

Full Length Research Paper

Study of optical constants in Se- In –Pb thin films of chalcogenide glasses

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Bulk glasses of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ (when $n = 0, 4, 6, 10$) systems and thin films have been prepared by the conventional melt quenching technique and by thermal evaporation technique, respectively. The optical constants (absorption coefficient (α), refractive index (n), extinction coefficient (k)) have been studied for Se-In-Pb thin films as a function of photon energy in the wavelength range (300-900 nm). Spectral dependence of transmittance (T) and reflectance (R) in the spectral range (300-900 nm) of glass Se-In-Pb have also been observed at various concentrations of Te and Pb. The effect of compositional variation on some optical constant has been observed and discussed in the present investigation.

Key words: optical constants, thin films, chalcogenide glasses.

INTRODUCTION

Chalcogenide glasses have been studied intensively in the last few years owing to their interesting properties and technological applications (Al-Ghamdi, 2006). They are materials used in optical and photonic devices. They have good electro-optic, thermo-optic, magneto-optic, acousto-optic properties, high refractive index (Barman and Sharma, 2013) and I R transparency (Zakery and Elliott, 2003). A good deal of information regarding the synthesis and opto–electro-structural properties of thin films of lead chalcogenides have been revealed by Kumar et al. (2005). The development of laser technology had opened up new application for narrow gap lead salts and their alloys. The polycrystalline thin films were deposited onto optically plane and chemically clean glass substrates by vacuum evaporation technique. The films were thin, uniform, smooth and tightly adherent to the substrates. Optical absorption spectroscopy, X-ray diffraction technique and current–voltage characteristics method were used to characterize the films.

Chalcogenide glasses material heating to melting is the form of a liquid and at some instance; it freezes the position of every atom by quenching. Even in this frozen

position, they retain short range order and the position of the nearest neighbour remains nearly the same. These glasses are useful in the preparation of passive devices like lenses, windows, fibers (Books et al., 1999; Hoede et al., 2001), active devices like laser fiber amplifiers (Schweitzer et al., 2001) and non-linear components (Dixit and Vijaya, 2001). The present work has been carried out in order to investigate some optical properties of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ system. The effect of incorporation of lead in Se-In alloy can change the structural and optical properties of the system.

METHODOLOGY

Glassy alloys of Se-In-Pb ($x=0, 4, 6, 10$) have been prepared by melt-quenching techniques. Extra pure materials (99.99%) were weighed according to their atomic percentage and sealed in 6 cm long quartz ampoules with diameter 6 mm in the vacuum of 10^{-5} torr. The sealed ampoules were kept in a furnace at 700°C and were held at the same temperature for about 10 h. The temperature of the furnace was raised slowly at a rate of 3-4°C/min. During heating, all the ampoules were constantly rocked for better homogenization of the alloys. This was achieved with the help of a

Table 1. Variation of Absorption coefficient (α) with photon energy in a $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films at room temperature.

S/N	Photon energy E (eV)	Absorption coefficient (α) in cm^{-1}			
		$\text{Se}_{75}\text{In}_{25}\text{Pb}_0$	$\text{Se}_{75}\text{In}_{21}\text{Pb}_4$	$\text{Se}_{75}\text{In}_{19}\text{Pb}_6$	$\text{Se}_{75}\text{In}_{15}\text{Pb}_{10}$
1	1.377	15555.556	7777.778	N/A	3888.889
2	1.458	15555.556	7777.778	3888.889	3888.889
3	1.549	14000.00	6222.222	4666.667	4666.667
4	1.906	22555.556	6222.222	17888.889	23333.333
5	2.065	38888.889	15555.556	27222.222	38888.889
6	2.253	62222.222	29555.556	49777.778	56000.000
7	2.478	79333.333	42000.000	73888.889	70000.000
8	2.753	101111.111	56000.000	101111.111	101111.111
9	3.540	112777.778	88666.667	163333.333	136111.111
10	4.130	217777.778	217777.778	256666.667	256666.667

ceramic rod to which all the ampoules were tucked away in the furnace. Rotating the same rod after every five minutes interval of time did this. Thereafter, the obtained melts were cooled rapidly by removing the ampoules from the furnace and quenching into the ice cold water. The quenched samples were taken out by breaking the ampoules. The amorphous nature of the glassy alloys was identified by X - Ray diffraction. Thin films of glassy alloys of thickness (~300 nm) were prepared by thermal evaporation technique in which substrate was kept at room temperature at a base pressure of 10^{-4} torr using the molybdenum boat; the film was kept inside the deposition chamber for 24 h to achieve the stable equilibrium (Ogusk et al., 2004). The thickness of the film was measured by a single crystal thickness monitor. In order to measure the optical absorption reflection, transmission as a function of wavelength (300-900 nm), a double UV/VIS/NIR computerized spectrophotometer (JASCO V-500) has been used.

RESULTS AND DISCUSSION

The value of optical absorption coefficient (α) as a function of incident photon ($h\nu$) for deposited thin films of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ where $x=0, 4, 6, 10$ at room temperature are shown in Table 1. The absorption coefficient (α) has been obtained directly from the absorbance against wavelength curves using the relation

$$\alpha = \text{OD}/t \quad (1)$$

Where OD is the optical density measured at a given layer thickness (t).

It has been observed in Table 1 that the value of absorption coefficient (α) increases linearly with the increase in photo energy of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$. According to Mott and Davis (1979), the absorption of light by amorphous solids depends on the energies of the incident photon and on the optical band gap of the material. Thus the behavior may be represented by the following equation.

$$\alpha h\nu = B (h\nu - E_g) \quad (2)$$

Where B is a constant which depends on the transition

probability, $h\nu$ is energy of incident photon, E_g is optical band gap of the material, r is an index which depends on the nature of transition (Hasegawa et al., 1978) where $r = 1/2$ and $r = 2$ for allowed direct transition and indirect transition, respectively.

The present system obeys the rule of indirect transition and the relation between optical gap, optical coefficient (α), and the energy $h\nu$ of the incident photon is given by

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (3)$$

Where α obeys - Urbach relation (Urbach, 1953)

$$\alpha = \exp [A(h\nu - h\nu_0)]/kT \quad (4)$$

Where A is a constant of the order of unity, ν_0 is the constant corresponding to the lowest excitonic frequency.

The variation of $(\alpha h\nu)^{1/2}$ with photon energy $h\nu$ for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ films are shown in Figure 1. The value of indirect optical band gap (E_g) has been calculated by taking the intercept on the x-axis. The calculated values of E_g are given in Table 2. It is evident from the table that the value of optical band (E_g) increases from 1.24 to 1.32 with increasing Pb content in $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$. The increase in the E_g with increasing Pb may be due to increase in grain size, the reduction in the disorder, and decrease in density of defect states.

The value of E_g decreases from 1.32 to 1.25 with increasing Pb concentration in $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ sample, since the optical absorption depends on the short range order in the amorphous state and defects associated with it. The decrease in the optical band gap in the present system may be due to reduction of the amount of disorder in the system and increase in the density of defect state. It may be due to (Borgogro et al., 1982) the shift in Fermi level whose position is determined by the distribution of electrons over the localized states (Miller et al., 1988). The values of the variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ films are given in Table 3.

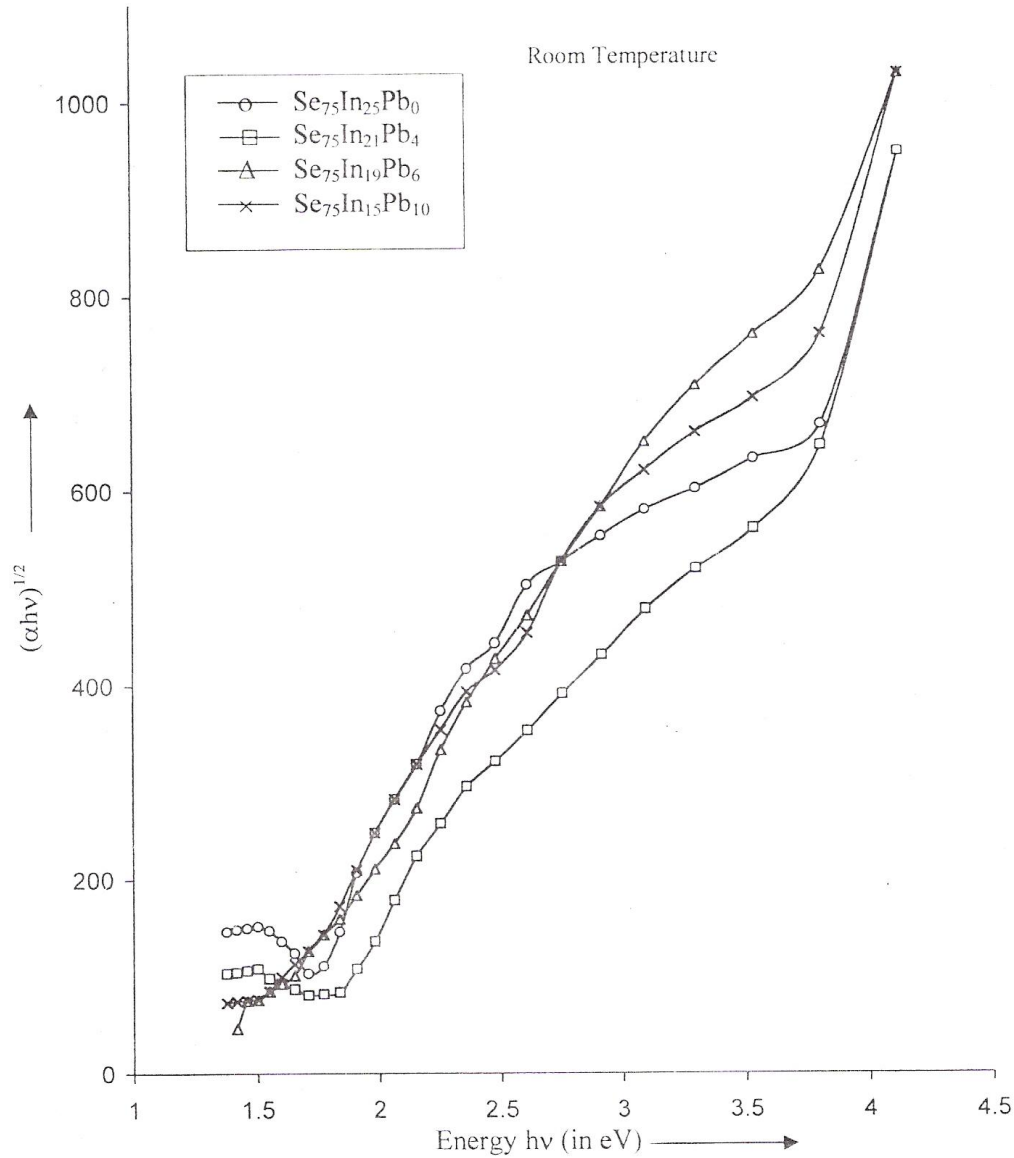


Figure 1. Variation of $(\alpha hv)^{1/2}$ with photon energy in a $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films at room temperature.

Table 2. Optical parameter in $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin film at 700 nm at RT.

X	E_g (eV)	α (cm^{-1}) (10^4)	N	k (10^{-3})	ϵ_r'	ϵ_r''	R%	T%
0	1.50	0.7	2.016	0.390	4.067	0.00157	15.63	65.625
2	1.24	0.388	2.575	0.2167	6.630	0.0011	29.16	70.625
6	1.32	1.166	5.279	0.6502	27.868	0.00686	75.62	58.33
10	1.25	1.166	2.660	0.6502	7.080	0.00346	31.25	64.166

The variation of reflectance (R) in percentage for the present system of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ is shown in Table 4. The table shows that the reflectance (R) increases with the increase in wavelength. Similarly, the transmittance (T)

has also been shown for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ in Table 3. It is evident from the table that the percentage in the transmission increases with respect to wavelength. It is clear from the table that the value of the transmission

Table 3. Variation of $(\alpha \text{ hv})^{1/2}$ with photon energy in a - $\text{se}_{75}\text{In}_{25-x}\text{Pbx}$ thin films at room temperature.

S/N	Photon energy E (eV)	Absorption coefficient (α) in Cm^4			
		$\text{Se}_{75}\text{In}_{25}\text{Pb}_0$	$\text{Se}_{75}\text{In}_{21}\text{Pb}_4$	$\text{Se}_{75}\text{In}_{19}\text{Pb}_6$	$\text{Se}_{75}\text{In}_{15}\text{Pb}_{10}$
1	1.377	146.338	103.477	N/A	73.169
2	1.441	150.581	106.477	75.290	75.290
3	1.511	147.250	98.167	85.015	85.015
4	1.588	124.172	87.803	101.386	113.353
5	1.674	111.310	82.966	143.701	143.701
6	1.770	207.351	108.906	184.659	210.896
7	1.877	283.382	179.227	237.095	283.382
8	1.998	374.392	258.032	334.867	355.180
9	2.136	443.382	322.608	427.898	416.485
10	2.294	527.629	392.666	527.629	527.629
11	2.478	580.761	478.404	649.311	620.860
12	2.693	631.849	560.250	760.395	694.142
13	2.950	948.379	948.379	1029.579	1029.579
14	3.261	N/A	N/A	N/A	N/A

N/A, Not available.

Table 4. Variation of reflection (R) in % with wavelength in a- $\text{se}_{75}\text{In}_{25-x}\text{Pbx}$ thin films at room temperature.

S/N	Wave length in nm	Reflection (R) in %			
		$\text{Se}_{75}\text{In}_{25}\text{Pb}_0$	$\text{Se}_{75}\text{In}_{21}\text{Pb}_4$	$\text{Se}_{75}\text{In}_{19}\text{Pb}_6$	$\text{Se}_{75}\text{In}_{15}\text{Pb}_{10}$
1	900	87.500	62.500	31.250	28.125
2	800	70.833	54.583	60.417	13.750
3	700	15.625	29.167	75.625	31.250
4	600	46.875	14.583	30.208	41.667
5	500	31.667	32.500	41.667	28.125
6	400	30.208	31.250	36.458	31.667
7	300	28.333	22.917	29.167	22.917

Table 5. Variation of transmission (T) in % with wave length in a $\text{se}_{75}\text{In}_{25-x}\text{Pbx}$ thin films at room temperature.

S/N	Wave length in nm	Transmission (T) in %			
		$\text{Se}_{75}\text{In}_{25}\text{Pb}_0$	$\text{Se}_{75}\text{In}_{21}\text{Pb}_4$	$\text{Se}_{75}\text{In}_{19}\text{Pb}_6$	$\text{Se}_{75}\text{In}_{15}\text{Pb}_{10}$
1	900	40.000	56.250	75.000	82.500
2	800	44.792	61.458	78.125	85.938
3	700	65.625	70.625	58.333	64.167
4	600	14.583	48.958	19.792	21.771
5	500	2.083	15.625	3.125	3.438
6	400	N/A	3.125	0.208	0.229
7	300	N/A	0.208	N/A	N/A

N/A, Not available.

starts decreasing after about 600 nm (Table 5). The refractive index (n) and extinction coefficient (k) have been calculated by using the theory of reflectivity of light for the above sample discussed. According to this theory, the reflectance of light from this film can be expressed in turn of fresnel's coefficient. The reflectivity (Scott et al.,

1982) on a interface can be given by:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)$$

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

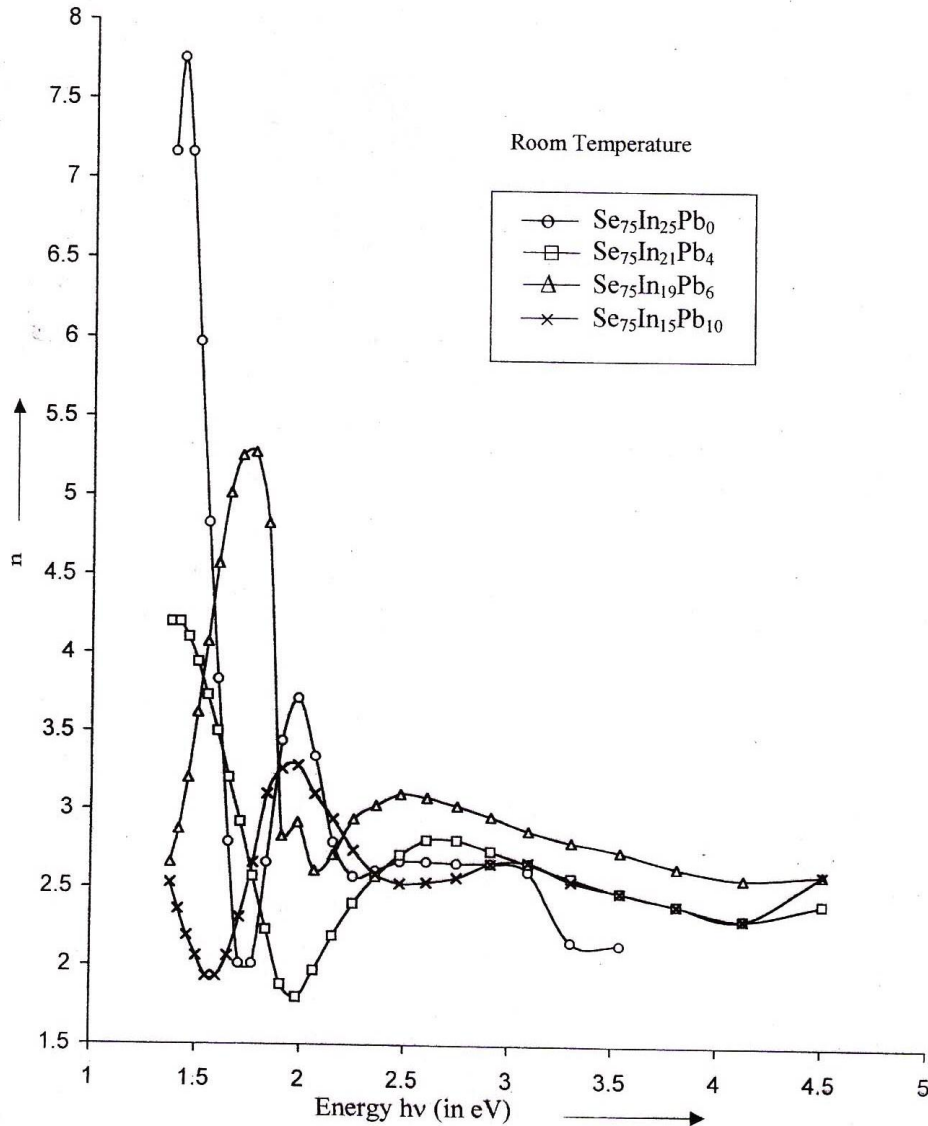


Figure 2. Variation of refractive index (n) with photon energy in a $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films at room temperature.

Where λ is the wavelength

The spectral dependence of refractive index (n) and extinction coefficient (k) for $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films are shown in Figures 2 and 3, respectively. The value of refractive index (n) and the value of extinction coefficient (k) increases with increasing photon energy conclusion.

Conclusion

In this paper we systematically studied the chemical modification of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ glass system incorporated with Pb. It was found in the optical investigations that the optical band gap increases up to

4% of Pb concentration in $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$; with further increase of Pb content, the optical band gap decreases in the present system. The increase in the optical band gap with increasing Pb content may be due to the increase in the grain size, the reduction in the disorder and decrease in the density of defect states. The value of optical band gap (E_g) decreases at higher Pb concentration. The decrease in the optical band gap in the present system may be due to reduction in the amount of disorder in the system and increase in the density of defect states. From the reflectance and transmittance studies of the film of $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$, it may be concluded that the refractive index (n) decreases, while the value of the extinction coefficient k increases with photon energy.

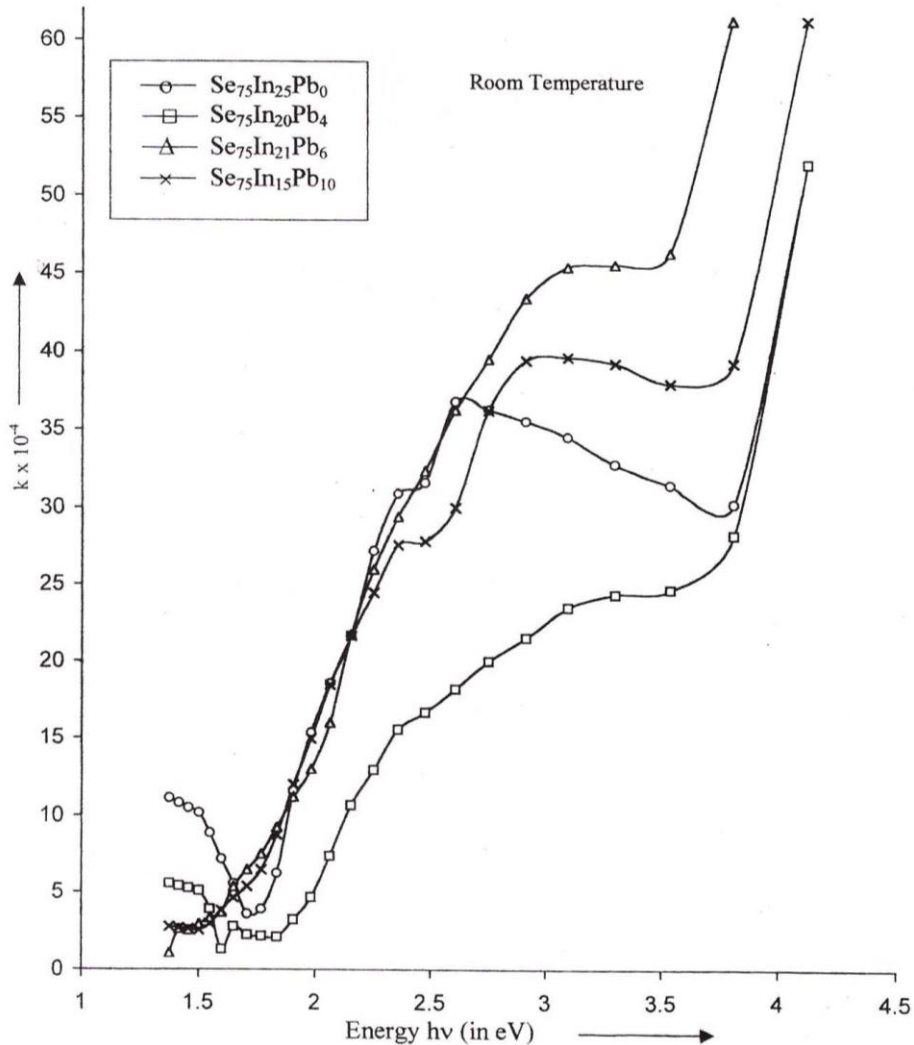


Figure 3. Variation of extinction coefficient (K) with photon energy in a $\text{Se}_{75}\text{In}_{25-x}\text{Pb}_x$ thin films at room temperature.

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