# Effect of morphology and microstructure on the thermal conductivity of chalcogenide thermoelectric materials

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# Summary

In this thesis, I have investigated the structure and morphology of some typical thermoelectric materials and their effects on the performance of these materials. In our world, the energy crisis and environmental pollution are two major problems that people need to address. Thermoelectric materials have received a lot of attention in this respect due to their ability to convert directly between heat and electricity, while doing so in a pollution-free, highly reliable and maintenance-free manner.

In this thesis four materials, $Pb_{0.49}Ge_{0.51}Te$, $Pb_{1-x}Te$, $Cu_2S$, and $Cu_{2+x}X_{0.01}Se$, are synthesised by high-temperature solid-state methods with controlled cooling procedures. The main purpose is to regulate the Seebeck coefficient and thermal conductivity by controlling the structure and morphology of the materials, with the ultimate goal of improving the thermoelectric performance and increasing the prospect of application of the materials.

Chapter 1 provides an introduction to the thermal effects involved, the factors that influence the performance of thermoelectric materials, and it also reviews the state of the art regarding several promising materials. The second chapter provides an introduction to the preparation and characterization methods used to investigate the materials in this thesis.

In Chapter 3, the focus is on regulating the effect of phase separation phenomena and how this influences the thermal conductivity of $Pb_{0.49}Ge_{0.51}Te$. It is shown that phase separation can be controlled by the cooling procedure used from the liquid phase during sample preparation. The PbTe-GeTe system undergoes spinodal decomposition, leading to a complex microstructure comprised of Ge- and Pb-rich domains. The changes in microstructure that occur are investigated from the beginning to the end of the spinodal

decomposition process using a combination of X-ray diffraction, scanning electron microscopy and transmission electron microscopy to precisely analyze the structure and morphology of the materials as well as to determine the elemental compositions of different domains.

In Chapter 4, non-stoichiometric $Pb_{1-x}Te$ single crystals with several different morphologies, as well as polycrystalline material with the same composition, are grown by the rapid cooling of liquid-phase Pb-Te in vacuum. Previous studies of PbTe have almost exclusively focused on stoichiometric samples, thus the fact that Pb-deficient $Pb_{1-x}Te$ can be stabilised provides greater scope and more options for optimizing PbTe-based thermoelectric materials.

In Chapter 5, the same simple method of rapid cooling from the melt is used to stabilize $Cu_2S$ samples containing both monoclinic and tetragonal phases. The precise cooling procedure used determines the microstructure and distribution of the two phases, which in turn has a significant influence on the thermal conductivity. The stability and thermoelectric properties of these mixed-phase samples are investigated.

In Chapter 6, copper selenide samples with rhombohedral symmetry and containing an excess of Cu ($Cu_{2+x}Se$, where x = 0.12 to 0.15) are obtained by rapid quenching from high temperature. It is shown that doping with the rare-earth elements Gd, Ho and Yb improves the Seebeck coefficient and thus the ZT value by energy band engineering. In particular, the power factor $S^2/\rho$ is greatly enhanced in the region below 400 K, leading to room temperature thermoelectric performance that promises to be at least as good as $Bi_2Te_3$, the best material known for this temperature range.

In summary, this thesis provides new insight into how the cooling procedure and rate during the material preparation process can be used to control the chemical composition and microstructure of systems that tend to segregate into different chemical and/or structural phases. This is an effective way to influence the thermal conductivity and hence to further optimize various materials with excellent thermoelectric performance.