



Physical properties of $\text{Bi}_2(\text{Te, Se})_3$ and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ prepared using solid-state microwave synthesis

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ABSTRACT

$\text{Bi}_2(\text{Te, Se})_3$ and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ bulk products were synthesised using standard solid-state microwave synthesis. The $\text{Bi}_2(\text{Te, Se})_3$ and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ were then deposited thermally onto glass substrates at a pressure of 10^{-6} Torr. The structure of the samples was analysed using X-ray diffraction (XRD), and the powders and thin films were observed to be polycrystalline and rhombohedral in structure. The surface morphology of the samples was determined using scanning electron microscopy (SEM). From the measurements of optical properties, the energy gap values for the Bi_2Te_3 , Bi_2Se_3 , and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ thin films were 0.43, 0.73, and 0.65 eV, respectively.

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1. Introduction

Narrow-gap binary chalcogenides such as Bi_2Te_3 and Bi_2Se_3 function as thermoelectric materials at room temperature (300 K) [1]. Their crystal structures are rhombohedral with space group D_{3d}^5 ($R\bar{3}m$). These crystal structures can be represented as a stack of hexagonally arranged atomic planes, each consisting of only one type of atom. Five atomic planes are stacked in a close-packed (fcc) fashion with a (Te,Se)1-Bi-(Te,Se)2-Bi-(Te,Se)1 arrangement [2,3]. Recently, some new techniques have been developed for the preparation of $\text{Bi}_2(\text{Te, Se})_3$, including a simple chemical route [4], microwave-assisted synthesis [5], and solid-state microwave synthesis [6]. Interestingly, solid-state microwave synthesis provides a faster, simpler and more economically feasible method for the preparation of binary group chalcogenides such as Bi_2Te_3 and Bi_2Se_3 . Compounds prepared using solid state microwave synthesis may possess improved physical properties compared with those synthesised using other techniques [6]. To the best of our knowledge, there have been no previous reports describing a mixture of Bi_2Te_3 and Bi_2Se_3 , such as $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$, prepared via solid-state microwave synthesis. In the present study, the successful growth of Bi_2Te_3 , Bi_2Se_3 , and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ bulk products using solid-state microwave synthesis was reported. The corresponding thin films were deposited onto glass substrates via thermal evaporation of the bulk products. Their structural and optical properties were then examined.

2. Experimental

The Bi, Te, and Se used in the current work were of high-purity powder (99.999%). Preparation of Bi_2Te_3 was carried out by a mixture of Bi (0.5219 g) and Te (0.4781 g), and that for Bi_2Se_3 was carried out by a mixture of Bi (0.6383 g) and Se (0.3617 g) in a molar ratio of 2:3. A typical element ratio for the preparation of $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ is as follows: (0.5630 g) Bi, (0.1276 g) Se, and (0.3094 g) Te. All elements were mixed and ground for 20 min using a mortar and pestle. The materials were placed in a quartz ampoule under a vacuum of 10^{-5} mbar. The ampoule was inserted into a vertical alumina crucible. The sample was irradiated in an 800 W microwave oven (MS2147C) for 10 min with periodic shaking. Selected portions of the samples were imaged using a scanning electron microscope (SEM; JSM-6460). The Bi_2Te_3 , Bi_2Se_3 and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ bulks products were deposited onto ultrasonic cleaned glass substrates using thermal evaporation technique (Alcatel-101). The thermal evaporation runs were carried out at a pressure of 10^{-6} mbar. The substrate was held at room temperature throughout the depositions. The thicknesses of the thin films were determined to be approximately 0.42 μm using the Filmetrics F20 measurement system. XRD patterns of the resulting powders and thin films were recorded using an X-ray diffractometer system (PANalytical X'Pert PRO MRD PW3040). The optical properties were then measured using an FTIR spectrometer (PERKIN ELMER SPECTRUM GX) over the wavelength range of 1–5 μm .

3. Results and discussion

The XRD spectra illustrated in Fig. 1(a) and (b) for the Bi_2Te_3 , Bi_2Se_3 and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ powders and thin films indicate that these

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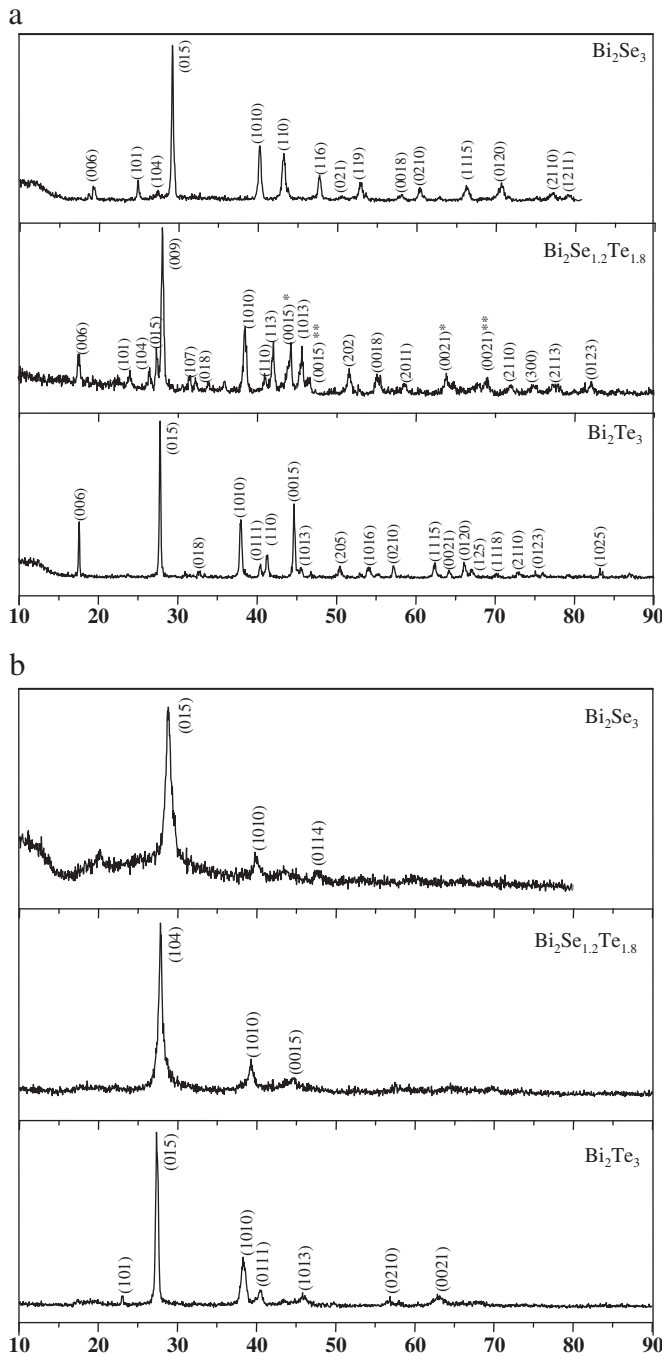


Fig. 1. (a) XRD of the powders, * refers to Bi_2Te_3 and ** refers to Bi_2Se_3 and (b) XRD of the thin films.

substances are polycrystalline and are rhombohedral in structure at 300 K. They are also in good agreement with the JCPDS values of Bi_2Te_3 and Bi_2Se_3 (Card No. 15-0863 and 33-0214). The rhombohedral crystal structure can be represented as a stack of hexagonally arranged atomic planes such that the lattice constant of the rhombohedral unit cell a_R for the powders can be determined using the following relationship [7]:

$$a_R = \frac{1}{3} \sqrt{3a_H^2 + c^2} \quad (1)$$

where a_H is the lattice constant for the hexagonal phase structure. This lattice constant can be calculated using the following equation [7]:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a_H^2} \right) + \frac{l^2}{c^2} \quad (2)$$

The values of a_H , c , and a_R are shown in Table 1.

The crystallite size (D) of the thin films was calculated via the Scherer's formula [7] from the X-ray diffraction pattern using the maximum intensity peak for each compound:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (3)$$

where β is the full width at the peak's half maximum intensity. The D values for the thin films were 237, 208, and 227 Å for Bi_2Te_3 , Bi_2Se_3 , and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$, respectively. Interestingly, the crystallite size of the films was observed to decrease with an increase in Se content.

From the SEM images, the bulk products reveal a non-uniform distribution of grain and are characterised by some void spaces as shown in Fig. 2(a), (b), and (c). To understand the variations in optical properties for the samples with varying selenium contents, ascertaining what is the actual composition of the as-prepared bulk samples is necessary. Fig. 2 also shows the nominal compositions and actual compositions measured by EDX for the Bi_2Te_3 , Bi_2Se_3 , and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ bulk products, respectively.

The optical properties of the Bi_2Te_3 , Bi_2Se_3 , and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ thin films were measured after obtaining the infrared absorbance and transmittance spectra. These absorbance data were used in conjunction with the Lambert law in order to obtain the absorption coefficient, α , using the following equation [8]:

$$\ln(I_0/I) = 2.303 \text{ Abs.} = \alpha t \quad (4)$$

where (I_0/I) is the ratio of the incident light intensity to the transmitted light intensity, Abs. is the absorbance, and t is the thickness of the film. The results in Fig. 3(a) indicate that the α for Bi_2Se_3 is $1.1 \times 10^4 \text{ cm}^{-1}$, a value higher than that reported for the Bi_2Te_3 and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ films. To calculate the band gap energy of the samples, the following equation was used [8]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (5)$$

where h is Planck's constant, ν is the frequency, A is a constant that depends on the transition probability, E_g is the energy band gap, and the parameter n depends on the transmissions type. Notably, Fig. 3(b) shows a plot of $(\alpha h\nu)^n$ as a function of $h\nu$ based on the assumption that $n = 2$. This finding indicates that the possible optical transition in the thin films is direct and does not rely on phonons. The values of the optical band gap E_g were 0.43 and 0.65 eV for Bi_2Te_3 and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$, respectively, whereas a band gap of 0.73 eV was estimated for the Bi_2Se_3 thin films. The values of E_g increased with an increase in Se content.

Table 1
Structural parameters of Bi_2Te_3 , Bi_2Se_3 and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ powders.

Parameters	Bi_2Te_3 -JCPDS	Bi_2Te_3 -powder	Bi_2Se_3 -JCPDS	Bi_2Se_3 -powder	$\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ -powder
a_H (Å)	4.3852	4.3724	4.1396	4.143	4.2932
c (Å)	30.483	30.26322	28.636	28.63602	30.10116
a_R (Å)	10.472	10.399	9.84	9.84047	10.335

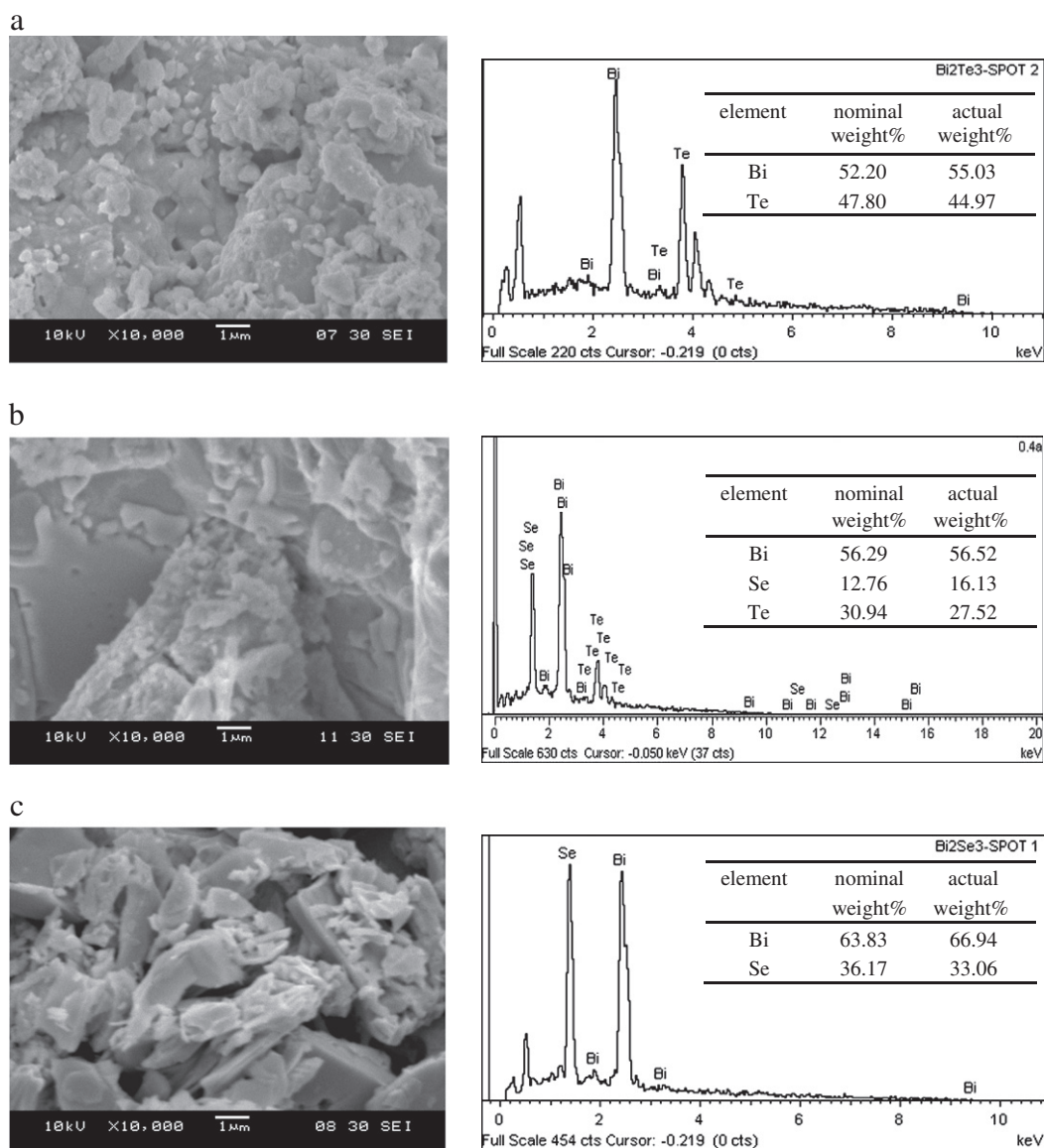


Fig. 2. SEM images and EDX results of the (a) Bi_2Te_3 , (b) $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ and (c) Bi_2Se_3 bulk products.

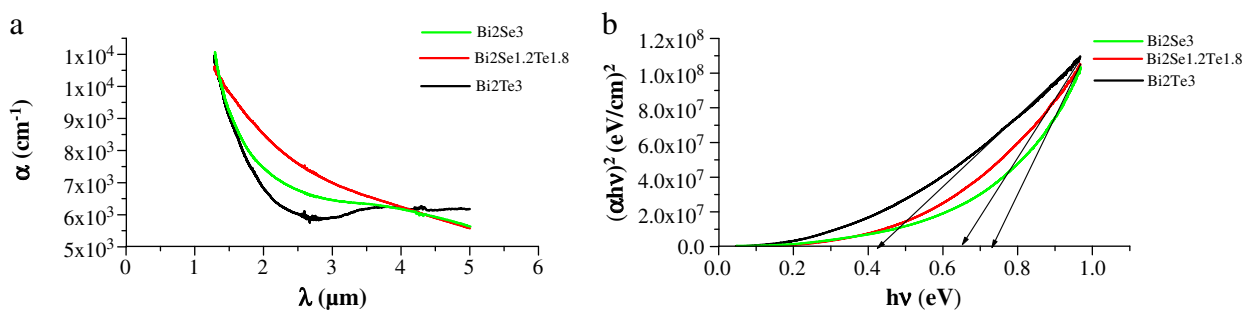


Fig. 3. (a) Absorption coefficient α as a function of wavelength λ and (b) $(\alpha h\nu)^2$ as a function of photon energy $h\nu$.

4. Conclusions

Rhombohedral Bi_2Te_3 , Bi_2Se_3 , and $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$ microstructures were produced successfully by inexpensive solid-state synthesis. Thin films of these compounds were deposited onto glass substrates via thermal

evaporation. Interestingly, the crystallite size was found to decrease with an increase in Se composition. From the optical measurements reported in the current paper, Bi_2Te_3 , $\text{Bi}_2\text{Se}_{1.2}\text{Te}_{1.8}$, and Bi_2Se_3 were found to have direct energy gap values of 0.43, 0.65, and 0.73 eV, respectively, which increased with an increase in Se content.

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