PRAMANA — journal of physics
© Indian Academy of Sciences
Vol. 78, No. 2
February 2012
pp. 309–318

Optical characterization of a-$Se_{85-x}Te_{15}Zn_x$ thin films

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MS received 24 September 2010; revised 13 July 2011; accepted 8 August 2011

Abstract. Thin films of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10) glassy alloys have been deposited onto a chemically cleaned glass substrate by thermal evaporation technique under vacuum. The analysis of transmission spectra, measured at normal incidence, in the spectral range of 400–2500 nm helped us in the optical characterization of thin films under study. From the analysis of transmission spectra, the optical parameters such as refractive index (n), extinction coefficient (k), absorption coefficient (α), real and imaginary dielectric constants (ε' and ε'') have been calculated. It is observed that the parameters n, k, ε', ε'' and α decrease with increase in wavelength (λ) and increase with Zn content. Optical band gap (E_g) has also been calculated and found to decrease with Zn content in $Se_{85-x}Te_{15}Zn_x$ glassy system which could be correlated with increase in the density of defect states.

Keywords. Chalcogenide glasses; thin films; optical parameters.

PACS Nos 78.20.Ci; 61.43.Fs; 61.43.Dq

1. Introduction

Chalcogenide glasses have recently gained much importance as, unlike conventional oxide glasses, they show semiconducting properties and hence can be used in various solid-state devices. These materials, in particular selenium glasses, exhibit the unique property of reversible transformation [1], which makes these glasses useful as optical memory devices. Glassy alloys of Se–Te system based on Se have become materials of considerable commercial, scientific and technological importance. They are widely used for various applications in many fields such as optical recording media because of their excellent laser writer sensitivity, xerography and electrographic applications such as photoreceptors in photocopying and laser printing, infrared spectroscopy and laser fibre techniques [2–4]. Amorphous Se–Te alloys have greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects than pure Se [5]. As these glasses have poor thermo-mechanical properties, in order to enlarge their domain of applications, it is necessary to increase their softening temperature and mechanical strength by adding a third element.

The third element behaves as a chemical modifier as it is reported to expand the glass-forming region and also creates compositional and configurational disorder [6–8]. Thus the incorporation of a third element like Zn to Se–Te binary is expected to change the optical and electrical properties of the host alloy, which play a major role in device preparation. The reason for selecting Zn as a chemical modifier in the Se–Te system is based on its attractive and important applications in chalcogenide glasses. Like Ag, Zn can also be used for photo-doping in chalcogenide glasses [9–12]. There are reports of successful doping of $ZnSe_xTe_{1-x}$ in the literature that are suitable for developing light emitting diodes and lasers.

The optical band gap, refractive index and extinction coefficient are the most significant parameters in amorphous semiconducting thin films. The optical behaviour of a material is utilized to determine its optical constants. Films are ideal specimens for reflectance and transmittance type measurements. Therefore, an accurate measurement of the optical constants is extremely important. Chalcogenide glasses have been found to exhibit a change in refractive index [13–16] under the influence of light, and so these materials can be used to record not only the magnitude but also the phase of illumination.

The aim of the present investigation is to study the effect of Zn incorporation on the optical properties of Se–Te matrix. The optical transmission spectra of films of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10) are measured in the wavelength range 400–2500 nm by spectrophotometer (Perkin-Elmer, model Lambda-750). The well-known Swanepoel's method is employed to determine the optical parameters. In the present case, optical parameters like refractive index (n), film thickness (d), extinction coefficient (k), absorption coefficient (α), real and imaginary dielectric constants (ε' and ε'') and band gap (E_g) have been calculated for $Se_{85-x}Te_{15}Zn_x$ glassy system.

Sections 2 and 3 describe the experimental details and the results respectively. The conclusions are presented in the last section.

2. Experimental details

Bulk samples of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10) were prepared by melt quenched technique. High purity elements (99.999% pure), selenium, tellurium and zinc were weighed by electronic balance (Shimadzu, AUX 220) according to their atomic percentages, with a least count of 10^{-4} g. The properly weighed materials were put into clean quartz ampoules (length ∼5 cm and internal diameter ∼8 mm) and then sealed under vacuum of 1.3×10^{-3} Pa. These sealed ampoules were heated in an electric furnace up to 1000°C and kept at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate of 3–4°C/min. During the heating process, ampoules were constantly rocked, by rotating the ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain a homogeneous glassy alloy.

After rocking for about 10 h, the ampoules were rapidly quenched by removing the ampoules from the furnace and dropping into ice-cooled water. The quenched samples of the glassy alloys were taken out by breaking the quartz ampoules. The glassy nature of the samples was ascertained by the X-ray diffraction pattern as shown in figure 1. Compositional analysis was performed using electron probe microanalysis (EPMA) technique.

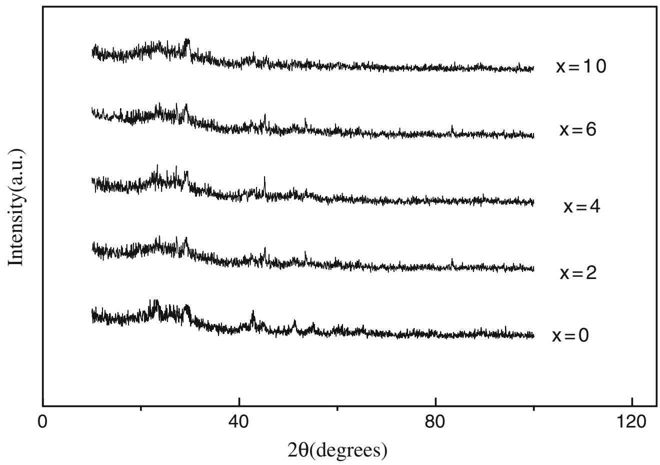

Figure 1. X-ray diffraction pattern of $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6, 10$).

Thin films of $Se_{85-x}Te_{15}Zn_x$ glassy alloys were prepared by vacuum evaporation technique keeping the glass substrate at room temperature. The thin films were kept in the deposition chamber in the dark for 24 h before using them. This was done to allow sufficient annealing at room temperature so that a metastable thermodynamic equilibrium may be attained in the samples as suggested by Abkowitz [17].

The normal incidence transmission spectra of $Se_{85-x}Te_{15}Zn_x$ thin films have been taken by a double beam UV-VIS-NIR spectrophotometer in the transmission range 400–2500 nm. The spectrophotometer was set with a suitable slit width of 1 nm in the measured spectral range.

3. Results and discussions

3.1 *Determination of optical parameters* (*a method of calculation*)

Figure 2 shows the transmission spectra as a function of wavelength for thin films of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10). The plot shows fringes due to interference at various wavelengths.

The optical behaviour of the material is generally utilized to determine its optical constants, i.e. refractive index (n), extinction coefficient (k) absorption coefficient (α) etc. These optical constants are determined using Swanepoel's method [18–21]. According to this method the transmission spectrum can roughly be divided into four regions. Interference fringes can be used to calculate the optical constants of the film. The basic equations for the four regions are as follows:

(i) In the transparent region ($\alpha = 0$), the refractive index n is given by

$$n = [M + (M^2 - s^2)^{1/2}]^{1/2}, \tag{1}$$

where

$$M = (2s/T_m) - (s^2 + 1)/2 \tag{2}$$

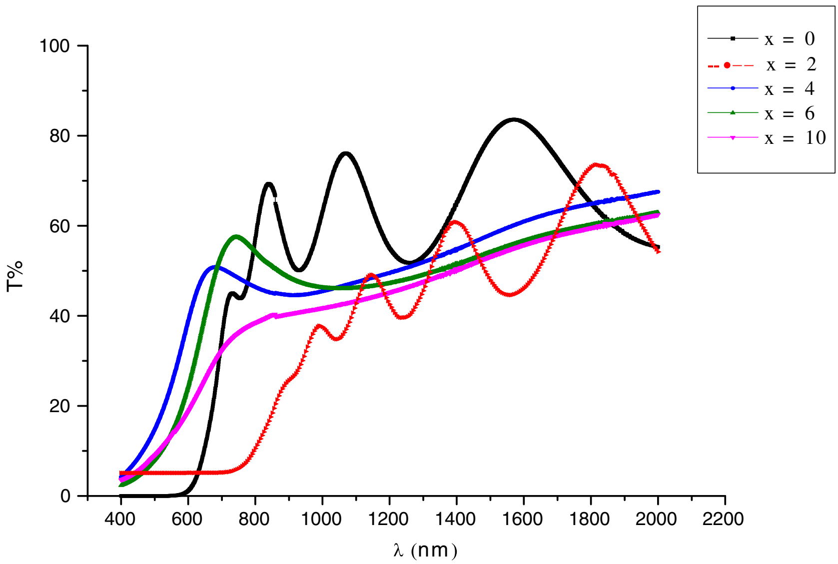

Figure 2. Variation of the transmittance (T) with wavelength (λ) in $Se_{85-x}Te_{15}Zn_x$ thin films.

and T_m is the envelope function of the transmittance minima, s is the refractive index of the substrate.
(ii) & (iii) In the region of weak and medium absorptions ($\alpha \neq 0$), n is given by

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}, \quad (3)$$

where

$$N = [2s(T_M - T_m)/T_M T_m] + (s^2 + 1)/2 \quad (4)$$

and T_M is the envelope function of the transmittance maxima. For extinction coefficient k, the absorbance x is given in terms of the interference extremes using the following relation:

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

where

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

and

$$x = \exp(-4\pi kd/\lambda). \quad (7)$$

(iv) In the region of strong absorption where the interference maxima and minima converge to a single curve, the absorbance x is given by [21]

$$x \approx \frac{T_0\ (n+1)^3\ (n+s^2)}{16n^2 s}. \quad (8)$$

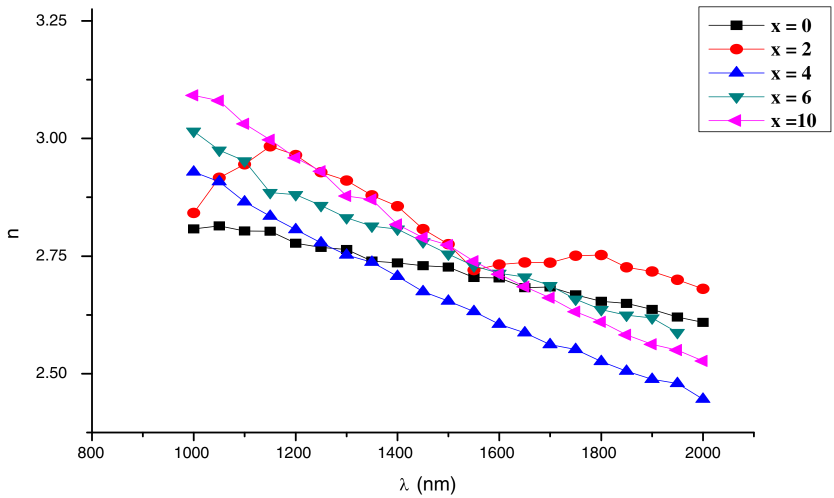

Figure 3. Variation of refractive index (n) with wavelength (λ) in $Se_{85-x}Te_{15}Zn_x$ thin films.

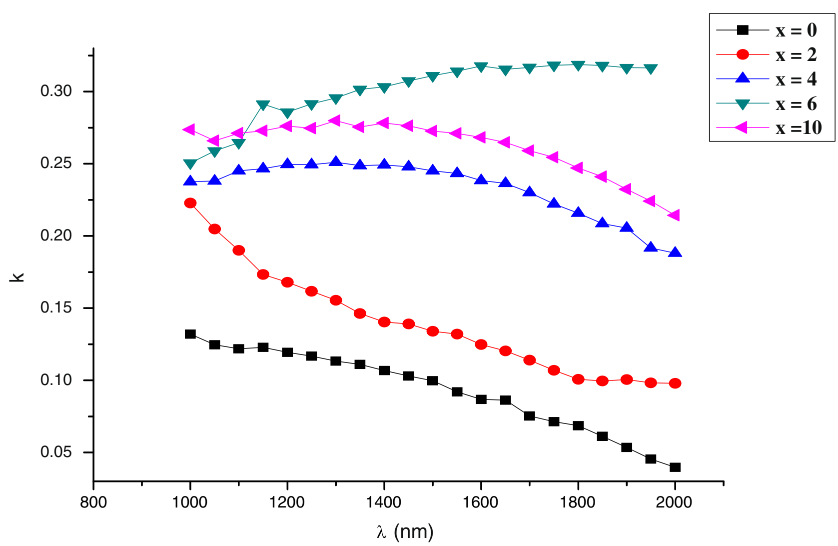

Figure 4. Variation of extinction coefficient (k) with wavelength (λ) in $Se_{85-x}Te_{15}Zn_x$ thin films.

Figures 3 and 4 show the spectral dependence of n and k for thin films of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10). It is clear from the figures that n and k decrease with an increase in λ. This behaviour is due to the increase in transmittance and decrease in absorption coefficient with wavelength. The decreases in n with λ show the normal dispersion behaviour

Table 1. Values of refractive index (n), extinction coefficient (k), real and imaginary dielectric constants (ε' and ε'') for $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6$ and 10) thin films.

Glassy samples	Refractive index (n)	Extinction coefficient (k)	Real dielectric constant (ε')	Imaginary dielectric constant (ε'')
$Se_{85}Te_{15}$	2.80	13.20×10^{-2}	7.87	0.74
$Se_{83}Te_{15}Zn_2$	2.84	22.27×10^{-2}	8.03	1.27
$Se_{81}Te_{15}Zn_4$	2.93	23.76×10^{-2}	8.52	1.39
$Se_{79}Te_{15}Zn_6$	3.02	25.04×10^{-2}	9.03	1.51
$Se_{75}Te_{15}Zn_{10}$	3.09	27.36×10^{-2}	9.48	1.69

of the material. The calculated values of n and k for different concentrations of Zn are given in table 1. It is also evident from the figures and table that n and k increase with Zn content.

3.2 *Determination of dielectric constants*

The dielectric constant of the films can be calculated with the help of n and k [22]. The real dielectric constant (ε') can be calculated by the relation:

$$\varepsilon' = n^2 - k^2 \tag{9}$$

while the imaginary dielectric constant (ε'') can be calculated by the relation:

$$\varepsilon'' = 2nk. \tag{10}$$

The variation of both ε' and ε'' with λ for the investigated thin films are shown in figures 5 and 6, respectively, and the calculated values are also given in table 1 for all compositions of $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6$ and 10). The variation of ε' and ε'' with λ follows almost the same trend as that of n and k.

3.3 *Determination of absorption coefficient (α) and optical band gap (E_g)*

The absorption coefficient α of the thin films was calculated using the following relation:

$$\alpha = 4\pi k/\lambda. \tag{11}$$

The calculated values of k obtained by Swanepoel's method are being used in the above relation. A plot of α as a function of photon energy ($h\nu$) is given in figure 7 and the values are given in table 2. The value of α is found to increase with increase in $h\nu$ for $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6$ and 10) glassy system.

The analysis of the absorption coefficient has been carried out to obtain the optical band gap (E_g). The optical band gap has been determined from absorption coefficient data as a function of $h\nu$ by using Tauc relation [23–25]

$$(\alpha\nu h)^{1/2} = A\ (h\nu - E_g), \tag{12}$$

where A is the edge width parameter representing the film quality, which is calculated from the linear part of this relation and E_g is the optical band gap of the material. The

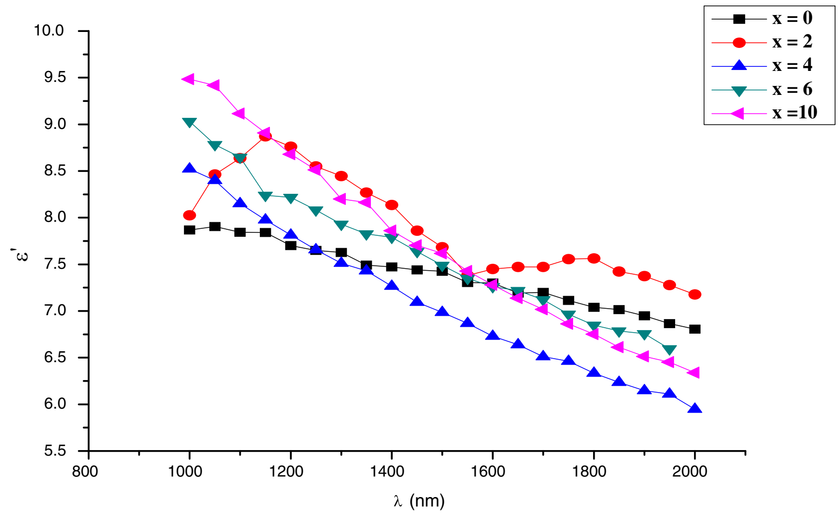

Figure 5. Variation of real dielectric constant (ε') with wavelength (λ) in $Se_{85-x}Te_{15}Zn_x$ thin films.

usual method for determining E_g involves a plotting of $(\alpha h\nu)^{1/2}$ against $h\nu$ as shown in figure 8 and the values of E_g are given in table 2 for the investigated samples. It is found that E_g decreases with the incorporation of Zn in $Se_{85}Te_{15}$ binary glassy alloy. The decrease in E_g indicates an increase in the density of localized states (DOS). Similar trend

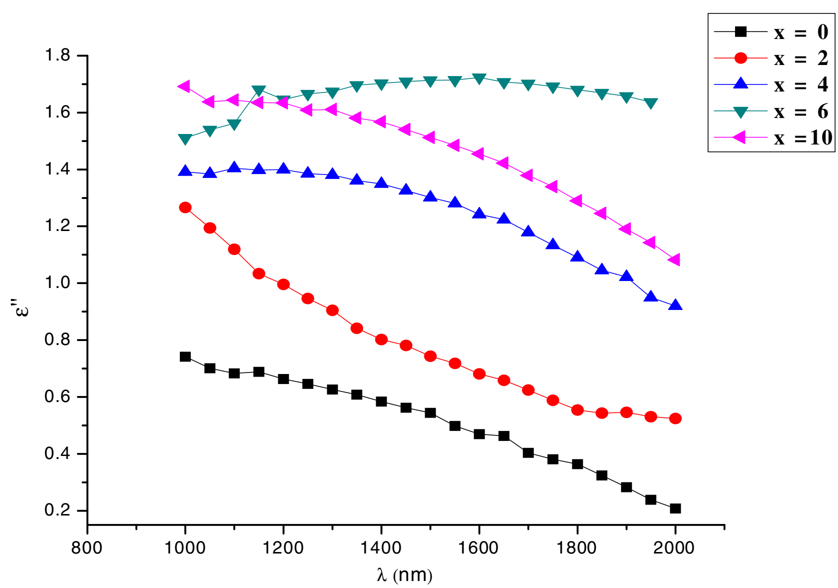

Figure 6. Variation of imaginary dielectric constant (ε'') with wavelength (λ) in $Se_{85-x}Te_{15}Zn_x$ thin films.

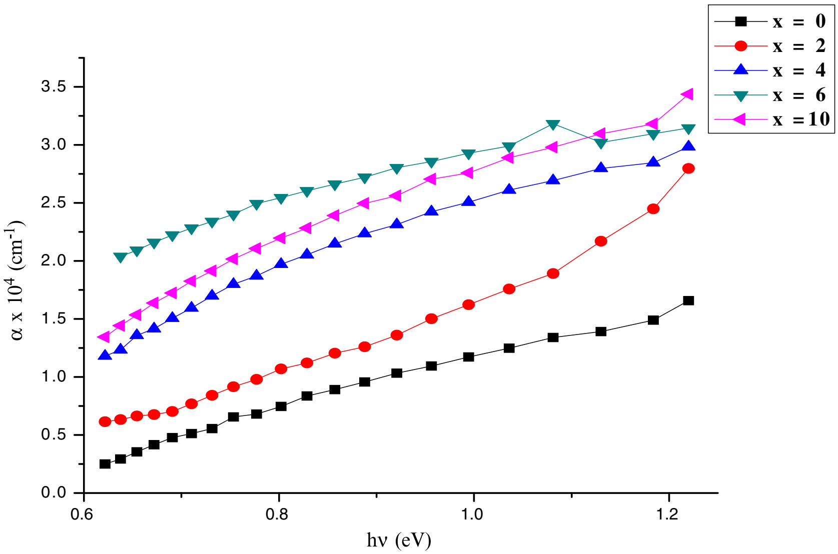

Figure 7. Variation of absorption coefficient (α) with photon energy ($h\nu$) in $Se_{85-x}Te_{15}Zn_x$ thin films.

of DOS with increasing Zn content has already been reported by Krishna Ji *et al* [26]. We have also found an increase in DOS with Zn incorporation in our SCLC measurements.

The decrease in E_g along with the increase in the density of defect states may also be correlated with the electronegativity difference of the elements involved. It has been reported by Kastner *et al* [27] that the valence band in chalcogenide glasses is constituted by lone pair p-orbitals contributed by the chalcogen atoms. These lone pair electrons will have a higher value of energies adjacent to electropositive atoms than those of the electronegative atoms. Thus, the addition of an electropositive element to the electronegative element may raise the energy of lone pair states, which is further responsible for the broadening of the valence band inside the forbidden gap. The electronegativities of Se, Te and Zn are 2.4, 2.1 and 1.7, respectively. Since Zn has lower electronegativity than Se, the substitution of Zn for Se may raise the energy of lone pair states, which may be further

Table 2. Optical band gap (E_g) and absorption coefficient (α) for $Se_{85-x}Te_{15}Zn_x$ ($x = 0, 2, 4, 6$ and 10) thin films.

Glassy samples	Optical band gap (E_g) (eV)	Absorption coefficient (α) (m^{-1}) at 999 nm
$Se_{85}Te_{15}$	1.08	1.66×10^4
$Se_{83}Te_{15}Zn_2$	0.92	2.80×10^4
$Se_{81}Te_{15}Zn_4$	0.70	2.98×10^4
$Se_{79}Te_{15}Zn_6$	0.63	3.14×10^4
$Se_{75}Te_{15}Zn_{10}$	0.56	3.44×10^4

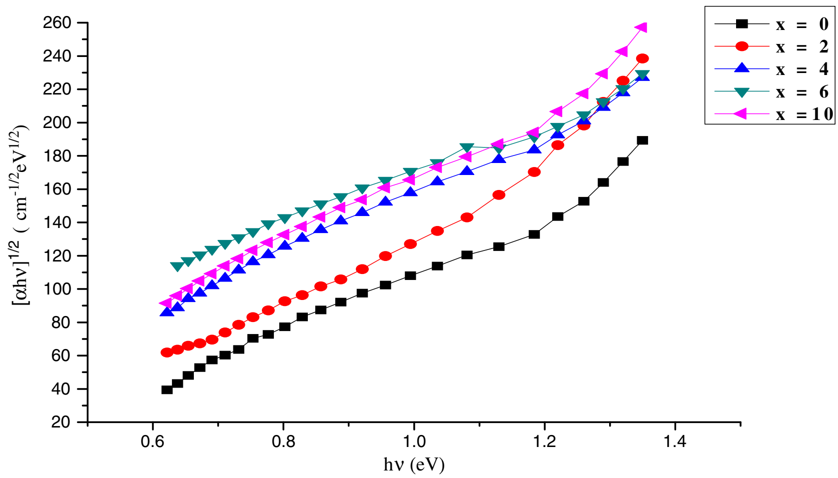

Figure 8. Variation of $[\alpha h\nu]^{1/2}$ with photon energy ($h\nu$) in $Se_{85-x}Te_{15}Zn_x$ thin films.

responsible for the broadening of the valence band. This leads to band tailing and hence shrinking of the band gap. Therefore, E_g decreases with Zn content.

4. Conclusions

The optical transmission spectra of the thin films of $Se_{85-x}Te_{15}Zn_x$ ($x = 0$, 2, 4, 6 and 10) glassy alloys are measured in the wavelength range of 400–2500 nm by spectrophotometer. The optical parameters are calculated by using the envelope method proposed by Swanepoel. The results indicate that values of n, k, α, ε' and ε'' increase by adding Zn to $Se_{85}Te_{15}$ binary glassy alloy. It is also observed that optical band gap decreases with Zn content. The decrease in band gap has been correlated to increase in the density of localized states in the present glassy system. The decrease in band gap could also be explained in terms of electronegativity difference between the elements involved in making the aforesaid glassy systems.

Acknowledgements

The authors are very much grateful to the Department of Science and Technology (DST), New Delhi, India for the financial assistance during this work. The authors also thank Prof. R C Budhani and Prof. Y M Mohapatra, Department of Physics, IIT, Kanpur for providing them the facility to obtain XRD data and optical measurements respectively.

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