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Crystal structure, oxygen nonstoichiometry and thermal expansion of the layered NdBaCo_{2-x} M_x O_{5+ δ} (*M* = Ni, Cu)



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ABSTRACT

The homogeneity range and crystal structure of the NdBaCo_{2-x} $M_xO_{5+\delta}$ ($0.0 \le x \le 0.5$ for M = Ni and $0.0 \le x \le 1.1$ 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- δ} and Zr_{0.85}Y_{0.15}O_{2- δ} were investigated within the temperature range 1173–1373 K in air.

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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 NdBaCo₂O_{5+ δ} were studied in detail [1–9] recently. It was found that oxygen content in the NdBaCo₂O_{5+ δ} 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 $\delta \ge 0.75$ and $\delta \le 0.4$ 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 NdBaCo₂O_{5+ δ} oxides with $0.4 \le \delta \le 0.75$ 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 NdBaCo₂O_{5+δ} 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 $0.0 \le x \le 1.4$ for M = Fe and $0.0 \le x \le 0.4$ 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 $1.5 \le x \le 2.0$ 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+ δ} 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_x O_{5+ δ} 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 Nd₂O₃ (with 99.99% purity), barium carbonate BaCO₃ (special purity grade), copper oxide CuO and nickel acetate Ni(CH₃COO)₂ × 4H₂O (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



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 Table 1

 The structural parameters and *R*-factors refined by the Rietveld method for the NdBaCo_{2-x} M_x O_{5+δ} (M = Ni, Cu) solid solutions.

	$NdBaCo_2O_{5^+\delta}$	NdBaCo _{2-x} Ni _x O _{5+δ}				NdBaCo _{2-x} Cu _x O _{5+δ}						
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 (03)	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 _{со–О3} (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 CoO₂ 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+δ} oxides were performed at 1273 K during 100–120 h with intermediate grindings and NdBaCo_{2-x}Ni_xO_{5+δ} 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 ($\lambda = 1.5418$ Å) with pyrolytic graphite monochromator within the angle range $20^\circ \leq 2\Theta \leq 70^\circ$ (scan step 0.04 with the exposure time 7–10 s). The unit cell parameters were calculated using the "Cellef 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 μ g; 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% H₂–90% 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 heat-ing/cooling rate of 5 K/min. The samples for the measurements were preliminary compacted into the form of a bar with the sizes about $2 \times 4 \times 15$ mm and sintered



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

at 1323–1473 K in air during 24 h, with subsequent slow cooling (\sim 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.

Table 2

Calculated mean oxidation state of 3d-transition metals and oxidation state of cobalt ions in the assumption that all copper and nickel ions are in the Cu^{2+} and Ni^{2+} form.

x	5 + δ	Mean oxidation state of 3d-transition metal	Oxidation state of Co ions in the assumption of Me ²⁺		
$NdBaCo_{2-x}Ni_{x}O_{5+\delta}$					
0.0	5.74 ^a	3.24	3.24		
	5.73 ^b	3.23	3.23		
0.1	5.70 ^a	3.20	3.26		
0.2	5.67 ^a	3.17	3.30		
0.3	5.65 ^a	3.15	3.35		
0.4	5.59 ^a	3.09	3.36		
0.5	5.58 ^ª	3.08	3.44		
NdBaCo _{2-x} Cu _x O ₅₊₅					
0.2	5.69 ^b	3.19	3.32		
0.4	5.55ª	3.05	3.31		
0.6	5.42 ^a	2.92	3.31		
0.8	5.31 ^a	2.81	3.35		
1.1	5.09 ^b	2.59	3.31		

^a Data of iodometric titration (error ±0.05).

^b Data of TGA (error ±0.01).



Fig. 3. Temperature dependence of oxygen content in the NdBaCo_{2-x} M_x O_{5+ δ} in air.

Table 3

Average thermal expansion coefficients (TECs) of NdBaCo_{2-x} $M_xO_{5+\delta}$ (M = Ni, Cu) in air and the temperature of interaction between NdBaCo_{2-x} $M_xO_{5+\delta}$ and Ce_{0.8}Sm_{0.2}O_{2- δ} electrolyte.

М	x	$\alpha \times 10^{6}$, K^{-1} , 298–1373 K	x	Interaction temperature (K)
Ni	0.0 0.2 0.4	22.4 22.1 21.2	0; 0.1 0.3; 0.5	>1373 1373
Cu	0.2 0.4	22.7 21.4	0.2 0.8	>1273 1273

Chemical stability of the NdBaCo_{2-x} $M_xO_{5+\delta}$ (M = Ni, Cu) relative to the electrolyte materials Ce_{0.8}Sm_{0.2}O₂ and Zr_{0.85}Y_{0.15}O₂ has been studied within the temperature range 1173–1373 K, by means of annealing of the corresponding mixtures with 1:1 weight ration during 24 h in air with following XRD analysis.

3. Results and discussion

In order to check a homogeneity range for partial substitution of 3*d*-transition metals (Ni and Cu) for Co in the NdBaCo₂O_{5+ δ} a



Fig. 4. Linear thermal expansion of the NdBaCo_{2-x} M_x O_{5+ δ} ceramics in air: M = Ni with x = 0.2 (a) and x = 0.4 (b), M = Cu with x = 0.2 (c) and x = 0.4 (d).

number of samples with overall composition NdBaCo_{2-x} M_x O_{5+ δ} within the range 0.0 $\leq x \leq$ 0.7 (for M = Ni) and 0.0 $\leq x \leq$ 2.0 (for M = Cu) with steps in x of 0.1 were prepared by glycerin-nitrate technique. According to the results of XRD analysis the homogeneity range for the nickel-substituted cobaltites NdBaCo_{2-x}Ni_xO_{5+ δ} appears within 0.0 $\leq x \leq$ 0.5, which is slightly less than the values reported earlier (x = 0.6) [12]. This difference can be caused by the difference in synthesis temperatures: 1373 K in present work and 1523 K in [12]. According to XRD results the samples with nickel content x = 0.6 and 0.7 were multi-phase and together with saturated solid solution NdBaCo_{1.5}Ni_{0.5}O_{5+ δ} contained barium cobaltite BaCoO_{3- δ} and oxides Nd₂O₃ and NiO.

According to the results of XRD analysis of the NdBaCo_{2-x}Cu_xO_{5+δ} ($0.0 \le x \le 2.0$) samples, the substitution of Co by Cu leads to the formation of two types of solid solutions with limited homogeneity ranges. The copper substituted cobaltites NdBaCo_{2-x}Cu_xO_{5+δ} within the range $0.0 \le x \le 1.1$ were single phase and isostructural to the undoped neodymium barium cobaltite NdBaCo₂O_{5+δ}, while the oxide with x = 1.9 was similar to the undoped neodymium barium cuprite Nd₃Ba₃Cu₆O_{14-δ} (x = 2.0). The samples of the nominal composition NdBaCo_{2-x}Cu_xO_{5+δ} with copper contents $1.2 \le x \le 1.8$ con-



Fig. 5. XRD pattern of the NdBaCo_{2-x}Ni_xO_{5+δ} samples in contact with the Ce_{0.8}Sm_{0.2}O_{2-δ} fired at 1373 K in air (a) and NdBaCo_{2-x}Cu_xO_{5+δ} samples in contact with the Zr_{0.85}Y_{0.15}O_{2-δ} fired at 1173 K in air (b).

sisted of the two saturated solid solution: $NdBaCo_{0.9}Cu_{1.1}O_{5+\delta}$ and $Nd_3Ba_3(Cu_{1.9}Co_{0.1})_3O_{14-\delta}$.

Similar to undoped NdBaCo₂O_{5+ δ}, the crystal structure of both solid solutions NdBaCo_{2- $x}Ni_xO_{5+<math>\delta$} with $0.0 \le x \le 0.5$ and NdBaCo_{2- $x}Cu_xO_{5+<math>\delta$} with $0.0 \le x \le 1.1$ can be described within the tetragonal unit cell $a_p \times a_p \times 2a_p$ (sp. gr. *P4/mmm*). Fig. 1 illustrates X-ray diffraction patterns for the NdBaCo_{1.6} $M_{0.4}O_{5+\delta}$ (M = Ni, Cu) refined by the Rietveld analysis. The structural parameters for all single phase samples NdBaCo_{2- $x}M_xO_{5+\delta}$ are listed in Table 1. The crystal structure of complex oxides Nd₃Ba₃Cu₆O_{14- δ} (x = 2.0) and Nd₃Ba₃Cu_{5.7}Co_{0.3}O_{14- δ} (x = 1.9) can be described within the tetragonal unit cell $a_p \times a_p \times 3a_p$ (sp. gr. *P4/mmm*) with the unit cell parameters a = 3.882(1) Å, c = 11.629(1) Å for Nd₃Ba₃Cu_{5.7}Co_{0.3}O_{14- δ}, that agrees with the data reported in [14,15].</sub></sub></sub>

The dependencies of the unit cell parameters for a series of NdBaCo_{2-*x*}*M_x*O_{5+δ} (*M* = Ni, Cu) solid solutions versus nickel and copper content (*x*) are shown in Fig. 2. The substitution of nickel or copper into the cobalt sublattice leads to a slight variation of the *a* parameters and a gradual increase of the *c* parameters and the unit cell volume. Such behavior can be explained by the size factor since the ionic radius of nickel ($r_{Ni^{2+}/Ni^{3+}} = 0.79/0.72$ Å, CN = 6) and copper ($r_{Cu^{2+}/Cu^{3+}} = 0.87/0.68$ Å, CN = 6) are larger than ionic radius of cobalt ($r_{Co^{3+}/Co^{4+}} = 0.75/0.67$ Å, CN = 6) [16]. The anisotropy in the unit cell parameter changes with increasing of the dopant content is more obvious for the Cu-substituted samples. One can be perplexed why the substitution in the B site influences the values of a and *c* parameters differently. The probable reason of such anisotropy can be related with the peculiarity of oxygen vacancies location in the structure of double perovskites $LnBaCo_2O_{5+\delta}$. It is well recognized that oxygen vacancies are not randomly distributed in the lattice, but located in the Ln–O planes [5]. As it will be shown below, the substitution of Co ions by Ni or Cu leads to the increase of oxygen vacancies concentration and as a result can strongly affect the distances between the layers along *c*-axis while the values of *a* parameter change in a smaller extent. Similar variations of the unit cell parameters while cobalt was substituted by nickel were also detected by Kim and Manthiram [12]. Simultaneous influence of different although linked parameters (such as, oxidation states of 3*d*-transition metals, oxygen content in particular crystallographic planes) causes a nonlinear change of the unit cell parameters with the dopant concentration changes. However the substitution of Fe for Co in the rare earth and barium cobaltates that leads to the increase of oxygen content also yields same anisotropic increase of the *a* and *c* parameters [10,17,18]. Therefore the explanation of this anisotropy effect is more complicated and not so obvious.

The results of TGA measurements for NdBaCo_{2-x} M_x O_{5+ δ} (M = Ni, Cu) versus temperature in air are shown in Fig. 3. Solid lines represent the data obtained in dynamic regime (cooling rate 2 K/min), points correspond to the values measured in static regime (isothermal dwells for 10 h). It can be seen that oxygen exchange between the solid and gaseous phases has started at about 550 K. An excellent agreement between the data, obtained in dynamic and static regimes suggests that the oxygen exchange process and, hence, equilibration between the solid oxides and gaseous phase is fast enough. The substitution of nickel or copper for cobalt sites results in a decrease of oxygen content. Such behavior can be explained by the fact that nickel and copper are more electronegative elements in comparison to cobalt (χ_{Co} = 1.88; χ_{Ni} = 1.91; χ_{Cu} = 2.00 in the Pauling scale [19]) and therefore they act partially or completely as the acceptors of electrons (Ni'_{Co} and Cu'_{Co}). The negatively charged acceptor defects in the oxide are balanced by the corresponding amount of positively charged oxygen vacancies $(V_0^{\bullet\bullet})$, and/or electron holes. Similar behavior was observed in the ordinary perovskite system $Ln_{1-x}M_xCo_{1-y}Ni_yO_{3-\delta}$ (*M* = alkali earth metals) [20,21]. It is interesting to note that as expected the increase of acceptor dopant (Ni'_{Co} and Cu'_{Co}) content yields to the decrease of mean oxidation state of 3d-transition metals, however if we assume that all acceptor impurities (Ni or Cu) possesses the oxidation state equal to 2+, the values of oxidation state of the Co ions remain practically (at least for the Cu containing phases) constant (Table 2). In other words, the substitution of cobalt ions with oxidation state larger than 2+ by the Cu²⁺ is accompanied with the release of oxygen from the lattice in the equivalent amount according to the electroneutrality condition that allows maintaining the oxidation state of cobalt at the constant value.

The dependencies of relative linear expansion for the NdBaCo_{2--x} $M_xO_{5+\delta}$ (M = Ni, Cu with x = 0; 0.2; 0.4) versus temperature within the range 298–1273 K in air, obtained during heating and cooling sufficiently coincide with each other (Fig. 4). The average values of thermal expansion coefficients (TECs), calculated from experimental results are listed in Table 3. It can be seen that the average values of TEC remains practically unchanged for the 0.2 nickel or copper substituted cobaltites, while further increase of 3*d*-transition metal content leads to the decrease of TEC values.

In order to check possible chemical interactions the NdBaCo_{2-x} M_x O_{5+ δ} samples (M = Ni with x = 0; 0.1; 0.3; 0.5 and M = Cu with x = 0.2; 0.8) were mixed with the solid electrolyte

materials Ce_{0.8}Sm_{0.2}O₂ and Zr_{0.85}Y_{0.15}O₂ in mass ratio 1:1 and fired during 24 h at 1173 K, 1273 K and 1373 K in air. It was found that NdBaCo_{2-x}Ni_xO_{5+ δ} (x = 0; 0.1) is chemically inert to Ce_{0.8}Sm_{0.2}O₂ within all temperature range studied. Further increase of nickel content leads to the decrease of chemical stability of layered perovskite relative to the electrolyte materials. The XRD patterns of the NdBaCo_{2-x}Ni_xO_{5+ δ} (x = 0.3; 0.5) with Ce_{0.8}Sm_{0.2}O_{2- δ} mixtures annealed at 1373 K revealed additional reflections corresponding to the BaCe_{1-v}Nd_vO_{3- δ} and Ni_{1-z}Co_zO (Fig. 5a). Similar results were obtained for the copper substituted cobaltites. The sample of the nominal composition NdBaCo_{1.8}Cu_{0.2}O_{5+ δ} has not interacts with the Ce_{0.8}Sm_{0.2}O_{2- δ} at 1273 K, while the NdBaCo_{1.2}Cu_{0.8}O_{5+ δ} in contact with the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ reveals the formation of interaction products. The interaction temperatures between NdBaCo_{2-x} $M_xO_{5+\delta}$ (*M* = Ni, Cu) oxides and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte are listed in Table 3.

On the contrary $Zr_{0.85}Y_{0.15}O_{2-\delta}$ solid electrolyte started to react with all studied perovskite materials NdBaCo_{2-x} M_x O_{5+ δ} (*M* = Ni with x = 0; 0.1; 0.3; 0.5 and M = Cu with x = 0.2; 0.8) even at 1173 K forming low conducting barium zirconate BaZrO₃ [22]. Fig. 5b illustrates the results of XRD patterns of the NdBaCo_{2-x}Cu_xO_{5+ δ} (x = 0; 0.8) and $Zr_{0.85}Y_{0.15}O_2$ mixtures annealed at 1173 K as an example.

4. Conclusion

The homogeneity range, crystal structure, oxygen nonstoichiometry and thermal expansion of layered perovskite phases NdBaCo_{2-x} M_x O_{5+ δ} (*M* = Ni, Cu) were investigated. It was shown that the crystal structure of NdBaCo_{2-x} M_x O_{5+ δ} (*M* = Ni with $0.0 \le x \le 0.5$ and M = Cu with $0.0 \le x \le 1.1$) oxides can be described within the tetragonal $a_p \times a_p \times 2a_p$ structure (sp. gr. P4/ mmm) regardless of the dopant nature. The oxygen content is shown to decrease with increasing temperature and dopant (Ni, Cu) content. The values of average thermal expansion coefficients of the NdBaCo_{2-x} M_x O_{5+ δ} (*M* = Ni, Cu) within the temperature range 298-1273 K in air calculated from the dilatometric measurements varied from $21\times 10^{-6}\,K^{-1}$ to $23\times 10^{-6}\,K^{-1}.$ It was found that NdBaCo_{2-x} M_x O_{5+ δ} (*M* = Ni, Cu) oxides interacts with the Zr_{0.85}Y_{0.15-} $O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$, therefore they cannot be considered as a potential cathode material for the fuel cells based on these electrolytes or special precautions have to be taken.

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