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PHYSICAL AND CHEMICAL PROPERTIES OF $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ SOLID SOLUTIONS SYNTHESIZED BY DIFFERENT METHODS

By using solid-state and sol-gel technologies solid solutions of the $BiFeO_3$ – $LaCoO_3$ system were synthesized. The parameters of their crystal lattice were determined. The temperature dependence of electrical conductivity and thermal expansion of the $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ (x = 0; 0.05; 0.1; 1.0) samples was studied in air in the temperature range of 300–1,050 K. It was shown that the use of sol-gel technology reduces the temperature and the time of synthesis. The samples obtained by solid-phase method have lower coefficients of thermal expansion and specific conductivity.

Introduction. Multiferroics, i.e. materials that combine both ferromagnetic and ferroelectric properties are of great interest for the development of new magnetoelectric materials in which electrical properties can be controlled by the magnetic field and, conversely, the magnetic properties can be modulated by the electric field. This suggests that ferroelectromagnets with the large magnitude of magnetoelectric effect can be used in various fields of sensor electronics for creation of storage devices with ultra-high density of recording, and are promising not containing toxic lead piezoelectric materials with low sintering temperature [1–5].

The most famous of the multiferroics is $BiFeO_3$ in which dipole ordering of about 1,100 K and antiferromagnetic ordering at ≈640 K occur, which gives the possibility to use this material at room temperature [6, 7]. Moreover, a variety of solid solutions can be made on its basis, which further enhances the importance of these compounds. However, the preparation of ceramic-phase $BiFeO_3$ is somewhat complicated because the phase diagram of the system Bi_2O_3 – Fe_2O_3 significant areas are occupied by two more binary compounds – $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ [8, 9].

Therefore, in this work one carried out the investigation of physicochemical properties of solid solutions of iron-cobaltites of bismuth-lanthanum $Bi_{1-x}La_xFe_{1-x}Co_xO_3$, formed as a result of simultaneous isovalent substitution of ions Bi^{3+} with ions La^{3+} in $BiFeO_3$ and the equivalent of quantity of iron ions Fe^{3+} with ions Co^{3+} obtained by using the sol-gel technology and the solid phase method (SPM).

Experimental technique. For the synthesis of polycrystalline solid solutions $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ (x = 0; 0.05; 0.1; 1.0) by solid phase reaction method Bi_2O_3, Fe_2O_3, La_2O_3 and Co_3O_4 were used. Lanthanum oxide La_2O_3 was being previously calcined in air at 1,000°C for 1 h. The powders of compounds taken in predetermined molar ratios were mixed and milled for 30 min in a planetary mill Pulverizette 6 with the addition of ethanol. The obtained charge with the added ethanol was compressed under the pressure of 50–75 MPa into tablets with the diameter of 25 mm and the height of 5–7 mm, and then burnt at 800°C in air for 8 h. After the precalcination the tablets were crushed, milled, compressed into bars of 30 mm in length and with the section of 5×5 mm^2. Synthesis conditions in air ranged widely depending on the composition of the samples: T_1 = 800°C (8 h), T_2 = 830°C (30 min) for the samples x = 0; 0.05; 0.1 and T_2 = 1,150°C (2 h) for x = 1.0.

To obtain iron-cobaltites of bismuth-lanthanum $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ (x = 0; 0.05; 0.1; 1.0) with the help of the sol-gel technology we used a previously developed technique to obtain solid solutions with perovskite structure manganites [10]. The powders obtained by the sol-gel method (SGM), were compressed into tablets and calcinated in the air at temperatures: T_1 = 650ºC (2 h), T_2 = 750ºC (0.5 h) for x = 0, T_2 = 800ºC (0.5 h) for x = 0.05, T_2 = 820ºC (0.5 h) for x = 0.1, T_2 = = 1,100ºC (2 h) for x = 1.0.

X-ray diffraction patterns were obtained on a D8 ADVANCE diffractometer using CuK_α-radiation. The parameters of the crystal structure were determined with the help of X-ray spreadsheet processor RTP and the data catalogs of the International Centre for Diffraction Data (ICDD JCPDS).

Electrical conductivity was measured at constant current in the air in the temperature range of 300–1,000 K by a four-contact method using silver electrodes applied on the face of the samples of size 5×5×4 mm in a thin layer by means of brazing silver paste.

Thermal expansion of the samples investigated in the air in the range of temperatures of 300–1,000 K with a quartz dilatometer in a dynamic (heating and cooling to 3–5 $K \cdot min^{-1}$) mode.

Results and their discussion. The studies of solid solutions of the binary systems of $BiFeO_3$ – $LnFeO_3$ (Ln – rare earth element) in which $BiFeO_3$ and $LnFeO_3$ have rhombohedral and orthorhombic perovskite structure respectively are widely represented in the literature. In the $BiFeO_3$ – $LaCoO_3$

system both components have crystalline structure of rhombohedrally distorted perovskite. Radiographs of samples of the $BiFeO_3$ – $LaCoO_3$ system (Fig. 1) obtained by solid phase reaction method at the synthesis temperature T_1 = 800°C (8 h), T_2 = 830°C (30 min) at x = 0; 0.05; 0.1 and T_2 = 1,150°C (2 h) with x = 1.0 showed that these $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ solid solutions had a rhombohedral distortion of the unit cell of perovskite. The crystal structure of $BiFeO_3$ was characterized by the following unit cell parameters a = 3.963 Å and α = 89°44', which is consistent with the literature data [11]. In this case, the X-ray patterns for $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ ($0 \le x \le 0.1$) samples presented $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ impurity phases, the number of which for the $BiFeO_3$ sample was ≈5%. With the increase of the degree of substitution x the content of mullite phase ($Bi_2Fe_4O_9$) and sillenite phase ($Bi_{25}FeO_{39}$) slightly increased indicating the thermal instability of $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ and complex mechanism of the solid phase reaction in systems based on bismuth ferrite having the melting point (T = 950°C) much less than the melting point of the second component of $LaSoO_3$ system (1,600°C) [12].

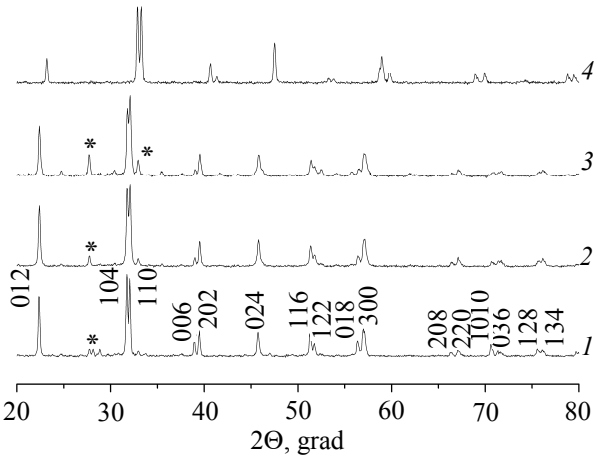

Fig. 1. Radiographs of $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ samples synthesized by the solid phase method, at different values of x:
1 – 0; *2* – 0.05; *3* – 0.1; *4* – 1.0;
* – of phase $Bi_{25}FeO_{39}$, $Bi_2Fe_4O_9$

The results of X-ray phase analysis of $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ (x = 0; 0.05; 0.1; 1.0) samples obtained by the sol-gel technology showed that the crystallization process in powders of xerogels begin already during the heat treatment for at least 2 h at 650°C, as evidenced by the appearance of the X-ray diffuse reflections corresponding to the position of the reflections on the main phase of the synthesized solid solutions $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ (Fig. 2). However, the samples with a degree of substitution of x = 0.05 and 0.1 had also had $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ impurity phases, the number of which was insignificant compared to the corresponding samples obtained by solid-phase method.

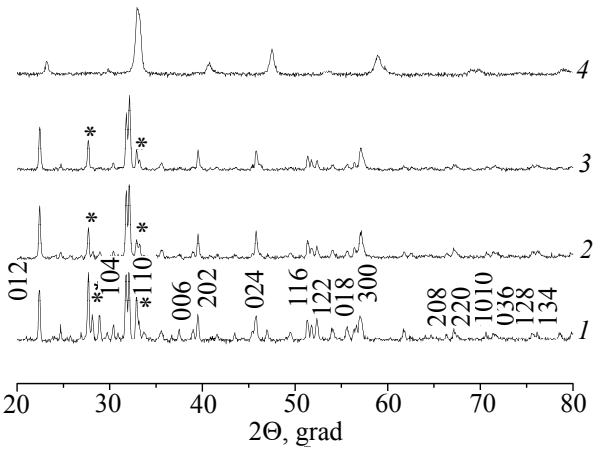

Fig. 2. Radiographs of $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ samples synthesized by the sol-gel method at different values of x:
1 – 0; *2* – 0.05; *3* – 0.1; *4* – 1.0;
* – of phase $Bi_{25}FeO_{39}$, $Bi_2Fe_4O_9$

$Bi_{1-x}La_xFe_{1-x}Co_xO_3$ (x = 0; 0.05; 0.1; 1.0) samples obtained by the sol-gel method at 650°C were subsequently additionally calcinated at temperature above 650°C. Such heat treatments affected the phase composition of the samples differently. For example, calcination at 800°C (30 min) of the sample with x = 0.05 and 820°C (30 min) of the sample with x = 0.1 resulted in a significant decrease in the content of impurities. For the sample corresponding to the composition of the pure bismuth ferrite x = 0), after heat treatment at 750°C (30 min) diffraction patterns showed increase in the amount of impurities and decrease in the main phase. Perhaps bismuth ferrite formation begins at temperature T < 650ºC, and at T > 650ºC $BiFeO_3$ decomposes to form impurity phases. Heat treatment of the powder, equivalent to lanthanum cobaltite $LaCoO_3$ (x = 1) already at 650ºC (2 h) yielded pure phase of rhombohedrally distorted perovskite (Fig. 2). Thus, in the synthesis of samples of iron-cobaltites of bismuth-lanthanum $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ by the sol-gel technology leads to the decrease in temperature and the time of synthesis in comparison with solid-phase method for their obtaining from the corresponding metal oxides.

The results of measurements of specific conductivity (Fig. 3) showed there that σ of the samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ is in the temperature range 300–1,000 K and increases exponentially with temperature raise indicating a semiconducting conductivity. Increase in the degree of substitution x ions Bi^{3+} with ions La^{3+} and ions Fe^{3+} with ions Co^{3+}, which also leads to a gradual increase of value σ. The values σ for samples σ for the samples of solid

solutions $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ obtained using the sol-gel method are slightly higher than for the corresponding samples iron-cobaltites bismuth-lanthanum synthesized by solid phase reaction method. For example, at a temperature of 850 K, the conductivity of the sample $Bi_{0,95}La_{0,05}Fe_{0,95}Co_{0,05}O_3$ increases the from $1.56 \cdot 10^{-2}$ Sm · cm^{-1} for the sample synthesized by solid phase reaction method to 11.08 Sm · cm^{-1} for the corresponding solid solution obtained by the sol-gel method (Fig. 3, curves *1*, *1**). In addition, the samples of solid solutions, obtained by the sol-gel method, have a lower value of the activation energy of conductivity (Fig. 4, Table 1). This may indicate a higher concentration of charge carriers in these samples.

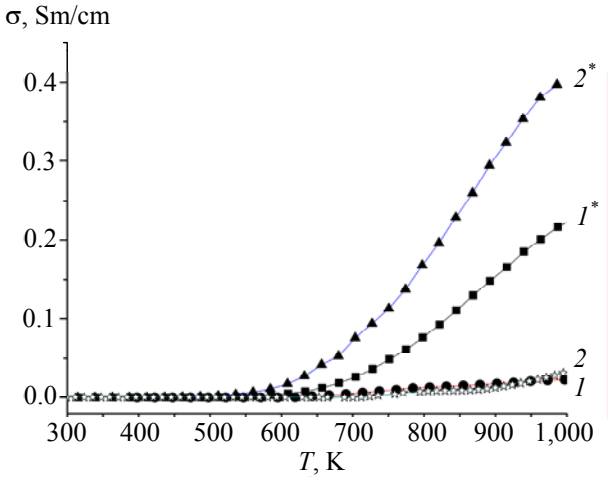

Fig. 3. Temperature dependence of the specific conductivity (σ) samples $Bi_{1-x}La_xFe_{1-x}Co_xO$ synthesized by solid-phase (*1*, *2*) and sol-gel (*1**, *2**) methods at different *x*: *1*, *1** – 0.05; *2*, *2** – 0.1

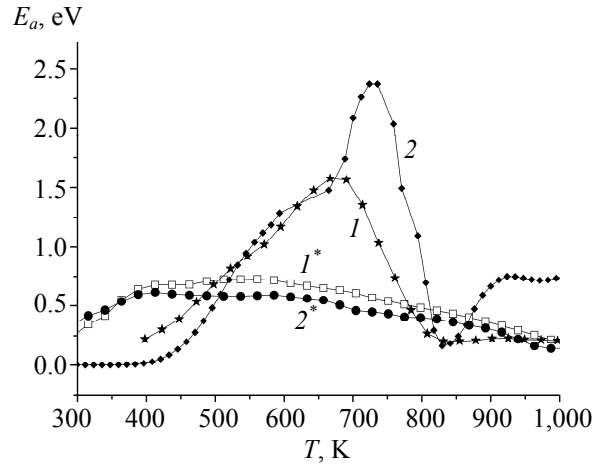

Fig. 4. The temperature dependence of the energy of electrical activation (E_a) of the samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ synthesized by solid-phase (*1*, *2*) and sol-gel (*1**, *2**) methods at different *x*: *1*, *1** – 0.05; *2*, *2** – 0.1

Table 1

The activation energy of conductivity (E_a) of intermediate temperatures calculated by linear sections depending on lnσ of T^{-1} for samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$

$Bi_{1-x}La_xFe_{1-x}Co_xO_3$ at *x*	E_a, eV	Δ*T*, K	E_a, eV	Δ*T*, K
	SGM		SPM	
0	–	–	0.45	634–776
0.05	0.685	340–800	0.72	445–628
0.1	0.584	360–750	1.26	545–712
1.0	–	–	0.45	396–557

The temperature dependence of relative elongation $\Delta l / l_0$ of samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$, synthesized by sol-gel method are obtained by dilatometric method (Fig. 5); they show that for the whole temperature range 300–1,100 K, the linear relationship $\Delta l / l_0 = f(T)$ for samples with the degree of substitution of $x = 0$; 0.05 and 0.1 is observed. Such behavior is also observed for samples $x = 0$; 0.05 and 0.1, obtained by the solid-phase method. This may indicate a lack of phase transitions in these samples within the temperature range investigated. For a sample with the degree of substitution of $x = 1.0$ in the temperature range 300–1,100 K the $\Delta l / l_0 = f(T)$ is nonlinear, which may be due to the transition of cobalt ions from low- to intermediate- and/or high-spin condition accompanied by the increase in cell volume.

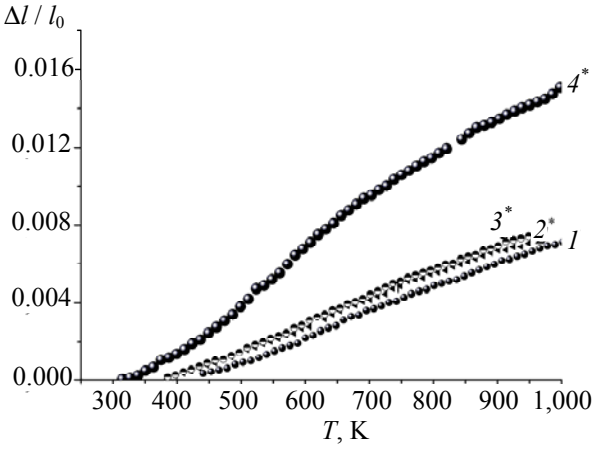

Fig. 5. The temperature dependence of the relative elongation $\Delta l / l_0$ of samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$, synthesized by solid-phase (*1*) and sol-gel (*2**, *3**, *4**) methods at different *x*: *1* – 0; *2** – 0.05; *3** – 0.1; *4** – 1.0

The values of the mean linear thermal expansion coefficient (α) of samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$, calculated for the temperature range in which the linear dependence of $\Delta l / l_0$ on *T* is observed are shown in Table 2. In this table there are also extended temperature range (ΔT_1, ΔT_2, ΔT_3)

for which the linear dependence of $\Delta l / l_0$ on T is observed.

Table 2

The average linear thermal expansion coefficients (α) for samples $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ at low, intermediate and high temperatures (α_1, α_2, α respectively) and temperature ranges ΔT_1, ΔT_2, ΔT_3 for low-, intermediate- and high-temperature linear sections of dependencies $\Delta l / l_0$ from T respectively

x	$\alpha_1 \cdot 10^6$, K^{-1}	ΔT_1, K	$\alpha_2 \cdot 10^6$, K^{-1}	ΔT_2, K	$\alpha_3 \cdot 10^6$, K^{-1}	ΔT_3, K
0 SPM	–	–	11.8	415–955	–	–
0.05 SGM	–	–	13.2	385–900	–	–
0.05 SPM	–	–	10.7	380–890	–	–
0.1 SGM	–	–	13.8	398–866	–	–
0.1 SPM	–	–	11.6	330–740	–	–
1.0 SGM	18.9	340–440	29.3	510–680	19.7	715–930
1.0 SPM	17.7	300–430	24.2	450–700	21.6	710–1,070

The values of the mean coefficient of linear thermal expansion of the investigated solid solutions obtained using the sol-gel technology were slightly higher than for the corresponding samples synthesized by the solid phase reaction method.

Conclusion. By using solid-phase and sol-gel methods solid solutions of the $BiFeO_3$ – $LaCoO_3$ system were synthesized. The sol-gel technology developed for obtaining precursors allowed to lower the temperature and reduce the time of synthesis of the solid solutions based on bismuth ferrite, to obtain samples of $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ solid solutions with a small amount of impurity phases. However, in the sample of $BiFeO_3$ obtained by the sol-gel method the content of $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ impurity phases was more substantial than for bismuth ferrite synthesized by the solid phase method. According to the results of the investigation it was shown that the values of the electrical conductivity and the linear coefficient of thermal expansion of the $Bi_{1-x}La_xFe_{1-x}Co_xO_3$ solid solutions obtained by the sol-gel method were slightly higher and the activation energy of the electrical conductivity was less than for the corresponding samples synthesized by the solid phase reaction method.

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