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Article in *Physics of the Solid State* · April 2008

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# Effect of Oxygen Nonstoichiometry on the Thermal and Electrophysical Properties of Layered Ferrocuprates $LnBaCuFeO_{5+\delta}$ ( $Ln = La, Pr$ ; $(0 \leq \delta \leq 0.5)$ )

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Received August 20, 2007

**Abstract**—The influence of the oxygen content ( $5 + \delta$ ) on the structure, thermal expansion, and electrical properties of the  $LnBaCuFeO_{5+\delta}$  phases ( $Ln = La, Pr$ ) is investigated. It is found that, for  $0 \leq \delta \leq 0.25$ , the unit cell parameters of the ferrocuprates decrease and the linear thermal expansion coefficient increases linearly with increasing  $\delta$ . In the range  $0.25 \leq \delta \leq 0.50$ , the thermal expansion coefficient and the structural parameters of the samples depend weakly on their oxygen nonstoichiometry  $\delta$ . The  $LnBaCuFeO_{5+\delta}$  ferrocuprates ( $0 \leq \delta \leq 0.48$ ) are  $p$ -type semiconductors with the electrical resistivity  $\rho$ , thermopower coefficient  $S$ , and activation energy for electrical conduction  $E_A$  decreasing with increasing  $\delta$  and the dependence  $E_A = f(\delta)$  being close to linear.

PACS numbers: 61.50.Nw, 78.30.-j, 65.40.De, 74.25.Fy

DOI: 10.1134/S1063783408040033

## 1. INTRODUCTION

The structure and properties of many oxygen-deficient complex perovskite-type oxides (superconducting cuprates  $RBa_2CuO_{7-\delta}$ , layered cobaltites and manganites  $RBaMe_2O_{6-\delta}$  (where  $R$  is a rare-earth element and  $Me = Co$  or  $Mn$ )) depend strongly both on their nonstoichiometry  $\delta$  and on the degree of oxygen vacancy ordering in the crystal lattice [1–5].<sup>1</sup> These parameters can be modified by properly varying the thermal prehistory of a sample ( $T$  and  $p(O_2)$ ) during annealing, heating–cooling rate, etc.). Layered rare-earth and Ba ferrocuprates  $RBaCuFeO_{5+\delta}$  (0112-type phases) belong to the perovskite family and possess sensor [6] and catalytic [7] properties, and, therefore, investigation of the effect of oxygen nonstoichiometry on their structure and properties is of interest both for the development of novel functional materials and in order to gain a deeper understanding of the composition–structure–property interrelations for layered oxides of the perovskite family.

The  $PrBaCuFeO_{5+\delta}$  phase has a tetragonal structure (space group  $P4/mmm$ ,  $Z = 1$ ,  $a = b = a_c = 3.923(2)$  Å,  $c \approx 2a_c = 7.759(2)$  Å for  $\delta = 0.35(2)$  [8]) formed by double  $(Cu,Fe)_2O_5$  layers of vertex-shared pyramids  $CuO_5$  and  $FeO_5$ ; the barium ions are located in the layers, and the praseodymium ions, between the layers, thus joining them. The unit cell doubling of the  $ABO_3$  perovskite results from the ordered arrangement of barium and

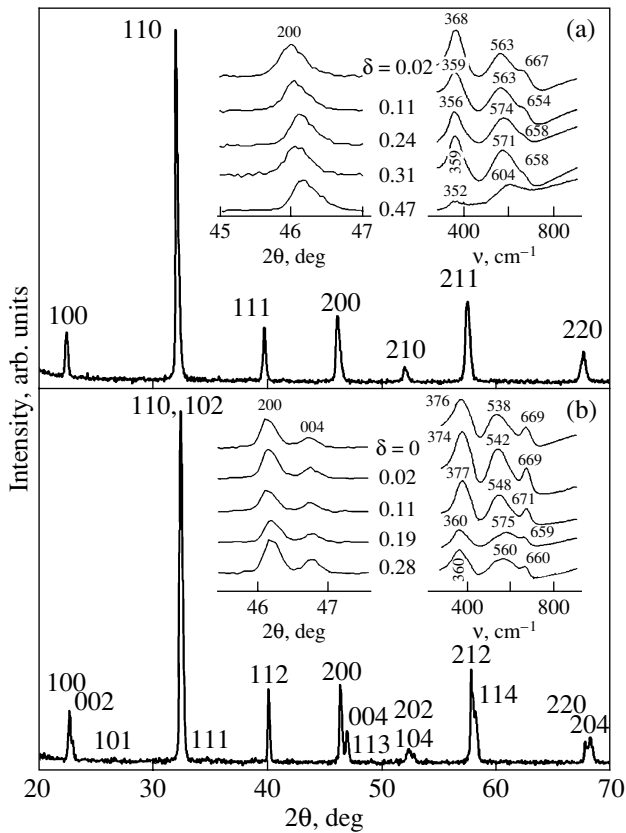
praseodymium ions along the  $c$  axis, which is accompanied by ordering of the  $(1 - \delta)$  oxygen vacancies in the  $PrO_\delta$  layers. The lanthanum–barium ferrocuprate has a very nearly cubic structure (space group  $Pm3m$ ,  $a_c = 3.9256(6)$  [9],  $3.92330(5)$  [10],  $3.924$  Å [11]) because of the  $La^{3+}$  and  $Ba^{2+}$  ions, which are close in radii [12], being statistically distributed over the  $A$  positions of the  $LaBaCuFeO_{5+\delta}$  phase. The  $LnBaCuFeO_{5+\delta}$  ferrocuprates are  $p$ -type antiferromagnetic semiconductors [11, 13] with the Néel temperature  $T_N = 70$  K [10] and 68 K [14] for  $Ln = La$  and  $T_N = 280(5)$  K for  $Ln = Pr$  at  $\delta = 0.35(2)$  [8].

We have synthesized ceramic samples of the  $LnBaCuFeO_{5+\delta}$  perovskite phases ( $Ln = La, Pr$ ) with different oxygen contents ( $5 + \delta$ ), determined their crystal structure parameters, and studied the effect of the nonstoichiometry  $\delta$  on the thermal expansion, electrical resistivity, and thermopower of the lanthanum (praseodymium)–barium layered ferrocuprates.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Polycrystalline samples of  $LnBaCuFeO_{5+\delta}$  ( $Ln = La, Pr$ ) were synthesized by the ceramic technique from a mixture of lanthanum nitrate  $La(NO_3)_3 \cdot 6H_2O$  (reagent grade) with oxides  $Pr_6O_{11}$  (reagent grade),  $Fe_2O_3$  (special-purity grade 2-4), and  $CuO$  (special-purity grade 9-2) and barium carbonate  $BaCO_3$  (high-purity grade) by calcination in air at 1173 K for 40 h [11]. The powders thus obtained were pressed at (1–

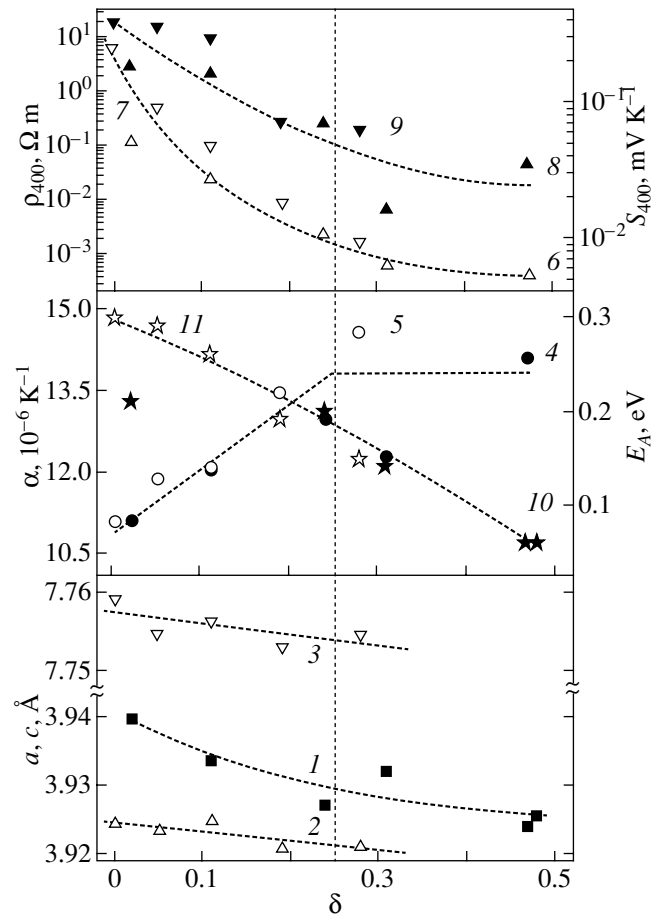
<sup>1</sup> A classical example is the stepped dependence of the superconducting transition temperature  $T_c$  of the high-temperature superconductor  $YBa_2Cu_3O_{7-\delta}$  on its oxygen nonstoichiometry  $T_c = f(\delta)$  [2].



**Fig. 1.** X-ray powder diffraction patterns of (a)  $\text{LaBaCuFeO}_{5.47}$  and (b)  $\text{PrBaCuFeO}_{5.28}$ . The insets show the IR absorption spectra and the (200) reflections for  $\text{LaBaCuFeO}_{5+\delta}$  and the (200) and (004) reflections for  $\text{PrBaCuFeO}_{5+\delta}$  with different oxygen contents ( $5+\delta$ ).

$3) \times 10^3 \text{ kg/cm}^2$  into pellets measuring  $\approx 5 \times 4 \times 30 \text{ mm}$ , which were subsequently sintered in air at 1273 K for 5–10 h. The sintered bars were used in studies of thermal expansion and thermopower, and the platelets ( $\approx 5 \times 5 \times 3 \text{ mm}$  in size) cut from these bars, in measurements of the electrical resistivity of the samples. To measure the electrophysical properties, Ag electrodes were prepared on the surface of the samples by firing silver paste at 1073 K for 15 min. To obtain samples with different oxygen contents, the powders and the sintered ceramic (with the Ag contacts fired in) were additionally maintained at 473–1073 K for 10–15 h in flowing oxygen ( $(p(\text{O}_2) = 10^5 \text{ Pa})$  or nitrogen ( $(p(\text{O}_2) = 10^2 \text{ Pa})$ ), followed by slow cooling (with a rate of 2–6 K/min) to room temperature, without taking them out of the furnace and disconnection of the gas supply.

The oxygen content ( $5+\delta$ ) in the samples was determined iodometrically with an error  $\Delta\delta = \pm 0.01$ . The x-ray diffraction measurements of the powder samples were performed on a Bruker D8 XRD diffractometer ( $\text{CuK}\alpha$  radiation, Ni filter). The errors in the calculation of the ferrocuprate unit cell parameters were  $\Delta a = \pm 0.004 \text{ \AA}$  and  $\Delta c = \pm 0.008 \text{ \AA}$ . The IR absorption spectra



**Fig. 2.** Dependences of (1–3) the unit cell parameters (1, 2)  $a$  and (3)  $c$ , (4, 5) the linear thermal expansion coefficient  $\alpha$ , (6, 7) the electrical resistivity  $\rho_{400}$ , (8, 9) the thermopower  $S_{400}$ , and (10, 11) the activation energy for electrical conduction  $E_A$  of the (1, 4, 6, 8, 10)  $\text{LaBaCuFeO}_{5+\delta}$  and (2, 3, 5, 7, 9, 11)  $\text{PrBaCuFeO}_{5+\delta}$  ferrocuprates on the excess oxygen content  $\delta$  in the samples.

of the powder samples were recorded using pelletized mixtures with KBr (reagent grade) containing  $\approx 0.5\%$   $\text{LnBaCuFeO}_{5+\delta}$  on a Fourier spectrometer Nexus (Thermo Nicolet) in the frequency interval 300–1500  $\text{cm}^{-1}$ . The error of vibration frequency determination did not exceed  $\pm 2 \text{ cm}^{-1}$ . Thermal expansion, electrical resistivity  $\rho$ , and thermopower  $S$  of the polycrystalline samples were studied in air in the temperature interval 280–520 K<sup>2</sup> to within  $\delta(\rho) \leq 5\%$  and  $\delta(S) \leq \pm 10\%$  by the techniques described elsewhere [15]. The experimental values of  $\rho$  of the ceramic were reduced to zero porosity as described in [15, 16]. The values of the linear thermal expansion coefficient  $\alpha$  and the electrical conduction activation energy  $E_A$  were derived from the linear parts of

<sup>2</sup> Oxygen exchange between lanthanum (praseodymium)–barium ferrocuprates and the ambient medium for  $T < 520 \text{ K}$  was found to be practically nonexistent [11, 17]. This was substantiated in our study by the reproducibility of the properties of the ceramic during its thermal cycling.

the dependences  $\Delta l/l_0 = f(T)$  and  $\ln(p/T) = f(1/T)$  (with a correlation coefficient  $R \geq 0.999$ ) to within  $\delta(\alpha) \leq \pm 5\%$  and  $\Delta E_A \leq 0.01$  eV, respectively.

### 3. RESULTS AND DISCUSSION

The  $\text{LaBaCuFeO}_{5.47}$  phase prepared in air ( $p(\text{O}_2) = 10^5$  Pa) was cubic, and its reflections were indexed on the basis of space group  $Pm\bar{3}m$  (Fig. 1a) with the parameter  $a = 3.924$  Å, which agrees with the data reported in [9–11]. The structure of the lanthanum–barium ferrocuprate remained cubic with decreasing oxygen content (Fig. 1a); the  $\text{LaBaCuFeO}_{5+\delta}$  unit cell increased in size with  $\delta$  decreasing in the  $0 < \delta < 0.25$  interval, while being practically independent of  $\delta$  within  $0.25 < \delta < 0.50$  (see table and Fig. 2). The anomalously large value of the  $a$  parameter for the  $\text{LaBaCuFeO}_{5.31}$  composition ( $a = 3.932$  Å) should be attributed to the specific experimental conditions. This sample was prepared by a reducing annealing of  $\text{LaBaCuFeO}_{5+\delta}$  in the nitrogen environment ( $p(\text{O}_2) = 10^2$  Pa) at 673 K; as reported in [18], it is in this temperature interval that the unit cell of the lanthanum–barium ferrocuprate increases in size ( $\Delta a$ ) as a result of oxygen vacancies in the  $\text{LaO}_\delta$  layers of its crystal structure becoming disordered. The values of  $\Delta a$  resulting from the annealing of  $\text{LaBaCuFeO}_{5+\delta}$  in air [18] and in nitrogen coincide ( $\Delta a = 0.05\%$ ), which suggests that the degree of ordering of the oxygen sublattice of the lanthanum–barium ferrocuprate near 673 K does not depend on the gradient of the chemical potential of oxygen ( $\text{grad}\mu(\text{O}_2)$ ) between the sample and ambient air.

As follows from x-ray diffraction measurements (Fig. 1b), the  $\text{PrBaCuFeO}_{5+\delta}$  samples had a tetragonal structure (space group  $P4/mmm$ ) with the parameters  $a = 3.921$ – $3.924$  Å and  $c = 7.755$ – $7.760$  Å (see table), which agree well with [8, 10, 13]. The dependences  $a = f(\delta)$  and  $c = f(\delta)$  for the praseodymium–barium ferrocuprate were fairly weak (Fig. 2), which is in accord with the results obtained for the  $\text{PrBaCuFeO}_{5+\delta}$  and  $\text{PrBaCo}_2\text{O}_{5+\delta}$  phases [8, 19, 20].

The IR absorption spectra of the  $\text{LnBaCuFeO}_{5+\delta}$  phases (Figs. 1a, 1b) exhibit three absorption bands peaking at 352–377 ( $\nu_1$ ), 538–604 ( $\nu_2$ ), and 654–671 ( $\nu_3$ )  $\text{cm}^{-1}$ , which can be assigned to bending ( $\nu_1$ ) and stretching ( $\nu_2$ ) vibrations of the metal–oxygen bonds in  $\text{Cu}(\text{Fe})\text{O}_2$  layers, as well as to stretching vibrations of the apical oxygen in the Cu–O–Fe bonds ( $\nu_3$ ) in the structure of the rare-earth and barium ferrocuprates [11, 21]. We readily see (Fig. 1) that a decrease in the oxygen content in a sample brings about a shift of the  $\nu_2$  bands toward lower, and the  $\nu_3$  bands, toward higher frequencies. This means that the metal–oxygen interaction energy in the  $\text{Cu}(\text{Fe})\text{O}_2$  layers decreases, and that in the Cu–O–Fe chains, increases with decreasing  $\delta$ , which gives rise to growth of the anisotropy of interac-

Unit cell parameters  $a$  and  $c$ , unit cell volume  $V$ , linear thermal expansion coefficient  $\alpha$ , and activation energy for electrical conduction  $E_A$  of lanthanum (praseodymium)–barium ferrocuprates with different oxygen contents ( $5 + \delta$ )

| $\delta$                       | $a$ , Å | $c$ , Å | $V$ , Å <sup>3</sup> | $\alpha \times 10^6$ , K <sup>-1</sup> | $E_A$ , eV |
|--------------------------------|---------|---------|----------------------|--|------------|
| <b>LaBaCuFeO<sub>5+δ</sub></b> |         |         |                      |  |            |
| 0.48                           | 3.926   | –       | 60.51                | –                                      | 0.06       |
| 0.47                           | 3.924   | –       | 60.42                | 14.1 [18]                              | 0.06       |
| 0.31                           | 3.932   | –       | 60.79                | 12.3                                   | 0.14       |
| 0.24                           | 3.927   | –       | 60.56                | 13.0                                   | 0.20       |
| 0.11                           | 3.934   | –       | 60.88                | 12.0                                   | 0.26       |
| 0.02                           | 3.940   | –       | 61.16                | 11.1                                   | 0.21       |
| <b>PrBaCuFeO<sub>5+δ</sub></b> |         |         |                      |  |            |
| 0.28                           | 3.921   | 7.755   | 119.2                | 14.6 [18]                              | 0.15       |
| 0.19                           | 3.921   | 7.753   | 119.2                | 13.5                                   | 0.19       |
| 0.11                           | 3.925   | 7.756   | 119.5                | 12.1                                   | 0.26       |
| 0.05                           | 3.923   | 7.755   | 119.3                | 11.9                                   | 0.29       |
| 0.00                           | 3.924   | 7.760   | 119.5                | 11.1                                   | 0.30       |

tions in the structure of the  $\text{LnBaCuFeO}_{5+\delta}$  ferrocuprates ( $\Delta\nu = \nu_3 - \nu_2$  increases for  $\text{Ln} = \text{Pr}$  from 100  $\text{cm}^{-1}$  ( $\delta = 0.28$ ) to 131  $\text{cm}^{-1}$  ( $\delta = 0$ ), and for  $\text{Ln} = \text{La}$ , from 0  $\text{cm}^{-1}$  ( $\delta = 0.47$ ) to 104  $\text{cm}^{-1}$  ( $\delta = 0.02$ )). A comparison of our results with those reported in [11] permits a conclusion that a decrease in  $\delta$  and an increase in  $R_{\text{Ln}^{3+}}$  exert the same effect on the strength of metal–oxygen interactions in the structure of layered ferrocuprates.

The temperature dependences of relative elongation  $\Delta l/l_0 = f(T)$  of ceramic  $\text{LnBaCuFeO}_{5+\delta}$  samples were linear (Fig. 3), their linear thermal expansion coefficients increased linearly in the interval  $0 < \delta < 0.25$  and were practically independent of  $\delta$  with increasing  $\delta$  until they finally reached the limiting value  $\alpha = (14\text{--}15) \times 10^{-6}$  K<sup>-1</sup> (Fig. 2, table) (the anomalously low linear thermal expansion coefficient of the  $\text{LaBaCuFeO}_{5.31}$  ferrocuprate ( $\alpha = 12.3 \times 10^{-6}$  K<sup>-1</sup>) is the result, as already pointed out, of the maximum disorder in its oxygen sublattice).

A comparison of the x-ray diffraction with dilatometric measurements suggests a conclusion that structural characteristics of layered ferrocuprates depend strongly on their oxygen nonstoichiometry for  $\delta < 0.25$  (when the  $\text{LnO}_\delta$  layer is filled by oxygen ions to less than one fourth) and vary only weakly for larger  $\delta$  ( $0.25 < \delta < 0.50$ , and the oxygen filling  $\Theta$  of the  $\text{LnO}_\delta$  layer varies within the interval  $1/4 < \Theta < 1/2$ ). We note that the anomalous course of the concentration dependences of the properties oxygen-deficient oxides in the

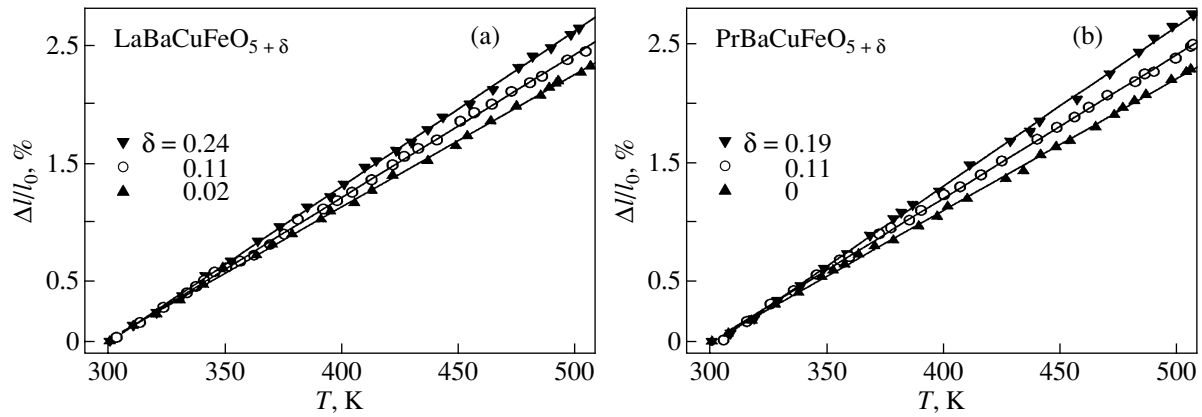


Fig. 3. Temperature dependences of the relative elongation of the (a)  $\text{LaBaCuFeO}_{5+\delta}$  and (b)  $\text{PrBaCuFeO}_{5+\delta}$  ferrocuprates.

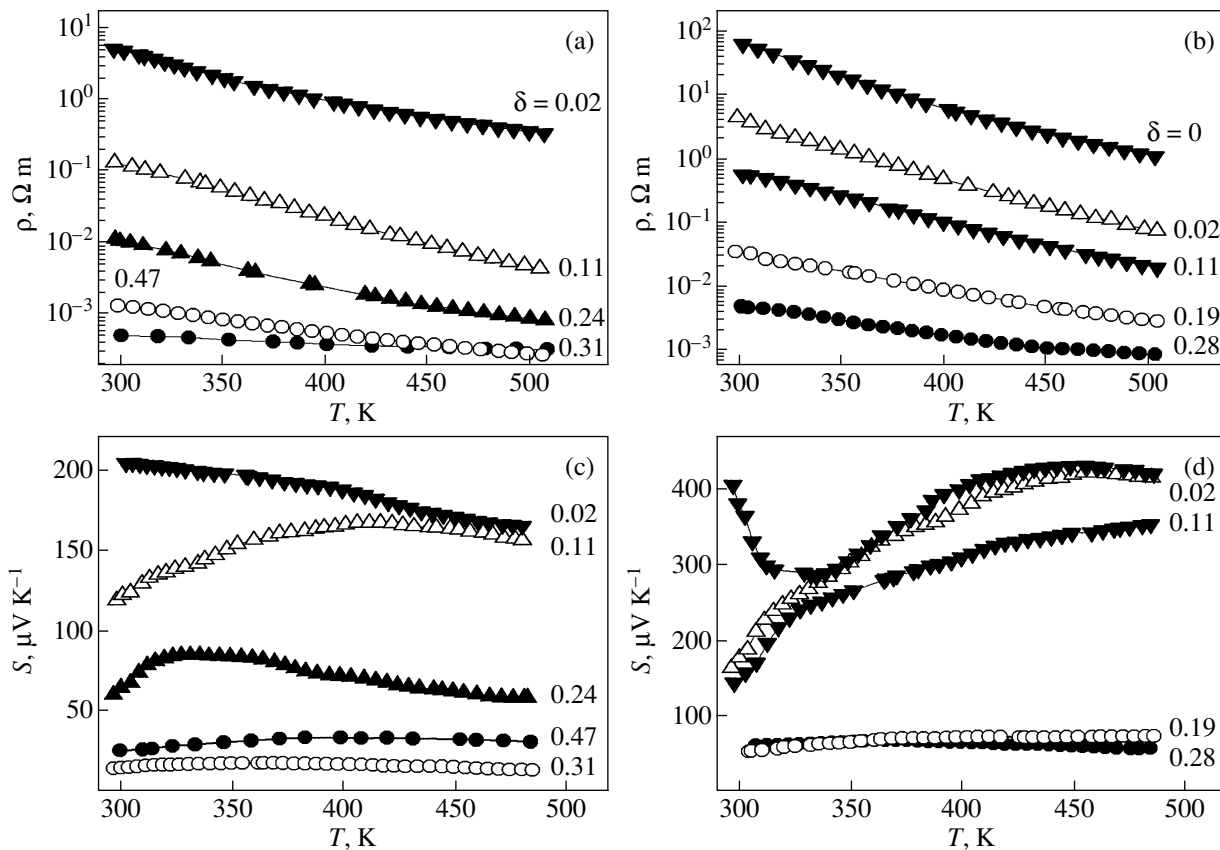


Fig. 4. Temperature dependences of (a, b) the electrical resistivity  $\rho$  and (c, d) the thermopower  $S$  of the (a, c)  $\text{LaBaCuFeO}_{5+\delta}$  and (b, d)  $\text{PrBaCuFeO}_{5+\delta}$  ferrocuprates.

region  $\Theta \approx 1/4$  was observed more than once before, in particular, in the dependences of the superconducting transition temperature  $T_c = f(\delta)$  for high-temperature superconductors of the type of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (near  $\delta \approx 0.5$ , which corresponds to  $\Theta \approx 1/4$ ) [1, 2], as well as in the dependence of the activation energy of conduction for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  cuprates in the normal state [22, 23].

As seen from Fig. 4, all the  $\text{LnBaCuFeO}_{5+\delta}$  ferrocuprates studied are  $p$ -type semiconductors with the electrical resistivity and thermopower increasing with decreasing oxygen content in a sample. The thermopower of compositions with  $\delta > 0.25$  was small, not over  $80 \mu\text{V K}^{-1}$ ; for strongly reduced samples, the values of  $S$  were considerably larger and reached 0.2–0.4  $\text{mV K}^{-1}$  (Figs. 4c, 4d). The dependences  $\rho = f(T)$

and  $S = f(T)$  exhibited slight hysteresis in heating–cooling cycles. As shown in [17], for  $T < 520$  K, oxygen exchange between the gas phase and the  $\text{LaBaCuFeO}_{5+\delta}$  ceramic is practically zero. The observations reported in [17], as well as the fact that the values of  $\rho$  and  $S$  of a sample were reproducible under repeated thermal cycling, suggest that the observed hysteresis is a result of rearrangement in the oxygen sublattice of the samples (ordering–disordering of oxygen vacancies in the  $\text{LnO}_\delta$  layers) subjected to heating–cooling cycling. It is appropriate to note here that the electrical resistivities of the praseodymium–barium ferrocuprate ceramic determined by us agree well with the values of  $\rho$  for  $\text{PrBaCuFeO}_{5+\delta}$  samples ( $\delta = 0, 0.25$ ) presented in [13].

The activation energies of electrical conduction  $E_A$  of the  $\text{LnBaCuFeO}_{5+\delta}$  ferrocuprates, calculated from the dependences  $\ln(\rho/T) = f(1/T)$ , are listed in the table and presented in Fig. 2. We readily see that the value of  $E_A$  of the samples, 0.06–0.30 eV, falls off practically linearly with increasing content of excess oxygen in a sample. Correlation of the concentration dependences of the electrophysical properties of ferrocuprates, namely,  $\rho_{400} = f(\delta)$ ,  $S_{400} = f(\delta)$ , and  $E_A = f(\delta)$  (Fig. 2), suggests that the values of  $\rho$  and  $S$  of the ceramic increase with a decrease in both  $\delta$  and the lanthanide radius  $R_{\text{Ln}^{3+}}$ , while the activation energy of electric transport in the layered lanthanum (praseodymium)–barium ferrocuprates is determined primarily by the content of excess oxygen in the  $\text{LnO}_\delta$  layers.

#### 4. CONCLUSIONS

We have studied the effect of oxygen nonstoichiometry on crystal structure parameters, thermal expansion, electrical resistivity, and thermopower of lanthanum–barium and praseodymium–barium perovskite ferrocuprates  $\text{LaBaCuFeO}_{5+\delta}$  ( $0.02 \leq \delta \leq 0.48$ ) and  $\text{PrBaCuFeO}_{5+\delta}$  ( $0 \leq \delta \leq 0.28$ ).

It has been shown that, for  $0 < \delta < 0.25$  ( $0 < \Theta < 1/4$ ), the unit cell size of the ferrocuprates decreases and their linear thermal expansion coefficient increases linearly, whereas for  $0.25 < \delta < 0.50$  ( $1/4 < \Theta < 1/2$ ), structural characteristics of the  $\text{LnBaCuFeO}_{5+\delta}$  phases only weakly depend on their oxygen nonstoichiometry  $\delta$ .

The decrease in the oxygen content in the sample gives rise to an increase in the energy of metal–oxygen interaction in the Cu–O–Fe chains and its decrease in the  $\text{Cu(Fe)O}_2$  layers of crystal structure of the layered perovskite ferrocuprates.

The  $\text{LnBaCuFeO}_{5+\delta}$  phases ( $\text{Ln} = \text{La, Pr}$ ) are  $p$ -type semiconductors whose electrical resistivity and thermopower decrease with increasing oxygen content in a

sample and the radius of the  $\text{Ln}^{3+}$  cation, while the activation energy of electric transport depends on the oxygen nonstoichiometry of a sample  $\delta$  only, with the dependence  $E_A = f(\delta)$  being very nearly linear.

#### ACKNOWLEDGMENTS

This study was supported by the State Coordinated Research Program “Crystal and Molecular Structures” (project no. 33) and the Belarussian Republican Foundation for Fundamental Research (projects no. X03M-049).

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*Translated by G. Skrebtsov*