High temperature thermoelectric properties of oxygen-deficient $Ca_3Co_4O_9$

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Since the discovery of large thermoelectric power in the layered compounds $NaCo_2O_4$ and $Ca_3Co_4O_9$,[1-4] misfit-layered cobalt oxides particularly have attracted much interest as candidates for thermoelectric (TE) materials. The structural formula becomes $[Ca_2CoO_3]_{0.62}CoO_2$. Such an incommensurate modulation induces periodic positional displacement of constituent ions. Among the first nearest ionic bonds, Co-O bonds in the RS-type BL have the most significant modulation in this compound. Shimoyama *et al*.[5] have reported that some oxygen sites become deficient in the RS-type BL upon heating by which the chemical formula becomes $[Ca_2CoO_{3-\delta}]_{0.62}CoO_2$, where the oxygen deficiency, δ, changes from 0 to 0.14 and should preferentially occur at sites where the Co-O bonds are highly modulated. Sugiyama *et al*.[6] have presented that $[Ca_2CoO_{3-\delta}]_{0.62}CoO_2$ indicates the existence of two magnetic transitions at around T_{SDW} = 100K and T_{SS} = 400 ~ 600K; the former is a transition from a paramagnetic state to an incommensurate spin-density wave (SDW) state. The latter is a transition of the spin state (SS) of Co ions, i.e., the populations of the low-spin (LS), intermediate-spin (IS), and high-spin (HS) states are most likely to vary gradually with increasing temperature above T_{SS}^{end}=380K. However, detailed study of the temperature dependence of the transition and its effect on the Co valence, which is controlled by the partial substitution for Ca ions and/or the oxygen deficiency, δ have not been reported. Recently, we have studied the modulated crystal structure of divalent Pb ion doped $Ca_3Co_4O_9$ polycrystalline samples.[7] In this study, we have employed a high-resolution powder neutron diffraction technique to investigate the weak modulated crystal structure of oxygen-deficient $Ca_3Co_4O_9$ polycrystalline samples. As shown in Fig.1, we have measured the electrical resistivity of both $Ca_3Co_4O_9$ and oxygen-deficient $Ca_3Co_4O_9$ samples in temperature range from 80 K to 900 K. We will also discuss the Seebeck coefficient, the modulation of the atomic positions and the magnetic susceptibilities in order to investigate the valence state of Co ions.

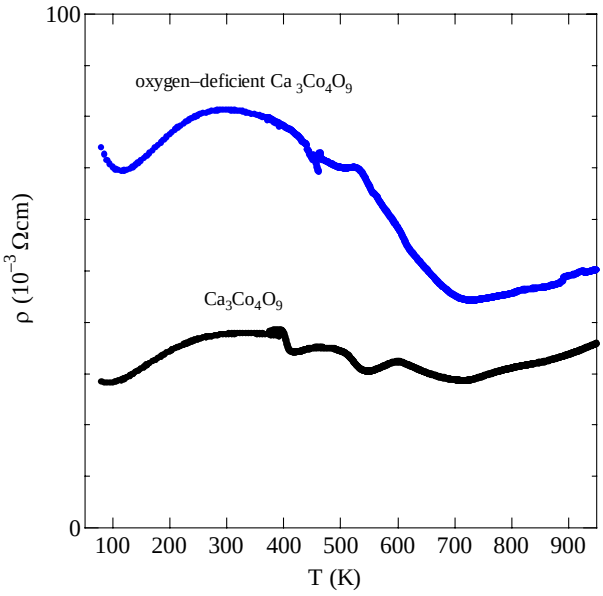

Fig.1 Temperature dependence of electrical resistivity.

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