Effect of vacuum thermal annealing on optical properties of amorphous (Se$_{80}$Te$_{20}$)$_{94}$Ag$_{6}$ chalcogenide thin films prepared by thermal evaporation technique

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Abstract. Amorphous (Se$_{80}$Te$_{20}$)$_{94}$Ag$_{6}$ thin films are prepared at room temperature by using thermal evaporation technique. The as-prepared thin films are annealed both at higher and lower temperatures than glass transition temperature $T_g$. X-ray diffraction of annealed film above $T_g$ confirms the presence of different phases. The glass transition temperature of as-prepared glass is evaluated with the help of DSC measurement. Transmittance measurements are used to find the value of optical parameters and optical band gap $E_g$. Refractive index and extinction coefficient increases with increase in annealing temperature. The band gap show an increase for the annealing temperature less than $T_g$ and decrease for the temperature greater than $T_g$. Mott and Davis Model forms the basis for the explanation of change in optical band gap.

1. Introduction
In recent years, high potential applications in optics, optoelectronics, optical memories, ultra-fast optical switches and optical amplifiers attract the researcher towards the S, Se, Te based chalcogenide glasses. The refractive index for these materials is generally found to be on higher side and also these materials possess low phonon energy. In addition to above properties they also have good transparency in the range of visible to infrared region [1-3]. In their pure state Se glass has a remarkable property of phase reversal [4-7] which is applicable in optical memory devices, but it has some drawback also like low sensitivity and short lifetime. One of the highlighted points about Se-Te alloy is that aside of greater hardness, high photosensitivity and lower aging effect, they also possess high $T_c$ which makes these alloys more useful for technological aspects [8-13]. These alloys can be a good choice for optical recording media as they exhibit excellent laser writing sensitivity [14]. The expectation from Se-Te based chalcogenide glasses is high regarding their use as good phase change media between the two states i.e. amorphous and crystalline. Due to the technological importance of optical properties of chalcogenide glasses thin films, they became the centre point of number of studies.
A thin film of amorphous chalcogenide has potential applications in the technology of optically recorded memories. Silver doped chalcogenide thin films have the unique potential in the field of photodoping, relief grating, microlenses, imprint and photo-lithography, optical imaging and phase change optical recording technology [15-22]. The third element silver is doped into Se-Te system in order to exaggerate the utilization of thin films of the SeTeAg ternary alloy in the fields of optical memories, optical switches and phase change technology. In this work, we are dealing with the determination of some optical parameters in annealed and un-annealed (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ thin films by utilizing the transmission spectra in the wavelength region of 700-1800 nm.

2. Experimental
Bulk (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ glass was prepared by melt quenching technique. Constituents element Se, Te and Ag were sealed in evacuated ($10^{-5}$ Torr) quartz ampoule. The sealed ampoules were heated at 1150°C for 24 hours under continuous rocking. Quenching of the obtained melt was done in ice cooled water. The amorphous natures of quenched samples were confirmed by X-ray diffraction. Differential Scanning Calorimetry (DSC) (Shimadzu TA-60) measurement are done under nitrogen atmosphere from 300 K to 600 K. Approximate 10 mg fine powder of bulk glass is sealed in alumina pan and inserted into the DSC. The DSC scan was taken at constant heating rate 5 K/min. Thin films of prepared glass were deposited by thermal evaporation technique. Transmittance of all the thin film samples were measured using a (Shimadzu UV-3600) spectrophotometer, in the wavelength range 700-1800 nm. Annealing process of thin film was performed under nitrogen atmosphere in vacuum $10^{-3}$ Torr for 2 hours. After annealing, films are examined under X-ray diffractometer.

3. Results and discussion
Thin films deposited by thermal evaporation are annealed at 330 K and 355 K. Thin films are annealed below and above the glass transition temperatures because the glass transition temperature $T_g$ and crystallization temperature $T_c$ of as-prepared glass are found at 335 K and 365 K respectively.

![Figure 1. X-ray diffraction of as-prepared and annealed (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ thin films.](image1)

![Figure 2. DSC trace of as-prepared (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ bulk glass.](image2)

From the X-ray diffraction it reveals that the crystalline phases Se$_8$, Te, Ag$_2$Se and Ag$_2$Te are present in the annealed films [23]. The average size of crystallites is determined by using the Debye-Scherrer formula
where $k$ is the Scherrer constant, $\beta$ is line width of X-ray diffraction peak (full width at half maxima), $\theta$ is the Bragg’s angle at which X-rays are reflected and $\lambda$ is the wavelength of incident X-rays. The average size of crystallites is 13 nm and 16 nm when films are annealed at temperatures 330 K and 355 K respectively. According to the Debye-Scherrer formula, the grain size increases with the annealing temperature which indicating that the crystallization increases with increasing annealing temperature. The glass transition temperature of as-prepared (Se80Te20)94Ag6 glass has been find out from the DSC scan. Fig. 2 shows the DSC trace of bulk (Se80Te20)94Ag6 glass. DSC trace clearly indicates the position of glass transition temperature $T_g$ and crystallization temperature $T_c$.

3.1 Optical Properties

The room temperature transmission spectra of the as-prepared and annealed films are shown in fig 3. The average transmittance goes on decreasing as the annealing temperature increased. It may be explained by the X-ray pattern of annealed films. It reveals that the peaks in XRD pattern continue to enlarge with increase in annealing temperature. Polycrystalline phases are developed in the film layer during the annealing. The grain boundaries of these micro-crystallites scatter and reflect the light [24] leading to the decrease in the average transmittance.

3.1.1. Determination of optical constants. In this work only transmission spectra is used in order to measure the optical parameters, like refractive index, absorption coefficient, extinction coefficient etc. Swanepoel’s method [25, 26] is used to calculate the above mentioned parameters. The refractive index is given by

$$n = \left\{N + (N^2 - n_0^2)^{1/2}\right\}^{1/2}$$

(2)

Where

$$N = 2n_s \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}}T_{\text{min}}} + \frac{n_s^2 + 1}{2}$$

(3)

and $n_s^2 = 1.52$, refractive index of the glass substrate.

$T_{\text{max}}$ = upper extreme point of transmission.

$T_{\text{min}}$ = lower extreme point of transmission.
The extinction coefficient $k$ can be calculated from the following relation

$$d = \frac{\lambda_a \lambda_b}{2(\lambda_a n_1 - \lambda_b n_2)}$$  \hspace{1cm} (4)

Where $n_1$ and $n_2$ are the refractive indices of adjacent maxima or adjacent minima corresponding to the wavelength $\lambda_a$ and $\lambda_b$ respectively.

The extinction coefficient $k$ can be calculated from the following relation

$$k = \frac{\lambda}{4\pi d} \log \frac{1}{A}$$  \hspace{1cm} (5)

and

$$A = \frac{E_M - (E_M^2 - (n^2 - 1)^3(n^2 - n_e^2))^{1/2}}{(n - 1)^3(n - n_e^2)}$$  \hspace{1cm} (6)

where $A$ is called absorbance and

$$E_M = \frac{8n^2n_e}{T_{max}} + (n^2 - 1)(n^2 - n_e^2)$$  \hspace{1cm} (7)

Figure 3. Transmission spectra of (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ thin films.

The presence of upper and lower extremes at the same wavelength position in the observed transmission spectra indicates that the deposited films are optically homogeneous. The thickness of the film can be obtained by the relation

Figure 4. Plot of refractive index ($n$) vs. wavelength ($\lambda$) in (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ films.

3.1.2. Measurement of real and imaginary part of dielectric constant. The above equations (2) and (5) are used to calculate real and imaginary dielectric constant respectively [27].

$$\epsilon' = n^2 - k^2$$  \hspace{1cm} (8)

$$\epsilon'' = 2nk$$  \hspace{1cm} (9)

And dissipation factor, $\tan \delta$, can be calculated as

$$\tan \delta = \frac{\epsilon''}{\epsilon}$$  \hspace{1cm} (10)

Figure 5. Plot of extinction coefficient ($k$) vs. wavelength ($\lambda$) in (Se$_{80}$Te$_{20}$)$_{94}$Ag$_6$ films.
3.1.3. Determination of optical energy gap. The analysis of optical absorption of the amorphous films was found suitable with the Tauc’s [28] relation given as

\[ a\nu v = B(\nu v - E_{g}^{opt})^{m} \]  

(11)
The optical band gap \( E_{g}^{opt} \) can be determined from the plot between \( (a\nu v)^{1/2} \) and \( \nu v \) as shown in fig.9. The intercept on the \( \nu v \) axis of the extrapolating of linear portion of curve gives the band gap. It is found that the values of band gap of as-prepared, annealed below \( T_{g} \) and above \( T_{g} \) films are 1.10 eV, 1.05 eV and 1.15 eV respectively. Fig.9 shows that optical bandgap increases when the film annealed below \( T_{g} \) while it further decreases when annealed between \( T_{g} \) and \( T_{c} \).

**Figure 6.** Plot of real dielectric constant (\( \varepsilon' \)) vs. wavelength (\( \lambda \)) in (Se_{80}Te_{20})_{94}Ag_{6} thin films.

**Figure 7.** Plot of imaginary dielectric constant (\( \varepsilon'' \)) vs. wavelength (\( \lambda \)) in (Se_{80}Te_{20})_{94}Ag_{6} thin films.

**Figure 8.** Plot of dissipation factor \( \tan(\delta) \) vs. wavelength (\( \lambda \)) in (Se_{80}Te_{20})_{94}Ag_{6} thin films.

**Figure 9.** Plot of \( (a\nu v)^{1/2} \) vs. photon energy (\( \nu v \)) for (Se_{80}Te_{20})_{100-x}Ag_{x} thin films.
When the thin film are annealed below $T_g$, there occur an increase in optical band gap which is due to the decrease in localized states [29], this can be explained by taking reference of Mott-Davis model. In this process the disorder developed during deposition are removed which lead to an increase in optical gap. Annealing above $T_g$ produces surface dangling bonds around the crystallites [30] and also it crystallizes the amorphous layer. These crystallites will breakdown on further increase in annealed temperature [31] due to which additional dangling bonds are generated on the surface of grain boundaries. Now the gap have an increased concentration of localized states resulting in a decrease in optical band gap.

4. Conclusions
Thin films of as-prepared glass were deposited by thermal evaporation technique. Glass transition temperature and crystalline temperature were found with the help of DSC measurement. X-ray diffraction reveals that film crystallizes on heat treatment. Annealing temperature show an impact on the refractive index of the system it increases with increase in temperature also the increase in extinction coefficient ($k$) is observed with rise in annealing temperature. The optical band gap also show changes with annealing temperature. Davis-Mott model is considered as the reference in explaining these changes.

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