STEM Observation and Carrier Transport Properties of Layered Ca$_x$CoO$_2$ Epitaxial Film

K. Sugiura$^1$, R. Huang$^2$, T. Saito$^2$, Y. Ikuhara$^{2,3}$, Y. Ishida$^4$, K. Nomura$^5$, H. Hosono$^{6,7}$, H. Ohta$^1$, and K. Koumoto$^1$

$^1$Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
$^2$Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 466-8587, Japan
$^3$Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan
$^4$RIKEN SPring-8 Center, Hyogo 679-5148, Japan
$^5$ERATO-SORST, JST, in Frontier Collaborative Research Center (FCRC), Tokyo Institute of Technology, Yokohama 226-8503, Japan
$^6$FCRC, Tokyo Institute of Technology, Yokohama 226-8503, Japan
$^7$Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

Introduction
A series of layered cobalt oxides, $A_x$CoO$_2$ ($A$ = Li, Na, Ca etc.), has attracted much attention because of their good thermoelectric performance [1] and the superconductivity in hydrated Na$_{0.3}$CoO$_2$ ($T_c < 5$ K) [2]. Past extensive researches provided with a lot of intriguing electronic/magnetic properties in this system. On the other hand, various ordered structures of interlayer cations between conductive CoO$_2$ layers were suggested. Therefore, one of the most important issue in this system is to verify whether the distribution of the interlayer cation can affect their physical properties. For this purpose, we chose Ca$_x$CoO$_2$ among several layered cobalt oxides because Ca-based cobaltite is chemically stable as compared to Na or Li-based one. This advantage can lead to suitable observation of cation-arrangements by scanning transmission electron microscopy (STEM). Further, we can fabricate high-quality epitaxial film of this Ca$_x$CoO$_2$ by ion-exchange of Na$_x$CoO$_2$ epitaxial film, although bulk single crystals of Ca-Co-O are considered to be very difficult to obtain. Here we report fabrication, structural analysis, and hole transport properties of Ca$_x$CoO$_2$ epitaxial films with two different Ca-sublattice.

Experimental
The high-quality epitaxial films of Ca$_x$CoO$_2$ ($x = 0.33$) were fabricated by the reactive solid-phase epitaxy (R-SPE) [3] method followed by the ion-exchange treatment. First, Na$_{0.8}$CoO$_2$ epitaxial films were fabricated by the R-SPE method [4]. Then, the Na$_{0.8}$CoO$_2$ film was heated at 300°C in air with Ca(NO$_3$)$_2$ powder, which was put on the film directly, to convert the film into Ca$_{0.33}$CoO$_2$ film [5]. Sample observations were performed on a Cs-corrected STEM operating at 200kV (JEM-2100F) equipped with Gatan Enfina EELS system. The electrical resistivity ($\rho$) and Seebeck coefficient ($S$) of the films were measured by the dc four-point probe method in the van der Pauw configuration and a conventional steady state method, respectively, in the temperature range below 400 K.

Results
1. Structural characterization: Only the intense diffraction peaks of 000/$f$ Ca$_x$CoO$_2$ together with 0006 $\alpha$-Al$_2$O$_3$ peak were observed in the out-of-plane XRD pattern, indicating that the film is highly c-axis oriented. Moreover, a step-like structure composed of well-oriented hexagonal domains was clearly observed in the topographic AFM image, indicating high crystal quality of the Ca$_x$CoO$_2$ epitaxial film. The Ca-content, $x$ in the film was evaluated to be Ca$_{0.33}$CoO$_2$ by X-ray fluorescence (XRF) analysis. Cross-sectional HAADF-STEM image along the [1120] zone axis of the film [Fig. (c)] reveals that Ca-sublattice is $\sqrt{3}a \times \sqrt{3}a$ hexagonal ordered structure as illustrated in Fig (e). After the thermal annealing of the film, dramatic change of Ca-sublattice structure was observed keeping the Ca content. The in-plane XRD pattern revealed that Ca-sublattice is $2a \times \sqrt{3}a$ orthorhombic structure as illustrated in Fig. (d). These results indicate that two types of Ca$_{0.33}$CoO$_2$ epitaxial films with different Ca-arrangements were successfully fabricated in spite of the same Ca-doping concentration.
2. **Carrier transport properties**: Figure (a) shows the temperature dependence of $\rho$ for the Ca$_{0.33}$CoO$_2$ epitaxial films with different Ca-arrangements. Typical metallic conductivity was observed in the $\sqrt{3}a \times \sqrt{3}a$ hexagonal Ca-arranged film. The $\rho$ value increases proportionally to $T^2$ below ~140 K likely due to electron-electron interaction, while it is saturated ($\sim 10^{-3}$ $\Omega$cm) [inset of Fig. (a)]. Thus, degenerate Fermions dominate the hole conduction below 140 K, though correlated hopping is dominant above 140 K. On the other hand, the $2a \times \sqrt{3}a$ orthorhombic Ca-arranged film exhibits insulating behavior. The slope of log $\sigma$ - $T$ curve was proportional to $-1/3$ below ~300 K, suggesting that the variable-range-hopping-like conduction is dominant at low temperatures, while it was $-1$ above ~300 K, suggesting that the nearest-neighbor-hopping-like conduction is dominant at high temperatures. This mechanism clearly suggests that the random potential barriers are formed near the valence band edge, resulting in localization of holes from itinerant state. This is likely due to random distribution of Ca-vacancies because the occupancy of Ca-site in the orthorhombic Ca-arrangement is only $\sim 66\%$, though that in the hexagonal one is $100\%$. The present results clearly demonstrate that Ca-distribution of Ca$_x$CoO$_2$ affects not only crystallographic symmetry but also electron transport significantly.

**Summary**

We herein demonstrated that the distribution of Ca-ions sandwiched by two conducting CoO$_2$ layers significantly affects hole transport properties by using high-quality epitaxial films of Ca$_{0.33}$CoO$_2$ with different Ca-arrangements. The present result strongly suggests that a design of the interlayer is essential to understand a lot of strange physical properties and to improve thermoelectric performance in the series of cobaltites.

**References**


---

**FIG.** (a) Temperature dependence of $\rho$ for the Ca$_{0.33}$CoO$_2$ epitaxial films. Inset shows the $\rho$ - $T^2$ curve of the metallic film. The HAADF-STEM images of Ca$_{0.33}$CoO$_2$ films (b: as-prepared, c: annealed at 400°C). Ca-ordered structure corresponding to each image is also shown (d,e).