

THERMOELECTRIC PROPERTIES OF COBALTITE THIN FILMS – FROM BASICS TO APPLICATIONS

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The interest in thermoelectric materials that can convert waste heat into electricity is steadily growing. A new avenue for fundamental and application-oriented research on metal-oxides has recently been established by advances in the synthesis of epitaxial thin films, heterostructures, and multilayers with tailored lattice structure and electronic density of states. The potential of such systems for research on thermoelectricity is just beginning to be recognized. Material parameters to be optimized for applications are combined to a figure of merit, ZT , for the thermoelectric performance ($ZT = S^2 \sigma T / \kappa$, with S being the thermopower (also called Seebeck coefficient), σ the electrical and κ the thermal conductivity) which should be as large as possible as, at least larger than unity for practical applications. Amongst the best thermoelectric oxides found so far, the layered cobaltites including Na_xCoO_2 , Sr_xCoO_2 , Ca_xCoO_2 as well as $\text{Ca}_3\text{Co}_4\text{O}_9$ play a prominent role. Especially, the incommensurate misfit layered cobalt oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ has been extensively studied in single crystalline and bulk polycrystalline forms and substantially less as thin films. Theoretical activities until now have been concentrated more on calculations of the Seebeck coefficient and much less on than thermal conductivity or ZT . There are two different approaches to explain the high Seebeck coefficient of the cobaltites. One is based on first principles band structure calculations in combination with standard Boltzmann transport theory, where correlation effects are neglected in a first approximation. The other one employs the Hubbard model, the paradigmatic model for strongly correlated systems.

Our experimental work has been motivated by the excellent thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ as well as its remarkable thermal and chemical stability at high temperatures. The crystal structure of $\text{Ca}_3\text{Co}_4\text{O}_9$ is monoclinic with the alternate stacking of CdI_2 -type CoO_2 layers and two-dimensional triangular lattice rock-salt-type Ca_2CoO_3 layers with a distorted square lattice along the c -axis. Additionally, it is the only cobaltite with the Co ion in different valence states for two adjacent layers. Using conventional pulsed laser deposition techniques we have grown ultrathin $\text{Ca}_3\text{Co}_4\text{O}_9$ single layer films in the thickness range of 20nm to 150nm on various substrates such as SrTiO_3 , MgO and Al_2O_3 and characterized them by X-ray diffractometry, as well as charge- and entropy transport measurements from room temperature up to 700°C . We found that our films are stable in oxygen environment at least up to 700°C and show for those grown on SrTiO_3 a thickness dependent Seebeckcoefficient, S , up to $700 \mu\text{V/K}$ resulting in a powerfactor of $4.5 \times 10^{-3} \text{ W/mK}^2$. Films grown on MgO and Al_2O_3 show values for S of about $150 \mu\text{V/K}$ to $200 \mu\text{V/K}$ and nearly thickness independent powerfactors of $(0.2 - 0.4) \times 10^{-3} \text{ W/mK}^2$. The results are discussed with respect to strain related effects due to lattice mismatch as well as interface related electronic reconstructions.