SUMMARY OF Ph.D. DISSERTATION

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Title

Electronic Structure and Physical Properties in Layered Co Oxides A_xCoO_2 (A=Na, Pd)

Abstract

Layered Co oxides A_xCoO_2 (A is an alkaline metal or a transition metal, and x is a composition ratio) exhibit exotic features due to A site atoms, such as thermoelectric behaviors of Na_xCoO_2 (A=Na). However, the origins of the physical properties of these materials have not been studied. We used a combined computational-experimental approach from the electronic point of view. The purpose of this study is to make clear the physical nature of A_xCoO_2 (A=Na, Pd) for explaining the relationship between the electronic states and their thermoelectric properties.

In Chapter 1, the relation between the intrinsic inhomogenity and thermoelectric properties in layered Co oxides and the purpose of this study are described. In Chapter 2, the electronic states and physical properties of Na_xCoO_2 are described. We investigated transport properties of Na_xCoO_2 with the effects of the A-site ion potentials on charge disproportionation of Co ions. We found anomalous magnetoresistive effects (MR) in several Na(x)–modified samples synthesized in our NaOH-flux methods. The x=0.5 and 1.0 samples show negative MR, –10% and –45% respectively, though there are no negative MR in any other samples. We performed the electronic structure calculation with LDA+U method considering the various Na arrangements and found that length of the Co–Na bond determines the valence states of Co ions. In Chapter 3, the electronic states and physical properties of $PdCoO_2$ are described. $PdCoO_2$ shows canonical metallic conduction without any electron correlation effects. However we found that the Co onsite Coulomb repulsion energy of $PdCoO_2$ is 4~5eV indicating strong electron correlation from XPS and cluster calculations. We found the electronic states around the Fermi-level mainly consist of Pd4*d* orbital from the valence band analysis. This result indicates that Pd4*d*-electron screen the electron correlation effects on the CoO_2 layers. In Chapter 4, the thermoelectric properties of Na_xCoO_2 calculated from the electronic states are described. We calculated the thermopower of Na_xCoO_2 from the electronic structure and the Boltzmann transport equation. Our calculation indicated that the carrier densities of Na_xCoO_2 are in the range of $1\sim3\times10^{22}cm^{-3}$ coincided with experimental data taken from the thermopower and the Hall measurements. We also investigated the non-rigid-band effect on the thermoelectric properties and found that the slight compression (0.9%) in the direction of c-axis of the CoO_2 layers lead to increase the thermopower of Na_xCoO_2 by 45%. Chapter 5 gives the conclusion of this study and offers future prospects.

In conclusion, we explained the origins of the physical properties of A_xCoO_2 (A=Na and Pd) and the relationship between the electronic states and their thermoelectric properties. Our results contribute to the improvement of the thermoelectric performance in layered Co oxides.