Structural Properties of Thermally Evaporated $Bi_2(Te_{1-x}Se_x)_3$ Thin Films

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A polycrystalline $Bi_2(Te_{1-x}Se_x)_3$ with variable composition x (where $0 \leq x \leq 1$) has been prepared using Bridgman method. Thin films of the prepared alloys with different compositions were deposited onto ultra clean glass substrates by the thermal evaporation technique. The as-deposited $Bi_2(Te_{1-x}Se_x)_3$ thin films were investigated by electron scanning microscope (ESM), energy dispersive spectroscopy (EDAX) and X-ray diffraction (XRD) for surface morphological, compositional and structural studies. X-ray diffraction study confirmed that the bulk materials with different compositions are polycrystalline in nature having rhombohedral structure. The as-deposited films have amorphous structure but the films annealed at temperatures more than 400 K are polycrystalline. The effect of selenium content and the thermal annealing on various structural parameters was also investigated. The thin films exhibit preferential orientation along the [015] direction for the films annealed at temperatures more than 400 K, together with other abundant planes (101) and (110). Various structural parameters such as lattice constants, crystallite size, strain and density have been calculated and they are found to be compositional dependent.

1. Introduction:

There is an increasing interest in thermoelectric materials for refrigeration applications in industry and other areas like space, defense, biology, and photonics as well as sensor applications. More interest is expected to develop with advances and discoveries in nanotechnologies and microsystems. Ternary alloys prepared out of semiconductor materials can be grouped as a class of semiconductors in which lattice parameter, energy band-gap and other operational parameters could be continuously varied as per requirements by selecting the constituents and their relative concentrations suitability. The use of thin film polycrystalline semiconductors has attracted much interest in an expanding variety of applications e.g. in various electronic and optoelectronic devices [1-5]. Group V_2VI_3 compounds are known as good thermoelectric

materials. These thermoelectric materials have been widely applied to cool electronic devices such as integrated circuit packages, laser diodes and infrared detectors, because quick and precise control of temperature is possible with almost no noise during operation [6-8]. In particularly the binary semiconductors Bi_2Te_2 and Bi_2Se_3 and their solid solutions, which have attracted much attention because of their potential application in the micro-fabrication of integrated thermoelectric devices, and they have very high value of figure of merit [9 - 12].

Solid solutions formed by melting of Bi, Se and Te are well known to be the best materials for thermoelectric refrigeration at room temperature. The more interesting solid solution is of the system $Bi_2(Te_{1-x}Se_x)_3$ (where $0 \leq x \leq 1$). Structural parameters directly affect the optical and electrical properties of thin films of this system [13]. The preferential orientation in particular plays a major role in the determination of physical properties of these films.

In many cases, neither the compositions nor the crystal structure of the films of the system $Bi_2(Te_{1-x}Se_x)_3$ with different compositions, (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) have been studied in sufficient detail to allow knowledge of the correct avenue to follow in order to improve the properties. Even though, a large volume of work has been done on this system with compositions x = 0, 0.1 and 1 [14-22], there is no literature available on the structural, optical and electrical properties of the system $Bi_2(Te_{1-x}Se_x)_3$ (where x = 0.2, 0.4, 0.6, 0.8) . The aim of this work is to synthesis compounds of the system $Bi_2(Te_{1-x}Se_x)_3$ with different x values and to give a detailed study on the structural characterization of thermally evaporated $Bi_2(Te_{1-x}Se_x)_3$ thin films where x ranges between 0 and 1 in steps of 0.2. Correlation between compositions as well as thermal annealing, with the different structural parameters will be also investigated.

2. Experimental Techniques:

2.1. Preparation of $Bi_2(Te_{1-x}Se_x)_3$ ingot.

There are several methods for preparing the original bulk materials of semiconducting compounds, belong to the family of V_2VI_3 and their alloys, from its constituents elements [23- 28]. Among these methods, we have used the Bridgman technique for obtaining $Bi_2(Te_{1-x}Se_x)_3$ compounds with different values of x. In this method, silica tube is used which has a constricted sharp end at the bottom to facilitate seeding in the growth process. The silica tube is washed with hot distilled water and pure alcohol, and then coated with a thin layer of graphite to prevent contamination of the charge on the inner surface of the silica tube. Elements of 99,999% pure bismuth, selenium and tellurium (Aldrich Mark) weighed in stoichiometric ratio using electric balance,

sensitivity 10^{-4} gm (Sartorius Mark). The mixture of each composition was taken in a silica tube, sealed under vacuum $\approx 1.5 \times 10^{-4}$ Pa.

At the beginning of the growth runs, the silica tube was held in the hot zone of the furnace about 24 hours for complete melt of the composition. Then the tube was shaking during heating several times for homogenization. The rate of propagation of the crystallization front was 1.7 mm /h. The temperature of the middle zone is ranges from 870 K to 995 K corresponding to the crystallization temperature of the prepared samples with different compositions. The duration time for producing the compound as crystal is about twelve days. The product crystal was 1.5 cm diameter and 1.5 cm in length.

2.2. Preparation of Thin Films:

Thin films of $Bi_2(Te_{1-x}Se_x)_3$ were prepared by depositing the original bulk material on suitable substrates, held at room temperature (300 K) during the deposition process, by conventional thermal evaporation technique. The substrates were carefully cleaned by hot water, chromic acid, distilled water, and ethyl alcohol, successively. A high vacuum coating unit (Edwards 306 A) with a single source was employed for thin film preparation at high vacuum of $\sim 5 \times 10^{-4}$ Pa. The plate holder can be rotated by means of an electric motor with different speeds so that homogenous film thickness can be obtained.

In each evaporation process, the quantity of the bulk material was completely evaporated to avoid spillage and/or decomposition of the material by overheating during evaporation. The thermal evaporation rate was kept constant at ~ 3 nm/s allover the deposition time. The film thickness, t, was monitored by a quartz crystal thickness monitor (Edward, FTM4) and it was also measured interferometrically [34]. The as-deposited films were annealed at 323, 373, 423, and 473 K for 1 h under a vacuum of 1.5×10^{-1} Pa .

The elemental composition of the bulk material as well as the as-deposited films was determined using an energy-dispersive X-ray spectrometer (EDXS) unit, interfaced to a scanning electron microscope (SEM; Philips XL) operating at an accelerating voltage of 30 kV. The relative error of determining the indicated elements does not exceed 5 %.

X-ray diffractograms were obtained with computer controlled X-ray diffractometer (formally made by Diano corporation U.S.A.) has a measuring range (2θ) from -20° to +150°. The reproducibility 2θ is ±0.01° and the diameter of the measuring circle is 401 mm. the detector is scintillation counter with a dead time of less than 10^{-6} sec. Fe filtered Co radiation was used. The X-ray tube was energized at 45 kV and 10 mA. The X- diffraction patterns were recorded automatically using the software Diano corporation XPEX.

3. Determination of Structural Parameters:

3.1 Lattice Constant:

The thermally evaporated $Bi_2(Te_{1-x}Se_x)_3$ with variable composition x (where $0 \leq x \leq 1$) thin films posses the rhombohedral structure with space group R3m. It is confirmed by comparing the peak position (2θ) of the XRD pattern of the film with the standard X-ray powder diffraction data file for the binary samples [35]. The lattice constants "a" and "c" for the hexagonal phase structure is determined by using the relation [36]

$$1/d^2 = (4/3)\ \{h^2 + hk + k^2\}\ /\ a^2 + l^2/c^2$$

3.2. Size and Strain:

The size (D) and strain (ε) developed in the $Bi_2(Te_{1-x}Se_x)_3$ thin films are calculated using Dehlez method [37.].

3.3 Dislocation Density

The dislocation density is estimated using the relation [38].

$$\rho = 15\ \varepsilon\ /\ a\ D$$

where "a" is the lattice constant, D is the particle size and ε is the micro-strain.

3.4. Number of Crystallites:

Once the crystallite size is estimated, the number of crystallites per unit surface area can also be obtained by using the relation [39]

$$N = t\ /\ D^3$$

where D is the mean crystallite size and t is the thickness of the film.
Along with all these properties, the volume of the unit cell and the axial ratio (c/a) were also estimated for all samples with various compositions.

4. Results and Discussion:

Compositional analysis and crystal homogeneity are verified by powder X-ray analysis, and energy dispersive X-ray analysis (EDAX). The particle size and morphology of the samples was examined by the transmission electron microscopy (TEM).

The weight percentage of the elemental compositions of the prepared materials of $Bi_2(Te_{1-x}Se_x)_3$ compounds with indicated x, and their thin films are computed from the analysis of energy dispersive X-ray spectrometry (EDXS). The calculated contents of Bismuth, Tellurium and Selenium wt % were comparable with those included in the starting mixture, indicating that the synthesized material are very nearly stoichiometric for all the investigated

samples (Table 1). Fig. (1) shows the EDAX spectrum of $Bi_2(Te_{0.4}Se_{0.6})_3$ material as a representative one.

Table (1) Initially included and actually existing, using EDAX wt % of $Bi_2(Te_{1-x}Se_x)_3$ solid solutions.

Somposition	Actual wt% calculated			Experimental wt%		
	Bi	Te	Se	Bi	Te	Se
Bi_2Te_3	40	60	-	40.77	59.23	-
$Bi_2Te_{2.4}Se_{0.6}$	40	48	12	40.93	49.23	9.84
$Bi_2Te_{1.8}Se_{1.2}$	40	36	24	38.22	36.64	25.14
$Bi_2Te_{1.2}Se_{1.8}$	40	24	36	37.52	28.34	34.14
$Bi_2Te_{0.6}Se_{2.4}$	40	12	48	36.76	13.87	49.37
Bi_2Se_3	40		60	39.97	-	60.03
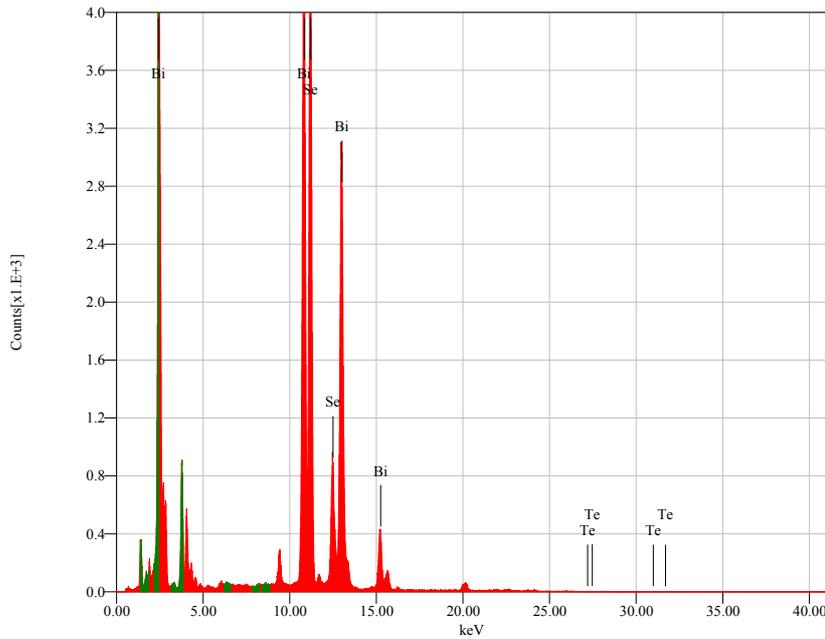
Fig. (1): EDAX spectra of $Bi_2(Te_{0.4}Se_{0.6})_3$ in powder form.

The deviation from stoichiometry in prepared samples is comparable with the experimental error (± 2 %).

Figure (2 a-c) shows the transmission electron microscope image of as-deposited (300K) $Bi_2(Te_{0.8}Se_{0.2})_3$ thin films and annealed at different temperatures (373 K and 473 K). The grain size was measured to be in the range of micron. The electron diffraction pattern carried out for the same sample as a representative one for the investigated system, of both as-deposited (300 K) and annealed in vacuum of 1.5 x 10^{-1} Pa at 373 K and 473 K are illustrated in Fig. (2 d-f). The rings are diffused in the as-deposited sample indicating the amorphous structure, but the films annealed at 373 K, 473 K show well defined spots, indicating polycrystalline structure.

The X-ray powder diffractogram of the synthesized material in a fine powder of the system $Bi_2(Te_{1-x}Se_x)_3$ (where x = 0, 0.2, 0.4 , 0.6, 0.8 and 1) are represented in Fig. (3), which indicating that, all the investigated samples have a polycrystalline structure. Although, the general form has the same feature, the peak positions shift slightly on passing from one composition to other. Matching between the observed reflecting planes and those of the standard data indicated no extra peaks corresponding to the precipitation of elements or binary alloys along the whole measured 2θ range, indicating the formation of a single phase.
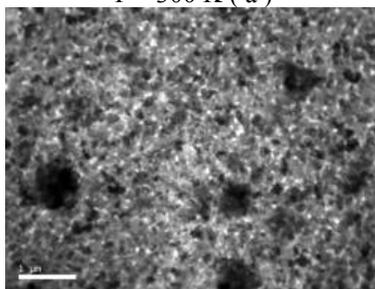
The correspondence between the diffraction lines with different compositions indicates that all the compounds have the same crystal structure (isostructural), as shown in Fig. (3).
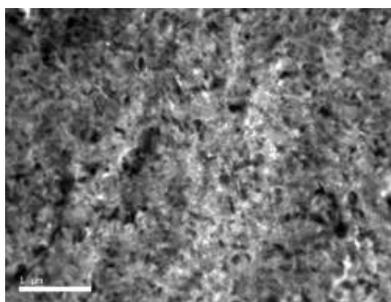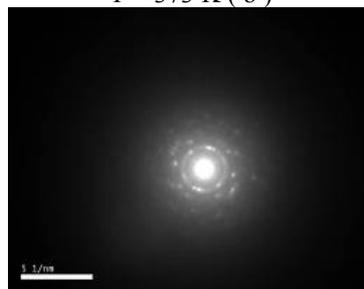

T = 300 K (a)
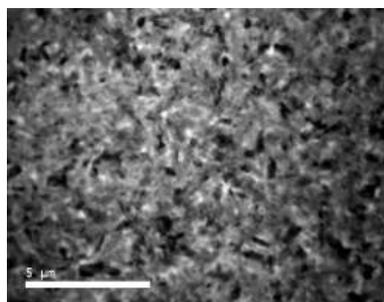
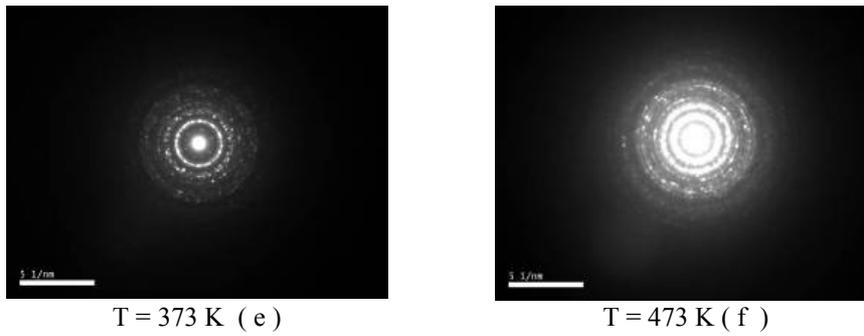T = 373 K (b)

T = 473 K (c)

T = 300 K (d)

T = 373 K (e)   T = 473 K (f)

Fig. (2): Transmission and electron microscope (a-c) and electron diffraction (d-f) images of $Bi_2(Te_{0.8}Se_{0.2})_3$ thin films annealing at different temperatures
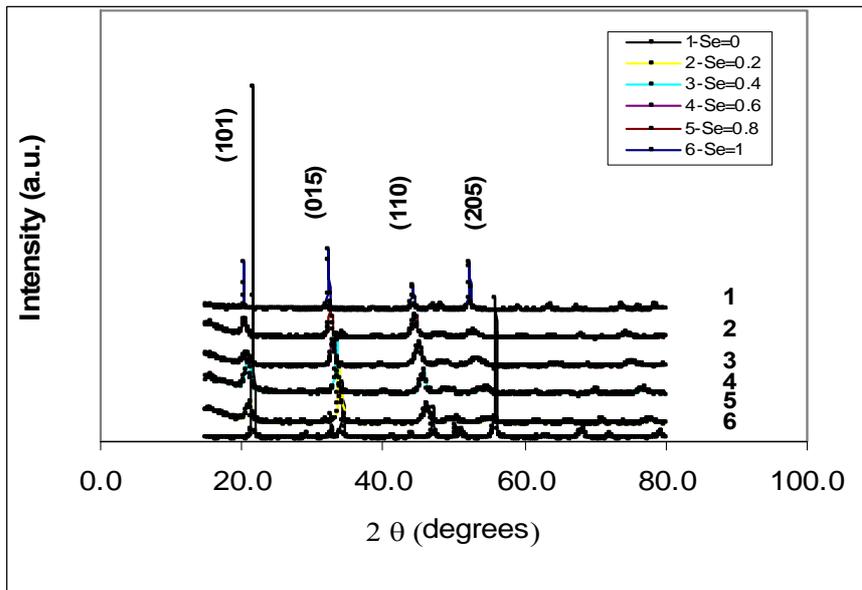

Fig. (3): XRD of $Bi_2(Te_{1-x}Se_x)_3$ powder of different compositions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0)

The structure of the synthesized binary samples Bi_2Se_3 and Bi_2Te_3 in powder form, is in quite agreement with the standard XRD data (International Center for Diffraction Data ICDD) for Bi_2Se_3 card No 33-021415-863 and for Bi_2Te_3 card No 82-0358) and have rhombohedral system [a = 4.127 Å and c = 28.58 Å for Bi_2Se_3 and a = 4.395 Å, c = 30.44 Å for Bi_2Te_3] having space group R3m [40]. Since no references in the ICDD files were found for the investigated ternary system, the X-ray diffractograms were subjected to the

indexing process in order to calculate unit cell dimensions of the compounds under investigation. Consequently, the observed reflecting planes were indexed and the unit cell parameters were determined using the Divol-91 computer program [41]. The analysis has indicated that the ingot material is a single phase polycrystalline material corresponding to the rhombohedral type structure with space group R3m. It was found that the interplaner spacing d decreases with increasing Se content as shown in Fig. (4).
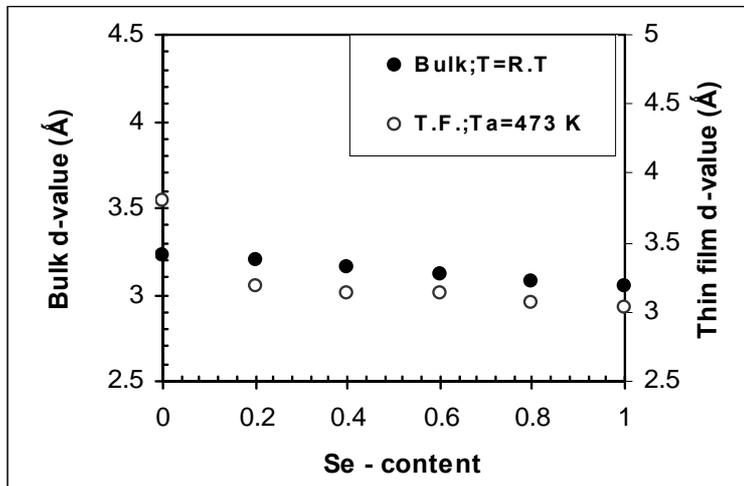

Fig. (4): Variation of the d-values of $Bi_2(Te_{1-x}Se_x)_3$ bulk and thin films with composition.

Plots of the lattice parameters (a, c) and the axial ratio (c/a) as a function of composition, is shown in Fig.(5 A,B). It is clear from this figure that, the parameters (a, c, c/a) decrease with increasing Se contents. The increase of c/a of $Bi_2Te_{1.8}Se_{1.2}$ thin film may be due to the low value of the lattice constant a, for this composition. Consequently, it is concluded that the substitution of Te by Se in the system $Bi_2(Te_{1-x}Se_x)_3$, only effect the unit cell parameters [42 and 43]. This behaviour may be referred to the difference in ionic radii and atomic weight of selenium and tellurium as well as their electronegativity.

Figure (6) shows the X-ray diffractograms of the prepared thin films of different compositions annealed at 473 K which idicates that, the position of the peaks shifts slightly on passing from one composition to other, a behaviour which is similar to that of the bulk.
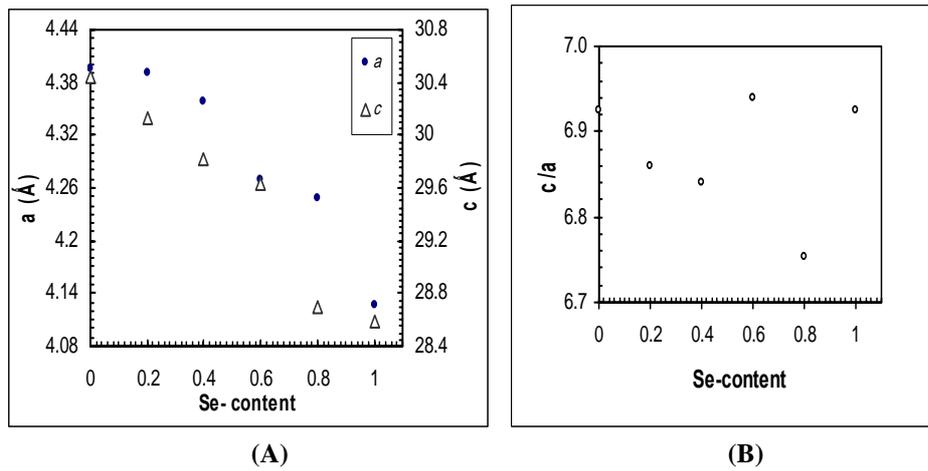
Fig.(5): Variation of lattice parameters: **A)** a and c, and **B)** c/a with Se-content for $Bi_2(Te_{1-x}Se_x)_3$ compound.

Figure (7) represents the X-ray diffractograms of the as deposited $Bi_2(Te_{0.8}Se_{0.2})_3$ thin film and that annealed in vacuum ($1.5x10^{-1}Pa$) at different temperatures as a representative example for the investigated system $Bi_2(Te_{1-x}Se_x)_3$, which show that, the as-deposited films and those annealed at 323 K, have the amorphous structure, but films annealed at 423 K and 473 K have polycrystalline one. Fig. (7) indicates also that, all films of different compositions exhibit strong (015) orientation associated with minor peaks of the reflection planes (110) and (205), while Bi_2Te_3 (x = 0) has a high degree of preferred orientation along [110] direction. It has been observed also that, there are some changes in the intensity and peak positions with increasing the peak intensity appreciably with increasing the annealing temperature for all investigated samples. This increase in the peak intensity associated with annealing indicates that, the grains have essentially random orientation, and substantial atomic arrangement can take place upon annealing.

Variation of the microstrain (ε) versus the annealing temperature shows a decreasing trend. This behaviour is an acceptable one due to the fact that the strain in general released and decreased normally with raising the annealing temperature. On the other hand, however at constant annealing temperature the strain decreases by increasing Se content in all the investigated films except that film with x = 0.8 as shown in Fig. (8). Changing the selenium content leads to a change in the lattice parameters as well as other structural parameters. This may be interpreted either in terms of outward relaxation at the particle faces so that two or three interplaner spacing are appreciably distorted [44, 45] or on the

basis of surface tension consideration [46, 47]. The sign of the surface energy can give rise to which of the two forces is dominated [48].
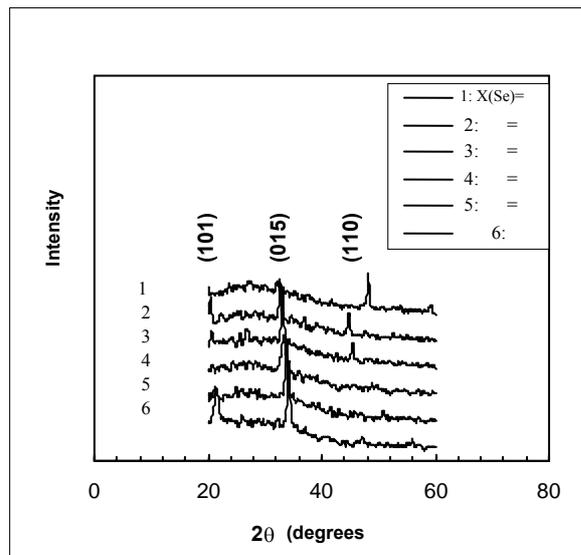

Fig. (6): XRD of $Bi_2(Te_{1-x}Se_x)_3$ thin films with composition x at T= 437K.

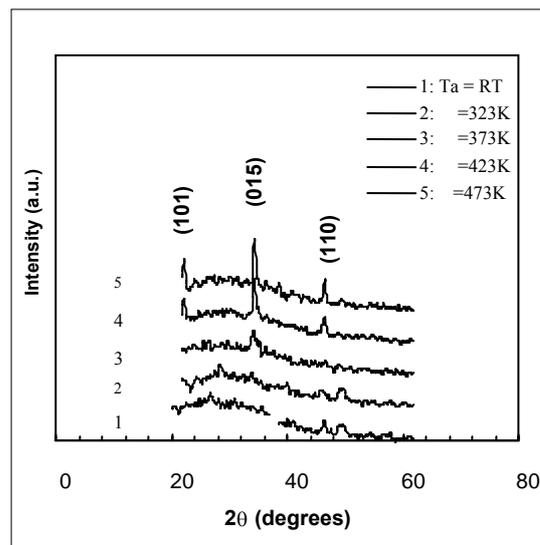**Fig. (7):** XRD of $Bi_2(Te_{08.}Se_{0.2})_3$ thin films annealed at different temperatures.

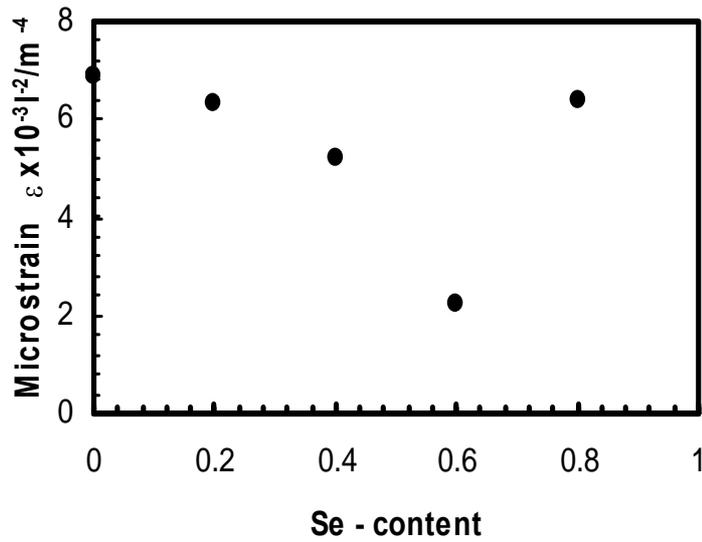**Fig. (8):** Variation of microstrain of $Bi_2(Te_{1-x}Se_x)_3$ films with Se content (T_{ann} = 473 K)

It is observed that, the dislocation density (ρ) exhibits slow decreasing with selenium content, see Fig. (9), the decrease of ε and ρ with increasing Se contents can be referred to the difference in the physico- chemical properties Se and Te.

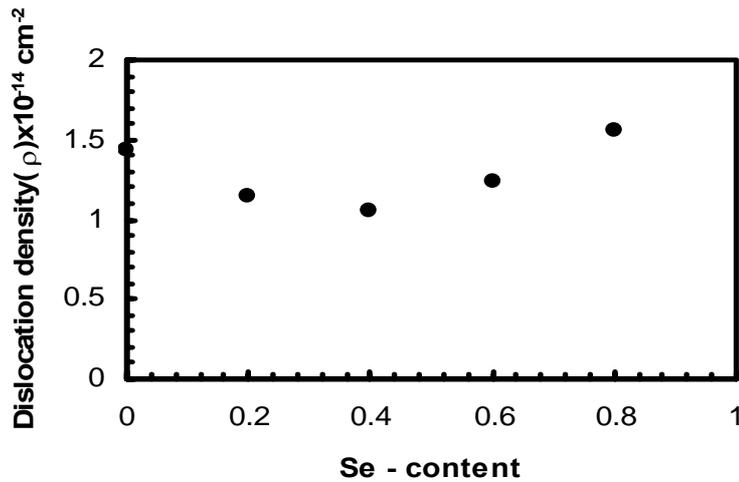**Fig. (9):** Variation of dislocation density of thin films annealed at 473 K with Se content (T_{ann} = 473 K)

The grain size (D) of the investigated samples annealed at 473 K represents in Fig. (10), and shows a compositional dependence. The minimum value of the grain size at x = 0.6 may be attributed to the formation of newer smaller grains over the larger grains. Figure 11 represents a plot of the grain size as a function as a of the annealing temperature of the prepared $Bi_2(Te_{0.8}Se_{0.2})_3$ thin films as a representative example. From Fig. (11) it is clear that, the grain size increases with increasing the annealing temperature. This result is correlates with the observed increase of crystallinity obtained from the X-ray diffraction. A plot of the number of crystallite (N) for unit surface area of $Bi_2(Te_{0.8}Se_{0.2})_3$ thin films as a representative case as a function of the annealing temperature given in Fig. (12). It is clear that, N decreases as the annealing temperature increases, which supports the change in grain size with annealing temperature. Similar results were observed in semiconductor chalcogenides thin films [49 and 50].
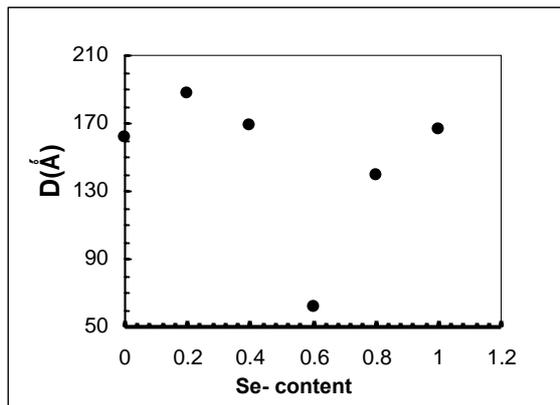

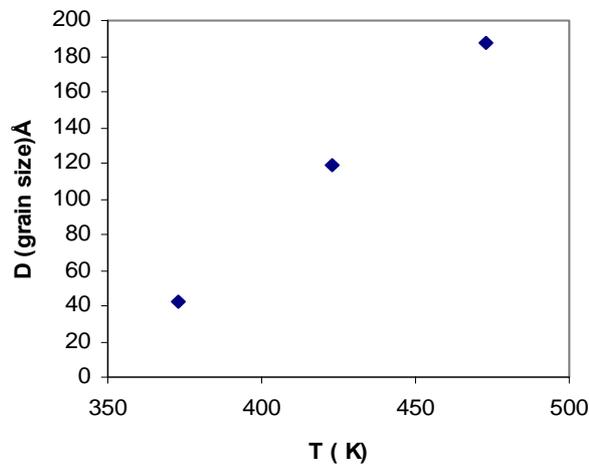**Fig. (10):** Variation of grain size of $Bi_2(Te_{1-x}Se_x)_3$ films with Se content ($T_{ann} = 473$ K)

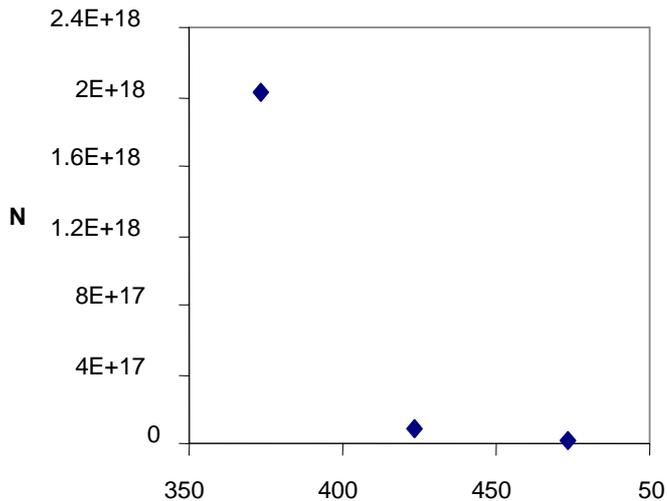**Fig.(11):** Variation of grain size(Å) $Bi_2(Te_{0.8}Se_{0.2})_3$ films annealed at different temperatures.

Fig. (12): Variation of N of $Bi_2(Te_{0.8}Se_{0.2})_3$ films annealed at different temperatures.

5. Conclusion:

The system $Bi_2(Te_{1-x}Se_x)_3$, (where x = 0, 0.2, 0.4, 0.6, 0.8 and 1) in the polycrystalline form was obtained by Bridgman method, and thin films were prepared by thermal evaporation technique. Crystal structural analysis of the investigated samples revealed that the as-deposited films are amorphous. An amorphous to crystalline phase transition with a single phase of the rohombohedral type structure as that of the prepared bulk material, was obtained for films annealed in vacuum at T ≥ 423 K. It is also found that, the different structural parameters such as lattice constants, crystallite size, microstrain and dislocation density are depend on both composition and the annealing temperature.

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