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Crystal structure, oxygen nonstoichiometry and thermal expansion of the layered $NdBaCo_{2-x}M_xO_{5+\delta}$ (M = Ni, Cu)

T.V. Aksenova, A.S. Urusova, L.Ya. Gavrilova, V.A. Cherepanov *

Department of Chemistry, Institute of Natural Sciences, Ural Federal University, Yekaterinburg, Russia

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ABSTRACT

The homogeneity range and crystal structure of the $NdBaCo_{2-x}M_xO_{5+\delta}$ ($0.0 \leqslant x \leqslant 0.5$ for M = Ni and $0.0 \leqslant x \leqslant 1.1$ for M = Cu) solid solutions were determined by X-ray diffraction. The crystal structure of the $NdBaCo_{2-x}M_xO_{5+\delta}$ was described as tetragonal (sp. gr. *P4/mmm*). The structural parameters were refined using Rietveld full-profile analysis. It was shown that parameter *a* remains practically constant while parameter *c* gradually increases with the increase of nickel or copper content. The changes of oxygen content in $NdBaCo_{2-x}M_xO_{5+\delta}$ versus temperature were determined by thermogravimetric analysis. Gradual substitution of cobalt by copper or nickel leads to the decrease of oxygen content. The average thermal expansion coefficients for the $NdBaCo_{2-x}M_xO_{5+\delta}$ (M = Ni, Cu) samples were calculated within the temperature range 298–1273 K in air. The chemical stability of complex oxides $NdBaCo_{2-x}M_xO_{5+\delta}$ (M = Ni, Cu) in contact with the electrolyte materials $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Zr_{0.85}Y_{0.15}O_{2-\delta}$ were investigated within the temperature range 1173–1373 K in air.

1. Introduction

The perovskite type oxides with the formula $LnBaCo_2O_{5+\delta}$ (Ln = Nd–Ho) have potential applications as gas sensors, catalysts or cathode materials for intermediate temperature-operating solid oxide fuel cells (IT-SOFCs) [1–4] due to the high electronic-ionic conductivity and high oxygen diffusivity.

The crystal structure and physicochemical properties (such as, electrical conductivity, magnetic characteristics, and thermal expansion) of undoped neodymium barium cobaltite $NdBaCo_2O_{5+\delta}$ were studied in detail [1–9] recently. It was found that oxygen content in the $NdBaCo_2O_{5+\delta}$ can vary significantly within the range δ = 0.0–1.0 depending on the conditions used (temperature and partial oxygen pressure) and the values obtained at room temperature are strongly dependent on the synthetic route and cooling rate. The crystal structure of single phase samples with $\delta \geqslant 0.75$ and $\delta \leqslant 0.4$ can be described within the tetragonal unit cell $a_p \times a_p \times 2a_p$ (sp. gr. *P4/mmm*), where a_p is the unit cell parameter of parent perovskite. On the other hand the $NdBaCo_2O_{5+\delta}$ oxides with $0.4 \leqslant \delta \leqslant 0.75$ crystallized in the orthorhombic unit cell $a_p \times 2a_p \times 2a_p$ (sp. gr. *Pmmm*) [6,8,9].

The introduction of 3*d*-transition metal (M = Fe, Ni, Cu, Mn) into the cobalt sublattice of the $NdBaCo_2O_{5+\delta}$ affects the value of oxygen content and correspondingly the crystal structure and therefore physicochemical properties of the oxide. It was reported that depending on the 3*d*-transition metal content (x) partially substituted neodymium barium cobaltites $NdBaCo_{2-x}M_xO_{5+\delta}$ can crystallized in either tetragonal structure with $0.0 \leqslant x \leqslant 1.4$ for M = Fe and $0.0 \leqslant x \leqslant 0.4$ for M = Ni (sp. gr. *P4/mmm*), or orthorhombic structure with x = 0.4 for M = Ni (sp. gr. *Pmmm*), or in cubic structure with $1.5 \leqslant x \leqslant 2.0$ for M = Fe (sp. gr. *Pm-3m*) [10–12]. The substitution of cobalt by iron leads to the gradual increase of oxygen content in the $NdBaCo_{2-x}Fe_xO_{5+\delta}$ oxides and improves chemical stability, but hampers the transport properties [10,11]. The incorporation of nickel into the cobalt sublattice results in a decrease of oxygen content and electrical conductivity of the materials [12].

The influence of the nature of 3*d*-transition metal (M = Ni, Cu) partially substituted for Co in the crystal structure, oxygen nonstoichiometry and thermal properties of the $NdBaCo_{2-x}M_xO_{5+\delta}$ solid solutions is presented in this paper.

2. Experimental

Polycrystalline $NdBaCo_{2-x}M_xO_{5+\delta}$ (M = Ni, Cu) samples were prepared using glycerin nitrate technique. Neodymium oxide Nd_2O_3 (with 99.99% purity), barium carbonate $BaCO_3$ (special purity grade), copper oxide CuO and nickel acetate $Ni(CH_3COO)_2 \times 4H_2O$ (both of pure for analysis grade) and metallic cobalt were used as starting materials. Metallic cobalt was obtained by reducing of cobalt oxide (pure for analysis grade) in the hydrogen flow at 673–873 K. Before weighting the starting materials (oxides and barium carbonate) were preliminary annealed in order to remove adsorbed gases and water. According to the glycerin nitrate technique the required amounts of the starting materials were dissolved in nitric acid, and then glycerin in the amount needed for a complete reduction of nitrate ions was added. The obtained solutions were dried to viscous gels that further transformed to brown powders, and then fired at 773–1173 K. Final anneals of

* Corresponding author. Tel.: +7 3432517927; fax: +7 3433507401.
E-mail addresses: vladimir.cherepanov@usu.ru, vl_cherepanov@mail.ru (V.A. Cherepanov).

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Table 1
The structural parameters and *R*-factors refined by the Rietveld method for the $NdBaCo_{2-x}M_xO_{5+\delta}$ (M = Ni, Cu) solid solutions.

	$NdBaCo_2O_{5+\delta}$	$NdBaCo_{2-x}Ni_xO_{5+\delta}$					$NdBaCo_{2-x}Cu_xO_{5+\delta}$					
x	0.0	0.1	0.2	0.3	0.4	0.5	0.2	0.4	0.6	0.8	1.0	1.1
P4/mmm space group, Nd(1d) (0.5; 0.5; 0.5), Ba(1c) (0.5; 0.5; 0), Co/Me(2 g) (0; 0; *z*), O1(1a) (0; 0; 0), O2(1b) (0; 0; 0.5), O3(4i) (0; 0.5; *z*)[a]												
a (Å)	3.903(1)	3.903(1)	3.904(1)	3.904(1)	3.905(1)	3.906(1)	3.904(1)	3.909(1)	3.910(1)	3.911(1)	3.909(1)	3.907(1)
c (Å)	7.614(1)	7.616(1)	7.617(1)	7.618(1)	7.621(1)	7.623(1)	7.616(1)	7.628(1)	7.639(1)	7.649(1)	7.668(1)	7.679(1)
V (Å)^3	116.02(2)	116.03(1)	116.14(1)	116.16(1)	116.21(1)	116.29(1)	116.11(1)	116.55(1)	116.78(1)	116.97(1)	117.17(1)	117.22(2)
z (*Co/Me*)	0.252(1)	0.251(4)	0.251(2)	0.251(4)	0.250(4)	0.250(4)	0.254(1)	0.254(1)	0.256(1)	0.258(1)	0.255(1)	0.255(1)
z (*O3*)	0.281(1)	0.288(3)	0.291(2)	0.283(4)	0.285(4)	0.286(3)	0.288(2)	0.294(1)	0.295(1)	0.295(2)	0.296(1)	0.292(1)
Occ.	0.674(3)	0.650(1)	0.624(1)	0.602(1)	0.587(2)	0.556(2)	0.666(3)	0.534(3)	0.461(4)	0.381(4)	0.297(4)	0.209(1)
d_{Nd-Co} (Å)	3.343(4)	3.344(2)	3.350(9)	3.354(2)	3.355(2)	3.356(2)	3.335(5)	3.339(5)	3.334(6)	3.324(6)	3.340(6)	3.342(3)
d_{Nd-O3} (Å)	2.563(5)	2.528(2)	2.516(9)	2.558(2)	2.549(2)	2.540(2)	2.532(2)	2.507(7)	2.500(7)	2.506(8)	2.504(8)	2.513(5)
d_{Ba-Co} (Å)	3.363(4)	3.362(2)	3.359(9)	3.354(2)	3.355(2)	3.356(2)	3.372(5)	3.378(5)	3.388(6)	3.401(6)	3.388(7)	3.396(3)
d_{Ba-O3} (Å)	2.901(6)	2.940(2)	2.957(9)	2.910(2)	2.920(2)	2.933(2)	2.938(9)	2.976(9)	2.989(9)	2.986(9)	2.995(9)	2.983(7)
d_{Co-O1} (Å)	1.920(7)	1.920(3)	1.912(2)	1.901(3)	1.910(3)	1.910(3)	1.937(9)	1.942(9)	1.957(9)	1.980(9)	1.969(2)	1.960(2)
d_{Co-O2} (Å)	1.887(7)	1.890(3)	1.897(2)	1.901(3)	1.910(3)	1.910(3)	1.871(9)	1.872(9)	1.872(1)	1.844(9)	1.875(9)	1.880(2)
d_{Co-O3} (Å)	1.964(1)	1.972(6)	1.977(3)	1.968(6)	1.971(6)	1.973(5)	1.969(2)	1.978(2)	1.979(2)	1.975(2)	1.979(3)	1.974(5)
R_{Br} (%)	5.88	5.35	9.03	6.06	7.73	7.59	4.93	2.97	3.71	3.99	6.05	5.21
R_f (%)	6.18	5.93	11.0	7.14	6.95	8.23	4.74	3.32	4.85	4.84	7.37	5.07
R_p (%)	8.52	13.1	14.5	14.0	15.4	14.8	7.98	7.64	7.74	8.28	8.81	9.73

[a] Oxygen atoms labeled as O1 correspond to the oxygen in BaO planes, those labeled as O2 correspond to the oxygen in NdO_δ planes (thus, the occupancy factor found is given), and those labeled as O3 correspond to the oxygen in CoO_2 planes.

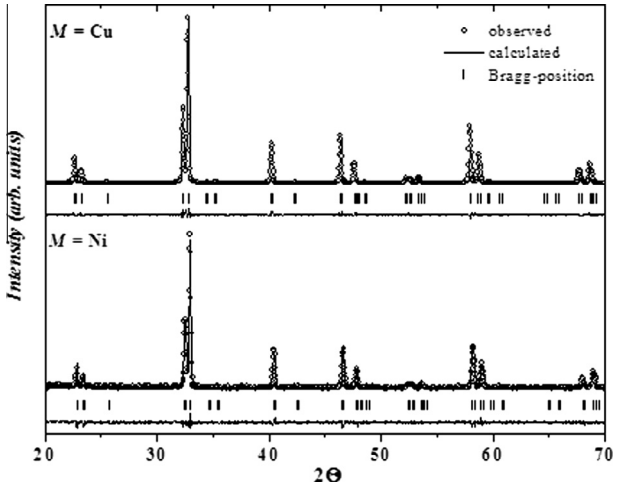

Fig. 1. XRD pattern for $NdBaCo_{1.6}M_{0.4}O_{5+\delta}$ refined by Rietveld analysis. Points represent the experimental data and the solid curve is the calculated profile. A difference curve is plotted at the bottom. Vertical marks represent the position of allowed Bragg reflection.

the $NdBaCo_{2-x}Cu_xO_{5+\delta}$ oxides were performed at 1273 K during 100–120 h with intermediate grindings and $NdBaCo_{2-x}Ni_xO_{5+\delta}$ oxides – at 1373 K in air, followed by slow cooling down to room temperature at a rate of about 100°/h.

Obtained oxides were characterized by XRD using a DRON-6 and DRON-UM1 diffractometers in Cu Kα radiation (λ = 1.5418 Å) with pyrolytic graphite monochromator within the angle range $20° \leqslant 2\Theta \leqslant 70°$ (scan step 0.04 with the exposure time 7–10 s). The unit cell parameters were calculated using the "CelRef 4.0" program and refined using the full profile Rietveld analysis. The convergence between experimental XRD data and calculated profile was estimated by a set of standard factors: R_{wp} – weighed profile factor, R_p – profile factor, R_f – structural factor, R_{Br} – Bragg-factor and R_{exp} – expected factor.

Thermogravimetric measurements (TGA) were carried out using STA 409PC Netzsch GmbH (weight resolution of 1 μg; sample weight of 1–2.5 g) within the temperature range from 298 K to 1373 K in air in static (isothermal dwells for 8–12 h) and dynamic (heating/cooling rate 2 K/min) regimes. The absolute values of oxygen content in the sample were determined by two methods: direct reduction of the complex oxides in the TG cell by hydrogen (10% H_2–90% Ar) at 1273 K and iodometric titration of the samples slowly cooled down to room temperature. The iodometric titration technique was described elsewhere [13].

Thermal expansion measurements were carried out within the temperature range 298–1273 K in air using the dilatometer (Netzsch GmbH DIL 402C) at a heating/cooling rate of 5 K/min. The samples for the measurements were preliminary compacted into the form of a bar with the sizes about 2 × 4 × 15 mm and sintered at 1323–1473 K in air during 24 h, with subsequent slow cooling (~1.5 K/min). The density of the polished ceramic samples was not less than 90% of their theoretical values calculated from the XRD data.

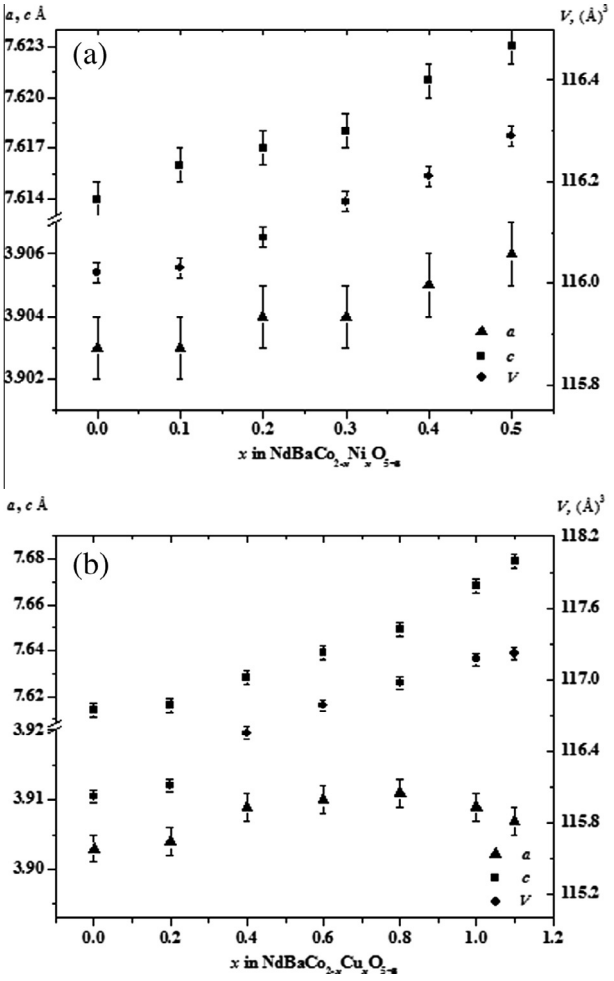

Fig. 2. The dependence of the unit cell parameters for the $NdBaCo_{2-x}M_xO_{5+\delta}$ solid solution versus 3*d*-transition metal content: M = Ni (a) and M = Cu (b).