E_S are the activation energies of electrical conductivity and thermo-EMF, E_S meets the excitation energy of polarons and E_m is energy of its transfer (at $E_m > 0$ charge transfer is thermally activated and carried out by small radius polarons (SRP) for hopping mechanism) [11]. As can be seen from given in Table 2 values of E_A, E_S and E_m, charge carriers in $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ are the small radius polarons. Values of activation energy of electrical conductivity (E_A), determined from the linear parts of $\ln(\sigma T) = f(1/T)$ dependences, decreased at increasing of substitution degree of bismuth by neodymium and of iron by manganese (Fig. 3, Table 2). Activation energy of transfer of SRP, in the whole, increased at x decreasing, but value of excitation energy of SRP shanged nonmonotonously and for all the samples studied was less than E_m.

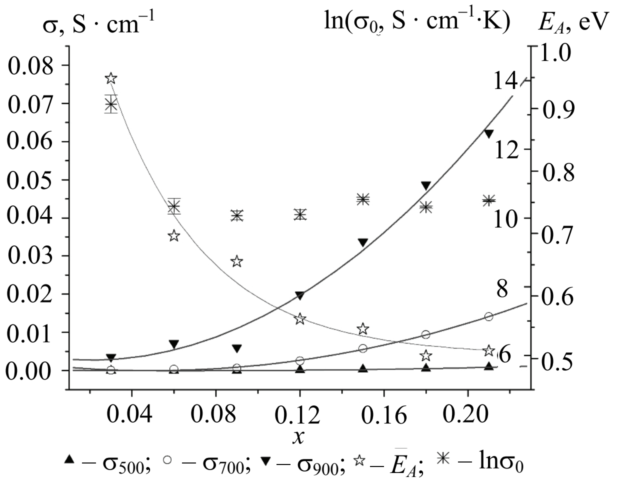


Fig. 3. Concentration dependences of electrical conductivity (σ), activation energy of electrical conductivity (E_A) and logarithm of preexponential factor ($\ln\sigma_0$)

Conclusion. Thus, in this work crystal structure, thermal expansion, electrical conductivity and thermo-EMF of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ $(0.0 < x \le 0.21)$

solid solutions prepared by solid-state reactions method were studied. It was found that solid solution with $x = 0.03$ possessed rhombohedrally distorted perovskite structure ($BiFeO_3$ structure) and in the samples with $0.06 \leq x \leq 0.21$ the coexistence of rhombohedral and orthorhombic phases of $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$, perovskites was observed and at substitution degree the amount of orthorhombic phase is increased. It was shown that $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ oxides are *p*-type semiconductors which electrical conductivity increased and thermo-EMF coefficient slightly changed at x increasing. Activation energy of electrical conductivity as well as energy of SRP transfer decreased at substitution degree of bismuth by neodymium and of iron by manganese.

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