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New anion-deficient cubic perovskites: $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$ ($0 \leqslant x \leqslant 0.8$) and $Ba_{2-x}La_xCoInO_{5+\delta}$ ($0.2 \leqslant x \leqslant 0.8$)

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The new compound $Ba_2InCoO_{5+\delta}$, which has a cubic perovskite structure ($a = 4.1587(3)$ Å) at high temperatures, was prepared by heating mixtures of $BaCO_3$, In_2O_3 and Co_3O_4 in air at 1150 °C for 20 h. Heat treatment of $Ba_2InCoO_{5+\delta}$ in air at 850 °C for 72 h revealed a phase transformation into a brownmillerite-type structure. To stabilize a cubic perovskite phase at moderate temperatures, the solid solutions $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0 \leqslant x \leqslant 0.7$ and $Ba_{2-x}La_xCoInO_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ were prepared. X-Ray diffraction revealed that the cubic perovskite structure is stable only for $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0.4 \leqslant x \leqslant 0.6$ and $Ba_{1.2}La_{0.8}CoInO_{5+\delta}$, $Ba_{1.4}La_{0.6}CoInO_{5+\delta}$ upon heat treatment in air at 850 °C for 72 h.

Introduction

An exciting feature of some families of complex transition metal oxides is the ability to conduct oxide ions at elevated temperatures. Oxide conductors are important materials for the construction of SOFCs (solid oxide fuel cells), which are able to directly transform energy of a chemical reaction (*e.g.* $H_2 + O_2$) into electrical energy. Dense membranes made of oxides with both electronic and ionic conductivity are able to separate oxygen without the need for external power and are particularly attractive for syngas production directly from natural gases such as methane. Other applications of oxide ion conducting materials are oxygen sensors *etc.*

One group of oxide ion conductors includes compounds with the perovskite structure. Some of the best perovskite-based oxide ion conductors with negligible electronic conductivity are $La_{0.9}Sr_{0.1}Ga_{1-x}M_xO_{3-\delta}$, M = Mg, In, Al.[1,2] High ionic and electronic conducting perovskites $La_{1-x}Sr_xCo_{1-y}Fe_yO_z$ were first reported by Teraoka *et al.* 10 years ago[3] and now these materials are widely studied as mixed oxide ion conductors.

The oxide ion conductivity in perovskites is normally higher for cubic compounds with disordered oxygen vacancies. All anion positions then have the same energy in contrast to the case of distorted perovskite structures. The decrease in oxide ion conductivity with increasing deviation from cubic symmetry was shown by Ishihara *et al.*[4] for the series $(La_{0.9}Ln_{0.1})_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-y}$, Ln = Y, Nd, Sm, Gd and Yb. Another example is $Ba_2In_2O_5$ which has the brownmillerite structure, a vacancy ordered variant of the perovskite. At $T \geqslant 800$ °C it transforms into cubic perovskite with a random distribution of oxygen vacancies in the structure and the value of conductivity jumps by 2 orders of magnitude.[5] One of the ways to stabilize the cubic form of $Ba_2In_2O_5$ at lower temperature is a partial substitution of indium by other cations, *e.g.* $Ba(Zr_{1-x}In_x)O_{3-y}$.[5]

As was mentioned above there is an interest in materials with mixed ionic and electronic conductivity. Such compounds can be found among complex cobalt oxides with perovskite structure due to the variable oxidation state (from +2 to +4) and easy transition between different coordination environments of cobalt atoms. This makes complex cobalt oxides promising candidates to prepare new highly efficient mixed conductors. Recently a new compound Ba_2ScCoO_5[6] with a cubic perovskite structure and a high concentration of oxygen vacancies has been reported. We have searched for analogues of this phase among cobalt containing double perovskites with another trivalent cation. In the present paper we report the preparation and study of $Ba_2InCoO_{5+\delta}$ having a cubic perovskite structure at high temperature. In order to stabilize the cubic phase at low temperatures, the solid solutions $Ba_2In_{1-x}Co_{1+x}O_5$, $0 \leqslant x \leqslant 0.8$ and $Ba_{2-x}La_xCoInO_{5+\delta}$, $0.0 \leqslant x \leqslant 0.8$ have been prepared.

Experimental

Samples of $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0.0 \leqslant x \leqslant 0.8$ with the step 0.1 and $Ba_{2-x}La_xCoInO_{5+\delta}$, $0.0 \leqslant x \leqslant 0.8$ with the step 0.2 were prepared from stoichiometric mixtures of $BaCO_3$, In_2O_3, Co_3O_4 and La_2O_3 pressed into pellets and annealed in air at 1150 °C for 20–24 h whereafter they were quenched in air. To test the stability of the prepared phases at lower temperatures, the samples were annealed in air at 850 °C for 72 h. Iodometric titration was used to determine the oxygen content in as-prepared samples. About 50 mg of the sample under investigation was placed in a flask containing 20 ml of a 20% water solution of KI. Then, several drops of concentrated HCl were added to the solution. The flask was kept in a dark place until the entire sample had dissolved. The released elementary iodine was titrated by a standard $Na_2S_2O_3$ solution with starch added as an indicator.

Electron diffraction studies (ED) and EDS analysis were carried out with a JEOL JEM 2000 FX instrument operated at 200 kV equipped with a LINK AN 10000 analytical system. Small amounts of the samples were crushed in *n*-butanol and used in the transmission electron microscopy (TEM) studies. A drop of this dispersion was put on a holey carbon film supported by a copper grid.

X-Ray powder diffraction (XRD) patterns were recorded with a FR-552 focusing camera using CuKα_1 radiation and germanium as an internal standard ($a = 5.6574$ Å). X-Ray powder diffractometer data were collected in symmetric transmission mode on a STOE STADI-P powder diffractometer

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equipped with a mini-PSD detector. The refinement of the crystal structures was performed with the CSD program package.[7]

Magnetization measurements were recorded with a SQUID magnetometer (MPMS 2 Quantum Design) as a function of temperature under a magnetic field of 1000 G on field-cooled powdered samples. Susceptibility values were corrected for the diamagnetic contribution.

Results

A single-phase sample of the new compound $Ba_2InCoO_{5+\delta}$ was obtained and reflections on the corresponding XRD patterns were indexed in a cubic unit cell with $a = 4.1587(3)$ Å. The absence of superstructure reflections was confirmed by the ED study, see Fig. 1(a) and (b). This indicates an absence of the ordering also at the scale of individual crystallites. However, the XRD pattern of the sample after annealing in air at 850 °C for 72 h had both additional superstructure reflections at low angles and clearly split perovskite subcell reflections. XRD patterns of $Ba_2InCoO_{5+\delta}$ before (I) and after (II) annealing in air are given in Fig. 2. The latter pattern could successfully be indexed in an orthorhombic cell with $a = 5.9433(4)$, $b = 15.810(1)$ and $c = 5.9872(5)$ Å, indicating the formation of a brownmillerite-type phase. This was also confirmed by ED study as shown in Fig. 3(a) and (b). This phase transformation is not surprising since the low-temperature form of $Ba_2In_2O_5$ is known to crystallize in the perovskite-related brownmillerite structure.[8]

To stabilize the high-temperature cubic phase at moderate temperature the solid solutions $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0 \leqslant x \leqslant 0.7$ and $Ba_{2-x}La_xCoInO_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ were prepared.

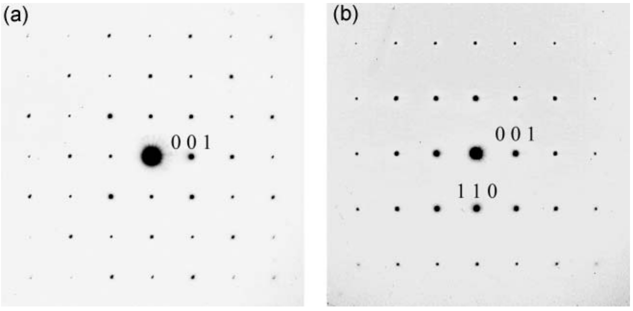

Fig. 1 Electron diffraction patterns for the high-temperature form of $Ba_2InCoO_{5+\delta}$ viewed along (a) [100] and (b) [$\bar{1}$10] confirming the cubic perovskite cell.

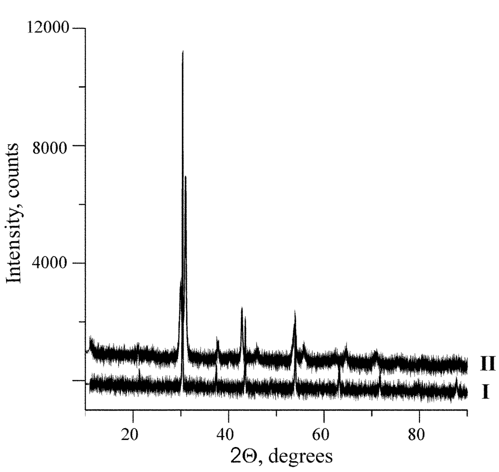

Fig. 2 XRD patterns for $Ba_2InCoO_{5+\delta}$ as-prepared (I) and after (II) annealing in air at 850 °C for 72 h.

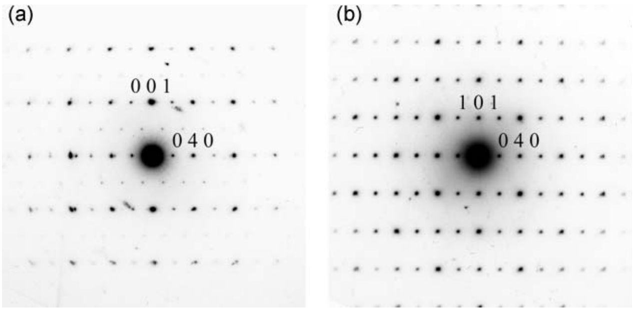

Fig. 3 Electron diffraction patterns for the low-temperature form of $Ba_2InCoO_{5+\delta}$ viewed along (a) [100] and (b) [$\bar{1}$01].

$Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$

XRD patterns of the single-phase samples of $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0 \leqslant x \leqslant 0.7$ with a cubic perovskite type structure were obtained. In the XRD pattern of the $x = 0.8$ sample two additional reflections (max intensity 5%) from admixture phase(s) were found. No superstructure or splitting of the main reflections was observed. The perovskite unit cell parameter for $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ *vs.* composition, shown in Table 1, exhibits a Vegard law behavior (Fig. 4) except for the $x = 0.8$ sample, which is not single phase. The observed decrease of the unit cell parameter with x is expected since the ionic radius of Co^{3+} (0.525 Å, low-spin) is smaller than In^{3+} (0.790 Å)[9]

The iodometric titrations showed that the oxygen contents of the samples change slightly with composition. For example, it was found that oxygen contents of the $x = 0.2$ and $x = 0.7$ samples correspond to the formulae $Ba_2In_{0.8}Co_{1.2}O_{5.20(2)}$ and $Ba_2In_{0.3}Co_{1.7}O_{5.12(2)}$, respectively. The oxidation state of cobalt decreases accordingly from +3.33 to +3.14.

The crystal structures of $Ba_2InCoO_{5+\delta}$, $Ba_2In_{0.3}Co_{1.7}O_{5+\delta}$,

Table 1 Unit cell dimensions of $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ (I) and $Ba_{2-x}La_xCoInO_{5+\delta}$, $0.2 \leqslant x \leqslant 0.8$ (II)

x	a/Å (I)	a/Å (II)
0	4.1587(3)	4.1587(3)
0.1	4.1501(7)	
0.2	4.1459(1)	4.1470(3)
0.3	4.1394(1)	
0.4	4.1330(2)	4.1368(6)
0.5	4.1270(5)	
0.6	4.1218(5)	4.1223(3)
0.7	4.1165(6)	
0.8	4.1061(8)	4.1167(6)

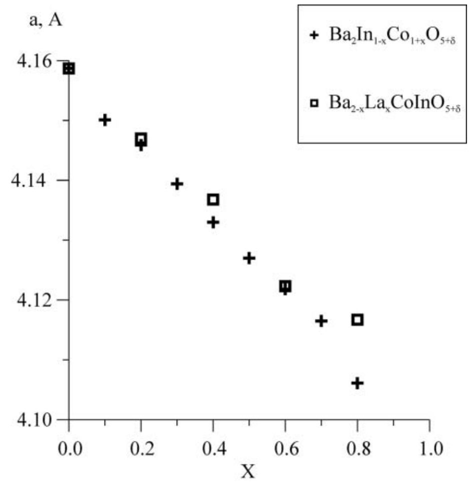

Fig. 4 Unit cell parameter for $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ and $Ba_{2-x}La_xCoInO_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ *vs.* composition.

$Ba_2In_{0.2}Co_{1.8}O_{5+\delta}$ were refined using X-ray powder diffraction data. The In/Co and oxygen occupancies were fixed according to the nominal composition and the values obtained from the iodometric titration of the samples. Refinements ended at the R_I-values of 0.03–0.05. However, high values of the atomic displacement parameters were found (B(Ba) = 2.83(5)–4.5(1) Å^2, B(Co/In) = 3.6(1)–5.2(2) Å^2 and B(O) = 4.6(3)–5.1(4) Å^2). Although there was no splitting, all of the reflections were highly asymmetric. This probably indicates a non-homogeneous distribution of cobalt, indium cations and oxygen vacancies in the crystallites. This is supported by the high values of the atomic displacement parameters for both cations and oxygen, indicating a high level of disorder in the structure, which is caused by a statistical occupation of the B-site by cations having appreciably different sizes ($r(In^{3+}) - r(Co^{3+}) > 0.25$ Å). The high values of the oxygen atomic displacement parameter could also indicate that the Co/In–O–Co/In bond is bent statistically in different directions. Such behavior has been found by Adler *et al.*[10] for $Ba(In_{0.67}Zr_{0.33})O_y$.

The magnetic susceptibility *vs.* temperature for $Ba_2InCoO_{5+\delta}$, $Ba_2In_{0.5}Co_{1.5}O_{5+\delta}$ and $Ba_2In_{0.3}Co_{1.7}O_{5+\delta}$ exhibited a paramagnetic behavior (Fig. 5). However, $1/\chi$ *vs.* T deviates from linear Curie–Weiss behavior. At 300 K the calculated magnetic moments per cobalt atom for $Ba_2InCoO_{5+\delta}$, $Ba_2In_{0.5}Co_{1.5}O_{5+\delta}$ and $Ba_2In_{0.3}Co_{1.7}O_{5+\delta}$ are 3.20, 2.89 and 2.98 μ_B, respectively. This difference cannot only be explained by a decreasing amount of Co^{4+} ($3d^5$, $\mu = 5.91\ \mu_B$) with increasing cobalt content. It could be also due to a variation of the amount of cobalt atoms in tetrahedral (Co^{3+}, high-spin (HS); $e^3t_2^3$, $\mu = 4.90\ \mu_B$) and octahedral coordination (Co^{3+}, HS $t_{2g}^4e_g^2$, $\mu = 4.90\ \mu_B$, low-spin (LS), $t_{2g}^6e_g$, $\mu = 0$ or intermediate spin (IS) $t_{2g}^5e_g^1$, $\mu = 2.83\ \mu_B$). The obtained magnetic moments therefore suggest that the amount of the Co^{3+} (LS and IS) in octahedral coordination increases with increasing cobalt content, x.

The cubic perovskite structure was found to be stable only for $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0.4 \leqslant x \leqslant 0.6$ upon heat treatment in air at 850 °C for 72 h. The unit cell parameters were within 2 e.s.d. of those for the as-prepared samples. On the X-ray pattern of the $x = 0.3$ sample one weak additional reflection was observed indicating that the composition is at the border of the stability range. The samples $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $0.7 \leqslant x \leqslant 0.8$ also contained, together with cubic perovskite phase, lines that can be referred to 2H-$BaCoO_3$. For the compositions $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, $x \leqslant 0.2$ a transformation of the cubic perovskite structure into a brownmillerite related one was observed.

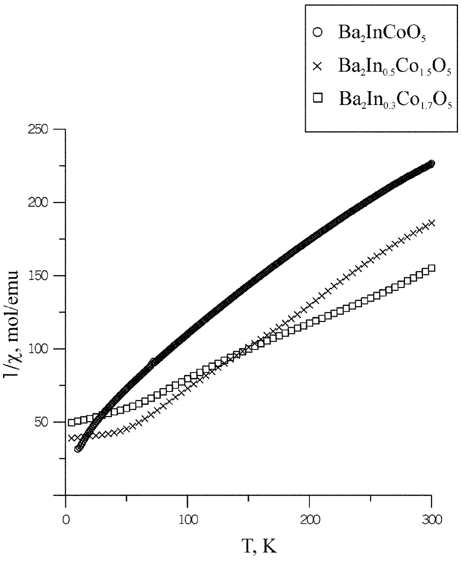

Fig. 5 $1/\chi$ *vs.* T for $Ba_2InCoO_{5+\delta}$, $Ba_2In_{0.5}Co_{1.5}O_{5+\delta}$, $Ba_2In_{0.3}Co_{1.7}O_{5+\delta}$.

$Ba_{2-x}La_xCoInO_{5+\delta}$

The XRD patterns of the $Ba_{2-x}La_xCoInO_{5+\delta}$, $x = 0.2$, 0.4 and 0.6 samples were single-phase, and could be indexed with a cubic cell with no superstructure reflections. The sample $Ba_{1.2}La_{0.8}CoInO_{5+\delta}$ contained together with the cubic perovskite phase about 5% of $La_{1-x}Ba_xCoO_3$. The unit cell parameters for $Ba_{2-x}La_xCoInO_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ are given in Table 1 and shown in Fig. 4. The decrease in the a-parameter of $Ba_{2-x}La_xCoInO_{5+\delta}$, $0 \leqslant x \leqslant 0.8$ with x is expected due to the smaller ionic radius of La^{3+} compared to Ba^{2+} (1.32 and 1.60 Å, respectively).

Annealing of the prepared samples in air at 800 °C for 5 days revealed that compositions $Ba_{1.2}La_{0.8}CoInO_{5+\delta}$ and $Ba_{1.4}La_{0.6}CoInO_{5+\delta}$ remained unchanged while additional broad reflections appeared in the XRD patterns of $Ba_{1.8}La_{0.2}CoInO_{5+\delta}$, and $Ba_{1.6}La_{0.4}CoInO_{5+\delta}$.

Discussion

It is well known that $BaCoO_3$ crystallizes in a 2H-$BaNiO_3$ structure. The structure consists of chains of face-shared octahedra along the c-axis. The stability of the structure depends on the size of the cation inside octahedra. A substitution of Co^{4+} with the larger In^{3+} leads to a high repulsion between two neighboring B-atoms which destabilizes the 2H structure. This can explain the stabilization of the cubic perovskite structure for substituted $BaCoO_3$. Our results show that even a substitution of ≈10% of cobalt by indium leads to a transformation to a cubic perovskite type structure.

However, the cubic perovskite $Ba_2InCoO_{5+\delta}$ is a high-temperature modification and transforms into the brownmillerite structure upon annealing at lower temperature, *e.g.* 850 °C. The brownmillerite structure ($A_2B_2O_5$) can be regarded as oxygen vacancy-ordered perovskite. It consists of layers of corner-shared octahedra separated by tetrahedra. In the low-temperature form of $Ba_2InCoO_{5+\delta}$, octahedral positions are most probably occupied by cobalt while tetrahedral positions are occupied by indium. With a partial substitution of indium by cobalt for $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$, cobalt atoms must enter the tetrahedral sites. However, tetrahedral coordination for Co^{3+} is not favorable, which leads to an instability of the brownmillerite structure in the case of $Ba_2In_{1-x}Co_{1+x}O_{5+\delta}$. This can explain why it is possible to stabilize the cubic perovskite phase by partial substitution of indium by cobalt. Another way to stabilize the cubic perovskite phase is by heterovalent substitution of Ba^{2+} by La^{3+}. To preserve the oxidation state of cobalt around +3 (which is normally stable in the experimental conditions used) it is necessary to increase the oxygen content of the phase. At some value of oxygen stoichiometry, which corresponds to the composition $Ba_{1.4}La_{0.6}CoInO_{5+\delta}$, the brownmillerite structure becomes unstable and this leads to the stabilization of the cubic perovskite phase.

These results demonstrate that high oxygen vacancy concentrations can be stabilised in the doped Ba_2InCoO_5 system, which may lead to useful new oxide ion conductors for SOFC or other applications.

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