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Nonstoichiometry, thermal expansion and oxygen permeability of $SmBaCo_{2-x}Cu_xO_{6-\delta}$

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ABSTRACT

Phase relationship analysis in the pseudobinary $SmBaCo_{2-x}Cu_xO_{6-\delta}$ system at 1000–1100 °C in air revealed the existence of solid solutions with the layered perovskite and 123-type structures, formed within the ranges of $0 \leq x \leq 1.2$ and $1.5 \leq x \leq 2.0$, respectively. The substitution of Cu^{2+} for $Co^{3+/4+}$ was found to induce phase transition from orthorhombic (space group *Pmmm*) into tetragonal (*P4/mmm*) polymorph at $x > 0.1$, and to increase oxygen deficiency studied by thermogravimetry and iodometric titration. The electrical conductivity and thermal expansion of Cu-substituted cobaltites decrease on doping, while the steady-state oxygen permeability exhibits an opposite trend, in correlation with the oxygen content variations. The average thermal expansion coefficient of $SmBaCo_{1.4}Cu_{0.6}O_{6-\delta}$ ceramics, where the level of ionic transport is comparable to that in most permeable cobaltite-based mixed conductors, is 16.9×10^{-6} K^{-1} at 25–1000 °C in air. At the same time, copper additions increase chemical reactivity of the materials with doped ceria electrolytes.

1. Introduction

Among the variety of promising mixed-conducting materials that can be used for solid oxide fuel cell (SOFC) electrodes and oxygen separation membranes, a significant attention of researchers is centered on the family of multicomponent solid solutions based on the layered perovskites $AA'Me_2O_{6-\delta}$ where A = Pr–Ho or Y, partially substituted by alkaline earth metal cations A′, and Me corresponds to the 3d-transition metal cations, primarily of Mn, Fe, Co and Ni [1–8]. Their advantages that are important for potential electrochemical applications include substantially high oxygen diffusivity, fast interfacial exchange kinetics and predominant electronic conductivity. In particular, numerous studies have been focused on cobalt-containing $ABaCo_2O_{6-\delta}$ [2–9] which exhibits, in addition to attractive transport and electrochemical properties, lower thermal expansion coefficients (TECs) compared to their disordered perovskite analogs $(A,A')CoO_{3-\delta}$. However, the TECs of the layered cobaltites are still essentially higher than those of common solid oxide electrolytes, limiting thermomechanical compatibility of these materials. In order to decrease contributions to the lattice expansion associated with oxygen nonstoichiometry variations and electronic transitions, cobalt is often replaced with other transition metal cations such as iron and copper [7,9–14]. In many cases, the latter type of doping makes it also possible to improve sintering of ceramic materials and, thus, to reduce temperatures necessary for the electrode and membrane fabrication (e.g., [15,16]). Continuing our previous report [17] dealing with iron-doped $SmBaCo_{2-x}Fe_xO_{6-\delta}$, the present work was centered on the analysis of phase relationships in the pseudobinary $SmBaCo_{2-x}Cu_xO_{6-\delta}$ system and studies of the crystal structure, defect chemistry, thermal expansion and mixed conductivity of Cu-substituted cobaltites.

2. Experimental

Powders of $SmBaCo_{2-x}Cu_xO_{6-\delta}$ $(0 \leq x \leq 2)$ were prepared by the glycine–nitrate technique using high-purity Sm_2O_3, $BaCO_3$, CuO, metallic Co, nitric acid and glycine as starting materials. Final thermal treatment was performed at 1000–1100 °C in air for 120 h, employing several annealing steps (~20 h each) and intermediate grindings. The synthesized single-phase powders were uniaxially pressed into disks and then sintered at 1200–1300 °C in air. The density of the sintered ceramic samples was higher than 90% of the theoretical values, calculated from the X-ray diffraction (XRD) data. In order to achieve equilibrium with atmospheric oxygen at low temperatures, all the samples were cooled down to room temperature at a rate of ~100 °C/h. XRD analysis was carried out employing a DRON-6 diffractometer (CuK_α-radiation, angle range was $2\Theta = 20°–120°$, step was 0.04°, 10 s/step) and an Equinox-3000 instrument (CuK_α-radiation, equipped by a curved position-sensitive detector CPS-590; the angle interval was $2\Theta = 10°–90°$, acquisition time was 1–2 h, step was 0.012°) at room temperature. The unit cell parameters were calculated using the CelRef v.4.0 software, and the structural parameters were refined by the full-profile Rietveld analysis

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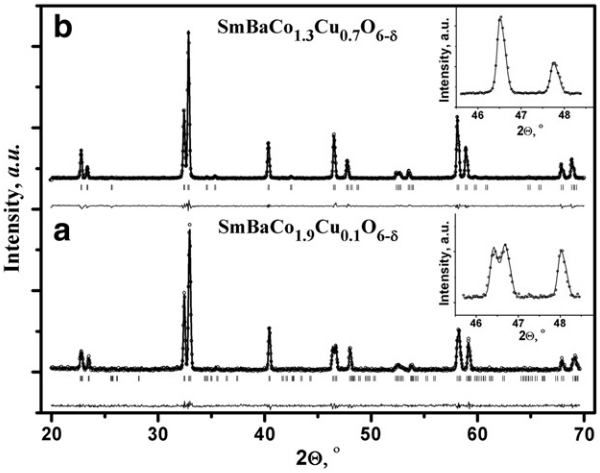

Fig. 1. Observed (circles), calculated (solid line) and difference (below) XRD profiles for the final Rietveld refinement of $SmBaCo_{2-x}Cu_xO_{6-\delta}$ with x = 0.1 and 0.7. Insets show characteristic fragments of the XRD patterns, indicating the differences between orthorhombic (a) and tetragonal (b) phases.

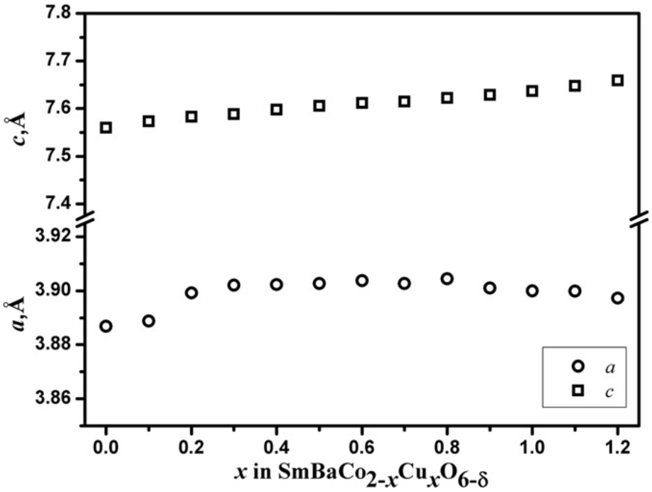

Fig. 2. Unit cell parameters vs. copper concentration in $SmBaCo_{2-x}Cu_xO_{6-\delta}$ (x = 0–1.2) at room temperature.

with a Fullprof 2008 package [18,19]. Ceramic microstructure was analyzed by scanning electron microscopy (SEM, Hitachi SU-70).

Thermogravimetric analysis (TGA) was carried out using a STA 409PC instrument (Netzsch) within the temperature range 25–1100 °C. In order to assess oxygen nonstoichiometry variations in air, two measurement regimes were employed, namely static (10 h dwells at a constant temperature, temperature steps of 25–50 °C) and dynamic (continuous heating/cooling rate of 1 °C/min). The absolute oxygen content was determined using a direct complete reduction by flowing hydrogen in the TGA instrument [17] and by iodometric titration. In the latter case, the powdered samples (0.2 g) were dissolved in a 2 M aqueous solution of hydrochloric acid in the presence of an excess amount of KI:

$$(Co_{2-x}Cu_x)^{z_{Me}+} + (4z_{Me} + x - 6)I^- \rightarrow (2-x)Co^{2+} + xCuI\downarrow + (2z_{Me} - 3)I_2 \quad (1)$$

where z_{Me} is the mean oxidation state of transition metal cations in the perovskite phase. The iodine formed in Reaction (1) was titrated by a standard $Na_2S_2O_3$ solution with a preliminary determined concentration; the equivalent point was registered using an automatic titrator Akvilon ATP-02.

Thermal expansion of the ceramic samples was measured using a vertical alumina dilatometer Linseis L75V/1250 in air (temperature range of 25–1100 °C, heating/cooling rate of 5°/min). The total electrical conductivity (σ) was studied by the 4-probe DC method at 25–1100 °C under atmospheric air, employing both cooling and heating regimes in order to ensure equilibration. The experimental technique used to determine steady-state oxygen permeation fluxes (j) through dense $SmBaCo_{2-x}Cu_xO_{6-\delta}$ membranes was described elsewhere [15,16]. The measurements were performed at 800–950 °C in the range of oxygen partial pressures at the membrane permeate side, $p(O_2)_{perm}$, from 0.01 to 0.21 atm. In all cases, the oxygen partial pressure at the membrane feed side, $p(O_2)_{feed}$, was equal to atmospheric pressure.

In order to assess possible interaction of $SmBaCo_{2-x}Cu_xO_{6-\delta}$ with solid oxide electrolytes, the corresponding mixtures with a 1:1 weight ratio were annealed at various temperatures (900–1100 °C) for 24 h in air and then examined by XRD.

3. Results and discussion

XRD analysis showed that the solid solution formation ranges in the pseudobinary $SmBaCo_{2-x}Cu_xO_{6-\delta}$ system at atmospheric oxygen pressure correspond to $0 \leq x \leq 1.2$ and $1.5 \leq x \leq 2.0$. No secondary phases are formed in these ranges; the end members of the two solid solution series were found to co-exist in the intermediate compositional range, x = 1.3–1.4. At x = 0.1 the crystal structure is orthorhombic (space group *Pmmm*), similar to undoped $SmBaCo_2O_{6-\delta}$ [17]. This structure can be described as $a_p \times 2a_p \times 2a_p$ where a_p is the primitive perovskite unit cell parameter. The Rietveld refinement results are presented in Fig. 1a and Table 1.

Table 1
Atomic positions in orthorhombic $SmBaCo_{1.9}Cu_{0.1}O_{6-\delta}$ and tetragonal $SmBaCo_{1.3}Cu_{0.7}O_{6-\delta}$, refined by Rietveld analysis.

$SmBaCo_{1.9}Cu_{0.1}O_{6-\delta}$ (S.G. *Pmmm*)					$SmBaCo_{1.3}Cu_{0.7}O_{6-\delta}$ (S.G. *P4/mmm*)				
Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
Sm	0.5	0.241 (1)	0.5	0.36 (4)	Sm	0.5	0.5	0	0.26 (4)
Ba	0.5	0.250 (1)	0	0.59 (4)	Ba	0.5	0.5	0.5	0.10 (4)
Co(Cu)1	0	0.5	0.265 (2)	0.89 (4)	Co(Cu)	0	0	0.235 (1)	0.59 (4)
Co(Cu)2	0	0	0.250 (2)	0.38 (4)	O1	0	0	0	0.68 (4)
O1	0	0	0	0.11 (5)	O2	0	0	0.5	1.09 (4)
O2	0	0.5	0	0.74 (4)	O3	0	0.5	0.195 (2)	0.73 (4)
O3	0	0.5	0.5	0.51 (5)					
O4	0	0	0.5	0.10 (4)					
O5	0.5	0	0.272 (3)	0.36 (5)					
O6	0.5	0.5	0.303 (3)	0.81 (5)					
O7	0	0.256 (2)	0.292 (1)	0.29 (4)					
a = 3.889 (1) Å; b = 7.822 (1) Å; c = 7.574 (1) Å; V = 230.42 (2) (Å)^3; R_{Br} = 6.41%; R_f = 9.58%; R_p = 11.7%					a = b = 3.900 (1) Å; c = 7.609 (1) Å; V = 115.72 (2) (Å)^3; R_{Br} = 4.99%; R_f = 4.73%; R_p = 7.65%				