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Nanostructured Telluride based Thermoelectric Materials

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Thermoelectric materials are promising candidates to tackle the problem of CO_2 emissions, when their efficiency is increased. Strategies to increase the figure of merit (ZT) for thermoelectric materials, include nanostructuring of the materials to reduce the thermal conductivity significantly. In this contribution we present recent results on two different important nanostructured materials, i.e. nanostructured Bi and Se double substituted GeTe (already known as phase change material, PCM) and superlattices of Bi_2Te_3/Sb_2Te_3.

Tellurium based PCM have a small band gap and a low thermal conductivity. Additionally, PCM´s are known to form complex nanostructures which make them ideal candidates for the application as thermoelectric materials [1]. To be able to control and understand the influence of the nanostructuring is an essential step in order to further reduce the thermal conductivity of these materials and hence to increase the ZT value.

$[GeTe]_{0.962}[Bi_2Se_{0.2}Te_{2.8}]_{0.038}$ and $[GeTe]_{0.937}[Bi_2Se_{0.2}Te_{2.8}]_{0.063}$ powder samples have been synthesized and compacted by spark-plasma sintering (SPS). Both samples were heat cycled. The high ZT value of $[GeTe]_{0.962}[Bi_2Se_{0.2}Te_{2.8}]_{0.038}$ remained stable but for the $[GeTe]_{0.937}[Bi_2Se_{0.2}Te_{2.8}]_{0.063}$ the ZT dropped from high to moderate ZT values after the first heating cycle due to a degradation of the electrical conductivity.

HRTEM micrographs have been recorded before and after the heat treatments of the $[GeTe]_{0.937}[Bi_2Se_{0.2}Te_{2.8}]_{0.063}$ specimen in order to identify real-structure property co-relationships. Before the heat treatments two major effects appearing on different length scales were noticed. Firstly, the precession electron diffraction (PED) measurements show a splitting of the reflections. Simulations show that the splitting is either due to a 91.3° rotation of domains or the formation of non-merohedral twins with a mirror plane along the {101} plane (figure 1a-c). Secondly, observed stripe like Moiré fringes appear on small nanometer sized areas in an ordered GeTe matrix (figure 1d). Preliminary simulations of the Moiré contrast indicate that the stripe like fringes rather arise from a change in the lattice constant than due to a rotation and/or translation of different GeTe grains. It is believed that the change of the lattice constant is due to an agglomeration of $Bi_2(SeTe)_3$. After the heat treatments the stripe like Moiré fringes vanished and planar defects were observed and also indicated via diffuse scattering in the FFT pattern (see figure 2) [1].

Artificial superlattices of Bi_2Te_3/Sb_2Te_3 as reported by Venkatasubramanian lead to a significant increase of the ZT value [2] with respect to bulk materials. However, the superlattice structure of Venkatasubramanian and thus the high ZT values have not been reproduced, in this form yet. In cooperation with the Fraunhofer IPM we show a similar superlattice structure prepared with the so-called nanoalloying approach [3] and report about the reproducibility of the thermoelectric performance.

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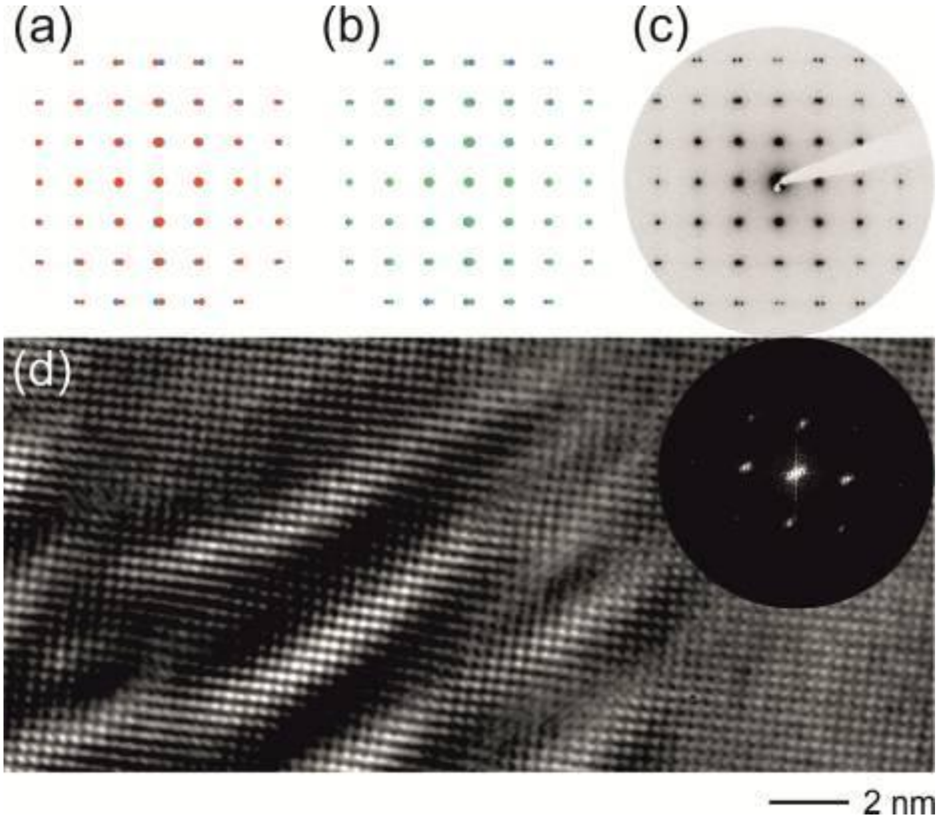

Figure 1. PED and Fourier filtered HRTEM micrograph of $[GeTe]_{0.937}[Bi_2Se_{0.2}Te_{2.8}]_{0.063}$ before the heat treatments. PED pattern of the sample shows a splitting of the reflections (c). Simulations indicate that the splitting is either due to a 91.3 ° rotation of different grains (a) or a twinning with a mirror plane along the {101} plane (b). HRTEM micrographs (d) show a stripe like Moiré contrast. The inset represents the corresponding FFT.

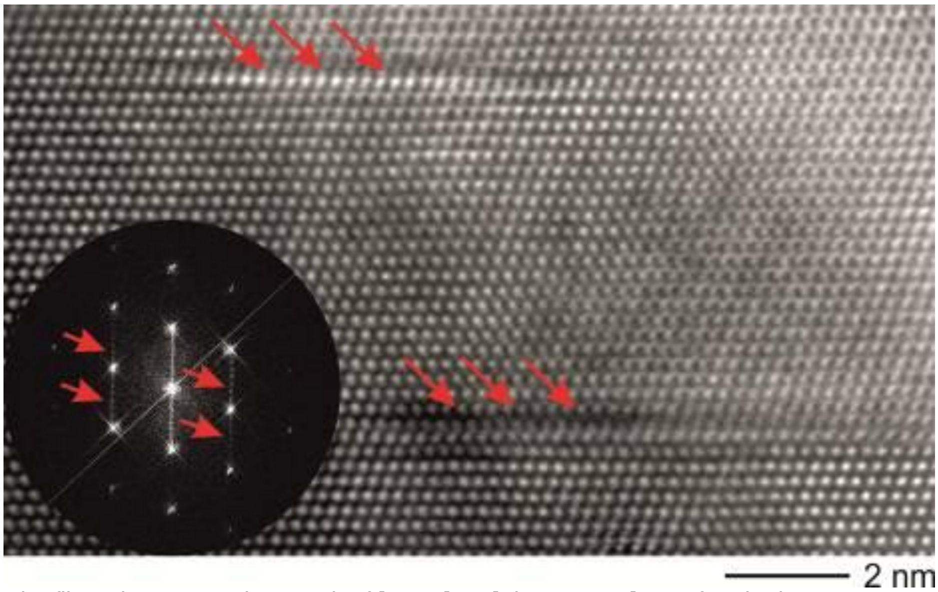

Figure 2. Fourier filtered HRTEM micrograph of $[GeTe]_{0.937}[Bi_2Se_{0.2}Te_{2.8}]_{0.063}$ after the heat treatments. Red arrows indicate planar defects. The inset represents the corresponding FFT. The diffuse intensities are due to the planar defects observed in the HRTEM micrograph [1].