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Structure and properties of $(CaOH)_kCoO_2$

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Abstract

We recently discovered two poly-type structural phases of the new cobalt-oxide system, $(CaOH)_{1.14}CoO_2$ and $(Ca_{0.85}OH)_{1.16}CoO_2$. The former phase is an orthorhombic form, while the latter phase is monoclinic one. Both the phases have layered structure that consists of CdI_2-type CoO_2 triangle-lattice layers and rock-salt-type CaOH double-atomic-plane slabs, alternately stacked along the *c*-axis. The two subcells have incommensurate periodicity along the *a*-axis, resulting in a modulated crystal structure. Each structure of the two phases is composed by different stacking manner of the CoO_2 blocks. The monoclinic phase accommodates hole-carriers generated by lattice defects of the Ca ions.

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1. Introduction

Recently, considerable interests have been focused on layered cobalt oxides because of their various unusual physical properties. Unconventional superconductivity found in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ [1] is one of them. It much stimulates our intellectual curiosity because the origin of the superconductivity seems to be associated with rather unusual electron pairing mediated by spin fluctuation. Another example of fascinating characteristic features of layered cobalt oxides is on large thermoelectric power. Unusually large Seebeck coefficients S with small resistivity ρ, resulting in large power factors S^2/ρ, have been reported in some of layered cobalt oxides such as γ-$NaCo_2O_4$ [2] or $Ca_3Co_4O_9$ [3]. These unusual properties seem to be essentially caused by strong electron correlation accompanied with spin frustration on the Co triangle-lattice planes, so that it seems to be very important for progress in solid-state physics to understand mechanism of these unusual quantum phenomena by precisely clarifying physical properties of compounds belonging to the class of layered cobalt oxides.

Stimulated by the current research on layered cobalt oxides, we have tried to search new related materials. The hope is that the search for new compounds will lead to an improved understanding of physics in the cobalt oxides and ultimately to discovery of new anomalous quantum phenomena such as anisotropic superconductivity. In the course of the phase-search experiments, we recently succeeded in synthesizing two new cobalt calcium hydroxides, $(CaOH)_{1.14}CoO_2$ [4] and $(Ca_{0.85}OH_{1.16}CoO_2)$ [5], using a high-pressure technique. Preliminary structure studies using X-ray and electron diffraction revealed that these compounds have different Bravais lattices, an orthorhombic form for $(CaOH)_{1.14}CoO_2$ and a monoclinic form for $(Ca_{0.85}OH)_{1.16}CoO_2$, but they have common structural features that they consists of two sub-lattices, a CdI_2-type CoO_2 lattice and a rock-salt-type double CaOH atomic-layers lattice, and that the two sub-lattices have incommensurate periodicity along the *a*-axis, resulting in a misfit-layered

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structure. It means that the phase mutually relates to each other as a poly-type phase. In order to develop the research on characterization of the two compounds, we very recently analyzed the modulated crystal structure using synchrotron X-ray diffraction data and precisely measured physical properties of the compounds. In this paper, we report on details of the crystal structure, resistivity, and thermoelectric power of the two new cobalt oxides, $(CaOH)_{1.14}CoO_2$ and $(Ca_{0.85}OH)_{1.16}CoO_2$.

2. Experimental

Polycrystalline samples were prepared from solid-state reaction of starting reagents, Co_3O_4, CaO_2, CaO, and $Ca(OH)_2$, using a high-pressure synthesis technique. The orthorhombic and monoclinic forms can be prepared distinctively for each by controlling the starting composition. The orthorhombic phase was made from the starting mixture with molar ratio of Ca:Co:O:H = 1.117:1:3.14:1.049, while the monoclinic phase was made from 1:1:3.333:1.167. The starting reagents with the compositions were mixed using an agate mortar in a glove box filled with dry Ar gas. Each mixture was sealed into a gold capsule, and then heated in a flat-belt-type high-pressure apparatus under 6 GPa at 1200 °C for 1 h, followed by quenching to room temperature before releasing the pressure. The as-grown products were washed in deionized water to remove the small amount of unreacted $Ca(OH)_2$.

Synchrotron X-ray diffraction data were measured on a high-resolution powder diffractometer installed at the BL15XU beam line of SPring-8 with Debye–Scherrer geometry, using a Ge(111) analyzer and a YAP detector. Incident beams from an undulator were monochromatized to a wavelength of 0.8 Å, with inclined Si(111) double-crystal monochromators. The fine-particle powder sample was loaded into a quartz-glass capillary tube (inner diameter 0.5 mm) and was rotated at a speed of about 1.2 cps during the measurement. The diffraction data were collected at room temperature in a 2θ angle range from 3° to 70°, in a step size of 0.005°, and a counting time of 5 seconds per step.

Electrical resistivity was measured from the conventional four-probe alternating current (AC) method using a commercial apparatus (Quantum Design, PPMS). Copper wires were attached onto the polished sample surface via an evaporated gold film using silver paste in order to make a good ohmic contact. An AC current of 0.5–0.01 mA at 60–300 Hz was applied to the sample for the measurement.

The Seebeck coefficient was measured from the PPMS using a thermal transport option (TTO) with the four probe configuration. Data were collected through a continuous mode while cooling at 0.3 K/min. Temperatures at the two temperature/voltage terminals were measured using thermometers (Cernox 1050). The temperature difference between the two terminals was controlled to within 3% of the measurement temperature.

3. Results and discussion

3.1. Structure

The crystal structures of the orthorhombic $(CaOH)_{1.14}CoO_2$ and the monoclinic $(Ca_{0.85}OH)s_{1.16}CoO_2$ were analyzed by the Rietveld method using the synchrotron X-ray diffraction data with a computer program PREMOS [6] on the basis of a superspace-group approach. In advance of the structure refinement, symmetry in superspace was studied using the electron diffraction data reported in Refs. [4,5]. As a result, the superspace groups, Cmca(p00)00s and C2/m(p00)s0, were adopted for the orthorhombic phase and the monoclinic one, respectively. Corresponding symmetry operators in the four-dimensional space are, $(0,0,0,0)+(1/2,1/2,0,1/2)+x,y,z,t$; $x,-y,-z,t$; $1/2-x,y,1/2-z,1/2-t$; $1/2-x,-y,1/2+z$, $1/2-t$; $-x,-y,-z,-t$; $-x,y,z,-t$; $1/2+x,-y,1/2+z$, $1/2+t$; $1/2+x,y,1/2-z,1/2+t$ for Cmca(p00)00s, and $(0,0,0,0)+(1/2,1/2,0,1/2)+x,y,z,t$; $+x,-y,-z,-t$; x, $-y,-z,1/2+t$; $-x,y,z,1/2-t$ for C2/m(p00)s0.

Initial models of the structures were constructed using the structure models proposed by van Smaalen et al. as references; The references were the poly-type phases of $(PbS)_{1.18}TiS_2$ [7,8]. The fundamental structures were determined from preliminary structure refinements. The obtained structure parameters are, $x=y=z=0$, $B=0.5$ (Å^2) for Co; $x=0$, $y=0.3238$, $z=0.0607$, $B=1.0$ for O; $x=0$, $y=0.1092$, $z=0.1697$, $B=1.0$ for Ca; $x=0$, $y=0.0241$, $z=0.2946$, $B=1.0$ for OH in case of the orthorhombic form, and $x=y=z=0$, $B=0.5$ (Å^2) for Co; $x=0.5$, $y=0.1928$, $z=0.1128$, $B=1.0$ for O; $x=0.25$, $y=0.0353$, $z=0.6624$, $B=1.0$, $g=0.85$ for Ca; $x=0.75$, $y=0.0182$, $z=0.6109$, $B=1.0$ for OH in case of the monoclinic form.

Structural modulation was determined from further precise analyses by refining variable Fourier amplitudes of modulation functions for fractional coordinates in superspace within the second order of the harmonics. Resultant R-factors (R_{wp}) of the Rietveld analysis were 0.0714 for the orthorhombic form and 0.0862 for the monoclinic form. Lattice parameters refined were $a_1=2.824(1)$ Å, $b=4.924(1)$ Å, and $c=17.270(5)$ Å with $k_1(=a_1/a_2)=0.576(1)$, *viz.*, $a_2=4.903$ Å, for the orthorhombic form, and $a_1=2.8180(4)$ Å, $b=4.8939(6)$ Å, $c=8.810(1)$ Å, and $\cos(\alpha)=-0.10021(5)$ with $k_1(=a_1/a_2)=0.57828(9)$, *viz.*, $a_2=4.873$ Å, for the monoclinic form.

Fig. 1 is the modulated crystal structures, illustrated using the refined structural parameters. The structures are built up with CoO_2 layers (subsystem-1) and rock-salt-type double CaOH layers (subsystem-2), alternately stacked along the c-axis. The CoO_2 layer is composed of edge-shared CoO_6 octahedra. The Co and O atoms form a triangle lattice for each atomic plane. Stacking manner of the CoO_6 octahedra is different for the two structural forms. Accordingly, the CoO_6 octahedra stack in order of ...*L*–*R*–*L*–*R*... for the orthorhombic form, and stack in order