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X-ray absorption spectroscopy study of parent misfit-layered cobalt oxide $[Sr_2O_2]_qCoO_2$

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ABSTRACT

Here we present a comprehensive X-ray absorption spectroscopy study carried out at Co-$L_{2,3}$, Co-*K*, O-*K* and Sr-*K* edges for the parent misfit-layered cobalt oxide phase $[Sr_2O_2]_{0.52}CoO_2$; comparison is made to another misfit-layered oxide $[CoCa_2O_3]_{0.62}CoO_2$ and the perovskite oxide $LaCoO_3$. A high-quality sample of $[Sr_2O_2]_{0.52}CoO_2$ was obtained through ultra-high-pressure synthesis using $Sr_3Co_2O_6$ and $Sr(OH)_2 \bullet 8H_2O$ as starting materials. Different dosages of $KClO_3$ were mixed with the raw materials as an oxygen source and tested, but it was found that the window for the redox control of $[Sr_2O_2]_{0.52}CoO_2$ is rather narrow. From Co-*K* and Co-$L_{2,3}$ spectra a mixed III/IV valence state is revealed for cobalt in $[Sr_2O_2]_{0.52}CoO_2$, but the average valence value is a little lower than in $[CoCa_2O_3]_{0.62}CoO_2$. Then, Sr-*K* spectrum indicates that the $[Sr_2O_2]$ double-layer block in $[Sr_2O_2]_{0.52}CoO_2$ clearly deviates from the cubic SrO rock-salt structure, suggesting a more complicated coordination environment for strontium. This together with a somewhat low Co-valence value and the fact that the phase formation of $[Sr_2O_2]_{0.52}CoO_2$ required the presence of $Sr(OH)_2 \bullet 8H_2O$ in the high-pressure synthesis suggest that the $[Sr_2O_2]$ block contains –OH groups, *i.e.* $[Sr_2(O,OH)_2]_{0.52}CoO_2$.

1. Introduction

Misfit-layered cobalt oxides [1,2] can be described with the formula $[M_mA_rO_{m+r}]_qCoO_2$ (M=*e.g.* Co, Bi, Pb, Tl; A=*e.g.* Ca, Sr, Ba), where the rock-salt (RS) and CdI_2-type hexagonal (H) sub-blocks stack alternatively along the *c*-axis. Crystallographically, the superspace group developed earlier for misfit-layered chalcogenides could be applied to describe their structures [3]. Incommensurability along the *b*-axis denoted with the misfit-factor q ($\equiv b_H/b_{RS}$) induces structural modulation. Such self-assembled multilayer compounds simultaneously possess good electrical conductivity (σ), mainly through the hexagonal CoO_2 lattice, and low thermal conductivity (κ) as a result of phonon scattering across the two sub-blocks, and are hence promising thermoelectric materials particularly for high-temperature applications, like the related Na_xCoO_2 compound [4]. As the aforementioned general formula of misfit-layered cobalt oxides indicates, the number of layers in the RS slab $[M_mA_rO_{m+r}]$ may be systematically varied (Fig. 1), from single-layer (m=0, r=1) compounds with A=alkali metal through double-layer (m=0, r=2; A=Sr [5,6] or Ca [7,8]) and triple-layer (*e.g.* $[CoCa_2O_3]$ [9,10]) compounds to quadruple-layer compounds (*e.g.* $[Bi_2Sr_2O_4]$ [11]). Accordingly, the misfit-parameter q and the physical properties are changed. Another way to control the properties of these compounds is to adjust their oxygen contents and thereby Co-valence values [12,13].

Among the $[M_mA_rO_{m+r}]_qCoO_2$ phases, the double-RS-layer (m=0, r=2) phases are different from the rest of the known misfit oxides in the sense that they do not form in ambient air but require synthesis routes carried out in an evacuated and sealed quartz tube, in a hydrothermal vessel or under ultra-high pressure [5–8,14]. Synthesis in a sealed quartz tube using SrO_2 as an "internal" oxygen source yielded polycrystalline $[Sr_2O_2]_qCoO_2$ with a commensurate layer stacking, *i.e.* q=0.5, and a monoclinic tilting angle β=96.3°. Minor impurities including $SrCO_3$ and Co_3O_4 were always present giving semiconductive resistivity about two orders higher in magnitude than those of typical misfit-layered cobalt oxides [5]. Single-crystalline $[Sr_2O_2]_qCoO_2$ samples obtained through ultra-high pressure synthesis showed somewhat different results. Electron diffraction analysis revealed an incommensurate structure with q=0.53 and less monoclinic tilting (β=93°). Compared to the room-temperature thermopower value determined for commensurate $[Sr_2O_2]_{0.5}CoO_2$ ($S_{300\ K}\approx 85$ μV/K) [5], the high-pressure-synthesized product gave a slightly lower one ($S_{300\ K}\approx 75$ μV/K) [15]. Finally, the average Co valence determined from the $1/\chi$ – *vs.* – T curve was around +3.0–3.3, *i.e.* lower than expected from the ideal formula of $[Sr_2O_2]_{0.53}CoO_2$.

Misfit-layered cobalt oxides are one of the most promising options among bulk thermoelectric oxides. Nevertheless, except

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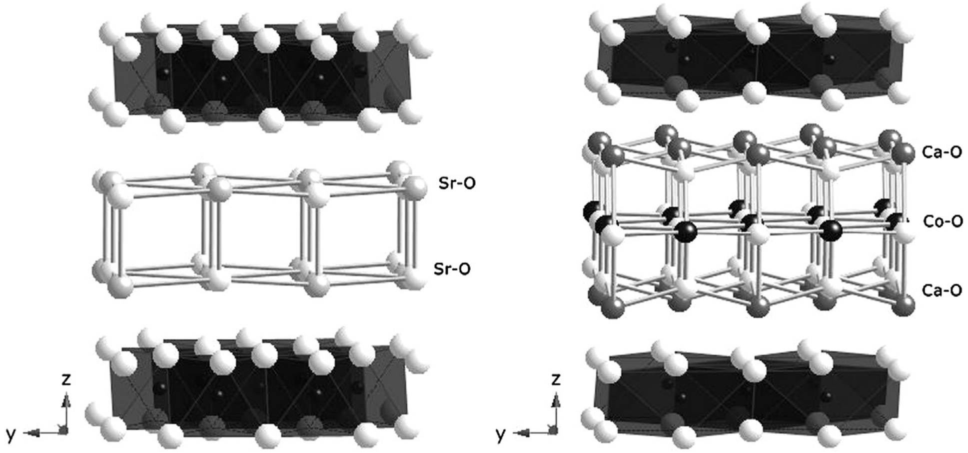

Fig. 1. A schematic illustration of the crystal structures of $[Sr_2O_2]_{0.52}CoO_2$ (left) and $[CoCa_2O_3]_{0.62}CoO_2$ (right), wherein the Sr_2O_2 double-RS-layer and $CoCa_2O_3$ triple-RS-layer blocks, respectively, are sandwiched in between two hexagonal CoO_2 layer blocks.

the impressively high figure-of-merit ($Z \equiv S^2/\rho\kappa$, with S, ρ and κ being Seebeck coefficient, electrical resistivity and thermal conductivity, respectively) values discovered in epitaxial thin films or single crystals at elevated temperatures [16,17], the progress has been halted in these few years. Thus, we have revisited the simplest double-RS-layer phase $[Sr_2O_2]_qCoO_2$ producing it under high pressure and also another well-known misfit-layered cobalt oxide $[CoCa_2O_3]_{0.62}CoO_2$ for comparison. Since the valence of Co in the CoO_2 sub-block determines the transport properties of misfit-layered compounds, we took advantages of synchrotron X-ray absorption spectroscopy (XAS) at different edges to figure out the electronic states and local structures of each of the target atom.

2. Experimental

Oxygen-deficient Ruddlesden–Popper structured $Sr_3Co_2O_6$ was prepared by a citrate-gel process for the precursor for the high-pressure synthesis of $[Sr_2O_2]_qCoO_2$. Stoichiometric amounts of $SrCO_3$, $Co(NO_3)_2$•$6H_2O$ and anhydrous citric acid were dissolved in distilled water and heated at ~100 °C with mild stirring. After removing the organic residues through calcination in air at 600 °C the resultant powder was finely ground and then fired in air at 1000 °C following by quenching to room temperature. Next, in the high-pressure synthesis, the precursor was mixed with $Sr(OH)_2$•$8H_2O$ and $KClO_3$ and sealed in a gold capsule in an Ar-filled glove box. The mixture was compressed and heated in a cubic-anvil high-pressure apparatus at 950 °C and 2 GPa for 30 min and then cooled down to room temperature before releasing the pressure. To remove residual KCl, the product was pulverized and washed with distilled water in an ultrasonic cleanser several times.

Stoichiometric amounts of $CaCO_3$, $Co(NO_3)_2$•$6H_2O$ and anhydrous citric acid were used for synthesizing $[CoCa_2O_3]_{0.62}CoO_2$. The final phase was obtained by sintering in air at 920 °C with an intermittent grinding and pelletizing.

All the samples were first checked by X-ray powder diffraction (PANanalytical X′pert) for phase purity using monochromatized Cu*K*α irradiation. Zero-field and field-cooled magnetic susceptibilities (χ) as a function of temperature were recorded without any and with 1 T magnetic field in the superconducting quantum interference device magnetometer (SQUID; Quantum Design: MPMS-XL5), respectively, between 5 and 300 K. Electron diffraction was carried out in the transmission electron microscope (JEOL JEM-2200FS, acceleration voltage = 200 kV). The specimen was ground and dispersed in pure ethanol and then dropped on a Cu grid. The crystallite was aligned to the incidence electron beam by using a liquid-nitrogen-cooled double-tilt holder.

Soft X-ray absorption spectra were collected at the BL 20 A high-energy spherical grating monochromator (HSGM) beamline in National Synchrotron Radiation Research Center (NSRRC, Taiwan). The incidental photon flux (I_0) was monitored by the gold-coated mesh placed before the entrance of the ultrahigh vacuum (~10^{-10} Torr) chamber. At O-*K* edge, the spectra were recorded in total-fluorescence-yield (TFY) mode by using a microchannel-plate (MCP) detector. However, the Co-*L* spectra were recorded in total-electron-yield (TEY) mode only. Energy resolution was ~0.2 eV in the scanning region and the photon energies were calibrated by using the known absorption features of CoO single-crystal reference located in the light path. Measurements at Co-*K* and Sr-*K* edges were carried out at the BL 01C1 beamline in transmission mode at room temperature. Si (1 1 1) double-crystal monochromators give an energy resolution $\Delta E/E$ better than 2×10^{-4}. All the spectra were then normalized to unity in the absorption coefficient across the edge.

3. Results and discussion

Generally the high-pressure high-temperature synthesis yields products of high densities and accordingly structures with atoms at their highest coordination numbers [18]. Fig. 2 presents X-ray powder diffraction patterns for the Sr–Co–O products obtained with three different cooling rates. The pattern for the quenched sample could be indexed according to the cubic/pseudo-tetragonal cell of $SrCoO_x$ ($x \geq 2.75$) [19]. A *c*-axis-oriented misfit-layered phase was found to exist when the cooling rate was lowered enough, *e.g.* to 15 °C/min. (It should be noted that in order to confirm the absence of phases other than the misfit phase we plotted the full diffraction pattern in log scale; not shown here). A mixture of the two aforementioned phases was found in samples obtained after a rapid cooling to room temperature within a minute. It was moreover found that $Sr(OH)_2$•$8H_2O$ and $KClO_3$ were both needed to be included among the starting materials to develop the misfit-layered structure. The chlorate $KClO_3$ decomposes to KCl and O_2 around 550 °C and provides the excess oxygen needed to oxidize cobalt beyond the trivalent state; the decomposition temperature of $KClO_3$ only slightly depends on pressure within the synthesis conditions we used [20]. The residual KCl is – as has been widely applied in flux growth of single crystals – likely to facilitate the melting, reconstruction of the melt and the uni-axial stacking. Recently we carried out a series of experiments in a Teflon-line