

Proton-induced changes on the optical parameters of a-(Ge₂₀Se₈₀)_{0.96}Ag_{0.04} thin films

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Nonoxide, chalcogenide glasses are of interest for application in infrared technology, including the fabrication of optical elements such as mirrors and filters. The low characteristic vibrational frequencies of chalcogenide bonds allow them to transmit far out into the infrared [1]. These glasses show a variety of photostimulated phenomena when exposed to light or other radiations [2, 3]. When these glasses are irradiated with high energy particles or light, bond breaking and bond rearrangement can take place, which results in the change in local structure of the glassy materials. These include subtle effects such as shifts in the absorption edge (photobleaching and photodarkening), and more substantial atomic and molecular reconfiguration such as photoinduced refractive index changes and photodoping effects [4]. In general, these phenomena are associated with the changes in the optical constants [5] and absorption edge shift [6], allowing the use of these materials in the fabrication of a large number of optical devices. This clearly underlines the importance of these glassy materials by accurate determination of their optical constants, refractive index, and extinction coefficient, as well as the corresponding optical band gap.

Chalcogenide glasses like Ge–Se are known to be very good covalently bonded glass formers. The dominant feature of the network is fourfold coordinated Ge. The structure of these glasses is a function of composition [7]. A discontinuity in various physical properties of these glasses has been observed at a composition when the average coordination number $\langle r \rangle = 2.4$. The coordination number of Ge is 4 and Se is 2, so at $x = 20$, the value of $\langle r \rangle = 2.4$ in a-Ge_xSe_{100-x} system. In the Se-rich zone, the structure consists of Se chains linked by Ge atoms tetrahedrally coordinated by Se atoms, i.e., the structure consists of chains of corner-shared GeSe_{4/2}. As the Ge concentration increases the corner-shared tetrahedrons give place to edge-shared ones [7]. It has been reported that at a concentration about 20 at.% of Ge, a new noncrystalline compound GeSe₄ exists in the Ge–Se system [8]. It has also been reported that the addition of Ag has dual chem-

ical role as an additive in Ge–Se chalcogenide glasses [9, 10]. In Se-rich compositions ($x < 1/3$), Ag acts as a network modifier and phase separates into an Ag₂Se-rich glass, leaving the Ge₇Se_{1-t} backbone Se-deficient ($t > x$), while in Ge-rich compositions ($x \geq 2/5$), Ag becomes a network former. As a network modifier, a bimodal glass transition temperature (T_g) is reported and attributed to a phase separation of Ag-centered structures (resembling α -Ag₂Se) from the host matrix [9, 10].

Therefore, we have decided to study the optical properties of such a technically important material, i.e., a-(Ge₂₀Se₈₀)_{0.96}Ag_{0.04} thin films before and after the proton irradiation. In this paper, a relative simple method [11, 12] for determining the optical constants has been used. Optical transmission spectra have been taken in the wavelength range 400–2000 nm. The optical parameters like refractive index (n), absorption coefficient (α), oscillator strength (E_d), oscillator energy (E_0), and optical gap (E_g) have been calculated. The effect of proton irradiation has been studied on these optical parameters. It has been observed that these parameters change after the proton irradiations.

Glassy alloy of a-(Ge₂₀Se₈₀)_{0.96}Ag_{0.04} is prepared by quenching technique as described elsewhere [13]. Thin films of the alloy are prepared by vacuum evaporation technique on well-degassed Corning 7059 glass substrates at room temperature and base pressure of $\sim 2 \times 10^{-5}$ mbar using a molybdenum boat. Amorphous nature of the sample has been checked by X-ray diffraction technique. No prominent peak has been observed in the thin film.

The samples are irradiated at room temperature in vacuum ($\sim 10^{-6}$ Torr), using 1×10^{15} ions/cm² at 3 MeV proton energy from Chandigarh Cyclotron. The beam was focused using a circular collimator so that an area of ~ 0.75 cm² on the films received a uniform ion dose. The normal incidence transmission spectra of the substrate with and without a-(Ge₂₀Se₈₀)_{0.96}Ag_{0.04} thin film have been measured by a double-beam UV/VIS/NIR computer-controlled spectrometer [Hitachi-330], in the transmission

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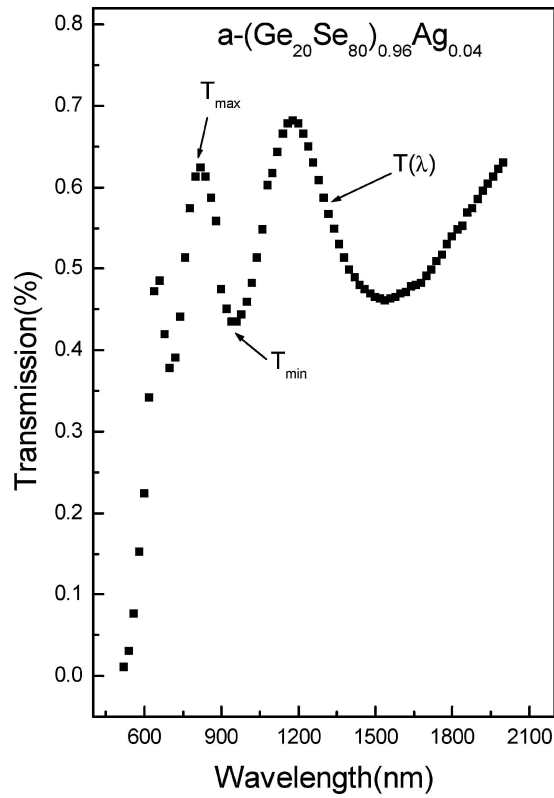


Figure 1 Optical transmission spectrum, $T(\lambda)$ for $a-(\text{Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$ thin film before irradiation.

range 400–2000 nm. The spectrometer was set with a suitable slit width of 1 nm, in the spectral range. All optical measurements have been performed at room temperature (300 K).

The model behind Swanepoel's method [11, 12] assumes that the sample is a thin film of nonuniform thickness deposited on a transparent substrate having a refractive index 's'. The system is surrounded by air, whose refractive index is $n_0 = 1$. The film has a complex refractive index $n^* = n - ik$, where n is the refractive index and k the extinction coefficient. The refractive index in the region where the absorption coefficient, α is ≈ 0 is calculated by the equation [11]

$$n = \sqrt{N + \sqrt{N^2 - S^2}} \quad (1)$$

where

$$N = 2s \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}} + \frac{s^2 + 1}{2} \quad (2)$$

T_{\max} and T_{\min} are the envelope values at the wavelengths at which the upper and lower envelopes and the experimental transmission spectrum are tangent, respectively, as shown in Fig. 1. The accuracy to which λ can be measured is ± 1 nm. Fig. 1 shows the normal incidence optical transmission spectra of $a-(\text{Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$ thin film before proton irradiation. Similar type of transmission spectra

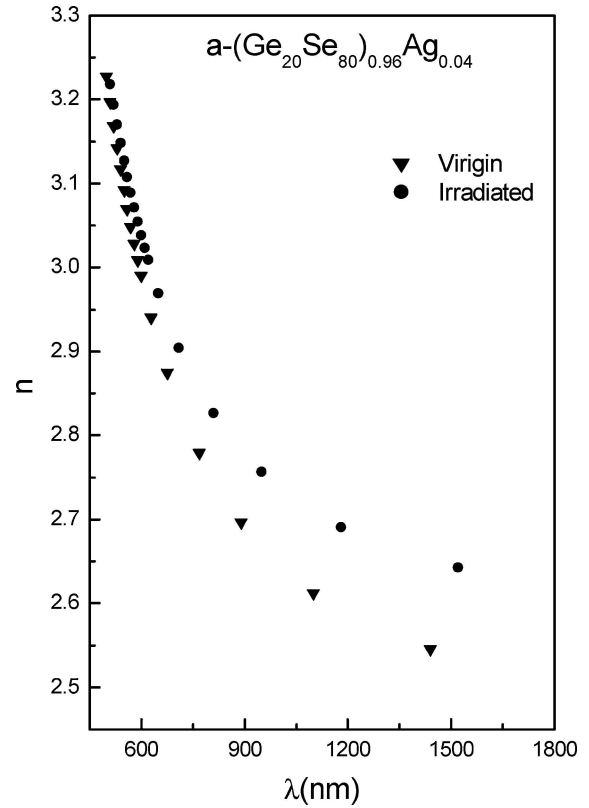


Figure 2 Variation of n with wavelength (λ) in virgin and irradiated states.

has been observed for the proton-irradiated sample also (figure not shown here). The envelopes of the transmission spectrum, T_{\max} and T_{\min} have been observed from this figure.

The values of 'n' are calculated using Equation 1 at wavelengths corresponding to the tangent points. If n_1 and n_2 are the refractive indices at two adjacent tangent points at λ_1 and λ_2 , then according to the basic equation for interference fringes:

$$2nt = m\lambda \quad (3)$$

where 'm' is an order number. The thickness (t) is given by

$$t = \frac{\lambda_1 \lambda_2}{4(\lambda_1 n_2 - \lambda_2 n_1)} \quad (4)$$

Using Equation 3, new more precise values of the refractive index and the film thickness were determined by a procedure which was explained in detail in [11, 12]. The calculated values of refractive index at different wavelengths have been plotted in Fig. 2. The data on the dispersion of the refractive index, $n(\lambda)$ have been calculated using the single-effective-oscillator model proposed by Wemple and DiDomenico [14, 15]. They found that all the data can be described to an excellent approximation

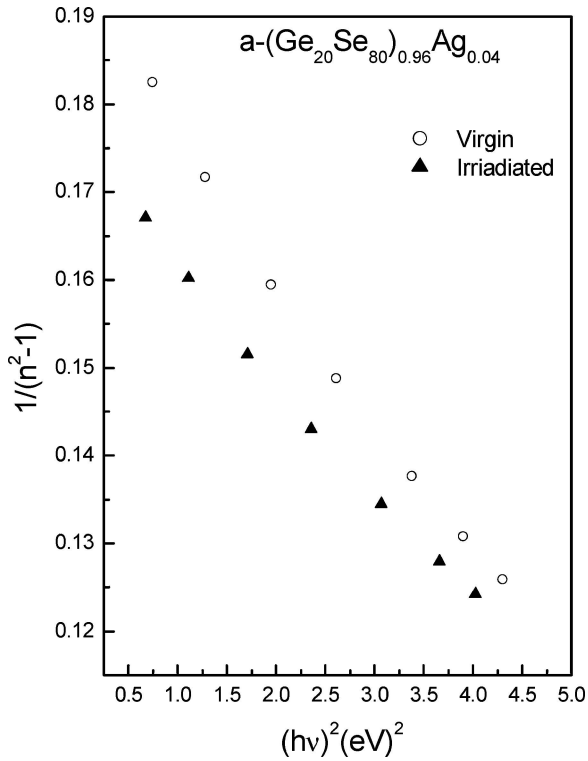


Figure 3 Plot between $1/(n^2-1)$ and $(hv)^2$ in virgin and irradiated states.

by the following relation:

$$n^2(\hbar\omega) = 1 + \frac{E_d E_0}{E_0^2 - (\hbar\omega)^2} \quad (5)$$

where $\hbar\omega$ is the photon energy. Plotting $(n^2-1)^{-1}$ vs. $(\hbar\omega)^2$ allows us to determine the oscillator parameters, by fitting a linear function to the smaller energy parameters. Fig. 3 shows the plot of $(n^2-1)^{-1}$ vs. $(hv)^2$, which is a straight line. E_d and E_0 can be directly determined from the slope, $(E_d E_0)^{-1}$ and the intercept, E_0/E_d , on the vertical axis. The values of E_0 , E_d , and the static refractive index, $n(0)$ (i.e., extrapolated to $\hbar\omega \rightarrow 0$) for this alloy thin film is similar to that of the other Se-rich alloys reported in the literature [5, 6]. After the proton irradiation, the values of $n(0)$ and E_d increase from $(2.531 \pm 0.004) - (2.629 \pm 0.004)$ and $(18.9 \pm 0.01) - (20.8 \pm 0.01)$ eV, respectively. The value of E_0 decreases from (3.72 ± 0.01) to (3.65 ± 0.01) eV.

The absorption coefficient (α) [16] can be calculated from the relation

$$x = \exp(-\alpha t) \quad (6)$$

where x is the absorbance as described elsewhere [11, 12]. The absorption coefficient of amorphous semiconductors in the strong-absorption region ($\alpha \geq 10^4 \text{ cm}^{-1}$), assuming parabolic valence- and conduction band edges, is given by [16]

$$\alpha(\hbar\omega) = B(\hbar\omega - E_g^{\text{opt}})^2 / (\hbar\omega) \quad (7)$$

where E_g^{opt} is the energy distance between the valence and conduction band mobility edges. The parameter B given by the slope of the plots is an interesting parameter, since it can be taken as a measure of the disorder.

Finally, the optical gap (E_g^{opt}) is calculated from the intersection of the plot $(\alpha\hbar\omega)^{1/2}$ vs. $\hbar\omega$ with the abscissa axis (result not shown here). The values of E_g^{opt} and $B^{1/2}$ decrease from (1.85 ± 0.01) to (1.81 ± 0.01) eV and $784-762 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$, respectively.

Amorphous $\text{Ge}_{20}\text{Se}_{80}$ alloy has the structure of Se-Se bridges linked with $\text{GeSe}_{4/2}$ edge-sharing units [8]. In Ge-Se-Ag system, interstitial voids are chemically ordered around the cation-centered structural units [$\text{Ge}(\text{Se})_4$ tetrahedral]. Extrinsic atoms (Ag) are assumed to occupy these interstitial voids, thereby reducing the disorder in the system [17]. Dwivedi *et al.* [18] have made the Raman measurements on 1 MeV Kr^{++} ion irradiated $\text{a-Ge}_{21.5}\text{Se}_{78.5}$ thin films. They have observed the band positions at 201 cm^{-1} [$\text{Ge}(\text{Se})_{4/2}$ corner-sharing tetrahedral], 215 cm^{-1} [vibrations of Se atoms in the four-member rings composed of two edge-sharing tetrahedral], and a band near 263 cm^{-1} [Se-Se bonds in Se chains]. Upon Kr^{++} irradiation, the intensity of the vibrational mode at 263 cm^{-1} related to Se-Se bonds in chains increases. Also, upon comparing the relative areas of the spectra, they found that upon irradiation, the relative area of band at 201 cm^{-1} is unchanged which indicates that the irradiation does not affect the number of $\text{Ge}(\text{Se})_{4/2}$. They have also shown that irradiation converts Se-Se bridges linked with [8] edge sharing $\text{Ge}(\text{Se})_{4/2}$ units to Se-Se linear chains. The full width half maximum (FWHM) of the band at 201 cm^{-1} decreases after irradiation. The observed decreases in the width of this peak upon irradiation may mean a decrease in disorder. This decrease also indicates that irradiation increases ordering in the local structures [18].

Using the same arguments, we can explain the observed increase in the refractive index (n) and the oscillator strength (E_d). Upon irradiation in $\text{a-(Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$ thin films with proton (3 MeV), Se-Se bridges linked with edge-sharing $\text{GeSe}_{4/2}$ units, are converted into Se-Se linear chains. Ag may form the heteropolar bonds with these Se-Se chains. Upon irradiation, this material may phase separate into an Ag_2Se -rich glass and decreasing the disorder in the material as suggested by Mitkova *et al.* [9]. In Se-rich compositions, Ag acts as a network modifier and phase separates into an Ag_2Se -rich glass. They have made the Raman measurements on Se-rich $(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y$ glassy system. Their Raman results suggest that Ag, present at triangular interstitial sites with coordination number (CN) = 3 in $\alpha\text{-Ag}_2\text{Se}$, may be a good representation of the glass structure. Such a network will possess $n_c = 3.33$ and from equation $n_c = (5/2)r_m - 3$, yield $r_m = 2.53$. Here the symbols n_c and r_m are known as mean constraints per atom and mechanical effective connectivity of the network. This value of r_m reside close to the critical connectivity (r_c) = 2.40 to optimize

the glass forming tendency within the constrain counting theory [19]. The decrease in the value of $B^{1/2}$ from 784 to $762 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$ also indicates that a decrease in the disorder of $a\text{-(Ge}_{20}\text{Se}_{100-x})_{100-x}\text{Ag}_{0.04}$ glassy system takes place after the proton irradiation. The decrease of E_g^{opt} from (1.85 ± 0.01) to $(1.81 \pm 0.01) \text{ eV}$ is explained by the fact that the binding energy of the Ag–Se bond ($202.5 \text{ kJ mol}^{-1}$) is smaller than that of the Ge–Se bonds (484 kJ mol^{-1}). Therefore, there is a smaller energy splitting taking place between the states of the valence and the conduction bands.

From the above discussions one can conclude that upon irradiation with 3 MeV protons in $a\text{-(Ge}_{20}\text{Se}_{80})_{0.96}\text{Ag}_{0.04}$, the values of n , E_d increase and E_0 decreases. The values of E_g^{opt} and $B^{1/2}$ also decrease after irradiation. The dispersion of the refractive index is explained in terms of the single oscillator model. The results have been explained in terms of the structural changes upon proton irradiation.

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