Thermoelectric properties and crystal structures in layered Co oxides

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Polycrystalline samples were prepared by a conventional solid-state reaction method. Appropriate amount of starting from a mixture of CaCO3 (99.9%) and Co3O4 (99.9%) powders were mixed with an agate mortar and pressed into pellets. The pellets were calcined in air at 920 ℃ for 12h and sintered at 920 ℃ for 24h under pure flowing oxygen gas. The samples were furnace cooled to room temperature, ground and pelletized again. This process was repeated three times in order to obtain well-crystallized single-phase sample. In addition, one of the obtained well-crystallized single-phase samples were annealed in pure flowing Ar gas at 740 ℃ for 48h and then quenched in distilled water to control oxygen nonstoichiometry δ. In this work, we prepare two samples: "Sample A" and "Sample B". The former is the obtained well-crystallized single-phase sample, and the latter is the annealed sample to control oxygen nonstoichiometry δ in reduction atmosphere.

Neutron powder diffraction (ND) data were collected at room temperature using a Kinken powder diffractometer for the high-efficiency and high-resolution measurements (HERMES) of Institute for Materials Research (IMR), Tohoku University, installed at a JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI). The ND data were collected on thoroughly ground powders in a multiscanning mode in the 2 θ range from 3.0 to 153.9 °with a step width of 0.1 °.The incident neutron beam was monochromatized to a wavelength of 1.8205 Å.The XRD and ND data were simultaneously analyzed using a Rietveld refinement program PREMOS 91 designed for modulated structure analyses. We adopt a superspace group of C2/m(1p0)s0 because the CdI2-type [CoO2] subsystem has a C2/m symmetry, whereas the RS-type BL subsystem has a C21/m symmetry. The crystal structures and interatomic distance plots were obtained using the PRJMS and MODPLT routines, respectively; both are included in the PREMOS 91 package.

Figure 1(a) shows the observed, calculated and difference intensities of the HERMES data for Sample A. Short vertical lines below the patterns indicate the peak positions of the main (upper) and satellite (lower) reflections of the two subsystems. The final Rwp factor is 5.37 % and the lattice parameters are refined to a = 4.83353(4) Å, bCoO2 = 2.82380(7) Å, c = 10.8455(3) Å and β = 98.141(5) °for the [CoO2] subsystem and bRS = 4.55757(8) Å for the RS-type BL subsystem. The resulting p = bCoO2/bRS = 0.61958(5) ～0.62 corresponds to the structural formula [Ca2CoO3.08]0.62CoO2.

The crystal structure of Sample B was also analyzed in a similar manner. Figure 1(b) shows the observed, calculated and difference intensities of the HERMES data for Sample B. Short vertical lines below the patterns indicate the peak positions of the main (upper) and satellite (lower) reflections of the two subsystems. The final Rwp factor is 4.69 % and the lattice parameters are refined to a = 4.83804(6) Å, bCoO2 = 2.82533(1) Å, c = 10.86027(2) Å and β = 98.135(8) °for the [CoO2] subsystem and bRS = 4.55128(9) Å for the RS-type BL subsystem. The resulting p = bCoO2/bRS = 0.62077(6) ～0.62 corresponds to the structural formula [Ca2CoO3.08 − δ]0.62CoO2.

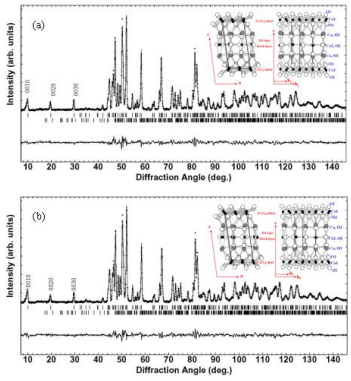

Fig. 1. Fig.1 Observed, calculated and difference intensities of powder ND data for (a) Sample A and (b) Sample, respectively.The inset is the final crystal structure.