Summary PhD thesis

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"Structural, chemical, and thermoelectric properties of Bi_2Te_3 Peltier materials: bulk, thin films, and superlattices"

Thermoelectric materials are used for power-generation and solid-state refrigeration devices. At room temperature, Bi_2Te_3 bulk materials are widely used Peltier materials since they are known for their large thermopower, large electrical conductivity, low thermal conductivity, and thereby a high thermoelectric figure of merit $ZT = 1$ at $T = 300$ K. The research on thermoelectric materials is based on solid state physics which predicts that it is difficult to improve one transport coefficient without changing the others in an unfavourable way. The reason is that the transport coefficients are determined by common fundamental parameters of the electron and phonon systems.

A new approach to an increased thermoelectric figure of merit are nanostructured materials. Thermoelectric quantum well systems based on Bi_2Te_3 were proposed by Hicks and Dresselhaus in 1993. In 1999, Venkatasubramanian manufactured Bi_2Te_3/Sb_2Te_3 superlattices [artificial nanostructure (ans)] with a period of 6 nm and a spectacular thermoelectric figure of merit of $ZT > 2$. The ans yielded a reduced lattice thermal conductivity which was attributed to a reduction of the phonon mean free path due to the structural disorder introduced by the ans. The ans showed a significantly increased ZT compared to bulk materials and was a boost for the synthesis of nanostructured materials for thermoelectric applications.

In Bi_2Te_3, in the literature there are a large number of published measurements of transport properties, a small number of structural analyses, however no data of combined measurements. It is still an open question, why the lattice thermal conductivity of bulk Bi_2Te_3 is so small. Preliminary investigations by transmission electron microscopy (TEM) yielded a structural modulation [natural nanostructure (nns)] with a wavelength of 10 nm in bulk Bi_2Te_3. In this work, the nature of the nns was analysed and the correlations to the transport coefficients, particularly the lattice thermal conductivity, is discussed.

Transmission electron microscopy combined with energy dispersive X-ray spectrometry is the method of choice for a study of the correlations between structure, chemical composition, and physical properties in thermoelectric materials. Particularly, stress fields and chemical compositions can be analysed at an unrivalled lateral resolution, a high sensitivity, and a high accuracy. In this work, experimental methods will be presented for the first time, yielding an accurate quantitative analysis of the chemical composition and of stress fields in Bi_2Te_3 and in compounds with similar structural and chemical microstructures.

This work can be subdivided as follows: (I) *N*-type $Bi_2(Te_{0.91}Se_{0.09})_3$ and *p*-type $(Bi_{0.26}Sb_{0.74})_{1.98}(Te_{0.99}Se_{0.01})_{3.02}$ bulk materials synthesised by the Bridgman technique, which are used in commercially available Peltier devices. (II) Bi_2Te_3 thin films and $Bi_2Te_3/Bi_2(Te_{0.88}Se_{0.12})_3$ superlattices epitaxially grown by molecular beam epitaxy (MBE) on BaF_2 substrates with periods of 6-12 nm at the Fraunhofer-Institut für Physikalische Messtechnik (IPM). (III) Experimental methods, i.e., TEM specimen preparation, high-accuracy quantitative chemical analysis by EDX in the TEM, and image simulations of dislocations and the nns according to the two-beam dynamical diffraction theory.

The striking microstructural feature is the presence of a structural modulation (nns) in *n*-type and *p*-type Bi_2Te_3 bulk materials, in Bi_2Te_3 thin films, and $Bi_2Te_3/Bi_2(Te,Se)_3$ superlattices.

Therefore, the nns is of general character for Bi_2Te_3 materials. The nns was analysed in detail by stereomicroscopy and by image simulation and was found to be a pure sinusoidal displacement field with (i) a displacement vector parallel to <5,-5,1> and an amplitude of about 10 pm and (ii) a wave vector parallel to {1,0,10} and a wavelength of 10 nm. The results obtained here showed a significant amount of stress in the samples, induced by the nns which was still not noticed and identified. The stress fields directly affect the lattice thermal conductivity in particular.

Both kinds of nanostructures, artificial (ans) and natural (nns) nanostructures, yielded in thermoelectric materials a low lattice thermal conductivity which was beneficial for the thermoelectric figure of merit *ZT*. The reason is a reduction of the phonon mean free path due to the structural disorder introduced by the ans and the nns. The ans and the nns are the key to an increased *ZT* after several decades of stagnancy, and therefore are currently a main topic of research and application.