Crystal structure, thermal and electrotransport properties of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ ($0.02 \leq x \leq 0.20$) solid solutions

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Abstract
Using solid-state reactions method, the solid solutions of layered oxygen-deficient perovskites NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ ($0.02 \leq x \leq 0.20$) were prepared; their crystal structure, thermal stability, thermal expansion, electrical conductivity and thermopower were studied. It was found that NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ phases crystallize in tetragonal syngony (space group $P4/mmm$) and are $p$-type semiconductors, whose conductivity character at high temperatures changed to the metallic one due to evolution from the samples of so-called weakly-bonded oxygen. Partial substitution of barium by strontium in NdBaFeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ leads to the small decreasing of unit cell parameters, thermal stability and thermopower of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ solid solutions, increasing of their electrical conductivity values and slightly affects their linear thermal expansion coefficient and activation energy of electrical transport values.

1. Introduction

Layered oxygen-deficient double perovskites of LnBaMeM'Me'O$_{5\pm\delta}$ (Ln = Y, rare-earth element (REE), Me, Me' = 3d-metal) have a complex of unique properties, including large values of electrical conductivity and thermopower, and contain in their structure labile oxygen, so they may be used as functional materials for different purposes: high-temperature oxide thermoelectrics, electrode materials for solid-oxide fuel cells (SOFC), materials for working elements of semiconducting chemical gas sensors, catalysts of hydrocarbons oxidation, etc. [1–6].

LnBaCo$_{0.5}$O$_{5\pm\delta}$ phases demonstrate high electrochemical performance in oxygen reduction reaction (ORR) [4–8], but values of their linear thermal expansion coefficient (TEC, $\alpha$) are too large (circa $(15–29)\times10^{-6}$ K$^{-1}$) [7–9]) in comparison to the TEC of commonly used in SOFC zirconia, ceria, or perovskite-like based solid electrolytes, which are equal to $(10–11)\times10^{-6}$ K$^{-1}$, $(12–13)\times10^{-6}$, and $(10–13)\times10^{-6}$ K$^{-1}$ respectively [10], which limits the practical implementation of these phases as cathode materials in SOFC.

Many studies [8,9,11–18] have demonstrated that partial substitution in LnBaCo$_{0.5}$O$_{5\pm\delta}$ of cobalt by other 3d-metal or barium by strontium essentially improves electrochemical performance of solid solutions forming at such substitution and reduces their TEC value. So, partial substitution of cobalt by iron in LnBaCo$_{0.5}$O$_{5\pm\delta}$ (Ln = Pr, Nd) leads to the reducing of TEC and polarization resistance of materials forming at this substitution and also improves their long-term stability at implementation as cathode materials of SOFC [12,13,15]. Doping of barium by strontium and of cobalt by copper or iron in YBaCo$_{0.5}$O$_{5\pm\delta}$ lead to the reducing of TEC of forming solid solutions, improving of their structural stability and electrochemical performance [9,16].

So, obtaining and studying of solid solutions, including complex substituted ones, on the basis of layered oxygen-deficient double perovskites is an actual task, having scientific and practical interest.

In this work we studied the effect of partial substitution of barium by strontium in NdBaFeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ on the crystal structure, thermal and electrotransport properties of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5\pm\delta}$ solid solutions as perspective cathode materials for intermediate-temperature SOFC.
2. Experimental

Ceramic samples of NdBa$_x$Sr$_{1-x}$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ ($x = 0.02, 0.05, 0.10,$ and $0.20$) solid solutions were prepared by means of solid-state reactions method from Nd$_2$O$_3$ (NO-L), BaCO$_3$ (pure), SrCO$_3$ (pure), Fe$_2$O$_3$ (super pure 2–4), Co$_3$O$_4$ (pure), and CuO (pure for analysis) in air at temperature of 1173 K within 40 h with consequent sintering during 9–18 h in air at temperatures of 1223–1273 K according to the methods, described in [19,20].

Identification of the samples and determination of their lattice constants was performed by means of X-ray diffraction analysis (XRD) (X-ray diffractometer Bruker D8 Advance XRD, Cu Kα-radiation). Apparent (effective) density of the sintered ceramics was investigated using DIL 402 PC quartz dilatometer in air within 1100 K temperature interval. IR-absorption spectra of the samples were recorded in the mixtures with KBr within 300–1100 cm$^{-1}$ (Thermo Nicolet Nexus Fourier-Transform Infrared Spectrometer). Apparent (effective) density of the sintered ceramics ($\rho_{\text{eff}}$) was determined from the mass and dimensions of the samples, and their porosity ($\Pi$) was calculated using Eq. (1):

$$\Pi = (1 - \rho_{\text{eff}}/\rho_{\text{XR}})100\%,$$

where $\rho_{\text{XR}}$ - X-ray density of the samples.

Thermal expansion of the sintered ceramics was investigated using DIL 402 PC quartz dilatometer in air at temperatures of 1100–1100 K [21]. Electrical conductivity and thermopower of NdBa$_x$Sr$_{1-x}$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ solid solutions were studied in air within 300–1100 K according to the methods, described in detail in [20]. Values of TEC and apparent activation energies of electrical conductivity ($E_a$) and thermopower ($E_S$) were calculated from the linear parts of

$$\Delta l/l_0 = f(T), \ln(\sigma T) = f(1/T), \text{ and } S = f(1/T) \text{ dependences, respectively.}$$

3. Results and Discussion

After final stage of the synthesis, all the samples of the NdBa$_x$Sr$_{1-x}$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ solid solutions were single phase, within XRD accuracy (Fig. 1a), and had a structure of tetragonally distorted double perovskite of YBaCuFeO$_5$ type ($a \approx 8\mu m = 2a_p$) [1], and their reflections were indexed in the framework of the $P4/mmm$ space group with unit cell parameters of $a = 3.903–3.914 \text{ Å}$ and $c = 7.707–7.715 \text{ Å}$. (Table 1).

As can be seen from the Table 1, increasing of the substitution degree of larger Ba$^{2+}$ ion by smaller Sr$^{2+}$ one (for C.N. = 12 $R(Ba^{2+}) = 1.60 \text{ Å}, R(Sr^{2+}) = 1.44 \text{ Å}$) leads to the decreasing of the size of the unit cell of the NdBa$_x$Sr$_{1-x}$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ phases. Porosity of the sintered ceramics enlarged at $x$ increasing (Table 1), which let us conclude that partial substitution of barium by strontium in NdBaFeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ slightly reduces sinterability of this perovskite.

On the IR-absorption spectra of the samples were detected some absorption bands with extrema at 351–353 cm$^{-1}$ ($\nu_1$), 467–470 cm$^{-1}$ ($\nu_2$), 576–582 cm$^{-1}$ ($\nu_3$), and 660–665 cm$^{-1}$ ($\nu_4$) (Fig. 1b), which were attributed, according to [23], to the stretching ($\nu_1$, $\nu_3$, and $\nu_4$) and bending vibrations ($\nu_2$) of the (Fe,Co,Cu)–O–(Fe,Co,Cu) bonds in the [(Fe,Co,Cu)O$_2$] basal planes ($\nu_1$, $\nu_3$), as well as stretching vibrations of apical oxygen of (Fe,Co,Cu)–O–(Fe,Co,Cu) bonds along $c$ axis ($\nu_4$) in the structure of NdBa$_x$Sr$_{1-x}$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ phases. At $x$ increasing the $\nu_3$ and $\nu_4$ bands shifted to the larger values.

![Fig. 1 X-ray powder diffractograms (a) and IR-absorption spectra (b) of NdBa$_x$Sr$_{1-x}$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+8}$ solid solutions: $x = 0.02$ (1); 0.05 (2); 0.10 (3); 0.20 (4)](image-url)
which pointed out to increasing of energy of metal-oxygen interactions in the crystal structure of these phases. Results of IR-absorption spectroscopy correlate with the XRD results, showing that increasing of substitution degree of barium by strontium in NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ solid solutions leads to the shrinking of their unit cell. According to the results of thermal analysis, near the room temperature all the samples were thermally stable, but, beginning from the temperatures of 623–663 K ($T_b$) the small mass loss (0.6–0.8%) was detected (Fig. 2a), which took place due to the evolution of the labile (weakly-bonded) oxygen from the samples into environment [24]. Values of $T_b$ decreased at $x$ increasing (Fig. 2c, Table 2), which indicated increasing of mobility of weakly-bonded oxygen in the structure of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ solid solutions at increasing of substitution degree of barium by strontium. On the temperature dependences of the relative elongation ($\Delta L/L_0$) of materials studied an anomaly in a kink near $T_k = 640–680$ K accompanied by the increase the TEC value was detected (Fig. 2b, Table 2), which took place due to the rearrangement of oxygen sublattice of the samples with consequent evolution of oxygen from them in air [24]. TEC values of ceramics in high-temperature region ($\alpha_{HT}$, $T > T_b$) were 15–24% larger than in the low-temperature one ($\alpha_{LT}$, $T < T_b$) (Table 3). Values of TEC of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ solid solutions in both temperature regions slightly varied but temperature of anomaly ($T_k$) essentially decreased (Fig. 2d) at $x$ increasing.

As can be seen from the data given in the Fig. 3a,b, materials studied are p-type ($S > 0$) semiconductors ($\partial S/\partial T > 0$). Their conductivity character at high temperatures ($T > T_{max}$) changed to the metallic one ($\partial S/\partial T < 0$), which was accompanied by the change of the sign of the $\partial S/\partial T$ derivative ($\partial S/\partial T < 0$ at $T < T_{min}$ and $\partial S/\partial T > 0$ at $T > T_{min}$). Observed anomalies of electrotransport properties of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ phases as well as described earlier anomaly of thermal expansion were due to the evolution of the weakly-bonded oxygen from the samples [24]. Note that temperatures of $S$ and $T$ anomalies, $T_{max}$ and $T_{min}$ respectively, at $x$ increasing shifted to the smaller temperatures (Fig. 3c,d, Table 2) like $T_b$ and $T_k$ temperatures. It is interesting that values of $T_b$, $T_k$, and $T_{min}$ temperatures were rather close to each other, but $T_{max}$ value was essentially larger (Table 2, Figs. 2c,d, 3c,d). Values of all critical temperatures ($T_{LT}$: $T_b$, $T_k$, $T_{max}$, and $T_{min}$) decrease at increasing of strontium content in the NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ solid solutions, hereby dependence $T_{LT} = f(x)$ was almost linear for $T_b$, underlinear for $T_k$ and $T_{min}$ and overlinear for $T_{max}$ increased despite of the

| Table 1 | The unit cell parameters (a, c, c/2a, V), effective density ($D_{eff}$) and porosity (I) of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ layered perovskites finally sintered at 1273 K |
|---------|---------------------------------|---------|-----------------|-----------------|--------|
| x       | a, Ǻ   | c, Ǻ   | c/2a, Ǻ       | V, Å$^3$       | $D_{eff}$, g/cm$^3$ | I, %  |
| 0.02    | 3.913(1) | 7.715(1) | 0.9860       | 118.11(1)       | 5.54   | 10   |
| 0.05    | 3.914(1) | 7.711(1) | 0.9851       | 118.11(1)       | 5.62   | 8    |
| 0.10    | 3.912(1) | 7.707(2) | 0.9853       | 117.91(1)       | 5.54   | 12   |
| 0.20    | 3.903(1) | 7.708(1) | 0.9876       | 117.51(1)       | 4.84   | 21   |

| Table 2 | Values of critical temperatures ($T_b$, $T_k$, $T_{max}$, and $T_{min}$) of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ ceramics |
|---------|---------------------------------|---------|---------|---------|---------|
| x       | $T_b$, K | $T_k$, K | $T_{max}$, K | $T_{min}$, K |
| 0.02    | 663       | 680       | 734       | 685       |
| 0.05    | 631       | 670       | 733       | 665       |
| 0.10    | 631       | 660       | 730       | 650       |
| 0.20    | 623       | 640       | 709       | 650       |

Fig. 2 Temperature dependences of mass loss (a) and relative elongation (b) of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{6+x}$ samples: $x = 0.02$ (1); 0.05 (2); 0.10 (3); 0.20 (4). Dilatometric curves are shifted from each other by 0.1% for the clarity of presentation. Insets shows concentration dependences of temperatures of mass loss onset (c) and kink of the $\Delta L/L_0 = f(T)$ dependences (d)
fact that porosity of the samples enlarged at increasing of strontium content (Table 1). So, our results show that partial substitution of barium by strontium in NdBaFeCoO$_{5+x}$ is an effective way to increase its electrical conductivity.

Layered oxygen-deficient double perovskites LnBaMe’Me°O$_{5+x}$ possess polaronic character of charge transfer [1,19,24], and temperature dependences of their electrical conductivity and thermopower obey Eqs. (2–3)

\[ \sigma = \frac{A}{T} \exp\left(-\frac{E_\sigma}{kT}\right), \]
\[ S = \left(\frac{k}{e}\right)\left(-\frac{E_m}{kT} + B\right), \]

where $E_\sigma = E_{\text{m}} + E_{\text{s}}$ and $E_m$ – activation energies of electrical conductivity and thermopower respectively, $E_{\text{s}}$ is also activation energy of charge carriers – polarons, and $E_m$ is energy of their transfer [25].

As can be seen from the data given in the Table 3, values of energies of activation of electrical transport, in the whole, slightly varied at varying strontium content in the samples. Comparing obtained in this work results with the data of [24], where for NdBaFeCo$_{0.5}$Cu$_{0.5}$O$_{5+x}$ layered perovskite was found that $E_\sigma = 0.245$ eV, $E_m = 0.048$ eV, and $E_m = 0.200$ eV, we can conclude that partial substitution of barium by strontium in this parent phase does not affect practically the value of activation energy of charge carriers – polarons, but results in essential reducing of transfer energy of charge carriers.

### Table 3 Values of TEC (\(\alpha\)) and apparent activation energy of electrical transport (\(E_{\text{m}}, E_{\text{s}}, E_{\text{m}}\)) for the sintered NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+x}$ ceramics

| \(x\) | \(10^5 \cdot \alpha_T\), K$^{-1}$ | \(10^3 \cdot \alpha_{\text{curr}}\), K$^{-1}$ | \(E_{\text{m}}, \text{eV}\) (350–700 K) | \(E_{\text{s}}, \text{eV}\) (400–650 K) | \(E_{\text{m}}, \text{eV}\) |
|------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 0.02 | 15.8                          | 19.3                          | 0.190                         | 0.047                         | 0.143                         |
| 0.05 | 16.3                          | 20.0                          | 0.203                         | 0.044                         | 0.159                         |
| 0.10 | 16.6                          | 19.1                          | 0.200                         | 0.054                         | 0.146                         |
| 0.20 | 16.4                          | 20.4                          | 0.167                         | 0.038                         | 0.129                         |

### 4. Conclusions

By means of solid-state reactions method the ceramic samples of NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+x}$ (\(x = 0.02, 0.05, 0.10, \) and 0.20) solid solutions were prepared, and their crystal structure and physico-chemical properties were studied. In was found that obtained materials had tetragonal structure, whose unit cell parameters slightly depend on their cationic composition, and are p-type semiconductors, whose conductivity character changes to the metallic one at high temperatures due to the evolution of oxygen from their crystal structure into environment. It was established that partial substitution of barium by strontium in NdBaFeCo$_{0.5}$Cu$_{0.5}$O$_{5+x}$ results in the increasing of electrical conductivity, reducing of energy activation of electrical conductivity, thermopower and thermal stability of solid solutions forming at this substitution NdBa$_{1-x}$Sr$_x$FeCo$_{0.5}$Cu$_{0.5}$O$_{5+x}$.

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