

Effect of indium incorporation on the optical properties of Ge-Se glassy semiconductors

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Optical properties viz. refractive index (n), extinction coefficient (k) has been studied by analyzing the transmission spectrum of thin films of $\text{Ge}_{17}\text{Se}_{83-x}\text{In}_x$ ($x = 0, 3, 6, 9, 12, 15$). The spectrum was obtained in the range 400 – 1500 nm. Tauc's extrapolation has been used to determine optical band gap of thin films. The variation in the optical parameters for different thin films are explained on the basis of presence of defect states and change in average bond energy of the system. The real and imaginary parts of dielectric constants and optical conductivity of the thin films has also been calculated.

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1. Introduction

Chalcogenide glasses are the chains of random lengths and random orientations formed by bonding of chalcogen elements sulphur (S), selenium (Se) and tellurium (Te) and alloys containing these chalcogen as the major constituents. Systematic research on chalcogenide glasses started at the middle of the twentieth century. Chalcogenide glasses have been of enormous interest for infrared optics since 1950 [1]. Chalcogenide glasses possess high optical transparency in IR region. These have low phonon energy, high photosensitivity, easy fabrication and processing leads to various photonic application such as ultrafast optical switches, frequency converters, optical amplifiers, optical recording devices, integrated optics, infrared lasers and infrared transmitting optical fibers [2-4]. Ge-Se-In system is of special interest because of the fact that it forms glasses over a wide domain of compositions [5] and the incorporation of In to Ge-Se alloy expands the glass forming area and creates compositional and configurational disorder in the system. The glass-forming region in the ternary Ge-Se-In system extends to about 20 at% In and about 60–90 at% Se, with the rest being Ge [6]. Therefore, it is a suitable system for the investigation of the variation of certain optical properties. The optical properties of chalcogenide glasses depend on the structural configuration of the system and addition of In creates the structural disorder. So authors have decided to work out for the optical properties of $\text{Ge}_{17}\text{Se}_{83-x}\text{In}_x$ ($x = 0, 3, 6, 9, 12, 15$) in detail. The present work deals with determination of optical band gap (E_g^{opt}), absorption coefficient (α), refractive index (n) and extinction coefficient (k) for $\text{Ge}_{17}\text{Se}_{83-x}\text{In}_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films by analyzing transmission spectrum in the wavelength range from 400 - 1500 nm. The dielectric

constants and optical conductivity are determined using n , k and α .

2. Experimental details

Bulk sample of $\text{Ge}_{17}\text{Se}_{83-x}\text{In}_x$ ($x = 0, 3, 6, 9, 12, 15$) were prepared using melt quench technique. Materials (99.999% purity) were weighed according to their atomic percentages and sealed in quartz ampoules in a vacuum $\sim 10^{-4}$ Pa. The sealed ampoules were heated up to 950 °C at a rate of 2-3 °C/min and rocked for 12 hours at the highest temperature to make the melt homogeneous. The quenching was done in ice-cold water immediately after taking out the ampoules from the furnace. Thin films of the bulk samples were prepared on cleaned glass substrates by thermal evaporation technique [Vacuum coating unit HINDHIVAC 12A4D Model] at base pressure of $\sim 10^{-4}$ Pa. Amorphous nature of the bulk samples and thin films was confirmed by X-ray diffraction technique as no sharp peak was observed. The normal incidence transmission spectra of $\text{Ge}_{17}\text{Se}_{83-x}\text{In}_x$ thin films have been taken by a double beam UV-Vis-NIR spectrophotometer [Perkin Elmer lambda 750] in the transmission range 400 - 1500 nm. The spectrophotometer was set with a suitable slit width of 1 nm in the measured spectral range. All measurements were obtained at room temperature (300 K).

3. Results and discussion

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 $\text{Ge}_{17}\text{Se}_{83-x}\text{In}_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films. According to Swanepoel's method [7] the envelope of the interference maxima and minima of transmission spectra can be used for deducing optical

parameters. The extinction coefficient (k) can be neglected in the region of weak and medium absorption ($\alpha \neq 0$). Therefore, this approximation is valid over most part of the spectra. The presence of maxima and minima on nearly same wavelength position confirms the optical homogeneity of the deposited film *i.e.* no scattering or absorption occurs at long wavelength. This method has been used in chalcogenide glasses by various workers [8,9].

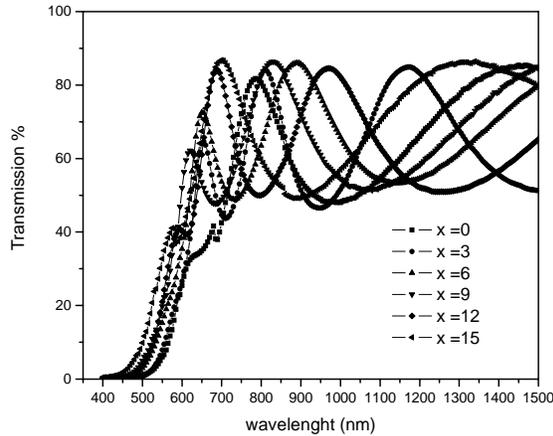


Fig. 1. Plot of optical transmission versus wavelength for $Ge_{17}Se_{83}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films.

3.1 Determination of refractive index and extinction coefficient

The refractive index (n) of the thin films is obtained by the envelope method proposed by Swanepoel [7], by making use of the following expressions. In the transparent region, where the absorption coefficient ($\alpha \approx 0$), the refractive index (n) is given by

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

where

$$N = \frac{2s}{T_m} - \frac{(s^2 + 1)}{2} \quad (2)$$

T_m is the envelope function of minimum transmittance and s is the refractive index of substrate of value 1.5. In the weak region where absorption coefficient ($\alpha \neq 0$), the transmittance decreases due to the influence of α and the value of N in equation (1) is given by

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{(s^2 + 1)}{2} \quad (3)$$

where T_M is the envelope function of maximum transmittance. The accuracy of the refractive index can be

increased by calculating thickness of the thin film (d), taking into account the basic interference equation

$$2nd = m\lambda \quad (4)$$

where $m = 1, 2, 3, \dots$ at the maximum points in the transmission spectrum and $m = 1/2, 3/2, 5/2, \dots$ at minimum points in the transmission spectrum. If n_1 and n_2 are the refractive indices of two adjacent maxima or minima at wavelengths λ_1 and λ_2 , then the thickness of the film is given by

$$d = \lambda_1 \lambda_2 / 2(\lambda_1 n_2 - \lambda_2 n_1) \quad (5)$$

The extinction coefficient k can be calculated using the relation

$$k = \frac{\lambda}{4\pi d} \ln\left(\frac{1}{x}\right) \quad (6)$$

where d is the thickness of the film and x is the absorbance. In the region of weak and medium absorption using the transmission maxima, x can be calculated by

$$x = \frac{E_M - [E_M^2 - (n^2 - 1)^3(n^2 - s^4)]^{0.5}}{(n - 1)^3(n - s^2)} \quad (7)$$

where

$$E_M = \frac{8n^2 s}{T_M} + (n^2 - 1)(n^2 - s^2) \quad (8)$$

The variation of refractive index (n) and extinction coefficient (k) with wavelength is shown in Fig. 2 and 3. From Fig. 2 and 3 it is clear that both refractive index and extinction coefficient decreases with the increase of wavelength for the thin films under investigation. This decrease in the refractive index and the extinction coefficient with the increase in wavelength may be attributed to the increase in the transmittance and decrease in the absorption coefficient with increasing wavelength. The decrease in the value of the refractive index with wavelength shows the normal dispersion behaviour of the material. Moreover, this decrease in the extinction coefficient with an increase in wavelength also shows that the fraction of light lost due to scattering and absorbance process decreases. Further very less values of extinction coefficient shows that films deposited are homogeneous.

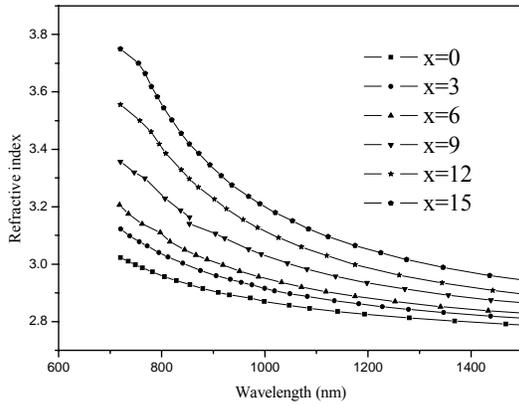


Fig. 2. Plot of refractive index versus wavelength for $Ge_{17}Se_{83-x}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films.

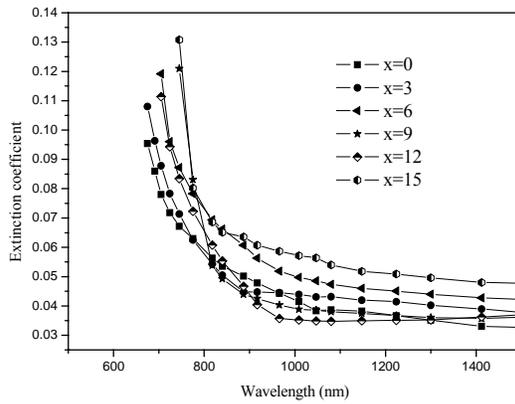


Fig. 3. Plot of extinction coefficient versus wavelength for $Ge_{17}Se_{83-x}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films.

3.2 Determination of absorption coefficient and optical band gap

The absorption coefficient (α) of $Ge_{17}Se_{83-x}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films can be calculated using the well-known relation [7]

$$\alpha = (1/d)\ln(1/x) \quad (11)$$

The optical band gap has been estimated from absorption coefficient data as a function of wavelength by using Tauc relation [10]

$$\alpha h\nu = B(h\nu - E_g^{opt})^n \quad (12)$$

where $h\nu$ is the photon energy, α is the absorption coefficient, E_g^{opt} the optical band gap, B is band tailing parameter and $n = 1/2$ and 2 for direct and indirect band gap respectively. Fig. 4 shows the variation of $(\alpha h\nu)^{1/2}$

with $h\nu$. Optical band gap E_g^{opt} can be determined by the extrapolation of best fit line between $(\alpha h\nu)^{1/2}$ and $h\nu$ to intercept the $h\nu$ axis ($\alpha = 0$) for $Ge_{17}Se_{83-x}In_x$ system.

The change in optical band gap may be understood in terms of decrease in average bond energy [11] of the system with In incorporation. Since band gap is sensitive to average bond energy so explains the decrease in optical band gap with In addition to Ge-Se system.

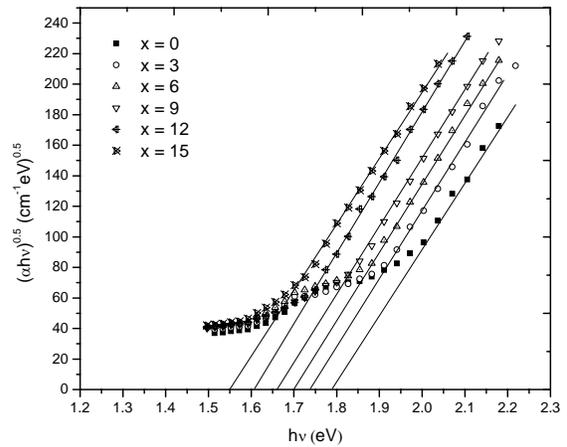


Fig. 4. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for $Ge_{17}Se_{83-x}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films.

3.3 Determination of dielectric constants and optical conductivity

The dielectric constant of $a-Ge_{17}Se_{83-x}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films can be calculated with the help of refractive index (n) and extinction coefficient (k) [12].

While real dielectric constant (ϵ_r) can be calculated from the relation

$$\epsilon_r = n^2 - k^2 \quad (13)$$

and the imaginary dielectric constant (ϵ_i) can be calculated from the following relation

$$\epsilon_i = 2nk \quad (14)$$

For $a-Ge_{17}Se_{83-x}In_x$ thin films the variation of both real and imaginary dielectric constants (ϵ_r and ϵ_i) with wavelength follows the same trend as that of refractive index and extinction coefficient. The optical parameters i.e. n , k , ϵ_r and ϵ_i decreases with increasing wavelength.

The values of ϵ_r and ϵ_i are given in Table 1 at 800 nm.

Table 1. Values of refractive index (n), extinction coefficient (k), real part of dielectric constant (ϵ_r), imaginary part of dielectric constant (ϵ_i) and optical conductivity (σ) are given at 800 nm, optical band gap (E_g^{opt}) and thickness (d) for $Ge_{17}Se_{83-x}In_x$ ($x = 0, 3, 6, 9, 12, 15$) thin films.

x	d (nm) ± 30 nm	n	k	α (cm^{-1}) $\times 10^4$	E_g^{opt} (eV)	ϵ_r	ϵ_i	σ (s^{-1}) $\times 10^{13}$
0	715	2.59	0.0032	1.81	1.78	7.51	0.0118	0.98
3	669	2.68	0.0046	1.79	1.74	8.13	0.0537	1.31
6	689	2.76	0.0058	1.71	1.70	9.06	0.0311	1.45
9	705	2.84	0.0067	1.65	1.66	8.70	0.0927	1.74
12	676	2.98	0.0081	1.61	1.61	8.90	0.0053	2.01
15	709	3.11	0.0097	1.52	1.55	8.97	0.0041	4.45

Fig. 5 shows the variation of optical conductivity ' σ ' with wavelength. The optical conductivity is determined using the relation [13]

$$\sigma = \alpha nc/4\pi \quad (15)$$

where ' c ' is the velocity of light, ' α ' is absorption coefficient and ' n ' is refractive index. Optical response is most conveniently studied in terms of optical conductivity. It has the dimensions of frequency which are valid only in Gaussian system of units. The optical conductivity directly depends on the absorption coefficient and refractive index and found to increase sharply for higher energy values due to large absorption coefficient and refractive index for these values.

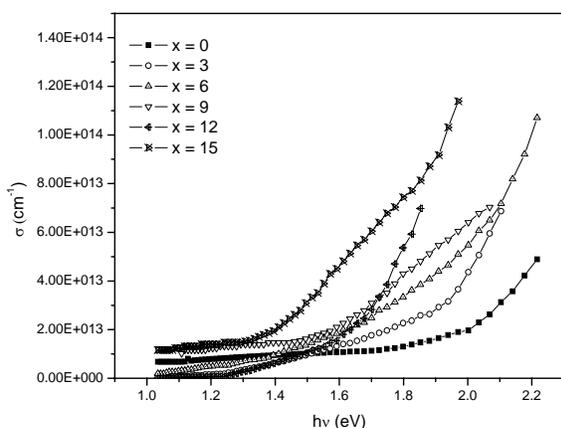


Fig. 5. Plot of optical conductivity (σ) versus wavelength for $Ge_{17}Se_{83-x}In_x$ thin films.

4. Conclusion

Optical properties have been calculated for $a-Ge_{17}Se_{83-x}In_x$ system. The optical absorption in given system seems to be of non direct transition. Optical band

gap has been found to be decreasing with In content. Refractive index follows the normal dispersion for all samples under investigation. The dielectric constants and optical conductivity were also determined from the optical parameters and found to decrease with the increase in wavelength.

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