Thermoelectric properties of the layered oxides LnBaCu(Co)FeO$_{5+\delta}$ (Ln = La, Nd, Sm, Gd)

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The crystal structure, electrical conductivity and thermo-e.m.f. of layered oxides LnBaCu(Co)FeO$_{5+\delta}$ (Ln=La, Nd, Sm, Gd) of perovskite structure have been studied. The LnBaCu(Co)FeO$_{5+\delta}$ compounds have cubic structure for Ln = La and tetragonal one for the Ln = Nd–Gd and are p-type semiconductors (except for LaBaCoFeO$_{5+\delta}$ having negative S values). The activation energy of electric transport, thermoelectric coefficients (Seebeck, Peltier and Thomson) and the power factor of the oxides studied have been determined. The power factor of LnBaCu(Co)FeO$_{5+\delta}$ phases has been found to depend on the nature of rare earth elements and $3d$-metals in their structure and to be maximum for SmBaCuFeO$_{5+\delta}$, GdBaCuFeO$_{5+\delta}$ and NdBaCoFeO$_{5+\delta}$. The layered perovskites can be considered as a base for development of the new thermoelectric oxide materials.

Исследованы кристаллическая структура, электропроводность и термо-ЭДС слоистых оксидов LnBaCu(Co)FeO$_{5+\delta}$ (Ln–La, Nd, Sm, Gd) со структурой перовскита. Соединения LnBaCu(Co)FeO$_{5+\delta}$ имеют кубическую структуру для Ln = La и тетрагональную — для Ln = Nd–Gd и являются полупроводниками p-типа (кроме LaBaCoFeO$_{5+\delta}$, для которого $S < 0$). Определены значения энергии активации процессов электропереноса, термоэлектрических коэффициентов (Зеебека, Пельтье и Томсона) и фактора мощности изученных оксидов. Найдено, что значения фактора мощности фаз LnBaCu(Co)FeO$_{5+\delta}$ зависят от природы входящих в их состав редкоземельных элементов и $3d$-металлов и максимальны для SmBaCuFeO$_{5+\delta}$, GdBaCuFeO$_{5+\delta}$ и NdBaCoFeO$_{5+\delta}$. Показано, что слоистые перовскиты можно рассматривать как основу для разработки новых оксидных термоэлектрических материалов.

The direct conversion of heat into electric power is based on the Seebeck effect and is realized in the thermo-electrogenerators (TEG). The TEG efficiency depends on the figure-of-merit (ZT) of thermoelectric materials (TEM) used in the TEG. The ZT value of a TEM is determined as (1):

$$ZT = \frac{S^2 \sigma}{\kappa} T. \qquad (1)$$

It is seen from Eq. (1) that to reach high ZT values, a TEM should exhibit high thermo-e.m.f. (S) and electrical conductivity (σ) and low thermal conductivity (κ).

Such possess it is just the layered bismuth and antimony tellurides as well as silicides of iron and other metals that show such a complex of properties. These materials are used in the thermoelectroconverters [1].

As to the high-temperature operation in air, metal oxides have obvious advantages due to their high thermal and chemical stability. It is known that the layered cobaltites (Na$_x$CoO$_2$ [2–4], Ca$_3$Co$_2$O$_6$ [2, 5–7], Ca$_3$Co$_4$O$_9$ [2]) and some perovskites (BaPbO$_3$ [2], LaCoO$_3$ [2, 8]) show a high thermoelectric efficiency, but search for and development of the new oxide thermoelectric materials (OTE) is a very important

problem. In this work, the thermoelectric properties of the layered perovskite oxides LnBaCu(Co)FeO$_{5+\delta}$ (Ln = La, Nd, Sm, Gd) is studied and the practical usability of these phases as OTE is estimated.

The LnBaCu(Co)FeO$_{5+\delta}$ (Ln = La, Nd, Sm, Gd) compounds were prepared by ceramic method from the BaCO$_3$ (pure grade) and other metal oxides (pure or better than pure grade) in air within 1173–1473 К temperature range [9, 10]. The samples were identified using X-ray analysis (Bruker D8 XRD diffractometer, CuK$_\alpha$-radiation, 40 kV, 40 mA; 5–100° 2θ range; 0.05° scan step) and IR absorption spectroscopy (Fourier spectrometer Nexus ThermoNicolet; 300–1500 cm^{-1} frequency range, in pellets containing finely ground mixture of oxide compound with KBr in a mass ratio of 1/200). The oxygen content in the samples (5 + δ) was determined iodometrically (Δδ = ±0.01). The electrical conductivity (σ) of the sintered samples was measured using DC ($I{\leq}50$ mA) four-probe method (digital voltmeters V7-58, V7-53; power supply B5-47) in air within 300–1100 K range in dynamic mode at heating and cooling rate of 3 to 5 K·min^{-1} at an error δ(σ)≤±5 % [9, 10]. The σ values for the ceramics studied were recalculated to zero porosity as described in [10, 11]. The thermo-e.m.f. of the ceramics was determined with reference to silver (digital voltmeter V7-65/3) in air within 300–1100 K range at an error δ(S)≤±10 % [9, 10]. The temperature gradient between the hot and the cold ends of the sample was maintained at the 20–25 K level during the measurements. Prior to measurements of the electrophysical properties, Ag electrodes were deposited on the sample surface by fusing silver paste at 1073 K for 15 min. The chromel-alumel thermocouples were employed to measure the temperature. Using reference data of the absolute Seebeck coefficients for silver (S_{Ag}) [12, 13], the absolute Seebeck coefficients of layered oxides LnBaCu(Co)FeO$_{5+\delta}$ were found from the results of thermo-e.m.f. measurements. From these values, the values of the absolute Peltier's (Π) and Thomson's coefficients (μ) of the LnBaCu(Co)FeO$_{5+\delta}$ oxides at different temperatures had been calculated using the equations (2) [13]:

$$\Pi = ST, \quad \mu = T\frac{dS}{dT}. \qquad (2)$$

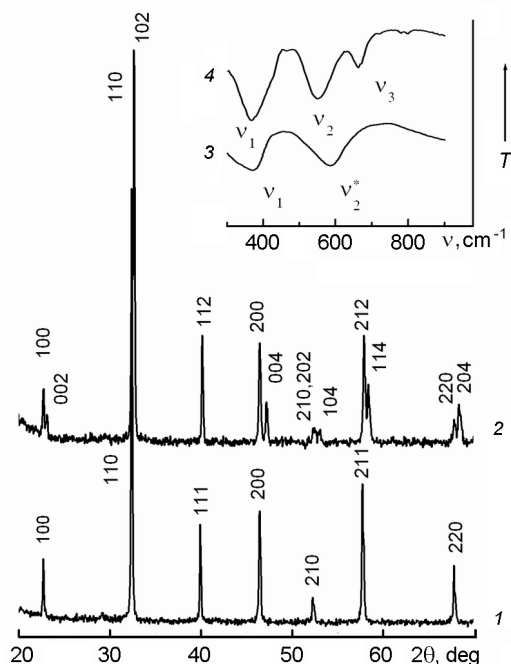The power factors (P) of the ceramic samples were calculated as:

Fig. 1. X-ray powder diffraction patterns (CuK$_\alpha$ radiation) and IR absorption spectra of the LaBaCoFeO$_{5.97}$ (1), NdBaCoFeO$_{5.65}$ (2), SmBaCoFeO$_{5.37}$ (3) and SmBaCuFeO$_{5.08}$ (4) phases.

$$P = S^2\sigma. \qquad (3)$$

After the final synthesis stage in air, the samples of the LnBaCu(Co)FeO$_{5+\delta}$ phases were single-phase ones within the error of X-ray diffraction analysis, and had perovskite structure with reflections indexed in the cubic crystal system (space group $Pm3m$) for Ln = La and in the tetragonal crystal system (space group $P4/mmm$) for Ln = Nd, Sm, Gd (Fig. 1). The unit cell parameters of the samples diminished at decreasing rare-earth element (REE) ionic radii [14] and as a whole, were larger for the ferrocuprates than for the ferrocobaltites due to the higher concentrations of the weakly bound oxygen (δ) in the ferrocobaltites (see Table). The unit cell parameters of the ferrocuprates LnBaCuFeO$_{5+\delta}$ agree well with the literature data [15–18].

IR absorption spectrum of the LaBaCoFeO$_{5.97}$ phase has a diffuse character with the poorly expressed absorption maximum near 580 cm^{-1} (v_2^*). The IR absorption spectra of the LnBaCoFeO$_{5+\delta}$ (Ln = Nd, Sm, Gd) ferrocobaltites and LaBaCuFeO$_{5.47}$ phase exhibit two distinct bands with maxima at 368–370 (v_1) and 584–604 (v_2^*) cm^{-1},
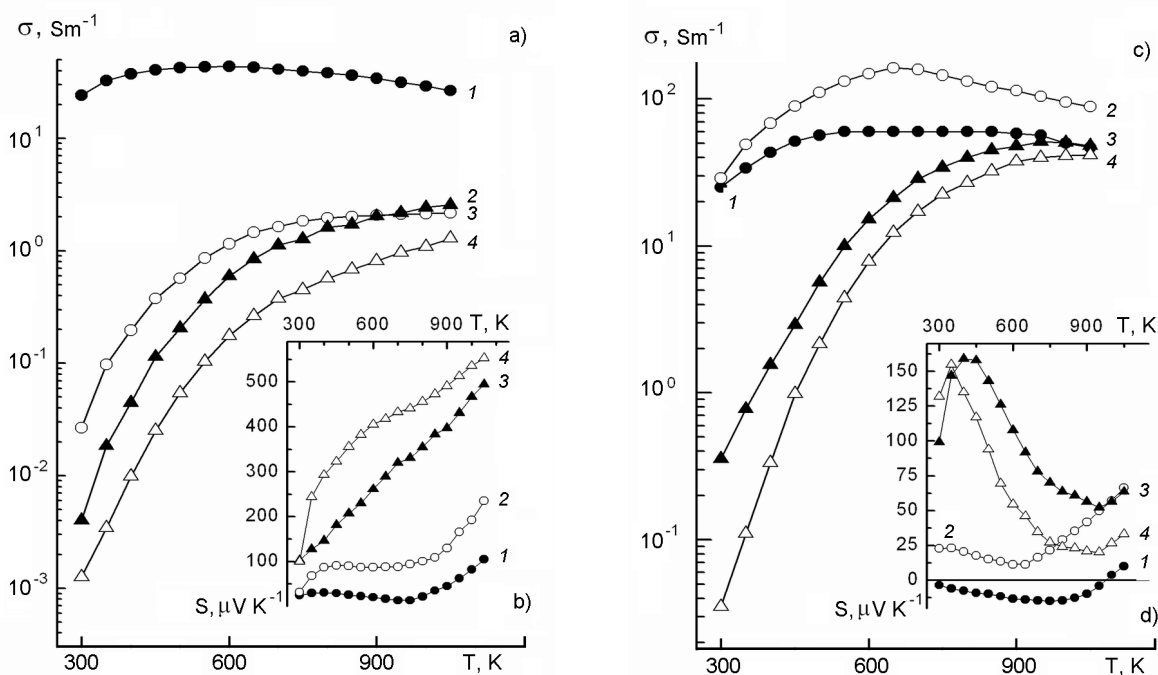
Fig. 2. Temperature dependences of the electrical conductivity (σ) (a, c) and Seebeck coefficient (S) (b, d) of the $LnBaCuFeO_{5+\delta}$ (a, b) and $LnBaCoFeO_{5+\delta}$ (c, d) phases. Ln = La (*1*), Nd (*2*), Sm (*3*), Gd (*4*).

and IR absorption spectra of the $LnBaCuFeO_{5+\delta}$ (Ln = Nd, Sm, Gd) ferrocuprates exhibit three distinct bands with maxima at 368–372 (ν_1), 544–553 (ν_2) and 660–664 (ν_3) cm^{-1} (Fig. 1), which are associated with the bending (ν_1) and stretching (ν_2) vibrations of the metal-oxygen bonds in the $[CuFeO_2]$ layers and the stretching vibrations (ν_3) of the (Cu/Fe)–O–(Cu/Fe) bonds containing apex oxygen atoms in the structures of $LnBaCuFeO_{5+\delta}$ phases [10, 19].

The absence of band peaked at ν_3 in the absorption spectra of the ferrocobaltites and

the fact that $\nu_2 < \nu_2^* < \nu_3$ let us conclude that $3d$-metal-oxygen ($3d$-metal = Fe, Co, Cu) interactions in the ferrocobaltites studied (as well as in the $LaBaCuFeO_{5.47}$ phase) are quasi-isotropic, whereas the $3d$-metal-oxygen distances in the $[(Cu,Co)FeO_2]$ layers of the ferrocuprates are larger than in the c direction (perpendicular to the $[CuFeO_2]$ layers).

All the oxides studied are the p-type semiconductors (except for $LaBaCoFeO_{5+\delta}$ with S values being negative at $T < 975$ K) (Fig. 2) and their σ values, as a whole, de-

Table. Values of the unit cell parameters (*a*, *c*) and volume (*V*), activation energy of electrical transport (E_S, E_m) as well as power factor (*P*) and Peltier's (Π) and Thomson's coefficients (μ) at $T = 1000$ K for the layered oxides $LaBaCu(Co)FeO_{5+\delta}$

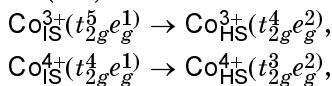| Sample	$a,$ nm	$c,$ nm	$10^3 \cdot V,$ nm^3	$E_S,$ eV	$E_m,$ eV	$P_{1000},$ $\mu W/(m \cdot K^2)$	$\Pi_{1000},$ mV	$\mu_{1000},$ mV/K
$LaBaCuFeO_{5.47}$	0.3924	–	60.42	0.020	0.045	19.7	81.4	0.402
$NdBaCuFeO_{5.12}$	0.3912	0.7737	118.4	0.016	0.185	8.48	200	0.640
$SmBaCuFeO_{5.08}$	0.3896	0.7706	117.0	–	–	54.1	477	0.663
$GdBaCuFeO_{5.08}$	0.3895	0.7693	116.7	–	–	31.3	535	0.473
$LaBaCoFeO_{5.97}$	0.3909	–	59.73	0.006	0.081	0.372	3.67	0.150
$NdBaCoFeO_{5.65}$	0.3909	0.7695	117.6	0.007	0.111	32.3	57.4	0.140
$SmBaCoFeO_{5.37}$	0.3908	0.7662	117.0	0.114	0.127	16.6	57.0	0.053
$GdBaCoFeO_{5.37}$	0.3908	0.7613	116.2	0.092	0.221	2.97	26.5	0.097
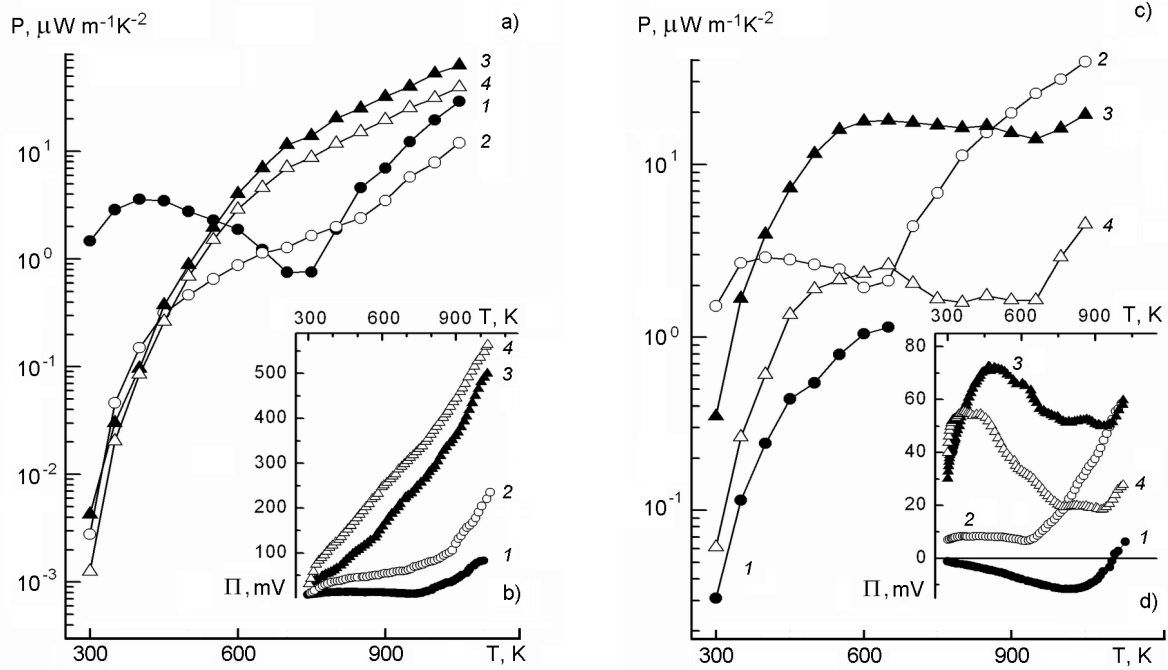
Fig. 3. Temperature dependences of the power factor (P) (a, c) and Peltier coefficient (Π) (b, d) of the $LnBaCuFeO_{5+\delta}$ (a, b) and $LnBaCoFeO_{5+\delta}$ (c, d) phases. Ln = La (*1*), Nd (*2*), Sm (*3*), Gd (*4*).

creased but S values increased when REE ionic radii increased. The ferrocobaltites have higher σ values ($\sigma_{max} \approx 1.6 \cdot 10^4$ S·m^{-1} near 650 K for $NdBaCoFeO_{5+\delta}$ (Fig. 2c)) but the ferrocuprates have higher S values ($S_{max} \approx 500-550$ μV·K^{-1} near 1000–1050 K for $GdBaCuFeO_{5+\delta}$ (Fig. 2b)).

At high temperatures, the electrical conductivity character of the ferrocobaltites and $LnBaCuFeO_{5+\delta}$ (Ln = La, Nd) phases changes from semiconducting ($\partial\sigma/\partial T > 0$) to metallic ($\partial\sigma/\partial T < 0$) (Fig. 2a,c), while the S values start to rise sharply (Fig. 2b,d). This is caused by the release of the weakly bound oxygen (δ) from the crystal lattice of these phases [20].

In the $S = f(T)$ dependences for $SmBaFeCoO_{5+\delta}$ and $GdBaFeCoO_{5+\delta}$ phases, a maximum is observed near 350 К and 450 К, respectively (Fig. 2d). The S increasing for $LnBaCoFeO_{5+\delta}$ (Ln = Sm, Gd) within 300–350 (450) К range seems to be caused by a change in the spin state of the cobalt cations Co^{3+}, Co^{4+} in their crystal structure from intermediate-spin (IS) to high-spin state (HS)

$$Co^{3+}_{IS}(t_{2g}^5 e_g^1) \rightarrow Co^{3+}_{HS}(t_{2g}^4 e_g^2),$$
$$Co^{4+}_{IS}(t_{2g}^4 e_g^1) \rightarrow Co^{4+}_{HS}(t_{2g}^3 e_g^2),$$

similarly to the spin state transition of Co^{3+} cations in the perovskite cobaltites of REE $LnCoO_3$ [21].

The temperature dependences of electrical conductivity and Seebeck coefficient for materials with polaronic charge transport (the perovskite layered oxides belong to these materials [9, 10, 20]) can be described by relations (4):

$$\sigma = A/T \cdot \exp(-(E_S + E_m)/kT), \qquad (4)$$
$$S = \pm k/e(-E_S/kT + B),$$

where E_S is the excitation energy of the charge carrier (polaron) and E_m is its transport energy ($E_m \approx 0$ for non-activated charge transport with large polarons (LP); if $E_m > 0$, the charge transport is thermally activated and is due to the small-polaron (SP) hopping [22]).

The E_S and E_m values determined from linear fractions of the $\ln(\sigma \cdot T) = f(1/T)$ and $S = f(1/T)$ plots for the oxides studied are presented in the Table. As is seen, the charge carriers in the $LnBaCu(Co)FeO_{5+\delta}$ phases are the small polarons ($E_m > 0$). The electrical transport activation energy values (E_S and E_m) in these phases increase when the REE ionic radius decreases and, as a

whole, are larger for the ferrocuprates than for the ferrocobaltites (see Table).

The power factors (P) calculated using the experimental σ and S values for the LnBaCu(Co)FeO$_{5+\delta}$ oxides are shown in Fig. 3a,c and in the Table. It is seen that, as a whole, the P values for the oxides studied increase at temperature increasing and depend heavily on the nature of the REE and 3d-metals in the crystal structure. The maximum P values (among the oxides studied) are observed for SmBaCuFeO$_{5+\delta}$, GdBaCuFeO$_{5+\delta}$, and NdBaCoFeO$_{5+\delta}$ (54.1; 31.3; and 32.3 μW·m^{-1}·K^{-2}, respectively, at $T = 1000$ K, see Table). These values are considerably lower than power factors for the sodium-cobalt oxide bronzes (for NaCo$_{1.8}$Cu$_{0.2}$O$_4$, for example, $P = 3.08$ mW·m^{-1}·K^{-2} at 1073 К [4]), but are close to the P values for ceramics based on Ca$_3$Co$_2$O$_6$ (for (Ca,Bi)$_3$(Co,Cu)$_2$O$_6$ solid solutions, $P \approx 30-50$ μW·m^{-1}·K^{-2} near 1173 К [5, 6], while for Ca$_{2.85}$Er$_{0.15}$Co$_2$O$_6$ phases, $P = 10.66$ μW·m^{-1}·K^{-2} at $T = 1073$ K [7]) and LaCoO$_3$ (for LaCo$_{0.80}$Ti$_{0.20}$O$_{2.86}$ and LaCo$_{0.80}$Ni$_{0.20}$O$_{2.95}$, the power factor values are 28.2 and 9.5 μW·m^{-1}·K^{-2}, respectively, at 1243 К [8]).

Thus, although LnBaCu(Co)FeO$_{5+\delta}$ oxides cannot compete with effective OTE based on NaCo$_2$O$_4$, comparison of our results with the data from [5–8] let us conclude that layered perovskite oxides may be used as a basis for development of new thermoelectric materials.

The absolute Peltier (Π) and Thomson (μ) coefficients for the LnBaCu(Co)FeO$_{5+\delta}$ oxides calculated using Eqs. (2) are presented in Fig. 3b,d, 4, and in the Table. As is seen, the Π values for LnBaCuFeO$_{5+\delta}$ phases increase when REE ionic radii decrease and temperature rises (for Ln = Sm, Gd, the $\Pi = f(T)$ dependences are nearly linear) (Fig. 3b). Values of Π for LnBaCoFeO$_{5+\delta}$ phases were considerably lower than for LnBaCuFeO$_{5+\delta}$ ones (by more than 10 times for Ln = La, Gd near 1000 К) and their temperature dependences were less pronounced than for the ferrocuprates (Fig. 3d).

The Thomson coefficient (μ) values for LnBaCu(Co)FeO$_{5+\delta}$ phases vary non-monotonously when temperature increases and have a minimum (for SmBaCuFeO$_{5+\delta}$ phase, a maximum) in the temperature region 500–700 К (Fig. 4). The μ values for ferrocuprates LnBaCuFeO$_{5+\delta}$ (Ln = Sm, Gd) are positive within the whole temperature range
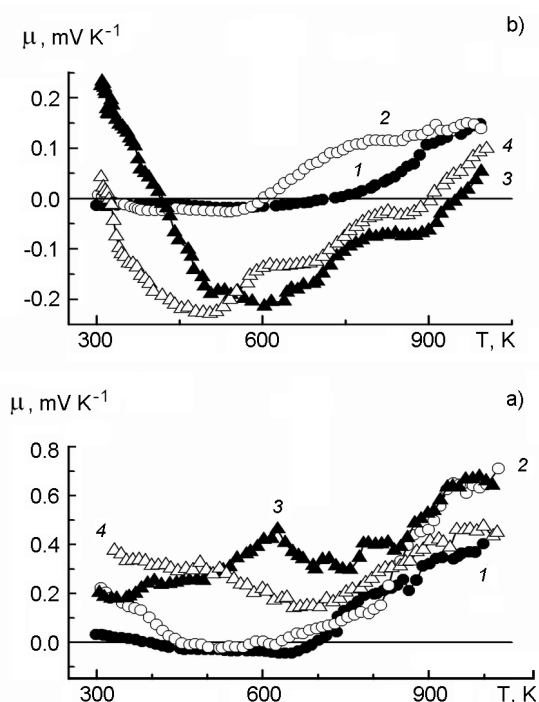

Fig. 4. Temperature dependences of the Thomson's coefficient (μ) of the LnBaCuFeO$_{5+\delta}$ (a) and LnBaCoFeO$_{5+\delta}$ (b) layered oxides: Ln = La (*1*), Nd (*2*), Sm (*3*), Gd (*4*).

studied. For other oxides studied, the μ values are positive near room temperature and at high temperatures (near 1000 K) but negative at intermediate temperatures (Fig. 4). The Thomson coefficients for the ferrocuprates are considerably higher than for the ferrocobaltites (by more than 10 times for Ln = Gd near 1000 К) (Fig. 4, Table).

The main results of the experimental study of thermoelectric properties of layered oxides LnBaCu(Co)FeO$_{5+\delta}$ can be summarized as follows. The LnBaCu(Co)FeO$_{5+\delta}$ compounds are semiconductors of n–(LaBaCoFeO$_{5+\delta}$) and p-type (the other oxides) with electrophysical properties depending strongly on the nature of the REE and 3d-metals in their structure. The charge transport in LnBaCu(Co)FeO$_{5+\delta}$ phases occurs due to hopping of small polarons, the activation energy of small-polaron hopping increasing when REE ionic radii decrease. The power factor values of LnBaCu(Co)FeO$_{5+\delta}$ oxides let us consider those as a potential base for development of new oxide thermoelectric materials.

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Термоелектричні властивості шаруватих оксидів LnBaCu(Co)FeO$_{5+\delta}$ (Ln = La, Nd, Sm, Gd)

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Досліджено кристалічну структуру, електропровідність та термо-ЕРС шаруватих оксидів LnBaCu(Co)FeO$_{5+\delta}$ (Ln=La, Nd, Sm, Gd) зі структурою перовскіту. Сполуки LnBaCu(Co)FeO$_{5+\delta}$ мають кубічну структуру для Ln = La та тетрагональну — для Ln = Nd–Gd та є напівпровідниками p-типу (окрім LaBaCoFeO$_{5+\delta}$, для якого $S < 0$). Визначено значення энергії активації процесів електроперенесення, обчислено величини термоелектричних коефіцієнтів (Зеебека, Пельтьє та Томсона) і фактора потужності досліджених оксидів. Виявлено, що значення фактора потужності фаз LnBaCu(Co)FeO$_{5+\delta}$ залежать від природи рідкісноземельних елементів та 3d-металів, які входять до їх складу, і є максимальними для SmBaCuFeO$_{5+\delta}$, GdBaCuFeO$_{5+\delta}$ та NdBaCoFeO$_{5+\delta}$. Показано, що шаруваті перовскіти можна розглядати як основу для розробки нових оксидних термоелектричних матеріалів.