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Structure and Properties of the $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ (Ln', Ln" – REE) Solid Solutions

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Abstract *The ceramic samples of the layered ferrocuprates $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ (Ln', Ln" – La, Pr, Sm, Gd, Yb) solid solutions using solid-state reactions method were prepared and their crystal structure, oxygen nonstoichiometry, thermal expansion, electrical conductivity and thermo-EMF were investigated. It is found, that $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ oxides are the p-type semiconductors. It is shown, that structural characteristics, oxygen nonstoichiometry, linear thermal expansion coefficient and activation energy of electrical conductivity of layered ferrocuprates depend on sizes of REE cations in their composition, but electrical conductivity and thermo-EMF values depend on electronic configuration of ones.*

Keywords: Layered perovskites, solid solutions, crystal structure, thermal expansion, electrical conductivity, thermo-EMF.

INTRODUCTION

The layered peroskite-like ferrocuprates of rare-earth elements (REE) and barium are considered as prospective base for development of new semiconducting chemical sensors of gases [1, 2], electrode materials for intermediate-temperature solid-oxide fuel cells [3], as well as components of thermoelectric generators operating at elevated temperatures [4, 5], which stipulates the great interest to these compounds.

It is known that functional characteristics of oxide materials can be essentially improved at partial iso- and heterovalent substitution of cations in their structure, so development of the methods of chemical modification of layered ferrocuprates of REE and barium is actual task, which has a great scientific and practical interest.

In this work the influence of partial substitution of one REE by another on the crystal structure, oxygen stoichiometry, thermal expansion and electrical properties of the ferrocuprates $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ (Ln', Ln" – La, Pr, Sm, Gd, Yb) solid solutions was investigated.

MATERIALS AND METHODS

The ceramic samples of $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$, $Pr_{0,5}Sm_{0,5}BaCuFeO_{5+\delta}$, $Sm_{0,5}Gd_{0,5}BaCuFeO_{5+\delta}$, $Gd_{0,5}Yb_{0,5}BaCuFeO_{5+\delta}$ ferrocuprates solid solutions were prepared from La_2O_3 (pure grade), Pr_6O_{11} (pure grade), Sm_2O_3 (pure grade), Gd_2O_3 (pure grade), Yb_2O_3 (pure grade), CuO (super pure grade 9–2) and Fe_2O_3 (super pure grade 2–4) and $BaCO_3$ (pure grade) using solid-state reactions method in air at 1173–1273 K according to the method described in [6].

Identification of the samples and determination of their lattice constants using X-ray diffraction analysis (XRD) (diffractometer D8 Advance Bruker AXS (Germany), CuK_α – radiation) and IR absorption spectroscopy (Furier-spectrometer Nexus ThermoNicolet) were performed. The oxygen nonstoichiometry index of the samples (δ) was determined using iodometry.

The apparent density of the samples (ρ_{exp}) was calculated 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 using methods described in [4–6]. Values of the linear thermal expansion coefficient (LTEC, α) and activation energy of electrical conductivity (E_A) of the samples were calculated from linear parts of $\Delta l/l_0 = f(T)$ and $\ln(\sigma \cdot T) = f(1/T)$ dependences respectively.

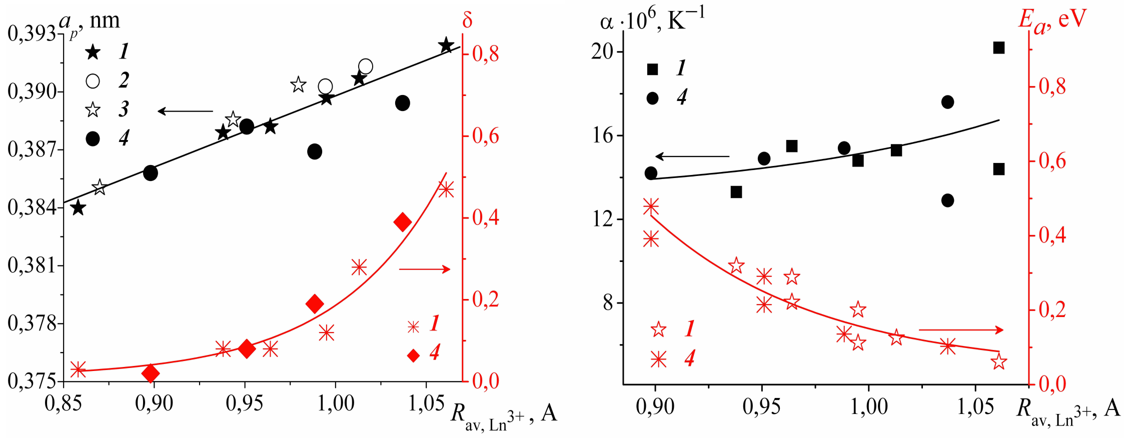
RESULT AND DISCUSSION

After final stage of annealing the $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ samples were monophase, within XRD accuracy, and had perovskite structure – quasi-cubic ($a \approx a_p$) for the $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$, $Pr_{0,5}Sm_{0,5}BaCuFeO_{5+\delta}$ oxides and $YBaCuFeO_{5+\delta}$ type tetragonally distorted ($a \approx a_p$, $c \approx 2a_p$) [7] for the $Sm_{0,5}Gd_{0,5}BaCuFeO_{5+\delta}$, $Gd_{0,5}Yb_{0,5}BaCuFeO_{5+\delta}$ solid solutions. The lattice constants of $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ phases obtained by us (table) are in a good accordance with the literature data [6, 9, 10]. As can be seen from the fig. 1, *a*, perovskite cell parameter (a_p) and oxygen nonstoichiometry index (δ) of the layered ferrocuprates of REE and barium expectedly decrease at decreasing of average ionic radius of REE, and the $a_p = f(R_{av,Ln}{}^{3+})$ dependence are close to the linear.

Table

Values of the lattice constants (*a*, *c*, *V*, *a*$_p$), oxygen nonstoichiometry index (δ) and wavenumbers of absorption maxima (ν$_1$, ν$_2$, ν$_3$) of $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ solid solutions

Compound	δ	*a*, nm	*c*, nm	$10^3 \cdot V$, nm^3	a_p, nm	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
$La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$	0,39	0,3894	–	59,05	0,3894	370	553	612
$Pr_{0,5}Sm_{0,5}BaCuFeO_{5+\delta}$	0,19	0,3869	–	57,92	0,3869	378	579	608
$Sm_{0,5}Gd_{0,5}BaCuFeO_{5+\delta}$	0,08	0,3896	0,7706	116,8	0,3882	372	557	663
$Gd_{0,5}Yb_{0,5}BaCuFeO_{5+\delta}$	0,02	0,3873	0,7656	114,8	0,3858	366	571	656



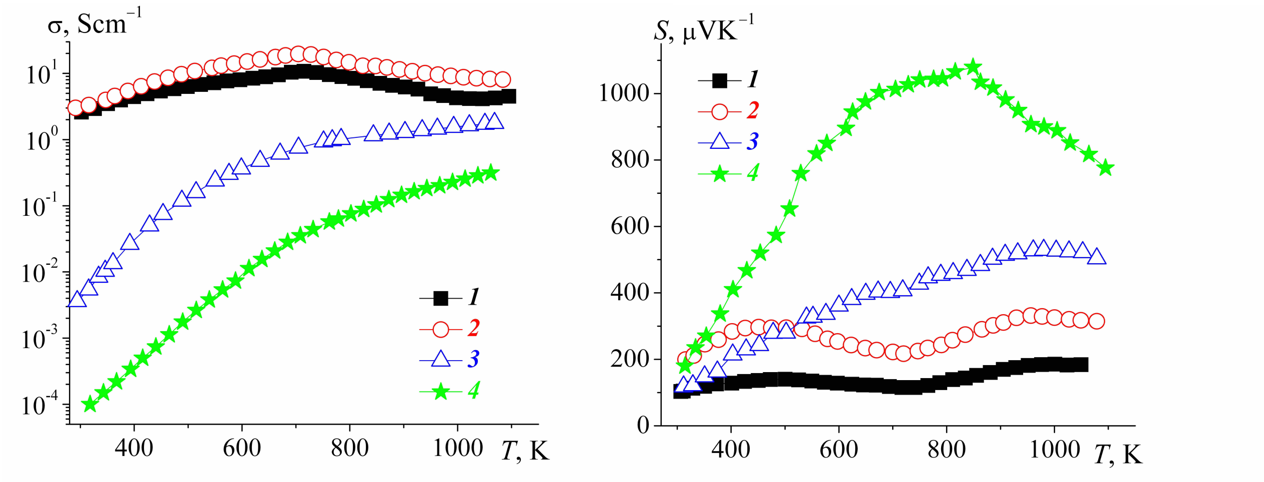
a *b*

Fig. 1. Dependences of the perovskite cell parameter (a_p), oxygen nonstoichiometry index (δ) (*a*), LTEC (α) and activation energy of electrical conductivity (E_A) (within 400–1000 K) (*b*) of the layered ferrocuprates of REE and barium on the average radius of REE cation ($R_{av,Ln^{3+}}$) [8]: *1* – $LnBaCuFeO_{5+\delta}$ (Ln – La, Pr, Nd, Sm, Gd, Yb) [6], *2* – $La_{1-x}Eu_xBaCuFeO_{5+\delta}$ [9], *3* – $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ (Ln', Ln'' – Nd, Sm; Nd, Y; Lu, Y) [10], *4* – results of this work

IR absorption spectra of the $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ solid solutions contained three pronounced bands with extrema at 366–378 (ν_1), 553–579 (ν_2) and 608–663 (ν_3) cm^{-1} (table). According to [11], these bands correspond to the bending (ν_1) and stretching vibrations (ν_2) of (Cu/Fe)–O–(Cu/Fe) bonds in the basal $[(Cu/Fe)O_2]$ layers and stretching vibrations (ν_3) of apical oxygen of (Cu/Fe)–O–(Cu/Fe) bonds in the structure of $YBaCuFeO_{5+\delta}$ type phases. On the base of obtained results one can conclude that anisotropy degree of metal-oxygen interactions ($\Delta\nu = \nu_3 - \nu_2$) in the tetragonally distorted $Sm_{0,5}Gd_{0,5}BaCuFeO_{5+\delta}$, $Gd_{0,5}Yb_{0,5}BaCuFeO_{5+\delta}$ ferrocuprates ($\Delta\nu = 85–106\ cm^{-1}$) is higher than in the quasi-cubic $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$, $Pr_{0,5}Sm_{0,5}BaCuFeO_{5+\delta}$ phases ($\Delta\nu = 29–59\ cm^{-1}$). Anisotropy of the crystal structure of the last two oxides obtained by means of IR absorption spectroscopy is small and do not manifested on the X-ray diffractograms of the powders. So, vibrational absorption spectroscopy in comparison with XRD is more sensitive to the small distortions of the crystal structure of the layered perovskite-like oxides.

On the temperature dependence of relative elongation of $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$ phase near 650 K the anomaly in a kink was observed, which was accompanied with increasing of LTEC values of the sample from $12,9 \cdot 10^{-6}\ K^{-1}$ to $17,6 \cdot 10^{-6}\ K^{-1}$. According to the [6], this anomaly takes place due to the rearrangement of the oxygen sublattice of this oxide and beginning of evolution of weakly-bonded oxygen (δ) from its volume to the gas phase. The $\Delta l/l_0 = f(T)$ dependences of other ferrocuprates studied were practically linear; so, we can conclude, that within temperature interval investigated the structural changes in these oxides is absent or proceeded with negligible intensity and can't be detected by means of dilatometry. As can see from the data given in the fig. 1, *b*, the LTEC value of the layered ferrocuprates of REE and barium slightly decreses at decreasing of average cationic radius of REE.

The prepared by us $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ solid solutions were *p*-type semiconductors; for $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$, $Pr_{0,5}Sm_{0,5}BaCuFeO_{5+\delta}$ samples near 700–750 K the conductivity character changed from semiconducting into metallic and thermo-EMF began to increase due to the evolution of weakly-bonded oxygen (δ) from the samples to the gas phase (fig. 2). The values of activation energy of electrical conductivity of $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ phases varied within 0,103–0,479 eV and increased at decreasing of average radius of REE cation (fig. 1, *b*) in their structure, which is in a good accordance with the results of [6].



a *b*

Fig. 2. Temperature dependences of electrical conductivity (*a*) and thermo-EMF (*b*) of solid solutions of $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$ (*1*), $Pr_{0,5}Sm_{0,5}BaCuFeO_{5+\delta}$ (*2*), $Sm_{0,5}Gd_{0,5}BaCuFeO_{5+\delta}$ (*3*), $Gd_{0,5}Yb_{0,5}BaCuFeO_{5+\delta}$ (*4*)

Comparison of results obtained in this work with the literature data [4, 6] let us conclude that electrical conductivity of the layered ferrocuprates of REE and barium, in a whole, decreases, and thermo-EMFincreases at increasing of *f*-electrons number (*n*) (decreasing of radius) of REE cation; moreover the $\sigma = f(n)$, $S = f(n)$ dependences are unmonotonous and possess «sawtooth» character: the values of electrical conductivity and thermo-EMF of $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ solid solutions, with few exceptions[1], very different from the arithmetic mean for the $Ln'BaCuFeO_{5+\delta}$, $Ln''BaCuFeO_{5+\delta}$ phases (fig. 3).

It should be noted that electrical characteristics of $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ solid solutions also very differ from those of their isoelectronic analogues: so, for example, for $Gd_{0,5}Yb_{0,5}BaCuFeO_{5+\delta}$ (Gd^{3+}: $[Xe]4f^7$, Yb^{3+}: $[Xe]4f^{13}$: $n = 10$) at 1000 K $\sigma = 0{,}243\ S \cdot cm^{-1}$ and $S = 873\ \mu V \cdot K^{-1}$, while for $HoBaCuFeO_{5+\delta}$ ferrocuprate (Ho^{3+}: $[Xe]4f^{10}$: $n = 10$) $\sigma_{1000} = 0{,}678\ S \cdot cm^{-1}$, and $S_{1000} = 720\ \mu V \cdot K^{-1}$ [4]; for $Sm_{0,5}Gd_{0,5}BaCuFeO_{5+\delta}$ solid solution (Sm^{3+}: $[Xe]4f^5$, Gd^{3+}: $[Xe]4f^7$: $n = 6$) $\sigma_{1000} = 1{,}45\ S \cdot cm^{-1}$, while for isoelectronic by its (by REE) $EuBaCuFeO_{5+\delta}$ phase (Eu^{3+}: $[Xe]4f^6$: $n = 6$) $\sigma_{1000} = 0{,}108\ S \cdot cm^{-1}$ [6].

So, electrical properties of the layered ferrocuprates of REE and barium strongly depend on electronic configuration of REE cations in their composition: in particular, conductivity of phases which contain REE cations with odd number of 4*f*-electrons, is larger than conductivity of ferrocuprates on the base of REE with even number of 4*f*-electrons; the marked regularity is more pronounced for the phases in which the average charge of transition metal cations (iron and copper) closes to the +2,5 ($\delta \approx 0$). At the

[1] Thermo-EMF of $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$ solid solution ($S_{1000} = 188\ \mu V \cdot K^{-1}$) is practically equal to the half of sum of thermo-EMF of $LaBaCuFeO_{5+\delta}$ ($S_{1000} = 81{,}5\ \mu V \cdot K^{-1}$) and $PrBaCuFeO_{5+\delta}$ phases ($S_{1000} = 301\ \mu V \cdot K^{-1}$); reason for this is that the concentration of charge carriers ("holes") in the layered ferrocuprates of barium and lanthanum (praseodymium) is determined mainly by their oxygen nonstoichiometry (δ); value δ for $La_{0,5}Pr_{0,5}BaCuFeO_{5+\delta}$ is 0,39 that close to the half the sum of δ for ferrocuprates of lanthanum and barium (0,47) and praseodymium and barium (0,28) [6].

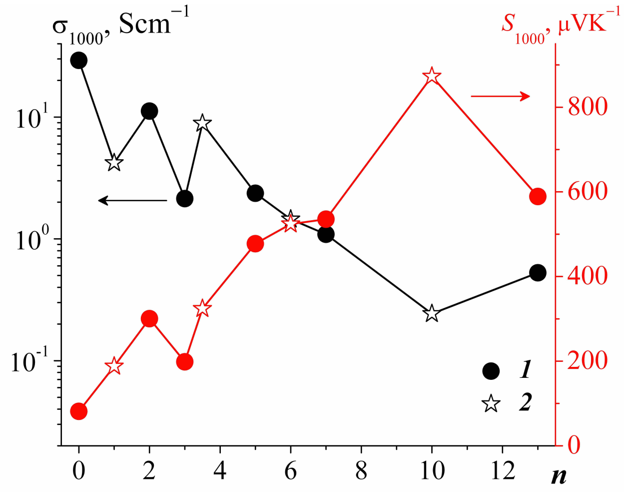


Fig. 3. Dependences of electrical conductivity (σ_{1000}) and thermo-EMF (S_{1000}) of layered ferrocuprates of REE and barium on the average number of *f*-electrons of REE cation (*n*) [8]: *1* – $LnBaCuFeO_{5+\delta}$ (Ln – La, Pr, Nd, Sm, Gd, Yb) [4, 6], *2* – results of this work

same time¸ as follows from the $E_A = f(R_{av,Ln}{}^{3+})$ dependence (fig¸1, *b*), energetic of electrical transport in layered ferrocuprates depends more strongly on the radius of cation than on its electronic structure.

Thus, results of this work indicate the possibility separate regulation of electrical characteristics (values of electrical conductivity and thermo-EMF) and energetic of charge transfer in the layered ferrocuprates of REE and barium by means of directed partial substitution of one REE by another in their crystal structure, and regulation efficiency increases at decreasing of amount of weakly-bonded oxygen in the samples (δ)

CONCLUSION

By means of ceramic method the polycrystalline samples of the layered perovskite-like ferrocuprates $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ (Ln', Ln" – La, Pr, Sm, Gd, Yb) solid solutions were prepared, their lattice constants and oxygen nonstoichiometry were determined and their thermal expansion, electrical conductivity and thermo-EMF were studied. It is shown that $Ln'_{0,5}Ln''_{0,5}BaCuFeO_{5+\delta}$ phases are *p*-type semiconductors. It is established that values of structural characteristics, oxygen nonstoichiometry, linear thermal expansion coefficient and activation energy of electrical conductivity of these phases strongly depend on the size of REE cations in their structure, but values of electrical conductivity and thermo-EMF of the samples strongly depend on the electronic configuration of the REE cations.

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