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Phase diagram of $SrO–InO_{1.5}–CoO_x$ and a new compound $Sr_3In_{0.9}Co_{1.1}O_6$

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ABSTRACT

$Sr_3In_{0.9}Co_{1.1}O_6$, isostructural to $Ca_3Co_2O_6$, is revealed by the study of the phase relations in the system $SrO–InO_{1.5}–CoO_x$ (1000 °C). The structure of $Sr_3In_{0.9}Co_{1.1}O_6$ is refined by the combination of powder X-ray and neutron diffraction. $Sr_3In_{0.9}Co_{1.1}O_6$ crystallizes in a trigonal lattice with the cell parameters $a=b=9.59438(3)$ Å, $c=11.02172(4)$ Å with the space group *R*-3*c*. Its structure possesses 1D $(In/Co)O_3$ chains running along the *c*-axis constructed by alternating face-sharing CoO_6 octahedra and $(In_{0.9}Co_{0.1})O_6$ trigonal prisms. The co-occupation of In^{3+} and Co^{3+} at the trigonal prismatic site is evidenced by elementary analysis and determined by the structure refinement. $Sr_3In_{0.9}Co_{1.1}O_6$ is paramagnetic, and the susceptibility is consistent with the occupation of Co^{3+} at 10% of the trigonal prismatic positions in a high spin state (HS, $S=2$). The HS Co^{3+} is well separated by diamagnetic CoO_6 octahedra and InO_6 trigonal prisms and shows a *g* factor of 2.0 in the magnetic measurements.

1. Introduction

Hexagonal perovskite related compounds with the general formula $A_3B'BO_6$ have attracted considerable attention due to their interesting structural features and physical properties [1–8]. In this family, A is typically Ca or Sr, and B' and B can be the same, as in $Ca_3Co_2O_6$, or different cations, with B'=Y, Sc, In, Na, Mg, Ni, Cd, Zn, Co, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, and B=Ru, Rh, Ir, Pd, Pt, Cr, Ni, Bi [6]. The structure of $A_3B'BO_6$ consists of infinite chains formed by alternating face-sharing $B'O_6$ trigonal prisms and BO_6 octahedra and each chain is surrounded by six chains separated by the *A* cations. These compounds possess quasi-1D structures in which the interaction within the chains is much stronger than that between the chains. Among them, $Ca_3Co_2O_6$ is a well investigated one [1,3,9–14]. It presents a ferromagnetic ordering of the magnetic Co^{3+} cations along the chains and antiferromagnetic correlations between chains at low temperature. Its magnetization curve displays steps at low temperature, which is considered as the result of interchain frustration. Due to the similar chemistry of Ca^{2+} and Sr^{2+} the larger size of Sr^{2+} accommodates more *B* and/or *B′* cations, so substitution of Ca^{2+} by Sr^{2+} results in a series of $Sr_3B'BO_6$ compounds [6].

In an effort to explore new compounds in the $Sr_3B'BO_6$ family, we focused on the system $SrO–InO_{1.5}–CoO$. In the related systems, no binary compound was revealed in the system $InO_{1.5}–CoO$, and only one compound, $SrIn_2O_4$, with a $CaFe_2O_4$-type structure was reported in $SrO–InO_{1.5}$ [15], while the system $SrO–CoO_x$ was complicated [5,7,16–22], in which $SrCoO_{2.52}$, $Sr_6Co_5O_{15}$, $Sr_5Co_4O_{12}$, $Sr_{24}Co_{19}O_{57}$, $Sr_4Co_3O_9$, $Sr_{14}Co_{11}O_{33}$, and $Sr_3Co_2O_{7-y}$ ($0.94 \le y \le 1.22$ were revealed. $SrCoO_{2.52}$ (JCPDF 40-1018) has an oxygen deficient hexagonal perovskite structure. $Sr_6Co_5O_{15}$, $Sr_5Co_4O_{12}$, $Sr_{24}Co_{19}O_{57}$, $Sr_4Co_3O_9$, and $Sr_{14}Co_{11}O_{33}$ belong to the hexagonal perovskite family Sr_xCoO_3 [6–7,18–22] and $Sr_3Co_2O_{7-y}$ ($0.94 \le y \le 1.22$) is an oxygen-deficient $n=2$ member of the Ruddlesden–Popper phase [23]. These strontium–cobalt complex oxides present various coordination configurations of cobalt, including octahedra, trigonal prisms, and intermediate polyhedra formed from octahedra and trigonal prisms, and accordingly there are a variety of magnetic and other physical properties [5,7,16–23].

This work presents the phase diagram of $SrO–InO_{1.5}–CoO_x$ at 1000 °C. A new ternary compound $Sr_3In_{0.9}Co_{1.1}O_6$, isostructural to $Ca_3Co_2O_6$, is revealed. In the 1D $B'BO_6$ chain formed by face-sharing octahedra and trigonal prisms, octahedral positions are fully occupied by Co^{3+} in the low spin state (LS, $S=0$) and trigonal prismatic positions are occupied by In^{3+} and Co^{3+} in the ratio of 9:1, where Co^{3+} are in the high spin state (HS, $S=2$) and well separated by In^{3+} and Co^{3+} (LS). This compound is paramagnetic due to the 10% occupancy of Co^{3+} (HS) in the trigonal prismatic positions.

2. Experimental

2.1. Materials and preparation

The samples were synthesized by conventional solid state reaction. $SrCO_3$, In_2O_3, and Co_3O_4 of analytical grade were mixed

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stoichiometrically and ground in an agate mortar. The mixture was calcined at 1000 °C under atmosphere for 3–5 days with several intermediate grindings and XRD examination. The samples in and near the SrO–CoO binary line were quenched in air. At the composition n_{Sr}:n_{In}:n_{Co}=3:1:1, a new compound was detected and it was revealed later that the product contained a small amount of $SrIn_2O_4$ impurity. The chemical and structural analysis indicates the new compound has a composition of $Sr_3In_{0.9}Co_{1.1}O_6$ and the experiment at the composition n_{Sr}:n_{In}:n_{Co}=3:0.9:1.1 gave rise to an almost pure phase.

2.2. *Measurement and characterization*

The powder XRD data for phase identification was collected in a Rigaku D/Max 2000 diffractometer using CuK_α radiation (λ=1.5418 Å) at room temperature(25 °C). The elementary analysis was carried out on an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). The sample obtained at the composition n_{Sr}:n_{In}:n_{Co}=3:1:1 was dissolved in 0.1 M HCl with a small amount of insoluble impurity $SrIn_2O_4$ remaining. After filtration, the solution was used for the ICP-AES analysis. Work curves were established in the analysis to calibrate the contents of In and Co. The molar ratio of In/Co in the solution corresponded to that in $Sr_3In_{0.9}Co_{1.1}O_6$. The oxidation state of cobalt in $Sr_3In_{0.9}Co_{1.1}O_6$, +2.98(2), was determined by iodimetric titration.

The powder XRD data used for structure determination was collected on a Bruker AXS D8 Discover X-Ray Diffractometer with CuK_α radiation (λ=1.5418 Å) and a graphite monochromator at the secondary beam. The powder neutron diffraction data was collected on the high resolution powder diffractometer for thermal neutrons (HRPT) of Swiss Spallation Neutron Source SINQ at the Paul Scherrer Institut, Switzerland, with the wavelength 1.494 Å at different temperatures (1.5, 4, 30, 60, 90, 120, 150,180, 210, 240, 270, 298 K). The electron diffraction patterns were taken on a JEOL JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV and a camera length of 150 cm. The magnetic measurements were carried out on a Quantum Design MPMS-SS superconducting quantum interference device (SQUID) magnetometer in the temperature range 2–300 K at 0.1 T.

3. Results and discussion

3.1. *Quasi-ternary phase diagram SrO–InO$_{1.5}$–CoO$_x$*

The quasi-ternary phase diagram SrO–InO$_{1.5}$–CoO$_x$ at 1000 °C under atmosphere is shown in Fig. 1. The cobalt oxide is CoO, under these conditions, and the oxidation state of cobalt varies in other cobalt-containing compounds. $SrIn_2O_4$ is observed in the SrO–InO$_{1.5}$ binary line. In the SrO–CoO$_x$ system, $SrCoO_{2.52}$, $Sr_5Co_4O_{12}$, and $Sr_3Co_2O_{7-y}$ are identified, but $Sr_6Co_5O_{15}$, $Sr_4Co_3O_9$, $Sr_{14}Co_{11}O_{33}$, and $Sr_{24}Co_{19}O_{57}$ were not observed. $Sr_6Co_5O_{15}$ and $Sr_4Co_3O_9$ exist below ~900 and 940 °C, respectively [7,18–21], and $Sr_{14}Co_{11}O_{33}$ and $Sr_{24}Co_{19}O_{57}$ were previously obtained as single crystals grown from a mixture of $SrCO_3$, $CoCO_3$, and KOH in the Sr:Co:K molar ratio 1:1:10 [22]. $Sr_3Co_2O_{7-y}$ is not stable in air. It absorbs water quickly and then transforms to a hydrate phase [23]. With the substitution of Co by In, $Sr_3Co_2O_y$ extends to a solid solution $Sr_3Co_{2-x}In_xO_{7-\delta}$ ($0 \leq x \leq 0.27$) and $Sr_5Co_4O_{12}$ extends to $Sr_5Co_{4-x}In_xO_{7-\delta}$ ($0 \leq x \leq 0.56$).

There are four binary regions (A–D) and seven ternary regions (shown in different symbols) in the phase diagram, as depicted in Fig. 1. A new ternary compound, $Sr_3In_{0.9}Co_{1.1}O_6$, is identified. It exists as a sharp compound instead of a solid solution. The structure and properties of this compound are discussed in the following.

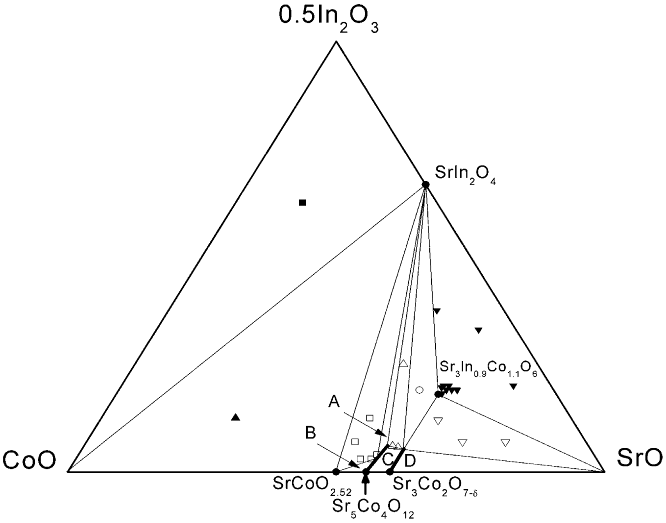

Fig. 1. Phase diagram of SrO–InO$_{1.5}$–CoO at 1000 °C in atmosphere. The two short black lines spreading from $Sr_5Co_4O_{12}$ and $Sr_3Co_2O_{7-\delta}$ indicate the In-substituted solid solution lines $Sr_5In_xCo_{4-x}O_{12}$ ($0 \leq x \leq 0.56$) and $Sr_3Co_{2-x}In_xO_{7-\delta}$ ($0 \leq x \leq 0.27$). Details of the binary phase region are shown in Fig. S1. The characters and symbols in the diagram are: (A) $SrIn_2O_4$+$Sr_5In_xCo_{4-x}O_{12}$ ($0.28 \leq x \leq 0.56$); (B) $SrCoO_{2.52}$+$Sr_5In_xCo_{4-x}O_{12}$ ($0 \leq x \leq 0.28$); (C) $Sr_5In_xCo_{4-x}O_{12}$ ($0 \leq x \leq 0.56$)+$Sr_3Co_{2-x}In_xO_{7-\delta}$ ($0 \leq x \leq 0.27$); (D) $Sr_3Co_{2-x}In_xO_{7-\delta}$ ($0 \leq x \leq 0.27$)+SrO; (■) In_2O_3+CoO+$SrIn_2O_4$; (▲) $SrIn_2O_4$+CoO+$SrCoO_{2.52}$; (□) $SrIn_2O_4$+$SrCoO_{2.52}$+$Sr_5In_xCo_{4-x}O_{12}$ (x=0.28); (△) $Sr_5In_xCo_{4-x}O_{12}$ (x=0.56)+$Sr_3Co_{2-x}In_xO_{7-\delta}$ (x=0.27)+$SrIn_2O_4$; (▽) SrO+$Sr_3Co_{2-x}In_xO_{7-\delta}$ (x=0.27)+$Sr_3In_{0.9}Co_{1.1}O_6$; (○) $Sr_3In_{0.9}Co_{1.1}O_6$+$SrIn_2O_4$+$Sr_3Co_{2-x}In_xO_{7-\delta}$ (x=0.27); (▼) $Sr_3In_{0.9}Co_{1.1}O_6$+$SrIn_2O_4$+SrO.

3.2. *Structure of $Sr_3In_{0.9}Co_{1.1}O_6$*

The indexing of the powder XRD data of $Sr_3In_{0.9}Co_{1.1}O_6$ by PowderX [24] shows a rhombohedral lattice with a=9.59 Å and c=11.02 Å in hexagonal expression, which is confirmed by electron diffraction patterns of a tilt series (Fig. 2). The peaks with $l=2n+1$ of $h-hl$ indices are all absent, indicating the existence of a c-glide; hence the space group R-3c is selected. Since the XRD pattern of $Sr_3In_{0.9}Co_{1.1}O_6$ is similar to that of $Ca_3Co_2O_6$, the atom coordinates of $Ca_3Co_2O_6$ were taken as the initial parameters for $Sr_3In_{0.9}Co_{1.1}O_6$ in the structure analysis. The structure parameters were refined by powder X-ray diffraction data and high resolution neutron diffraction data using the program Fullprof [25]. The Rietveld analysis results by X-ray are summarized in Tables S1 and S2 in the Supporting information. The data collection conditions and the results of Rietveld analysis by neutron data (298 K) are summarized in Table 1. The atomic coordinates, isotropic thermal factors, and occupancies (298 K) are listed in Table 2 and the selected bond lengths and angles are listed in Table 3. The Rietveld refinement plot of neutron data (298 K) is shown in Fig. 3. We also carried out the refinements using anisotropic thermal factors and the results from the neutron data (298 K) are provided in Table S3. The refined results of neutron data at 1.5 K are provided in Tables S4 and S5. The Rietveld refinement plots at 1.5 K, 30 K, and 180 K are provided in Figs. S2–Fig. S4 in the Supporting information. The variation of cell parameters of $Sr_3In_{0.9}Co_{1.1}O_6$ with temperature is listed in Table S6.

From the neutron diffraction data, the positions and the occupancies of oxygen atoms can be accurately determined. The structure refinement indicates that In^{3+} and Co^{3+} are located at the center of the trigonal prisms randomly in a ratio of 0.92(1):0.08(1) and all the octahedral positions are occupied by Co^{3+} atoms, which is consistent with the elementary analysis result n(In):n(Co)=0.91:1.09. It is noteworthy that we did not