STRUCTURE, THERMAL, AND PHYSIC-CHEMICAL PROPERTIES OF SOME CHALCOGENIDE ALLOYS

by

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Bulk products of crystalline $Bi_2Se_{3-x}Te_x$ alloys (x =0.0, 0.1, 0.3, 0.5) were prepared using simple melting synthesis. Crystalline features, microstructure, and surface morphologies of the synthesized samples were examined via X-ray diffraction, scanning electron microscope, and energy dispersive X-ray spectrometer. Elemental distribution was studied by energy dispersive analysis of X-ray spectroscopy. Polycrystalline of rhombohedral crystal structure was observed for the concerned samples. Perfect crystallinity and micro-scalability of the prepared were also reflected by the physic-chemical properties of each sample. Thermal behavior was studied throughout differential scanning calorimetry and thermogravimetric analysis showing that the samples are of high stability over high temperature range. Physic-chemical properties were determined in terms of experimental density. These properties were compactness value, molar volume and the percentage of free volume. Density of Bi_2Se_3 alloy was obtained at 7.37 gm/cm^3. The Te doping enhanced the density of the $Bi_2Se_{3-x}Te_x$ system. The most Te doped alloy showed density of 9.018 gm/cm^3. All other physic-chemical properties showed strong dependence on the Tea amounts in the system.

Key words*: chalcogenides, crystal structure, thermal behavior, physic-chemical properties*

Introduction

Compounds of Bi-based chalcogenides such as Bi_2Se_3 and Bi_2Te_3 are well known as layered materials of narrow bandgap. Crystalline asymmetric band structure with rhombohe-

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dral unit cell has been observed for these compounds [1]. Narrow band gap chalcogenide semiconductors of layer structure show interest and high potential for thermoelectric and Hall-effect applications in addition to interesting electrophysical and galvanomagnetic features [2].

As reported, chalcogenides are promising candidates for photodetectors, electrochemical cells and many optoelectronic applications [3, 4]. Experimentally, it was found that Bi_2Se_3 and Bi_2Te_3 are van der Waals layered compounds with metallic surface states which is of high technological importance in topological insulators applications, as topological insulating features were discovered in Bi_2Se_3 and Bi_2Te_3 chalcogenides.

The Bi_2Se_3 and based chalcogenides have shown much interesting for optoelectronic applications. In addition, layers of nanocrystalline Bi_2Se_3-Bi_2Te_3 are quite interesting for applications in quantum electronics and information storage devices. Due to low-cost, thin layers of Bi_2Se_3-Bi_2Te_3 are very promising for solar cells fabrication. Not only this but also $Bi_2Te_{3-x}Se_x$ alloys have long been investigated for thermoelectricity owing to their promising physical, electrical and thermal properties which make them ideal candidates for thermoelectric power generation applications [5-7]. On the other hand, investigations of the unique structural and physical properties of binary chalcogenides of the V_2VI_3 group are feasible towards applications in the field of optoelectronic devices and thermo-electric modules [8]. For example, bulk materials of $(Bi,Sb)_2(Te,Se)_3$ were reported to exhibit high seebeck coefficient value demonstrating high applicability in applications such as thermoelectric based refrigerators [9]. Additionally, Bi_2Te_3 and based alloys have long been known as one of the best candidate compounds for low temperature and room temperature waste heat recovery. As reported, devices based on thermoelectric technology can work in reverse mode as a heat pump to produce cooling (refrigeration) with the many advantages including high reliability, small size and no noise, as well. By these measures of performance, thermoelectric technology is highly competitive [10-14].

As well known, the material's properties are strongly dependent on the internal structure and crystal features. Therefore, we present in this article a systematic study on the structural and physic-chemical features of the crystalline $Bi_2Se_{3-x}Te_x$ alloys prepared by simple melting method. To the best of knowledge, few limited data can be found on physic-chemical properties of bismuth chalcogenides. Therefore, a comprehensive study on crystal structure, grain size, density and other based structural properties of $Bi_2Se_{3-x}Te_x$ alloys is present in this research.

Experimental procedures

Bulk crystalline samples of $Bi_2Se_{3-x}Te_x$ system were prepared from pure powders of Bi, Se, and Te elements (99.999% purity). The appropriate weights of the pure elements constituting the alloy were determined by electrical analytical microbalance (AINSWORTH) with sensitivity 10^{-4} g. The weighted elements were then charged into silica tubes with the dimensions of 1 cm diameter and 15 cm length, sealed under vacuum (10^{-5} mbar). The tubes were washed using first order distilled water and then carbonized with high purity acetone. The mixture inside the quartz tubes were placed in programmable furnace (VOP VULCAN D-550) at 1100 °C for 10 hours. During melting, the mixture was shaken and agitated to ensure homogeneity of the melt alloy. The molten mixture was then cooled inside the oven by furnace cooling till room temperature. Worth mentioning that the melting process was performed at a temperature higher than the melting point of the each of the working elements (Bi of melting point 271.5 ºC, Se melts at 217.0 °C, and Te of 449.5 °C). Also, the temperature

used (1100 °C) is much higher than the melting temperature of Bi_2Se_3 phase (705 ºC), and that of Bi_2Te_3 phase (586 ºC). However, it was much proper to prepare better crystalline compounds due to the super-heating effect. The alloying period was extended to about 10 hours, which was found very proper to perform the required reaction. The internal microstructure, morphologies and elemental distribution in the prepared samples were investigated by XRD (with Cu K_α radiation at λ = 1.5406 Å) besides SEM technique (Model: FEINOVA NANO-SEM-200) attached with an energy-dispersive X-ray (EDX) spectrometer, respectively. Estimations of the crystallite size were performed with the aid of the known Williamason-Hall formula. Moreover, essential information such as phase purity and lattice parameters were obtained from the conducted analysis. Thermal characteristics were examined using differential scanning calorimetry (DSC) technique. Physic-chemical properties were experimentally estimated for the studied and the effect of tellurium addition on the properties was also studied.

Results and discussions

Crystal structure and phase purity of as-prepared bulk $Bi_2Se_{3-x}Te_x$ alloys were examined with the aid of XRD analysis using Cu K_α radiation source with λ = 1.5406 Å). Figure 1 shows the diffractograms for powder samples taken from the grounded bulk alloys. As illustrated in the figure, all diffractions peaks are in well matching with the standard JCPDS cards of Bi_2Te_3 and Bi_2Se_3.

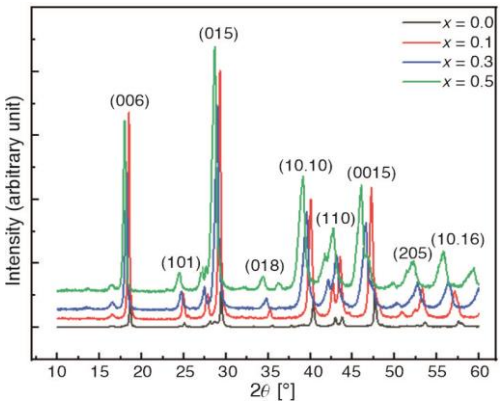

Figure 1. The XRD curves of $Bi_2Se_{3-x}Te_x$ powder alloys

Essential information such as purity, lattice parameter and crystallite size were revealed from XRD analysis. Identification of the present phases are believed to be responsible for the physic-chemical and thermal properties of the prepared compositions.

Sharp peaks at 2θ = 29.439º and 18.639º were observed indicating a hexagonal phase of Bi_2Se_3 corresponds to (006) and (015) planes, respectively. The Te doped samples exhibited strongest main peak at 2θ = 27.719º corresponding to the orientation plane (015) as preferable growth orientation direction. Appearance of many peaks on the diffractograms is attributed to the different orientations of the crystallite structure and the polycrystalline nature of the compounds. All observed peaks in the XRD patterns were clearly identified from the JCPDS standard cards of polycrystalline Bi_2Se_3 compound [15]. It can be observed that Te atoms crystallize in the same place and shape of the Se atoms in the $Bi_2Se_{3-x}Te_x$ system. Introducing Te atoms is revealed by a notable shift detected for all main. The main peak shists to the left side due to different atomic radii of Se and Te atoms [16].

Lattice parameters of the prepared systems were determined from the most intense diffraction peaks. The determined lattice parameters are tabulated in tab. 1. Data in tab. 1 reveal good agreement with previously reported values. On the other side, the crystallite-sizes of the pristine and doped samples were estimated using the Williamason-Hall relation expressed:

$$\beta\cos\theta = 4\varepsilon\sin\theta + \frac{0.9\lambda}{D_t} \tag{1}$$

where β [radians] is the full width at half maximum (FWHM) of the most intense peaks, D_t [nm] – the magnitude of crystallite diameter, λ [nm] – the wavelength of the used X- rays, θ [°] – the diffraction angle, and ε – the micro-strain.

The calculated values of the crystallite size are tabulated in tab. 1. As shown, a remarkable increase can be seen as the Te content increases. Such increase is attributed to the larger ionic radius of Te with respect to that of Se.

Table 1. The EDAX results, grain size, lattice parameters, crystallization temperature, and peak melting temperature of $Bi_2Se_{3-x}Te_x$ bulk alloys

Sample	EDAX results			D_t [nm]	Lattice parameters [Å]		T_c [K]	T_m [K]
	Bi%	Se%	Te%		*a*	*c*		
$x = 0.0$	40.43	59.57	0.0	45	4.139	28.636	684	851
$x = 0.1$	40.16	52.93	6.91	51	4.218	29.420	659	873
$x = 0.3$	40.13	48.94	10.93	55	4.219	29.421	658	885
$x = 0.5$	40.03	23.01	36.96	69	4.219	29.579	656	902

Morphological properties and composition of the samples were obtained from SEM coupled with EDAX analyzer. The SEM analysis was carried out for rough (as-prepared) surface of the bulk samples. The SEM micrographs of Bi_2Se_3 and $Bi_2Se_{3-x}Te_x$ samples are shown in fig. 2. The SEM images indicate uniform surface without cracks indicating high density for the prepared materials. Clearly, surface of each sample would be considered as a strong agglomeration of micro-sized grains stacked together compactly. Noticeable variation in shape and size in the morphological properties can been seen in each compound. Obviously, Te-doping changes the appearance, color and density of the material. With higher Te amounts much compact and much denser materials are developed. The SEM observations are in well matching with density calculations and other determined parameters.

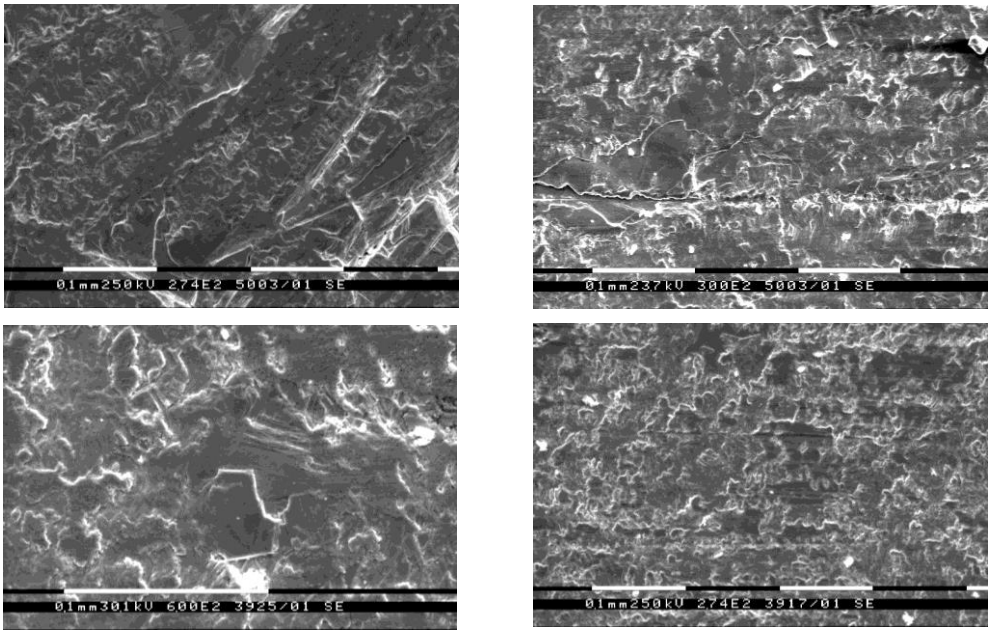

Figure 2. The SEM micrographs of $Bi_2Se_{3-x}Te_x$ bulk alloys

A quantitative analysis to detect the presence percentages of Bi, Se, and Te elements in the prepared alloys was performed with the aid of energy dispersive analysis of X-ray spectroscopy (EDAX). The obtained data of the EDAX analysis are illustrated in tab. 1. As shown in the table, the ratios of elements are in well agreement with the stoichiometric ratio of $Bi_2Se_{3-x}Te_x$. Investigations on the structural characteristics and thermal behavior of the studied samples were carried out using thermal analysis. Differential scanning calorimetry (DSC) technique was employed for this purpose. The DSC technique was mainly used check out the phase transitions, specific heat, melting and crystallization temperatures, degree of crystallinity, oxidative stability and thermos-kinetics. As known the thermal stability provides important information on the maximum working temperature of the material. Additionally, thermogravimetric analysis (TG) is helpful for purposes of quantitative characterizations related to mass changes and/or decomposition versus temperature. Therefore, a complete study of the thermal behavior of $Bi_2Se_{3-x}Te_x$ was conducted using simultaneous thermal analysis (STA) which represents the simultaneous measurement ofDSC and TGA. Simultaneous TGA-DSC studies were carried out at the heating rate of 10 K per minute in air atmosphere. The used amounts of each sample in the analysis were around 12.30-12.50 mg, powder materials. The analysis was performed over a wide range of temperature from 300-973 K.

Crystallization temperature, T_c, is exhibited referring to an exothermic reaction, which occured due to a sudden change in specific heat [17]. The Crystallization temperature of each sample was recorded and shown in tab. 1. Also, peak melting temperature, T_m, was calculated and tabulated in tab. 1.

Notably, T_m increases with increasing the amounts of Te in the Bi_2Se_3 lattice. Such behavior is discussed with the concept of chemical-network model. As more Te incorporated into the Bi_2Se_3 lattice, more bonds are formed by Te atoms with Bi atoms, rather than with Se. Consequently, the average bond energy of the system decreases and thus the T_m increases because the bond energy of Bi-Se bond, about 170.4 kJ/mol, is larger than the reported bond energy of Bi-Te, around 125.6 kJ/mol, whilst the value of T_c decreases.

Study of physic-chemical parameters such as density and compactness is important in determination of the order of atoms and the type of connection between the structural units of the material. Moreover, the free volume percentage and molar volume were estimated for the studied materials. The density was measured with Archimedean immersion method using a simple piknometeric and distilled water as immersion fluid.

Density was calculated using the formula [18]:

$$\rho = \frac{m}{m + m_1 - m_2}\rho_0 \tag{2}$$

where m, m_1, m_2, and ρ_0 are mass of the alloy sample, mass of piknometer, mass of the used water, and density of the water, respectively. Density of water was taken as 0.998 gm/cm^3.

Behavior of density *vs.* Te amounts is illustrated in fig. 3. Obviously, the density of $Bi_2Se_{3-x}Te_x$ system increases with increasing the Te amounts. The notable increase can be attributed to the fact that atomic weight of Te is much greater than that of Se. The parent Bi_2Se_3 alloy showed density of 7.37 gm/cm^3. The most Te doped alloy showed density of 9.018 gm/cm^3 with enhancement of 22%.

Compactness of the synthesized samples, σ, was determined from density measurements. The following equation was employed:

$$\sigma = \frac{\sum_i \frac{C_i A_i}{\rho_i} - \sum_i \frac{C_i A_i}{\rho}}{\sum_i \frac{C_i A_i}{\rho}} \tag{3}$$

As present in fig. 3(b), σ increases with Te increasing which is expected due to the proportional between compactness and the density. The more tellurium content is added, the more compact the structure becomes.

For more investigations on the physic-chemical properties, molar volume, V_m, was estimated for the $Bi_2Se_{3-x}Te_x$ system as [19]:

$$V_m = \frac{1}{\rho}\sum_i C_i M_i \tag{4}$$

Noting that M_i and C_i refer to the atomic weight and the molecular concentration of the i^{th} component in the $Bi_2Se_{3-x}Te_x$ system, respectively.

The dependence of the molar volume on the Te content is shown in fig. 3(c). A notable reduction in the value of the molar volume with tellurium addition can be observed. The reduction can be ascribed to the nature of the dependence between the material's density and its molar volume.

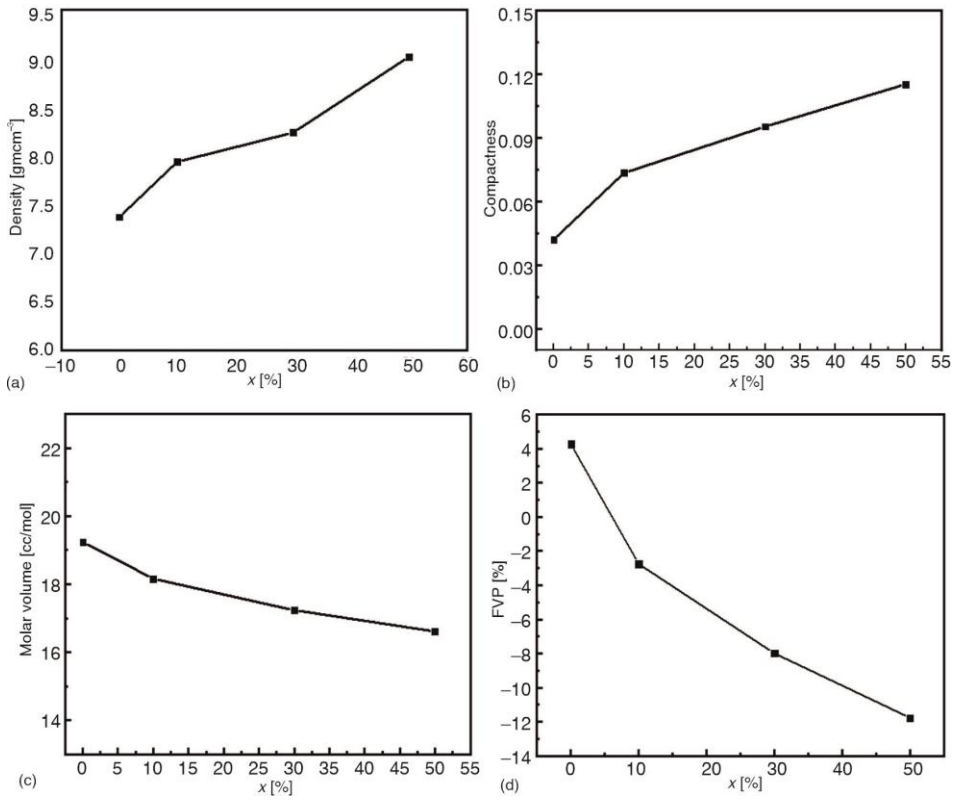

Figure 3. Physic-chemical properties of $Bi_2Se_{3-x}Te_x$ bulk alloys, in terms of density (a), compactness (b), molar volume (c), and free volume percentage (d)

Another important parameter in examination of the structural and internal characteristics of the crystal is free volume percentage (FVP). The free volume percentage in the synthesized alloys was calculated using the formula:

$$FVP = \frac{V_M - V_T}{V_M} 100\% \tag{5}$$

where V_M is the molar volume and V_T is the theoretical volume. The theoretical volume was estimated according to the relation:

$$V_T = XV_A + YV_B + ZV_C \tag{6}$$

where V_A, V_B, and V_C represent the atomic volumes of the elements while X, Y, and Z refer to the atomic fraction of each element of the alloy's constituting elements. Dependence of the free volume percentage on the Te amounts in the $Bi_2Se_{3-x}Te_x$ system is demonstrated in fig. 3(d). The exhibited negative values are because of the theoretical volumes are higher than the molar volumes for some alloys. On the other side, FVP showed significant reduction as the Te content increases, which is due to the reduction in the degrees of freedom, resulting in enhancing of the mechanical stability of the material.

Conclusion

Bulk samples of $Bi_2Se_{3-x}Te_x$ ingots were prepared via direct melting of pure powders of Bi, Se, and Te elements in quartz tubes at high temperature. The crystal structure and surface morphology of the prepared compounds were investigated with the aid of XRD, SEM, and EDAX analyses. The XRD studies revealed polycrystalline nature of the alloys with hexagonal Bi_2Se_3 phase. The SEM characterizations showed dense and compact structure of high homogeneity. The DSC and TGA analyses were employed to the studies of thermal properties of the studied materials. Crystallization temperature and peak melting point were obtained and investigated. Physic-chemical properties such as density and based structural properties were examined, showing strong dependence on the composition of alloy. The findings of the current work proved that the addition of Te altered and enhanced the physic-chemical properties.

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