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Synthesis and Crystal Structure of the New Complex Cobalt and Nickel Oxide $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$

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Abstract—The complex cobalt and nickel oxide $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ has been synthesized by the citrate method. The oxygen content of the oxide has been determined by iodometric titration. The crystal structure of the compound has been refined using X-ray powder diffraction data ($a = 3.7951(2)$ Å, $c = 19.700(1)$ Å, $\chi^2 = 1.15$, $R_F^2 = 0.0586$, $R_p = 0.0365$, $R_{wp} = 0.0462$). $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ has the structure of the second member of the Ruddlesden–Popper series $A_{n+1}B_nO_{3n+1}$.

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Interest in complex cobalt oxides $Sr_{1-x}R_xCoO_{3-y}$ with a perovskite structure stems from the possibility of their use for producing electrodes for high- and low-temperature fuel cells and as oxygen-permeable membranes [1, 2]. It was recently found that the Sr^{2+} and R^{3+} cations in the crystal structure of some cobaltites $Sr_{1-x}R_xCoO_{3-y}$ (R = Eu–Ho, Y) are ordered, which entails ordering of oxygen vacancies and leads to the formation of so-called 314 phases $Sr_3RCo_4O_{10.5}$ [3]. The latter have some interesting physical properties. In particular, depending on the oxygen content, the 314 phases are either antiferromagnets with semiconducting properties ($Sr_{2/3}Y_{1/3}CoO_{2.66}$) or ferromagnets with metallic conductivity ($Sr_{2/3}Y_{1/3}CoO_{2.70}$) [4, 5]. Therefore, it is of interest to synthesize and study the crystal structure and electrophysical properties of the 314 phases in which cobalt is partially substituted by other transition-metal cations, for example, by nickel. In this paper, we report the synthesis and crystal structure of the new phase $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$.

EXPERIMENTAL

Samples of $Sr_3YCo_{4-x}Ni_xO_{10.5}$ ($0 \le x \le 3$, $\Delta x = 1$) were synthesized by the citrate method. Calculated amounts of yttrium oxide were dissolved in melted citric acid taken in a 50-fold molar excess. After the melt became transparent, $SrCO_3$ (pure for analysis) and, then, $(NiOH)_2CO_3$ (pure for analysis) were introduced. After they were dissolved, a solution of $Co(NO_3)_2 \cdot 6H_2O$ (pure for analysis) in a minimal possible amount of water was added to the melt. The mixture was heated by a gas burner until a brown solid mass was formed, which was annealed at 650°C for 24 h. Then, the resulting powder was pressed in tablets and annealed at 1100°C for 48 h. The phase composition of samples was monitored by X-ray powder diffraction. X-ray powder diffraction pattern were obtained on an FR-552 high-resolution focusing monochromator camera ($CuK_{\alpha1}$ radiation, $\lambda = 1.54060$ Å) at room temperature. Germanium was added as an internal reference. To refine the crystal structure of the synthesized oxide, diffraction data obtained on a STADI-P (STOE) diffractometer was used ($CuK_{\alpha1}$, $\lambda = 1.54060$ Å).

The oxygen content in the single-phase samples obtained was determined by iodometric back titration. A small amount of the sample (of about 0.03 g) was placed in a flask containing 20 mL of a 20% KI solution. The solution was acidified with 2 mL of HCl (conc.), sealed with a rubber stopper, and left in the dark until the sample was completely dissolved. The released iodine was titrated with a standard $Na_2S_2O_3$ solution.

The cationic composition was determined using electron probe X-ray microanalysis (EPXMA) on a JEOL JSM-820 scanning electron microscope (accelerating voltage, 15–20 kV) equipped with a LINK AN10000 microanalysis system.

High-resolution electron diffraction and microscopy were carried out on a JEOL JEM 3010 UHR transmission microscope (Stockholm University, Sweden).

RESULTS AND DISCUSSION

X-ray powder diffraction showed that all $Sr_3YCo_{4-x}Ni_xO_{10.5}$ samples ($0 < x \le 3$, $\Delta x = 1$) were not

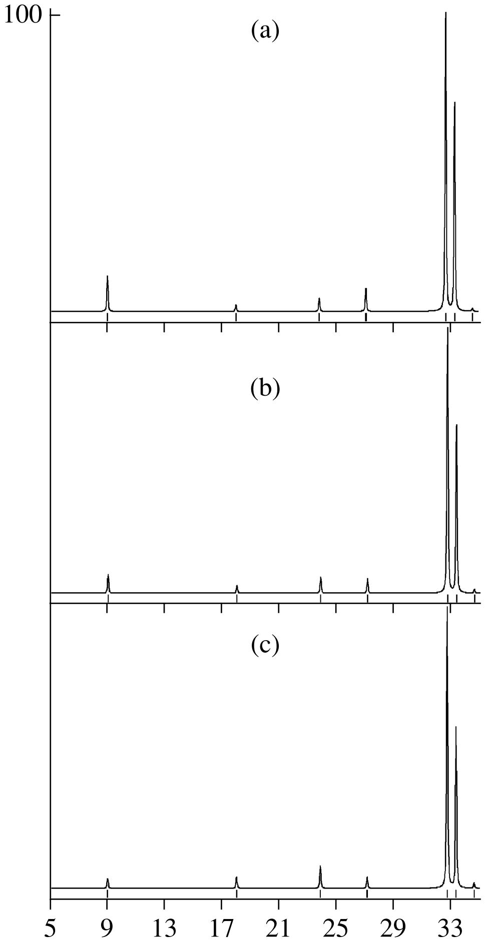

Fig. 1. Calculated X-ray powder diffraction patterns for $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ at (a) $g = 0.0$, (b) $g = 0.5$, and (c) $g = 1.0$.

single-phase. The sample with the composition $Sr_3YCo_2Ni_2O_z$ contains, in addition to nickel oxide (NiO), a tetragonal phase with an *I*-centered lattice and the following unit cell parameters: $a = 3.8012(5)$ Å and $c = 19.754(2)$ Å. In the search for an isostructural compound, the $Sr_2Y_{0.8}Ca_{0.2}Co_2O_6$ phase was revealed [6].

Assuming that the oxidation states of nickel and cobalt in the new tetragonal phase are, respectively, +2 and +3 and taking into account the Sr/Y ratio in the initial sample, we derived its composition $Sr_{2.25}Y_{0.73}Co_{1.25}Ni_{0.75}O_6$. A sample of this composition was synthesized under the same conditions. The X-ray powder diffraction pattern of the single-phase sample was completely indexed in terms of a tetragonal *I*-centered cell ($a = 3.7944(5)$ Å and $c = 19.695(4)$ Å). The cationic composition of the resulting phase was confirmed by EPXMA: Sr : Y : Co : Ni = 49(3) : 14(2) : 24(3) : 11(2) (calculated ratio, Sr : Y : Co : Ni = 45 : 15 : 25 : 15). Standard deviations calculated from the results of eight measurements are parenthesized. Iodometric titration showed that the oxygen composition of the phase corresponds to the formula $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84(1)}$. To change the oxygen content of the phase, the sample was annealed in a nitrogen atmosphere at 800°C. According to iodometric titration, the oxygen content of the resulting compound decreased and corresponded to the formula $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.57(1)}$. The unit cell parameters of the phase after heat treatment in nitrogen were $a = 3.8195(5)$ Å and $c = 19.652(4)$ Å. The same trends in the unit cell parameters with a decrease in the oxygen content were observed for $(Sr,Y,Ca)Co_2O_{6+y}$ [6].

Table 1. Crystallographic data for $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$

Space group	*I*4/*mmm*
Unit cell parameters, Å	$a = 3.7951(2)$ $c = 19.700(1)$
Reliability factors	$\chi^2 = 1.15$; $R_F^2 = 0.0586$; $R_p = 0.0365$, $R_{wp} = 0.0462$

To study the homogeneity range of the $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ phase, we synthesized $Sr_2YCoNiO_6$ and $Sr_{1.75}Y_{1.25}Co_{0.75}Ni_{1.25}O_6$ samples. According to X-ray powder diffraction, both samples are multiphase and contain, in addition to the tetragonal phase $(Sr,Y)_3(Co,Ni)_2O_{6+y}$, a large amount of impurity phases.

The refinement of the crystal structure of $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ was carried out with the GSAS program [7]. The atomic coordinates in the crystal structure of $Sr_2Y_{0.8}Ca_{0.2}Co_2O_6$ [6] were taken as the initial ones. The oxygen atom displacement parameters were refined in the block. Taking into account close atomic scattering factors of the cations Sr^{2+} ($Z = 38$) and Y^{3+} ($Z = 39$), as well as Co ($Z = 27$) and Ni ($Z = 28$), only Y and Co cations were placed in the corresponding positions. The refinement of the structure converged with $R_F^2 = 0.0918$ and $\chi^2 = 1.26$. The presence of the extra (as compared to the stoichiometric composition) oxygen atoms in the structure allowed us to assume that they occupy the 2*a* (0,0,0) position. The occupancy of this position ($g = 0.84$) was calculated based on the iodometric titration data and was not refined. As a result, the residual factors considerably decreased ($R_F^2 = 0.0586$ and $\chi^2 = 1.15$). The theoretical X-ray powder diffraction patterns of $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6+y}$ were calculated for three different oxygen contents ($y = 0$, 0.5, and 1.0). The oxygen content was varied by changing the occupancy of the O(3) position ($g = 0.0$, 0.5, and 1.0, respectively). The calculated X-ray powder diffraction patterns are shown in Fig. 1. The X-ray diffraction patterns show that there is a correlation between the occupancy of the O(3) position and small-angle reflection intensities.

Table 1 presents the crystallographic data for $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$. The final atomic coordinates, site occupancies, and atomic displacement parameters are summarized in Table 2. Selected interatomic distances are listed in Table 3. Figure 2 shows the experimental, calculated, and difference X-ray powder diffraction profiles for $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84(1)}$.

Table 2. Atomic coordinates and isotropic thermal displacement parameters for $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$

Atom	Position	g	x	y	z	U_{iso}, Å^2
Y1	2*b*	1.0	0.0	0.0	0.5	0.035(3)
Y2	4*e*	1.0	0.0	0.0	0.3192(2)	0.026(2)
Co1	4*e*	1.0	0.0	0.0	0.0979(4)	0.024(2)
O1	4*e*	1.0	0.0	0.0	0.196(1)	0.050(4)
O2	8*g*	1.0	0.0	0.5	0.0823(7)	0.050(4)
O3	2*a*	0.84	0.0	0.0	0.0	0.050(4)

Table 3. Selected interatomic distances (Å) in the structure of $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$

Y1–O2 (×8)	2.50(1)	O2 (×4)	2.71(1)
O3 (×4)	2.6836(1)	Co1–O1 (×1)	1.94(2)
Y2–O1 (×1)	2.42(2)	O2 (×4)	1.922(3)
O1 (×4)	2.701(2)	O3 (×1)	1.928(8)

The $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ sample was studied by electron diffraction and high-resolution transmission electron microscopy. Electron diffraction confirmed the correctness of the choice of the space group and unit cell parameters. The electron diffraction image along the [010] direction is shown in Fig. 3. The lack of superstructure reflections points to the absence of ordering of oxygen vacancies in the crystal structure of $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$. The electron diffraction image along the [010] direction and the corresponding Fourier transform of a part of this image are shown in Fig. 4. The crystal structure of the compound $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ is an oxygen-deficient analogue of the structure of the second member of the Ruddlesden–Popper series $A_{n+1}B_nO_{3n+1}$ (Fig. 5). Among cobalt complex oxides, $Sr_3Co_2O_{7-y}$ ($0.94 \le y \le 1.22$) [8] and $Sr_2Ln_{0.8}Ca_{0.2}Co_2O_{6+y}$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, and Y) [9] have the same crystal structure. Oxygen vacancies in the structures of these compounds are located in the plane passing through the axial oxygen atoms linking two neighboring layers of CoO_6 octahedra:

$$\ldots AO\ CoO_2\ AO_{1-x}\square_x\ CoO_2\ AO\ OA\ldots,$$

where A is Sr or Ln and □ is the oxygen vacancy. As a result, the structure has two crystallographically different positions for A cations with the coordination number (CN) 9 and 8 (for the stoichiometry $A_2Co_2O_6$).

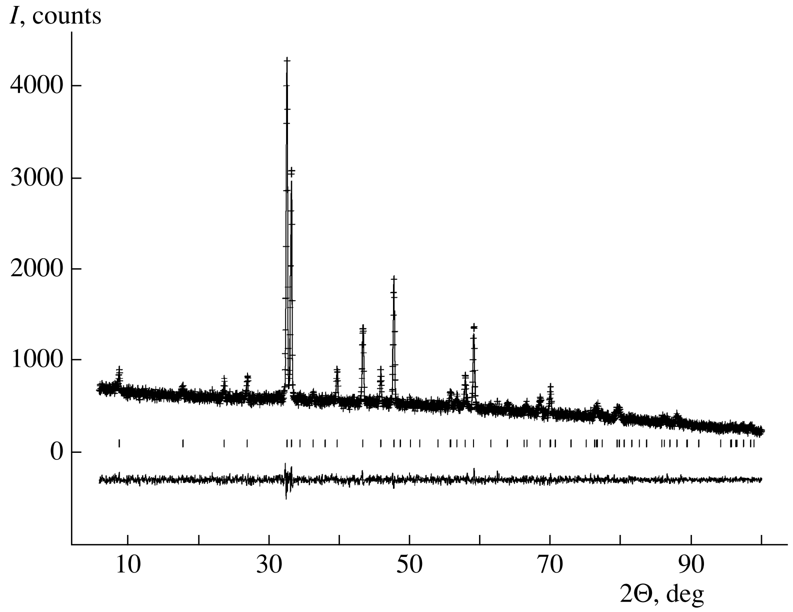

Fig. 2. Experimental, calculated, and difference profiles for $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84(1)}$.

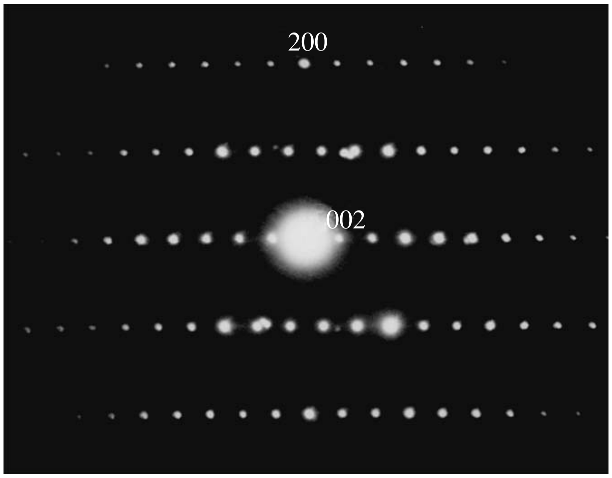

Fig. 3. Electron diffraction image along the [010] direction.

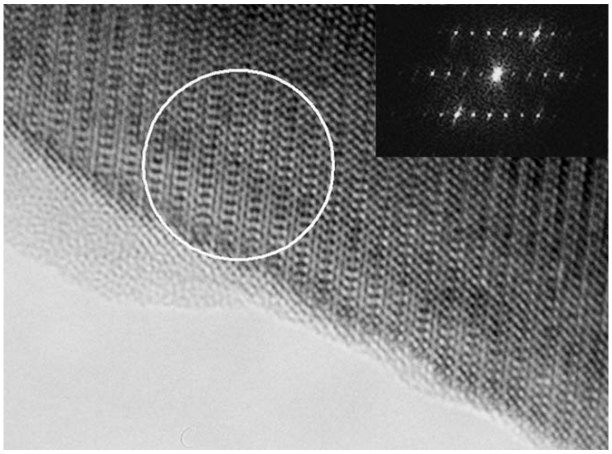

Fig. 4. Electron diffraction image along the [010] direction and the corresponding Fourier transform.

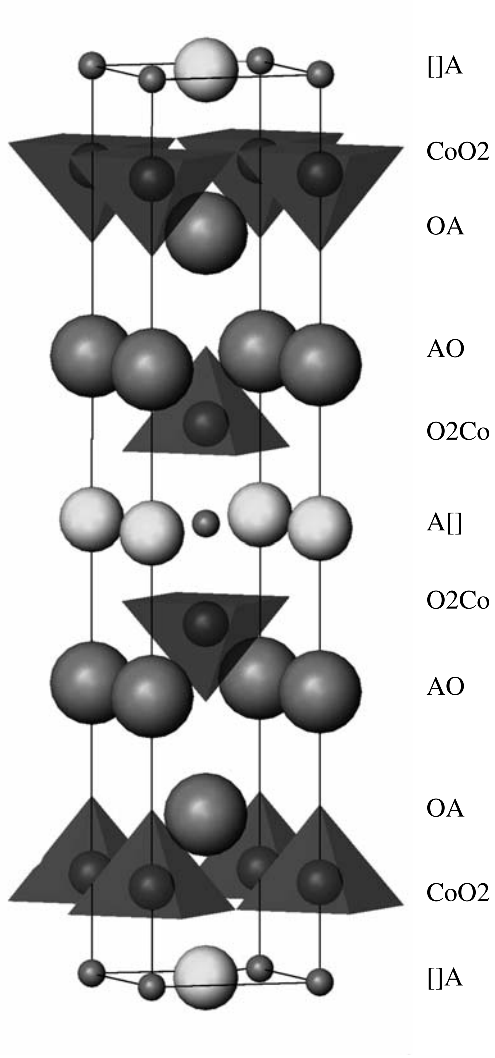

Fig. 5. Crystal structure of the compound $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$.

In particular, positions with the smaller CN (CN = 8) in $Sr_2Y_{0.8}Ca_{0.2}Co_2O_6$ [6] are occupied by small cations Ca^{2+} and Y^{3+}, whereas positions with CN= 9 are occupied by large Sr^{2+} cations. The coordination polyhedron of the cobalt atoms in this case is a square pyramid. In the structure of $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$, only 16% of the oxygen positions are vacant. In this case, only 16% of the Co/Ni cations have a square-pyramidal coordination environment, whereas the rest of the Co/Ni atoms have an octahedral environment. The mean formal oxidation state of Co/Ni in $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ is +3.47. It should be noted that this compound was synthesized in air (p_{O_2} = 0.2 atm) and has a high oxygen content (~7). For example, a close oxygen content (6.79) is achieved in cobaltites $(Sr,Y,Ca)_3Co_2O_{6+y}$ only when the synthesis is carried out under high pressure [6], whereas attempts to increase the oxygen content in $Sr_3Co_2O_{6-y}$ lead to the decomposition of the phase [8]. Lanthanum nickelates $La_2Ni_2^{+2.42}O_{6.92}$ with the structure of the second member of the Ruddlesden–Popper series, synthesized at high temperatures (1200°C) in air [10], have a high oxygen content. It is likely that the high oxygen content in nickel-substituted cobaltite with the structure of $Sr_{2.25}Y_{0.75}Co_{1.25}Ni_{0.75}O_{6.84}$ is caused by the presence of Ni^{3+} for which CN = 6 is stable.

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