Effect of Bi Content on Optical Properties of Se-Sb-Bi Chalcogenide Amorphous Thin Films

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Abstract— Se90-xSb10Bix (x=0, 2, 4, 6, 8 & 10) chalcogenide glasses were prepared by well-established melt quenching technique. The glassy nature was verified by X-ray diffraction (XRD). Thin films of these samples were deposited on glass substrate using thermal evaporation technique at room temperature. The transmission spectra of thin films have been taken using UV-VIS-NIR spectrophotometer (Varian Cary 500) in the wavelength range 200 nm to 1500 nm. The refractive index and film thickness are calculated by using envelope method proposed by Swanepoel. The results indicate that n increases with the increasing Bi content which is related to the increased polarizability of the larger Bi atomic radius 1.46 Å compared with the Se atomic radius 1.16 Å. The value of absorption coefficient (α) and hence extinction coefficient (k) has been determined from transmission spectra. Optical band gap (Eg) is estimated using Tauc's extrapolation and is found to decrease from 1.46eV 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. The variation of optical band gap with Bi content has been studied. This study is aiming to examine such structures if they are employed as photonic devices such as photo-detectors, LED's and optical switches.

Key words: Chalcogenide thin films, optical properties, Band gap, XRD

I. INTRODUCTION

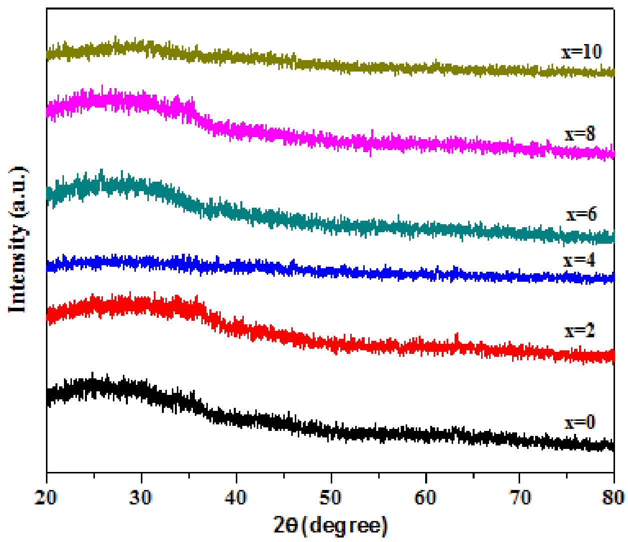
In recent years, the optical memory effects in chalcogenide semiconducting films have been investigated and utilized for various applications. Due to their high refractive index (ranging between 2.0 and 3.5) and optical band gap lying in the sub-band gap region, chalcogenide glasses are used as core materials for optical fibres which is further used for transmission, especially when short length and flexibility is required [1-2]. Selenium exhibits the unique property of reversible phase transformation. Its various device applications such as rectifiers, photocells, xerography, switching and memory, etc., have made it attractive, but pure selenium has disadvantages such as short lifetime and low sensitivity [3]. Due to high glass forming ability of Se, it represents a good host matrix for the investigation of chalcogenide glasses in the bulk and thin film forms. Thus, the above problems can be overcome by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, As, etc.), which gives higher sensitivity and crystallization temperature, and smaller aging effects [4]. Here we have chosen Sb as an additive due to its ability to improve the thermal stability of the Se drastically [5]. The addition of third element expands the glass forming area and also creates compositional and configurationally disorder in the system. The addition of impurities like Bi has produced a remarkable change in the optical and electrical properties of chalcogenide glasses. The conductivity of chalcogenide glasses changes from p to n type due to Bi addition [6]. The aim of the present investigation is to study the effect of Bi incorporation on the optical properties of Se-Sb matrix. A method proposed by Swanepoel [7-8] which is based on the use of extremes of the interference fringes of the transmittance spectrum, enables us to calculate the value of refractive index and film thickness.

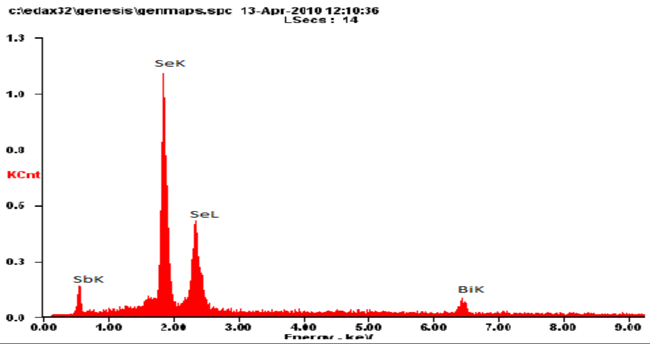
II. EXPERIMENTAL DETAILS

The bulk material of $Se_{90-x}Sb_{10}Bi_x$(x=0, 2, 4, 6, 8, 10) were prepared by the conventional melt-quenching technique. High-purity (99.999%) Se, Sb and Bi in appropriate atomic weight proportions were sealed in a quartz ampoule under a vacuum of 10^{-5} Torr. The ampoules (length 10.5 cm and 8 mm internal diameter) were then heated at 900 ^{0}C for about 18 hours with continuous rotation to facilitate homogenization of the sample. The molten samples were rapidly quenched in ice-cooled water. Thin films of these glassy materials were prepared using thermal evaporation technique at room temperature under the vacuum of 5×10^{-6} Torr. The amorphous nature of the thin film was ascertained using X-ray diffractometry (Bruker AXS D-8 Advance Diffractometry) with Cu Kα-radiation source (λ= 1.540 Å). The XRD pattern of $Se_{86}Sb_{10}Bi_4$ thin film is shown in Figure 1. The absence of any sharp peak in the XRD pattern confirms the amorphous nature of the film. The possible differences between the compositions of the evaporation source material and the film deposited onto the substrate were determined by Energy-Dispersive X-ray Analysis (EDAX), by making use of a field emission scanning electron microscopy (FEI Quanta 200F model) shown in **Figure 2**. The results show that the composition of the thin films grown is equal to that of the bulk source material within 2 atomic %. Transmission spectra have been taken using UV-VIS-NIR spectrophotometer (Varian Cary 5000).

III. RESULTS AND DISCUSSION

The X-ray diffractograms of typical as-deposited films on glass substrate kept at room temperature do not reveal any peak corresponding to Bragg's condition, as shown in Figure 1, thus, the as deposited films were found to be amorphous. The compositions of as-deposited $Se_{90-x}Sb_{10}Bi_x$(x=0, 2, 4, 6, 8 & 10) thin films were investigated using energy dispersive X-ray analysis (EDAX). Figure 2 shows the spectral distribution of the constituent elements for the $Se_{86}Sb_{10}Bi_4$ thin films. The atomic percentage ratio of Se, Sb and Bi are listed below in Table 1 Optical transmission T is a very complex function and is strongly dependent on the absorption coefficient.





Sample	EDAX Data			Optical band gap (eV)
	Se (at. %)	Sb (at. %)	Bi (at. %)	
$Se_{90}Sb_{10}$	91.4	9.6	-	1.46
$Se_{88}Sb_{10}Bi_2$	88.2	9.8	1.9	1.41
$Se_{86}Sb_{10}Bi_4$	86.4	9.7	3.9	1.39
$Se_{84}Sb_{10}Bi_6$	84.5	9.8	5.7	1.35
$Se_{82}Sb_{10}Bi_8$	82.4	9.8	7.8	1.31
$Se_{80}Sb_{10}Bi_{10}$	80.4	9.7	9.9	1.24

Table 1: The EDAX data and optical band gap for Se90-xSb10Bix(x=0, 2, 4, 6, 8, 10 at %) thin film

A. Optical band gap

A spectral change in the optical absorption near the band edge is characterized by α (ν) which increase exponentially with hν obeying the exponential relation:

$$\alpha(\nu) = \alpha_o \exp(h\nu / E_s)$$

Where α_o is constants and E_s is interpreted as the width of tails of the localized states in the gap, it represents the degree of disorder. We have performed UV-visible absorption spectroscopy before and after annealing to study the variation of band gap Eg in the film. The energy gap *Eg* can be determined by absorption coefficient data as the function of photon energy (*hv*) using this eqn .

$$\alpha hv = A(hv - Eg)^n$$

Where *A* is a constant and *n* characterizes the transition process. We can see $n = 2$ and 2/3 for direct allowed and forbidden transitions, respectively, and $n = 1/2$ and 1/3 for indirect allowed and forbidden transitions, Tauc relation[11] this method has been used in chalcogenide glasses by various workers [12-15].

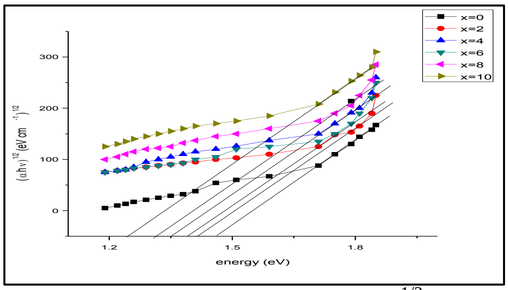


Fig. 2: Curve of hυ and $(\alpha h\upsilon)^{1/2}$

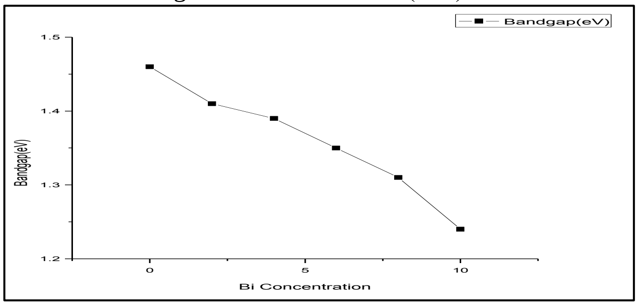


Fig. 3: Variation of band gap (Eg) with Bi concentration

The values of optical band gap Eg are also given in Table 1 for each sample. It is evident from the table that optical band gap Eg are estimated to be range 1.46 to 1.24 eV (Fig2) decreases with Bi-content. The optical band gap is a bond sensitive property [16].

IV. CONCLUSION

The transmission spectra of vacuum evaporated $Se_{90-x}Sb_{10}Bi_x$ thin films taken at normal incidence have been analyzed in the spectral range 200-1500 nm and the various optical parameters are calculated. The refractive index and film thickness are calculated by using envelope method proposed by Swanepoel. 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 1.39 to 1.24 eV by the addition of Bi content.

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