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# Structure and Electrical and Transport Properties of Cation-Deficient Samples of Perovskite Ferrocuprates $R\text{BaCuFeO}_{5+\delta}$ ( $R = \text{Y, La}$ )

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**Abstract**—The structure, thermal expansion, and electrical properties of cation-deficient ferrocuprates  $R\text{BaCuFeO}_{5+\delta}$  ( $R = \text{Y, La}$ ), which are  $p$ -type semiconductors, are investigated. The linear thermal expansion coefficient of the yttrium–barium ferrocuprate decreases upon formation of vacancies in the  $A$  sublattice ( $\text{Y, Ba}$ ), while the unit cell parameters remain practically unchanged upon the formation of vacancies in different sublattices ( $\text{Y, Ba, Cu/Fe}$ ) of the crystal structure. From analyzing the results of the thermopower measurements, it is assumed that the  $\text{YBaCuFeO}_{5+\delta}$  ferrocuprate is actually a “nanocomposite” consisting of nanoregions of the  $\text{Y}_2\text{Cu}_2\text{O}_5$  and  $\text{BaFeO}_{3-\delta}$  phases. The lanthanum deficiency brings about an increase in the  $\text{LaBaCuFeO}_{5+\delta}$  unit cell while leaving very nearly unaffected its linear thermal expansion coefficient and electrical properties. The formation of cation vacancies in extended  $[\text{Ba}(\text{Cu,Fe})_2\text{O}_5]$  blocks of the  $\text{LaBaCuFeO}_{5+\delta}$  phase gives rise to tetragonal distortion of its cubic structure, a decrease in the linear thermal expansion coefficient, and an increase in the electrical resistivity of the samples, the latter resulting primarily from an increase in the carrier transport energy in  $(\text{Cu,Fe})\text{O}_2$  layers of  $\text{LaBaCuFeO}_{5+\delta}$ .

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## 1. INTRODUCTION

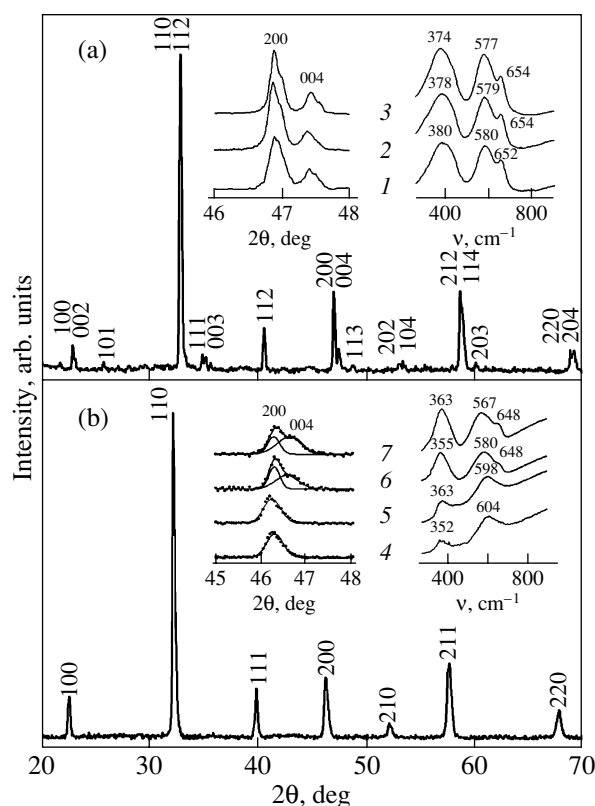
We have been recently witnessing a surge of research activities in the field of layered perovskite oxides, which include superconducting cuprates  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $R = \text{Y, rare-earth element}$ ) [1], magnetoresistive manganites  $R\text{BaMn}_2\text{O}_{6-g}$  [2], and cobaltites  $R\text{BaCo}_2\text{O}_{5+\delta}$  [3], as well as  $R\text{BaCuFeO}_{5+\delta}$  ferrocuprates, including the yttrium–barium ferrocuprate first described in [4].

The structure of the tetragonal ferrocuprate  $\text{YBaCuFeO}_{5+\delta}$  is formed by double  $(\text{Cu,Fe})_2\text{O}_5$  layers of vertex-shared  $\text{CuO}_5$  and  $\text{FeO}_5$  pyramids which are oriented perpendicular to the  $c$  axis; the  $\text{Ba}^{2+}$  ions are located inside the double layers, and the  $\text{Y}^{3+}$  ions, between them. The doubling of the perovskite unit cell is the result of the  $\text{Ba}^{2+}$  and  $\text{Y}^{3+}$  cation ordering along the  $c$  axis [4]. Because of the  $\text{La}^{3+}$  and  $\text{Ba}^{2+}$  cations, which are close in radius ( $R_{\text{La}^{3+}} = 1.32 \text{ \AA}$ ,  $R_{\text{Ba}^{2+}} = 1.60 \text{ \AA}$  for the coordination number of 12 [5]), being statistically distributed over the  $A$  positions of the  $\text{LaBaCuFeO}_{5+\delta}$  ferrocuprate, its structure is close to cubic [6, 7], with the perovskite unit cell parameters  $a_p = 3.9256(6)$  [6],  $3.92330(5)$  [7], and  $3.924 \text{ \AA}$  [8]; neutron diffraction measurements suggest that, at low temperatures ( $T = 15 \text{ K}$ ), the unit cell of  $\text{LaBaCuFeO}_{5+\delta}$  is orthorhombically distorted ( $a > b \approx$

$\sqrt{2}a_p$ ,  $c \approx 2a_p$ ,  $a = 5.5586(8) \text{ \AA}$ ,  $b = 5.5550(9) \text{ \AA}$ ,  $c = 7.8155(2) \text{ \AA}$ ) [7].

The  $R\text{BaCuFeO}_{5+\delta}$  layered ferrocuprates have an application potential as materials for chemical catalysts [9] or semiconducting gas sensors [10, 11]; the catalytic or sensor properties of these phases can be improved by partial heterovalent substitution of the cations in their composition. One of the ways in which one can modify the properties of perovskite-based functional materials consists in their self-doping, i.e., in creating cation nonstoichiometry [12, 13]. This method makes use of the ability of a perovskite ( $\text{ABO}_3$ ) to retain its crystal structure under formation of 5–10% cation vacancies  $A$  or  $B$  sublattice [12]. This method has an attractive aspect in that the properties of functional materials are tailored without an increase in the number of components entering into their composition, i.e., without making the system chemically more complex.

We report here on a study of the effect of  $A$  or  $B$  cation deficiency on the crystal structure, thermal expansion and electrical properties of layered oxygen-deficient yttrium–barium ( $\text{YBaCuFeO}_{5+\delta}$ ) and lanthanum–barium ( $\text{LaBaCuFeO}_{5+\delta}$ ) perovskite ferrocuprates.



**Fig. 1.** X-ray powder diffraction patterns of (a)  $\text{YBaCuFeO}_{5.04}$  and (b)  $\text{LaBaCuFeO}_{5.47}$ . The insets show the (200) and (004) reflections and IR absorption spectra of (1)  $\text{YBaCuFeO}_{5.04}$ , (2)  $\text{Y}_{0.95}\text{BaCuFeO}_{4.97}$ , (3)  $\text{YBa}_{0.95}\text{CuFeO}_{4.99}$ , (4)  $\text{LaBaCuFeO}_{5.47}$ , (5)  $\text{La}_{0.95}\text{BaCuFeO}_{5.43}$ , (6)  $\text{LaBa}_{0.95}\text{CuFeO}_{5.45}$ , and (7)  $\text{LaBaCu}_{0.95}\text{FeO}_{5.44}$ .

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Polycrystalline samples of  $R_{0.95}\text{BaCuFeO}_{5+\delta}$ ,  $R\text{Ba}_{0.95}\text{CuFeO}_{5+\delta}$ ,  $R\text{BaCu}_{0.95}\text{FeO}_{5+\delta}$ , and  $R\text{BaCuFe}_{0.95}\text{O}_{5+\delta}$  ( $R = \text{Y, La}$ ) were prepared by the ceramic technique. The  $\text{Y}_2\text{O}_3$  (It-OV),  $\text{La}_2\text{O}_3$  (reagent grade),  $\text{Fe}_2\text{O}_3$  (special-purity grade 9-2),  $\text{CuO}$  (special-purity grade 9-2) oxides and the  $\text{BaCO}_3$  (high-purity grade) carbonate taken in the required molar ratios were mixed in an agate mortar with a small addition of ethyl alcohol. The mixtures thus prepared were pelletized and calcined in air at 1173 K for 40 h. To study thermal expansion, electrical resistivity and thermopower, the powders were pressed at  $(1-3) \times 10^3 \text{ kg/cm}^2$  into pellets (9 mm in diameter and 3–5 mm thick) and  $5 \times 5 \times 30$ -mm bars, which were sintered subsequently at 1273 K for 5–10 h.

The x-ray powder diffraction analysis of the samples was performed on DRON-3 and Bruker D8 XRD diffractometers ( $\text{CuK}_\alpha$  radiation). The errors of unit cell parameter determination for the ferrocuprates were  $\Delta a = \pm 0.004 \text{ \AA}$ , and  $\Delta c = \pm 0.008 \text{ \AA}$ . IR absorption spectra of the ferrocuprates in the form of pelletized mix-

tures with KBr (reagent grade) were recorded on a Nexus Fourier spectrometer (ThermoNicolet) in the frequency region  $300-1500 \text{ cm}^{-1}$ . The vibration frequencies were measured to within  $\pm 2 \text{ cm}^{-1}$ . The content of excess oxygen  $\delta$  in the samples was determined iodometrically with an accuracy  $\Delta\delta = \pm 0.01$ .

The thermal expansion of the sintered ceramic samples was studied with a specially designed quartz dilatometer in air with a vertical quartz piston; the measurements were performed in the temperature range 300–1100 K in a dynamic mode with an average heating-cooling rate of 3–5 K/min. The linear thermal expansion coefficient  $\alpha$  of the samples was derived from linear parts of the  $\Delta l/l_0 = f(T)$  plots with an error  $\delta(\alpha) \leq \pm 5\%$ .

The electrical resistivity  $\rho$  of the ceramic was measured by the four-point probe dc technique in air at  $T = 300-1100 \text{ K}$  in a dynamic mode, with a heating and cooling rate of 3–5 K/min ( $\Delta\rho \leq 5\%$ ). The experimental values of the electrical resistivity of the ceramic,  $\rho_P$ , were reduced to zero porosity ( $\rho_{P=0}$ ) using the relation  $\rho_{P=0} = \rho_P(1 + P^{2/3})/(1 + P^{2/3} + P)$  [14]. The porosity of sintered samples was determined from the relation  $P = (d_{x\text{-ray}} - d_{\text{exp}})/d_{x\text{-ray}}$ , where  $d_{x\text{-ray}}$  and  $d_{\text{exp}}$  are the x-ray and the apparent densities derived from the mass and geometric size of a sample. The thermopower coefficient  $S$  of the ferrocuprates was determined with reference to silver in air, in the temperature interval 300–1000 K in a dynamic mode, with a heating and cooling rate of 3–5 K/min to within  $\delta(S) \leq \pm 10\%$ . The temperature gradient between the hot and cold ends of the sample was maintained at the 20–25-K level during the measurements. 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  $S = f(1/T)$ , respectively (the correlation coefficient  $R \geq 0.999$ ). Prior to measurements of the electrophysical properties, Ag electrodes were deposited on the sample surface by firing silver paste at 1073 K for 15 min. The chromel–alumel thermocouples were employed to measure the temperature.

## 3. RESULTS AND DISCUSSION

The yttrium–barium ferrocuprate  $\text{YBaCuFeO}_{5.04}$  synthesized by us had a tetragonal structure (space group  $P4/mmm$ , Fig. 1a) with the unit cell parameters  $a = 3.875 \text{ \AA}$  and  $c = 7.669 \text{ \AA}$ , which agree well with the literature data  $a = 3.867 \text{ \AA}$ ,  $c = 7.656 \text{ \AA}$  [4];  $a = 3.872 \text{ \AA}$ ,  $c = 7.681 \text{ \AA}$  [9];  $a = 3.8740(2)$ ,  $c = 7.6676(5) \text{ \AA}$  [15]; and  $a = 3.878$ ,  $c = 7.672 \text{ \AA}$  [16]. The samples of the cation-deficient yttrium–barium ferrocuprates were single-phase and had tetragonal structure corresponding to that of  $\text{YBaCuFeO}_{5+\delta}$  (Fig. 1a) with unit cell parameters  $a = 3.873-3.882 \text{ \AA}$  and  $c = 7.661-7.674 \text{ \AA}$  (Table 1), which coincides within experimental error with the unit cell dimensions of the  $\text{YBaCuFeO}_{5.04}$  phase. The oxygen content in the samples, as derived from iodometric

measurements, varied within  $4.96 \leq (5 + \delta) \leq 4.99$ , i.e., formation of cation vacancies in the yttrium–barium ferrocuprate was accompanied by formation of oxygen vacancies. The contents of  $\text{Cu}^{3+}$  in the cation-deficient samples and  $\text{YBaCuFeO}_{5.04}$  were equal ( $[\text{Cu}^{3+}] = 8$  at. %).

The lanthanum–barium ferrocuprate  $\text{LaBaCuFeO}_{5.47}$  had a cubic structure (space group  $Pm\bar{3}m$ , Fig. 1b) with the unit cell parameter  $a = 3.924$  Å, a figure fitting the data of [6–8]. Following the anneal at 1273 K, cation-deficient lanthanum–barium ferrocuprate samples were single-phase and had a perovskite structure. The oxygen content in these samples was close to that in the starting phase (Table 1), which suggests that formation of cation vacancies in the lanthanum–barium ferrocuprate is accompanied by an increase in the degree of copper oxidation (from +2.94 for  $\text{LaBaCuFeO}_{5.47}$  to  $\approx +3.00$  for the other samples). The  $\text{LaBaCuFeO}_{5.43}$  ferrocuprate, just as the  $\text{LaBaCuFeO}_{5.47}$  phase, was cubic (Fig. 1b), with formation of cation vacancies in the  $\text{LaO}_\delta$  layers bringing about the expected increase in the perovskite unit cell size  $a$  (Table 1).

The formation of cation vacancies in  $[\text{Ba}(\text{Cu},\text{Fe})_2\text{O}_5]$  blocks of the  $\text{LaBaCuFeO}_{5+\delta}$  ferrocuprate brought about tetragonal distortion of its cubic structure, which is evidenced by the more complicated shape of the x-ray diffraction patterns of the cation-deficient samples. For instance, the (200) singlet produced by the cubic phase in the angular interval  $2\theta = 46^\circ\text{--}47^\circ$  is replaced by a doublet (200) + (004), which is characteristic of layered tetragonal ferrocuprates (Fig. 1). An increase in the average degree of copper oxidation brought about compression of the perovskite unit cell of the samples in the direction perpendicular to the  $(\text{Cu},\text{Fe})\text{O}_2$  layers (Table 1).

The IR absorption spectra of yttrium-containing samples (Fig. 1a) reveal absorption bands peaking at frequencies of 374–380 ( $\nu_1$ ), 577–580 ( $\nu_2$ ), and 652–654  $\text{cm}^{-1}$  ( $\nu_3$ ) corresponding to the stretching ( $\nu_2$ ) and bending ( $\nu_1$ ) vibrations of the metal–oxygen bonds in the  $[\text{Cu}(\text{Fe})\text{O}_2]$  plane, as well as to the stretching vibrations of the apical oxygen in  $\text{Cu}\text{--}\text{O}\text{--}\text{Fe}$  bonds ( $\nu_3$ ) in the  $\text{YBaCuFeO}_{5+\delta}$  structure [17]. The closeness of the values of  $\nu_1\text{--}\nu_3$  for the cation-deficient samples and the  $\text{YBaCuFeO}_{5+\delta}$  phase permits a conclusion that the energy of the metal–oxygen bonds in the yttrium–barium layered ferrocuprate practically does not change in the formation of cation vacancies in its structure.

The IR absorption spectra of lanthanum-containing samples (Fig. 1b) exhibit two distinct bands with extrema at 350–360 ( $\nu_1$ ) and 567–604  $\text{cm}^{-1}$  ( $\nu_2$ ), which can be identified with the bending ( $\nu_1$ ) and stretching ( $\nu_2$ ) vibrations of the  $(\text{Cu},\text{Fe})\text{--}\text{O}\text{--}(\text{Cu},\text{Fe})$  bonds in their structure [8, 17]. The IR absorption spectra of the  $\text{LaBaCuFeO}_{5.47}$  and  $\text{La}_{0.95}\text{BaCuFeO}_{5.43}$  phases very nearly coincide, thus supporting the above conclusion

**Table 1.** Unit cell parameters of yttrium (lanthanum)–barium ferrocuprates

Sample	$a$ , Å	$c$ , Å	$V$ , Å <sup>3</sup>
$\text{YBaCuFeO}_{5.04}$	3.875	7.669	115.2
$\text{Y}_{0.95}\text{BaCuFeO}_{4.97}$	3.876	7.674	115.3
$\text{YBa}_{0.95}\text{CuFeO}_{4.99}$	3.875	7.666	115.1
$\text{YBaCu}_{0.95}\text{FeO}_{4.99}$	3.873	7.661	114.9
$\text{YBaCuFe}_{0.95}\text{O}_{4.96}$	3.874	7.666	115.1
$\text{LaBaCuFeO}_{5.47}$	3.924	–	60.42
$\text{La}_{0.95}\text{BaCuFeO}_{5.43}$	3.928	–	60.61
$\text{LaBa}_{0.95}\text{CuFeO}_{5.45}$	3.924	7.803	120.1
$\text{LaBaCu}_{0.95}\text{FeO}_{5.44}$	3.925	7.794	120.1
$\text{LaBaCuFe}_{0.95}\text{O}_{5.42}$	3.922	7.793	119.9

on a weak influence of defects on the lanthanum sublattice on the structure of the lanthanum–barium ferrocuprate, which was derived from the x-ray powder diffraction data. The position of the maximum in the absorption band  $\nu_2$  for the other ferrocuprates, namely,  $\text{LaBa}_{0.95}\text{CuFeO}_{5.45}$ ,  $\text{LaBaCu}_{0.95}\text{FeO}_{5.44}$ , and  $\text{LaBaCuFe}_{0.95}\text{O}_{5.42}$ , shifts successively toward lower frequencies as compared to the  $\text{LaBaCuFeO}_{5+\delta}$  phase. An additional absorption band peaking at 650  $\text{cm}^{-1}$  ( $\nu_3$ ) appears in the IR absorption spectra of these phases, whose intensity grows with decreasing oxygen content in a sample. Said otherwise, formation of cation vacancies in  $[\text{Ba}(\text{Cu},\text{Fe})_2\text{O}_5]$  blocks of  $\text{LaBaCuFeO}_{5+\delta}$  brings about distortion of the  $\text{BO}_n$  polyhedra ( $B = \text{Cu}, \text{Fe}$ ;  $n = 5, 6$ ) making up these blocks, i.e., compression of these polyhedra along the preferred direction. Thus, the results obtained in the x-ray powder diffraction and IR absorption spectroscopy measurements of the layered ferrocuprates correlate and lead one to the same conclusions.

The dependences  $\Delta l/l_0 = f(T)$  for the  $\text{YBaCu}_{0.95}\text{FeO}_{5+\delta}$  and  $\text{YBaCuFe}_{0.95}\text{O}_{5+\delta}$  samples measured in the 310–1100-K interval were found to be linear, and their linear thermal expansion coefficient was close to that of the  $\text{YBaCuFeO}_{5+\delta}$  phase (Table 2). The linear thermal expansion coefficient of the  $\text{Y}_{0.95}\text{BaCuFeO}_{5+\delta}$  and  $\text{YBa}_{0.95}\text{CuFeO}_{5+\delta}$  samples at  $T^* = 525$  K increased from  $\approx 1.0 \times 10^{-5} \text{ K}^{-1}$  to  $(1.3\text{--}1.5) \times 10^{-5} \text{ K}^{-1}$  (Table 2). The decrease in the linear thermal expansion coefficient of the yttrium–barium ferrocuprate upon formation of yttrium and barium vacancies (the A positions) correlates with the observation [18] that the linear thermal expansion coefficient of the lanthanum–strontium perovskite ferrocuprate decreases when cation vacancies form in its A sublattice.

The dependences  $\Delta l/l_0 = f(T)$  for the lanthanum–barium ferrocuprates exhibits an anomaly in the form of a kink at  $T^* = 630\text{--}725$  K (Table 3), which should be

**Table 2.** Linear thermal expansion coefficients  $\alpha$  and activation energies of electrical conduction  $E_A$  for cation-deficient samples of the yttrium–barium ferrocuprate

Sample	$\alpha \times 10^5, \text{K}^{-1}$		$T^*, \text{K}$	$E_A, \text{eV}$		$T^\#, \text{K}$
	300 K– $T^*$	$T^*$ –1100 K		300 K– $T^\#$	$T^\#$ –1100 K	
YBaCuFeO <sub>5+<math>\delta</math></sub>	1.43		–	0.24		–
Y <sub>0.95</sub> BaCuFeO <sub>5+<math>\delta</math></sub>	0.96	1.51	525	0.19	0.44	440
YBa <sub>0.95</sub> CuFeO <sub>5+<math>\delta</math></sub>	0.96	1.33	525	0.16	0.65	380
YBaCu <sub>0.95</sub> FeO <sub>5+<math>\delta</math></sub>	1.35		–	0.16	0.47	385
YBaCuFe <sub>0.95</sub> O <sub>5+<math>\delta</math></sub>	1.45		–	0.34		–

**Table 3.** Linear thermal expansion coefficients  $\alpha$  and activation energies of electrical transport  $E_A$ ,  $E_S$ , and  $E_m$  for cation-deficient samples of the lanthanum–barium ferrocuprate

Sample	$\alpha \times 10^5, \text{K}^{-1}$		$T^*, \text{K}$	$E_A, \text{eV}$	$E_S, \text{eV}$	$E_m, \text{eV}$
	300 K– $T^*$	$T^*$ –1100 K				
LaBaCuFeO <sub>5+<math>\delta</math></sub>	1.41	2.04	650	0.07	0.02	0.04
La <sub>0.95</sub> BaCuFeO <sub>5+<math>\delta</math></sub>	1.26	2.09	725	0.11	0.03	0.08
LaBa <sub>0.95</sub> CuFeO <sub>5+<math>\delta</math></sub>	1.40	1.92	720	0.17	0.02	0.15
LaBaCu <sub>0.95</sub> FeO <sub>5+<math>\delta</math></sub>	1.10	1.81	685	0.16	0.03	0.13
LaBaCuFe <sub>0.95</sub> O <sub>5+<math>\delta</math></sub>	1.06	1.68	630	0.17	0.03	0.14

assigned to rearrangement of their oxygen sublattice due to release of oxygen [8]. The value of  $T^*$  for *B* deficient samples (630–685 K) is close to  $T^*$  for LaBaCuFeO<sub>5+ $\delta$</sub>  (650 K), and for the *A* deficient ones it is shifted toward higher temperatures (720–725 K). The values of  $\alpha$  for  $T < T^*$  are smaller than those for  $T > T^*$ , because, in the latter case, formation of oxygen vacancies contributes additionally to expansion of LaBaCuFeO<sub>5+ $\delta$</sub> . The values of  $\alpha$  for cation-deficient lanthanum–barium ferrocuprates were smaller than those for LaBaCuFeO<sub>5+ $\delta$</sub>  (Table 3), which is stronger pronounced for  $T < T^*$  and correlates with the data reported in [18] according to which formation of cation vacancies in the structure of the La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3– $\delta$</sub>  perovskite brings about a decrease in its linear thermal expansion coefficient.

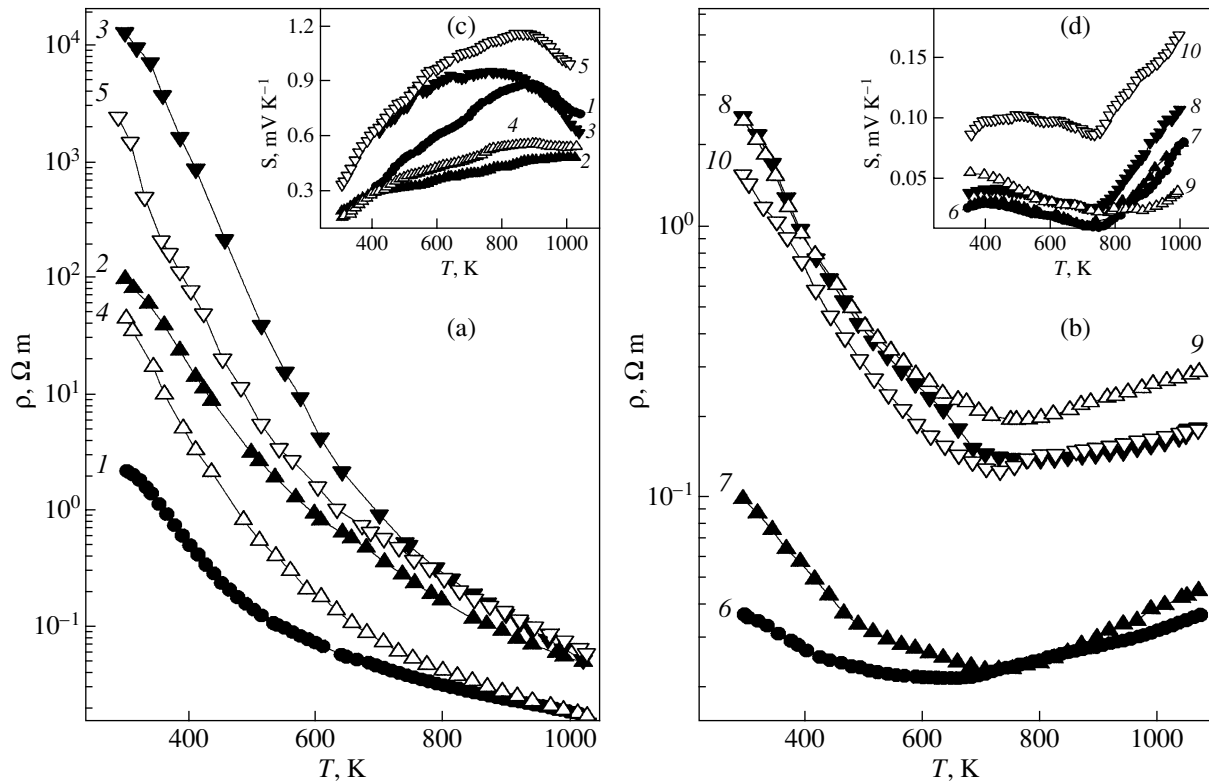
All the ferrocuprates studied were *p*-type semiconductors (Fig. 2) whose electrical resistivity increased because of the formation of cation vacancies, a predictable effect (Figs. 2a, 2b). The electrical resistivity of the lanthanum–barium ferrocuprates changed its pattern from the semiconducting ( $\partial\rho/\partial T < 0$ ) to metallic signature ( $\partial\rho/\partial T > 0$ ) (Fig. 2b), while the thermopower coefficient  $S$  started to grow sharply near 750 K (Fig. 2d), which should be assigned to thermal dissociation of these phases becoming active in air at  $T \approx 670$  K [8].

Table 2 lists the values of the apparent activation energy of electrical conduction  $E_A$  of the yttrium–barium ferrocuprates. As seen from Table 2, formation of cation vacancies in the YBaCuFeO<sub>5+ $\delta$</sub>  structure gives

rise to a growth of  $E_A$  of the ceramic (by a factor 2.0–2.5 for  $T^\# < T$ ); this suggests that charge transport in defective yttrium–barium ferrocuprates involves considerable energy for its initiation.

The variation in the cation composition of the yttrium–barium ferrocuprate affected strongly both its thermopower coefficient  $S$  and the shape of the dependence  $S = f(T)$  (Fig. 2c); interestingly, vacancy formation in the yttrium and copper positions (Y<sub>0.95</sub>BaCuFeO<sub>5+ $\delta$</sub>  and YBaCu<sub>0.95</sub>FeO<sub>5+ $\delta$</sub>  samples) and barium and iron positions (YBa<sub>0.95</sub>CuFeO<sub>5+ $\delta$</sub>  and YBaCuFe<sub>0.95</sub>O<sub>5+ $\delta$</sub>  samples) produced practically the same or similar effect on the thermopower of the samples. These observations can be explained if we assume that the YBaCuFeO<sub>5+ $\delta$</sub>  yttrium–barium ferrocuprate is essentially a nanocomposite made up of nanoregions of the Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> and BaFeO<sub>3– $\delta$</sub>  phases.

The electrical resistivities of the La<sub>0.95</sub>BaCuFeO<sub>5+ $\delta$</sub>  and LaBaCuFeO<sub>5+ $\delta$</sub>  phases were close in magnitude, particularly at elevated temperatures, whereas the values of  $\rho$  for the LaBa<sub>0.95</sub>CuFeO<sub>5+ $\delta$</sub> , LaBaCu<sub>0.95</sub>FeO<sub>5+ $\delta$</sub> , and LaBaCuFe<sub>0.95</sub>O<sub>5+ $\delta$</sub>  ferrocuprates were considerably higher and close in magnitude (Fig. 2b). As follows from our measurements, formation of cation defects (vacancies) in the conducting [Ba(Cu,Fe)<sub>2</sub>O<sub>5</sub>] blocks exerts the strongest (and practically the same) effect on the magnitude of  $\rho$  for the lanthanum–barium layered ferrocuprate. The values of the thermopower coefficient of the lanthanum–barium ferrocuprates were found to be close in magnitude, with the exception



**Fig. 2.** Temperature dependences of (a, b) the electrical resistivity and (c, d) the thermopower of the ceramics (1)  $\text{YBaCuFeO}_{5+\delta}$ , (2)  $\text{Y}_{0.95}\text{BaCuFeO}_{5+\delta}$ , (3)  $\text{YBa}_{0.95}\text{CuFeO}_{5+\delta}$ , (4)  $\text{YBaCu}_{0.95}\text{FeO}_{5+\delta}$ , (5)  $\text{YBaCuFe}_{0.95}\text{O}_{5+\delta}$ , (6)  $\text{LaBaCuFeO}_{5+\delta}$ , (7)  $\text{La}_{0.95}\text{BaCuFeO}_{5+\delta}$ , (8)  $\text{LaBa}_{0.95}\text{CuFeO}_{5+\delta}$ , (9)  $\text{LaBaCu}_{0.95}\text{FeO}_{5+\delta}$ , and (10)  $\text{LaBaCuFe}_{0.95}\text{O}_{5+\delta}$ .

of  $\text{LaBaCuFe}_{0.95}\text{O}_{5+\delta}$ , throughout the temperature interval covered (Fig. 2d). The comparatively large values of  $S$  of the iron-deficient lanthanum–barium ferrocuprate should be probably assigned to the maximum degree of imperfection of the oxygen sublattice (Table 1).

The activation energies of electrical conduction  $E_A$  of the cation-deficient lanthanum–barium ferrocuprates, as derived from the linear parts of the dependence  $\ln(\rho/T) = f(1/T)$  ( $T < 750$  K,  $\delta \approx \text{const}$ ), are listed in Table 3. Formation of cation vacancies in the structure of the lanthanum–barium ferrocuprate gives rise to growth of  $E_A$  by a factor of 1.5–2.5, from 0.07 eV for  $\text{LaBaCuFeO}_{5+\delta}$  to 0.17 eV for  $\text{LaBa}_{0.95}\text{CuFeO}_{5+\delta}$ . The activation energies of thermopower ( $E_S$ ) of the cation-deficient lanthanum–barium ferrocuprates were 0.02–0.03 eV, which is close to the value  $E_S = 0.02$  eV for the  $\text{LaBaCuFeO}_{5+\delta}$  starting phase (Table 3).

The studies of electric transport properties of the layered lanthanum–barium ferrocuprate within the small-radius polaron (SRP) model [19] permit one, in particular, from measurements of the electrical resistivity and thermopower, to derive the charge transport parameters, namely, the excitation energy of the SRP carrier ( $E_S$ ) and the SRP transport activation energy ( $E_m = E_A - E_S$ ). As seen from the data in Table 3, forma-

tion of cation defects (vacancies) in the  $\text{LaBaCuFeO}_{5+\delta}$  structure affects only weakly the excitation energy of carriers, thus increasing considerably (two- or three-fold) the activation energy of their transport, which is most pronounced in samples with defects in the conducting  $[\text{Ba}(\text{Cu},\text{Fe})_2\text{O}_5]$  blocks of the layered lanthanum–barium ferrocuprate structure.

#### 4. CONCLUSIONS

We have studied the effect of cation deficiency on the structure and properties of layered yttrium–barium  $\text{YBaCuFeO}_{5+\delta}$  and lanthanum–barium  $\text{LaBaCuFeO}_{5+\delta}$  ferrocuprates. It has been established that the unit cell parameters of the  $\text{YBaCuFeO}_{5+\delta}$  phase practically do not change, the linear thermal expansion coefficient decreases substantially when vacancies arise in the A sublattice, and the electrical resistivity grows when cation vacancies are formed in different positions of its structure. Thermopower measurements suggest that the  $\text{YBaCuFeO}_{5+\delta}$  ferrocuprate is nanostructured and consists of nanoregions of the  $\text{Y}_2\text{Cu}_2\text{O}_5$  yttrium cuprate and  $\text{BaFeO}_{3-\delta}$  barium ferrite.

It has been found that lanthanum deficiency in a sample gives rise to an increase in the unit cell size in  $\text{LaBaCuFeO}_{5+\delta}$  and only insignificantly influences its

thermal expansion and electrical properties. Cation vacancy formation in the  $[\text{Ba}(\text{Cu},\text{Fe})_2\text{O}_5]$  blocks of the lanthanum–barium ferrocuprate brings about tetragonal distortion of its cubic structure, a decrease in the linear thermal expansion coefficient of the samples and an increase in their electrical resistivity. It has been shown that the decrease in the electrical conductivity of the samples originates from increasing carrier transport energy in the  $(\text{Cu},\text{Fe})\text{O}_2$  layers of the lanthanum–barium ferrocuprate  $\text{LaBaCuFeO}_{5+\delta}$ .

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#### REFERENCES

1. Yu. D. Tret'yakov and E. A. Gudilin, *Usp. Khim.* **69**, 3 (2000).
2. I. O. Troyanchuk, S. V. Trukhanov, and G. Szymczak, *Kristallografiya* **47** (4), 716 (2002) [*Crystallogr. Rep.* **47** (4), 658 (2002)].
3. S. Roy, I. S. Dubenko, M. Khan, E. M. Condon, J. Craig, and N. Ali, *Phys. Rev. B: Condens. Matter* **71**, 024419 (2005).
4. L. Er-Rakho, C. Michel, Ph. LaCorre, and B. Raveau, *J. Solid State Chem.* **73**, 531 (1988).
5. R. D. Shannon, and C. T. Prewitt, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **25**, 946 (1969).
6. L. Er-Rakho, C. Michel, F. Studer, and B. Raveau, *J. Phys. Chem. Solids* **48**, 377 (1987).
7. H. Rando, W. A. Ortiz, F. M. Araujo-Moreira, L. Suescun, B. Toby, E. Quagliata, C. A. Negreira, K. Prassides, and A. W. Mombro, *Physica C (Amsterdam)* **313**, 105 (1999).
8. A. I. Klyndyuk and E. A. Chizhova, *Neorg. Mater.* **42** (5), 611 (2006) [*Inorg. Mater.* **42** (5), 550 (2006)].
9. T. Rentschler, *Thermochim. Acta* **284**, 367 (1996).
10. A. Klyndziuk, G. Petrov, S. Kurhan, Ye. Chizhova, A. Chabatar, L. Kunitski, and L. Bashkirov, *Chem. Sens.* **20** (Suppl. B), 854 (2004).
11. A. I. Klyndyuk, E. A. Chizhova, and I. A. Taratyn, *Tr. Belaruss. Gos. Tekh. Univ., Ser. III: Khim. Tekhnol. Neorg. Veshchestv* **XIII**, 54 (2005).
12. T. N. Kol'tsova and G. D. Nipan, *Zh. Neorg. Khim.* **41** (12), 1944 (1996) [*Russ. J. Inorg. Chem.* **41** (12), 1844 (1996)].
13. I. O. Troyanchuk, *Fiz. Tverd. Tela (St. Petersburg)* **48** (5), 653 (2006) [*Phys. Solid State* **48** (5), 898 (2006)].
14. A. K. Tripathi and H. B. Lal, *Mater. Res. Bull.* **15**, 233 (1980).
15. M. J. Ruiz-Aragon, E. Maron, U. Amador, J. L. Martinez, N. H. Andersen, and H. Ehrenberg, *Phys. Rev. B: Condens. Matter* **58**, 6291 (1998).
16. J. Linden, M. Kochi, K. Lehmus, T. Pietari, M. Karpinen, and H. Yamauchi, *J. Solid State Chem.* **166**, 118 (2002).
17. Y. K. Atanassova, V. N. Popov, G. G. Bogachev, M. N. Iliev, C. Mitros, V. Psycharis, and M. Pissas, *Phys. Rev. B: Condens. Matter* **47**, 15201 (1993).
18. G. Ch. Kostoglouidis and Ch. Ftikos, *Solid State Ionics* **126**, 143 (1999).
19. N. Mott and E. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford University Press, Oxford, 1979; Mir, Moscow, 1982).

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