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EFFECT OF Zn INCORPORATION ON OPTICAL PROPERTIES OF AMORPHOUS Se-Te THIN FILMS

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Measurements of optical properties have been made on alloyed samples of Se and Te with Zn prepared under vacuum by quenching the melt into water. The optical transmission spectra of films of $Se_{70}Te_{30-x}Zn_x$ (x = 0, 8) are measured in the wavelength range 400–2000 nm by spectrophotometer. It is observed that refractive index (n), real dielectric constant (ε`), extinction coefficient (k), imaginary dielectric constant (ε") decrease with increase in wavelength (λ). The absorption coefficient (α) increases with photon energy (hν). The optical energy gap (E_g) has been calculated from optical coefficient data, which is found to increase with Zn content.

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1. Introduction

Chalcogenide glassy semiconductors continue to attract the attention of scientists, because they possess very attractive properties and offer new approaches in engineering. Chalcogenide glasses are transparent in the VIS and IR spectral ranges [1-4], with relatively high refractive index ($2 \le n \le 3.7$), low optical losses (≤0.3dB/cm) [5]. It is well known that number of photo induced phenomena and structural transformations appear upon irradiation with band gap light. This makes them appropriate materials for optical recording [6], diffractive grating [7], holography and micro-optics [8].

The optical behavior of material is utilized to determine optical constants. The optical band gap, refractive index and extinction coefficient are the most significant parameters in amorphous semiconducting thin films. Therefore, an accurate measurement of optical constant is extremely important.

In the present work, the optical transmission spectra of films of $Se_{70}Te_{30-x}Zn_x$ (x = 0, 8) are measured in the wavelength range 400–2000 nm by spectrophotometer. It is observed that refractive index (n), real dielectric constant (ε`), extinction coefficient (k), imaginary dielectric constant (ε") decrease with increase in wavelength (λ). The absorption coefficient (α) increases with photon energy (hν). The optical energy gap (E_g) has been calculated from optical coefficient data, which is found to increase with Zn content.

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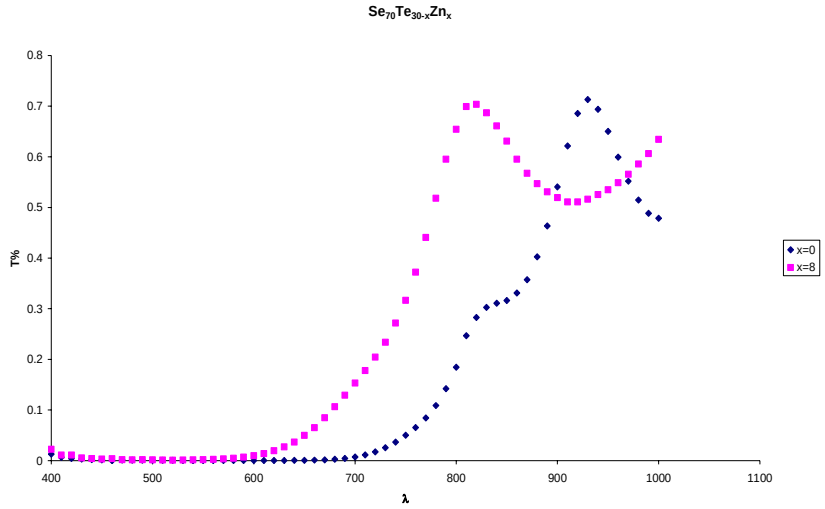

Fig. 1Variation of transmittance (T) with wavelength ((λ) in Se $_{70}$Te $_{30}$ and Se$_{70}$Te $_{22}$Zn$_{8}$ thin films

The reason of the selection of Zn as chemical modifier in Se-Te system is based on its attractive and important applications in chalcogenide glasses [9-15]. Like silver, Zn can also be used for photo-doping of chalcogenide glassy semiconductors [9-13].There are reports of successful doping of $ZnSe_xTe_{1-x}$ in literature [14] that results in the development of light-emitting diodes and lasers. Development of $ZnSe_xTe_{1-x}$ p-type contacts for high efficiency tandem structures has been recently reported [15] for the tandem solar cell devices, which have been under development in various configurations because of their promise of high efficiency.

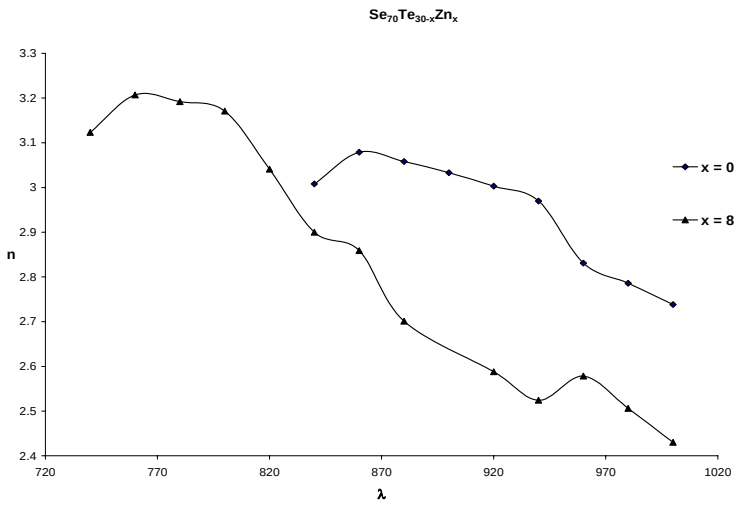

Fig.2 Variation of refractive index (n) with wave length (λ) in Se$_{70}$Te$_{30}$ and Se$_{70}$Te$_{22}$Zn$_{8}$ thin films

Section 2 describes the experimental details of sample preparation and optical transmission. Results have been presented and discussed in section 3.The last section deals with the conclusions of the present work.

2. Experimental

Glassy alloys of $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ are prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Zn elements, in accordance with their atomic percentages, are 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 ampoules containing material are heated to 1000 ^{0}C and were 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 ampoules are constantly rocked, by rotating a ceramic rod to which the ampoule was tucked away in the furnace. This is done to obtain homogeneous glassy alloys. After rocking for about 12 hours, the obtained melt was then rapidly quenched in ice cooled water. The quenched sample is then taken out by breaking the quartz ampoule. The glassy nature of the alloy was ascertained by X-ray diffraction.

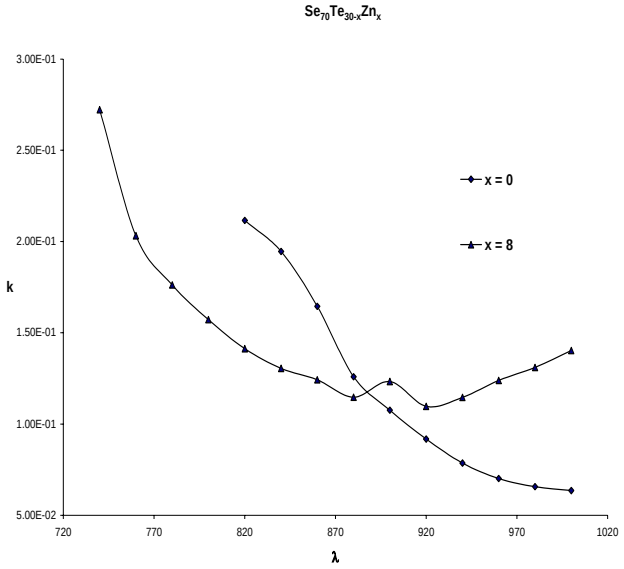

Fig.3. Variation of refractive index (k) with wave length (λ) in $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ thin films

Thin films of glassy alloys were prepared by vacuum evaporation technique, in which the substrates are kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The films are 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 thin films as a function of wavelength of the incident light.

3. Results and discussion

The optical transmission spectra of films of $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ are measured in the wavelength range 400-2000 nm using a Computer Controlled Spectrometer as mentioned in section 2.Fig 1 shows the results of these measurements, which indicates defined maxima and

minima due to interference phenomenon. These maxima and minima are used to calculate the optical parameters in the present case.

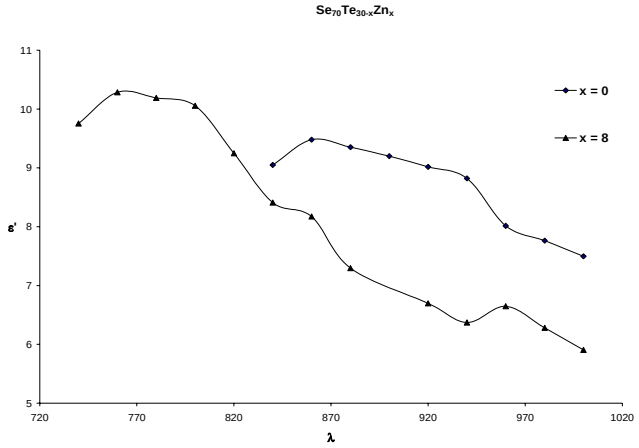

Fig. 4. Variation of real dielectric constant (∈`) with wave length (λ) in $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ thin films

The optical system under consideration is amorphous homogeneous and uniform. Optical transmission(T) is very complex function and is strongly dependent on absorption coefficient (α).

According to Swanepoel's method [16], which is based on Mainfacer [17], the envolpe of the interference maxima and minima occured in the spectrum can be utilized for obtaining 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 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 wavelength. This method has been used in chalcogenide glasses by various workers [18-22].

3.1 Determination of optical constants

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

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

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, the refractive index n is given by,

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

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 maximum.

In the region of strong absorption, the transmittance decreases drastically due almost exclusively to the influence of α and n can be estimated by extrapolating the values in the other regions. Because the thickness of our film is uniform, interference gives rise to the spectrum as

shown in Fig.1. The fringes can be used to calculate the refractive index n of the film using Eqs. (1) and (2) as indicated previously.

The extinction coefficient k can be calculated from the relation,

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

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,

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

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

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

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 $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ are shown in Fig.2 and Fig.3, respectively, and the calculated values are also given in the Table1.

Table 1.

Sample No.	Sample	Refractive index(n)	Exinction coefficient(k)	Real dielectric constant(ε`)	Imag. dielectric constant(ε")	Film thickness (d) nm.
1.	$Se_{70}Te_{30}$	3.003	0.92×10^{-1}	9.02	5.51×10^{-1}	2374
2.	$Se_{70}Te_{22}Zn_8$	2.588	1.1×10^{-1}	6.70	5.68×10^{-1}	1955

3.2 Determination of dielectric constants

The dielectric constant of the films can be calculated with the help of refractive index n and extinction coefficient k [23]. Real dielectric constant (ε`) can be calculated by the relation,

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

While the imaginary dielectric constant (ε") can be calculated by the relation,

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

The spectral distribution of both real and imaginary dielectric constants for $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ films is shown in Fig. 4 and 5, respectively, and the calculated values are also given in Table 1.

3.3 Absorption coefficient and optical band gap

The absorption coefficient α of films can be calculated using the well-known relation,

$$\alpha = 4\pi k / \lambda$$

where k is substituted by its value obtained from Fig. 3. The spectral distribution of absorption coefficient α for $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ films is shown in Fig. 6 and calculated values are also given in Table 2. The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for these films are shown in Fig. 6. 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.

Table 2.

S. No.	Sample	Optical band gap (E_g)	Absorption coefficient(α)in m^{-1} at 920 nm
1.	$Se_{70}Te_{30}$	1.26	9.98×10^4
2.	$Se_{70}Te_{22}Zn_8$	1.34	11.9×10^4

It is evident from the Table2 that optical band gap E_g increases with Zn content. The Zn additive in $Se_{70}Te_{30-x}$ must bring about a compositional change of host material i.e., the alloying effect as the optical band gap is found to vary with Zn concentration .The increase in band gap may be understood as follows:

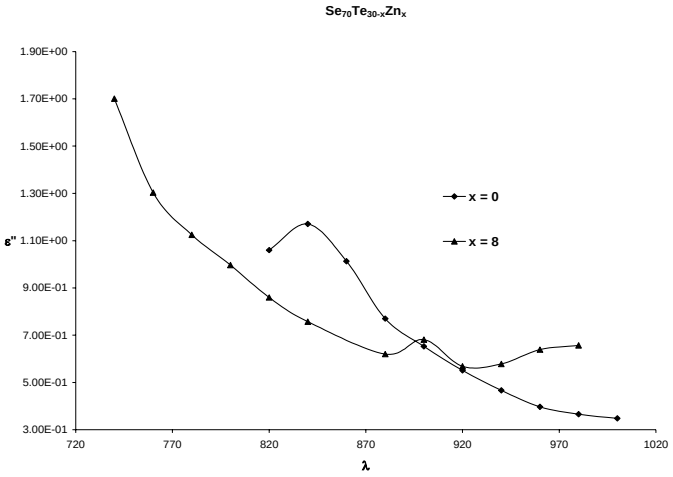

Fig. 5. Variation of imaginary dielectric constant (∈") with wave length (λ) in $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ thin films

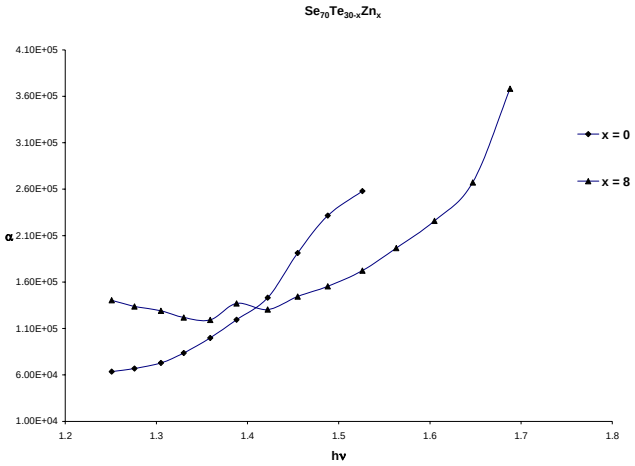

Fig.6 Variation of absorption Coefficient (α) with photon Energy (hν) in $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ thin films

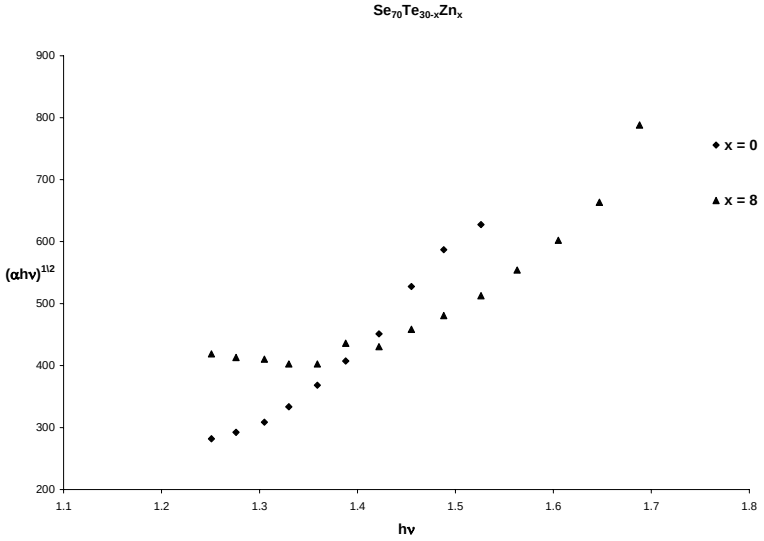

Fig.7 Variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) for $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ films.

Pauling [24] defines the electronegativity of an atom as the power to attract an electron to itself in a molecule. When the two atoms, which differ in their electronegativity values, combines to form an alloy , then the element of higher electro negativity attracts an electron pair more towards itself and behave as anion whereas the other element behave as a cation. Using Sanderson's principle [25] of equalization of electonegativity, electonegativity (X_c) between Se-Te and Se-Te-Zn alloys has been calculated using Hussain et al. [26] values for different elements. The calculated values are given in Table 3. When the electronegativity difference is large, it is expected that the probability of defect formation will be more. It has been observed that electonegativity (X_c) decreases on increasing Zn content. Therefore, the defect density should decrease with Zn concentration, which in turn should increase the band gap. In the present system also, we observed that the optical band gap (E_g) increases with Zn concentration, which may be due to the decrease in electonegativity(X_c) of the sample.

Table 3.

S.No.	Elements	Electonegativity(X_c)
1.	Se	2.5
2.	Te	2.1
3.	Zn	1.65

4. Conclusion

The optical transmission spectra of amorphous thin films of $Se_{70}Te_{30}$ and $Se_{70}Te_{22}Zn_8$ are measured in the wavelength range 400–2000 nm by spectrophotometer. It is observed from optical transmission measurements that optical energy gap (E_g) increases with Zn content. It is also found that refractive index (n), real dielectric constant (ε`), extinction coefficient (k), imaginary dielectric constant (∈") decreases with wavelength (λ). The absorption coefficient (α) increases with photon energy (hν). The increase of E_g with Zn content can be explained in terms of the electeronegativty of the third element.

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