

Transport phenomena in the non-stoichiometric oxide δ - Na_xCoO_2

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Abstract

Recently, there is strong interest in developing novel thermoelectric materials for energy conversion. In this context the highly anisotropic cobalt oxide Na_xCoO_2 exhibits promising thermoelectric properties. Thermoelectric properties are characterised by the figure of merit ZT with the absolute temperature T and $Z = S^2/\sigma$ with the electrical conductivity σ . Seebeck coefficient S and the thermal conductivity κ . In spite of intense effort in the past materials with ZT of the order of 2 or higher are still awaited. Due to a Seebeck coefficient of $150 \mu\text{V/K}$, an electrical conductivity of 300 S/cm in combination with low thermal conductivity 1.2 W/mK the non-stoichiometric oxide Na_xCoO_2 may be considered an alternative to the conventional high temperature thermoelectric materials for power generation. Advantages to the state-of-the-art material PbTe from a manufactures point of view are the low specific weight, the lower environmental hazards, ability of metallurgic processing of the material and oxidation stability. Besides the potential for an application in power generation Na_xCoO_2 exhibits most interesting transport phenomena subject to the Na non-stoichiometry. Depending on composition and reaction temperature four different phases are known: δ - Na_xCoO_2 ($0.9 < x < 1$), δ' - Na_xCoO_2 ($x = 0.75$), δ'' - Na_xCoO_2 ($0.55 < x < 0.6$) and δ''' - Na_xCoO_2 ($0.55 < x < 0.74$). All phases differ significantly in their thermoelectric properties. This paper focuses on the correlated transport properties of δ - Na_xCoO_2 featuring a still rising Seebeck coefficient while the electrical conductivity is already dominated by bipolar effects representing the breach with the classic understanding based on a simple two-band model. The transport of spin entropy contributing to a high Seebeck coefficient will be discussed as well as the potential to expand the temperature range beyond extrinsic conductivity representing the classic limit of the band model for thermoelectric energy conversion.