Synthesis, Fabrication, and Characterization of Multidimensional Nanoparticle Based Thermoelectric Materials Composed of Bismuth, Antimony, and Tellurium.

Derrick Mott, Nguyen T. Mai, Nguyen T. B. Thuy, Teruyoshi Sakata, Mikio Koyano, and Shinya Maenosono
School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

ABSTRACT

With the event of nanotechnology, the field of thermoelectric (TE) materials has been re-invigorated with many recent advances towards materials with high thermoelectric efficiency (dimensionless figure of merit, ZT). The realization of such materials opens up new avenues to the creation of devices that can be used in freon-less refrigeration, micro-electronic cooling, or for harnessing lost heat energy from sources such as car engines. In our own research work, we have successfully devised a synthetic technique towards nanoparticles composed of bismuth, antimony, and tellurium that has proven highly versatile in tuning both the composition and shape/structure of the resulting nanoparticles. The ability to control the nanoparticle composition and shape/structure are highly important as these are critical parameters that dictate the resulting devices TE activity. In a modified polyol synthetic technique, it was found that many complex composition, shape, and structure combinations could be obtained for the nanoparticles including Bi-Sb nanodiscs with controllable size, a heterostructure composed of Sb_2Te_3 nanodiscs deposited on Te nanowires, or small particles deposited on a $(Bi_{0.5}Sb_{0.5})_2Te_3$ wire, just to name a few. By simply changing the capping ligands used in the synthesis, the nanoparticles resulting composition, morphology and structure could be changed, leading to a straightforward route towards TE nanoparticles with interesting properties. This presentation focuses on our recent study of the synthesis of bismuth, antimony, and tellurium composite nanoparticles with applications in thermoelectric materials in terms of understanding the underlying mechanisms of the synthetic technique, and characterization of the resulting nanomaterial properties.

INTRODUCTION

In the field of thermoelectric (TE) materials, the use of nanotechnology has been recognized as an effective avenue to increase the efficiency (ZT value) of the existing bulk materials [1]. The creation of TE materials with a nanoscale structure increases the phonon scattering along grain boundaries, ultimately suppressing the thermal conductivity, which increases the overall thermoelectric efficiency of the device [2]. As a result there has been renewed interest in this field with many researchers focusing on imparting nanoscale dimensions to the most promising bulk thermoelectric materials such as Bi_2Te_3 or $(Bi_xSb_y)Te_{100-x-y}$ [1,3]. While simple nanostructuring has been demonstrated to be effective in increasing the TE efficiency, the use of true nanoparticles with controllable size, shape, structure and composition have the potential to be the most effective in this field [3]. This approach is however a challenge, with few successful studies overcoming such difficulties as avoiding oxidation, or controlling the size, shape and other properties of the resulting nanocrystals. In our own recent research, we have demonstrated the effectiveness of a modified polyol method towards the synthesis of nanoparticles composed of bismuth, antimony and tellurium with controllable shape and composition that could be tuned by simply changing the identity of the capping ligand used in the synthesis [4]. The synthetic route has proven to be highly versatile and has led to the creation

of many complex composition/structure combinations for this class of nanoparticle. Nanoparticles with controllable composition, shape and structure are expected to be the most promising for TE materials because the particles can be assembled into large superlattices, thereby taking advantage of the tailorable crystal grain boundaries (suppressing thermal conductivity). This study details our continued work in modifying the synthetic parameters in terms of tuning the identity of the capping ligands toward controlling the size, shape, composition and structure for nanoparticles composed of bismuth, antimony and tellurium. In this work a wide range of synthetic conditions has been tested with various amounts or ratio of capping species. To simplify the experimental results only the most important key products are discussed.

EXPERIMENT

Chemicals: bismuth trichloride, antimony trichloride, tellurium tetrachloride, oleic acid (OAC), oleylamine (OAM), 1,2-hexadecanediol and di-octylether as well as other common solvents were obtained from Aldrich.

S*ynthetic Technique:* 5.0×10^{-4} moles total of bismuth, antimony and tellurium precursors with equimolar ratio was mixed with 25 ml di-octylether, then 1.5×10^{-3} moles of 1,2-hexadecanediol was added along with the capping species, the identity of which was used to manipulate the morphology of the resulting nanostructures. In general, various ratios of oleic acid or oleylamine were used, which is described more fully in the text. The mixture was purged with argon under vigorous stirring. At this point the mixture temperature was raised to 105 ^{o}C for 10 minutes to remove water, which also caused the reactants to completely dissolve in the solvent (a light grey color in the solution). After this, the temperature was increased to 200 ^{o}C and was held for 1 hour. The formation of particles within this time was evidenced by the solution color change from light grey to dark grey or black depending on the capping species used. After reaction, the nanoparticle solution was cooled to room temperature and the particles were purified by precipitation in ethanol. The materials could be briefly re-suspended (precipitation occurs in about 1 day) in hexane with additional OAC/OAM. The resulting nanomaterials were then analyzed.

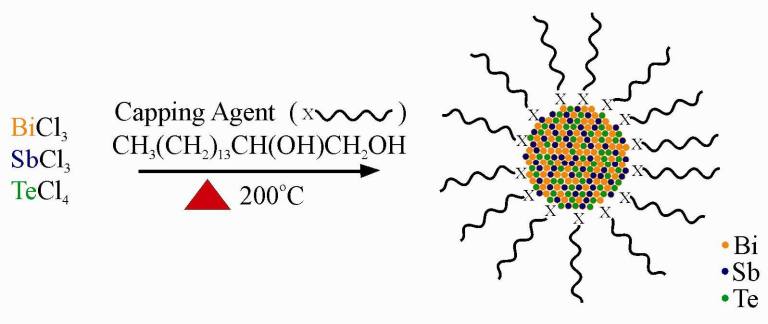
Instrumentation and Measurements: Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) were used to characterize the size, shape, composition and structure of the nanoparticles. TEM analysis was performed on an Hitachi H-7100 transmission electron microscope operated at 100kV. TEM samples were prepared by dropping the suspended particles onto a carbon coated copper grid and drying in air overnight. Samples for XRD measurements were prepared in powder form after cleaning the reaction product with ethanol and drying in a vacuum evaporator.

DISCUSSION

The discussion section covers two main areas. First the synthesis results are discussed in terms of the resulting morphology of the nanoparticles. Second, the composition and structure properties are assessed by using XRD. The use of OAM and OAC capping species is focused on because these give some of the most promising particles in terms of uniform composition or structure. Scheme 1 shows the general approach used towards the organic ligand encapsulated bismuth, antimony and tellurium containing nanoparticles. In this synthesis we begin with bismuth, antimony, and tellurium chloride precursors in a wet chemical synthesis scheme. The technique allows us to take advantage of organic capping ligands to control the morphology,

composition and structure of the resulting particles. Such an ability is highly exciting for the creation of nanostructured TE materials with enhanced efficiency as it is the nanoscale structure (i.e. wires, discs, etc) that serve to minimize the thermal conductivity (most often accomplished through increased phonon scattering at crystal boundaries in the material [1,2]).

Scheme1: General synthetic route towards molecular encapsulated nanoparticles composed of bismuth, antimony and tellurium.



In the first experimental example bimetallic particles composed of bismuth and antimony were synthesized. Here, only bismuth and antimony precursors were used, excluding tellurium. Figure 1 shows the TEM images collected for two different types of nanoparticles synthesized. Figure 1A shows a TEM image for nanodiscs synthesized using OAM capping species (0.32 ml). The nanodiscs have an approximate diameter of 50 nm with all discs appearing to lie flat on the TEM grid. All of the particles appear to be discs with many of them displaying a hexagonal shape. Figure 1B shows the results of the synthesis when both OAM (0.16 ml) and OAC (0.17 ml) are used as a capping species system. In this case the particles appear to be generally smaller in size (about 20 nm in diameter). These particles also appear to be disc-like in shape, which is more readily observed in this image as several particles can be seen lying partially on edge (propped up by neighboring particles). In terms of morphology, it seems that the addition of OAC to the synthesis caused the resulting particle size to generally be smaller. This ability allows the control of particle size by controlling the ratio of capping species used in the synthesis.

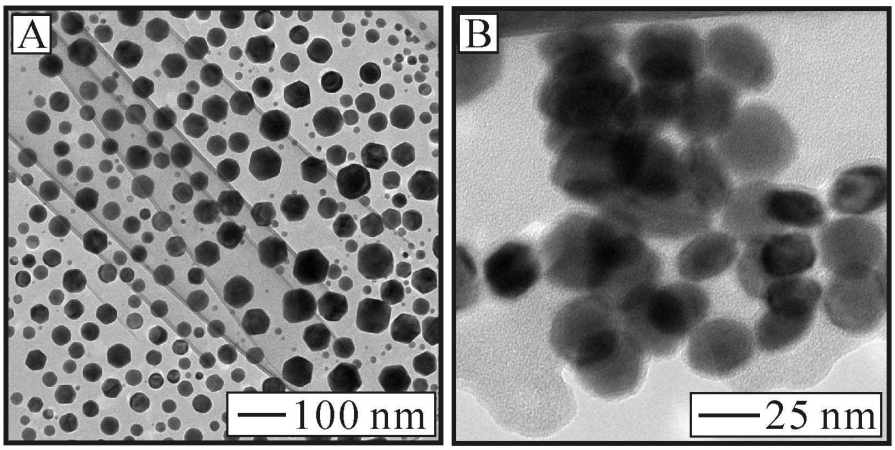


Figure 1: TEM images of nanodiscs synthesized with OAM (A) and OAM/OAC (B).

In the second experimental example, all three metallic precursors were used with OAC (0.32 ml) as a capping species. Figure 2 shows the TEM images collected for the trimetallic synthesis. As can be observed, these particles have a complex heterostructure, which is similar to another result observed previously [5]. In this case the particles appear to be composed of a long central nanowire studded with smaller discs (Figure 2A). The wires can be fully loaded with discs which grow from the side walls of the wire (Figure 2B). This nanoparticle structure is highly complex and is intriguing from a standpoint of studying the resulting TE properties.

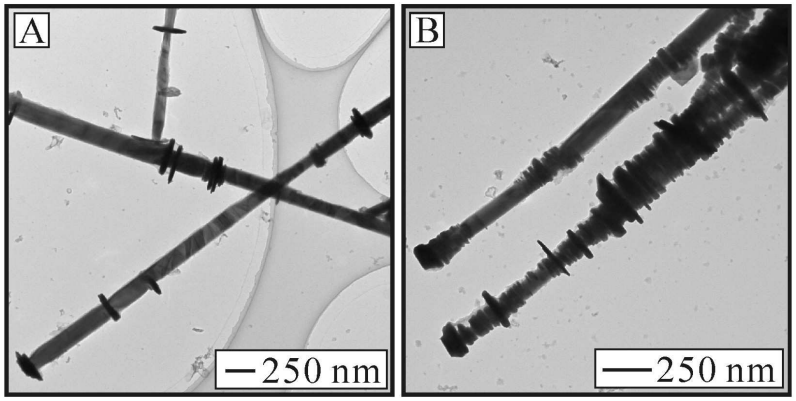


Figure 2: TEM images of nanowires studded with nanodiscs synthesized with OAC.

Finally, the third experimental example shows the results of a trimetallic synthesis using OAM (0.32 ml) as a capping species. Figure 3 shows the TEM images collected for the synthesis. In this case nanowires appear to form with a very high aspect ratio as observed in Figure 3A. However, upon closer inspection, it can be seen that these wires have smaller nanoparticles distributed over their surface. It may be that these small particles are the beginning of the formation of a similar heterostructure as shown in Figure 2. In general, the nanowires synthesized with OAM are much longer in length (several microns) than those synthesized with OAC (~1 micron). As well be discussed in the next section, these two samples have vastly different compositions.

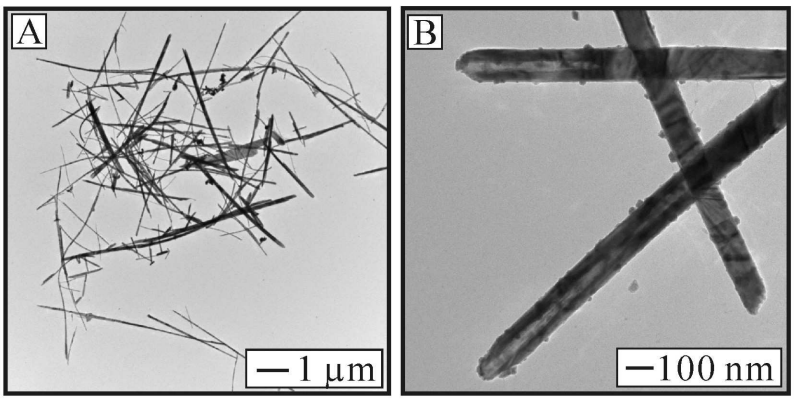


Figure 3: TEM images of nanowires synthesized with OAM (A), a magnified view of the nanowires shows small seed particles distributed over the wire surface (B).

Much insight is gained about these particles composition and structure when analyzed using XRD. Figure 4 shows the XRD patterns collected for the samples shown above. For each sample the component phases were identified by indexing the major peaks. These phases are labeled by the symbols ◆ for rhombohedral Bi-Sb, ● for hexagonal tellurium, ▲ for rhombohedral Sb_2Te_3, and ■ for $(Bi_{0.5}Sb_{0.5})_2Te_3$ [6]. For the nanodiscs synthesized with OAM (Fig. 4A) the sample is composed of a Bi-Sb compound. The particles also appear to have a small grain size, as evidenced by the significantly broad peaks in the pattern. This further reinforces the assertion that these particles are disc shaped in nature, reducing the apparent particle size. The nanodiscs synthesized with OAC (Fig. 4B) also shows peak positions consistent with a Bi-Sb compound. The low intensity peak (unlabeled) occurring below 45 degrees is indicative of monoelemental bismuth in the sample and may indicate a small degree of phase segregation for these particles. For the trimetallic containing particles synthesized with OAC (Fig. 4C), the XRD pattern is much more complex than for the bimetallic case. These particles are composed primarily of monoelemental Te and Sb_2Te_3 phases. Based on the peak intensities, the long central wire is composed of the Te and the discs studded on the particle surface are composed of Sb_2Te_3. The unlabeled peaks occurring at about 24 and 37.5 degrees arise from a minor component of Bi_2Te_3 phase present in the material as well. Finally, for the trimetallic particles synthesized using OAM, the sample appears to contain both Te (minor phases) and tri-elemental $(Bi_{0.5}Sb_{0.5})_2Te_3$ phases. The XRD results serve as a powerful tool to address the particles resulting composition and structure, providing key insight to the relationship between capping species used and the resulting particle characteristics.

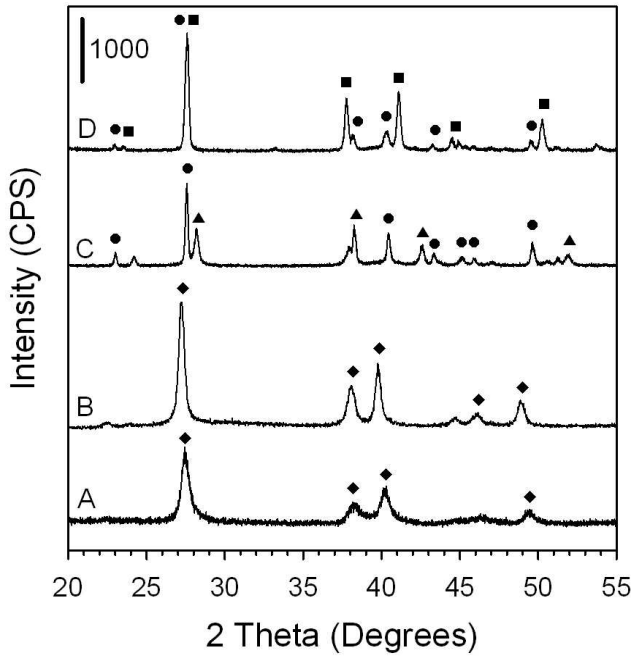


Figure 4: XRD patterns for Bi-Sb particles synthesized with OAM (A), OAC/OAM (B), and BiSbTe particles synthesized with OAC (C) and OAM (D). The peaks are marked with ◆ for rhombohedral Bi-Sb, ● for hexagonal tellurium, ▲ for rhombohedral Sb_2Te_3, and ■ for $(Bi_{0.5}Sb_{0.5})_2Te_3$ [6].

CONCLUSIONS

In conclusion, the use of a one pot synthesis based on the polyol method towards the synthesis of TE type nanoparticles composed of bismuth, antimony and tellurium has been demonstrated to be highly versatile in terms of controlling the particle size, shape, composition or structure by simply changing the capping species used. Such ability is important in creating highly functional TE devices as these are the parameters that give rise to the expected enhanced activity. This synthesis technique is expected to lead to more readily available nanoparticle based TE materials with promising properties. Part of the ongoing work focuses on the further control of the particle parameters as well as processing these materials into functional TE devices to study the TE efficiency.

ACKNOWLEDGMENTS

Derrick Mott gratefully acknowledges support by the Japan Advanced Institute for Science and Technology in addition to the Japanese Grant-in-aid for Scientific Research (C).

REFERENCES

1. Y. Ma, Q. Hao, B. Poudel, Y. Lan, B. Yu, D. Wang, G. Chen and Z. Ren, Nano Letters 8, 2580 (2008).
2. A. Purkayastha, Q. Yan, M. S. Raghuveer, D. D. Gandhi, H. Li, Z. W. Liu, R. V. Ramanujan, T. Borca-Tasiuc and G. Ramanath, Advanced Materials 20, 2679 (2008).
3. Y. Zhao and C. Burda, Applied Materials & Interfaces 6, 1259 (2009).
4. D. Mott, N. T. Mai, N. T. B. Thuy, Y. Maeda, T. P. T. Linh, M. Koyano and S. Maenosono, Physica Status Solidi A 208, 52 (2011).
5. W. Lu, Y. Ding, Y. Chen, Z. L. Wang and J. Fang, Journal of the American Chemical Society 127, 10112 (2005).
6. Reference data taken from the International Centre for Diffraction Data, PDF card numbers; Tellurium: 00-036-1452, Bi_2Te_3: 01-089-2009, Sb_2Te_3: 00-015-0874, Sb-Bi: 00-035-0517, and $(Bi_{0.5}Sb_{0.5})_2Te_3$: 01-072-1835.