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OPTICAL PROPERTIES OF AMORPHOUS $Se_{100-x}Sb_x$ THIN FILMS

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Optical transmission spectra in the wavelength range 400 – 1100 nm, has been used to calculate the optical parameters in amorphous thin films of $Se_{100-x}Sb_x$ (x = 2, 4, 6, & 10). Swanepole method has been used to calculate refractive index, real and imaginary dielectric constant, the extinction coefficient, absorption coefficient and optical band gap.

Keywords: Chalcogenide glasses, Amorphous semiconductors, Thin films, Optical properties and optical band gap.

1. Introduction

In recent years, the research has been focused on the special types of glasses like fluoride, chalcogenide and heavy metal oxide ones that can transmit the optical radiation. The attention in this paper is focused to discuss the optical properties of chalcogenide glasses. These glasses are oxygen-free inorganic glasses containing one or more kind of chalcogen elements [1-3] and most of them are infrared (IR) transparent. Chalcogenide glasses based on sulfides, selenide and telluride alloys in binary and multi-component systems have evoked much interest in terms of the understanding of basic physics of non-crystalline solids, as well as for the development of various semiconducting devices. These glasses are also promising material for various optical and photonic application [4].

Chalcogenide glasses have recently attracted a great deal of interest because of many applications as solid-state devices both in scientific and technological field [5]. Many amorphous semiconducting glasses, in particular selenium, exhibit [6] a unique property of reversible transformation. This property makes these glasses very useful in optical memory devices. Selenium based chalcogenide glasses have high transparency in the broad middle and far IR-region and have strong non linear properties [7]. Apart from these applications, amorphous Se has been found to have tremendous potential in Xeroxing application and therefore a lot of attempts have been made to improve its properties by alloying [8-9] it with other elements.

Alloying elements produce characteristics effects depending on the electronic structure of these elements. It has been reported [10] that the effect of alloying Sb with Se drastically improves the thermal stability of the Se.

The present paper reports the optical properties of amorphous $Se_{100-x}Sb_x$ (x = 2, 4, 6, & 10) thin films prepared by vacuum evaporation technique. The optical transmission spectra of these films are measured in the wavelength range 400-1100 nm by spectrophotometer. The straight forward analysis proposed by Swanepole has been successfully employed on the glasses to determine the optical constants. It is observed from optical transmission measurements that the optical band gap decreases on increase of Sb concentration in $Se_{100-x}Sb_x$ glasses. The values of refractive index and real dielectric constant decreases with photon energy while the values of extinction coefficient and imaginary dielectric constant increases with photon energy. It is found that the absorption coefficient, determined at strong absorption region, increases with photon energy. The chemical bond approach has been successfully applied to interpret the decrease of the optical band gap with increasing Sb concentration.

2. Experimental

Glassy alloys of $Se_{100-x}Sb_x$ were prepared by quenching technique. The exact proportions of high purity (99.999%) Se and Sb elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 800 ^{0}C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{0}C / minute. During heating, the ampoule was constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This was done to obtain homogeneous glassy alloy.

After rocking for about 12 hours, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampoule. The glassy nature of the alloy was ascertained by X-ray diffraction.

Thin films of glassy alloys of a $Se_{100-x}Sb_x$ were prepared by vacuum evaporation technique, in which the substrate was kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The films were kept inside the deposition chamber for 24 hours to achieve the metastable equilibrium. A Double UV/VIS/NIR Computer Controlled Spectrometer (Hitachi-330) is used for measuring optical transmission of $Se_{100-x}Sb_x$ thin films. The optical transmission was measured as a function of wavelength.

3. Results and Discussion

The optical system under consideration is amorphous, homogeneous and uniform. Optical transmission (T) is a very complex function and is strongly dependent on the absorption coefficient (α). Fig. 1 shows the variation of transmission (T) with wavelength (λ) in $Se_{100-x}Sb_x$ thin films. According to Swanepole's method [11], which is based on Mainfacer theory [12], the envelope of the interference maxima and minima occurs in the spectrum. The extinction coefficient (k) can be neglected in the region of weak and medium absorption ($\alpha \neq 0$).

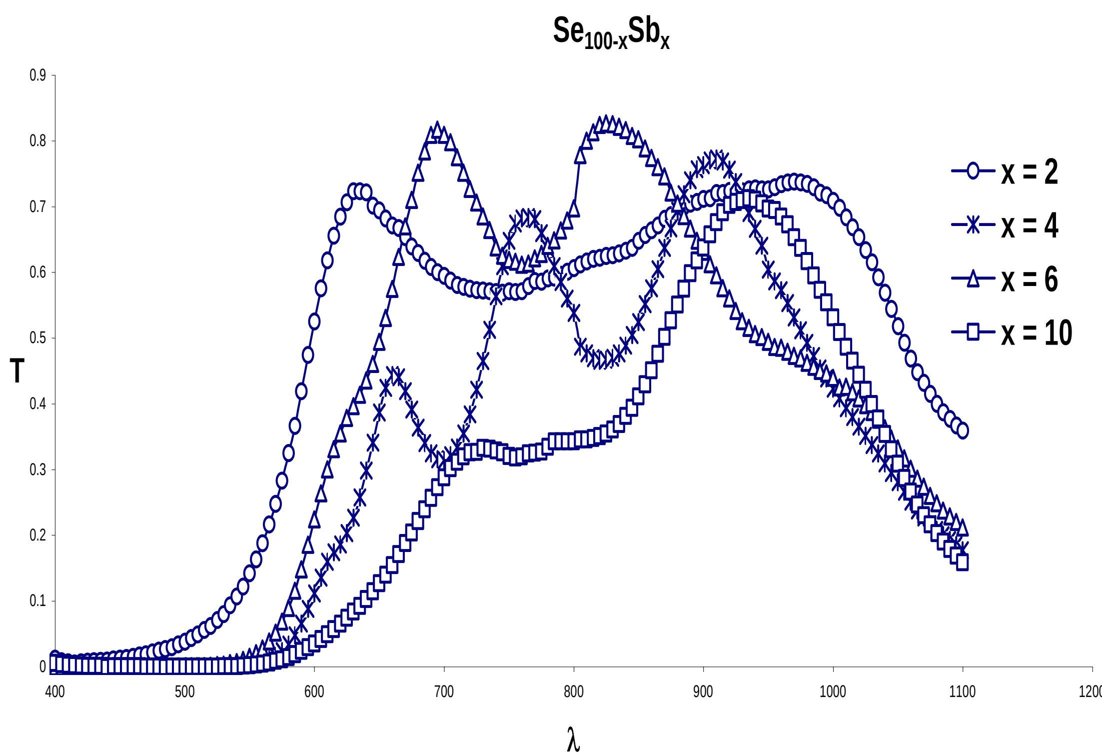

Fig. 1 Variation of transmittance (T) with wavelength (λ) in $Se_{100-x}Sb_x$ thin films.

Therefore, this approximation is valid over most spectrums. The presence of maxima and minima of transmission spectrum of the same wavelength position confirmed the optical homogeneity of the deposited film and that no scattering or absorption occurs at long wavelengths. This method has been used in chalcogenide glasses by various workers [13-16].

3.1 Determination of optical constants

For the method proposed by Swanepole, the optical constants are deduced from the fringe patterns in the transmittance spectrum. In the transmittance region where the absorption coefficient ($\alpha = 0$), the refractive index n is given by

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

where $N = (2s/ T_m) - (s^2 + 1)/2$

T_m is the envelope function of the transmittance minima and s is the refractive index of the substrate.

In the region of weak and medium absorption, where ($\alpha \neq 0$), the transmittance decreases mainly due to the effect of α and the refractive index n is given by

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

where $N = \{2s(T_M - T_m) / T_M T_m\} + (s^2 + 1)/2$

and T_M is the envelope function of the transmittance maxima.

In the region of strong absorption, the transmittance decreases drastically due almost exclusively to the influence of α and n which can be estimated by extrapolating the values in the other regions. Because the thickness of our film is uniform, interference give rise to the spectrum as shown in Fig. 1. The fringes can be used to calculate the refractive index n of the film using eqn. (1) and (2) as indicated previously.

The extinction coefficient k can be calculated from the relation

$$k = \alpha\lambda / (4\pi)$$
$$= (\lambda / 4\pi d) \ln(1/x) \qquad (3)$$

where x is the absorbance and d is the film thickness.

If n_1 & n_2 are the refractive indices at two adjacent maxima or minima at λ_1 & λ_2 then the thickness is given by

$$d = \lambda_1\lambda_2 / 2[\lambda_1 n_2 - \lambda_2 n_1] \qquad (4)$$

In the region of weak and medium absorption, using the transmission minima T_m, x is given by

$$x = [E_m - \{E_m^2 - (n^2 - 1)^3 (n^2 - s^4)\}^{1/2}] / [(n - 1)^3 (n - s^2)] \qquad (5)$$

where $E_m = [(8n^2 s/T_m) - (n^2 - 1)(n^2 - s^2)]$ (6)

The spectral distributions of both n and k for $Se_{100-x}Sb_x$ films are shown in Figs. 2 and 3 respectively. The calculated values are given in Table 1.

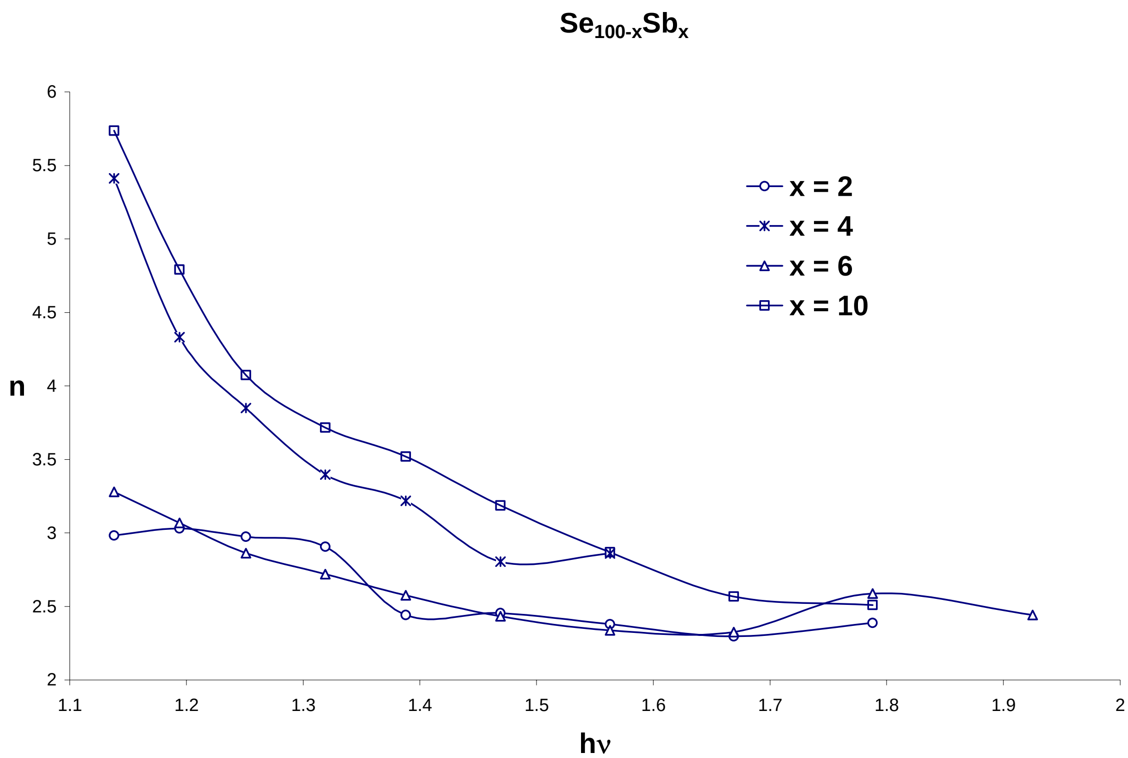

Fig. 2 Variation of refractive index (n) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

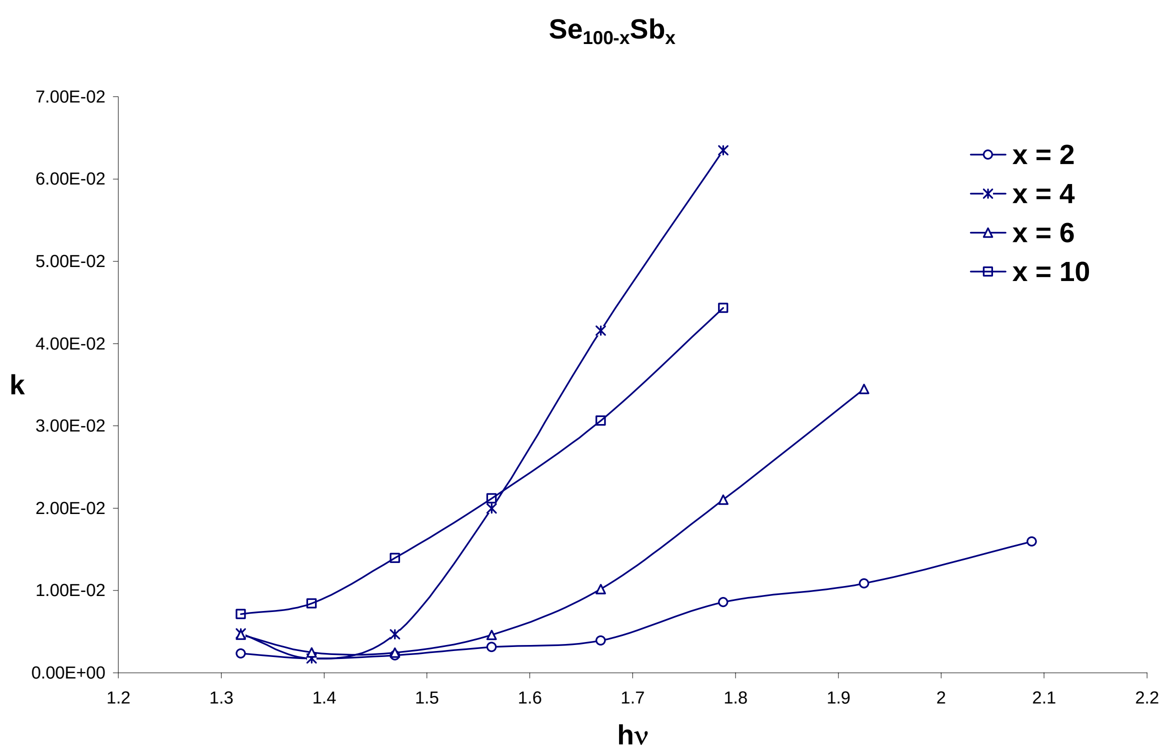

Fig. 3 Variation of extinction coefficient (k) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

Table 1

S. No.	Sample	Refractive index (n)	Extinction Coefficient (k)	Real Dielectric Constant (ε`)	Imag. Dielectric Constant (ε”)
1.	$Se_{98}Sb_2$	2.44	1.74×10^{-3}	5.99	0.85×10^{-2}
2.	$Se_{96}Sb_4$	3.22	1.75×10^{-3}	10.36	1.13×10^{-2}
3.	$Se_{94}Sb_6$	2.58	2.47×10^{-3}	6.44	1.27×10^{-2}
4.	$Se_{90}Sb_{10}$	3.52	8.42×10^{-3}	12.39	5.93×10^{-2}

3.2 Determination of dielectric constants

The dielectric constants of $Se_{100-x}Sb_x$ films can be calculated with the help of refractive index n and extinction coefficient k [17]. Real dielectric constant (ε`) can be calculated by the following eqn,

$$\varepsilon` = n^2 - k^2 \quad (7)$$

While the imaginary dielectric constant (ε”) dielectric constants can be calculated by the following eqn,

$$\varepsilon'' = 2nk \quad (8)$$

The spectral distribution of both real and imaginary dielectric constants for $Se_{100-x}Sb_x$ films is shown in Figs. 4 and 5 respectively. The calculated values are given in Table 1.

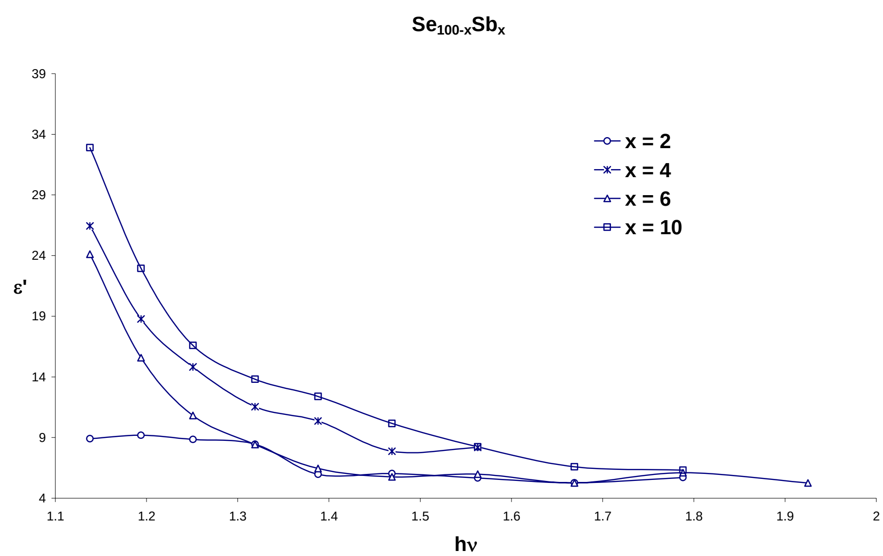

Fig. 4 Variation of real dielectric constant (ε’) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

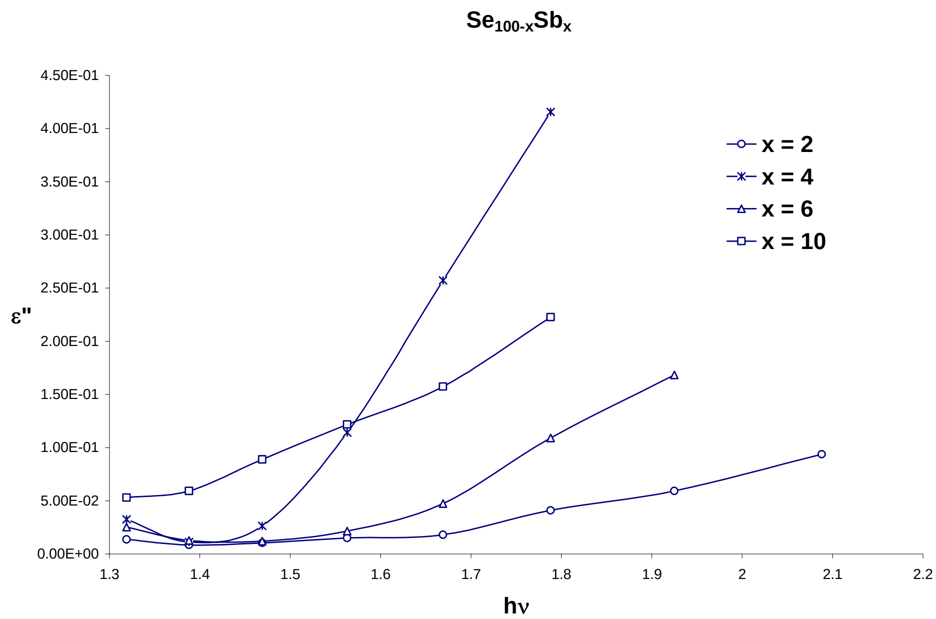

Fig. 5 Variation of imaginary dielectric constant (ε”) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

3.3 Absorption coefficient and optical band gap

The absorption coefficient α of $Se_{100-x}Sb_x$ films can be calculated using the well-known relation

$$\alpha = 4\pi k / \lambda \tag{9}$$

in which k is substituted by its value obtained from Fig. 3.

The spectral distribution of absorption coefficient α for $Se_{100-x}Sb_x$ films is shown in Fig. 6. The calculated values are given in Table 2.

The present system of $Se_{100-x}Sb_x$ obeys the role of non-direct transition and the relation between the optical band gap, absorption coefficient and energy (hν) of the incident photon is given by [18-20]:

$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g) \tag{10}$$

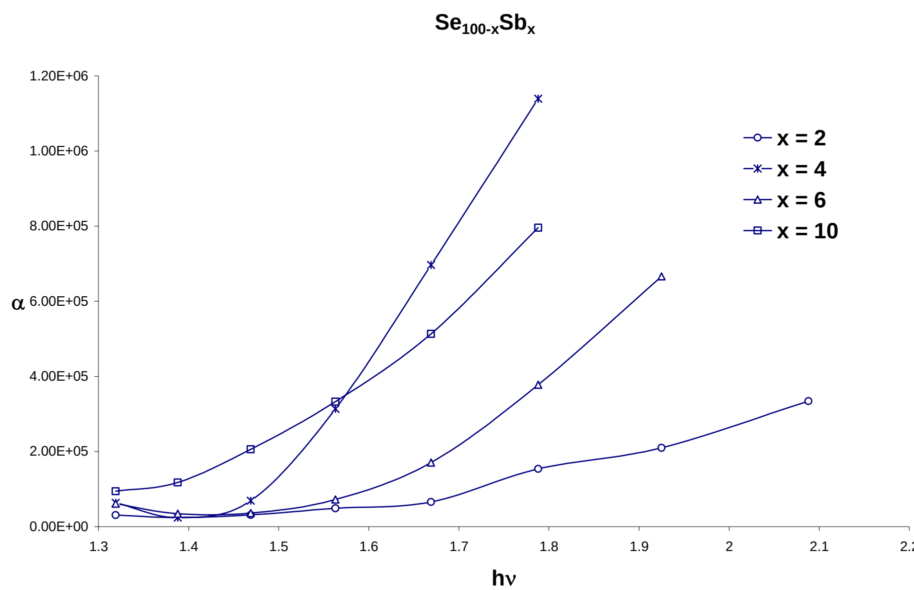

Fig. 6 Variation of absorption coefficient (α) with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

The variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) for $Se_{100-x}Sb_x$ films is shown in Fig. 7. The value of indirect optical band gap E_g has been calculated by taking intercept on x-axis. The values of optical band gap E_g are also given in Table 2 for each sample. It is evident from the table that optical band gap E_g decreases with Sb concentration. The chemical bond approach has been successfully applied to interpret the decrease of the glass optical band gap (E_g) with increasing Sb concentration.

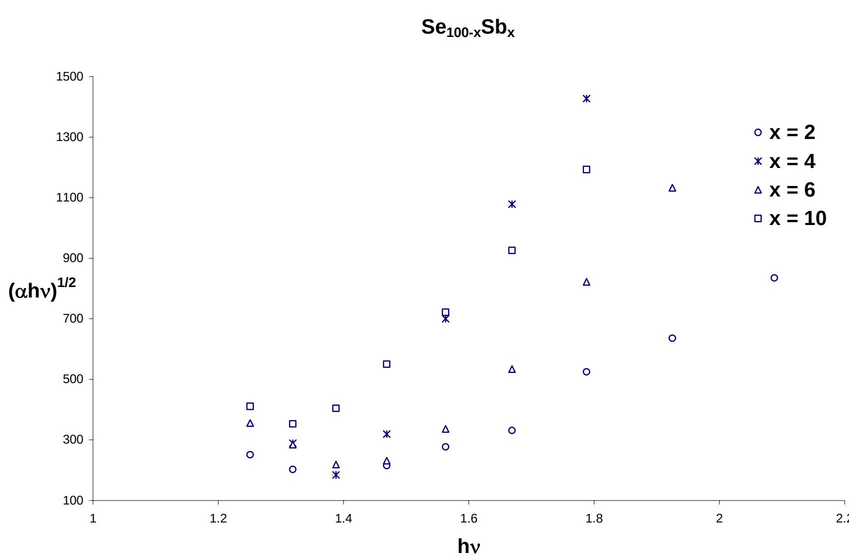

Fig. 7 Variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) in $Se_{100-x}Sb_x$ thin films.

Table 2

Sample No.	**Sample**	**Optical Band Gap (E_g)**	**Absorption Coefficient (α) in m^{-1}**
1.	$Se_{98}Sb_2$	1.48	2.48×10^4
2.	$Se_{96}Sb_4$	1.42	2.44×10^4
3.	$Se_{94}Sb_6$	1.39	3.45×10^4
4.	$Se_{90}Sb_{10}$	1.28	11.75×10^4

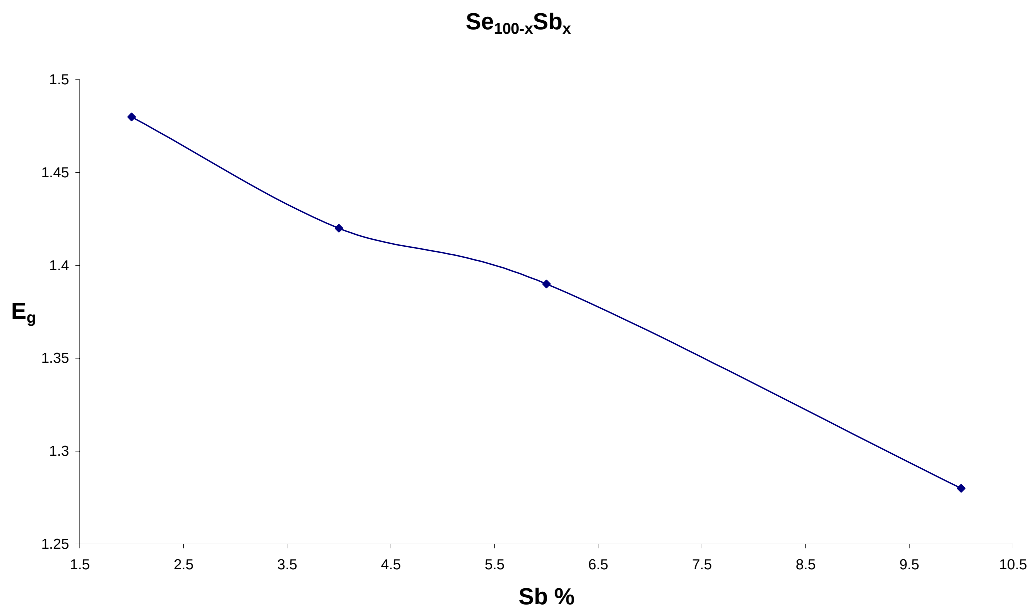

Fig. 8 Variation of optical energy gap (E_g) with Sb at %.

The decrease in the glass optical band gap (E_g) with increasing Sb concentration can be interpreted on the basis of the chemical bond approach proposed by Bicerano and Ovshinsky [21]. They assumed that atoms combine more favorably with atoms of different kinds than with the same kind. Bonds between like's atoms will then only occur if there is an excess of a certain type of atom. Bonds are formed in the sequences of decreasing bond energy until all the available valances of the atoms are saturated. Each constituent is co-ordinate by 8-N atoms, where N is the number of outer shell and this is equivalent to neglecting the dangling bonds and the other valence defects. Increasing Sb concentration at the expense of selenium leads to a shortage of Se-Se bonds, which may lead to lower average bond energy of the alloys. This may be the probable reason for the decrease of band gap with Sb concentration.

4. Conclusions

Optical transmission spectra in the wavelength range 400 – 1100 nm, has been used to calculate the optical parameters in amorphous thin films of $Se_{100-x}Sb_x$ (x = 2, 4, 6, & 10). Swanepole method has been used to calculate refractive index, real and imaginary dielectric constant, the extinction coefficient, absorption coefficient and optical band gap. A decrease in band gap is observed on increasing Sb concentration which is explained in terms of decrease of the concentration of Se-Se bonds.

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