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Optical band gap and optical constants in amorphous $Se_{70}Te_{30-x}Ag_x$ thin films

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This paper reports the study of optical properties of some Ag doped Se-Te chalcogenides glasses of $Se_{70}Te_{30-x}Ag_x$ (x = 2, 6 & 8). The optical transmission spectra of maxima and minima are measured in the wavelength range 400-2000 nm. It is found that optical band gap (E_g) increases with Ag-content and refractive index (n), extinction coefficient (k), dielectric constants [real (ε′) & imaginary (ε”) both] and absorption coefficient (α) decreases with Ag-content. A correlation between optical band gap (E_g) and electronegativity (X_c) of the alloys indicates that the optical band gap (E_g) increases with the decrease of electronegativity (X_c). Data are analyzed by Swanpoel method.

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1. Introduction

Chalcogenide glasses are based on the chalcogen elements S, Se and Te. These glasses are formed by the addition of other elements such as Ge, As, Ag, Sb, Ga, etc. These glasses are low-phonon energy materials and are generally transparent from the visible upto infrared. Chalcogenide glasses can be doped by rare-earth elements, such as Er, Nd, Pr, etc. and hence numerous applications of active optical devices have been proposed. These glasses are optically highly non-linear and could therefore be useful for all-optical switching (AOS). Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation and show a variety of photo-induced effects as a result of illumination. Various models have been put forward to explain these effects, which can be used to fabricate diffractive, wave-guide and fiber structures [1-3].

Chalcogenides glasses are also used as photographic materials and have gained much importance recently. The shortcomings of pure glassy Se&Te used for photographic drums are its short lifetime and low sensitivity [4]. Certain additives are used to improve these properties. The transmission limits of Se&Te glasses are now well known [5]. Selenium glasses exhibit a transmission range from 8 to 12 μm. but tellurium glasses offer the widest infrared transmission [6].

Glassy alloys of the Se-Te system based on selenium have become materials of considerable commercial importance and are widely used for optical recording media because of their excellent laser writing sensitivity [7] but these advantages depend on material stability [8]. Se-Te alloys have created extreme interest due to their greater hardness, higher photosensitivity, higher crystallization temperature, and lower aging effects as compared to pure amorphous Se [9-10]. It has been pointed out that the addition of Se into a Te alloy improves the corrosion resistance [11]. Therefore, Se-Te based alloys are thought to be a promising media, which make use of, a phase change between an amorphous state and a crystalline state.

The addition of different elements into chalcogenide glasses in order to modify their properties was popular even from the late 60′s. Ag-containing chalcogenide glasses have attracted much interest in glass science and technology for fundamental research of their structure, properties and preparation [12-16]. They have many current applications in optics, optoelectronics, chemistry and biology such as optical elements, gratings, photo-doping, optical memories, microlences, wave-guides, holography, bio and chemical sensors, solid electrolytes, batteries etc. [17-26].

The optical band gap, refractive index and extinction coefficient are the most significant parameters in amorphous semi conducting 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. The optical properties and photo-structural changes of Ag-doped chalcogenide glasses have been studied by various workers [27-29]. Thin films of chalcogenide glasses containing Ag have also been found to have application in erasable PC optical recording [30-35], but there are only a few studies reported on crystallization kinetics in these materials [36-38].

In the present work, we have incorporated Ag 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.

2. Experimental procedure

Glassy alloys of $Se_{70}Te_{30-x}Ag_x$ (x = 2, 6 & 8) were prepared by quenching technique. The exact proportions of high purity (99.999%) Se, Te and Ag 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 (~10^{-5} Torr) quartz ampoule (length ~ 5 cm and internal diameter ~ 8 mm). The ampoule containing material was heated to 1000 ^{o}C and was held at that temperature for 12 hours. The temperature of the furnace was raised slowly at a rate of 3 - 4 ^{o}C / 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 $Se_{70}Te_{30-x}Ag_x$ 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 $Se_{70}Te_{30-x}Ag_x$ 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 (α). Fig. (1) shows the variation of transmission (T) with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films. According to Swanepoel's method [39], which is based on Mainfacer [40], 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 glassy materials by various workers [41-44].

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:

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

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 absorption coefficients (α) and the refractive index (n) which is given by:

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

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 maxima.

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

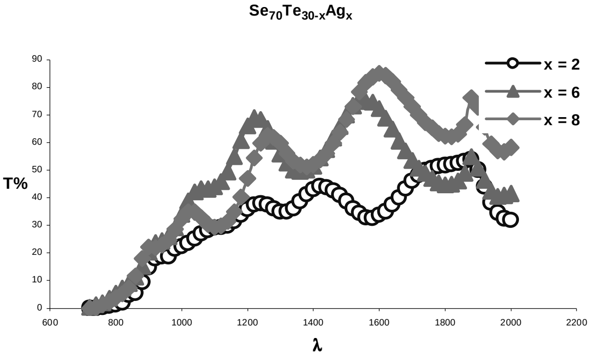

Fig. 1. Variation of transmission (T) with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films.

The extinction coefficient (k) can be calculated from the relation,

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

where x is the absorbance.

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

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

Where

$$E_m = [8n^2s/T_m] - (n^2-1)\ (n^2-s^2) \tag{5}$$

The spectral distribution of refractive index (n) and extinction coefficient (k) for $Se_{70}Te_{30-x}Ag_x$ is given in Figs. 2 and 3 respectively. The values of refractive index (n) and extinction coefficient (k) at a particular wavelength is given in Table 1 which shows that both these parameters decreases with Ag-content.

Fig. 2. Variation of refractive index (n) with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films.

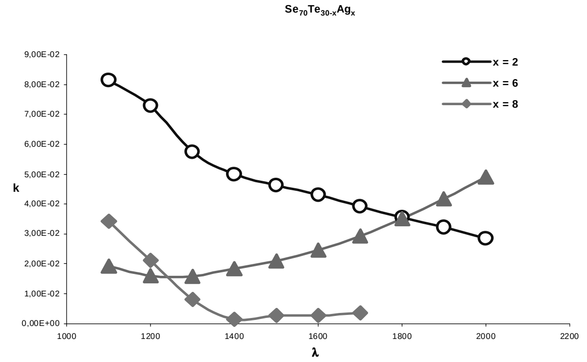

Fig. 3. Variation of extinction coefficient (k) with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films.

The real (ε') and imaginary (ε") parts of the dielectric constant of $Se_{70}Te_{30-x}Ag_x$ films have also been calculated by using the relation:

$$\varepsilon' = n^2 - k^2 \quad (6)$$

$$\varepsilon'' = 2\,n\,k \quad (7)$$

The variation of these parameters with wavelength (λ) is shown in Figs. 4 and 5 respectively. The values of real (ε') and imaginary (ε") parts of the dielectric constant at a particular wavelength is given in Table 1 which shows that both these parameters decreases with Ag-content.

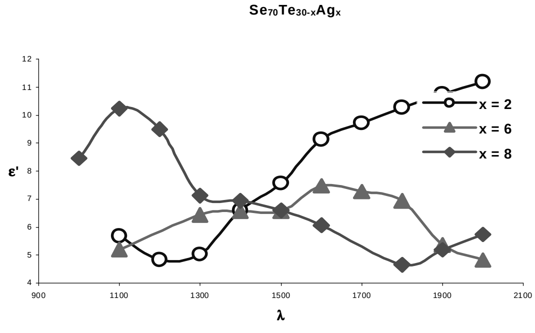

Fig. 4. Variation of real dielectric constant (ε') with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films.

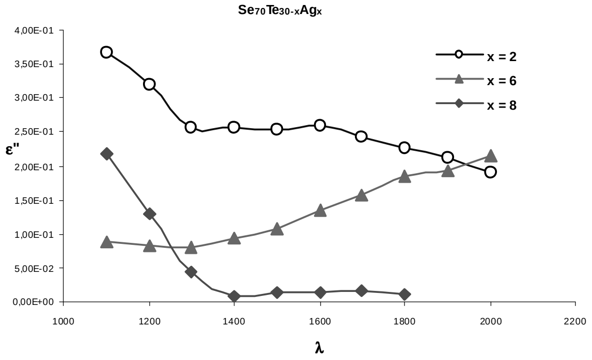

Fig. 5. Variation of imaginary dielectric constant (ε") with wavelength (λ) in $Se_{70}Te_{30-x}Ag_x$ thin films.

Table 1. Optical parameters in amorphous thin films of $Se_{70}Te_{30-x}Ag_x$.

No.	x at %	Optical band gap E_g (eV)	Absorption Coefficient (α) at 1600 nm. in (m^{-1})	Refractive index (n)	Extinction coefficient (k)	Real dielectric constant (ε')	Imaginary dielectric constant (ε")	Electro negativity (X_c)
1.	2	0.52	33.83	3.02	4.31×10^{-2}	9.12	26.04×10^{-2}	2.38
2.	4	0.61	19.24	2.73	2.45×10^{-2}	6.56	13.39×10^{-2}	2.37
3.	6	0.82	02.10	2.46	0.27×10^{-2}	6.07	1.33×10^{-2}	2.36

3.2 Absorption coefficient and optical band gap

The absorption coefficient (α) of $Se_{70}Te_{30-x}Ag_x$ films can be calculated using the well-known relation

$$\alpha = 4\pi k/\lambda \quad (8)$$

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

Table 2. Values of electronegativity (X_c) of different elements reported in reference [50].

No.	Elements	Electronegativity (X_c)
1.	Se	2.5
2.	Te	2.1
3.	Ag	1.9

The present system of $Se_{70}Te_{30-x}Ag_x$ obeys the role of non-direct transition and the relation between the optical band gap, absorption coefficient and energy (hν) of the incident photon is given by [45-47]:

$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g) \quad (9)$$

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

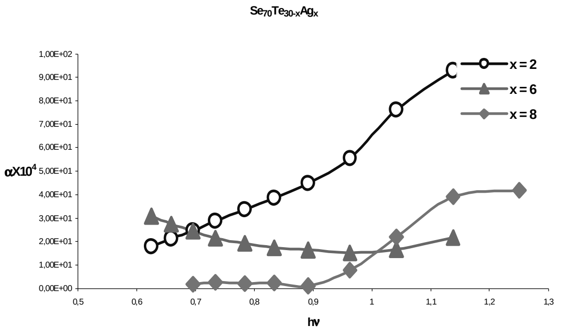

Fig. 6. Variation of absorption coefficient (α) with energy ($h\nu$) in $Se_{70}Te_{30-x}Ag_x$ thin films.

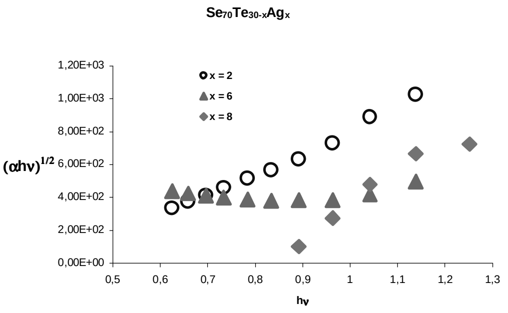

Fig. 7. Variation of $(\alpha h\nu)^{1/2}$ with energy ($h\nu$) in $Se_{70}Te_{30-x}Ag_x$ thin films.

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for $Se_{70}Te_{30-x}Ag_x$ films are shown in Fig. 7. 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) increases with Ag-content. The Ag additives in $Se_{70}Te_{30-x}$ 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 Ag concentration. The increase in band gap (E_g) may be understood as follows:

Pauling [48] defines the electronegativity of an atom as the power to attract electron to itself in a molecule. When the two atoms, which differ in their electronegativity value, combines to form an alloy, then the element of higher electronegativity attracts an electron pair more towards itself and behaves as anion whereas the other element behaves as a cation. Using Sanderson's principle [49] of equalization of electronegativity, electronegativity (X_c) between Se–Te and Se–Te–Ag alloys has been calculated using Husain et al. [50] values for different elements. The calculated values are given in Table 1. When the electronegativity difference is large, it is expected that the probability of defect formation will be more. The correlation of the electron affinity with the optical band gap [51] was considered by various workers. According to Mulliken [52], the electronegativity is the average of the ionization potential and the electron affinity. It is difficult to assign an electron affinity value for any semiconducting alloy, e.g. $Se_{70}Te_{30-x}Ag_x$ systems. Thus, it will be appropriate to correlate the electronegativity with optical band gap. In the present system, we observed that the optical band gap increases with decreasing electronegativity of a sample (see Table 1).

It is interesting to remark that in tha case of $Se_{85}Te_{15-x}Pb_x$ films prepared and studied by us [53] the energy gap decreases with the increase of Pb-content and this opposite effect can be understand by an increase of the electronegativity in the films.

4. Conclusion

Various parameters related to optical properties were calculated for various samples of $Se_{70}Te_{30-x}Ag_x$. The optical absorption in the Se-Te-Ag system seems to be due to non-direct transition. Energy gap (E_g) increases with increasing Ag-content. Absorption coefficient (α) decreases and is of the order 10^4 m^{-1} in all the alloys. Refractive index (n) and extinction coefficient (k) decreases with Ag-content. A correlation between optical band gap (E_g) and electronegativity (X_c) of the alloys indicates that the optical band gap (E_g) increases with the decrease of electronegativity (X_c).

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