



Calorimetric and optical study of amorphous $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ glassy alloy

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ABSTRACT

Bulk samples of $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ (where $x=0, 1, 2, 3, 4, 5$) glassy alloys are obtained by melt quenching technique. Differential scanning calorimetric (DSC) technique has been applied to determine the thermal properties of Se-rich $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ glassy alloys in the glass transition and crystallization regions at four heating rates (5, 10, 15, 20 K min^{-1}). The glass transition temperature (T_g) and peak crystallization temperature (T_p) are found to shift to a higher temperature with increasing heating rate. With Bi addition, the value of (T_g) increases. (T_p) is found to increase as Bi is introduced to the Se–Te host, however further increase in Bi concentration is responsible for the reduction of. Thin film of bulk samples are deposited on glass substrate using thermal evaporation technique under vacuum for optical characterization. Optical band gap is estimated using Tauc's extrapolation and is found to decrease from 1.46 to 1.24 eV with the Bi addition.

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1. Introduction

Chalcogenide glasses have attracted much interest in last couple of decades because of their interesting optical, electrical and physical properties which can be controlled by changing the chemical composition. This property of chalcogenide glasses makes these materials useful for technological applications such as infrared transmitting optical fiber, infrared lasers, optical amplifiers and blue laser diodes [1–3].

Amorphous selenium (Se) rich semiconducting alloys are of particular interest due to their current uses as photoconductors in high definition TV pick up tubes and particularly in digital X-ray imaging. Pure Se has short lifetime and low sensitivity and this problem can be overcome by alloying Se with certain elements which in turn gives high sensitivity, high crystallization temperature and smaller aging effects [4,5]. The substitution of Te for Se partly breaks up the Se_8 ring structure and increases the chain fraction. More recently it has been pointed out that Se–Te has some advantages over amorphous Se as far as their use in xerography is concerned [6]. The addition of third element expands the glass forming area and also creates compositional and configurational disorder in the system. The impurities like Bi have produced a remarkable change in the thermal and optical properties of chalcogenide glasses. The addition of Bi as a third element with simultaneous replacement of Se increases the glass transition temperature of the system [7–9] indicating the hardening of host Se–Te alloy. The glass forming ability of a sample is defined as the capacity to obtain amorphous phase when the sample is rapidly quenched. If the cooling rate is sufficiently high the crystallization is inhibited. In this case, the sample in liquid state at the melting

temperature (T_m) is rapidly quenched down to glass transition temperature where the liquid is transformed to amorphous phase. The composition dependence of glass forming ability is analyzed in the present system and it has been found to increase as Bi is introduced to host Se–Te alloy. However further increase of Bi reduces the glass forming ability. An increasing concentration of Bi in Se–Te glassy alloy is also responsible for the band tailing and broadening of valence band which is further known to reduce the width of optical band gap [10]. No work has been reported so far on the effect of Bi addition on thermal and optical properties of $\text{a-Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ chalcogenide alloy. In the present work DSC studies on bulk glasses have been carried out to determine (T_g), (T_p) and (T_m) as a function of heating rate as well as Bi concentration in the $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ chalcogenide system. Optical characterization has been carried out from the transmission spectra of the thin films of these glassy alloys at room temperature.

2. Experimental details

Glasses of $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$, where $x=0, 1, 2, 3, 4, 5$ were prepared by the melt quenching technique. The materials (5N pure) were weighed according to their atomic percentages and sealed in evacuated (at $\sim 10^{-4}$ Pa) quartz ampoules. The sealed ampoules were kept inside a furnace where the temperature was increased up to 1000 °C at a heating rate of 3–4 °C min^{-1} . The ampoules were frequently rocked for 15 h at the highest temperature to make the melt homogeneous. The quenching was done in ice-cold water. Glasses were obtained by breaking the ampoules. Thin films of $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ glasses were deposited on glass substrates which are subjected to cleaning with soap solution, ultrasonically cleaning by trichloroethylene, acetone followed by methyl alcohol. Then the substrate is washed by double ionized water and dried in oven. Thin films of the alloys are prepared by

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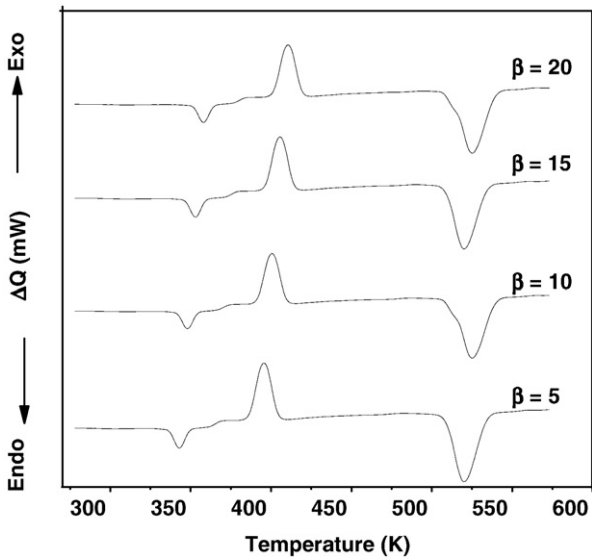


Fig. 1. Plot of DSC thermograms for $Se_{85-x}Te_{15}Bi_x$ ($x=5$) at different heating rates.

thermal evaporation technique at $\sim 10^{-4}$ Pa base pressure in a vacuum coating system (HINDHIVAC 12A 4D model). The bulk samples as well as their thin films have been characterized by the X-ray diffraction technique and both were found to be amorphous in nature as no prominent peak was observed in their spectra.

Thermal behavior of the sample is recorded using Mettler Toledo Star^c DSC system. In each study approximately 10 mg bulk material is used. DSC runs are taken at four heating rates (5, 10, 15, 20 $K\ min^{-1}$) for each of the composition so as to get (T_g), (T_p) and (T_m) for the system. The transmission spectra of the thin films in the spectral range 400–1500 nm were obtained using a double beam ultraviolet-visible-near infrared spectrophotometer (Perkin Elmer, λ 750). All the measurements reported were taken at 300 K.

3. Results and discussion

3.1. Thermal studies

Differential scanning calorimetric (DSC) thermograms were recorded for $Se_{85-x}Te_{15}Bi_x$ glassy alloys at different heating rates. Fig. 1 shows the thermograms of the as prepared $Se_{85-x}Te_{15}Bi_x$ (typically for

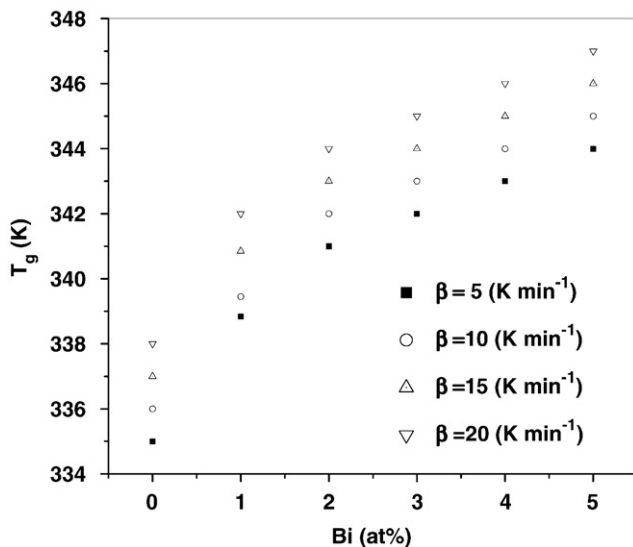


Fig. 2. Plot of (T_g) vs. Bi (at. %) for $Se_{85-x}Te_{15}Bi_x$ ($0 \leq x \leq 5$) alloy.

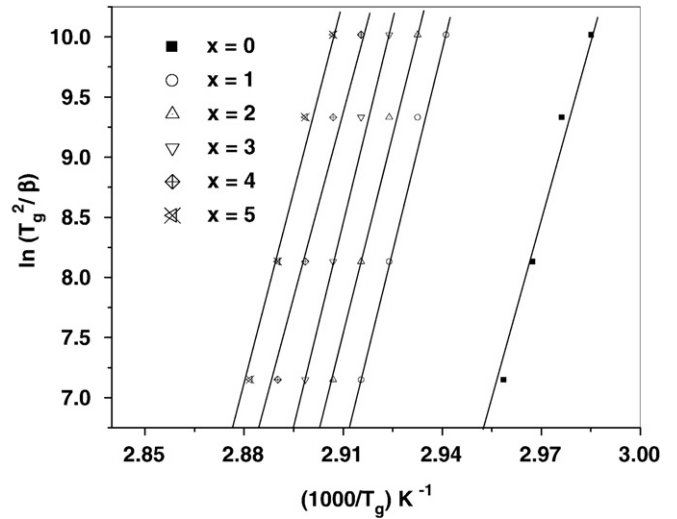


Fig. 3. Plot of $\ln(T_g^2/\beta)$ vs. $1000/T_g$ for $Se_{85-x}Te_{15}Bi_x$ ($0 \leq x \leq 5$) alloy.

$x=5$) glassy alloy at four heating rates (5, 10, 15 and 20 $K\ min^{-1}$). It has been observed from Fig. 1 that T_g and T_p shift towards higher temperature with increasing heating rate. Similar behavior is observed with other values of x . The value of crystallization temperature T_p of each alloy is found to be much higher than room temperature which is an advantage of these glassy alloys and is essential to prevent self transition of recording materials between two phases; amorphous and crystalline phase at room temperature.

Fig. 2 shows the increase of T_g with increasing Bi concentration. This behavior of T_g with Bi content can be explained on the basis of chemically ordered network model according to which heteropolar bonds are favored over homopolar bonds and bonds are formed in sequence of their decreasing bond energies. When Bi is added to the system it is expected to form bonds with Se rather than with Te. As the bond energy of Bi–Se bond (170.4 kJ/mol) is higher than the bond energy of Bi–Te (125.6 kJ/mol), the average bond energy of the system and hence the T_g increases. The value of T_g for studied composition at heating rate of 10 $K\ min^{-1}$ is given in Table 2. The apparent activation energy for glass transition E_t is calculated by using the Kissinger formula [11]

$$\ln \left[\frac{T_g^2}{\beta} \right] + \text{const.} = \frac{E_t}{RT_g} \quad (1)$$

where R is the gas constant and β is heating rate. Fig. 3 shows the plot of $\ln(T_g^2/\beta)$ as a function of $1000/T_g$ and is found to be linear for all the samples. The slope of the plot gives the value of E_t and is reported in Table 1. The glass activation energy is the amount of energy absorbed by a group of atoms in the glassy region so that a jump from one metastable state to another metastable state is possible. In other words the activation energy is involved in molecular motion and rearrangement of atoms around the glass transition temperature. In the present system under study, the activation energy for glass transition increases with Bi content. It implies that the probability of atoms to jump to the metastable state of lower internal energy

Table 1
Parameters determined from heating rate dependence of $Se_{85-x}Te_{15}Bi_x$ glassy system

x	B	E_t (kJ/mol)	E_c (kJ/mol) (Kissinger)	N	m	E_c (kJ/mol) (Matusita)
0	2.10	111.00	63.96	2.68	1.68	56.97
1	2.11	114.32	72.07	2.56	1.56	61.28
2	2.12	115.19	71.42	2.68	1.68	60.00
3	2.13	116.36	70.62	2.67	1.67	59.08
4	2.14	117.48	69.58	2.64	1.64	58.27
5	2.15	118.26	68.76	2.60	1.60	57.06

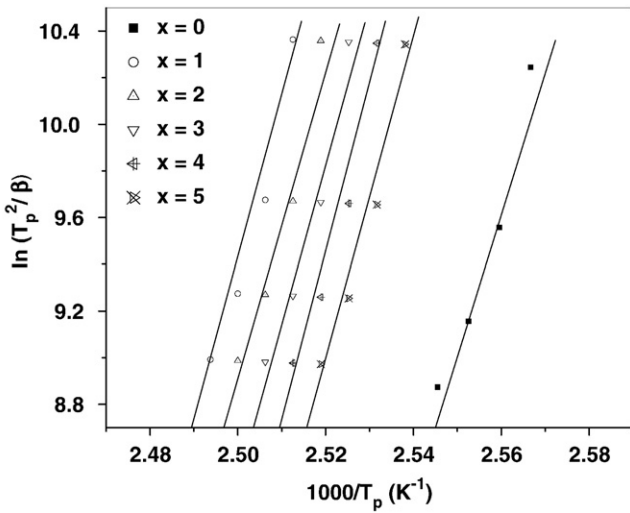


Fig. 4. Plot of $\ln(T_p^2/\beta)$ vs. $1000/T_p$ for $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($0 \leq x \leq 5$) alloy.

decreases with increasing Bi concentration and hence the stability of system decreases with Bi content. Activation energy for crystallization E_c is calculated from modified Kissinger equation [12,13]

$$\ln \left[\frac{T_p^2}{\beta} \right] + \text{const.} = \frac{E_c}{RT_g} \quad (2)$$

where E_c is determined from the slope of the plot of $\ln(T_p^2/\beta)$ vs. $1000/T_p$ as shown in Fig. 4. The calculated value of E_c for the studied composition using Kissinger formula is given in Table 1.

Now according to Matusita relation [14]

$$\ln[-\ln(1-V_F)] = -n \ln(\beta) - 1.052 \frac{mE_c}{RT} + \text{const} \quad (3)$$

where V_F is the volume fraction of crystals precipitated in the glass heated at uniform rate and is calculated by the relation $V_F = S_T/S$. [15].

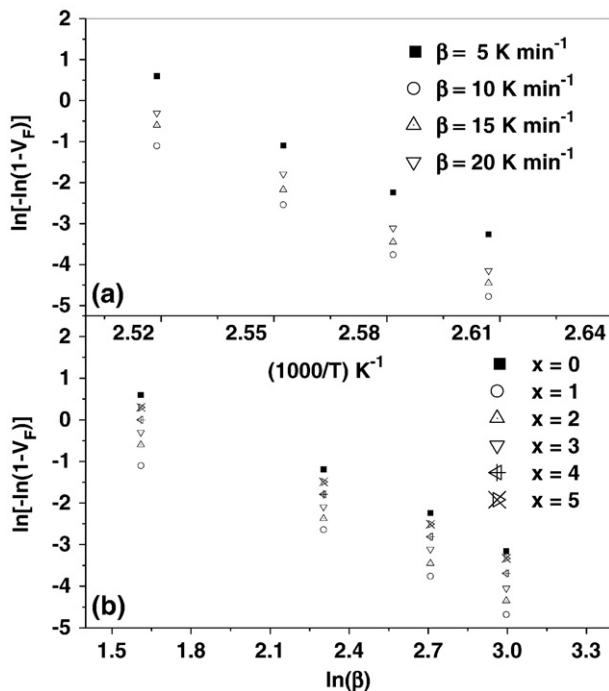


Fig. 5. Plots of (a) $\ln[-\ln(1-V_F)]$ vs. $\ln(\beta)$ and (b) $\ln[-\ln(1-V_F)]$ vs. $1000/T$ for a $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($0 \leq x \leq 5$) alloy at four heating rates, β' .

Table 2

Values of $(T_p - T_g)$, $(T_m - T_p)$, K_{gl} and T_{rg} calculated from DSC thermograms at 10 K/min heating rate, value of absorption coefficient at 1100 nm and optical band gap for the system

x	T_g (K)	T_p (K)	T_m (K)	$(T_p - T_g)$	$(T_m - T_p)$	K_{gl}	T_{rg}	E_g (eV)	α (cm^{-1})
0	335	376	519	41	143	0.29	0.645	1.46	1658.33
1	339	399	526	60	127	0.47	0.645	1.39	5800.17
2	341	398	527	57	129	0.44	0.647	1.33	7698.12
3	343	397	528	54	131	0.41	0.649	1.30	7890.54
4	344	396	529	52	133	0.39	0.65	1.27	10517.3
5	345	395	530	50	135	0.37	0.651	1.24	13538.3

In this relation S is the total area of exothermal peak and S_T is the area between starting point of exotherm and peak crystallization temperature. m and n are constants depending upon the morphology of growth [9]. For the present system the value of kinetic exponent n is determined from the slope of $\ln[-\ln(1-V_F)]$ vs. $\ln(\beta)$ as shown in Fig. 5b. Mean value of n as obtained for the studied composition is $2.60 \approx 3$. From the mean value of n it is possible to postulate a crystallization mechanism. It has been shown that n may be 4, 3, 2 or 1 [16], depending upon the type of nucleation and growth of the system. Since quenched samples were used in the present study the value of m is one less than n , i.e.; 2 indicating that bulk nucleation with two dimensional growth occurs in the system. The activation energy for crystallization is determined from the slope of $\ln[-\ln(1-V_F)]$ vs. $1000/T$ (see Fig. 5a), and is given in Table 1. The behavior of E_c is found to be similar from both the approaches. The difference between T_p and T_g which is an indication of the thermal stability of glasses against crystallization is maximum at Bi=1 at. % and further it decreases with increases in Bi content. The glass forming ability K_{gl} is calculated from Hurby's parameter [17]

$$K_{gl} = \frac{T_p - T_g}{T_m - T_p} \quad (4)$$

The ease in glass formation is determined by calculating the reduced glass transition temperature, $T_{rg} = T_g/T_m$ [18]. The value obtained obeys the two third rule which states that $T_{rg} = \frac{2}{3}$ and holds well for the studied composition. The value of K_{gl} and T_{rg} for the studied composition is reported in Table 2.

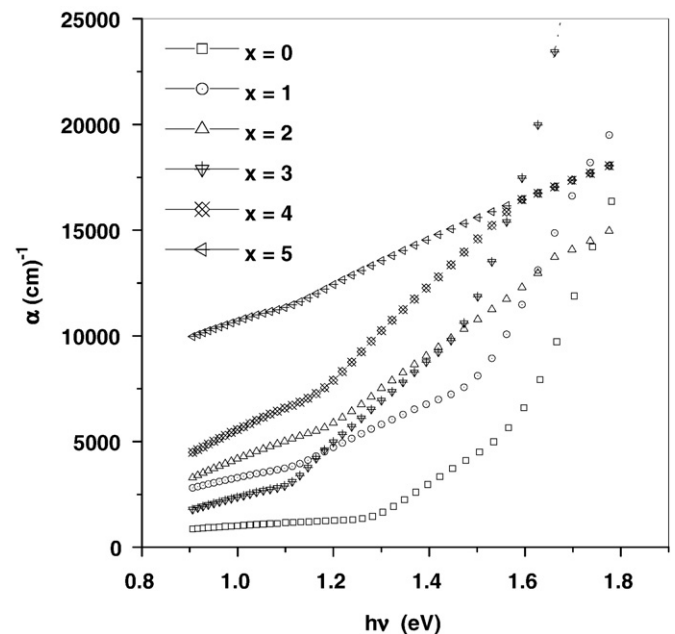


Fig. 6. Plot of absorption coefficient (α) vs. $h\nu$ for $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($0 \leq x \leq 5$) thin films.

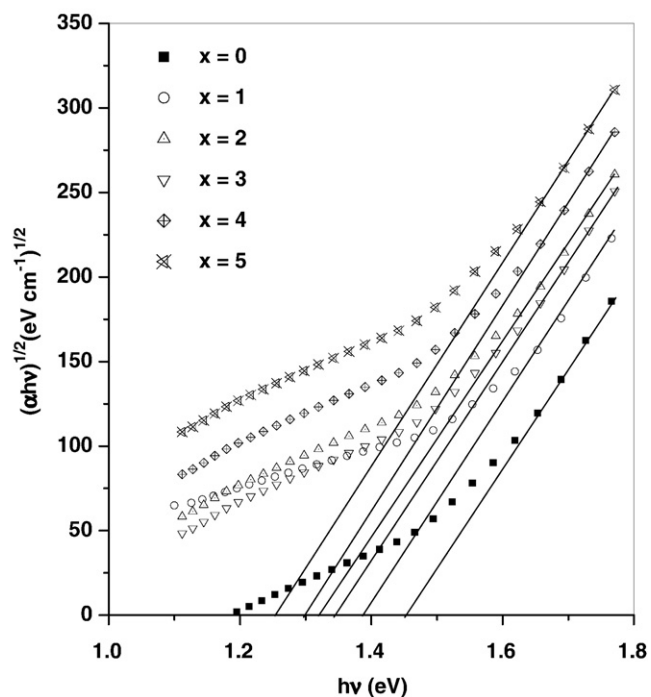


Fig. 7. Plot of $(\alpha hv)^{1/2}$ vs. hv for $Se_{85-x}Te_{15}Bi_x$ ($0 \leq x \leq 5$) thin films.

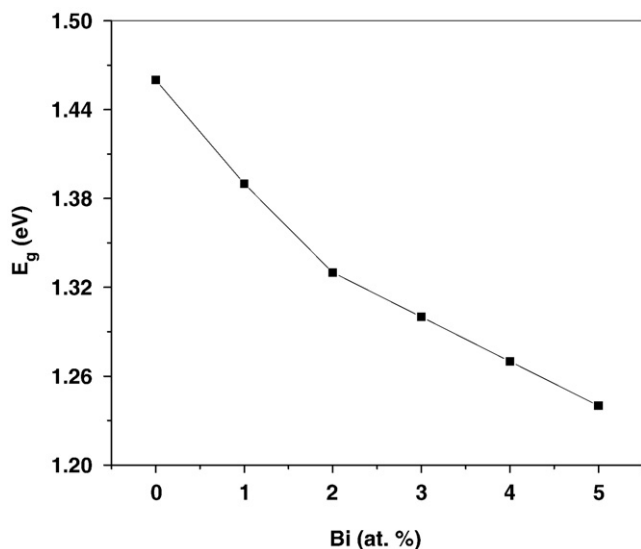


Fig. 8. Plot of band gap E_g vs. Bi (at.%) for $Se_{85-x}Te_{15}Bi_x$ ($0 \leq x \leq 5$) thin films.

3.2. Optical studies

The absorption coefficient (α) of $Se_{85-x}Te_{15}Bi_x$ thin films have been calculated by using well known relation

$$\alpha = \left(\frac{1}{d}\right) \ln \frac{1}{\omega} \quad (5)$$

Where d is the thickness of film and ω is the absorbance. The variation of (α) with energy (hv) is shown in Fig. 6 and is found to increase with increase in photon energy or decrease in wavelength. The value of (α) for $Se_{85-x}Te_{15}Bi_x$ thin films typically at 1100 nm are listed in Table 2.

The optical band gap (E_g) has been estimated from absorption coefficient data as a function of wavelength by using Tauc relation [19]

$$\alpha hv = B(hv - E_g)^\gamma \quad (6)$$

where B is a constant related to band tailing parameter. In the above equation $\gamma = 1/2$ for a direct allowed transition, $\gamma = 3/2$ for direct forbidden transition, $\gamma = 2$ for an indirect allowed transition and $\gamma = 3$ for indirect forbidden transition.

The graph between $(\alpha hv)^{1/2}$ and hv for $Se_{85-x}Te_{15}Bi_x$ films is shown in the Fig. 7. The non linear nature of the graph provides evidence that the transition in the forbidden gap is of indirect type. It is also evident from figure that optical band gap decreases with the addition of Bi content (Fig. 8). This decrease in optical band gap may be correlated with the electronegativity difference of the elements involved. According to Kastner et.al [20], the valence band in chalcogenide glasses is constituted by lone pair p-orbital's contributed by the chalcogen atoms. These lone pair electrons will have a higher value of energies adjacent to electropositive atoms than those of electronegative atoms. Therefore the addition of electropositive elements to the alloy may raise the energy of lone pair states which is further responsible for the broadening of valence band inside the forbidden gap. The electronegativities of Se, Te and Bi are 2.4, 2.1 and 2.0 respectively. From these electronegativity values it is clear that Bi is less electronegative than Se, so the substitution of Bi for Se may raise the energy of some lone pair states and hence broaden the valence band. This leads to band tailing and hence shrinking of the band gap. The value of optical band gap decreases from 1.46 to 1.24 eV as the Bi content is increased from 0 to 5 atomic percent in the Se–Te glassy alloy as is stated in Table 2.

4. Conclusion

DSC studies have been performed on the melt quenched $Se_{85-x}Te_{15}Bi_x$ chalcogenide glasses. The glass transition temperature has been found to increase from 335 to 345 K due to Bi addition. The stability is maximum for $x = 1$ and it decreases with Bi addition. It further leads to the conclusion that stable glasses are formed only with lower Bi concentration. DSC analysis also shows that bulk nucleation with two dimensional growth occurs in the system. The optical absorption in the given system seems to be of non direct type and the optical band gap obtained by Tauc's extrapolation is found to decrease from 1.46 to 1.24 eV by the addition of Bi content.

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