Thermoelectric properties of layered ferrocuprates LnBaCuFeO(5+delta) (Ln= La, Pr, Nd, Sm, Gd-Lu)

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Thermoelectric Properties of Layered Ferrocuprates $LnBaCuFeO_{5+\delta}$ (Ln = La, Pr, Nd, Sm, Gd–Lu)

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Abstract—The electrical resistivity ρ and the thermopower S of ceramic materials $LnBaCuFeO_{5+\delta}$ (Ln = La, Pr, Nd, Sm, Gd–Lu) are measured in air at temperatures in the range from 300 to 1100 K. All the studied ferrocuprates are p-type semiconductors. The electrical resistivity ρ and the thermopower S of these compounds increase with a decrease in the radius of the Ln^{3+} cation (with an increase in the number of $4f$ electrons n in Ln^{3+}). The nonmonotonic behavior of the dependences $\rho = f(n)$ and $S = f(n)$ indicates that the electrical properties of the layered ferrocuprates $LnBaCuFeO_{5+\delta}$ depend on the electronic configuration of the Ln^{3+} cation. The power factors P calculated for the $LnBaCuFeO_{5+\delta}$ ceramic materials from the experimental values of ρ and S increase with increasing temperature and, at $T = 1000$ K, reach the maximum values $P = 102.0$ and 54.1 μW m^{-1} K^{-2} for Ln = Pr ($4f^2$) and Sm ($4f^5$), respectively, and become close to each other and equal to 30–35 μW m^{-1} K^{-2} for Ln = Gd ($4f^7$), Dy ($4f^9$), and Ho ($4f^{10}$).

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1. INTRODUCTION

The direct conversion of the thermal (and also solar) energy into the electric power in thermoelectric generators requires the use of materials with a high thermoelectric efficiency. The measure of this efficiency is the dimensionless thermoelectric figure-of-merit (ZT): $ZT = (S^2T)/(\rho\kappa) = PT/\kappa$, where T is the absolute temperature, S is the thermopower coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and P is the power factor of the material [1]. The high thermoelectric efficiency has been observed for bismuth telluride Bi_2Te_3, antimony telluride Sb_2Te_3, and related solid solutions [1, 2]; skutterudites (for example, $Yb_yCo_4Sn_xSb_{12-x}$ [3]); and silicides of iron ($FeSi_2$) and other metals [1, 4]. However, for example, the use of tellurides at elevated temperatures in air has been limited by their low resistance to oxidation by atmospheric oxygen. A higher oxidation resistance has been observed for oxide thermoelectrics [5], which have been actively investigated since the discovery of the high thermoelectric efficiency ($P = 5 \times 10^{-3}$ W m^{-1} K^{-2} at $T = 300$ K) for $NaCo_2O_4$ single crystals by Terasaki et al. [6].

To date, the thermoelectric properties have been investigated for different oxides, including layered cobaltites of sodium [5, 7] and calcium [5, 8–11], as well as perovskite barium plumbates [5, 12] and rare-earth (RE) ferrites and cobaltites [5, 13–16]. The maximum values of the thermoelectric figure-of-merit have been achieved for materials based on $NaCo_2O_4$ ($ZT =$

1.2 at $T = 1073$ K for $Na_xCoO_{2-\delta}$ [5] single crystals) and $Ca_3Co_4O_9$ ($ZT = 0.2$ for $Ca_{2.5}Bi_{0.5}Co_4O_{9+\delta}$ ceramic materials [9] and $ZT = 0.27$ for $Ca_{2.7}Dy_{0.3}Co_4O_{9+\delta}$ [9] near $T = 1000$ K). However, the results obtained in [12–16] suggest that a further search for new efficient thermoelectric materials among layered oxides with a perovskite (or similar) structure holds much promise.

Layered ferrocuprates $LnBaCuFeO_{5+\delta}$ belong to the perovskite family and have a tetragonal structure (for $Ln \neq$ La) with the unit cell parameters $a = b = a_c$ ($c \approx 2a_c$ [17–20], which is formed by double $(Cu,Fe)_2O_5$ layers of vertex-shared pyramids CuO_5 and FeO_5; the Ba^{2+} ions are located inside the double layers, and the Ln^{3+} ions are arranged between them. The doubling of the perovskite unit cell (ABO_3) is the result of ordering of the Ba^{2+} and Ln^{3+} cations along the c axis. The lanthanum barium ferrocuprate has a nearly cubic structure [21, 22] due to the statistical distribution of the La^{3+} and Ba^{2+} cations with close radii [23] over the A positions of the $LaBaCuFeO_{5+\delta}$ phase.

In this study, the electrical resistivity and thermopower were measured and the power factors were calculated for layered rare-earth barium ferrocuprates $LnBaCuFeO_{5+\delta}$ with a perovskite structure. The influence of the oxygen nonstoichiometry δ and the nature of rare-earth elements on the thermoelectric properties of these phases was investigated. From a comparison of the obtained results with the data available in the literature [12–16], the conclusion was drawn that a further

search for new efficient thermoelectric materials among layered perovskite oxides holds much promise.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Polycrystalline samples of layered perovskite ferrocuprates $LnBaCuFeO_{5+\delta}$ (Ln = La, Pr, Nd, Sm, Gd–Lu) were synthesized by the ceramic technique from lanthanum nitrate hexahydrate (reagent grade), barium carbonate (high-purity grade), RE(III) oxides (reagent grade), iron(III) oxide (reagent grade), and copper(II) oxide (reagent grade) in air at temperatures in the range from 1173 to 1273 K for 40–80 h [20]. In order to investigate the electrical resistivity and thermopower, the 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 1273 K for 5–10 h.

The X-ray powder diffraction analysis of the samples thus prepared was performed on a DRON-3 diffractometer (CuK_α and CoK_α radiation). The oxygen content $(5 + \delta)$ in the samples was determined iodometrically with the error $\Delta\delta = \pm0.01$.

Prior to measurements of the electrophysical properties, Ag electrodes were applied to the surface of the sample by firing silver paste at a temperature of 1073 K for 15 min. The electrical resistivity ρ of the ceramic samples was measured by the four-point probe dc technique in air at temperatures $T = 300–1100$ K in the dynamic mode at a heating (or cooling) rate of 3–5 K/min. The relative error in the determination of the electrical resistivity ρ was less than 5%. The experimentally obtained values of the electrical resistivity for the ceramic samples were reduced to zero porosity according to the technique described in [24, 25]. The thermopower coefficient S of the layered ferrocuprates was determined with respect to silver in air at temperatures in the range from 300 to 1000 K in the dynamic mode at a heating (or cooling) rate of 3–5 K/min with the error of less than 10%. The temperature gradient between the hot and cold ends of the sample was maintained during the measurements at a level of 20–25 K. The temperature was measured with the use of chromel–alumel thermocouples. The power factor P of the ceramic sample was calculated according to the formula $P = S^2/\rho$ [1].

3. RESULTS AND DISCUSSION

The synthesized rare-earth barium ferrocuprates $LnBaCuFeO_{5+\delta}$ are single phase, to within the error of the X-ray powder diffraction analysis, and have a cubic (Ln = La) or tetragonal structure (Ln = Pr, Nd, Sm, Gd–Lu); the unit cell parameters are $a = 3.861(4)–3.924(4)$ Å and $c = 7.637(8)–7.756(8)$ Å and, on the whole, decrease with decreasing ionic radius of the lanthanide cation ($R_{Ln^{3+}}$), which is in good agreement with the data available in the literature [17–22]. The oxygen nonstoichiometry index δ of the $LnBaCuFeO_{5+\delta}$ ceramic samples, which was determined iodometrically, also decreases with decreasing ionic radius $R_{Ln^{3+}}$ and amounts to 0.47 for Ln = La, 0.28 for Ln = Pr, 0.12 for Ln = Nd, 0.08 for Ln = Sm and Gd, and 0.04–0.06 for Ln = Tb–Lu. The unit cell parameters a and c for the samples synthesized in the present work, as well as the oxygen content $(5 + \delta)$ in these samples, are close to the characteristics reported in [17, 18, 20, 21] for rare-earth barium ferrocuprates synthesized under similar conditions.

The dependences $\rho(T)$ for all samples (except for Ln = La and Pr) exhibit a semiconductor $(\partial\rho/\partial T < 0)$ behavior (Figs. 1a, 1b). The metallic behavior of the electrical resistivity $(\partial\rho/\partial T > 0)$ of the LaBaCuFeO$_{5+\delta}$ and PrBaCuFeO$_{5+\delta}$ samples at $T > 650$ K is determined by the thermal dissociation of the lanthanum (praseodymium) barium ferrocuprates, which begins to occur in air at temperatures close to 650 K [20]. The electrical resistivity of the layered ferrocuprates varies over a wide range (from $\rho_{min} = 2.3 \times 10^{-4}$ Ω m for Ln = La at $T = 550–650$ K to $\rho_{max} = 1.1 \times 10^5$ Ω m for Ln = Tm at $T = 300$ K) and increases nonmonotonically with an increase in the ionic radius $R_{Ln^{3+}}$ (with an increase in the number of $4f$ electrons n in Ln^{3+}). The dependences $\rho_T = f(n)$ (Fig. 2a) have maxima for Ln = Tb $(4f^8)$, Dy $(4f^9)$, Er$(4f^{11})$, and Tm $(4f^{12})$ and minima for Ln = Ho $(4f^{10})$ and Yb $(4f^{13})$, with the intensity decreasing with an increase in the temperature (Fig. 2a).

The activation energies of electrical conduction E_A of the studied samples, which were calculated from the linear parts of the dependences $\ln(\rho/T) = f(1/T)$, vary over a range from $E_A = 0.06$ eV for Ln = La to $E_A = 0.64$ eV for Ln = Tm and increase nonmonotonically with an increase in the ionic radius $R_{Ln^{3+}}$. The complex behavior of the curves $\rho = f(n)$, $\rho = f(R_{Ln^{3+}})$, $E_A = f(n)$, and $E_A = f(R_{Ln^{3+}})$ for the $LnBaCuFeO_{5+\delta}$ phases is caused by the periodicity of the properties of rare-earth elements [26], which have electronic configurations strongly affecting the electrical resistivity ρ of layered ferrocuprates [20, 27].

The thermopower coefficient of the layered ferrocuprates $LnBaCuFeO_{5+\delta}$ has a positive sign ($S > 0$) over the entire temperature range under investigation. This suggests that holes are the majority charge carriers in the aforementioned phases. The minima observed in the dependences $S = f(T)$ for the samples with Ln = La, Pr, and Nd at temperatures close to 700 K (Fig. 1c), as noted above, are determined by the thermal dissociation of these phases [20]. The dependences $S = f(T)$ for the samples with Ln = Tm and Ln = Lu exhibit a pro-
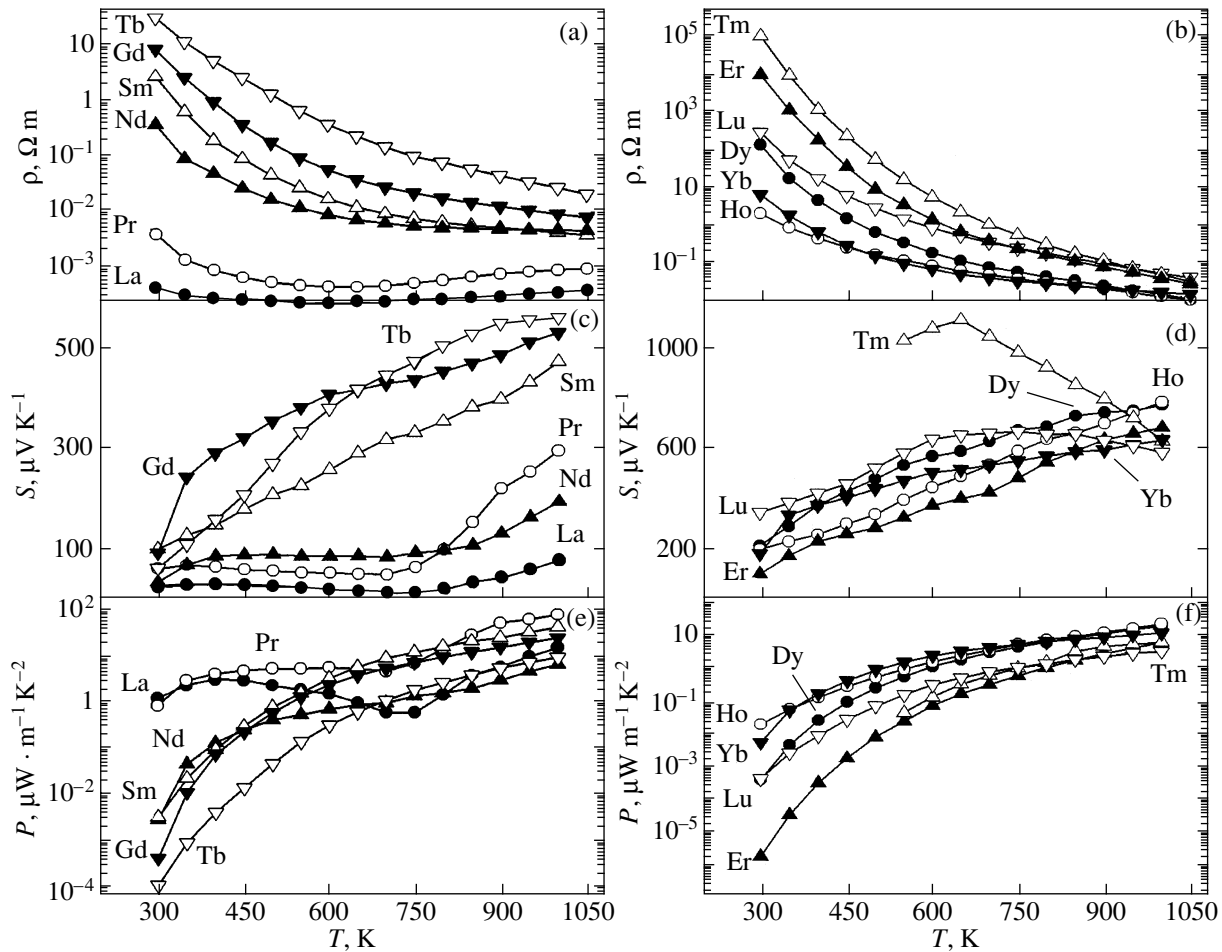
Fig. 1. Temperature dependences of (a, b) the electrical resistivity ρ, (c, d) the thermopower S, and (e, f) the power factor P for layered ferrocuprates $Ln\mathrm{BaCuFeO}_{5+\delta}$.

nounced maximum at $T = 650$ and 750 K, respectively (Fig. 1d). The thermopower coefficient S of the other samples increases monotonically with an increase in the temperature (Figs. 1c, 1d). The activation energies of thermopower E determined from the dependences $S = f(1/T)$ for the $Ln\mathrm{BaCuFeO}_{5+\delta}$ phases with $Ln =$ La, Pr, and Nd are equal to $E = 0.02$, 0.01, and 0.02 eV, respectively.

The activation energy of electrical conduction E_A for materials with a polaron character of the charge transfer, including layered ferrocuprates [20, 24, 27], satisfies the relationship $E_A = E + W$, where E is the excitation energy and W is the heat of polaron transfer ($W \approx 0$ for the activationless charge transfer by large-radius polarons and $W > 0$ for the thermally activated charge transfer by small-radius polarons through the hopping mechanism) [28]. It was found that, for the $\mathrm{PrBaCuFeO}_{5+\delta}$ and $\mathrm{NdBaCuFeO}_{5+\delta}$ phases, the activation energies of electrical conduction are $E_A = 0.13$ and 0.20 eV, respectively. A comparison of the quantities E_A and E for the layered ferrocuprates demonstrates that the excitation energy of small-radius polarons in

$Ln\mathrm{BaCuFeO}_{5+\delta}$ is approximately equal to 0.02 eV and hardly depends on the nature of the rare-earth element, whereas the heat of transfer of small-radius polarons increases with an increase the ionic radius $R_{Ln^{3+}}$ and amounts to 0.04, 0.12, and 0.18 eV for $Ln =$ La, Pr, and Nd, respectively.[1]

The dependences $S_T = f(n)$ for the $Ln\mathrm{BaCuFeO}_{5+\delta}$ phases, like the dependences $\rho_T = f(n)$, exhibit a complex behavior and pass through a maximum at $n = 9$, 10. In this case, the thermopower S for the compositions with $Ln =$ Dy and Ho reaches 710–720 μV K^{-1} at $T = 1000$ K (Fig. 2b). A strong positive correlation between the number of unpaired electrons of the Ln^{3+} cation and the thermopower of the ferrocuprate phases (Fig. 2b) indicates that the electrical properties of these phases

[1] An increase in the series La $\longrightarrow$ Pr $\longrightarrow$ Nd is also determined to some extent by a decrease in the content of weakly bound oxygen in the samples (as was noted above, the oxygen nonstoichiometry δ in $Ln\mathrm{BaCuFeO}_{5+\delta}$ is equal to 0.47, 0.28, and 0.12 for $Ln =$ La, Pr, and Nd, respectively).

(in particular, the concentration of charge carriers, i.e., small-radius polarons, in their conducting $Cu(Fe)O_2$ layers) are determined to a large extent by the electronic configuration of the rare-earth cation involved in their composition.

The power factors P of the $LnBaCuFeO_{5+\delta}$ ceramic samples at room temperature do not exceed 1.5 $\mu W\ m^{-1}\ K^{-2}$ (for Ln = La); however, their values increase[2] with increasing temperature (Figs. 1e, 1f). The nonmonotonic behavior of the dependences $P = f(n)$ is less pronounced as compared to the curves $\rho_T = f(n)$ and $S_T = f(n)$, especially, at high temperatures (Fig. 2c). In this case, there is a clear tendency toward a decrease in the power factor P of the layered ferrocuprates with a decrease in the ionic radius of the rare-earth cation (with an increase in the number n of $4f$ electrons in the rare-earth cation). The observed tendency is explained by the fact that, with an increase in n for the $LnBaCuFeO_{5+\delta}$ phases, the increase in the electrical resistivity ρ dominates over the increase in the thermopower S (moreover, in the range $10 \le n \le 14$, with an increase in n, the thermopower also decreases) (Fig. 2). The power factor of the $LnBaCuFeO_{5+\delta}$ ceramic samples reaches the maximum values for Ln = Pr and Sm: at T = 1000 K, P_{1000} = 102.0 and 54.1 $\mu W\ m^{-1}\ K^{-2}$, respectively. The values of P for the layered ferrocuprates with Ln = Gd, Dy, and Ho at T = 1000 K are close to each other and equal to 30–35 $\mu W\ m^{-1}\ K^{-2}$.

The power factors P of the most efficient oxide thermoelectrics based on layered sodium cobaltites are significantly higher: for example, $P = 5 \times 10^3\ \mu W\ m^{-1}\ K^{-2}$ for $NaCo_2O_4$ single crystals at T = 300 K [6] and $P = 3.08 \times 10^3\ \mu W\ m^{-1}\ K^{-2}$ for $Na(Co_{0.9}Cu_{0.1})_2O_4$ ceramic samples at T = 1073 K [7]. However, the use of $NaCo_2O_4$-based materials for high-temperature conversion of the thermal (or solar) energy into the electric power has been limited by the high volatility of Na_2O at high temperatures [5]. A higher thermal resistance is observed for materials based on layered calcium cobaltites ($Ca_3Co_2O_6$, $Ca_3Co_4O_9$), as well as perovskite cobaltites ($RCoO_3$), ferrites ($LaFeO_3$), and plumbates ($BaPbO_3$). The power factors P of these oxides are less than those for $NaCo_2O_4$ and equal to 50 $\mu W\ m^{-1}\ K^{-2}$ for $(Ca_{0.98}Bi_{0.02})_3Co_2O_6$ at T = 1170 K [8], 270 $\mu W\ m^{-1}\ K^{-2}$ for $Ca_{2.5}Bi_{0.5}Co_4O_{9+\delta}$ at T = 973 K [9], and 115 $\mu W\ m^{-1}\ K^{-2}$ for $Ca_3Co_4O_9$ at T = 973 K [11]. For $Sr_{0.6}Ba_{0.4}PbO_3$, the power factors are P_{773} = 310 and P_{1000} = 100 $\mu W\ m^{-1}\ K^{-2}$ [12]. For $La_{0.9}Sr_{0.1}FeO_3$, the power factor is P_{1100} = 110 $\mu W\ m^{-1}\ K^{-2}$ [13].

Fig. 2. Dependences of (a) the electrical resistivity ρ_T, (b) the thermopower S_T, and (c) the power factor P_T for ferrocuprates $LnBaCuFeO_{5+\delta}$ on the number n of f electrons in the Ln^{3+} cation at the temperatures T = (1) 300 and (2) 1000 K.

Therefore, layered rare-earth barium ferrocuprates cannot compete successfully with efficient oxide thermoelectrics based on $NaCo_2O_4$. However, a comparison of the results obtained in the present work with the data available in the literature [5, 8, 9, 11–13] suggests that a further search for layered perovskite oxide materials, which are suitable for the effective conversion of the thermal (or solar) energy into the electric power in thermoelectric generators at high temperatures, holds much promise.

4. CONCLUSIONS

Thus, the electrical resistivity and thermopower for ceramic samples of layered rare-earth barium ferrocuprates $LnBaCuFeO_{5+\delta}$ with a perovskite structure were investigated in air at temperatures in the range 300–1100 K, and the power factors of sintered ceramic materials were calculated. It was demonstrated that all

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[2] The minimum in the dependences $P = f(T)$ at temperatures close to T = 700 K for the $LaBaCuFeO_{5+\delta}$ and $PrBaCuFeO_{5+\delta}$ samples is determined by the small magnitude of their thermopower in the given temperature range.
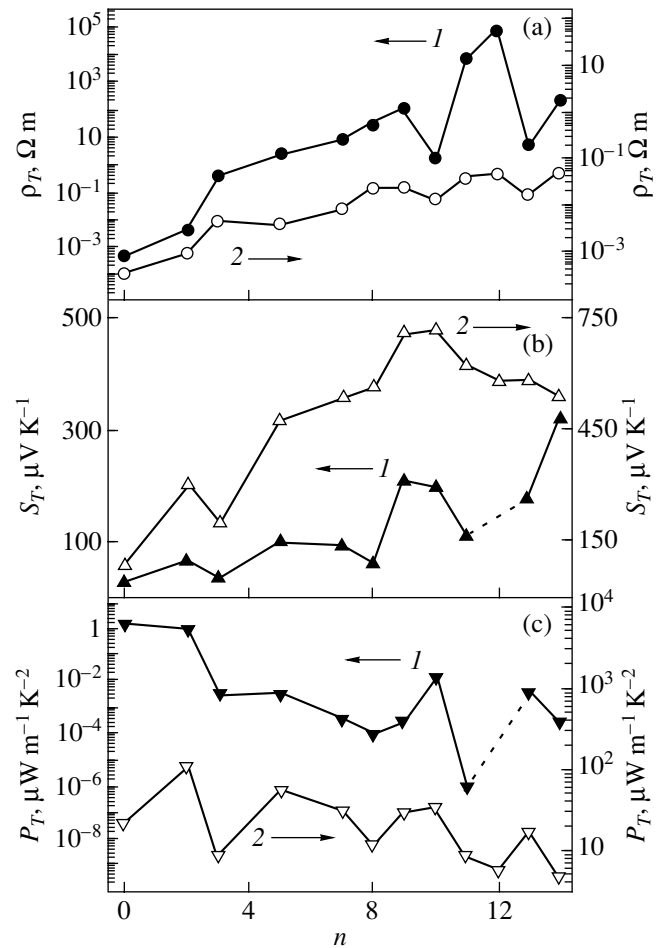
the studied ferrocuprates are *p*-type semiconductors and that the electrical resistivity and thermopower of these compounds increase with an increase in the number of 4*f* electrons in the Ln^{3+} cation (with a decrease in the ionic radius of Ln^{3+}). The complex behavior of the dependences $\rho = f(n)$, $S = f(n)$, and $P = f(n)$ indicates that the electrical properties of the $Ln\mathrm{BaCuFeO}_{5+\delta}$ phases strongly depend on the electronic configuration of the Ln^{3+} cation. It was established that the power factor increases with increasing temperature and, at $T = 1000$ K, reaches the maximum value $P = 102\ \mu\mathrm{W\ m^{-1}\ K^{-2}}$ for the composition $\mathrm{PrBaCuFeO}_{5+\delta}$.

A comparison of the obtained results with the data available in the literature allows us to draw the conclusion that a further search for new efficient thermoelectric materials among layered perovskite oxides holds much promise.

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