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New Perovskite Oxides $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$): Synthesis, Structure, and Properties

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Abstract—Perovskite oxides $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$) are synthesized, and the parameters of their crystal structure are determined in the temperature range 300–1100 K. The thermal stability, thermal expansion, electrical resistivity ρ , and thermopower S of the synthesized compounds are investigated. The compounds have a cubic structure with the unit cell parameter $a = 3.9085 \text{ \AA}$ for $M = \text{Fe}$ ($\delta = 0.97$) and $a = 3.9228 \text{ \AA}$ for $M = \text{Cu}$ ($\delta = 0.62$) and, at room temperature, are semiconductors (n -type for $M = \text{Fe}$ and p -type for $M = \text{Cu}$). At high temperatures, the thermopower and the coefficients $\partial\rho/\partial T$ and $\partial S/\partial T$ reverse sign due to the release of oxygen from the samples. Measurements of the magnetic susceptibility have revealed ferromagnetic ordering of the magnetic moments of the iron and cobalt cations in the $\text{LaBaFeCoO}_{5.97}$ compound at a temperature of 168 K.

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1. INTRODUCTION

Oxygen-deficient perovskites are layered oxides with a considerable correlation between the structure and the magnetic, thermal, and electrophysical properties. The strong overlap of the $3d$ electron orbitals of the transition metal cations and the $2p$ orbitals of the oxygen anions plays the key role in the behavior of these oxides, including high-temperature superconductors (HTSC) of the type $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ln is a rare-earth element) [1], magnetoresistive manganites $\text{LnBaMn}_2\text{O}_{6-\delta}$ [2, 3] and cobaltites $\text{LnBaCo}_2\text{O}_{5+\delta}$ [4, 5], as well as ferrites $\text{LnBaFe}_2\text{O}_{5+\delta}$ [6, 7] and chromites $\text{LnBaCr}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Gd}$) [8].

In recent years, intensive investigations have been performed with layered perovskites of the $\text{LnBaMe}'\text{Me}''\text{O}_{5+\delta}$ type in which the B sublattice is equally occupied by cations of different $3d$ transition metals (Me' , $\text{Me}'' = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$). Among these compounds, the first to be investigated were layered perovskite ferrocuprates of rare-earth elements and barium of the composition $\text{LnBaCuFeO}_{5+\delta}$ [9–12] because of their structural similarity to high-temperature superconductors $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In the literature, there have also been described layered cuprocobaltites $\text{LnBaCuCoO}_{5+\delta}$ ($\text{Ln} = \text{Y}$ [13, 14] and La [15, 16]) and the YBaMnCoO_5 phase [17].

Cobaltites are of special interest because cobalt in these compounds can be in different spin states, which is explained by the close values of the crystal-field splitting energy ($\Delta_{c.f.}$) and the intra-atomic exchange interaction energy (J_H) [15]. In oxygen-deficient perovskites, cobalt is contained predominantly in the

form of Co^{3+} cations, which 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. At low temperatures, the LS and IS states are energetically more favorable, whereas an increase in the temperature can be accompanied by the transitions $\text{LS} \rightarrow \text{IS}$ and $\text{IS} \rightarrow \text{HS}$ [4, 5, 15]. The YBaCuCoO_5 compound, which is the prototype of the series $\text{LnBaCuCoO}_{5+\delta}$, has a tetragonal structure (symmetry space group $P4/mmm$) with the unit cell parameters $a = 3.8679(1) \text{ \AA}$ and $c = 7.5674(2) \text{ \AA}$ [13] and is an antiferromagnet with the Néel temperature equal to 536 K (according to [13]) or 515 K (according to [14]). As follows from the data presented in [16], the antiferromagnetic ordering of the magnetic moments of the copper and cobalt cations in the $\text{LaBaCuCoO}_{5.6}$ phase is observed at temperatures below 205 K.

In this study, perovskite oxides $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$) were synthesized; the parameters of their crystal structure were determined; and the thermal stability, thermal expansion, magnetic susceptibility (for the $\text{LaBaFeCoO}_{5+\delta}$ phase), and electrophysical properties were investigated.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Polycrystalline samples of layered perovskites $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$) were synthesized by the ceramic technique from the oxides La_2O_3 (reagent grade), Fe_2O_3 (special-purity grade 2-4), CuO (special-purity grade 9-2), Co_3O_4 (analytical grade), and barium

carbonate BaCO_3 (high-purity grade) in air at temperatures in the range 1173–1473 K (for $M = \text{Fe}$) or 1173–1223 K (for $M = \text{Cu}$) for 60 h [12]. For the preparation of samples with a decreased oxygen content, a part of the $\text{LaBaFeCoO}_{5+\delta}$ powder was additionally annealed at a temperature of 1073 K for 10 h in a nitrogen flow ($p(\text{O}_2) = 10^2 \text{ Pa}$), followed by slow cooling (at a rate of 2–6 K/min) to room temperature, together with the furnace without switching off the gas supply. In order to investigate the thermal expansion, electrical resistivity, and thermopower, the prepared powders were pressed at a pressure of $(1\text{--}3) \times 10^3 \text{ kg/cm}^2$ into pellets (9 mm in diameter and 3–5 mm thick) and $5 \times 5 \times 30\text{-mm}$ bars, which were subsequently sintered in air at a temperature of 1223 K (for $M = \text{Cu}$) or 1473 K (for $M = \text{Fe}$) for 5–10 h.

The oxygen content ($5 + \delta$) in the samples was determined iodometrically with the error $\Delta\delta = \pm 0.01$. The X-ray powder diffraction analysis of the powdered samples was performed on a Bruker D8 XRD diffractometer ($\text{CuK}\alpha$ radiation, Ni filter). The IR absorption spectra of the powders in the form of pelletized mixtures containing $\approx 0.5\%$ $\text{LaBaMCoO}_{5+\delta}$ 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 did not exceed $\pm 2 \text{ cm}^{-1}$. The thermal stability of the $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$) powders was examined on a Mettler Toledo thermal analyzer in air at temperatures in the range from 293 to 1073 K. 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 [18] with the errors $\delta(\rho) \leq 5\%$ and $\delta(S) \leq \pm 10\%$. The experimentally obtained values of the electrical resistivity ρ for the ceramic samples were reduced to zero porosity according to the technique described in [18, 19]. The activation energies of electrical conduction E_A and thermopower E_S of the samples were derived from the linear parts of the dependences $\ln(\sigma T) = f(1/T)$ 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 linear parts of the dependences $\Delta l/l_0 = f(1/T)$ with the error $\delta(\alpha) \leq \pm 5\%$. The magnetic susceptibility of the $\text{LaBaFeCoO}_{5+\delta}$ compound was determined by the pondermotive method in the magnetic field $H = 8.6 \text{ kOe}$ at temperatures in the range from 77 to 950 K.¹

¹ The measurements were performed by S.S. Dorofeichik (Joint Institute of Solid-State and Semiconductor Physics, National Academy of Sciences of Belarus, Minsk, Belarus).

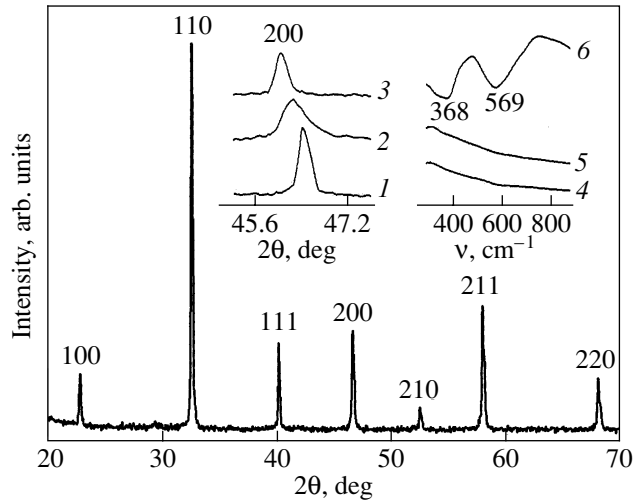


Fig. 1. X-ray powder diffraction pattern of the $\text{LaBaFeCoO}_{5.97}$ phase. The inset shows (1–3) the 200 reflections and (4–6) IR absorption spectra of the (1, 4) $\text{LaBaFeCoO}_{5.97}$, (2, 5) $\text{LaBaCuCoO}_{5.62}$, and (3, 6) $\text{LaBaFeCoO}_{5.53}$ phases.

3. RESULTS AND DISCUSSION

After the final stage of annealing in air ($p(\text{O}_2) = 0.21 \times 10^5 \text{ Pa}$), the samples of the perovskite oxides $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$) were single phase (Fig. 1), to within the error of the X-ray powder diffraction analysis, and had a cubic structure. The diffraction reflections of these phases were indexed in the symmetry space group $Pm\bar{3}m$ with the unit cell parameters $a = 3.9085 \text{ \AA}$ for $\text{LaBaFeCoO}_{5.97}$ and $a = 3.9228 \text{ \AA}$ for $\text{LaBaCuCoO}_{5.62}$ (Table 1). The differences in the unit cell parameters of the samples are associated both with the difference in the ionic radii of Fe^{3+} and Cu^{2+} cations (according to the data reported in [20], $R_{\text{Fe}^{3+}} = 0.645 \text{ \AA}$ and $R_{\text{Cu}^{2+}} = 0.730 \text{ \AA}$ for a coordination number of 6) and with the lower oxygen content in the lanthanum barium cuprocobaltite. The structure of $\text{LaBaFeCoO}_{5+\delta}$ upon its reduction in nitrogen ($p(\text{O}_2) = 10^2 \text{ Pa}$) remains unchanged, whereas the unit cell parameter regularly increases as a result of the decrease in the quantity δ (Table 1). The volume chemical expansion coefficient $\alpha_{\delta, V}$ of the $\text{LaBaFeCoO}_{5+\delta}$ phase,

Table 1. Unit cell parameters of the layered oxides $\text{LaBaMCoO}_{5+\delta}$

Sample	$a, \text{ \AA}$	$V, \text{ \AA}^3$
$\text{LaBaFeCoO}_{5.97}$	3.9085 ± 0.0010	59.709 ± 0.047
$\text{LaBaFeCoO}_{5.53}$	3.9415 ± 0.0010	61.235 ± 0.048
$\text{LaBaCuCoO}_{5.62}$	3.9228 ± 0.0012	60.365 ± 0.059

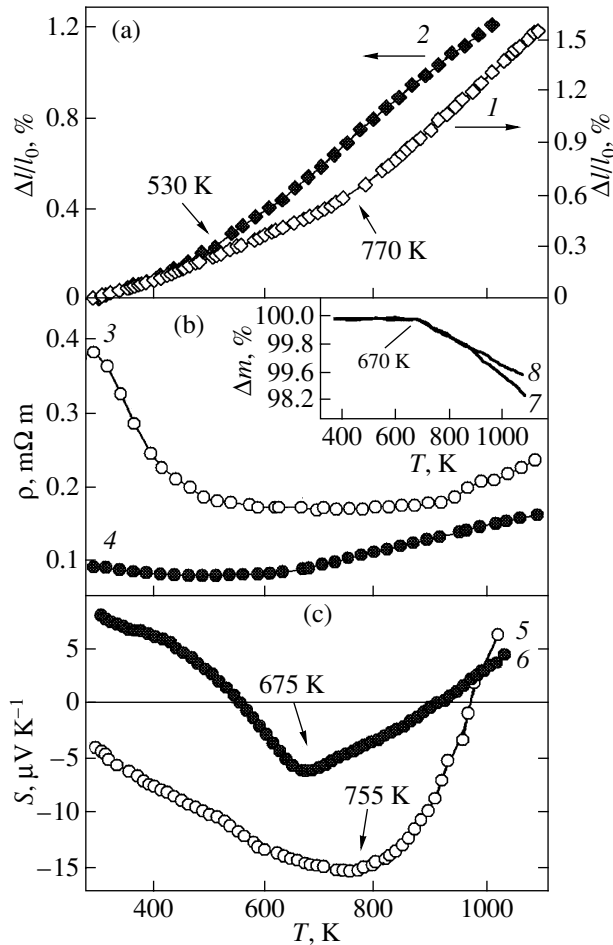


Fig. 2. Temperature dependences of (a) the relative elongation, (b) the electrical resistivity ρ , (c) the thermopower S , and (d) thermogravimetric curves (inset) for the (1, 3, 5, 7) LaBaFeCoO_{5+ δ} and (2, 4, 6, 8) LaBaCuCoO_{5+ δ} phases.

which was calculated according to the formula $\alpha_{\delta, v} = -\left(\frac{\partial \ln V}{\partial \delta}\right)$ [21], proved to be $\alpha_{\delta, v} = 0.057$, which agrees

Table 2. Linear thermal expansion coefficients α and activation energies of electrical transport processes E_A , E_S , and E_m for the perovskite oxides LaBaMCoO_{5+ δ}

Sample	LaBaFeCoO _{5+δ}	LaBaCuCoO _{5+δ}	
$\alpha \times 10^5, \text{K}^{-1}$	300– T^*	1.35	1.26
	T^* –1100	3.02	2.03
T^*, K	770	530	
$\alpha_T \times 10^5, \text{K}^{-1}$	1.32	1.15	
$\alpha_\delta \times 10^3$	17.3	15.7	
E_A, eV	0.087	0.042	
E_S, eV	0.006	0.021	
E_m, eV	0.081	0.021	

with the chemical expansion coefficient of the LaBaCuFeO_{5+ δ} ferrocuprate: $\alpha_{\delta, v} = 0.044$ in the range $0.00 < \delta < 0.25$ [21]. The perovskite unit cell parameters (a_p) calculated from the data reported in [15, 16] for the LaBaCuCoO_{5.61} [16] and LaBaCuCoO_{5.2} [15] phases are equal to $a_p = 3.9202 \text{ \AA}$ and $a_p = 3.9260 \text{ \AA}$, respectively, which is in good agreement with the results obtained in the present work (Table 1).

It should be noted that the investigations performed in [15, 16] with the use of high-resolution electron microscopy [15] and neutron diffraction [16] revealed the formation of superstructures due to the ordering of oxygen vacancies in the lattice of the lanthanum barium cuprocobaltite: $a = a_p$, $c \approx 5a_p$ (symmetry space group $P4/mmm$) for $\delta = 0.20$ [15] and $a < b \approx a_p$, $c \approx 3a_p$ (symmetry space group $Pmmm$) for $\delta = 0.61$ [16]. The fact that we have not revealed oxygen ordering in the structure of the LaBaCuCoO_{5+ δ} phase can be explained by the lower sensitivity of the X-ray powder diffraction analysis as compared to the neutron diffraction analysis, as well as by the differences in the thermal prehistory of the samples.

The IR absorption spectra of the LaBaFeCoO_{5.97} and LaBaCuCoO_{5.62} phases annealed in air have a diffuse character with weakly pronounced absorption maxima in the vicinity of 580 cm^{-1} , whereas the spectrum of the reduced lanthanum barium ferrocobaltite LaBaFeCoO_{5.53} exhibits two intense absorption bands with maxima at frequencies of $368 (\nu_1)$ and $569 (\nu_2) \text{ cm}^{-1}$ (Fig. 1), which are attributed to the bending (ν_1) and stretching (ν_2) vibrations of the $Me-O-Me$ ($Me = \text{Fe, Co}$) bonds in the structure of the layered perovskite LaBaFeCoO_{5+ δ} [12, 22]. The absence of additional absorption bands indicates the isotropy of the $Me-O-Me$ ($Me = \text{Fe, Co}$) bonds in the structure of the LaBaFeCoO_{5+ δ} ferrocobaltite, which is in agreement with the conclusions drawn regarding the cubic structure of this compound from the X-ray powder diffraction data.

The dependences $\Delta l/l_0 = f(T)$ for the phases LaBaMCoO_{5+ δ} ($M = \text{Fe, Cu}$) are characterized by an anomaly in the form of an inflection at the temperatures $T^* = 530 \text{ K}$ ($M = \text{Cu}$) and 770 K ($M = \text{Fe}$) (Fig. 2a, Table 2), which is accompanied by an increase in the linear thermal expansion coefficient of the samples by a factor of 2.2 and 1.6 for $M = \text{Fe}$ and $M = \text{Cu}$, respectively (Table 2). According to the results obtained from the thermogravimetric analysis (see the inset to Fig. 2), the release of weakly bound oxygen (δ) from the samples begins to occur at temperatures close to 670 K. Taking into account the thermogravimetric data and the results obtained in [12, 23], we can draw the conclusion that the observed increase in the linear thermal expansion coefficient of the samples is caused by the increase in the concentration of oxygen vacancies in the crystal lattice of these phases. Therefore, 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.

The separation of the thermal (linear thermal expansion coefficient α_T) and chemical (linear chemical expansion coefficient α_δ) contributions to the linear expansion of the samples was carried out according to the technique described in [23] with the use of the relationships $\alpha_T = \frac{1}{l_0} \left(\frac{\partial \Delta l}{\partial T} \right)_\delta$ and $\alpha_\delta = -\frac{1}{l_0} \left(\frac{\partial \Delta l}{\partial \delta} \right)$. In this case, we assumed that, to a first approximation, the degree of anharmonicity of the vibrations is determined only by the temperature and does not depend on the number of oxygen vacancies in the crystal lattice of the samples. The linear thermal expansion coefficients α_T and the linear chemical expansion coefficients α_δ of the $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe, Cu}$) phases are presented in Table 2. As can be seen from this table, the $\text{LaBaFeCoO}_{5+\delta}$ phase satisfies the relationship $3\alpha_\delta \approx \alpha_{\delta, V}$; i.e., the chemical expansion coefficients determined for this oxide from the dilatometric and X-ray powder diffraction data are in good agreement.

It can be seen from Fig. 2b that the $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe, Cu}$) compounds are 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 ($\partial\rho/\partial T > 0$). The observed behavior is explained by the thermal dissociation of these phases, which begins to occur in air at the temperature $T \approx 670$ K (see the inset to Fig. 2). At room temperature, the thermopower coefficient of the perovskite oxides $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe, Cu}$) has a negative sign ($S < 0$) for $M = \text{Fe}$ and a positive sign ($S > 0$) for $M = \text{Cu}$ (Fig. 2c). This suggests that the majority charge carriers are electrons in the lanthanum barium ferrocobaltite and holes in the cuprocobaltite. The thermopower coefficient of the $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe, Cu}$) compounds drastically increases at temperatures in the vicinity of 755 and 675 for $M = \text{Fe}$ and $M = \text{Cu}$, respectively (Fig. 2c), which, as noted above, is caused by the release of weakly bound oxygen from the ceramic samples.

For materials with a polaron character of the charge transfer, the temperature dependences of the electrical conductivity and the thermopower are described by the relationships $\sigma = \frac{A}{T} \exp(-E_A/kT)$ and $S = \frac{k}{e} (-E_S/kT + B)$, where $E_A = (E_S + E_m)$ and E_S are the activation energies of electrical conduction and thermopower, respectively [24]. 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).

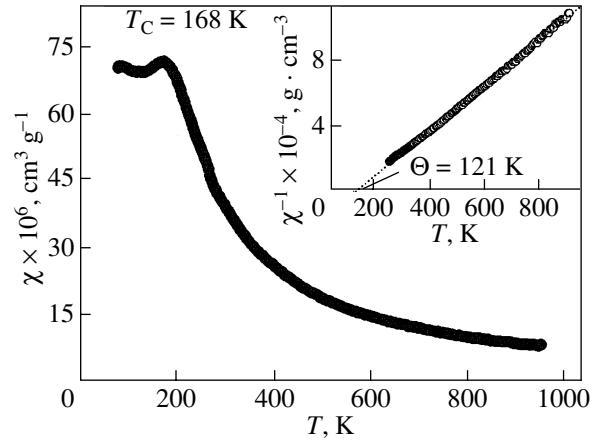


Fig. 3. Temperature dependence of the magnetic susceptibility χ for the $\text{LaBaFeCoO}_{5+\delta}$ ferrocobaltite. The inset shows the dependence $1/\chi = f(T)$ for the $\text{LaBaFeCoO}_{5+\delta}$ ferrocobaltite in the range of the applicability of the Curie–Weiss law.

The parameters E_A , E_S , and E_m calculated from the linear parts of the dependences $\ln(\rho/T) = f(1/T)$ and $S = f(1/T)$ ($T < 670$ K, $\delta \approx \text{const}$) for the perovskite oxides under investigation are presented in Table 2. As can be seen from this table, the energy of charge carrier excitation (E_S) in $\text{LaBaFeCoO}_{5+\delta}$ is considerably lower but the energy of charge carrier transfer (E_m) is considerably higher than those in $\text{LaBaCuCoO}_{5+\delta}$. Therefore, it can be concluded that the charge transfer between the copper and cobalt ions in $\text{LaBaCuCoO}_{5+\delta}$ is energetically more favorable than the charge transfer between differently charged cobalt ions in $\text{LaBaFeCoO}_{5+\delta}$.²

The dependence $\chi = f(T)$ for the $\text{LaBaFeCoO}_{5+\delta}$ phase exhibits a maximum at $T_f = 168$ K (Fig. 3) due to the order–disorder transition in the subsystem of $3d$ metal cations. In the temperature range 250–900 K, the dependence $1/\chi = f(T)$ for the lanthanum barium ferrocobaltite obeys the Curie–Weiss law $\chi = \frac{C}{T - \Theta}$, where

$C = 3.535 \text{ cm}^3 \text{ K mol}^{-1}$ is the Curie constant and $\Theta = 121$ K is the Curie paramagnetic point (effective temperature) (Fig. 3). The inequality $\Theta > 0$ indicates a ferromagnetic ordering of the magnetic moments of the iron and cobalt cations in $\text{LaBaFeCoO}_{5+\delta}$ (which is also indirectly confirmed by the close values of T_C and Θ). The effective paramagnetic moment ($p_{\text{eff}}^{\text{exp}}$) per formula unit of $\text{LaBaFeCoO}_{5.97}$ was calculated from the Curie constant C according to the formula $p_{\text{eff}}^{\text{exp}} =$

² According to the iodometric data, cobalt in $\text{LaBaFeCoO}_{5.97}$ and $\text{LaBaCuCoO}_{5.62}$ is in the form of Co^{3+} and Co^{4+} (copper in $\text{LaBaCuCoO}_{5.62}$ is in the form of Cu^{3+}).

$\sqrt{\frac{3Ck_B}{N_A\mu_B^2}} = 5.32\mu_B$, where k_B is the Boltzmann constant, N_A is the Avogadro number, and μ_B is the Bohr magneton. The theoretical value $p_{\text{eff}}^{\text{teor}}$ was determined from the relationship $p_{\text{eff}}^{\text{teor}} = \sqrt{\sum_i \mu_i^2} = 7.68\mu_B$, where μ_i is the magnetic moment of the cation in the i th magnetic subsystem ($\mu_i = \sqrt{n(n+2)}\mu_B$), n is the average number of unpaired electrons of the magnetic cation ($n = 5$ for $\text{Fe}_{\text{HS}}^{3+}$ and $\text{Co}_{\text{HS}}^{4+}$ and $n = 4$ for $\text{Co}_{\text{HS}}^{3+}$). The inequality $p_{\text{eff}}^{\text{exp}} < p_{\text{eff}}^{\text{teor}}$ (by 30%) can be explained by the high degree of covalency of the iron (cobalt)–oxygen bonds in the structure of the $\text{LaBaCuFeO}_{5+\delta}$ phase, as well as by the fact that part of the cobalt cations in this phase are not in the HS state but in the IS or even LS state.

4. CONCLUSIONS

Thus, in this work, the perovskite oxides $\text{LaBaMCoO}_{5+\delta}$ ($M = \text{Fe}, \text{Cu}$) were synthesized; the parameters of their crystal structure were determined; and the thermal stability, thermal expansion, and electrophysical properties were investigated. The synthesized compounds crystallize in the cubic system with the unit cell parameter $a = 3.9085 \text{ \AA}$ for $\text{LaBaFeCoO}_{5.97}$ and $a = 3.9228 \text{ \AA}$ for $\text{LaBaCuCoO}_{5.62}$ and, at room temperature, are semiconductors of the n -type for $M = \text{Fe}$ and the p -type for $M = \text{Cu}$. As the temperature increases, the thermopower and the temperature coefficients of thermopower and electrical resistivity reverse sign due to the release of oxygen from the samples. The charge transfer parameters of these phases were determined, and the thermal and chemical contributions to their expansion at high temperatures were separated. The results obtained from the measurements of the magnetic susceptibility revealed ferromagnetic ordering of the magnetic moments of the iron and cobalt cations in the $\text{LaBaFeCoO}_{5.97}$ compound at the Curie temperature $T_C = 168 \text{ K}$.

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