

Thermoelectric properties and crystal structures of chemically-modified layered thermoelectric materials

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Since the discovery of large thermoelectric power in the layered compounds, misfit-layered cobalt oxides particularly have attracted much interest as candidates for thermoelectric (TE) materials. We have employed a high-resolution neutron powder diffraction technique to investigate the modulated crystal structure of $[(\text{Ca}1-x\text{Pb}x)_2\text{CoO}_3]_{0.62}\text{CoO}_2$ polycrystalline samples. The solubility limit of Pb was determined on the basis of powder X-ray diffraction (XRD) intensities at room temperature using a JEOL JDX-3530 diffractometer ($\text{CuK}\alpha$). Neutron powder diffraction (ND) data were collected at room temperature using the Kinken powder diffractometer for high efficiency and high resolution measurements (HERMES) of Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai. Neutrons with a wavelength of 0.18265 nm were obtained by the 331 reflection of the Ge monochromator. The ND data were collected on thoroughly ground powders by a multiscanning mode in the 2θ range from 3.0° to 153.9° with a step width of 0.1° and were analyzed using a Rietveld refinement program, PREMOS 91, adopting a superspace group of $\text{C}2/m(1p0)s0$, where the CdI_2 -type $[\text{CoO}_2]$ subsystem has $\text{C}2/m$ symmetry while the RS-type BL $[\text{Ca}_2\text{CoO}_3]$ subsystem has $\text{C}21/m$ symmetry. The crystal structures and interatomic distance plots were obtained with the use of PRJMS and MODPLT routines, respectively; both were implemented in the PREMOS 91 package. Figure 1 shows Co1-O (upper panels) and Co2-O (lower panels) distances in the $[\text{CoO}_2]$ subsystem and the RS-type subsystem of (a) $x=0$ (left) and (b) $x=0.02$ (right) plotted against t . Among

these bonds, two apical Co2-O3 bonds are fairly shorter than the other four equatorial Co2-O2 bonds, ranging from 0.17 to 0.195 nm for $x=0$ and from 0.165 to 0.19 nm for $x=0.02$. The mean distance of Co2-O3 bonds for $x=0$ does not change very much as that of Co2-O3 bonds for $x=0.02$, i.e., both distances are 0.18 nm. This fact indicates that the Co ions in the RS-type subsystem are not replaced by tetravalent lead ions in the x range from 0 to 0.02. On the other hand, the four equatorial Co2-O2 bonds for $x=0$ (lower left panel) show small modulation amplitudes from 0.205 and 0.275 nm, relative to the $x=0.02$ (lower right panel) of 0.18 and 0.3 nm. However, the mean distances of the Co2-O2 bonds of the two phases are almost equal, i.e., 0.24 nm. In contrast to the Co2-O bonds, the six Co1-O1 bonds illustrated in the upper panels remain stable with increasing x , where the mean distance of the Co1-O1 bonds is 0.19 nm.

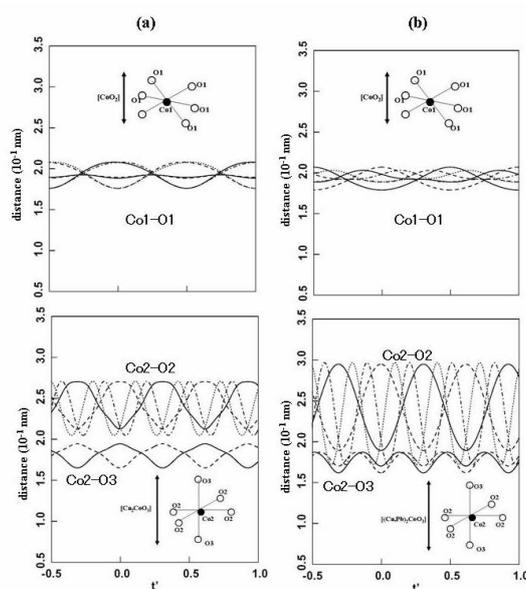


Fig. 1. Co1-O distances in the $[\text{CoO}_2]$ subsystem and Co2-O distances in the RS-type subsystem.