Hydrothermal synthesis of $Bi_2(Te_{1-x},Se_x)_3$, (x=0.1,0.3,0.5) nano-structure

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Abstract

In this work, $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.1}Se_{0.9}$ and $Bi_2Te_{1.5}Se_{1.5}$ powders were synthesized by a hydrothermal method, by using $BiCl_3$,Te, and Se powders as starting materials together with $NaBH_4$, NaOH and EDTA as the reductant, PH-value controller and additive, respectively. Then 100 nm thin films of powders fabricated by physical vapor deposition(PVD) . Morphology of the prepared samples were investigated by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) . Samples were characterized with FTIR spectroscopy. The hexagonal structure was observed for all of powders and thin films from the XRD results. The crystallite size of 8 to 20 nm were obtained using Scherrer equation . The thermoelectric measurement was carried out on the thin film samples .

Keywords: Hydrothermal, PVD, Thermoelectric properties, Seebeck cofficient

Introduction

The thermoelectric (TE) effect is the appearance of an electric field along a temperature gradient established in a material. The material which convert heat flow into electrical current and *vice versa* are known as thermoelectric materials [1]. The efficiency of TE materials is directly related to the dimensionless figure of merit, ZT, defined as $ZT=\alpha^2T/\rho\lambda$, where α is the seebeck coefficient, ρ is the electrical resistivity, λ is the thermal conductivity, and T is absolute temperature [2]. A good TE material should have large seebeck coefficient (α) to produce the required voltage, low thermal conductivity (λ) to keep the heat at the junction and low electrical resistivity (ρ) to minimize Joule heating [1]. TE materials are usually classified according to the temperatures at which For low temperature operation (0-250 ^{0}C), Bi_2Te_3-type semiconductors have primary been investigated because of their favourable ZT value in this temperature range [3]. Bi_2Te_3, Bi_2Se_3 and their solid solution crystals are narrow-band-gap semiconductors with asymmetric band structure, they have rhombohedral unit cell with symmetric space group $\bar{R}3m$ [4].Thin films of $Bi_2(Te_{1-x},Se_x)_3$ semiconductors are good candidates for small scale power generators, detectors, low weight refrigerators[5]. With increasing concerns on environmental protection and growing energy crisis, thermoelectricity based on solid-state physics theory draws comprehensive attention owing to its immense advantages, such as environmental friendliness, silent operation, absence of moving parts and high reliability [6]. An attractive Te-Free alternative to Bi_2Te_3 is the congeric Bi_2Se_3, which has remarkably similar structural properties. Furthermore, Se is 50 times more abundant than Te [6,7].

Experimental Method

Nanocrystalline $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.1}Se_{0.9}$ and $Bi_2Te_{1.5}Se_{1.5}$ were synthesized by a hydrothermal method by using $BiCl_3$, Te, and Se powders as starting materials together with $NaBH_4$, NaOH and ethylenediaminetetraacetic disodium salt (EDTA) as the reductant, PH-value controller and the organic complexing reagent, respectively. A Mixture of $BiCl_3$ (5mmol), Te and Se powders (7.5mmol), NaOH (0.875 g), EDTA (0.5 g) and a sufficient amount of $NaBH_4$ were put into a 50ml Teflon-lined autoclave in a Nitrogen atmospheric. The autoclave was then filled with distilled water up to 80% of its capacity. The autoclave was maintained at 150 ℃ for 48 h, followed by cooling to room temperature naturally. The products were filtered and washed with distilled water and ethanol in sequence. Finally, the dark products were dried in vacuum at 100℃ for 6 h. Thin films were deposited by convectional thermal evaporation of the synthesized powder onto glass substrate, using a high vacuum coating unit (Edwards 306A). The deposition rate was kept constant during the evaporation process at nearly 5Å/S. Deposition was performed at base pressure1.5×10^{-6} mbar and work pressure 5×10^{-6} mbar and temperature substrate at 150 ℃ . $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.1}Se_{0.9}$ and $Bi_2Te_{1.5}Se_{1.5}$ thin films of thickness 100 nm annealed at 150 ℃ for one hour. The thermoelectric measurement was carried out on the thin films samples.

Results and Discussion

The XRD Patterns of hydrothermal synthesized powders are showed in Fig. 1. All of them have the same space group $\bar{R}3m$ [7]. The crystallite size of 8 to 20 nm, 8 to 18 nm and 8 to 16 nm were obtained for $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.1}Se_{0.9}$ and $Bi_2Te_{1.5}Se_{1.5}$ powders, respectively using Scherer equation [8]. Crystallite size decreased with increasing content selenium. The enlarged (110) peaks of the XRD patterns shown in Fig. 1(b) display an apparent shift to high angel with increasing the selenium content by using Bragg's law, which mainly due to the smaller atomic radius of selenium (1.15 Å) compared with that of tellurium (1.4 Å). This also presumably verifies that the selenium atoms successfully enter into the crystal lattices Bi_2Te_3 to form ternary solid solutions [9].

Fig. 2 shows SEM images of the synthesized powders, the samples are flakelike and agglomerated. In addition, the size of them apparently decreased via increased selenium [7]. A comparison of FTIR values of powders is given in fig. 3. The bonds observed at 3440, 1440, 1000 and 660 cm^{-1} in all of powders can be attributed to O-H, C-N, C-H and Bi-O, respectively [10].

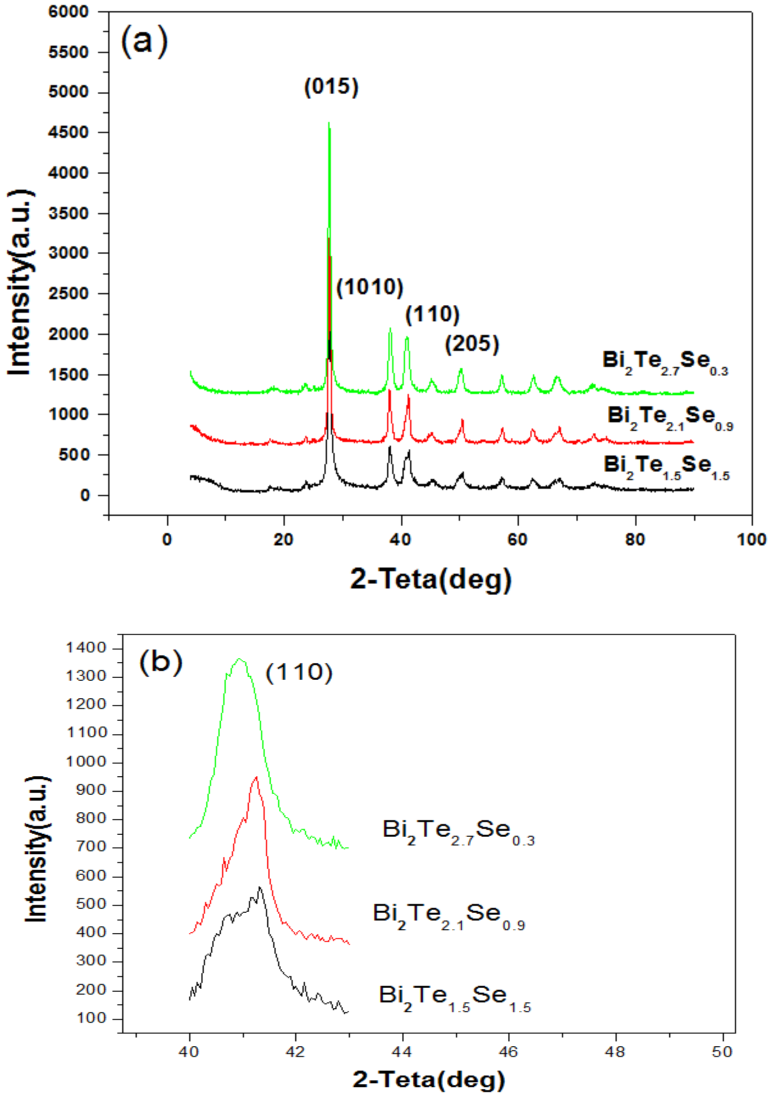

Fig. 1.(a) The XRD patterns and (b) the enlarged XRD patterns of (110) peak for different selenium content.

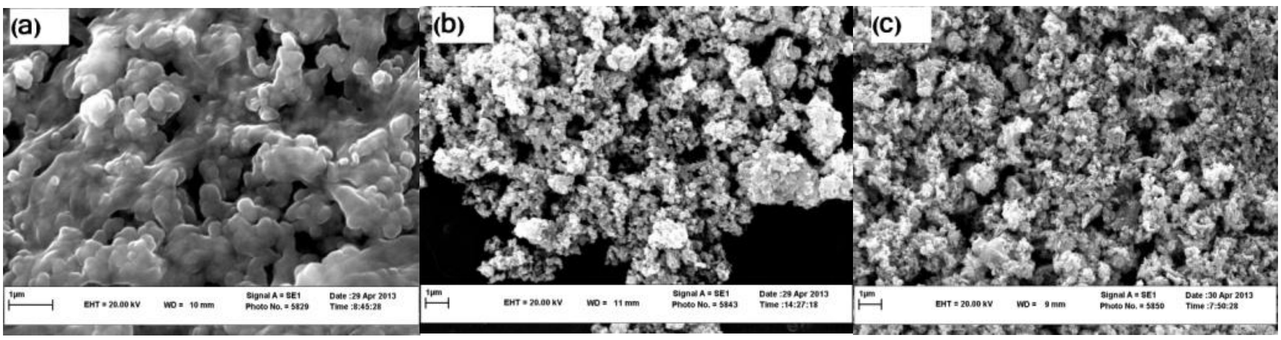

Fig 2.SEM images of $Bi_2Te_{2.7}Se_{0.3}$ (a),$Bi_2Te_{2.1}Se_{0.9}$ (b) $Bi_2Te_{1.5}Se_{1.5}$ (c)

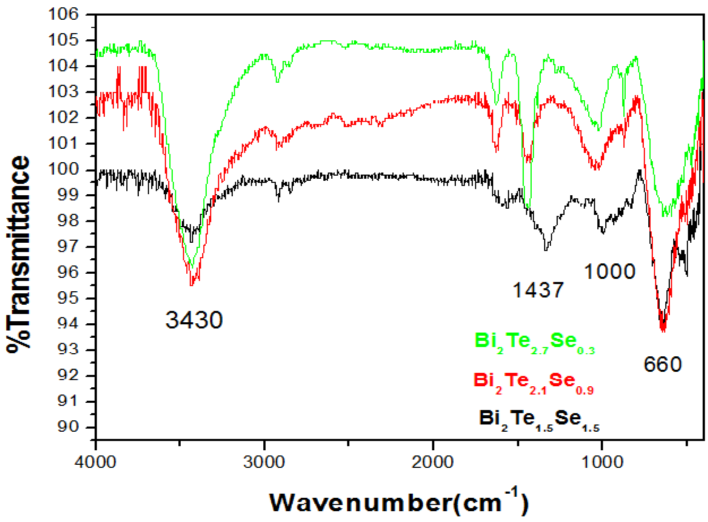

Fig 3. FTIR spectrum of samples

The thermoelectric measurement was carried out on the thin film sample. The Seebeck coefficients of -139.11, -120.0 and -98.85 µv/K, electrical resistivity of 7.03, 10.66 and 11.8µΩm and power factors of 2.748×10^{-3}, 1.354×10^{-3} and 0.85×10^{-3}W/mK^2 W/mk^2 were achieved for $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.1}Se_{0.9}$ and $Bi_2Te_{1.5}Se_{1.5}$ thin films, respectively [1].

Conclusion

Nanocrystalline $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.1}Se_{0.9}$ and $Bi_2Te_{1.5}Se_{1.5}$ thermoelectric compounds have been successfully synthesized via a hydrothermal route. The crystallite size of 8 to 20 nm were obtained using Scherrer equation. It is found the crystallite size of powders decreased with increasing content selenium. Then 100 nm thin films of them were fabricated by physical vapor deposition. The thermoelectric measurement were carried out on the thin films samples.

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