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Structure and Electrophysical Properties of Ferrocobaltites LnBaFeCoO$_{5 + \delta}$ (Ln = Tb, Dy, Ho, Y)

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Abstract—The ferrocobaltites LnBaFeCoO$_{5 + \delta}$ (Ln = Tb, Dy, Ho, Y) have been synthesized, and the parameters of their crystal structure have been determined. The thermal expansion, electrical resistivity ρ, and thermopower S of the synthesized compounds have been investigated in air at temperatures in the range from 300 to 1100 K. The compounds have a tetragonal structure (symmetry space group $P4/mmm$) with the unit cell parameters $a = 3.9000$ Å and $c = 7.5922$ Å (Ln = Tb, $\delta = 0.31$), $a = 3.8973$ Å and $c = 7.5679$ Å (Ln = Dy, $\delta = 0.34$), $a = 3.8970$ Å and $c = 7.5507$ Å (Ln = Ho, $\delta = 0.28$), and $a = 3.9029$ Å and $c = 7.5538$ Å (Ln = Y, $\delta = 0.25$). The ferrocobaltites under investigation are p-type semiconductors, and their electrical resistivity ρ and thermopower S decrease in the sequence Tb $\longrightarrow$ Ho $\longrightarrow$ Y $\longrightarrow$ Dy (at room temperature). The linear thermal expansion coefficient of the LnBaFeCoO$_{5 + \delta}$ phases in the vicinity of the temperatures ranging from 465 to 535 K increases from $(1.15–1.23) \times 10^{-5}$ to $(1.73–1.93) \times 10^{-5}$ K^{-1}. The parameters of charge transfer in these ferrocobaltites have been determined. It has been found that an increase in the temperature leads to an increase in the excitation energy of charge carriers and a decrease in the activation energy of charge carrier transfer.

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1. INTRODUCTION

Considerable interest expressed by researchers in layered perovskite oxides of the general formula LnBaMe_2O$_{5 + \delta}$ (Ln = Y, rare-earth (RE) element); Me = $3d$ metal) is caused by a unique combination of their electrophysical and magnetic properties. In particular, layered cobaltites LnBaCo$_2$O$_{5 + \delta}$ undergo a metal–insulator phase transition [1–5] and a series of magnetic phase transitions due to the interaction of spin, charge, and orbital degrees of freedom of their cobalt cations [2, 4, 6, 7]. The spin–orbital degeneracy of cobalt $3d$ electrons ensures high values of the thermopower coefficient for the LnBaCo$_2$O$_{5 + \delta}$ phases [8]. Layered cobaltites can be used as cathode materials in solid-oxide fuel cells [9]. Furthermore, owing to the high mobility of oxygen anions in the structure of these materials, they have provided the basis for the design of new oxygen ion conductors [10]. The large diversity of properties exhibited by the LnBaCo$_2$O$_{5 + \delta}$ cobaltites is associated primarily with the fact that these compounds have a two-dimensional structure and that cobalt in these phases can be in different spin states, which is explained by the close values of the crystal-field splitting energy ($\Delta_{\text{c.f.}}$) and the intra-atomic exchange interaction energy (J_H) [11]. Depending on the ratio between the crystal-field splitting energy $\Delta_{\text{c.f.}}$ and the intra-atomic exchange interaction energy J_H, the Co^{3+} cations can be in low-spin (LS, $t_{2g}^6 e_g^0$, $S = 0$), intermediate-spin (IS, $t_{2g}^5 e_g^1$, $S = 1$), and high-spin (HS, $t_{2g}^4 e_g^2$, $S = 2$) states, whereas the Co^{4+} cations can exist in LS ($t_{2g}^5 e_g^0$, $S = 1/2$), IS ($t_{2g}^4 e_g^1$, $S = 3/2$), and HS ($t_{2g}^3 e_g^2$, $S = 5/2$) states [1]. At low temperatures, the LS and IS states are energetically more favorable, whereas an increase in the temperature can be accompanied by the transitions LS $\longrightarrow$ IS and IS $\longrightarrow$ HS [8, 11, 12]. Layered ferrites LnBaFe$_2$O$_{5 + \delta}$ also exhibit interesting electrical and magnetic properties [13–16], which strongly depend on the oxygen content in these phases [15] and can change significantly due to charge ordering of iron cations in their structure (the Verwey transition) [15–17].

In recent years, apart from layered ferrites [13–17] and cobaltites [1–10, 12] of rare-earth elements and barium, intensive investigations have been performed with layered perovskites of the LnBa$Me'Me''$O$_{5 + \delta}$ type in which the B sublattice is equally occupied by cations of different $3d$ transition metals (Me', Me'' = Mn, Fe, Co, Ni, Cu). Examples of these compounds are provided by layered perovskite ferrocuprates LnBaCuFeO$_{5 + \alpha}$ [18–20], layered cuprocobaltites LnBaCuCoO$_{5 + \delta}$ (Ln = Y and La) [11, 21–24], and layered cobaltomanganites LnBaMnCoO$_{5 + \delta}$ (Ln = Y) [25] of rare-earth elements and barium, as well as the lay-
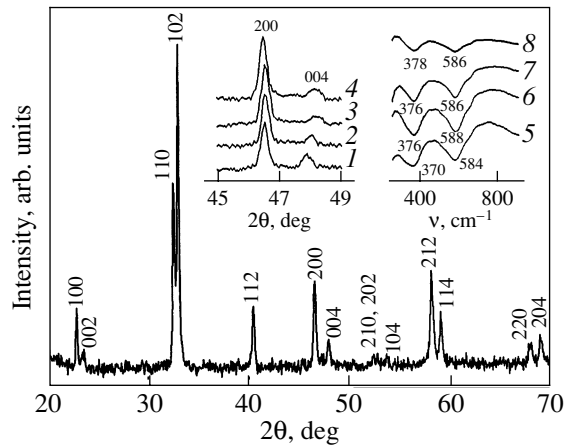
Fig. 1. X-ray powder diffraction pattern of the $TbBaFeCoO_{5.31}$ ferrocobaltite. The inset shows (*1–4*) the 200 and 004 reflections and (*5–8*) IR absorption spectra of the (*1, 5*) $TbBaFeCoO_{5.31}$, (*2, 6*) $DyBaFeCoO_{5.34}$, (*3, 7*) $HoBaFeCoO_{5.28}$, and (*4, 8*) $YBaFeCoO_{5.25}$ ferrocobaltites.

ered lanthanum barium ferrocobaltite $LaBaFeCoO_{5+\delta}$ described in our previous paper [24].

In this study, the layered perovskite ferrocobaltites $LnBaFeCoO_{5+\delta}$ (*Ln* = Tb, Dy, Ho, Y) were synthesized; the parameters of their crystal structure were determined; and the thermal stability, thermal expansion, and electrophysical properties (electrical conductivity and thermopower) were investigated.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Ceramic samples of layered perovskite ferrocobaltites $LnBaFeCoO_{5+\delta}$ (*Ln* = Tb, Dy, Ho, Y) were synthesized from the oxides Tb_2O_3 (reagent grade), Dy_2O_3 (DiO-3), Ho_2O_3 (GoO-1), Y_2O_3 (ItOV), Fe_2O_3 (special-purity grade 2–4), Co_3O_4 (analytical grade), and barium carbonate $BaCO_3$ (high-purity grade) in air at temperatures in the range 1173–1473 K for 60 h [20]. In order to investigate the thermal expansion, electrical resistivity, and thermopower, the prepared powders were pressed at a pressure of $(1–3) \times 10^3$ kg/cm^2 into pellets (9 mm in diameter and 3–5 mm thick) and $5 \times 5 \times 30$-mm bars, which were subsequently sintered in air at a temperature of 1473 K for 5 h.

The oxygen nonstoichiometry index δ of the $LnBaFeCoO_{5+\delta}$ samples was determined iodometrically with the error $\Delta\delta = \pm0.01$. The X-ray powder diffraction analysis of the powdered samples was performed on a Bruker D8 XRD diffractometer (CuK_α radiation, Ni filter). The IR absorption spectra of the powders in the form of pelletized mixtures containing approximately 0.5 wt % $LnBaFeCoO_{5+\delta}$ with KBr (reagent grade) were recorded on a ThermoNicolet Nexus Fourier transform infrared spectrometer in the frequency range 300–1500 cm^{-1}. The error in the determination of the vibrational frequencies $\Delta\nu \leq 2$ cm^{-1}. The thermal stability of the samples was examined on a Paulik–Paulik–Erdey MOM Q-1500D derivatograph in air at temperatures in the range from 293 to 1173 K at a heating rate of 10 K min^{-1}. The thermal expansion, electrical resistivity ρ, and thermopower S of the polycrystalline samples were investigated in air at temperatures in the range from 300 to 1100 K according to the techniques described earlier in [26] with the errors $\Delta(\rho) \leq \pm5\%$ and $\Delta(S) \leq \pm10\%$. The experimentally obtained values of the electrical resistivity ρ for the ceramic samples were reduced to zero porosity according to the technique described in [26, 27]. The activation energies of electrical conduction (E_A) and thermopower (E_S) of the samples were derived from the linear parts of the dependences $\ln(\rho/T) = f(1/T)$ and $S = f(1/T)$ (the correlation coefficient $R \geq 0.999$), respectively. The linear thermal expansion coefficients (α) of the samples were determined from the linear parts of the dependences $\Delta l/l_0 = f(T)$ with the error $\Delta(\alpha) \leq \pm5\%$.

3. RESULTS AND DISCUSSION

The ferrocobaltites $LnBaFeCoO_{5+\delta}$ (*Ln* = Tb, Dy, Ho, Y) synthesized in air are single phase (Fig. 1), to within the error of the X-ray powder diffraction analysis, and have a tetragonal structure. The diffraction reflections of these phases were indexed in the symmetry space group *P4/mmm* with the unit cell parameters $a = 3.8970–3.9029$ Å and $c = 7.5507–7.5922$ Å (Table 1). The unit cell parameters of the $LnBaFeCoO_{5+\delta}$ phases regularly decrease as a result of the decrease in the ionic radius of the lanthanide cation (according to the data reported in [28], $R_{Tb^{3+}} = 1.04$ Å, $R_{Dy^{3+}} = 1.03$ Å, and $R_{Ho^{3+}} = 1.02$ Å for the coordination number equal to eight) and have anomalously high val-

Table 1. Unit cell parameters of the ferrocobaltites $LnBaFeCoO_{5+\delta}$

Ln	δ	a, Å	c, Å	V, Å^3
Tb	0.31	3.9000 ± 0.0021	7.5922 ± 0.0065	115.479 ± 0.223
Dy	0.34	3.8973 ± 0.0021	7.5679 ± 0.0062	114.951 ± 0.213
Ho	0.28	3.8970 ± 0.0024	7.5507 ± 0.0073	114.671 ± 0.248
Y	0.25	3.9029 ± 0.0023	7.5538 ± 0.0069	115.065 ± 0.236

Table 2. Temperatures corresponding to inflections in the dependences $\Delta l/l_0 = f(T)(T^*)$, linear thermal expansion coefficients (α), and activation energies of electrical transport processes (E_A, E_S, and E_m) in different temperature ranges for layered ferrocobaltites LnBaFeCoO$_{5+\delta}$

Ln	$\alpha \times 10^5$, K^{-1}		T^*, K	E_A, eV	E_S, eV	E_m, eV
	$300-T^*$	T^*-1100				
Tb	1.15	1.93	500	0.384	0.066 ($T < 590$ K)	0.318 ($T < 590$ K)
					0.184 ($T > 590$ K)	0.200 ($T > 590$ K)
Dy	1.18	1.84	465	0.374	0.033 ($T < 580$ K)	0.341 ($T < 580$ K)
					0.106 ($T > 580$ K)	0.268 ($T > 580$ K)
Ho	1.23	1.79	535	0.359	0.022 ($T < 530$ K)	0.337 ($T < 530$ K)
					0.076 ($T > 530$ K)	0.283 ($T > 530$ K)
Y	1.22	1.73	520	0.345	0.046 ($T < 600$ K)	0.299 ($T < 600$ K)
					0.097 ($T > 600$ K)	0.248 ($T > 600$ K)

ues for the yttrium barium ferrocobaltite ($R_{Y^{3+}} = 1.015$ Å for the coordination number equal to eight [28]), which can be explained by the relatively low oxygen content in this phase (Table 1).

The oxygen nonstoichiometry index δ of the LnBaFeCoO$_{5+\delta}$ phases, which was determined iodometrically, varies in the range $\delta = 0.25$–0.34 and reaches the minimum value $\delta = 0.25$ for yttrium and the maximum value $\delta = 0.34$ for dysprosium (Table 1). According to the calculations carried out using the iodometric data, the mean oxidation numbers for cobalt cations in the LnBaFeCoO$_{5+\delta}$ phases are equal to +2.62, +2.68, +2.56, and +2.50 for Ln = Tb, Dy, Ho, and Y, respectively.

The IR absorption spectra of the rare-earth barium ferrocobaltites exhibit two intense absorption bands with maxima at frequencies of 370–378 (ν_1) and 584–588 (ν_2) cm^{-1} (Fig. 1), which are attributed to the bending (ν_1) and stretching (ν_2) vibrations of the Me–O–Me (Me = Fe, Co) bonds in the structure of these phases [20, 24, 29]. The absence of additional absorption bands indicates that the energies of the metal–oxygen interactions in the basal plane of the [Fe(Co)O$_2$] conducting layers are close to those in the direction of the c axis in the structure of the LnBaFeCoO$_{5+\delta}$ compounds. The values of ν_1 and ν_2 for the ferrocobaltites under investigation are respectively almost equal to each other (Fig. 1). This suggests that the energies of the metal–oxygen interactions in the structure of the LnBaFeCoO$_{5+\delta}$ phases have close values. Therefore, we can assume that the electrical resistivities of these phases should also be close to each other.

The results obtained from the thermal analysis indicate that the release of weakly bound oxygen from the powdered samples of the LnBaFeCoO$_{5+\delta}$ oxides begins to occur at temperatures close to 673 K. According to the calculations performed with the use of the iodometric and thermogravimetric data, the

LnBaFeCoO$_{5+\delta}$ phases at a temperature of 1073 K have the oxygen nonstoichiometry indices $\delta = 0.09$, 0.12, 0.09, and 0.06 for Ln = Tb, Dy, Ho, and Y, respectively.

The dependences $\Delta l/l_0 = f(T)$ for the rare-earth barium ferrocobaltites LnBaFeCoO$_{5+\delta}$ (Ln = Tb, Dy, Ho, Y) are characterized by an anomaly in the form of an inflection at the temperatures $T^* = 465$–535 K (Table 2), which is accompanied by an increase in the linear thermal expansion coefficient of the samples by a factor of 1.4–1.7. Taking into account the results obtained from the thermal analysis and the data reported in our previous papers [20, 24, 26], the observed increase in the linear thermal expansion coefficient of the samples can be explained by the increase in the concentration of oxygen vacancies in the crystal lattice of these phases. In other words, at $T > T^*$, the linear expansion of the samples exhibits both the thermal (an enhancement of the anharmonicity of vibrations) and chemical (an increase in the number of oxygen vacancies) nature.

It can be seen from Fig. 2 that the LnBaFeCoO$_{5+\delta}$ ferrocobaltites are p-type semiconductors and that, with an increase in the temperature, the character of their electrical resistivity changes from semiconducting ($\partial\rho/\partial T < 0$) to metallic ($\partial\rho/\partial T \geq 0$) due to the thermal dissociation of these phases. The electrical resistivity ρ of the ferrocobaltites under investigation decreases in the sequence Tb $\longrightarrow$ Ho $\longrightarrow$ Y $\longrightarrow$ Dy (at room temperature), but, on the whole, has close values (Fig. 2a). This result confirms the above conclusions drawn from the analysis of the IR absorption spectra of these compounds.

The dependences $S = f(T)$ for the LnBaFeCoO$_{5+\delta}$ ferrocobaltites are characterized by a maximum at the temperatures $T = 460$ K for Ln = Tb–Ho and $T = 410$ K for Ln = Y and by a minimum in the temperature range from 760 to 865 K (Fig. 2b). The observed increase in the thermopower coefficient S of the ferrocobaltites under investigation in the temperature range from 300
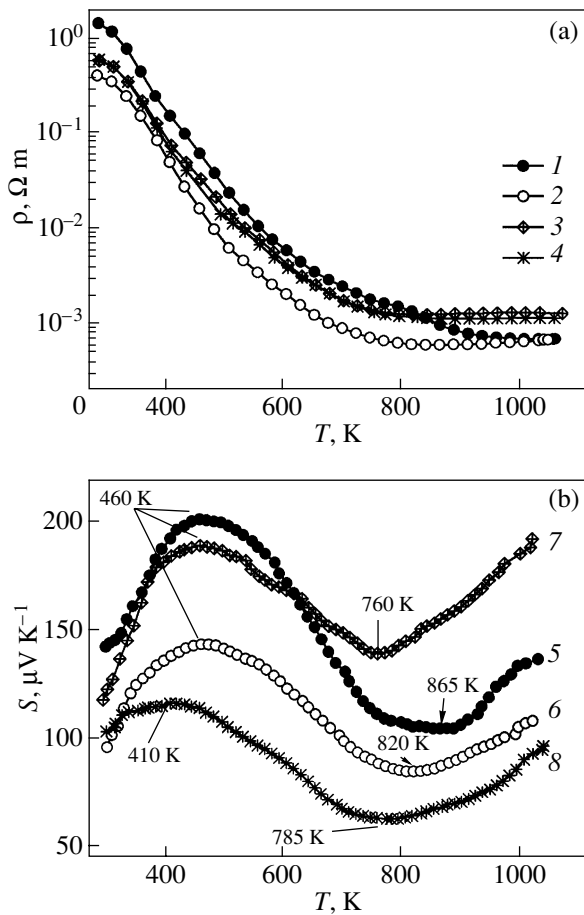
Fig. 2. Temperature dependences of (a) the electrical resistivity ρ and (b) the thermopower S for the LnBaFeCoO$_{5+\delta}$ ferrocobaltites. Ln = (1, 5) Tb, (2, 6) Dy, (3, 7) Ho, and (4, 8) Y.

Fig. 3. Dependences (a) $\ln(\rho/T) = f(1/T)$ and (b) $S = f(1/T)$ for the (1, 4) TbBaFeCoO$_{5+\delta}$, (2, 5) DyBaFeCoO$_{5+\delta}$, and (3, 6) YBaFeCoO$_{5+\delta}$ ferrocobaltites.

to 410 (460) K is most likely associated with the change in the spin state of the cobalt cations (Co^{2+}, Co^{3+}) in the composition of these compounds by analogy with the spin transitions in perovskite cobaltites of rare-earth elements [30], whereas the drastic increase in the value of S for the ferrocobaltite samples at high temperatures ($T > 760$–865 K) is caused by the release of weakly bound oxygen (δ) from their crystal lattice.

For a large number of layered oxides at high temperatures, the charge transfer has a polaron character [24, 26]. In this case, the temperature dependences of the electrical resistivity and the thermopower are described by the relationships $\rho = \rho_0 T\exp(E_A/kT)$ and $S = k/e(E_S/kT + B)$, where $E_A = (E_S + E_m)$ and E_m are the activation energies of electrical conduction and thermopower, respectively [31]. The quantities E_S and E_m correspond to the energies of polaron excitation and polaron transfer, respectively ($E_m \approx 0$ for the activationless charge transfer by large-radius polarons and $E_m > 0$ for the thermally activated charge transfer by small-radius polarons through the hopping mechanism).
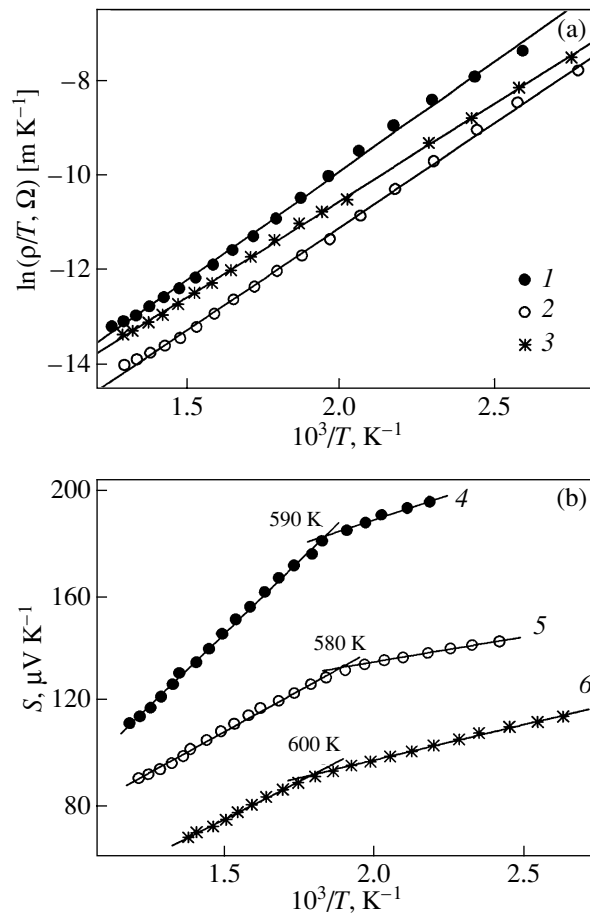
As can be seen from Figs. 3a and 3b, the dependences $\ln(\rho/T) = f(1/T)$ and $S = f(1/T)$ obtained for the LnBaFeCoO$_{5+\delta}$ ferrocobaltites exhibit a linear behavior over a wide range of temperatures. These results confirm the validity and applicability of the polaron model and the above relationships for the description of the electrical transport processes occurring in these materials.

The activation energies of electrical conduction E_A of the LnBaFeCoO$_{5+\delta}$ phases, which were calculated from the linear parts of the dependences $\ln(\rho/T) = f(1/T)$, decrease with a decrease in the ionic radius of the rare-earth element (Table 2). The activation energies of thermopower E_S determined from the linear parts of the dependences $S = f(1/T)$ for the LnBaCuFeO$_{5+\delta}$ ferrocobaltites increase with increasing temperature and reach 0.022–0.066 and 0.076–0.184 eV at temperatures below and above 530–600 K, respectively (Table 2).

It can be seen from the data presented in Table 2 that the excitation energy of small-radius polarons in the

LnBaCuFeO$_{5+\delta}$ ferrocobaltites increases by a factor of 2–3, whereas the transfer energy of small-radius polarons in the [Fe(Co)O$_2$] conducting layers of their crystal structure decreases by a factor of 1.2–1.6 in the temperature range close to the temperature at which oxygen begins to escape from the samples. This phenomenon is explained by the fact that the energy of the metal–oxygen interactions and the degree of lability of the oxygen sublattice of the layered perovskites change significantly at temperatures immediately preceding the thermal dissociation of these oxides.

4. CONCLUSIONS

Thus, the layered perovskite ferrocobaltites LnBaFeCoO$_{5+\delta}$ (Ln = Tb, Dy, Ho, Y) have been synthesized, and their crystal structure, thermal stability, and physicochemical properties have been investigated. It has been found that the synthesized compounds crystallize in the tetragonal crystal system (symmetry space group $P4/mmm$) and are p-type semiconductors. The parameters of charge transfer in these ferrocobaltites have been determined. It has been revealed that an increase in the temperature brings about an increase in the excitation energy of charge carriers and a decrease in the activation energy of charge carrier transfer.

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