

EFFECT OF ANTIMONY ADDITION ON THE OPTICAL BEHAVIOUR OF SnSeSb THIN FILMS

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The present work includes the optical properties of Sn₁₃Se_{87-x}Sb_x (x = 0, 3, 6, 9, 12) thin films prepared by vacuum evaporation technique (~ 10⁻⁴Pa). Thin films were characterized for the study of various optical properties like optical band gap (E_g^{opt}), absorption coefficient (α), refractive index (n) and extinction coefficient (k) by taking their transmission spectra in the range 400-2200 nm. The straightforward technique proposed by Swanepoel has been utilized to measure n and k . It has been observed that the value of n increases with the increase of Sb content. It has been observed that the optical gap is of indirect type and estimated using Tauc extrapolation. Optical gap decreases with increasing Sb content. The dielectric constants and optical conductivity has also been estimated using n , k and α .

(Received September 30, 2015; Accepted February 22, 2016)

Keywords: Chalcogenide; optical gap, thin films,

1. Introduction

Chalcogenide glasses are Group 16 elements of the periodic table (sulfur, selenium or tellurium) as a significant ingredient. Being covalently bonded materials they may be classified as molecular solids. Chalcogenide glasses shows special IR transmission and electrical properties which make these materials of great importance for use in several potential applications i.e. threshold switching, memory switching, inorganic photoresists, lenses for IR transmission and detection and optical waveguide for welding [1-3]. Due to specific optical properties like high photoconductivity, light sensitivity and the existence of a polar state the glasses of these systems can serve as the initial material for creating the media of optical information recording, radiation indicators, optical elements of IR technique, high voltage sources, ferroelectric glass-ceramics and other versatile applications [4-14]. Low phonon energy, high photosensitivity, easy fabrication and processing of chalcogenide glasses leads to various photonic applications i.e. frequency converters, optical amplifiers, optical recording devices, integrated optics, infrared lasers and infrared transmitting optical fibers [15-17]. Sn-Se-Sb system is of special interest due to the fact that it forms glasses over a wide domain of compositions [18]. Due to the large atomic radius as compared to oxygen and sulfur, selenium plays an important role in the nonlinear optical properties in selenide glasses. Working with Se induces some problems like short lifetime and low sensitivity. So to produce changes in the properties of new complex glass alloys, it is worth to add more than one element into selenium matrix to get rid of these problems. To overcome these problems, several workers [19-22] have used certain additives (Ge, Bi, As, etc.) to make binary alloys with selenium, which in turn gives high sensitivity, a high crystallization temperature and smaller aging effects. The incorporation of Sb to Sn-Se alloy increases the glass forming domain

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and creates compositional and configurational disorder in the system. The glass-forming region in ternary system groups with the addition of impurity [23]. Because of these merits it is a well suitable system for the investigation of various optical properties. The optical properties of chalcogenide glasses depends on the structural configuration of the system and addition of Sn creates the structural disorder.

The present work deals with the calculation of various optical parameters like optical band gap (E_g^{opt}), absorption coefficient (α), refractive index (n) and extinction coefficient (k) for $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films by analyzing transmission spectrum in the wavelength range from 400 - 2200 nm.

2. Experimental details

The materials of high purity (99.999%) were weighed according to their atomic percentages and they were sealed in evacuated (at $\sim 10^{-4}$ Pa) quartz ampoules. The sealed ampoules were held in reserve inside a furnace where the temperature was increased up to 800°C at a heating rate of $3\text{-}4^\circ\text{C}/\text{min}$. The ampoules were frequently rocked for 8 h at the highest temperature to make the thaw homogeneous. The quenching was then done in ice cold water. Thin films of glassy alloys were prepared on glass substrates by vacuum evaporation technique at room temperature and with the base pressure of $\sim 10^{-4}$ Pa. The bulks as well as thin films of the samples were prepared and are characterized by X-ray diffraction technique. The normal incidence transmission spectra within the transmission range 400-2200 nm of $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films were obtained by a double beam ultraviolet-visible-near infrared spectrophotometer [Perkin Elmer Lambda-750]. All measurements were performed at room temperature (300 K).

3. Results and discussion

The thin films of $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) bulk material were prepared by vacuum evaporation technique. The normal incidence transmission spectra in 400-2400 nm transmission range of $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films were obtained by a double beam ultraviolet-visible-near infrared spectrophotometer [Perkin Elmer Lambda-750] at the room temperature.

Fig. 1 shows the optical transmission spectra of $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films. The plot infers the fringes due to interference at various wavelengths. Optical transmission T being a very complex function strongly depends upon the absorption coefficient. According to Swanepoel's method [24] the envelope through the interference maxima and minima are drawn in the spectrum, the concept based on Manifacier theory [25]. The fact that optical homogeneity of the deposited film and that negligible scattering or absorption occurs at long wavelength is confirmed by the presence of maxima and minima of transmission spectra of the same wavelength position. This method has used in chalcogenide glasses by various workers [26-29]. The maxima and minima of spectra are used to calculate the various optical constants with the increasing antimony content the absorption edge shifts to higher wavelength along with maxima and minima of fringes.

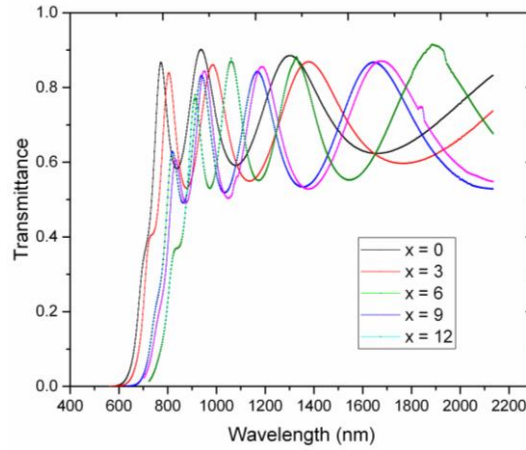


Fig. 1. Transmittance of $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films.

Fig. 2 shows the variation of refractive index with wavelengths for all the compositions. Refractive index has been estimated using straightforward technique proposed by Swanepoel [24]. The refractive index n is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (1)$$

where $N = \frac{2s}{T_m} - \frac{s^2 + 1}{2}$ for transparent region ($\alpha = 0$), T_m is the envelope function of the transmittance minima and s is the refractive index of the substrate and is given by

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{1/2} \quad (2)$$

In the region of weak and medium absorption ($\alpha \neq 0$), the factor N of equation (1) is given by $N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}$ and T_M is the envelope function of the transmittance maxima. In the

region of strong absorption, the transmittance decreases drastically to the influence of α and n and can be estimated by extrapolating the values from the other regions. Refractive index decreases with the increase in wavelength. The decrease in the refractive index with the increase in wavelength is directly correlated with the decrease in absorption coefficient. The decrease in the value of refractive index with wavelength presents normal dispersion in the material. The value of refractive index increases with increase in Sb content. This may be due to the increased density of the samples on addition of Sb content. Increase in the density of structure will lead to more compactness which further leads to the increase of refractive index. The increase of refractive index with Sb content may be explained on the basis of polarizability. Since substitution of more polarizable atom Sb [covalent radius = 1.40 Å] for Se [covalent radius = 1.16 Å] atom leads to the refractive index according to Lorentz-Lorentz relation [30]. The values of n at 800 nm are given in Table 1 for comparison sake.

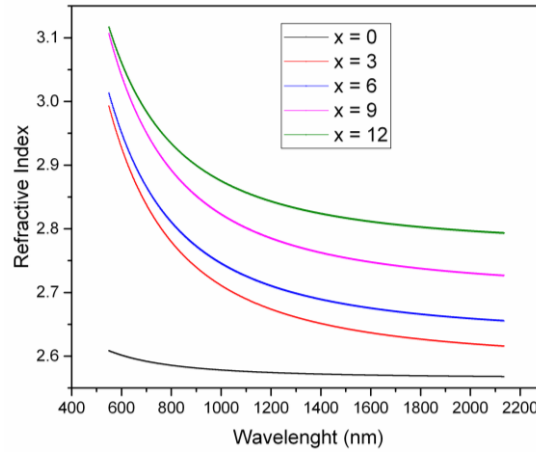


Fig. 2. Plot of refractive index with wavelength for $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films.

Table 1 Values of Refractive index (n) and extinction coefficient (k) at 800 nm, thickness (d), optical band gap (E_g^{opt}) of $\text{Sn}_{13}\text{Se}_{87-x}\text{Sb}_x$ ($x = 0, 3, 6, 9, 12$) thin films.

Composition	Thickness (d) nm	Refractive index (n)	Extinction Coefficient (k)	Optical energy gap (E_g^{opt} (eV))
$\text{Sn}_{13}\text{Se}_{87}$	1267	2.58	0.0437	1.60
$\text{Sn}_{13}\text{Se}_{84}\text{Sb}_3$	1320	2.78	0.0237	1.56
$\text{Sn}_{13}\text{Se}_{81}\text{Sb}_6$	1370	2.81	0.0866	1.49
$\text{Sn}_{13}\text{Se}_{78}\text{Sb}_9$	1287	2.89	0.1267	1.42
$\text{Sn}_{13}\text{Se}_{75}\text{Sb}_{12}$	1335	2.93	0.1903	1.35

Fig. 3 shows the extinction coefficient variation with wavelength. The extinction coefficient decreases with the increase in wavelength of the thin film under investigation. This may be due to decrease in the absorption coefficient. The extinction coefficient (k) is given by the relation $k = \alpha\lambda/4\pi$, where α is absorption coefficient and is given by

$$\alpha = (1/d)\ln(1/X) \quad (3)$$

where X is the absorbance [24] and d is the film thickness. If n_1 and n_2 are the refractive indices of two adjacent maxima and minima at λ_1 and λ_2 , then the thickness is given by

$$d = \lambda_1\lambda_2/2(\lambda_1n_2 - \lambda_2n_1) \quad (4)$$

The values of k at 800 nm and thickness (d) of thin films calculated using equation (4) are given in Table 1.

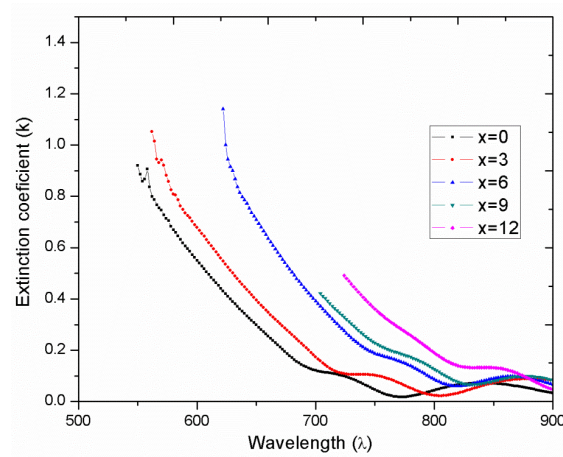


Fig. 3. Variation of extinction coefficient with wavelength for $Sn_{13}Se_{87-x}Sb_x$ ($x = 0, 3, 6, 9, 12$) thin films

Optical absorption study of the materials provides a simple method to explain some features of the band structure and energy gap of non metallic materials. The optical absorption coefficient (α) is calculated by using equation (3).

Fig. 4 shows the plot of absorption coefficient versus the photon energy. It is observed that α increases as the concentration of Sb increases for same energy values. With the substitution of Sb to Se energy losses are reduced due to multi phonon absorption. Thus multi phonon absorption edge shifts towards higher energy by increasing the amount of heavier Sb atoms. This fact leads to the increase in absorption coefficient.

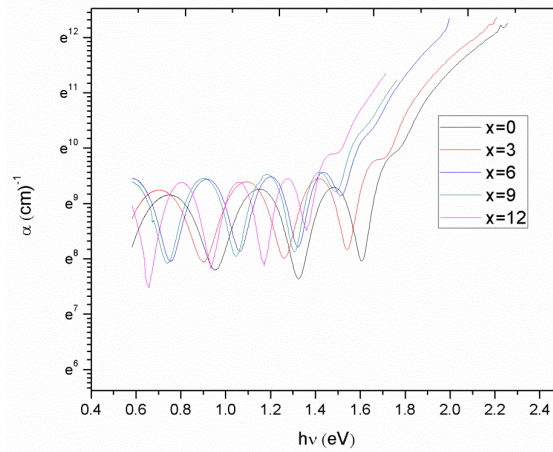


Fig. 4. Plot of absorption coefficient (α) versus the photon energy for $Ge_{17}Se_{83-x}Sb_x$ ($x = 0, 3, 9, 12$) thin films.

Fig. 5 shows the variation of $(\alpha h\nu)^{1/2}$ with $h\nu$. This figure is used to calculate optical gap (E_g^{opt}). This is observed by fitting different values of n in Tauc's relation [31] that transitions are of indirect type. The optical gap is calculated using Tauc extrapolation by putting the intercepts of extrapolations to zero with the photon energy axis $(\alpha h\nu)^{1/2} \rightarrow 0$. The band gap decreases with the increase in Sb content from 1.60 eV for $x = 0$ to 1.35 eV for $x = 12$ as shown in Table 1. This prominent decrease in the optical gap (E_g^{opt}) with increasing Sb content can be interpreted on the basis of CBA [32]. They assumed that atoms combine more preferably with atoms of different

types than with the same kind. Bonds between like atoms will then only occur if there is an excess of a certain type of atom. Bonds are created in the sequences of decreasing bond energy until all the available valences of the atoms are saturated. Each component is co-ordinate by 8-N atoms, where N is the number of outer shell and this is counterpart to neglecting the dangling bonds and the other valence defects. Increasing Sb content at the cost of selenium leads to the creation of heteropolar Se-Sb (42.9 kcal/mol) bonds at the cost of Se-Se (44.0 kcal/mol) bonds [33]. So formation of Se-Sb bonds reduces the average energy of the system. Since optical gap is a bond sensitive property and hence decrease in average bond energy of the system contributes to the decrease in optical gap with increasing Sb content. Further the decrease of optical gap with increase of Sb content can also be correlated with the decrease of average single bond energy $(\overline{H_s}/m)$ which is a measure of cohesive energy; i.e. decrease of $(\overline{H_s}/m)$ will lead to decrease of optical gap [34]. The decrease of optical gap with increase of Sb content may also be correlated with the electronegativity concept. Since electronegativity of Sb (2.05) is less than Se (2.55), so the substitution of Sb (more electropositive element than Se) for Se may raise some lone pair states energy and hence broaden the valence band. This will give rise to additional absorption over a broader range of energy leading to band tailing and hence shrinking the band gap.

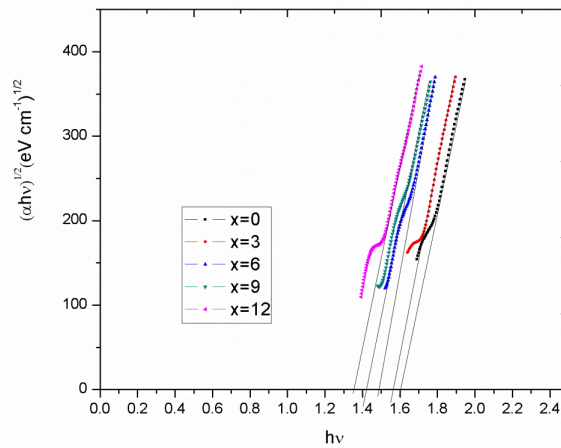


Fig. 5. Plot of $(ahv)^{1/2}$ with hv for $Sn_{13}Se_{87-x}Sb_x$ ($x = 0, 3, 6, 9, 12$) thin films.

4. Conclusions

Thin films of $Sn_{13}Se_{87-x}Sb_x$ ($x = 0, 3, 6, 9, 12$) glassy alloys were analysed for various optical properties by using their transmission spectra in the optical range 400–2200 nm. Refractive index has been found to increase with the increase of Sb content. The increase in refractive index with Sb content has been explained on the basis of polarizability. This is observed that α increases with Sb content. The interband transitions are of indirect type and optical gap has been estimated using Tauc method. The optical gap has been found to decrease from 1.60 eV for $x = 0$ to 1.35 eV for $x = 12$. The decrease of optical gap is mainly explained by using chemically ordered network model and the electronegativity concept.

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