Co-$L_{2,3}$ Edge Soft X-ray Absorption Spectroscopy of Topochemically Oxidized CaCoO$_3$ Thin Films

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Abstract
In this report, we present the characterization of CaCo^{IV}O$_3$ perovskite thin films prepared from the oxidation of CaCo^{III}O$_{2.5}$ brownmillerite films using a NaClO solution. The oxidation state and octahedral coordination of cobalt in CaCoO$_3$ is confirmed by comparing with that of SrCoO$_3$ via Co-$L_{2,3}$ edge soft X-ray absorption spectroscopy.

Keywords: Perovskite, Topochemistry, Cobalt

Background and Purpose

Oxides containing late transition metals with high oxidation states have been a fascinating playground for the study of exotic charge transfers, magnetic and electronic transport properties with notably ferromagnetism in SrCo^{IV}O$_3$, Sr$_2$Co^{IV}O$_4$[1–4] and BaFe^{IV}O$_3$[5] and negative thermal expansion (BiNi^{III}O$_3$, SrCu$_3$Fe$^{IV}_4$O$_{12}$, etc..).[6,7] The electronic structure of materials containing cations with high valence, Fe^{4+}, Co^{4+}, Ni^{3+} and Cu^{3+} is unusual with respect to conventional oxides. The high oxidation state of these small cations leads to unusually low lying partially-filled 3d bands which strongly hybridizes with O2p bands. This results in strong covalent bonds where a negative charge transfer (Δ) from the O2p to the 3d bands can occur resulting in the formation of holes $\underline{L}$ on the ligand so called "ligand-hole". The resulting electronic structure of the cations is considered as Co$^{3+}\underline{L}$ for Co^{4+} or Cu$^{2+}\underline{L}$ for Cu^{3+}.[8–17]

In this study, we investigated the oxidation state of cobalt in CaCoO$_3$ thin films, a perovskite containing the cobalt in the 4+ formal valence. While the bulk form has been reported to be obtainable via high pressure and high temperature synthesis,[18,19] here the perovskite was prepared from the topochemical oxidation of the CaCoO$_{2.5}$ brownmillerite films deposited onto a (LaAlO$_3$)$_{0.3}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT) substrate. The perovskite structure and the oxidation state of cobalt is confirmed by diffraction and soft X-ray absorption spectroscopy at the Co $L_{2,3}$-edge as well as comparison with SrCoO$_3$ films.

Experimental Summary

A polycrystalline target with a nominal composition CaCoO$_{2.5}$ was prepared by solid state reaction. A stoichiometric mixture of CaCO$_3$ (Rare Metallic, 99.99 %), SrCO$_3$ (Rare Metallic, 99.99 %) and Co$_3$O$_4$ (Wako, Practical Grade) was calcined in air at 700 ºC during 12 h for a complete decarbonation. The mixture was finely ground, pressed into pellets and sintered in air at 800 ºC for 24 h. Brownmillerite-type CaCoO$_{2.5}$ films were grown on LSAT (0 0 1) substrates (Crystal Base Co., Ltd.) (cubic, a_p = 3.868 Å) by

pulsed laser deposition (PLD). Deposition was carried out with a KrF excimer laser pulse with a λ = 248 nm wavelength, a 2 Hz frequency and 0.7 J/cm^2 energy density.   During the reaction, the O_2 pressure was kept at 5 Pa and the substrate temperature was set to 650-700 ºC. The film was grown for 20 minutes with a thickness estimated around 100 nm. Next, the films were cooled down to room temperature at a 20 ºC /min rate.

Precursor films were next oxidized by placing them in a NaClO solution (Wako, available chlorine 5.0 %). Oxidation of the films was monitored by a Smart Lab Rigaku Cu Kα X-ray diffractometer (Figure 1). The reaction was considered complete when the lowest angle $(0\ 0\ 1/2)_p$ peak that indicates the stacked octahedra and tetrahedra layers of the brownmillerite structure disappeared. Extinction of this peak suggested the sole presence of octahedral layers and therefore the main presence of a perovskite structure. Longer reaction times did not show difference on XRD patterns.

Oxidation of $SrCoO_3$ films could be achieved in one day as reported in ref. [1]. Once the reaction complete, samples were extracted from the NaClO solution and rinsed with deionized water. The crystal structures of the oxidized films were examined by a Cu Kα X-ray diffractometer (Smart Lab, Rigaku).

The XAS measurements around the Co L-edges were carried out at BL27SU of SPring-8, Japan. The XAS data were collected at 300 K using both surface-sensitive electron yield method and bulk-sensitive fluorescence yield. The energy resolution ΔE at Co L-edges was set to 150 meV.
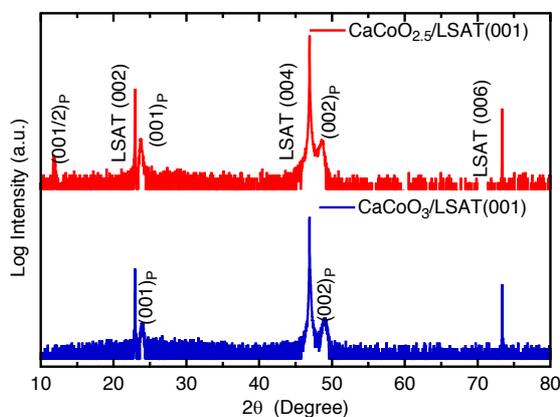

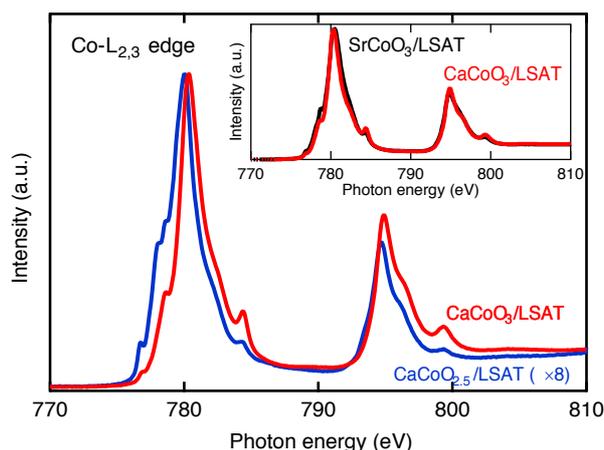Fig. 1. Out of plane XRD patterns of precursor film and after NaClO oxidization at room temperature for 6 days.

Fig. 2. XAS Co-$L_{2,3}$ edge spectra of precursor film and after NaClO oxidization at room temperature for 6 days. The inset compares the spectrum of $SrCoO_3$ and $CaCoO_3$ films.

Results and Discussion

Figure 1 shows the out-of-plane XRD patterns of as-grown $CaCoO_{2.5}$ films on LSAT indexed by (00l) reflections corresponding to the primitive perovskite unit cell ($a \sim 3.74$ Å). Presence of (00l/2) peaks due to the ordered oxygen deficiencies in the octahedra-tetrahedra-octahedra layers sequence of the brownmillerite structure can be observed in agreement with previous reports.[20] The c-axis lattice parameter estimated from the profiles was 14.96 Å (a_p = 3.74 Å), which is comparable to the 14.88 Å (a_p = 3.72 Å) and 14.92 Å values reported in previous thin film and single crystal studies.[20,21] The as-synthesized films were oxidized using a dilute NaClO solution at room temperature. This oxidizing agent was previously used by Ichikawa *et al.* to oxidize $SrCoO_{2.5}$ films to $SrCoO_3$ at RT within one hour.[1] Here, for $CaCoO_{2.5}$ films, six days were necessary to yield a supposed $CaCoO_3$. The longer time in the $CaCoO_{2.5}$ oxidation in comparison to $SrCoO_{2.5}$ (50 minutes)[1] may be due to the smaller ionic radius of Ca^{2+} (134 pm) in comparison to Sr^{2+} (144 pm).[22] Unlike the oxidation of $SrCoO_{2.5}$ which first oxidizes to $SrCoO_{2.87}$ and finally to $SrCoO_3$, no intermediates could be observed for the $CaCoO_{3-x}$ system.

As seen in Fig. 1, the (001) and (002) reflections that could be observed in the brownmillerite phase, remained after oxidation witnessing a topochemical intercalation of oxygen species. The out-of-plane lattice parameter of the obtained phase (3.72 Å) is fairly similar to that of the brownmillerite structure (a_p = 3.74 Å), which again is in marked contrast with the oxidation of $SrCoO_{2.5}$ with an out-plane lattice parameter evolving from 4.0 Å to 3.86Å and finally to 3.82 Å on LSAT.[1] The smaller lattice parameter observed in this case is due to the oxidation of the Co^{3+} to a smaller Co^{4+}.

To confirm the oxidation of the phase, we investigated the valence state of Co in brownmillerite-type $CaCoO_{2.5}$ films and oxidized films using soft-XAS measurements at the Co-$L_{2,3}$ edge (Fig. 2). The two peaks L_2 and L_3 at the Co-L edge originate from transitions of electrons from the Co-2p core-states to hole-states of the d character. The more intensive peak L_3 (2p$_{3/2}$ → 3d transition) is observed at lower

energy (780 eV) with respect to the L_2 peak ($2p_{1/2} \rightarrow 3d$ transition) (796 eV). Comparison of the absorption spectra for $CaCoO_3$ and $CaCoO_{2.5}$ (Fig. 2) reveals a shift of both L_2 and L_3 peaks (~ 0.2 eV) toward higher energy indicative of the oxidation of Co^{3+} to Co^{4+}. To confirm this, we compared the spectra of both $CaCoO_3$ films and $SrCoO_3$ (inset of Figure 2). Both patterns superimpose nearly ideally on one another, which indicates that both phases should be in the same oxidation state (Co^{4+}). Further evidence can be also obtained by observing the lack of difference not only in peak position but also in the shape and shoulders of these peaks that indicate similar local structural (octahedra only) and electronic features (Co^{4+}) for both materials.[23]

Challenges

We showed that the synthesis of $CaCoO_3$ films could be achieved by oxidation of a brownmillerite using a NaClO solution. Understanding the properties of the $CaCoO_3$ thin films will require further studies among which the determination of its genuine magnetic and spin state.

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