Physicochemical properties of the complex oxides in Sm-Ba-Me-Cu-O (Me = Fe, Co) systems

The present work was focused on the studies of crystal structure, oxygen non-stoichiometry, thermal expansion of SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$ and SmBaFe$_{2-x}$Cu$_x$O$_{6-\delta}$. Values of the oxygen content in complex oxides SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$ were determined over a wide temperature range in air using high temperature thermogravimetry and iodometric titration. Also, chemical stability with respect to Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ and Zr$_{0.85}$Y$_{0.15}$O$_{1.93}$ two common solid electrolyte materials used for SOFCs was evaluated.

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Introduction

Layered perovskites compounds A\textsuperscript{A'}B\textsubscript{2}O\textsubscript{6-\delta} wherein A is a lanthanide partially substituted by alkaline earth metal A', and B is 3d-atoms of metal (Ti, Cr, Mn, Fe, Co, Ni, Cu), are currently under scrutiny due to the successful combination of their physico-chemical properties\textsuperscript{1,3}.

Physico-chemical properties of the oxides formed in systems LnBaMe$_{2-x}$M$_{x}$O$_{6-\delta}$ are directly dependent on their crystal structure, the formation that can be significantly affected by an oxygen content. In this regard, information on the method of production, physico-chemical properties and stability of oxides A\textsuperscript{A'}B\textsubscript{2}O\textsubscript{6-\delta} under variation of the chemical composition and external thermodynamic conditions today is up-to-date. Therefore, the aim of this paper is to receive, and to analyze the crystallical structure and physico-chemical properties of complex oxide phases forming in the systems SmBaMe$_{2-x}$Cu$_x$O$_{6-\delta}$ (Me = Fe, Co).

The experimental part

Synthesis of the samples for the study was carried out on glycerol-nitrate technology. To prepare the samples samarium oxide Sm\textsubscript{2}O\textsubscript{3} and barium carbonate BaCO\textsubscript{3} were used as starting components; they were previously calcined to remove adsorbed moisture and gases, metallic cobalt, and iron oxalate FeC\textsubscript{2}O\textsubscript{4}×2H\textsubscript{2}O,
as well as nitric acid HNO₃ (qualification analytically pure), and glycerol (analytical grade qualification). Cobalt metal was prepared by reduction of corresponding oxides at 500–600°C in a stream of hydrogen. Thermogravimetric studies were carried out on the thermobalance STA 409 PC by Netzsch Gmbh., allowing to fixate changes in mass of the sample in dependence of the partial pressure of oxygen and temperature.

Measurements were carried out in static and dynamic modes. In the static mode, the sample (1–2 g), previously weighed in a platinum crucible, was heated to the temperature of the beginning of the measurements, it was held at this temperature for 10 hours to establish equilibrium between the solid and gas phases, and then the temperature was raised again and the constant of the weight of the sample was expected. Investigated temperature range of 300–1100 °C was held in the heating and cooling mode to 100 °C. In the dynamic mode the change in weight was continuously recorded during heating and cooling with a speed of 2 °C per min from room temperature to 1100 °C. The absolute value of oxygen deficiency was determined by direct reduction samples in hydrogen and iodometric titration methods. For this, the samples were slowly cooled to room temperature. Measurement of the linear coefficient of thermal expansion (LKTR) of ceramic materials is necessary to determine the possibility of obtaining of lasting contact in high-temperature electrochemical devices (such components are electrolytes, electrodes, electrical circuits, sealants, etc.).

Measurements of relative expansion of ceramic bars with increasing temperature were performed on dilatometer DIL402 C by Netzsch Gmbh in the temperature range 25–1100 °C with the heating and cooling rate of 5° per minute.

**Results and Discussion**

*Complex oxides SmBaCo₂₋ₓSₓO₆₋₅h:*

On glycerol-nitrate technology hard solutions were synthesized compositions SmBaCo₂₋ₓSₓO₆₋₅h where 0≤ₓ≤2. XRD revealed that single-phase complex oxides SmBaCo₂₋ₓSₓO₆₋₅h form in the composition range 0≤h≤1.2.

With minimal substitution of cobalt with copper (x = 0.1) a composite oxide is formed, which X-ray is satisfactorily described within the orthorhombic cell (pr. G. Pmmm).

Radiographs of the samples with a high content of copper (0.2≤h≤1.2) have been indexed within the tetragonal unit cell of the space group P4/mmm. In fig. 1 as an example of a complex oxide radiograph SmBaCo₁.₄S₀.₆O₅+₁₃ is represented. For all single-phase oxides unit cell parameters of the atomic coordinates were calculated. When the concentration of copper ions is increasing, an increase in parameters and volume of the unit cells of complex oxides SmBaCo₂₋ₓCuₓO₆₋₅h is observed. Such dependence can be explained in terms of size effects. Substitution of cobalt ions (r⁶+/r⁷⁺ = 0.75 / 0.67 Å, cn 6) with large size copper ions (r⁶+/r⁷⁺ = 0.87 / 0.68 Å, cn 6) [4] leads to a gradual increase in the bond lengths in the B-O, and as a consequence, increase in the size of the cell unit.

The phase composition of the samples SmBaCo₂₋ₓCuₓO₆₋₅h outside the homogeneity region is presented in Table 1.
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Table 1

<table>
<thead>
<tr>
<th>Nominal composition of the samples</th>
<th>Phase composition of the samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>SmBaCo$<em>{0.7}$Cu$</em>{1.3}$O$_{6-\delta}$</td>
<td>SmBaCo$<em>{0.8}$Cu$</em>{1.2}$O$_{6-\delta}$</td>
</tr>
<tr>
<td>SmBaCo$<em>{0.8}$Cu$</em>{1.2}$O$_{6-\delta}$</td>
<td>Sm$_3$Ba$_3$(Cu,Co)$<em>6$O$</em>{14-2\delta}$</td>
</tr>
<tr>
<td>SmBaCo$<em>{0.9}$Cu$</em>{1.1}$O$_{6-\delta}$</td>
<td>Sm$_3$Ba$_3$(Cu,Co)$<em>6$O$</em>{14-2\delta}$</td>
</tr>
<tr>
<td>SmBaCo$<em>{1.0}$Cu$</em>{1.0}$O$_{6-\delta}$</td>
<td>Sm$_3$Ba$_3$Cu$<em>6$O$</em>{14-2\delta}$</td>
</tr>
</tbody>
</table>

The compounds of nominal composition Sm$_3$Ba$_3$(Cu,Co)$_6$O$_{14-2\delta}$ are solid solutions Sm$_{3-x}$Sm$_x$(Cu,Co)$_6$O$_{7-4\delta}$. The crystal structure of these compounds has been described in terms of the tetragonal unit cell with triple option with $(a_p \times a_p \times 3a_p)$ space group $P4/mnm$.

Figure 2 shows the temperature dependence of the oxygen content of complex oxides SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$.

With the introduction of copper in cobalt sublattice a decrease in the value of the oxygen content is observed. This is due to the fact that the copper becomes totally or partially the electron acceptor (C$_{Cu}^-$) (EO$_{Cu}^-$ =1.75) and contributes to the oxygen vacancy ($V_O^-$) and/or electron holes.

Fig. 1 XRD pattern SmBaCo$_{1.4}$Cu$_{0.6}$O$_{6-\delta}$ treated by the method of Rietveld. Points are experimental data; solid top shedding is theoretical spectrum; solid bottom line is the difference between the experimental data and the theoretical curve.

Measuring of the relative increase in the size of the samples SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$ ($x=0; 0.4; 0.6$) was performed in air in the temperature range of $25-1100$ °C at a rate of heating and cooling $2^\circ$ per minute.

For this, the powders of the oxides were compressed under a pressure of 60 to 80 bar in the form of bars of size $2\times4\times20$ mm via a hydraulic press. The resulting bars were sintered in air at $1050-1200$°C for 14 hours and then slowly cooled to room temperature at a rate $100^\circ$ per hour.

The density of the sintered layered perovskites of samarium-barium SmBa-Co$_{2-x}$Cu$_x$O$_{6-\delta}$ is at least 90% of the calculated from the X-ray data.

Monotonic character of dilatometric dependencies for complex oxides SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$ indicates the absence of phase transitions. It has been established that the value of the CTE decreases with increasing concentration of copper in SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$.

Chemical compatibility of complex oxides SmBaCo$_{2-x}$Su$_x$O$_{6-\delta}$ ($x=0; 0.2; 0.4; 1.0$) with respect to the material of the electrolyte Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$ and Zr$_{0.85}$Y$_{0.15}$O$_{2-\delta}$ were studied by contact annealing at $900$°C, $1000$°C, $1050$°C, and $1100$°C in air.

Fig. 2. The dependence of the oxygen content of the temperature for SmBaCo$_{2-x}$Cu$_x$O$_{6-\delta}$.
XRD revealed that complex oxides SmBaCo$_{2-x}$Su$_x$O$_{5+δ}$, ex=0–0.4 do not react with a stabilized ceria oxide. And by annealing of the sample SmBaCoSuO$_{5-δ}$ with Ce$_{0.8}$Sm$_{0.2}$O$_{2-δ}$ at a temperature of 1000 °C, the diffraction patterns of the annealed mixtures present reflexes related to the cobaltites and cuprates samarium and barium.

The electrolyte based on zirconia at a temperature of 900 °C is reacted with all samples of SmBaCoSuO$_{5-δ}$. As the main impurity phase in the diffraction patterns of the annealed mixtures present reflexes related to BaZrO$_{3-δ}$.

Complex oxides SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$.

Solid solutions SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$, where 0.5≤x≤1.5 with 0.1 step were synthesized by the glycerol-nitrate technology. According to X-ray data, solid solutions SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$ with 0.7≤x≤1.3 are single-phase. Radiographs of oxides SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$ are satisfactorily described in terms of the tetragonal unit cell of the space group P4/mmm. Example radiographs of solid solution SmBaFe$_{1.2}$Su$_{0.8}$O$_{6-δ}$ treated by the method of full-profile Rietveld analysis are shown in Fig. 3.

For all single-phase oxides there were calculated unit cell parameters of the atomic coordinates. It was found that an increase in the concentration of copper in SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$ leads to a gradual increase in the parameters and the unit cell volume, which can be explained in terms of the size factor.

Conclusions

According to the results of the work, the following conclusions can be drawn:

1. The regions of homogeneous solid solution SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$ (0.7≤x≤1.3), SmBaCo$_{2-x}$Cu$_x$O$_{6-δ}$ (0≤x≤1.2) in the air are determined. The dependences of the unit cell parameters of the composition are drawn. It is shown that an increase in the degree of substitution of cobalt and iron in copper is a monotonic increase in the parameters and scope of the unit cells in oxides SmBaMe$_{2-x}$Cu$_x$O$_{6-δ}$;

2. It was found that the solid solutions SmBaCo$_{2-x}$Cu$_x$O$_{6-δ}$ in the range of compositions 0.1≤x≤0 crystallize in the orthorhombic cell (pr. G. Pmmm), and complex oxides SmBaFe$_{2-x}$Su$_x$O$_{6-δ}$ (0.7≤x≤1.3) and SmBaCo$_{2-x}$Cu$_x$O$_{6-δ}$ (0.2≤x≤1.2) in the tetragonal (sp. gr. P4/mmm);

3. High thermogravimetry and iodometric titration methods determined the values of oxygen content in the complex oxides formed in systems Sm-Ba-Co-Cu-O in a wide temperature range in air. It was found that the introduction of copper reduces the oxygen content in SmBaCo$_{2-x}$Me$_x$O$_{6-δ}$;

4. Coefficients of thermal expansion (CTE) of solid solutions SmBaCo$_{2-x}$Cu$_x$O$_{6-δ}$ (x=0; 0.4; 0.6) are calculated. It
is shown that the magnitude of the CTE decreases with increasing concentration of copper in the samples.

5. The chemical compatibility of complex oxides with the material of the solid electrolyte (Ce₀.₈Sm₀.₂O₂–δ and Zr₀.₈₅Y₀.₁₅O₂–δ) is researched at 900 ≤ T, °C ≤ 1100 and Pₒ₂=0.21 atm. It has been shown that solid solutions SmBaCo₂–ₓMeₓO₆–δ interact with stabilized zirconia at a temperature of 900 °C and do not interact with the stabilized cerium oxide to a temperature not higher than 900–1100°C depending on the concentration of copper ions.


