

Synthesis and Characterization of Bi₂Se₃ Thermoelectric Nanopowders

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Abstract: In order to synthesize Bi₂Se₃ nanopowders by a solvothermal synthesis method, ethylenediamine, dimethylformamide, acetone, absolute ethanol, and deionized water were respectively used as a solvent, using BiCl₃ and elemental Se powders as starting materials and KBH₄ as a reductant at 180°C for different times. X-ray diffraction was used for examining the phase composition of the products. The results showed that pure Bi₂Se₃ nanopowders were successfully synthesized only when deionized water was used as the solvent. Transmission electron microscopy observation revealed that the nanopowders consisted of big polygonal nanosheets and small irregular nanoparticles. The formation mechanism of the Bi₂Se₃ nanosheets and nanoparticles was proposed.

INTRODUCTION

Since 1993, when Hicks and Dresselhaus [1] reported that the dimensionless thermoelectric figure of merit ZT ($=\sigma\alpha^2T/\kappa$, here σ , α , and κ are the electrical conductivity, the Seebeck coefficient, and the thermal conductivity of the material, respectively, and T is absolute temperature) of a material can be markedly increased as its dimensionality is reduced, the preparation and thermoelectric properties of nanostructured materials have attracted more and more attention [2-9]. For example, Lin *et al.* [2, 3] studied the transport properties of Bi and Bi_{1-x}Sb_x nanowires and found that the Seebeck coefficient of Bi nanowires and the electrical conductivity of Bi_{1-x}Sb_x nanowires both dramatically increased as the diameter of the corresponding nanowires decreased. Harman *et al.* [10] reported $ZT \geq 2$ for PbTe-PbSeTe quantum-dot superlattices. Venkatasubramanian *et al.* [11] showed $ZT=2.4$ for p-type Bi₂Te₃-Sb₂Te₃ superlattices at room temperature and $ZT=1.2$ for n-type superlattices. Recently, Kanatzidis *et al.* [12] reported bulk AgPb₁₈SbTe₂₀ material with extremely high figure of merit ($ZT=2.1$ at 800K), and they considered that the material possessing so high ZT value probably due to Ag-Sb-rich nanocrystals embedded in PbTe matrix, which is conceptually akin to the one found in the artificial PbTe-PbSeTe superlattices [10].

Bi₂Se₃ is a promising thermoelectric material that can be used in thermoelectric cooling devices [13-14], and it can also be used as optical recording medium [15-16]. Usually, Bi₂Se₃ nanocrystallines are prepared by metallurgical melt processing [17], traveling heater method [18] or Bridgman method [19] at high temperatures (>500°C). Recently, preparation of Bi₂Se₃ nanostructured materials *via* wet chemical methods has attracted increasing attention due to low cost and convenient. For example, Qiu *et al.* [20] synthesized Bi₂Se₃ nanoparticles *via* sonochemical method using Bi(NO₃)₃, Na₂SeSO₃, EDTA and ascorbic acid as starting

materials; Cui *et al.* [21, 22] obtained Bi₂Se₃ nanobelts or nanotubes *via* the same method as in ref. [20], using BiCl₃, selenious acid and diamine hydrate as the starting materials; Wang *et al.* [23] synthesized Bi₂Se₃ nanopowders by a solvothermal method in ethylenediamine (en) using BiCl₃ and Se as starting materials and NaI as a reductant. Since selenium contained compounds are toxic, the influence of the fabrication route to Bi₂Se₃ upon the environment should be concerned. As elemental Se is less toxic compared with selenium contained compounds, in this paper, we selected Se powder as the Se source for the synthesis of Bi₂Se₃ nanopowders *via* a solvothermal method, in acetone, absolute ethanol, en, dimethylformamide (DMF), or deionized water, respectively. The phase composition and microstructure of the corresponding products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively.

EXPERIMENTAL DETAILS

Se powders with purity >99.5% and other chemicals with analytical purity were used. Absolute ethanol, acetone, en, DMF, and deionized water were respectively poured into five Teflon-lined autoclaves of 100 ml capacity until 80% of the volume was filled. Appropriate amount of BiCl₃, Se, KBH₄, and KOH were put into the autoclave sequentially. The autoclaves were sealed and maintained at 180°C for 24, 36, and 48 h, respectively, then naturally cooled to room temperature. The resultants were washed with diluted hydrochloride, deionized water and absolute ethanol in sequence for several times then filtered. Finally the dark products were dried in vacuum. XRD (Bruker D8 Advance) was used to characterize the dried products. The morphology and size of the products were examined by using TEM (Hitachi H-800).

RESULTS AND DISCUSSION

Fig. (1) shows the XRD patterns of the products synthesized at 180 °C for 24 h, using various solvents. It can be seen from Fig. 1 that using acetone or absolute ethanol as the solvent, their corresponding products have a similar XRD pattern and mainly contain elemental Bi and Se, with a little

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amount of Bi_4Se_3 . As en was used as the solvent, the product mainly contains Bi, with a small amount of Se and unknown phase, which is quite different from the result in ref. [23], where NaI was used as the reductant. The reason for the difference is considered that NaI is a very weak reductant ($E_{\text{I}_2/\text{I}^-}^0 = 0.535\text{V}$), while KBH_4 is very strong ($E_{\text{H}_2\text{O}/\text{BH}_4^-}^0 = -1.24\text{V}$). The latter can easily reduce Bi^{3+} into Bi ($E_{\text{Bi}^{3+}/\text{Bi}}^0 = 0.16\text{V}$).

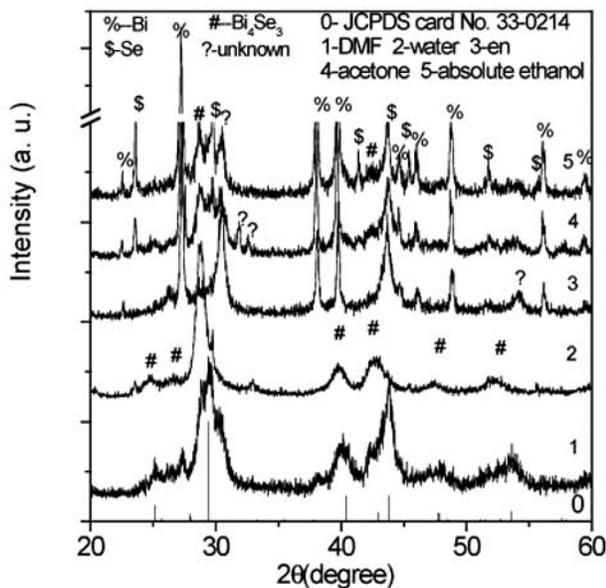


Fig. (1). XRD patterns of the product synthesized at $180\text{ }^\circ\text{C}$ for 24 h using various solvents, the reported data for Bi_2Se_3 is also given for comparison. The peaks marked by %, #, \$ and ? correspond to Bi, Bi_4Se_3 , Se, and unknown phase, respectively.

As DMF was used as the solvent, the product contains mainly Bi_2Se_3 (JCPDS card file, No. 33-0214), with some amount of Bi_4Se_3 , Bi and Se. As deionized water was used as the solvent, the product mainly contains Bi_4Se_3 (JCPDS 72-2065), with a little amount of Se and Bi_2Se_3 . These suggest that if we further prolong the holding time and/or increase the synthesis temperature, it is promising to obtain pure Bi_2Se_3 powders using DMF or deionized water as the solvent. Therefore, further experiments were only carried out using DMF or deionized water as the solvent and the results are shown as follows.

Fig. (2) shows the XRD patterns of products synthesized at $180\text{ }^\circ\text{C}$ for 36 or 48 h, using DMF and deionized water as the solvent, respectively. It can be seen from Fig. (2) that as DMF was used as the solvent and the holding time was 36 and 48 h, respectively, both the products contain Bi_2Se_3 , Bi_4Se_3 and Se_3 , only the product of the latter case has more Bi_2Se_3 . This indicates that, using DMF as the solvent, the product is still not pure even the holding time is 48 h. As deionized water was used as the solvent and the holding time was 36 h, besides the expected phase, Bi_2Se_3 , the product still contains Bi_4Se_3 , and little amount of unreacted Se, whereas as the holding time was prolonged to 48 h, all the XRD peaks (pattern 4 in Fig. 2) of the product correspond to the reflections of rhombohedral Bi_2Se_3 (JCPDS card file, No.

33-0214) with space group: R-3m (166). The calculated lattice constants, $a=4.130\text{ \AA}$ and $c=28.42\text{ \AA}$, from the XRD pattern agree with the reported data in JCPDS card file, No. 33-0214, $a=4.139\text{ \AA}$ and $c=28.63\text{ \AA}$. Therefore, the synthesized powder is rhombohedral Bi_2Se_3 .

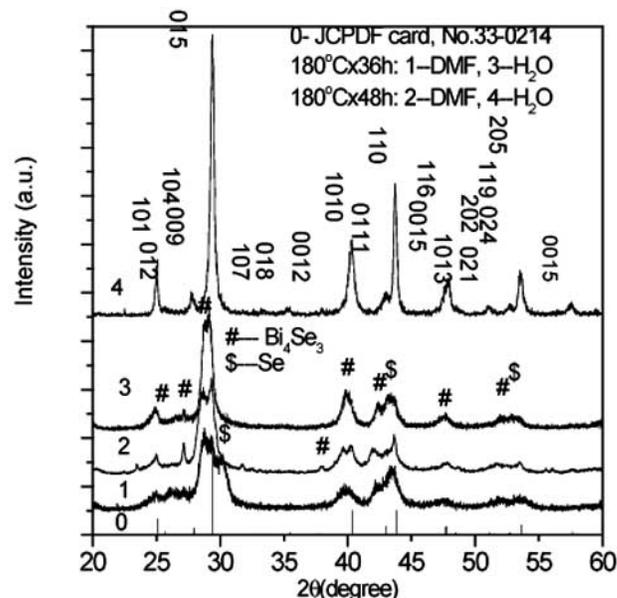


Fig. (2). XRD patterns of the product synthesized at $180\text{ }^\circ\text{C}$ for 36 or 48 h, using DMF and deionized water as the solvent, respectively, the reported data for Bi_2Se_3 is also given for comparison. The peaks marked by # and \$ correspond to Bi_4Se_3 and Se, respectively.

Pure Bi_2Se_3 cannot be successfully obtained under the present conditions when en, absolute ethanol, acetone or DMF was used as the solvent, which is probably because the physical and chemical properties of these solvents are different from those of deionized water. By comparing with the physical and chemical properties of the solvents used, it is found that deionized water has the biggest dielectric constant (dielectric constant= $78.304, 36.71, 25.7, 20.7, 12.9$ for deionized water, DMF, ethanol, acetone, and en, respectively) and that their other properties are similar [24]. Therefore, the dielectric constant of a solvent probably has a significant effect on the formation of the Bi_2Se_3 compound.

Fig. (3a) shows the TEM image of the product synthesized at $180\text{ }^\circ\text{C}$ for 36 h, using deionized water as the solvent. It can be seen from Fig. (3a) that the product contains some flake-like nanostructures with sizes of about 50 – 100 nm besides many small irregular nanoparticles. Fig. (3b) shows the TEM image of the product synthesized at $180\text{ }^\circ\text{C}$ for 48 h, using deionized water as the solvent. The morphology of the Bi_2Se_3 nanopowders is not uniform. The nanopowders contain two kinds of grains: one is small with size of $\sim 100\text{ nm}$, the other is bigger and regular with sizes in the range of 500-1000 nm. The bigger grains are in polygon and very thin, which can be seen from their contrast with the small grains (see the right upper corner hexagon). Therefore, we call them nanograins and nanosheets, respectively. Most nanosheets are hexagonal. If one takes a close look at the big hexagonal particle in the center of Fig. (3b), one will find

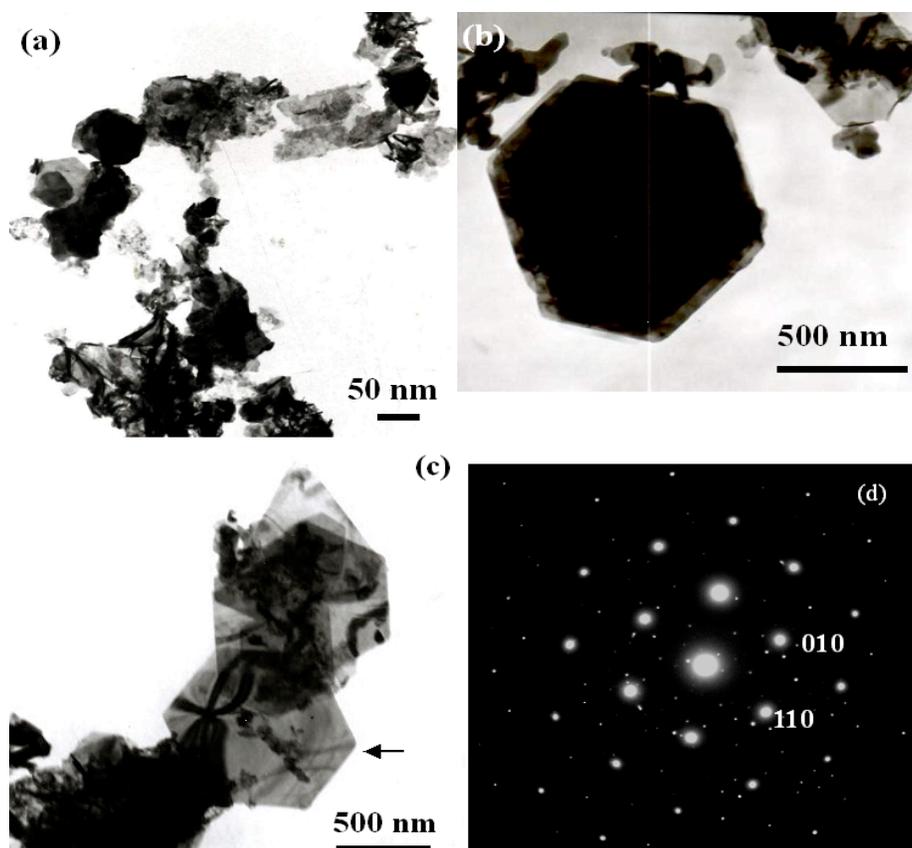


Fig. (3). TEM images of as the synthesized nanopowders at 180°C for 36 h (a), and 48 h (b) and (c), and the SAED pattern (d) recorded on the hexagonal nanosheet indicated by an arrow in (c).

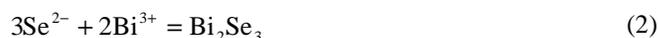
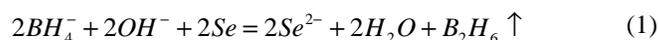
that in fact it consists of at least two hexagons with similar size. The hexagons are almost superpositioned, resulting in dark contrast. Fig. (3c) more clearly shows the morphology of the nanosheets, where several nanosheets are overlapped to some extent. Fig. (3d) shows the selected area electron diffraction (SAED) pattern normal to the plane of the hexagonal nanosheet indicated by an arrow in Fig. (3c). It reveals that the nanosheets are well crystallized and grow along the (0001) plane of the rhombohedral Bi_2Se_3 .

The crystal structure of Bi_2Se_3 consists of Bi and Se layers [22]. A Bi layer is composed of Bi atoms arranged to form a plane hexagonal structure, and a Se layer is formed by Se atoms arranged in the same way. In a unit cell, there are two different Se layers, named $\text{Se}^{(1)}$ and $\text{Se}^{(2)}$. A unit cell is packed with two Bi layers and three Se layers according to the sequence as follows: $\text{Se}^{(1)}$ -Bi- $\text{Se}^{(2)}$ -Bi- $\text{Se}^{(1)}$. Between two units, there is only the Van der Waals bond between the neighboring $\text{Se}^{(1)}$ planes. Because the Bi_2Se_3 has such layered structure and weak bonds between two unit layers, the nuclei forming from the solution are tiny thin crystals. And when the temperature is low, the formation rate of Bi_2Se_3 molecules and the growth rate of the crystals are low. It is easy to get small crystalline nanosheets with well-formed hexagonal morphology [22].

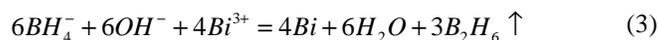
The synthesized Bi_2Se_3 powders possessing different morphologies must be related to their formation mechanisms. According to the redox potentials ($E^0_{\text{Se}/\text{Se}^{2-}} = -0.92 \text{ V}$

and others being given in above paragraphs), the Bi^{3+} and Se in the autoclave can be reduced into Bi and Se^{2-} , respectively, by KBH_4 . Although the former is easier to be reduced than the latter, the solubility of BiCl_3 in water is very limited especially at room temperature and it increases with increasing temperature. This suggests that the reduction process from Bi^{3+} to Bi in the system is slow. Therefore, there are two possible formation pathways of the Bi_2Se_3 . One is that the Bi^{3+} directly reacts with the reduced Se^{2-} and the other is that the reduced Bi reacts with the elemental Se. The reaction process is proposed as follows: a part of the Se is reduced into Se^{2-} and then the Se^{2-} directly reacts with Bi^{3+} into Bi_2Se_3 , whereas other Bi^{3+} ions in the solution are reduced into Bi atoms, then as the temperature increases the Bi atoms react with some Se to form Bi_4Se_3 , and finally the Bi_4Se_3 react with the remnant Se to form Bi_2Se_3 . The formation mechanisms can be expressed as follows.

The first pathway:



The second pathway:





The formation process of the Bi₂Se₃ is complicated as described above, resulting in the Bi₂Se₃ nanopowders not uniform. Combining the XRD and TEM results it can be deduced that the reactions (1) to (4) occur at early stage whereas the reaction (5) at late stage of the processing and that the nanosheets and the nanograins are the products of the first and the second pathway, respectively. The nanosheets formed at early stage of the processing grow up into regular shape as the temperature increases and the time is prolonged; therefore, they are bigger.

Based on the above results and discussion, we deduce that homogeneous Bi₂Se₃ nanopowders might be synthesized by adjusting the processing. For example, the Se powder is first fully reduced into Se²⁻ by KBH₄ according to the reaction (1) and then the Se²⁻ contained solution and BiCl₃ are put into the autoclave, Bi₂Se₃ nanopowders would finally form according to the first pathway. Using H₂SeO₃ or Na₂SeO₃ to replace Se may be another choice, as H₂SeO₃ or Na₂SeO₃ will be reduced to form Se and BiCl₃ will be reduced to form Bi according to the reaction (3). Bi₂Se₃ nanopowders would form according to the second pathway.

CONCLUSIONS

Pure Bi₂Se₃ nanopowders were successfully synthesized at 180°C for 48 h, using deionized water as solvent, whereas it was not successful using en, DMF, acetone or absolute ethanol as the solvent. There are two possible formation pathways of the Bi₂Se₃ nanopowders, which is probably the main reason that the nanopowders are not uniform.

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