EFFECT OF BI ADDITION ON THE OPTICAL BAND GAP OF Se$_{85}$Te$_{15}$ CHALCOGENIDE THIN FILMS

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This paper reports the influence of bismuth (Bi) addition on the optical properties of thin films of Se$_{85-x}$Te$_{15}$Bi$_x$ (x = 0, 1, 2, 3, 4, 5) chalcogenide glassy alloys. This has been done by analyzing the transmission spectra, measured at normal incidence, in the spectral range 400 to 1500 nm. Optical band gap *(E$_g$)* is estimated using Tauc's extrapolation and is found to decrease from 1.46 to 1.24 eV with the Bi addition. This behavior of optical band gap is interpreted in terms of electronegativity difference of the atoms involved and cohesive energy of the system.

1. Introduction

Chalcogenide glasses have attracted much interest in the 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]. The optical properties of chalcogenide vitreous semiconductors, i.e. the excellent transmittance in the infrared region (in the wavelength regions 3-5 μm and 8-14 μm), continuous shift in the optical absorption edge, the variation in the refractive index under the influence of light and a very strong correlation between the former properties and the corresponding chemical composition, explains the significant interest in these amorphous materials for the manufacture of filters, anti reflection coatings and in general, a wide variety of optical devices [4-6].

Among chalcogenides selenide materials have been identified as possible materials for non linear optical applications. Because of large atomic radius compared with oxygen in oxide glasses and sulfur in sulfide glasses, selenium plays an important role in the non linear optical properties in selenide glasses. However pure Se has short lifetime and low sensitivity. This problem can be overcome by alloying it with certain elements which in turn gives high sensitivity, high crystallization temperature and smaller aging effects [7, 8]. Impurity effects in chalcogenide glasses are important in the fabrication of glassy semiconductors. These impurity atoms are supposed to satisfy all the valence requirements when they enter the glassy network and therefore they are not supposed to play the role of acceptors or donors. The effect of impurity atoms in chalcogenide glasses depends upon the composition of the glasses, the chemical nature of impurity, and the value of impurity concentration. Several authors [9-11] have reported the impurity effects in various chalcogenide glasses. The substitution of Te for Se partly breaks up the

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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 for as their use in xerography is concerned [12]. The addition of third element like Bi expands the glass forming area and also creates compositional and configurational disorder in the system.. An increasing concentration of Bi in Se-Te glassy alloy is responsible for the band tailing and broadening of valence band which is further known to reduce the width of optical band gap. The present studies report the effect of Bi incorporation on the optical properties of Se-Te matrix.

2. Experimental details

Glasses of Se$_{85-x}$Te$_{15}$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 ~ 10^{-4} Pa) quartz ampoules. The sealed ampoules were kept inside a furnace where the temperature was increased up to 1000 $^\circ$C at a heating rate of 3–4 $^\circ$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 Se$_{85-x}$Te$_{15}$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 distilled water and dried in oven. Thin films of the alloys are prepared by thermal evaporation technique at ~10^{-4} Pa base pressure in a vacuum coating system (HINDHIVAC 12A 4D model). Rate of evaporation was kept low (~10 Å s^{-1}) and thickness of film was controlled by thickness monitor (DTM 101). The bulk samples as well as their thin films have been characterized by the X-ray diffraction technique (Rigaku Geiger Flex 3KW Diffractometer) using Cu Kα source and both were found to be amorphous in nature as no prominent peak was observed in their spectra. 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). The spectrophotometer was set with a slit width of 2nm in the measured spectral range. All the measurements reported were taken at 300 K.

3. Results and discussion

Fig. 1 shows the transmission spectra of Se$_{85-x}$Te$_{15}$Bi$_x$ thin films. The figure shows fringes due to interference at various wavelengths. The absorption coefficient α, of Se$_{85-x}$Te$_{15}$Bi$_x$ thin films have been calculated by using the well known relation

$$\alpha = \left(\frac{1}{d}\right)\ln\frac{1}{x} \qquad (1)$$
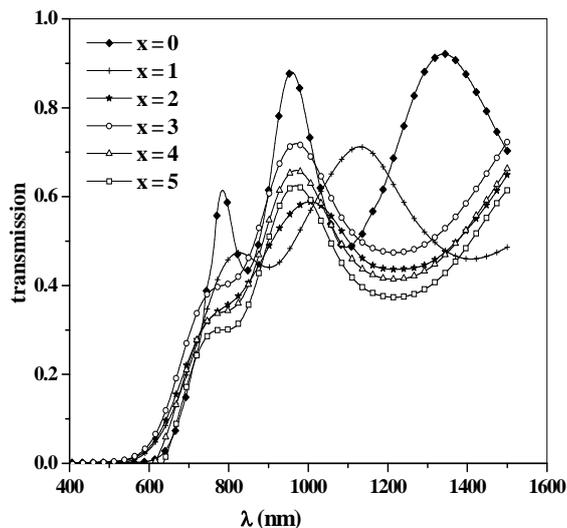
where x is the absorbance [10].

Fig 1

Fig. 1 Plot of Transmission versus Wavelength (nm) for Se$_{85-x}$Te$_{15}$Bi$_x$ thin films.

The variation of $\ln(\alpha)$ with $h\nu$ is shown in Fig. 2 and is found to increase with increase in photon energy. In amorphous semiconductors, the optical absorption edge spectra generally contains three distinct regions [13];
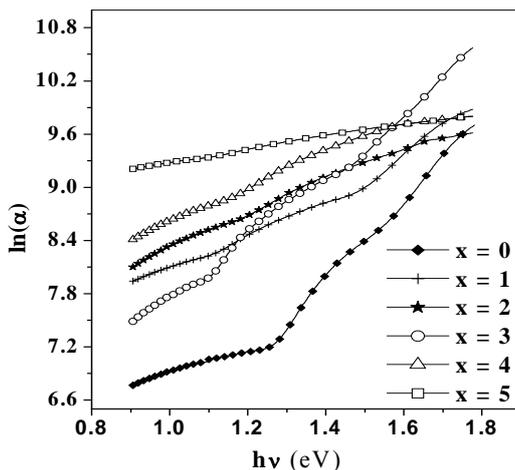

Fig 2

Fig. 2 Plot of absorption ln (α) versus $h\nu$ for Se$_{85-x}$Te$_{15}$Bi$_x$ thin films.

(a) High absorption region ($\alpha = 10^4$ cm^{-1}) which involves the optical transition between valence band and conduction band and determines the optical band gap. The absorption coefficient in this region is given by

$$\alpha h \nu = B(h\nu - E_g)^p \tag{2}$$

where E_g is defined as optical energy gap and B is a constant related to band tailing parameter. In the above equation $p = 1/2$ for a direct allowed transition, $p = 3/2$ for direct forbidden transition, $p = 2$ for an indirect allowed transition and $p = 3$ for indirect forbidden transition.

(b) Spectral region with $\alpha = 10^2 - 10^4 \, cm^{-1}$ is called Urbach's exponential tail region in which absorption depends exponentially on photon energy and is given by

$$\alpha h \nu = \alpha_0 \exp(h\nu / E_e) \tag{3}$$

where α_0 is a constant and E_e is interpreted as band tail width of localized states which generally represents the degree of disorder in amorphous semiconductor [14]. Fig. 2 shows a plot of $\ln(\alpha)$, as a function of $h\nu$ and it helps in interpreting the value of E_e (see table 1). In this region, most of the optical transitions take place between localized tail states and extended band states.

(c) The region ($\alpha \leq 10^2 \, cm^{-1}$) involves low energy absorption and originates from defects and impurities.

The optical energy gap (E_g), has been determined from absorption coefficient data as a function of photon energy ($h\nu$), using the eq. (2). After fitting all the values of p in the Tauc relation, the value of p equals to 2 is found to hold good leading to indirect transitions [13].
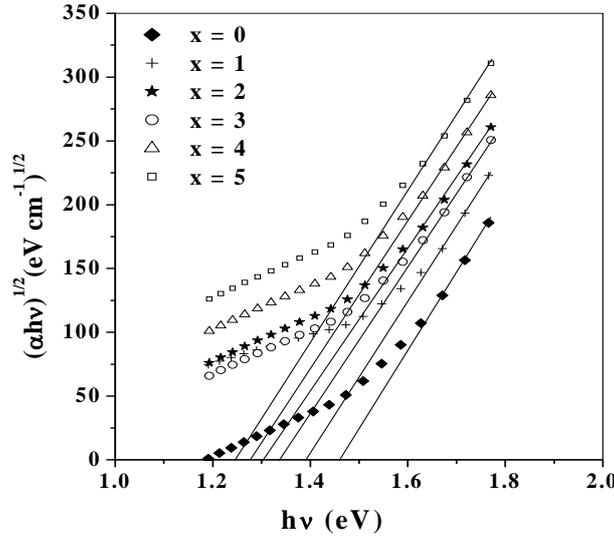

Fig 3

Fig. 3 Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $Se_{85-x}Te_{15}Bi_x$ thin films.

The graph between $(\alpha h\nu)^{1/2}$ and $h\nu$ for $Se_{85-x}Te_{15}Bi_x$ films is shown in the Fig. 3. 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. This decrease in optical band gap may be correlated with the electronegativity difference of the elements involved. According to Kastner et.al [15], 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. Since Bi is less electronegative than Se, the substitution of Bi for Se may raise the energy of some lone pair states, broadening the valence band. This leads to band tailing and hence shrinking of the band gap. It is also evident from table 1 that band tailing parameter E_e increases with increasing Bi content, which may be due to the formation of structural defects like unsatisfied bonds. The concentration of these defects also increases with Bi content. Therefore isolated centers of these defects can only introduce localized states at or near the band edges leading to an increase in the band tailing width. The values of band gap decreases from 1.46 to 1.24 eV as the Bi content is increased from 0 to 5 at. % in the Se-Te glassy alloy. The values of optical band gap for thin films under study are stated in table 1. Similar trend of optical band gap with increasing Bi concentration have been observed by Suri et. al [16] while studying the optical properties of Se-Te-Bi glassy alloys. Moreover Ilyas et. al. [17] also observed that the optical band gap decreases with increasing $Se_{98}Bi_2$ content in a-$(Se_{70}Te_{30})_{100-x}(Se_{98}Bi_2)_x$ thin films.

The optical band gap is a bond sensitive property [18]. Hence the decrease in optical band gap may also be interpreted in terms of cohesive energy of the system. The cohesive energy (CE), defined as stabilization energy of an infinitely large cluster of the material per atom is determined by summing the bond energies of the consequent bonds expected in the material. This behavior is equivalent to assuming a simplified model consisting of non interacting electron pair bonds highly localized between adjacent pair of atoms. The cohesive energy (CE) of prepared bulk samples is evaluated using the relation [19]

$$CE = \sum \left(C_i D_i / 100 \right) \tag{4}$$

where C_i and D_i are the number of expected chemical bonds and energy of each bond respectively. The bond energy of heteropolar bonds is calculated is by using Pauling method [20]. According to chemical bond approach (CBA) [21], atoms combine more favorably with atoms of different kind rather than with the same kind and bonds are formed in the sequence of decreasing bond energies until all the available valences are satisfied.

Consequently bonds between like atoms will only occur if there is an excess of a certain type of atoms. In the above mentioned system, Bi is expected to combine preferably with Se because the bond energy of Bi-Se (170.4 kJ/mol) bond is higher than that of Bi-Te (125.6 kJ/mol). This results in decrease of Se-Se (190.08 kJ/mol) bonds and is further responsible for lowering the average bond energy and hence CE of the system. The excess Se-Se bonds and CE of the system is calculated and tabulated in Table 1.

Table 1. Excess Se-Se bonds, cohesive energy (CE), band tailing parameter (E_e), and optical band gap (E_g) for $Se_{85-x}Te_{15}Bi_x$ (x = 0, 1, 2, 3, 4, 5) thin films.

x	Excess Se-Se bonds	CE (eV)	$E_e (eV)$	$E_g (eV)$
0	140	2.76	0.28	1.46
1	135	2.70	0.40	1.39
2	130	2.63	0.47	1.33
3	125	2.56	0.56	1.30
4	120	2.50	0.69	1.27
5	115	2.43	0.89	1.24

4. Conclusion

The transmission spectra of vacuum evaporated $Se_{85-x}Te_{15}Bi_x$ thin films taken at normal incidence have been analyzed in the spectral range 400-1500 nm and the various optical parameters are calculated. The optical absorption in the given system seems to be of non direct type and the optical band gap determined in the strong absorption region by Tauc's extrapolation is found to decrease from 1.46 to 1.24 eV by the addition of Bi content. The decrease in optical band gap is interpreted in terms of cohesive energy and electronegativity difference of the atoms involved.

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