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# THICKNESS DEPENDANT OPTICAL STUDY OF $Te_9Se_{72}Ge_{19-x}Sb_x$ ($8 \leq x \leq 12$) CHALCOGENIDE GLASSY THIN FILMS

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Antimony substituted quaternary chalcogenide glassy thin films have been synthesized by thermal vacuum evaporation technique. Glassy films possess the optical band gap ranging from 2.10 eV to 1.68 eV and high value of refractive index in between 2.52 to 2.90. The optical parameters such as refractive index (n), extinction coefficient (k), dielectric constant ($\mathcal{E}$') and optical band gap($E_g^{opt}$) have thickness dependency. Antimony has its own role in determining the optical constants but thickness is the dominating factor in reported work. Optical constants have the optimal values of optical constants which offer material applicability in photonic applications where high refractive index greater than 2.5 and tuneable optical band gap are of significant interest.

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*Keywords:* Optical Gap; Refractive Index; Chalcogenide Glass; Amorphous Materials

## 1. Introduction

The unique functionalities and properties of chalcogenides comprise the source material for photonic applications. Usually these glasses are transparent from visible to near IR region and can be moulded into lenses and fibers which play their own unique role in infrared optical fiber applications, televisions (vidicon camera tubes) and as a photo receptor in xerography [1-3].The high optical transparency of these glasses in mid and near IR region can be used for making optical fibers for remote sensing of the outer space, for bio sensing and under water pollutant detection [4-8]. Chalcogenide glasses have high third order optical nonlinearities with low losses and hence have been proposed for ultra fast optical switching in telecommunication systems [9-12]. These materials, based on their reversible switching properties between the amorphous and crystalline states have been used for optical rewritable data storage media [13-14].

A typical chalcogenide glass has relatively a sharp optical absorption edge and efficient photoexcited conductivity and luminescence, which are the characteristics of a clean band gap. But the doping experiments suggest that the Fermi level of chalcogenides is nearly pinned so the luminescence should occur at sub band gap energies [15]. Chalcogenide glasses exhibit a variety of photoinduced effects such as photodarkening and photoinduced anisotropy when exposed to radiation having energy comparable to the band gap [16-19]. Photoconductivity studies yield information about the defects and metastable structural states in amorphous solids. The lone pair electrons and valence alteration pairs play an important role in tuning the optical band gap and hence the properties of chalcogenide glassy alloy [20].

The allowed freedom in the preparation of glasses in different compositions induces changes in their short range order and thus makes it possible to tailor their optical and electrical properties as desired for technological applications. Se exhibits a unique property of reversible transformation .This property makes it very useful in optical memory devices. On addition of Ge to Se, it strengthens the average bond by cross-linking the Se chain structure, thereby increasing the glass transition temperature, resistivity and optical band gap, but on the other hand increases

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the intrinsic optical losses. This problem can be compensated with the addition of Sb in the glassy matrix. Red shift in absorption is observed with Sb addition in the Se-Ge glassy system, which improves the properties and reduces the optical losses.

## 2. Experimental Details

The bulk chalcogenide alloys, $Te_9Se_{72}Ge_{19-x}Sb_x$(x = 8, 9, 10, 11, 12) are prepared using 5N purity materials in appropriate amount according to their atomic weight percentage by the conventional melt quenching technique. The amorphous nature of bulk material has been confirmed using X-ray diffraction and SEM. The resultant glass products have good optical quality and meet the most optical needs. Thin films of the bulk materials have been deposited on cleaned microscopic glass substrates of refractive index (1.5) using vacuum thermal evaporation technique. The deposition of these thin films is carried out in the vacuum evaporation coating system (HINDHIVAC model 12A4D India). Two sets of thin films have been prepared to see the thickness dependent variation of optical constants. The vitreous nature of the films is confirmed through X-ray-diffraction as there is no prominent peak present in the patterns shown in Figure 1. The normal incidence optical-transmission and absorption spectra (not shown here) for these thin films have been recorded in 200–3300 nm spectral region, by a double-beam UV/Vis/NIR spectrophotometer (Perkin-Elmer, model Lambda-750). All optical measurements are carried out at room temperature.

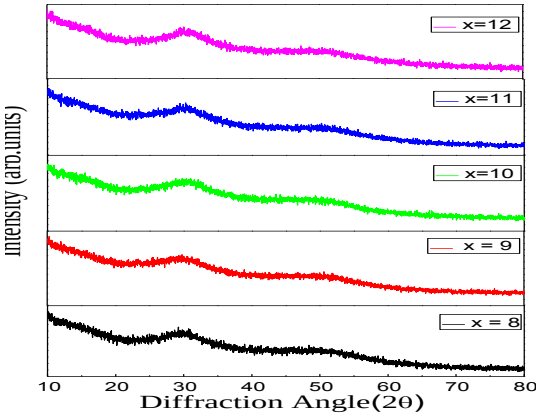


*Fig. 1 X-ray diffraction pattern of $Te_9Se_{72}Ge_{19-x}Sb_x$ ($8 \leq x \leq 12$) glassy thin films*

## 3. Results

### 3.1 Optical and Dielectric Parameters

The optical behaviour of material is generally described in terms of two basic parameters, optical band gap ($E_g^{opt}$) and refractive index ($n$). The refractive index of the material changes under the influence of light. The refractive index of the material is calculated by envelope method proposed by Swanepoel [21-22]. According to this method the value of the refractive index of film in the spectral region of medium and weak absorption is given by the expression

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

where

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \tag{2}$$

where $T_M$ and $T_m$ are the maximum and the corresponding minimum transmission at a certain wavelength ( λ) and s is the refractive index of the substrate on which thin films are deposited. In order to consider the effect of thickness on optical properties, two sets of thin films have been deposited on glass substrate and their transmission spectra are recorded and compared which are shown in Figure 2(a) and 2(b).

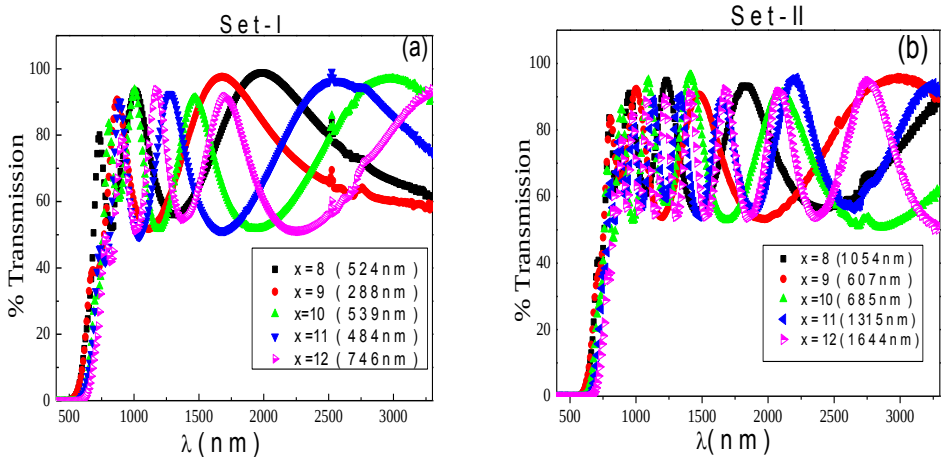


*Fig. 2 Transmission spectrum of $Te_9Se_{72}Ge_{19-x}Sb_x$ glass thin films of two sets (a) Set-I (b) Set-II*

Optical reflection (R) and transmission (T) are very complex functions and are found to be strongly dependent on the absorption coefficient ($\alpha$) evaluated from the relation

$$\alpha = \frac{1}{d} ln(\frac{1-R}{T}) \quad (3)$$

The extinction coefficient (*k*) has a dependence on the absorption coefficient and has been related as

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

where d is the thickness of the film and can be calculated by using the following relation

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_2 n_1 - \lambda_1 n_2)} \quad (5)$$

Here $\lambda_1$, $\lambda_2$ are the wavelengths of two consecutive maxima or minima and $n_1$, $n_2$ are their corresponding refractive indices. The optical energy band gap of the material has a strong dependence on the optical absorption spectrum. The absorption coefficient of chalcogenide glass changes rapidly for photon energies close to their band gap. According to Tauc, the optical absorption edge for many glassy and amorphous non-metallic materials can be divided into three regions [23]

(a) The absorption coefficient of an amorphous semiconductor in the high absorption region ($\alpha \geq 10^4$ cm$^{-1}$) can be calculated by using relation

$$\alpha h\nu = B(h\nu - E_g^{opt})^m \quad (6)$$

where B is the slope of Tauc edge called band tailing parameter that depends on the width of localized states in the band gap. In the above equation the value of m = 1/2 for a direct allowed transition, m = 3/2 for a direct forbidden transition, m = 2 for an indirect allowed transition and m = 3 for an indirect forbidden transition and $(E_g^{opt})$ is the optical band gap. The optical band gap of most of the chalcogenide glasses lie in the range 0.7 eV to 3.0 eV.

(b) The absorption coefficient for intermediate absorption ($10^1$ cm$^{-1}$ < $\alpha$ < $10^4$ cm$^{-1}$) follows the Urbach's [ 24] exponential relation given as

$$\alpha = \alpha_o \exp(h\nu/E_d) \quad (7)$$

where $\alpha_o$ is constant ,ν is the frequency of the radiation, h is Planck's constant and $E_d$ is defined as Urbach energy which is energy measured in terms of the width of the tail of localized states in the gap region.

(c) In weak absorption region ($\alpha \leq 10$ cm$^{-1}$), the shape and strength of absorption edge is found to depend on the preparation, purity, and perfection of material as well as thermal history of the material.

The values of absorption coefficient, optical band gap for thin films can be calculated from the Tauc relation given in equation (6) by plotting the graphs between $(\alpha h\nu)^{1/2}$ and $h\nu$ . Figures 3(a) and 3(b) show the plots of $(\alpha h\nu)^{1/2}$ versus hν and the variation of the extinction coefficient (k) with wavelength (λ) (inset) for thin films of Set-I and Set-II respectively.

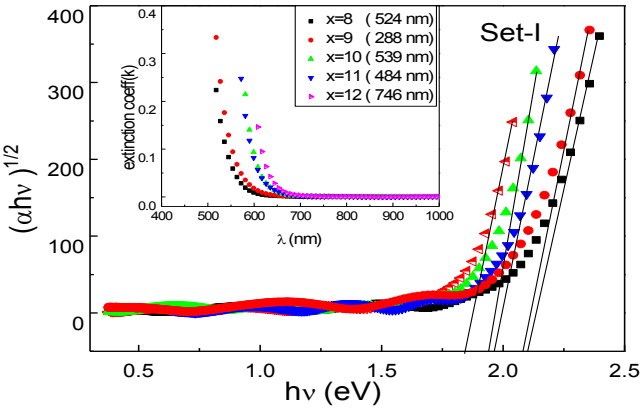


*Fig. 3(a) Plots of $(\alpha h\nu)^{1/2}$ versus hν and variation of extinction coefficient with wavelength (inset) for thin films (Set-I) for $Te_9Se_{72}Ge_{19-x}Sb_x$(x = 8, 9, 10, 11, 12)*

Optical constants like optical band gap, refractive index and extinction coefficient for thin films of different thickness of Set-I and Set-II are compared. The values of the optical energy gap $(E_g^{opt})$ have been obtained by extrapolating the curves of $(\alpha h\nu)^{1/2}$ versus hν for indirect allowed transition in thin films of $Te_9Se_{72}Ge_{19-x}Sb_x$ ($8 \leq x \leq 12$) by making $\alpha h\nu^{0.5} \rightarrow 0$ and are given in Table 1.

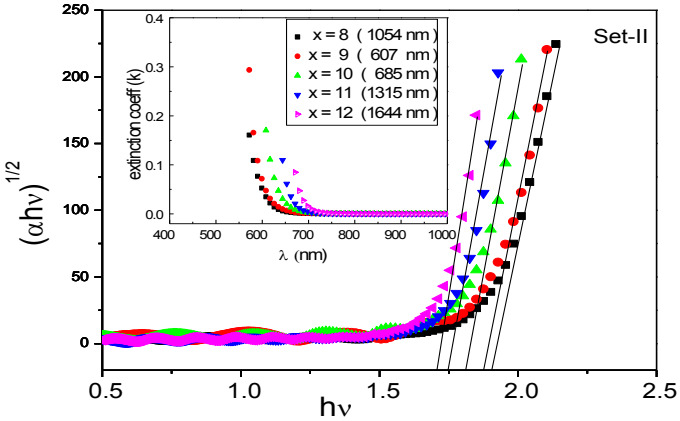


*Fig. 3(b) Plots of $(\alpha h\nu)^{1/2}$ versus hν and variation of extinction coefficient with wavelength (inset) for thin films (Set-II) for $Te_9Se_{72}Ge_{19-x}Sb_x$(x = 8, 9, 10, 11, 12)*

*Table 1 Values of thin film thickness (d), refractive index (n), extinction coefficient (k), optical energy gap $\left(E_g^{opt}\right)$ and real part ($\mathcal{E}_r$), imaginary part ($\mathcal{E}_i$) of dielectric constant for $Te_9Se_{72}Ge_{19-x}Sb_x$(x = 8, 9, 10, 11, 12) for two sets of thin films of different thickness.*

| Sample | Set –I | | | | | | Set-II | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | d (nm) | n | k | $E_g^{opt}$ (eV) | $\mathcal{E}_r$ | $\mathcal{E}_i$ | d (nm) | n | k | $E_g^{opt}$ (eV) | $\mathcal{E}_r$ | $\mathcal{E}_i$ |
| 8 | 524 | 2.66 | 0.0133 | 2.10 | 7.0754 | 0.0353 | 1054 | 2.52 | 0.0029 | 1.87 | 6.3504 | 0.0073 |
| 9 | 288 | 2.70 | 0.0185 | 2.08 | 7.2896 | 0.0501 | 607 | 2.75 | 0.0027 | 1.84 | 7.5625 | 0.0074 |
| 10 | 539 | 2.85 | 0.0198 | 1.94 | 8.1225 | 0.0566 | 685 | 2.74 | 0.0028 | 1.78 | 7.5076 | 0.0076 |
| 11 | 484 | 2.90 | 0.0201 | 1.96 | 8.3899 | 0.0581 | 1315 | 2.56 | 0.0020 | 1.72 | 6.5536 | 0.0052 |
| 12 | 746 | 2.79 | 0.0086 | 1.85 | 7.7840 | 0.0240 | 1644 | 2.74 | 0.0018 | 1.68 | 7.5076 | 0.0048 |

The polarization does not respond instantly to an applied field, there is some delay in response due to dielectric constant that results in dielectric loss expressed as permittivity (ε), which is complex and frequency dependent and is expressed as $\varepsilon = \varepsilon_r + i\varepsilon_i$, where($\varepsilon_r$) and ($\varepsilon_i$) are real and imaginary parts of permittivity, respectively. Here real part ($\varepsilon_r$) is dielectric constant and imaginary part ($\varepsilon_i$) is dielectric loss. The complex dielectric constant is a fundamental intrinsic property of the material. The real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant of thin films can also be calculated using the value of *n* and k *as* given [25] in the following equations

$$\varepsilon_r = n^2 - k^2 \tag{8}$$

$$\varepsilon_i = 2nk \tag{9}$$

## 4. Discussions

The observation of dielectric effects in the glasses implies that dipoles exist. Dielectric constant for a polar material is due to the contribution of electronic, ionic, orientational and space charge polarization. The total polarization of the material is the sum of all type of polarizations. The dielectric constant is the measure of the material's ability to respond to the external electrical field when subjected to it. On careful observation of two sets of thin films, we see that with the increase in thickness, there is a fall in the values of refractive index, optical band gap and dielectric constant. With the rise in thickness of thin films, there is increase in number of film layers where dangling bonds may satisfy themselves. This decreases the degree of polarization and hence the refractive index as $n \propto \sqrt{\varepsilon_r}$ . However, with rise in thickness there might be increase in degree of disorder and short range order (SRO) may tend towards medium range order (MRO) resulting in band tailing with consequent decrease in optical band gap. However compositional effect is difficult to observe as thickness effect is significant. The addition of Sb also affects the bonding structure of glassy matrix and affects the density of defect states contributing to variation of optical parameters. As Sb replaces Ge, defect states increases and it contributes to the reduction of the optical gap. Here the increase in the values of optical parameters such as refractive index (n) and extinction coefficient (k) may also be due to increasing Sb content. This can also be explained on the basis of polarizability. Due to the large atomic radius of the Sb (140 pm) as compared to Ge (122 pm), larger will be the atomic polarizability. Optical parameters have the direct dependence on material polarizability. Thus more polarisable Sb atoms in bonding glass matrix may also affect or increase the refractive index or optical constant of the material

## 5. Conclusion

a-$Te_9Se_{72}Ge_{19-x}Sb_x$ ($8 \leq x \leq 12$) glassy thin films have been prepared on glass substrate. Thickness based study has been made to see the effect of thickness on various optical properties. Dielectric constant depends upon the polarizability in the material which decreases with increase in thickness, hence the refractive index and extinction coefficient also. Thicker films have increased degree of disorder which causes band tailing and hence results decrease in the optical band gap. Increase in Sb also contributes to the reduction of the optical gap. Thin films of the material possess high value of refractive index and tuneable band gap which are attractive feature of these films for photonic applications such as optical fibers, waveguides and multiplexers.

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