Chemical Synthesis of Anisotropic Nanocrystalline Sb₂Te₃ and Low Thermal Conductivity of the Compacted Dense Bulk

Wenzhong Wang¹, *, Xiao Yan², Bed Poudel², Yi Ma², Qing Hao³, Jian Yang², Gang Chen³, and Zhifeng Ren², *

¹ College of Physics and Electrical Engineering, Central University for Nationalities, Beijing 100081, P. R. China
² Department of Physics, Boston College, Chestnut Hill, MA 02467, USA
³ Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

We describe a one-step, one-pot non-aqueous route for the synthesis of Sb₂Te₃ nanocrystals with hexagonal shape and highly anisotropic nanostructures. The as-prepared nanostructures were characterized by XRD, TEM and HRTEM. The effect of the stabilizers on the nanocrystal morphology has been discussed in detail. We have studied the thermal conductivity of the compacted bulk from the Sb₂Te₃ nanostructures. The results indicated that a very low thermal conductivity of about 1 W/mK at 300 K, comparing to 4.7 W/mK of the polycrystalline bulk, was achieved. The results indicated that nanostructured Sb₂Te₃ is potentially a good candidate for engineered nanocomposites that can lead to high thermoelectric figure-of-merit.

Keywords: Chemical Synthesis, Anisotropic Nanostructures, Antimony Telluride Thermal Materials.

The experimental investigations and theoretical calculations have recently suggested that if thermoelectric (TE) materials could be made on the nanoscale, their dimensionless figure-of-merit (ZT) should increase dramatically. Such high ZT materials would make TE coolers and power generators attractive in practical applications. Thus, there is a growing interest in nanostructured thermoelectric materials to improve ZT using the nanoscale size effect. In general, ZT is determined by several factors: thermopower, electrical and thermal conductivities, and absolute temperature. Increasing experimental results suggest that a good strategy is to use interfaces in nanostructures to reduce phonon thermal conductivity while maintaining the electron power factor. Anisotropic nanostructures, which are usually formed by self-assembly of individual preformed crystalline nanoparticles, may provide an alternative route to increase the phonon interfaces scattering, therefore leading to a lower thermal conductivity. Antimony telluride (Sb₂Te₃) belongs to layered semiconductors with tetradymite structures. This compound is often used with Bi₂Te₃ to form the best thermoelectric materials for near room temperature TE applications. Therefore, for exploring nanostructured thermoelectric materials with high ZT.

Here we report a one-step, one-pot non-aqueous synthesis of highly anisotropic Sb₂Te₃ nanostructures. This approach offers some advantages, for example, it does not require controlled removal of the protecting shell formed by the organic stabilizer before obtaining the desired anisotropic nanostructures.

In a typical synthesis, 10 mmol of SbCl₃ were first dissolved into 90 mL of ethanol completely, with the help of continuous stirring, following by adding appropriate amount of polyvinyl pyrrolidone (PVP) (MW: 130000), 15 mmol of Te powder, and 20 mmol of NaBH₄, and stirring for 10 min. The mixtures were transferred into a Parr reactor, sealed and kept at 200 °C for 24 h. The black precipitates were collected and washed with ethanol and distilled water for the characterizations of X-ray diffraction (XRD, Cu Kα, Bruker AXS), scanning electron microscope (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDS).

Figure 1 shows the typical 2-theta XRD pattern of the as-prepared Sb₂Te₃ anisotropic nanostructures in the presence of 0.90 mmol PVP (calculated by repeat unit of PVP). The diffraction pattern is well matched, not only at peak...
positions, but also peak intensity with that of rhombohedral Sb$_2$Te$_3$ structure (JCPDS No. 71-393, R-3m).

Figure 2 shows the TEM images of the Sb$_2$Te$_3$ nanostructures prepared with different amounts of surface modifier and assembling agent PVP (0.45, 0.90, and 2.7 mmol for Figures 2(a–c), respectively). The rod-like nanostructures with a diameter of about 60 nm are obtained at low PVP concentration (0.45 mmol, Fig. 2(a)). By increasing the amount of PVP to 0.90 mmol, the chain-like nanostructures are formed, and the diameter decreased to about 20 nm. A further increase of the PVP amount to 2.7 mmol leads to a significant diameter reduction to about 5 nm. Interestingly, a small fraction of the anisotropic nanostructures is branched, hereafter called multipod. Figure 2(d) shows a typical TEM image of one of the anisotropic multipods. The diameter of each of the three arms is slightly different.

Figure 3 shows the HRTEM images of the as-prepared Sb$_2$Te$_3$ anisotropic nanostructures. In these images, several common features of oriented attachment growth mechanism are observed, such as dislocations and misorientations. Figure 3(a) shows the HRTEM image of an individual Sb$_2$Te$_3$ anisotropic nanostructure. It is clearly shown that the nanostructure is formed by several particles...
of different sizes. The lattice planes of the particles are almost perfectly aligned through the contact area. However, a careful examination indicates that the nanostructure is not formed by perfectly oriented attachment of the nanoparticles. Two small misorientation areas are observed as shown by the white ellipses. The spacing of 0.316 nm corresponds to the (015) planes of Sb$_2$Te$_3$. Figure 3(b) shows an HRTEM image of the junction area of a tripod nanostructure. One can see that particles, as shown by I and II, form a rod-like structure. There is no observable misorientation in the lattice fringes throughout the whole nanorod, indicating that the nanorod is formed by an almost perfectly oriented attachment of two nanoparticles. A small misorientation is observed in the contact area between particle III and nanorods as shown by the white ellipse. In addition, some other complicated anisotropic nanostructures are shown in (c) (more than 3 branches) and (d) (C-like shape) of Figure 3.

When other stabilizers, such as hexadecyltrimethyl ammonium bromide (CTAB), were used, hexagonal nanoplates, shown in Figures 4(a) (SEM image) and 4(b) (TEM image), were obtained instead of anisotropic nanostructures. We also found that the concentration of the PVP had a great effect on the size of the nanostructures. Therefore, we conclude that PVP plays at least two important roles in the formation of anisotropic Sb$_2$Te$_3$ nanostructures. First, PVP serves as a stabilizer to prevent the particles from aggregating to larger particles. Second, the PVP serves as an “assembler” to induce the formation of Sb$_2$Te$_3$ anisotropic nanostructures through an effective adsorbing in a crystallographically specific manner. This is done to modify the oriented attachment mechanism by preventing contact between faces on which adsorption has occurred selectively, although the exact interaction between PVP and Sb$_2$Te$_3$ nanoparticles is still unclear.

All bulk 100% dense samples were compacted by hot pressing the respective particles using a Direct Current induced hot press.

Figure 5 shows the thermal conductivity of Sb$_2$Te$_3$ samples with different sizes and morphologies. Line A shows the thermal conductivity of Sb$_2$Te$_3$ anisotropic nanostructures prepared by using organic molecule PVP as size and structure controlling agent, and line B shows the thermal conductivity of Sb$_2$Te$_3$ hexagonal nanoplates synthesized by using cation surfactant CTAB as stabilizer. For comparison, data for Sb$_2$Te$_3$ polycrystals obtained from
Ref. [13] are included as shown in line C. It is easy to conclude that (i) the thermal conductivity can be reduced greatly with the size decrease of the Sb$_2$Te$_3$ crystals and (ii) the thermal conductivity of Sb$_2$Te$_3$ anisotropic nanostructures is about 1 W/mK that is reduced by a factor of about 5 compared with that (4.7 W/mK) of the polycrystals bulk at 300 K. The lower thermal conductivity of the anisotropic Sb$_2$Te$_3$ samples is mostly due to the presence of more interfaces since the starting nanoparticles are much smaller than hexagonal nanoparticles obtained from CTAB as a stabilizer.

However, due to the uncontrollable synthesizing conditions at the moment, we have not been able to achieve high ZT values yet because of either a low electrical conductivity or a low Seebeck coefficient. Nevertheless, we feel the low thermal conductivity is a very good first step towards achieving high ZT values in nanostructured bulk thermoelectric materials, and worth reporting while we are working on improving the electrical conductivity and Seebeck coefficient. We are confident we are going to reach our high ZT goal eventually.

In conclusion, we have developed a method to prepare anisotropic, single crystalline Sb$_2$Te$_3$ nanoparticles via a chemical method. These nanostructures were synthesized via a one-step, one-pot non-aqueous route by the oriented attachment of nanocrystals using organic molecule PVP as a stabilizer and assembler. When these particles are compacted into bulk form, an extremely low thermal conductivity of about 1 W/mK, much smaller than that (4.7 W/mK) of Sb$_2$Te$_3$ polycrystalline bulk at 300 K, was achieved. The results indicated that nanostructured Sb$_2$Te$_3$ is potentially a good candidate for engineered nanocomposites that can lead to high thermoelectric figure-of-merit.

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References and Notes

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