Enhanced Thermoelectric Performance at the Superionic Phase Transitions of Mixed Ion-Electron Conducting Materials

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Abstract

The quality of a thermoelectric material is judged by the size of its temperature dependent thermoeletric-figure-of-merit (zT). Superionic materials, particularly Zn_4Sb_3 and Cu_2Se, are of current interest for the high zT and low thermal conductivity of their disordered, superionic phase. In this work it is reported that the super-ionic materials Ag_2Se, Cu_2Se and $Cu_{1.97}Ag_{0.03}Se$ show enhanced zT in their ordered, normal ion-conducting phases. The zT of Ag_2Se is increased by 30% in its ordered phase as compared to its disordered phase, as measured just below and above its first order phase transition. The zT's of Cu_2Se and $Cu_{1.97}Ag_{0.03}Se$ both increase by more than 100% over a 30 K temperatures range just below their super-ionic phase transitions. The peak zT of Cu_2Se is 0.7 at 406 K and of $Cu_{1.97}Ag_{0.03}Se$ is 1.0 at 400 K. In all three materials these enhancements are due to anomalous increases in their Seebeck coefficients, beyond that predicted by carrier concentration measurements and band structure modeling. As the Seebeck coefficient is the entropy transported per carrier, this suggests that there is an additional quantity of entropy co-transported with charge carriers. Such co-transport has been previously observed via co-transport of vibrational entropy in bipolaron conductors and spin-state entropy in $Na_xCo_2O_4$. The correlation of the temperature profile of the increases in each material with the nature of their phase transitions indicates that the entropy is associated with the thermodynamcis of ion-ordering. This suggests a new mechanism by which high thermoelectric performance may be understood and engineered.

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