

OPTICAL BAND GAP AND OPTICAL CONSTANTS IN $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ THIN FILMS

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Thin films of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 0, 2, 4$ & 6) are deposited under vacuum on glass substrates by thermal evaporation technique. The optical constants (refractive index 'n', absorption coefficient ' α ', and extinction coefficient 'k') have been calculated in the wavelength range (400 – 2000 nm) using a transmission spectrum. The refractive index 'n' increases and extinction coefficient 'k' decreases with the wavelength. Data are analyzed by Swanepoel method. It has been found that optical energy gap E_g decreases with Pb content.

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1. Introduction

Studies on semiconducting chalcogenide glasses have received much attention because of their important optical application in IR region [1-6]. Impurity effects in chalcogenide glasses may have importance in the fabrication of glassy semiconductor devices. The most important application of chalcogenide glasses are now in the field of optics and arise chiefly from either their infrared transmitting properties or photo-induced effects exhibited by them. They have potential use in integrated optics, optical imaging, optical data storage and infrared optics [7–15].

The optical band gap, refractive index and extinction coefficient are the most significant parameters in amorphous semiconducting thin films. The optical behaviour of material is utilized to determine its optical constants. Films are ideal specimen for reflectance and transmittance type measurements. Therefore, an accurate measurement of the optical constant is extremely important.

Chalcogenide glasses have been found to exhibit the change in refractive index under the influence of light, which makes it possible to use these materials to record not only the magnitude but also the phase of illumination. The later is especially important in holographic optical data storage and in the fabrication of various integrated components and devices such as selective optical filters, mixers, couplers and modulators [16-18].

Most of the work has been carried out on chalcogenide thin films having Te as a major constituent. One of the limitations of Te based materials is their poor oxidation resistance. Hence, attempts have been made to investigate Se based chalcogenide thin films. Se has been selected because of its wide commercial applications. Its device applications like switching, memory and xerography etc made it attractive [19]. It also exhibits a unique property of reversible transformation. This property is very useful in optical memory devices. Hence, we have chosen Se-Te system to overcome these problems. In the present work, we have incorporated Pb in the Se-Te system. The addition of third element will create compositional and configurational disorder in the material with respect to the binary alloys.

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2. Experimental

Glassy alloys of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 0, 2, 4$ & 6) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Pb 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 ($\sim 10^{-5}$ Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 1000°C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of $3 - 4^\circ\text{C} / \text{minute}$. 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 then 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 $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 0, 2, 4$ & 6) 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 $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ ($x = 0, 2, 4$ & 6) thin films. The optical transmission was measured as a function of wavelength and incident photon energy.

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. According to Swanepoel's method [20], which is based on Mainfacer [21], 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 ($\alpha \neq 0$). 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 [22-25].

3.1 Determination of optical constants

For the method proposed by Swanepoel, 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

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

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 and 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 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 equation (1) and (2) as indicated previously.

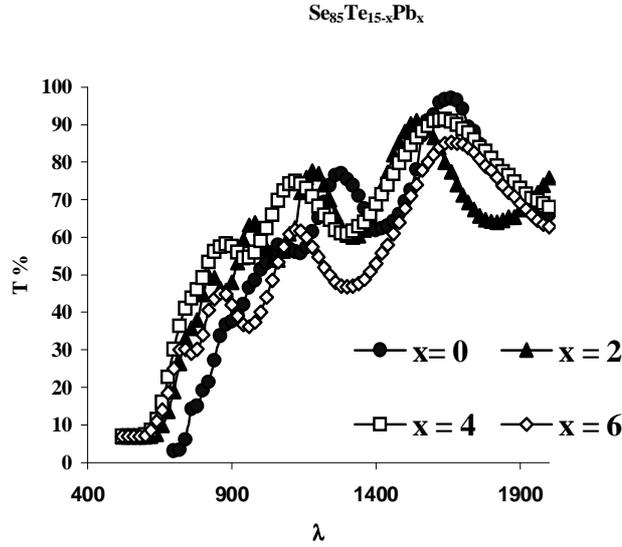


Fig. 1. Variation of transmittance (T) with wavelength (λ) in $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ thin films.

The extinction coefficient k can be calculated from the relation

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

where x is the absorbance.

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

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

Where $E_m = (8 n^2 s / T_m) - [(n^2 - 1) (n^2 - s^2)] \quad (5)$

The spectral distribution of both n and k for $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ is given in Figs. 2 and 3, respectively.

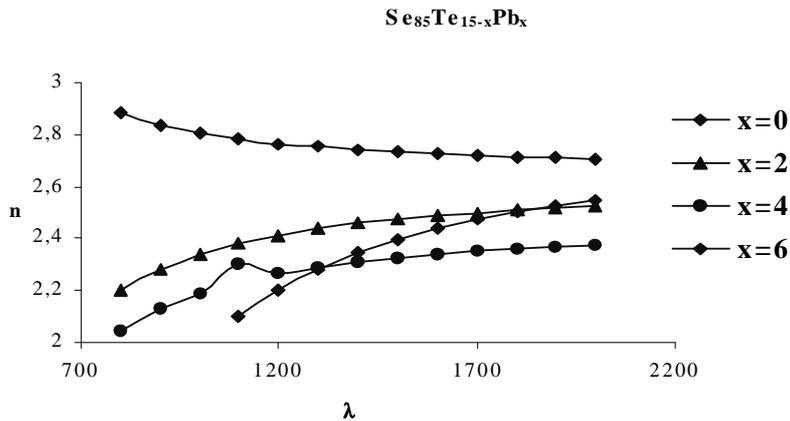


Fig. 2. Variation of refractive index (n) with wavelength (λ) in $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ thin films.

3.2 Absorption coefficient and optical band gap

The absorption coefficient α of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ films can be calculated using the well-known relation

$$\alpha = 4\pi k / \lambda \quad (6)$$

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

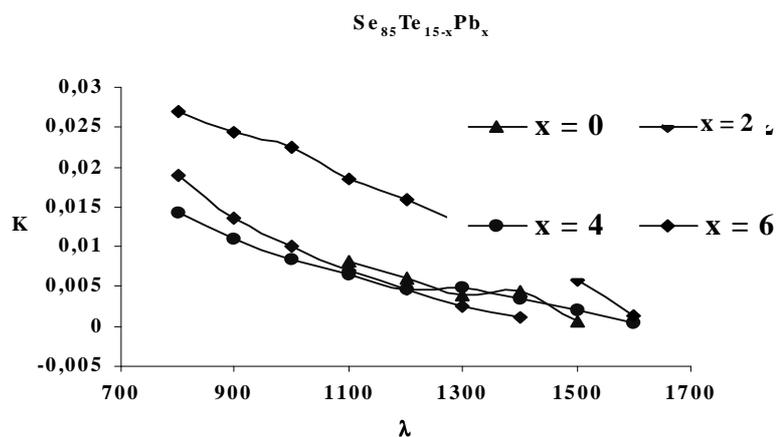


Fig. 3. Variation of extinction coefficient (k) with wavelength (λ) in $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ thin films.

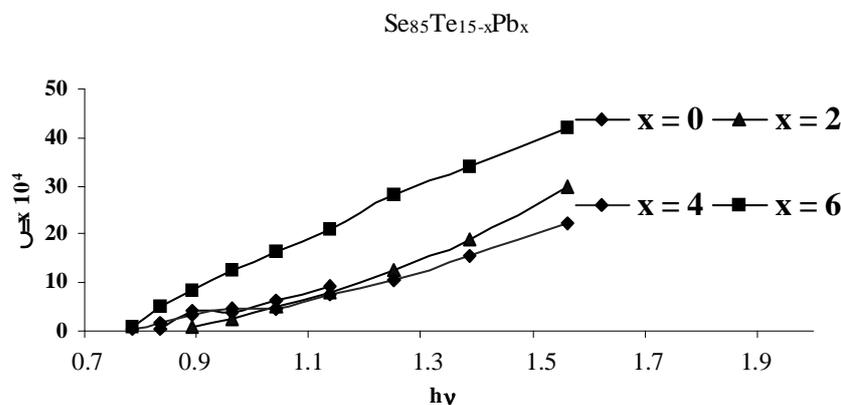


Fig. 4. Variation of absorption coefficient (α) with $h\nu$ in $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ thin films.

The present system of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ obeys the role of non-direct transition and the relation between the optical band gap, absorption coefficient and energy ($h\nu$) of the incident photon is given by [26-28]:

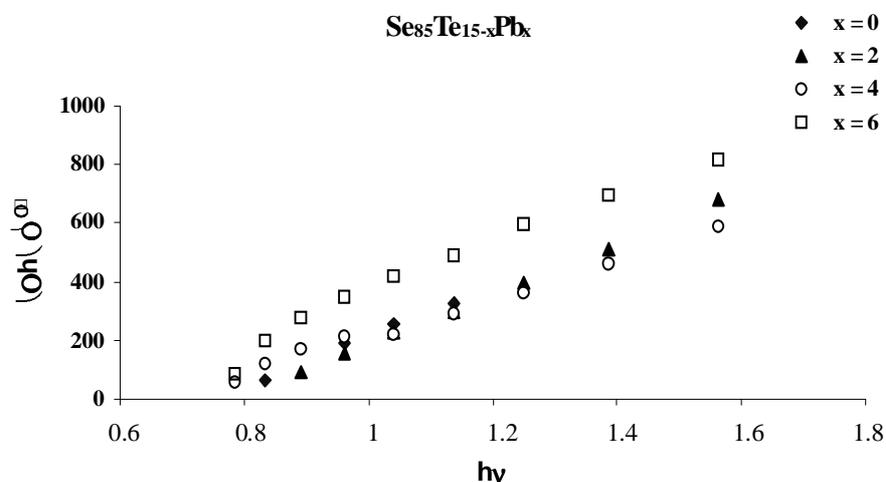
$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g) \quad (7)$$

The calculated values of absorption coefficient α are given in Table 1.

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ films are shown in Fig. 5. 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 1 for each sample. It is evident from the table that optical band gap E_g decreases with Pb-content.

Table 1.

No.	Sample	Optical band gap (E_g)	Absorption coefficient (α) in m^{-1} at 1200 nm	Refractive index (n)	Extinction coefficient (k)	Film thickness (d) nm
1.	$\text{Se}_{85}\text{Te}_{15}$	0.77	0.56×10^4	2.10	0.53×10^{-3}	3412
2.	$\text{Se}_{85}\text{Te}_{13}\text{Pb}_2$	0.76	1.11×10^4	2.20	1.10×10^{-3}	2244
3.	$\text{Se}_{85}\text{Te}_{11}\text{Pb}_4$	0.73	0.50×10^4	2.04	0.48×10^{-3}	2391
4.	$\text{Se}_{85}\text{Te}_9\text{Pb}_6$	0.62	1.33×10^4	2.71	1.27×10^{-3}	1518

Fig. 5. Variation of $(\alpha hv)^{1/2}$ with $h\nu$ in $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$ thin films.

The Pb additives in $\text{Se}_{85}\text{Te}_{15}$ must bring about a compositional change of the host material i.e., the alloying effect as the optical band gap is found to varies with Pb concentration. The decrease in band gap may be understood as follows:

The addition of Pb atoms in Se–Te may makes bonds with Se and Te separately with bond energy of Se–Pb (= 72.4 kcal/mol) and Te–Pb (= 60 kcal/mol). The bond energies of Se–Se is (= 79.5 kcal/mol) while that of Se–Te is (= 64 kcal/mol). The introduction of Pb in Se–Te system reduces the effective bond energy of [(Se–Se) + (Se–Te) – ((Se–Pb) + (Te–Pb))] = 11.1 kcal/mol. Maharajan et al also observed [29] that increase of Pb at % in the Se–Te system causes the decrease of T_g in the system. The reduction in the effective bond energy of the Se–Te–Pb system may be responsible for the observed decrease in optical band gap.

4. Conclusions

Various parameters related to optical properties were calculated for various samples of $\text{Se}_{85}\text{Te}_{15-x}\text{Pb}_x$. The optical absorption in the Se–Te–Pb system seems to be due to non-direct transition. Energy gap decreases with increasing Pb-content. Absorption coefficient is of the order of 10^4 m^{-1} in all the alloys.

References

- [1] A. R. Hilton, D. J. Hayes, M. D. Rehtin, J. Non-Cryst. Solids **17**, 319 (1975).
- [2] A. Vasko, in: Proceedings of the 11th International Congress on Glass **5**, Prague, 533 (1977).

- [3] D. Lezal, *J. Optoelectron. Adv. Mater.* **5**(1), 23 (2003).
- [4] P. Sharlandjev, B. Markova, *J. Optoelectron. Adv. Mater.* **5**(1), 39 (2003).
- [5] X. Zhang, H. J. Lucas, *J. Optoelectron. Adv. Mater.* **5**(5), 1327 (2003).
- [6] D. Lezal, J. Pedlikova, J. Zavadil, *J. Optoelectron. Adv. Mater.* **6**(1), 133 (2004).
- [7] J. S. Sanghara, I. D. Agarwal, *J. Non-Cryst. Solids* **256 & 257**, 6 (1999).
- [8] K. Schwartz in "The Physics of Optical Recording", Berlin, Springer-Verlag (1993).
- [9] A. Bradley in "Optical Storage for Computers Technology and Applications" Ellis Horwood Limited New York, (1989).
- [10] I. Shimizu, H. Kokado, E. Inoue, *Photogr. Sci. Engg.* **19**, 136 (1975).
- [11] T. Sirakawa, I. Shimizu, H. Kokado, E. Inoue, *Photogr. Sci. Engg.* **19**, 139 (1975).
- [12] Y. Ashara, T. Izumitani *Phys. Chem. Glasses* **16**, 29 (1975).
- [13] J. Bardangna, S. A. Keneman in "Holographic Recording Media" eds. H. M. Smith, Berlin, Springer-Verlag 229 (1977).
- [14] K. L. Tai, E. Ong, R. G. Vadimsky *Proc. Electro Chem. Sci.* **82-83**, 9 (1982).
- [15] J. Teteris, M. Reinfelde, *J. Optoelectron. Adv. Mater.* **5**(5), 1355 (2003).
- [16] A. M. Andriesh, V. V. Ponomar, V. L. Smirnov, A. V. Mironos, *Sov. J. Quantum Elect.* **16**, 721 (1986).
- [17] I. V. Kityk, E. Golis, J. Filipecki, J. Wasylak, V. M. Zacharko, *J. Mater. Sci. Lett.* **18**, 1292 (1995).
- [18] J. Wasylak, J. Kucharski, I. V. Kityk, B. Sahraui, *J. Appl. Phys.* **85**, 425 (1999).
- [19] S. R. Ovshinsky *Phys. Rev. Lett.* **21**, 1450 (1968).
- [20] R. Swanepoel, *J. Phys. E.* **16**, 1214 (1983).
- [21] J. C. Manificier, J. Gasiot, J. P. Fillard, *J. Phys. E. Sci. Instrum.* **9**, 1002 (1976).
- [22] S. M. Ei-Sayed, *Vaccum*, **72**, 169-175 (2004).
- [23] Ei-Sayed, M. Farg, *Optics & Laser Technology* [Article in Press].
- [24] H. S. Metcoally, *Vaccum* **62**, 345-351 (2001).
- [25] E. Marquez, A. M. Bernal-Oliva, J. M. Gonzalez-Leal, R. Pricto-Alcon, A. Ledesma, R. Jimenez-Garay, I. Martil, *Mater. Chem. and Phys.* **60**, 231-239 (1999).
- [26] J. Tauc, in: J. Tauc (Ed.), *Amorphous and Liquid Semiconductors*, Plenum Press, New York, 159 (1979).
- [27] F. Urbach, *Phys. Rev.* **92**, 1324 (1953).
- [28] K. Oe, Y. Toyoshiman, *J. Non-Cryst. Solids* **58**, 304 (1973).
- [29] N. B. Maharajan, N. S. Saxena, D. Bhandari, M. M. Imran, D. D. Paudyal, *Bull. Mater. Sci.* **23**, 369 (2000).