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Synthesis and Thermoelectric Properties of Bi_2S_3 Nanobeads

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ABSTRACT

Bismuth sulfide (Bi_2S_3), a direct band gap material with $E_g \cong 1.3$ eV, attracts high interest in thermoelectric investigations. In this work, nanometer-sized bismuth sulfide with unique morphology has been successfully prepared by a precipitation between bismuth 2-ethylhexanoate and thioacetamide in high-temperature organic solution with presence of proper capping/ stabilizing agents. By employing this technique, we are able to produce nanobeads of bismuth sulfide with an aspect ratio of ~ 5, typically ~10 nm wide and ~50 nm long according to the TEM observation. Characterization of XRD and TEM/HRTEM reveals that the as-prepared particles exist in single orthorhombic phase and possess high crystallinity. The composite ratio between Bi and S can be adjusted by varying the ratio between two precursors and was determined by using EDS (TEM) technique. Thermoelectric properties of these bismuth sulfide nanobeads were also investigated and will be discussed comparatively with those from commercial bulk materials.

INTRODUCTION

Bismuth sulfide (Bi_2S_3) is an important member of thermoelectric materials and is a typical semiconductor as well. In bulk form, it possesses a direct band gap of $E_g = 1.3$ eV [1]. It is generally accepted that the band gap changes when bulk materials are transferred into nanophase due to the quantum confinement effects. It is therefore believed that the thermoelectric efficiency of nanometer-sized Bi_2S_3 may be apparently improved.

Conventionally, Bi_2S_3 nanorods can be prepared by hydrothermal method [2-4], and Bi_2S_3 nanoparticles can be obtained using microwave irradiation [5] and thermal decomposition [6,7] routes. In this work, we employed a high temperature organic solution approach and produced, for the first time, Bi_2S_3 nanobeads with controlling the aspect ratio by selection of capping agent.

EXPERIMENTAL

The chart in Figure 1 illustrates the Material synthesis. In this approach, diphenyl ether was selected as a high boiling point reaction medium. Bismuth 2-ethylhexanoate, dissolved in diphenyl ether, was used as the bismuth precursor. Thioacetamide (TAA) was used as the precursor precipitating agent. Two part systems were prepared simultaneously. For part A, TAA (99+%, 0.8744g) was added into a round bottle flask containing 1-dodecanethiol (98+%, 4 ml), di(ethylene glycol) 2-ethylhexyl ether (98%, 2 ml) and diphenyl ether (99%, 8 ml) under argon stream. The system was gradually heated to 110 ^oC while being stirred untill TAA was

completely dissolved. For part B, oleic acid (90%, 2 ml; all above chemicals were from Aldrich) and a freshly-prepared solution of bismuth 2-ethylhexanoate (Alfa Aesar, 99.9%) in diphenyl ether (0.2M, 2 ml) were added into a three-neck flask that contains diphenyl ether (70 ml). Part A was injected into this reaction container while part B was stirred and heated to 180 ^{o}C under an Ar stream. The resulting solution was maintained at this temperature for 1 min before the heating source was removed. The mixture was then cooled down to room temperature, and Bi_2S_3 particles were precipitated by adding ethanol (60 ml) to the system and collected by centrifugation. The resulting Bi_2S_3 powder was kept in vacuum at room temperature overnight for further use. To characterize the conductivity, powder of as-prepared Bi_2S_3 was pressed into a pellet with a diameter of 9 mm and a thickness of ~1 mm. This pellet was sintered at 400 ^{o}C for 4 hours under argon atmosphere.

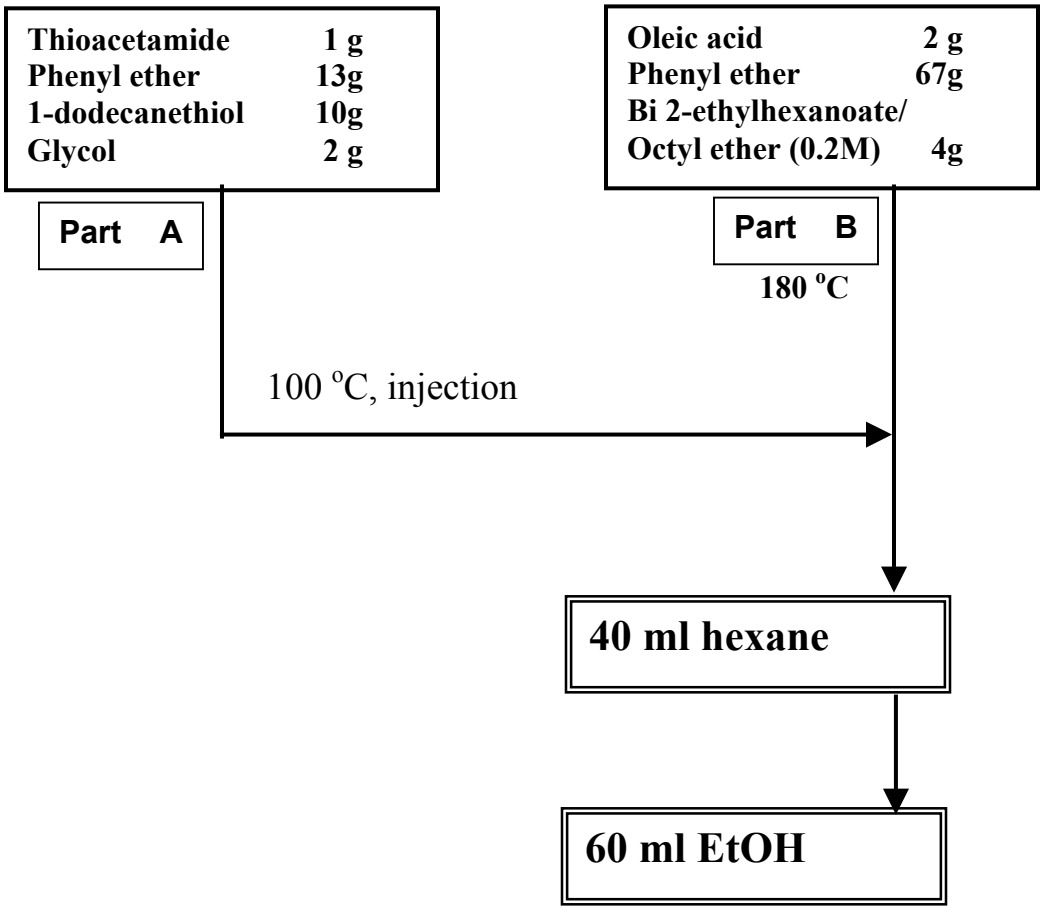

Figure 1. Flow chart for the preparation of Bi_2S_3 via high temprature solution processing.

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RESULTS AND DISSCUSION

The phase identification of as-prepared Bi_2S_3 powder was performed at room temperature using a (Cu Kα radiation) X-ray diffractometer (Philips X'pert System). All the peaks in this XRD pattern, as illustrated in Figure 2, were indexed as those from orthorhombic Bi_2S_3 crystal by the comparison with the standard ICDD PDF Card of Bi_2S_3 (17-0320). Confirmed by TEM diffraction pattern (Figure 3), this XRD pattern also indicates that our product possesses high crystallinity with a single orthorhombic phase.

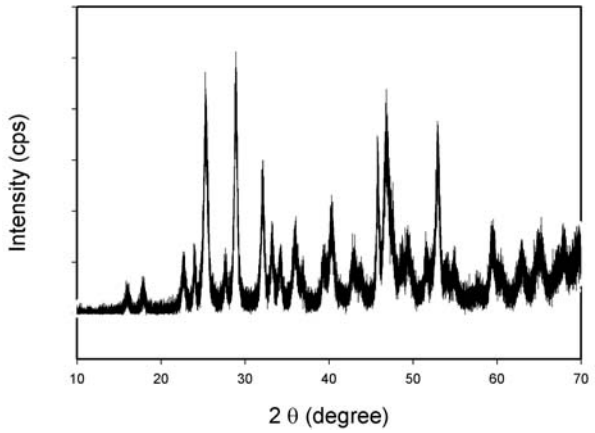

Figure 2. XRD trace of the Bi_2S_3 particles prepared at 180 ^oC

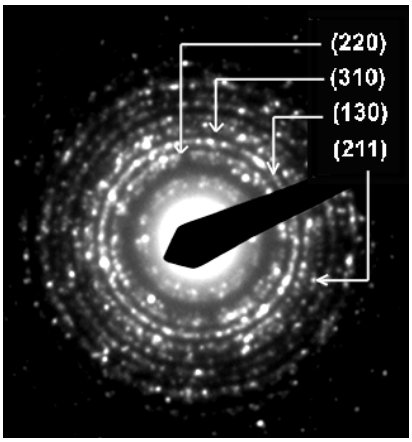

Figure 3. TEM image: Diffraction pattern of Bi_2S_3 particles

Figure 4 shows a light scattering result of as-prepared Bi_2S_3 particles dispersed in hexane, exhibiting the size distribution of particles. It demonstrates that the mean hydrodynamic radius of the sample is rather narrow, only ranging between 100 and 200 nm. As well known, the mean value of the size estimated using this technique is always larger than the actual one characterized by TEM due to the different instrumental nature of working function. Therefore, it is not true that both results can be always comparable. However, result from light scattering does provide the degree of particle distribution. We have also carefully checked the composition of the powder sample by using energy dispersive x-ray spectroscopy (EDS) in TEM. A typical spectrum is showed in Figure 5. The average elemental ratio between sulfur and bismuth was calculated as 58.7 to 41.3 (atomic percentage).

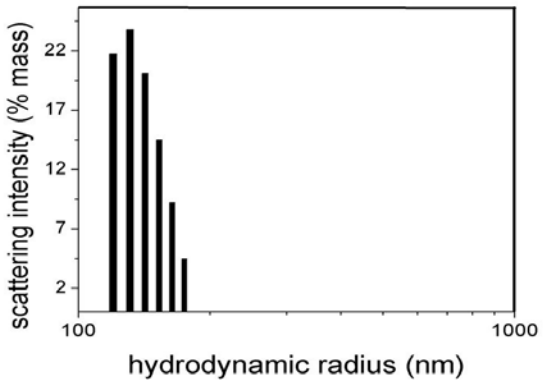

Figure 4. Bi_2S_3 particle size distribution

Figure 5 (a-c) are the transmission electron microscopy images of Bi_2S_3 particles prepared at 180 ^oC. Figure 5 (a) shows the morphology of the bead-shaped particles with average dimensions of ~15nm x 50nm. From our supporting experimental results, we noted that the formation of these elongated particles is most likely due to the related capping agent, i.e. 1-dodecanethiol in current investigation. Figure 5 (b) is an additional morphology image with higher magnification on selected zone, which indicates that all the elongated particles are highly crystalline. Figure 5 (c) is a high resolution TEM image showing the lattice structure on a single particle.

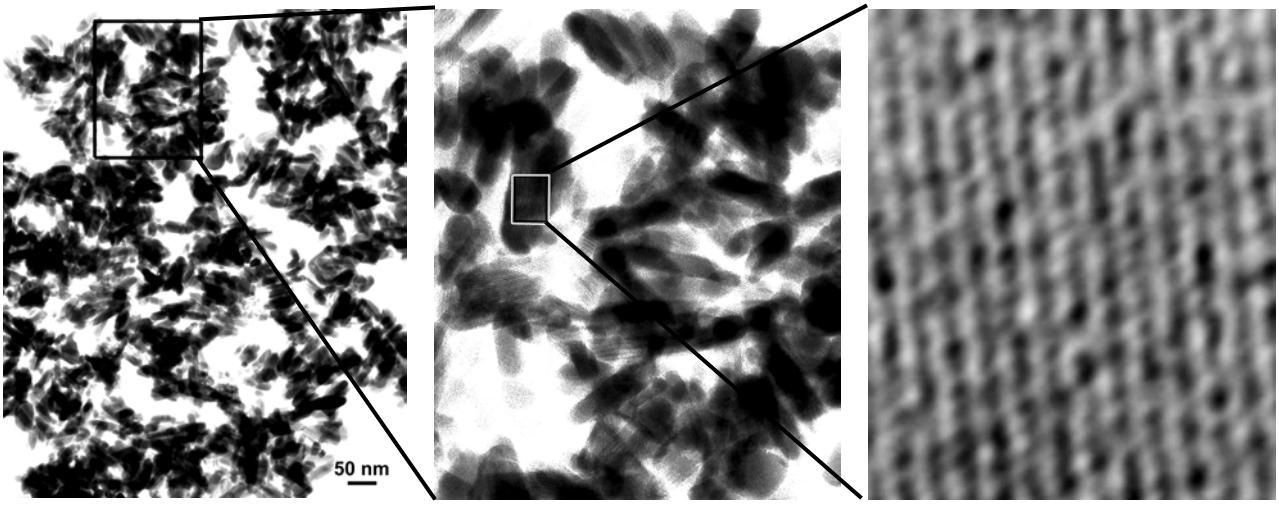

Figure 5. TEM images of Bi_2S_3. (a) morphology of Bi_2S_3 particles prepared at 180 ^oC; (b) morphology of selected Bi_2S_3 particles; and (c) HRTEM on a selected Bi_2S_3 particle

Most literature reports that Bi_2S_3 is semiconductor with a band gap of ~1.1-1.5 eV [8,9], except one research group [10], which reported metallic Bi_2S_3. We observed flat temperature dependence for resistivity (ρ) of our samples, shown as the solid curve in Figure 6. The inset of the figure was plotted in different scale to show the detailed temperature dependence of

resistivity. For comparison, we also plotted the data from Ref. [10] in dashed curve. We exclude the possibility of high scattering resistance due to defects, since our data is one order of magnitude smaller than that of metallic Bi_2S_3 at room temperature [10]. It is very likely our sample is semimetal. This is supported by the fact that our Seebeck coefficient (*S*) is only about 1/5 of that reported by others [10]. Figure 7 shows the Seebeck coefficient plotted against temperature. It has the shape typically observed in degenerated electron gas, except the magnitude, which is a little bit smaller than most semiconductors, possibly due to the cancellation of two bands of different sign of carriers, which is the case for semimetals. Ref. [10] argued that the sulfur deficiency in Bi_2S_3 made the sample metallic. Our data showed lower resistivity than Ref. [10] and the estimated sulfur deficiency is also higher than Ref. [10]. In this case the sample should be more metallic, while we observed semimetal-like resistivity. This could be explained by either the resistivity data reflects different levels of influence of grain boundaries, or could be something special due to the nature that our raw material is nano-composite. We are currently trying different sulfur concentration and different annealing temperature to investigate this problem.

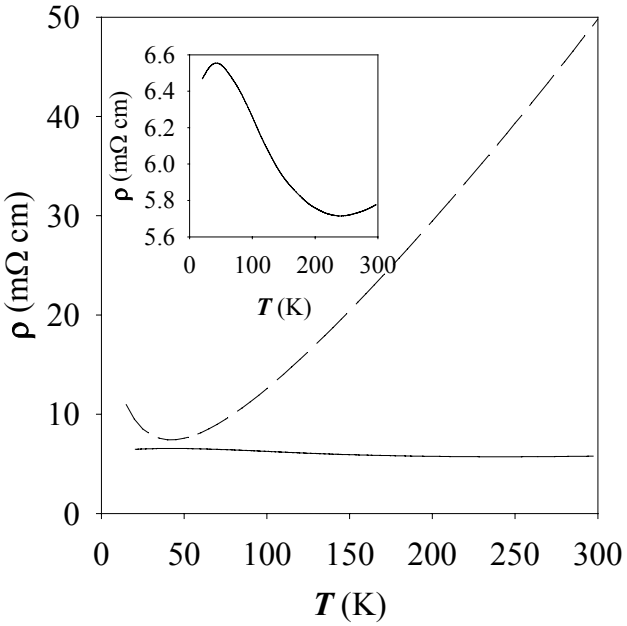

Figure 6. Comparison of resistivity of our Bi_2S_3 sample and the lowest from the literature. Solid curve is our data and the dashed curve is from Ref.[10]. Inset: same data of solid curve plotted in different scale.

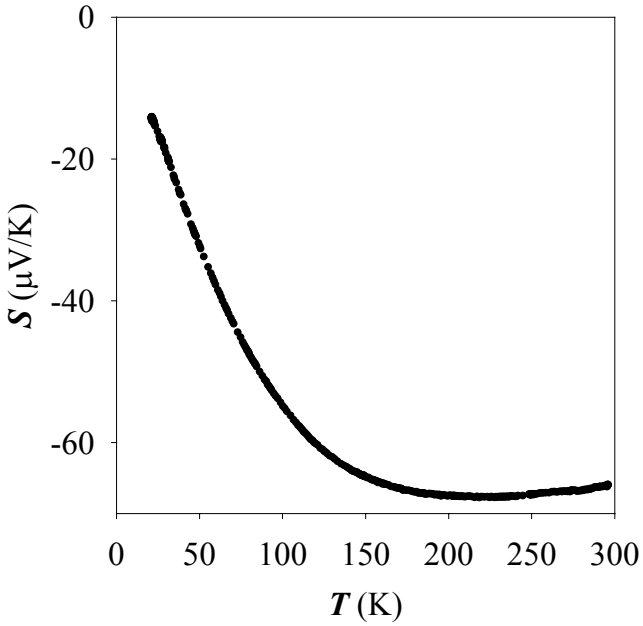

Figure 7. Seebeck coefficient for our Bi_2S_3 sample.

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CONCLUSIONS

Bismuth sulfide nanobeads have been successfully synthesized through a high temperature organic solution processing route. The crystallinity, particle size distribution, composite ratio and morphology of as-prepared powder were systemically analyzed using XRD, light scattering and EDS/TEM, respectively. Thermoelectric characterization indicates that our as-prepared nanostructured material is a semimetal, suggesting that sample sintered from these nanobeads of bismuth sulfide may be a promising thermoelectric material.

ACKNOWLEDGMENTS

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REFERENCES

[1] J. Black, E. M. Conwell, L. Seigle and C. W. Spencer, J. Phys. Chem. Solids, **2**, 240 (1957).
[2] M. W. Shao, M. S. Mo, Y. Cui, G. Chen and Y. T. Qian, J. Cryst. Growth, **233**, 799 (2001).
[3] W. Zhang, Z. Yang, X. Huang, S. Zhang, W. Yu, Y. Qian, Y. Jia, G. Zhou and L. Chen, Solid State Comm., **119**, 143 (2001).
[4] S. Yu, J. Yang, Y. Wu, Z. Han, Y. Xie and Y. Qian, Mater. Res. Bull. **33**, 1661 (1998).
[5] X. Liao, H. Wang, J. Zhu and H. Chen, Mater. Res. Bull., **36**, 2339 (2001).
[6] R. Nomura, K. Kanaya, H. Matsuda, Bull. Chem. Soc. Jpn., **62**, 939 (1989).
[7] A. Cyganski and J. Kobylecka, Thermochim. Acta, **45**, 65 (1981).
[8] R. K. Nkum, A. A. Adimado and H. Totoe, Mater. Sci. Eng. **B55** 102 (1998).
[9] Y. Ueda, A. Furuta, H. Okuda, M. Nakatake, H. Sato, H. Namatame and M. Taniguchi, J. Electron. Spectrosc. Relat. Phenom., **101-103** 677 (1999).
[10] B. Chen, C. Uher, L. Iordanidis, M. G. Kanatzidis, Chem. Mater. **9** 1655 (1997).