Crystal Structure and Electrotransport Properties of LaBa$_{1-x}$M$_x$CuFeO$_{5+\delta}$ (M – Sr, Ca, Mg) Solid Solutions at High Temperatures

Andrey I. Klyndyuk

Belarusian State Technological University, Sverdlova str., 13A, 220006, Minsk, Belarus,

ABSTRACT

The LaBa$_{1-x}$M$_x$CuFeO$_{5+\delta}$ (M – Sr, Ca, Mg) solid solutions had been prepared, their unit cell parameters had been determined, and their electrical conductivity and thermo–EMF in air at 300–1100 K had been measured. It has been found that LaBa$_{1-x}$M$_x$CuFeO$_{5+\delta}$ oxides have cubic structure and are the p–type semiconductors. On the $a_p = f(x)$, $\delta = f(x)$, $E_m = f(x)$, $E_p = f(x)$ dependences for LaBa$_{1-x}$Sr$_x$CuFeO$_{5+\delta}$ solid solutions at x = 0,25 the anomalies had been detected. These anomalies are connected, probably, with the ordering of La^{3+}, Ba^{2+} and Sr^{2+} cations in the LaBa$_{1-x}$Sr$_x$CuFeO$_{5+\delta}$ structure leading to the formation of the new chemical compound LaBa$_{3/4}$Sr$_{1/4}$CuFeO$_{5+\delta}$

Keywords: Layered perovskites, solid solutions, crystal structure, oxygen nonstoichiometry, electrical conductivity, thermo-EMF.

INTRODUCTION

Different functional materials belong to the perovskite family, including high-temperature superconductors (HTSC), magnetoresistive manganites, ferroelectrics, thermoelectrics, catalysts, chemical gas sensors etc. [1–6].

To obtain the functional materials with improved characteristics the perovskite-like oxides can be modified using charge control (heterovalent ionic substitution, creation of ionic nonstoichiometry [1–4,7]), spin control (isovalent cationic substitution in the perovskite structure by cations with other electronic configuration [1–3,8,9]) or size control (intersubstitution of cations of rare-earth (REE) or alkaline-earth elements (AEE) in the structure of perovskite or perovskite-like oxides [1,4,10,11]).

Change of perovskite oxides composition by means of charge or spin control let us effectively and strongly regulate their electrical and magnetic properties [1–3,7–9], but variation of their composition at size control (by means of «chemical pressure») can be considered as method of «soft» regulation of properties of functional materials [1,4,10,11]. Herewith optimization of parameters of materials is often reached at small substitutions degree of one AEE by another which demonstrates the complex character of interrelation of perovskite properties and size of cations in their structure. So, in work [12] is shown that the maximal value of critical current density (J_C) in

$YBa_{2-x}Sr_xCu_3O_{7-\delta}$ HTSC reaches at $x = 0,2$ and lower critical field (H_{C_1}) at $x = 0,4$. Authors of [13] found that partial substitution of Ba^{2+} by Sr^{2+} led to the increasing of corrosive stability of ceramics to the H_2O, and the maximal stability possesses the composition of $YBa_{1,8}Sr_{0,2}Cu_3O_{6,882}$.

Layered ferrocuprates $LnBaCuFeO_{5+\delta}$ ($Ln \neq La$) have tetragonally distorted ($a = b = a_p$, $c \approx 2\,a_p$) perovskite structure [14,15]) which consists of double layers of CuO_5 and FeO_5 pyramides connected by caps; Ba^{2+} ions are within these double layers, but Ln^{3+} ions are placed between them. The doubling of perovskite unit cell takes place due to the ordering of Ba^{2+} and Ln^{3+} ions along c axis. The structure of $LaBaCuFeO_{5+\delta}$ is quasicubic [16,17] due to the statistical representation of La^{3+} and Ba^{2+} cations which sizes are closed [18] in the structure of this phase. Ferrocuprates can be used as catalysts [19] or semiconducting gas sensors [20] which stipulates scientific and practical interest to these compounds.

In this work the influence of partial substitution of Ba^{2+} by M^{2+} (M – Sr, Ca, Mg) on the crystal structure and electrical properties of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ (M = Sr, Ca, Mg) solid solutions is studied.

MATERIALS AND METHODS

The powders of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ (M = Sr, Ca, Mg) solid solutions by means of ceramic method from $La(NO_3)_3 \cdot 6\,H_2O$ (chemically pure grade), $BaCO_3$ (pure grade), $SrCO_3$ (chemically pure grade), $CaCO_3$ (pure grade), $MgCO_3$ (chemically pure grade), Fe_2O_3 (ultra pure grade) and CuO (ultra pure grade) in air within 1173–1273 K during 40–80 h were prepared [21]. For measurements of electrical conductivity and thermo-EMF of the samples from the powders the pellets having diameter of 9 mm and thickness of 3–5 mm and bars having dimensions 5×5×30 mm at pressure of 1–3 MPa were presse and then sintered in air at 1273 K during 5–10 h.

X-ray diffraction (XRD) analysis of the samples on diffractometer DRON–3 (CuK_α–radiation) was performed. Accuracy of determination of perovskite cell dimension was $\Delta a_p = \pm 0,004$ Å. The oxygen nonstoichiometry index of the samples (δ) was determined using iodometry ($\Delta\delta = \pm 0,01$). Before measurements of electrical properties of the samples on their surface the Ag–electrodes were formed by means of burning of silver paste at 1073 K during 15 min. Electrical conductivity (σ) of ceramics using 4–probe method (direct current) in air at $T = 300$–1100 K in dynamical mode with heating and cooling rate of 3–5 K·min^{-1} ($\delta(\sigma) < 5\,\%$) was measured. The values of electrical conductivity of ceramics studied on the zero porosity using methodics [22,23] were recalculated. The coefficient of thermo-EMF (S) of the samples was determined in air within 300–1000 K in dynamical mode at heating at cooling rate of 3–5 K·min^{-1} ($\delta(S) < \pm 10\,\%$) at temperature gradient between hot and cool ends of the samples about 20–25 K.

RESULTS AND DISCUSSIONS

The phase of $LaBaCuFeO_{5.47}$ was cubic and its reflexes were indexed using $Pm3m$ space group with parameter $a = 3,924$ Å which is close to the data given in [16,17,21]. The samples of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ solid solutions after final stage of annealing at 1273 K were monophase, within XRD accuracy, and were also cubic with unit cell parameter $a_p = 3,885$–3,921 Å (see table). The size of unit cell of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases decreases at increasing of substitution degree of barium of other AEE and at decreasing of ionic radii of this AEE.

Nonlinearity of $a_p = f(x)$ dependences for $LaBa_{1-x}M_xCuFeO_{5+\delta}$ (Me = Sr, Mg) phases (table, fig. 1,a) is, probably, due to the decreasing of oxygen content in the samples at increasing of substitution

degree of Ba^{2+} by Sr^{2+}, Mg^{2+}. Effect δ on the value of unit cell of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases is in a good accordance with the data [25] and is proved by the fact, that a_p parameter of solid solutions with nearly equal substitution degree of barium by other AEE changes contrary to the content of oxygen in them (δ) (table). Existence of extrema at $x = 0,25$ on the dependences of $a_p = f(x)$, $\delta = f(x)$ (fig. 1, *a*, *b*) for the $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$ phases can be explained by the ordering of La^{3+}, Ba^{2+} and Sr^{2+} ions in their structure with formation of the new compound of $LaBa_{3/4}Sr_{1/4}CuFeO_{5.48}$ [26].

Table
Perovskite unit cell parameter (a_p) and values of activation energy of electrical transfer (E_p, E_m) of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ (M = Sr, Ca, Mg) solid solutions

Образец	a_p, Å	E_p, eV	E_m, eV
$LaBaCuFeO_{5,47}$	3,924	0,020	0,045
$LaBa_{0,95}Sr_{0,05}CuFeO_{5,45}$	3,921	0,029	0,052
$LaBa_{0,875}Sr_{0,125}CuFeO_{5,42}$	3,918	0,034	0,039
$LaBa_{0,8}Sr_{0,2}CuFeO_{5,45}$	3,912	0,038	0,033
$LaBa_{0,75}Sr_{0,25}CuFeO_{5,48}$	3,889	0,023	0,077
$LaBa_{0,7}Sr_{0,3}CuFeO_{5,42}$	3,895	0,035	0,024
$LaBa_{0,625}Sr_{0,375}CuFeO_{5,43}$	3,898	0,035	0,084
$LaBa_{0,55}Sr_{0,45}CuFeO_{5,37}$	3,885	0,022	0,035
$LaBa_{0,5}Ca_{0,5}CuFeO_{5,25}$	3,908	0,024	0,146
$LaBa_{0,75}Mg_{0,25}CuFeO_{5,31}$	3,914	0,037	0,080
$LaBa_{0,5}Mg_{0,5}CuFeO_{5,21}$	3,916	0,040	0,091

As can be seen from the fig. 2, the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ solid solutions are the *p*–type semiconductors which conductivity (σ) character changes from semiconducting ($\frac{\partial\sigma}{\partial T} > 0$) to metallic ($\frac{\partial\sigma}{\partial T} < 0$), but thermo-EMF coefficient (S) begins increasing near 700 K due to the evolution of the weakly-bonded oxygen from the samples into environment (δ) [21]. Electrical conductivity values of the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ solid solutions, in the whole, decreased at
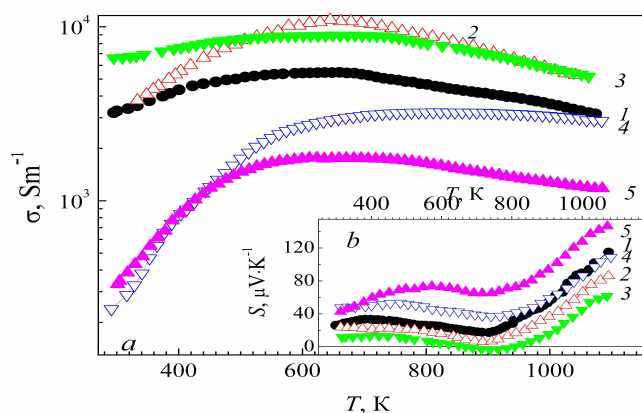
Fig. 2. Temperature dependences of electrical conductivity σ (*a*) and thermo-EMF S (*b*) of $LaBaCuFeO_{5+\delta}$ phase (*1*) and $LaBa_{1-x}M_xCuFeO_{5+\delta}$ solid solutions: M = Sr, x = 0,25 (*2*), 0,45 (*3*); M = Ca, x = 0,50 (*4*); M = Mg, x = 0,50 (*5*)

substitution of barium by calcium or magnesium and nonmonotonously changed at substitution of barium by strontium. The $\sigma = f(x)$ dependences for the $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$ phases at different temperatures were similar to the $\delta = f(x)$ (fig. 1, b) dependence, which proves the main role of oxygen sublattice state of ferrocuprates on their electrotransport properties.

The presence of the sharp maximum on the $\sigma = f(x)$ dependence for $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$ at $x = 0,25$ is additional reason to consider this composition as new individual compound $LaBa_{3/4}Sr_{1/4}CuFeO_{5+\delta}$ ($La_4Ba_3SrCu_4Fe_4O_{20+\gamma}$) [26]. The S value for the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases at room temperature was equal about $10–50\ \mu V \cdot K^{-1}$ (fig. 2, b) and, in the whole, increased at decreasing of oxygen content $(5+\delta)$ in the samples.

The charge transport in the layered ferrocuprates above room temperature usually described in the frame of model of small polarons hopping [22,25]. In this case the $\sigma = f(T)$ and $S = f(T)$ dependences described by equations (1):

$$\sigma = \sigma_0 \cdot T^{-1} \cdot \exp(-E_A / k \cdot T) ,$$
$$S = k/e \cdot (E_S / k \cdot T + B) , \qquad (1)$$

where $E_A = (E_p + E_m)$ and E_S are the activation energy of electrical conductivity and thermo-EMF respectively, but $E_p = E_S$ and E_m are the activation energy of charge carriers and activation energy of their transport [27].

As can be seen from the fig. 3,a,b, the $\ln(\sigma \cdot T) = f(1/T)$ and $S = f(1/T)$ dependences for the $La(Ba,M)CuFeO_{5+\delta}$ phases are linear within wide temperature interval (at $T < 700$ K, $\delta = const$), which proves the possibility to use the model of small polarons hopping at describing of their electrical properties. Values of E_p and E_m for the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ ferrocuprates are given in the
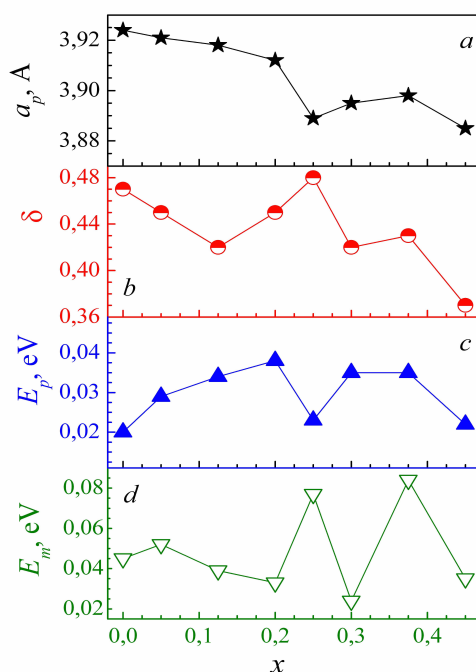
Fig. 1. Concentrational dependences of the perovskite unit cell parameter a_p (*a*), oxygen nonstoichiometry index δ (*b*), activation energy of the charge carriers E_p (*c*) and activation energy of their transfer E_m (*d*) for the phases of $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$
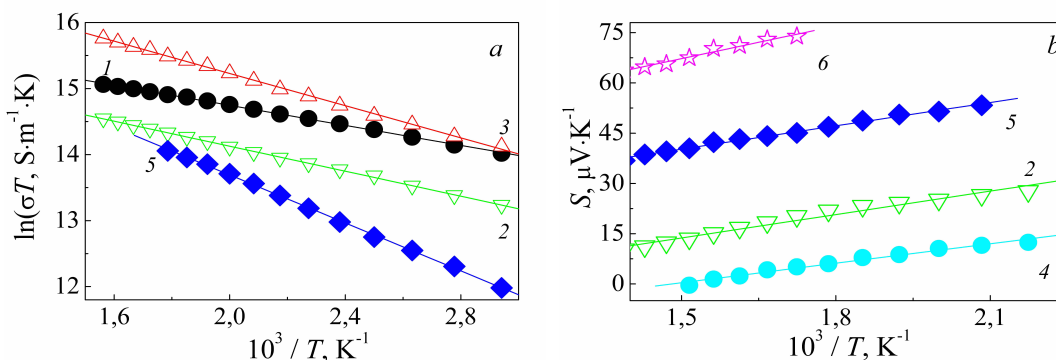
Fig. 3. Dependences of $\ln(\sigma \cdot T)$ (*a*) and thermo-EMF *S* (*b*) versus inverse temperature for the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases: *M* = Ba (*1*); *M* = Sr, *x* = 0,05 (*2*), 0,25 (*3*), 0,45 (*4*); *M* = Ca, *x* = 0,50 (*5*); *M* = Mg, *x* = 0,50 (*6*)

table and on the fig. 1,*c,d*. As it seen from the fig. 1, for the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases the $E_p = f(x)$ and $E_m = f(x)$ dependences are similar to the $a_p = f(x)$ and $\delta = f(x)$ dependences respectively. So, from the data obtained one can conclude that value of activation energy of charge carriers in $LaBa_{1-x}M_xCuFeO_{5+\delta}$ decreases at increasing of degree of overlapping of Cu(Fe) 3*d*– and O2*p*–orbitals, but activation energy of their transport in $(Cu,Fe)O_2$–layeres of these phases increases at decreasing of content of weakly-bonded oxygen in the LaO_δ layers.

The last conclusion is in contrary with the results of work [25] in which was shown that activation energy of electrical transport in $LaBaCuFeO_{5+\delta}$ increases at decreasing of oxygen content (5+δ) in it. One can eliminate this discrepancy by assuming that value of activation energy of transport of charge carriers in $LaBa_{1-x}M_xCuFeO_{5+\delta}$ solid solutions depends not only on value of oxygen nonstoichiometry of these phases but also on ordering degree of labile oxygen in the LaO_δ–layers of their crystal structure. In other words, extrema on the $E_m = f(x)$, $E_p = f(x)$ dependences (fig. 1,*c,d*) for the $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$ are due the same reasons that extrema on the $a_p = f(x)$, $\delta = f(x)$ dependences (fig. 1, *a*, *b*), namely, by ordering of cations of lanthanum and AEE (and, consequently, by ordering of oxygen vacancies) in the structure of these phases.

Thermo-EMF coefficient and electrical conductivity of some *p*-type semiconductors are binded with equation (2):

$$S = const - A \cdot \ln\sigma, \qquad (2)$$

where $A = \dfrac{k}{e}$ [27,28]. As it seen from the fig. 4, dependences of $S = f(\ln\sigma)$ for $LaBa_{1-x}M_xCuFeO_{5+\delta}$ ferrocuprates are linear, but value of *A* coefficient for the samples studied is equal only 30–33 $\mu V \cdot K^{-1}$, which is lower than theoretical value ($A = 86,17$ $\mu V \cdot K^{-1}$).

These low value of *A* in equation (2) for the layered ferrocuprates of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ are not unique; so, earlier for the layered cuprates of $(Nd_{2/3}Ce_{1/3})_4(Ba_{2/3}Nd_{1/3})_4Cu_6O_{16+x}$ [28] and $YBa_2Cu_3O_{7-\delta}$ [29–30] were obtained values $A = (43–44)$ $\mu V \cdot K^{-1}$, which, taking into account accuracy of experiment, is close to the values of *A*, which was found by us for the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases. To explain the obtained results, authors of [28] presumed that in cuprates of $(Nd_{2/3}Ce_{1/3})_4(Ba_{2/3}Nd_{1/3})_4Cu_6O_{16+x}$ and $YBa_2Cu_3O_{7-\delta}$ at high temperatures the charge carriers are bipolarons. Taking into account the structural

closeness of layered cuprates of $YBa_2Cu_3O_{7-\delta}$ type and ferrocuprates, one can presume, that in the latter electrical transport takes place by means of thermally activated transfer of bipolarons.
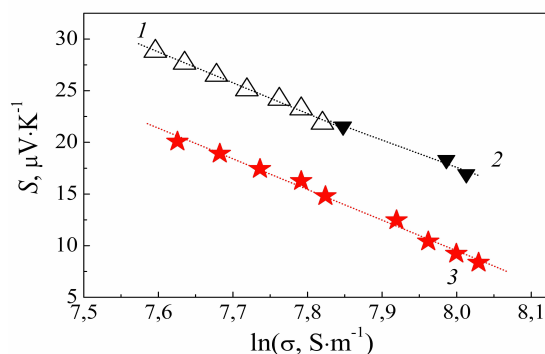
Fig. 4. Dependences of thermo-EMF S versus $\ln\sigma$ for the $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$
ferrocuprates: $x = 0,05$ (*1*), $0,125$ (*2*), $0,375$ (*3*)

CONCLUSION

In this work using ceramic method the $LaBa_{1-x}M_xCuFeO_{5+\delta}$ (M – Sr, Ca, Mg) ferrocuprates solid solutions are synthesized, their crystal structure and electrical properties are studied. It is found that $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases have cubic structure and are p–type semiconductors; the activation energy of electrical transport process in these oxides are determined. On the concentrational dependences of parameter of perovskite unit cel, oxygen nonstoichiometry index and parameters of electrical transport of $LaBa_{1-x}Sr_xCuFeO_{5+\delta}$ phases at $x = 0,25$ the anomalies are observed, which are connected with ordering of La^{3+}, Ba^{2+} and Sr^{2+} cations in their structure with formation of the new chemical compound of $LaBa_{3/4}Sr_{1/4}CuFeO_{5+\delta}$. On the base of complex analysis of electrical conductivity and thermo-EMF of $LaBa_{1-x}M_xCuFeO_{5+\delta}$ phases one can conclude that charge carriers in these phases are bipolarons.

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