

Electronic structure and the thermoelectric power of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Na}_{0.6}\text{CoO}_2$ layered cobalt oxides

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Angle resolved photoemission spectroscopy (ARPES) was performed on the two different layered cobalt oxides, $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Na}_{0.6}\text{CoO}_2$. The energy-momentum dispersion was clearly observed in ARPES spectra, indicating the presence of extended and coherent Bloch states, and consequently the Boltzmann-type electrical conduction. The Electronic structure near the Fermi level (E_F) in these Co oxides was consisting of the a_{1g} and e'_g bands from the CoO_2 layers. Making full use of electronic structure, we succeeded in qualitatively accounting for mechanism of the metallic electrical conduction with the large thermoelectric power: the large thermoelectric power is caused by the large electronic density of states at 100-200meV below E_F (van Hove singularity in e'_g), while the metallic conduction is brought about by the a_{1g} band.

Effect of Rare Earth-Doping on the thermoelectric Properties of ZnO

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We investigated the effects of doping of rare-earth ions (Ce, Pr, Nd, Sm, and Er) on the thermoelectric properties of ZnO, especially Seebeck coefficient. The samples were prepared by a wet sol-gel process: mixed aqueous solution of zinc acetate and rare-earth metal chlorides with the molar ratio of 0.4 % was hydrolyzed at room temperature; the recovered mixed hydroxide was washed and calcined at 500 °C, followed by sintering at 1400 °C for 10 hrs. The Seebeck coefficient and electric conductivity were measured as a function of temperature ranging from 100 °C to 800 °C. For reference, Al-doped ZnO samples with Al content of 0.1 – 0.4 % were also prepared and measured in the same way. The data were scattered more or less depending on the doping species, but it was commonly found that the rare-earth doped samples showed higher Seebeck coefficients with compared to those for Al-doped samples. The microscopic texture of the rare earth samples was also investigated and will be discussed in relation to the transportation properties.

Thermoelectric power performances of different transition-metal oxides at high temperature

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This work points towards the possible interest of LaCoO_3 phases for high T application due to its high Seebeck coefficient. Also, a sign change of the thermoelectric (TE) power was induced by tetravalent substitutions at the A- or B-site. This opens a new route to generate n- and p-type legs starting from the same oxide containing Co^{3+} . But, thermoelectric measurements at high T indicate that, independently of the S sign and value, S reaches a lower value of $\sim 80\mu\text{V.K}^{-1}$ for all at $T > 400\text{K}$. This is related to the Co^{3+} spin state transitions towards HS which is completed at 500K and leads to a metallic behavior. Migiakis et al. have reported for $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$ a $ZT(300\text{K}) \sim 0.02$ close to those obtained for NaCo_2O_4 . This result has motivated us to study the $\text{PrCo}_{1-x}\text{Ni}_x\text{O}_3$ series. The best performance, low resistivity ($0.02\Omega\text{.cm}$) and high S value ($\sim 140\mu\text{V.K}^{-1}$), has been obtained for $x=0.10$ at RT. But, at higher T, due to the spin state transition of the Co^{3+} , S decreases demonstrating the limitation for these perovskite cobaltites at high T. Some explanations will be given about the origin of those Seebeck coefficient temperature dependences in relation with the spin state dependence of Co^{3+} and the coordinence.

Crystal structure and thermoelectric properties of Pb doped $\text{Ca}_3\text{Co}_4\text{O}_9$

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Layered cobaltites have attracted much interest since the discovery of large thermoelectric power in NaCo_2O_4 . Several layered cobaltites have been discovered and all of these compounds possess a CdI_2 -type CoO_2 sheet in their structures, which is considered to be an essential constituent for realizing good thermoelectric performance. Various kinds of structural components called block layers can be inserted between the CoO_2 sheets to stabilize the structure of cobaltites and to supply charge carriers into the CoO_2 sheets. We have prepared Pb-substituted samples of $[(\text{Ca}_{1-x}\text{Pb}_x)_2\text{CoO}_3]_{0.62}\text{CoO}_2$ ($0.02 \leq x \leq 0.06$) and determined their crystal structure by a (3+1)-dimensional superspace group approach. In this study, the crystal structures were analyzed using a Rietveld analysis program PREMOS based upon the x-ray diffraction patterns. The thermoelectric power, the four-probe dc resistivity, and magnetic susceptibility were measured using a ResiTest8300 and a SQUID magnetometer (MPMS). By the Pb substitution, the modulation of Co-O distances in the $[\text{CoO}_2]$ subsystem of $x=0.03$ markedly decreased relative to that of $x=0.02$, whereas such a modulation amplitude in the $[\text{Ca}_2\text{CoO}_3]$ subsystem of $x \geq 0.04$ fairly increased.