



## Compositional dependence of optical parameters in Se–Bi–Te–Ag thin films

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### ABSTRACT

Compositional dependence of optical parameters in thermally evaporated amorphous  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  (for  $y=0, 1.0, 1.5$  and  $2.0$  at.%) quaternary thin films has been studied using well established Swanepoel method. The optical properties like, refractive index ( $n$ ), extinction coefficient ( $k$ ), absorption coefficient ( $\alpha$ ) and optical band gap ( $E_g$ ) have been determined from the transmission spectra in the spectral range from 500 to 2500 nm. The optical band gap ( $E_g$ ) has been estimated by using Tauc's extrapolation method and is found to increase with an increase in the Ag concentration. Present study shows that the refractive index, extinction coefficient and optical band gap increase with the increasing Ag content which is in agreement with the earlier studies. While the increase in the refractive index with Ag content over the entire spectral range can be attributed to the increased polarizability of larger Ag atomic radius (153 pm) compared to the Te atomic radius (135 pm), the increase in the optical band gap with increasing Ag concentration is correlated to an increase in the cohesive energy and decrease in the electronegativity of the films under study. The dielectric constant and optical conductivity ( $\sigma$ ) of the thin films under study are also found to increase with the Ag concentration.

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### 1. Introduction

Application of chalcogenide glasses in the field of laser power delivery, optical limiting, fiber amplifier and optical computing [1–3] has made them more interesting and useful materials. Moreover, immense value of nonlinear refractive index, low phonon energies and excellent transparency of amorphous chalcogenide thin films make them very promising materials for optical integrated circuits in optical communication systems [4,5]. Also, due to low optical losses in these materials, they are preferred as infrared optical materials [6]. Among chalcogenide glasses, Se–Te alloys have attracted much attention due to more superiority over amorphous Se. The addition of Te in Se is further known to improve the corrosion resistance property of selenium and reduce the electronic band gap of Se which makes the alloy important for their application in xerographic purposes [7]. Due to their unique properties, the Se–Te chalcogenide semiconducting alloys are of considerable significance in various fields like sensors, laser materials, solar cells, infrared detectors etc. but the thermal instability leading to crystallization is one of the major drawback of these alloys. The physical properties of these materials strongly depend on the method of doping and chemical nature of the impurities. It has been found that the metals like Ag, Sb, Bi, Cu, Sn etc. modify the properties of these semiconducting [8,9] materials, the reason for which they have received much attention in the recent

past. Several physical properties are found to be improved by the addition of certain metallic impurities [10–13]. The insertion of Bi to these alloys has been seen to produce remarkable changes [14–16] like, p to n type conduction, increase in chemical durability and broadening of the IR transparency region. But at the same time, it reduces the thermal stability of the material. On the other hand silver (Ag) easily alloys with the chalcogenide matrix by bridging chalcogenide chains and makes the structure more stable [17]. It is found that the addition of Ag results in various structural changes in the materials which in turn modify the band structure and hence electrical and optical properties of the materials. Due to their potential device applications in optoelectronics, biology and optics like optical memories, micro lenses, waveguides, gratings, photo doping [18–20] etc., Ag containing chalcogenide glasses have received adequate attention in glass science and technology. Multinary chalcogenides containing heavy main-group elements are attractive because of their abundant structural features [21] and distinctive physical properties that are applicable in thermoelectric devices. However, the present work seeks to study the effect of metal impurities on the optical properties of Se–Te based quaternary amorphous thin films. In Se excess chalcogenide materials, most of the researchers have chosen the Se content between 75 and 90 at.% [13,22–24], which seems to be thermally stable, so a midway concentration of Se is chosen. In view of the availability of considerable work on the ternary glasses, the present study focuses on the effect of Ag doping on the optical properties of Se–Te–Bi glass.

Since, films are the ideal specimen for reflectance and transmittance measurements, the accurate measurement of their optical

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constants is extremely important. The optical band gap ( $E_g$ ), refractive index ( $n$ ) and extinction coefficient ( $k$ ) are the significant parameters to be studied in amorphous semiconducting thin films. The change in refractive index of chalcogenide thin films under the influence of light makes them useful materials to record the magnitude as well as the phase of illumination. This property of such materials makes them important in holographic optical data storage and in the fabrication of various integrated devices such as couplers, modulators, mixers and optical fibers [25–27]. In the present work, effect of Ag addition on the optical properties of  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$ , ( $y=0, 1.0, 1.5$  and  $2.0$  at.%) thin films has been studied by analyzing the transmission spectra in the spectral range of 500–2500 nm. The optical parameters have been determined by using the well known Swanepoel's method [28] based on Manificier's idea [29]. In this method, the extremes of the interference fringes of transmission spectra are used to calculate the refractive index and film thickness in the transparent region. It has an advantage due to its nondestructive nature and it yields the dispersion relation over a large range of wavelength without any prior knowledge of the films thickness. The optical energy gap has been estimated by using Tauc's extrapolation method [30] and is found to increase with an increase in the Ag content. The variation in the optical band gap has been explained in terms of cohesive energy and electronegativity of the system.

## 2. Experimental details

The glassy alloys of  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  (for  $y=0, 1.0, 1.5$  and  $2.0$  at.%) in bulk form were prepared by conventional melt quenching technique. High purity (99.999%) elemental substances were weighed according to their atomic percentage and sealed in quartz ampoules (length 6 cm and internal diameter 8 mm), evacuated to a vacuum of  $10^{-5}$  Torr. The sealed ampoules were heated in a vertical furnace at an appropriate temperature of 1050 °C for 15 h by gradually increasing the temperature at the rate of 3–4 °C per minute. The ampoules were rocked frequently during heating in order to ensure homogenization of the melt. The ampoules were quenched in ice cooled water to obtain the glassy alloy. The samples were taken out from the ampoules by keeping the ampoules in  $\text{HF} + \text{H}_2\text{O}_2$  solution for about 48 h. The amorphous nature of the bulk samples was confirmed by X-ray diffraction as no prominent peak was observed in the spectra. Thin films were prepared on well cleaned microscopic glass substrates by thermal vacuum evaporation technique [Vacuum coating unit HINDHIVAC 12A 4D Model], at a vacuum of  $10^{-5}$  Torr, using a separate molybdenum boat for each sample. The substrates were kept at the room temperature. The films were grown at the rate of 13 Angstrom per second so as to achieve a film composition very near to the bulk material. The deposition parameters for all the films were kept identical so that the results could be compared. The thin films were kept inside the deposition chamber for about 24 h to achieve a metastable equilibrium. The composition of the films was checked by performing EDAX measurement using QUANTA-250, D-9393 Model. The EDAX measurements confirmed that the variation in the composition of the thin film with respect to bulk alloy is approximately about  $\pm 5\%$ . The amorphous nature of the thin films was again confirmed from the X-ray diffraction pattern. The transmission spectra of as-deposited thin films were recorded in the transmission range of wavelength 500 nm to 2500 nm, by using ultraviolet-visible-near infrared double beam spectrophotometer [Perkin Elmer Lambda-750]. All the measurements were carried out at the room temperature (300 K).

## 3. Results

The XRD pattern of thin films for different compositions is shown in Fig. 1. The absence of sharp structural peaks in XRD traces confirmed the amorphous nature of thin films. The transmittance  $T$  as a function of wavelength, of the incident light, for different compositions, is shown

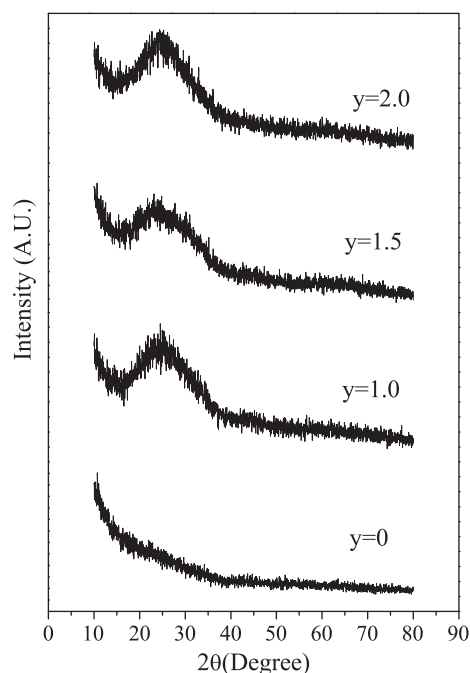


Fig. 1. XRD pattern of  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films for different compositions.

in Fig. 2. The occurrence of maxima and minima in the transmission spectra ensure the optical homogeneity of thin films. The optical transmission is a complex function and depends upon the refractive index of the substrate, refractive index of the film, film thickness and the wavelength of the incident light. The well established Swanepoel's method [28] is used to calculate the various optical parameters from the transmission spectra. According to Swanepoel, an envelop is drawn through the extremes of the transmission spectra because the envelop is a slow varying function of  $\lambda$  whereas the spectrum varies rapidly with  $\lambda$ .

### 3.1. Refractive index, film thickness and extinction coefficient

The values of refractive index, film thickness and extinction coefficient are calculated from transmission spectra using straight forward

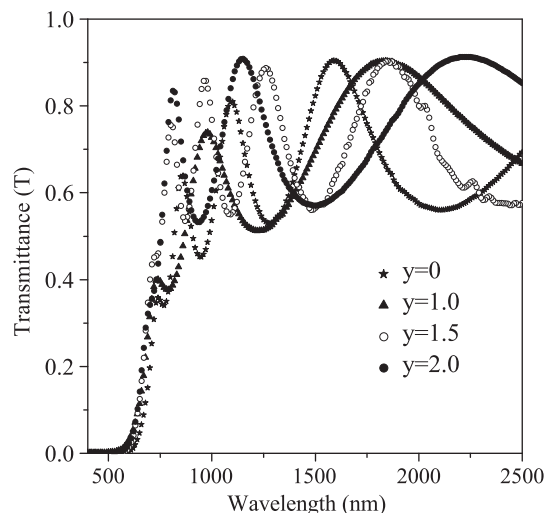


Fig. 2. Transmission spectra for  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films at different compositions.

technique propounded by Swanepoel. The first step in this method is to determine the transmittance envelop functions, i.e., transmission maximum  $T_M$  and corresponding minimum  $T_m$ , at a certain wavelength  $\lambda$ , respectively. The obtained values of  $T_M$  and  $T_m$ , at each  $\lambda$ , for different compositions are given in Table 1. The refractive index ( $n$ ) in the transparent region, when the absorption coefficient ( $\alpha$ ) is zero, can be obtained from the relation [28]

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

where

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

In Eq. (2)  $T_m$  is the envelope function of minimum transmittance and  $s$  is the substrate refractive index having value  $s=1.5$ . In the weak region where  $\alpha \neq 0$  the transmission decreases and the refractive index can be determined from Eq. (1) by using

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}, \tag{3}$$

here  $T_M$  is the envelop function of maximum transmittance. The values of refractive index for different compositions of the film, at each  $\lambda$ , are reported as  $n_1$  in Table 1. It is observed that for the entire spectral range, the refractive index increases with the increasing Ag concentration. Similar results for Ag doped ternary thin films are reported [31–33] in the literature.

The accuracy of the refractive index may be increased by calculating the film thickness using basic interference equation

$$2nd = P\lambda \tag{4}$$

where  $P$ , the order number is an integer, i.e.,  $P=1, 2, 3, \dots$ , for maxima and half integer, i.e.,  $P=1/2, 3/2, 5/2, \dots$ , for minima in the transmission spectra. In Eq. (4),  $n$  and  $d$  represent the refractive index and thickness of the film, respectively. If  $n_x$  and  $n_y$  are the refractive indices of two adjacent maxima (or minima) at

wavelengths  $\lambda_x$  and  $\lambda_y$ , respectively, then the thickness of the film can be determined [28] from the relation

$$d = T_M \frac{\lambda_x \lambda_y}{2(\lambda_x n_y - \lambda_y n_x)}. \tag{5}$$

Here, for two adjacent maxima or minima  $T_M=1$ . The values of film thickness  $d_1$  obtained from above equation are given in Table 1. The average value of film thickness  $\bar{d}_1$  along with the values of  $n_1$  and  $P$  is used to determine the order number  $P_0$ , from Eq. (4), at different extremes of the transmission spectra. By taking the exact integer or half integer value of  $P$ , the accuracy of film thickness can be increased significantly. The new film thickness  $d_2$  is obtained from Eq. (4) by using the values of  $n_1$  and  $P$  (integer and half integer for maxima and minima) for each value of  $\lambda$ . The values of new film thickness  $d_2$ ,  $P$  and  $P_0$  for different compositions of the film are given in Table 1. Now, using the exact value of  $P$  and film thickness  $d_2$ , Eq. (4) can be solved for  $n$  at each  $\lambda$ . The new values of the refractive index  $n_2$  are fitted to the Cauchy's relation [34], i.e.,  $n_2 = a + b/\lambda^2$ , to extrapolate the values of the refractive index for all wavelengths as shown in Fig. 3.

The extinction coefficient  $k$  is a measure of fraction of light lost due to scattering and absorption per unit distance of the medium. The value of extinction coefficient  $k$  for investigated compositions is calculated by using a well established relation [28]

$$k = \frac{\alpha\lambda}{4\pi}, \tag{6}$$

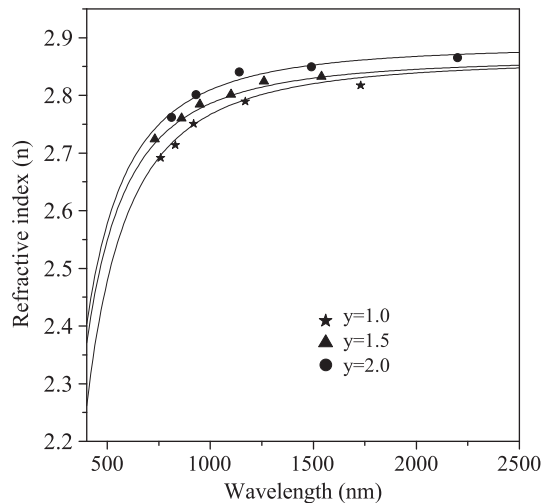
here  $\alpha$  is the absorption coefficient and is defined [28] as

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{X} \right), \tag{7}$$

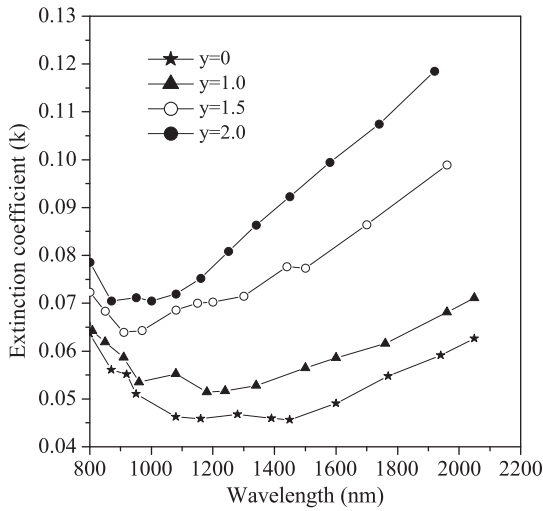
where  $d$  is the thickness of the film and  $X$  is the absorbance. The values of absorption coefficient obtained from Eq. (7) are used to calculate the extinction coefficient from Eq. (6). The extinction coefficient  $k$  as function of wavelength, for different compositions of  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films, is plotted in Fig. 4 which makes it clear that the extinction coefficient increases with an increase in the Ag concentration. Our results are in agreement with earlier [31] results for ternary thin films.

**Table 1**  
Values of  $\lambda$ , envelope functions  $T_M$  and  $T_m$ , refractive index  $n_1$ , film thickness  $d_1$  and  $d_2$ , and order number  $P_0$  and  $P$  for  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  ( $y=1.0, 1.5$  and  $2.0$ ) thin films.

$\lambda$ (nm)	$T_M$	$T_m$	$n_1$	$d_1$ (nm)	$P_0$	$P$	$d_2$ (nm)
<i>Se<sub>80.5</sub>Bi<sub>1.5</sub>Te<sub>17</sub>Ag<sub>1</sub></i>							
760	0.412	0.319	2.691	–	4.023	4.0	549.90
830	0.584	0.410	2.713	674.12	3.573	3.5	541.70
920	0.750	0.475	2.750	590.61	3.203	3.0	518.08
1170	0.845	0.502	2.789	394.66	2.637	2.5	524.34
1730	0.920	0.525	2.817	–	1.801	2.0	614.10
				$\bar{d}_1 = 553.13$			$\bar{d}_2 = 549.62$
<i>Se<sub>80.5</sub>Bi<sub>1.5</sub>Te<sub>16.5</sub>Ag<sub>1.5</sub></i>							
718	0.730	0.472	2.723	–	4.590	4.5	593.12
810	0.775	0.489	2.760	610.48	4.123	4.0	586.89
928	0.815	0.502	2.784	586.04	3.630	3.5	583.22
1090	0.853	0.512	2.801	593.75	3.110	3.0	583.58
1298	0.905	0.516	2.824	629.73	2.633	2.5	574.86
1590	0.920	0.517	2.832	–	2.155	2.0	561.36
				$\bar{d}_1 = 605.00$			$\bar{d}_2 = 580.44$
<i>Se<sub>80.5</sub>Bi<sub>1.5</sub>Te<sub>16</sub>Ag<sub>2</sub></i>							
768	0.807	0.498	2.762	–	3.068	3.0	417.07
925	0.870	0.512	2.801	432.15	2.583	2.5	412.74
1160	0.905	0.517	2.829	418.57	2.080	2.0	409.92
1548	0.915	0.518	2.839	428.82	1.564	1.5	408.94
2240	0.916	0.515	2.852	–	1.086	1.0	392.61
				$\bar{d}_1 = 426.52$			$\bar{d}_2 = 408.25$



**Fig. 3.** Refractive index ( $n$ ) versus wavelength ( $\lambda$ ) in  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films. Solid symbols represent the value of  $n$  at extremes and solid line represents the Cauchy's fitting.



**Fig. 4.** The extinction coefficient  $k$  as a function of wavelength  $\lambda$  in  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films.

### 3.2. Optical band gap

Chalcogenide glasses are found to exhibit highly reproducible optical edges which are insensitive to the preparation conditions. The absorption edges in crystalline materials are directly related to the conduction band and valence band whereas a different type of absorption edge is observed [35] in case of amorphous materials. In these materials, the absorption coefficient ( $\alpha$ ) is found to increase with the photon energy near the gap. This type of optical absorption edge is termed as the Urbach edge and is defined as

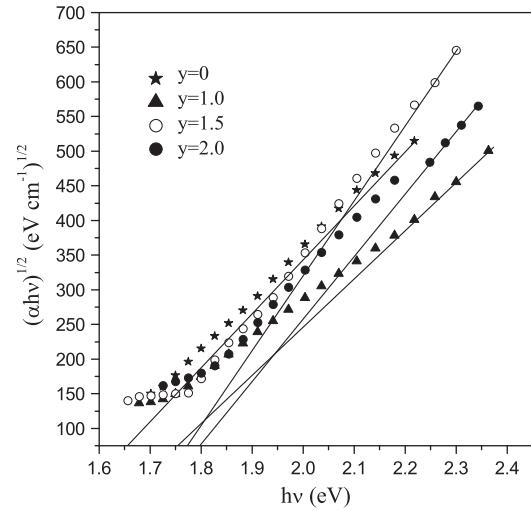
$$\alpha = \alpha_0 \exp(h\nu/E_e), \quad (8)$$

where  $\alpha_0$  is a constant and  $E_e$  is the Urbach energy that provide information about the extent of disorder or randomness in the materials [36]. Many of the chalcogenide materials are found [35] to exhibit this type of absorption edge. Absorption in this region depends upon the transition between extended states in one band and localized states in the exponential tail of the band. Thus, here the disorder refers to the electronic states within the material as compared to the irregularities in the atomic arrangement.

The optical energy gap  $E_g$  in  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films is calculated from absorption coefficient data using the non-direct transition model proposed by Tauc [37]. According to this model the absorption coefficient is related to the optical band gap  $E_g$  by the relation

$$\alpha h\nu = B(E_e - E_g)^L, \quad (9)$$

here  $B$  is the slope of the Tauc edge called band tailing parameter. It depends upon the width of the localized states in the bandgap which are attributed to the homopolar bonds in the chalcogenide glasses. In Eq. (9)  $L$  determines the type of transition and  $L = 1/2, 2, 3/2$  and  $3$  correspond to the direct allowed transition, indirect allowed transitions, forbidden transition and indirect forbidden transitions, respectively. It is shown that  $L = 2$  provides a best fit for the optical absorption data in many chalcogenide glassy materials [38].  $(\alpha h\nu)^{1/2}$  as a function of photon energy  $E_e = h\nu$  is plotted in Fig. 5. The values of the optical energy gap  $E_g^T$  for indirect allowed transition are obtained from the intercept by making  $(\alpha h\nu)^{1/2} \rightarrow 0$  and are given in Table 2. From Table 2 it is observed that the value of optical band gap increases with an increase in Ag concentration which is in agreement with the earlier studies [33,39–41] on ternary thin films.



**Fig. 5.** The dependence of  $(\alpha h\nu)^{1/2}$  on photon energy  $h\nu$  in  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films.

### 3.3. Dielectric constant and optical conductivity

The dielectric constant is an intrinsic property of a material and it affects the movement of the electromagnetic signals through the materials. The material with high dielectric constant makes the light travel slowly. The dielectric constant is a complex quantity. While its real part ( $\epsilon'$ ) explains the amount by which the material slows down the speed of light when passed through it, its imaginary part ( $\epsilon''$ ) shows how a dielectric material absorbs the energy from electric field due to dipole orientation.

The values of refractive index and extinction coefficient obtained above are used to determine [42] the dielectric response of the films under study. While real part of the dielectric constant ( $\epsilon'$ ) is calculated by using the relation

$$\epsilon' = n^2 - k^2, \quad (10)$$

imaginary part of the dielectric constant ( $\epsilon''$ ) is determined from the relation,

$$\epsilon'' = 2nk. \quad (11)$$

The values of the real and imaginary part of the dielectric constants for  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  thin films are listed in Table 3. It is observed that  $\epsilon'$  and  $\epsilon''$  increase with the increase in Ag content. The knowledge of real and imaginary part of the dielectric constant gives the dissipation factor  $\tan(\delta)$  and is defined as  $\tan(\delta) = \frac{\epsilon''}{\epsilon'}$ . The calculated values of dissipation factor are also reported in Table 3 which reveals that the dissipation factor also follows the same trend as that of  $\epsilon'$  and  $\epsilon''$ . The optical conductivity ( $\sigma$ ) shows the optical response of the material. It has a dimension of frequency which is valid only in Gaussian system

**Table 2**

Values of refractive index ( $n$ ) at 1280 nm, density ( $\rho$ ), optical band gap ( $E_g^T$ ), electronegativity ( $\chi$ ) and cohesive energy (CE) in  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  ( $y = 0, 1.0, 1.5$  and  $2.0$ ) thin films.

Ag (at.%)	$n$	$\rho$ (g/cm <sup>3</sup> )	$E_g^T$ (eV)	$\chi$	CE (kcal/mol)
0	2.73	5.190	1.656	2.420	43.71
1.0	2.79	5.229	1.752	2.416	43.87
1.5	2.81	5.248	1.782	2.412	43.95
2.0	2.83	5.290	1.801	2.403	44.02



**Table 3**

Values of optical band gap ( $E_g^S$ ), dielectric constants ( $\epsilon'$  and  $\epsilon''$ ), optical conductivity ( $\sigma$ ) and dissipation factor  $Tan(\delta)$  for  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$  ( $y=0, 1.0, 1.5$  and  $2.0$ ) thin films.

Ag (at.%)	$E_g^S$ (eV)	$\epsilon'$	$\epsilon''$	$\sigma(10^{13})$ ( $s^{-1}$ )	$Tan(\delta)$
0	1.572	6.8831	0.2826	3.93	0.0411
1.0	1.576	7.6436	0.3639	5.06	0.0476
1.5	1.580	7.7250	0.3812	5.30	0.0493
2.0	1.582	7.8844	0.4041	5.61	0.0512

of units. The optical conductivity of  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$  thin films is calculated by using the relation [43].

$$\sigma = \frac{\alpha n c}{4\pi}, \quad (12)$$

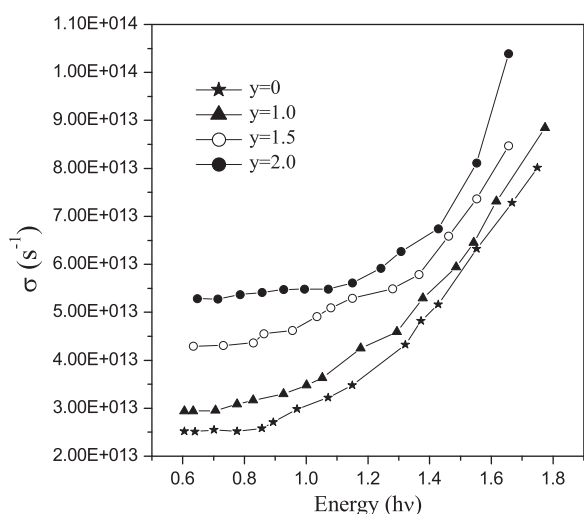
where  $c$  is the velocity of light. The values of optical conductivity for the different compositions of the thin films are given in Table 3. Fig. 6 illustrates the variation of  $\sigma$  with photon energy  $h\nu$  for different compositions of  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$  thin films. Since, the optical conductivity is directly related to the refractive index, it increases with an increase in the Ag concentration.

#### 4. Discussion

From Table 1 it is evident that the refractive index in  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$  thin films, increases with an increase in Ag contents. It may be due to the fact that the addition of Ag ( $\rho=10.49g/cm^3$ ) leads to the increase in the density of the glass matrix making the system rigid and compact. Various empirical and theoretical relations correlating the refractive index  $n$  with density  $\rho$  of the glasses are given [44,45] in the literature. Our results for refractive index show a similar trend to the one found [45,46] in permanently densified glasses. Moreover, the increase in  $n_1$  with Ag concentration may also be explained [47] in terms of the mean polarizability  $\alpha$  of the system. According to the Lorentz–Lorenz relation [48], the refractive index is directly related to the mean polarizability of the material as

$$\frac{n^2-1}{n^2+1} = \frac{1}{3\epsilon_0} \sum_i Z_i \alpha_i, \quad (13)$$

where  $\epsilon_0$  is the permittivity of free space and  $Z_i$  is the number of polarizable units of type  $i$  per unit volume with polarizability  $\alpha_i$ . The



**Fig. 6.** Variation of optical conductivity  $\sigma$  with photon energy  $h\nu$  for  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$  thin films.

atomic radius of Ag (153 pm) is greater than that of Te (135 pm), Se (116 pm) and Bi (146 pm). So, larger the atomic radius of the atom, larger will be its polarizability and consequently larger will be the refractive index. Thus, the change in refractive index  $n$  by Ag doping can be attributed [46,49]: (i) to the change in  $\rho$  caused by the structural rearrangement in the glass under study and (ii) change in mean polarizability caused by the formation of heteropolar bonds. From the above discussion we can say that the density  $\rho$  and mean polarizability  $\alpha$  are the two major factors [49] that contribute to the variation in refractive index.

For the system under consideration, the values of optical band gap vary from 1.656 eV to 1.801 eV for  $y=0$  to 2 at.%. This increase in optical band gap can be explained on the basis of Mott and Davis model [35]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defect present in the amorphous structure. Addition of Ag modifies the glass network and favors the formation of strong Se–Ag bonds with consequent decrease in defect states and reduction in tailing of bands [50]. Increase in the optical band gap with an increase in the Ag content is also reported [33,39–41] which shows that the increase is due to the decrease in the density of defects state. This increase can further be explained in terms of the electronegativity ( $\chi$ ), described [51] as the average of ionization potential and electron affinity. Since, it is difficult to assign an electron affinity value for a semiconductor alloy, say,  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$ , it will be appropriate to correlate the electronegativity with the optical bandgap,  $E_g$ . According to Pauling [52] the electronegativity of an atom in a molecule has the power to attract an electron toward itself. When the elements with different electronegativity values combine to make an alloy, the element of higher electronegativity attracts a pair of electron toward itself behaving as an anion, and the other element behaving as a cation. The electronegativity for the present samples is calculated by using Sanderson's principle [53]. According to this principle, electronegativity of an alloy is the geometric mean of electronegativity of its constituent elements. The calculated values of electronegativity for different concentration of Ag are listed in Table 2 where one can see that the electronegativity of  $Se_{80.5}Bi_{1.5}Te_{18-y}Ag_y$  thin films decreases from 2.420 to 2.403 with increasing concentration of Ag. In our case,  $E_g$  increases while  $\chi$  decreases with the increasing content of Ag as reported for other chalcogenide materials [54,55]. Different empirical relations are proposed [56–58] in the literature that correlate the electronegativity with the optical band gap. It is pertinent to mention here that larger the difference between the electronegativity of the combining atoms larger the band gap [58]. In Se–Te–Bi–Ag system the electronegativity value of Ag, Te, Bi, and Se are 1.93, 2.1, 2.02 and 2.55, respectively.

The variation of optical band gap can also be explained on the basis of chemical bond approach by estimating the cohesive energy of the system under investigation. The cohesive energy (CE) is the stabilization energy of an infinitely large cluster of a material per atom and is calculated by using the chemical bond approach (CBA) method [59]. The calculated values of cohesive energy are given in Table 2. Here, it is observed that the cohesive energy increases with an increase in Ag content in the system. The increase in the cohesive energy may be due to the fact that the addition of Ag results in heavily cross-linked structure which in turn makes the system stable. It is thus clear that the addition of Ag leads to the stability [17] of the system. The increase in CE implies an increase in the average stabilization energy and higher bonding strength that lead to an increase in the optical band gap. Thus, it may be concluded that the addition of Ag in  $Se_{80.5}Bi_{1.5}Te_{18}$  material leads to the increase in the optical band gap of the material which is in agreement with the earlier reported results [33,39–41] for ternary systems. As such, the increase in the optical band gap with an increase in Ag concentration can be ascribed to the decrease in density of defect states, increase in the grain size and reduction in the disorder which further results in the reduction of tailing of bands [23,31,35,40,50,60].

The optical band gap  $E_g$  in amorphous alloys can also be described by Shimakawa's simple relation [61], i.e.,  $E_g(AB)(Y) = YE_g(A) + (1 - Y)E_g(B)$ , where  $Y$  is the volume fraction of the element  $A$ ,  $E_g(A)$  and  $E_g(B)$  are the optical band gaps of the elements  $A$  and  $B$  respectively. The volume fraction calculations are done by using atomic mass and density of the elements used. The calculated values of optical band gap using Shimakawa's relation for present films are listed in Table 3. Calculated values of optical band gap using Shimakawa's method are smaller than those obtained from transmission spectra using Tauc's relation. The difference in the values of  $E_g$  by two methods may be attributed to the approximation used in the Shimakawa's relation. In Tables 2 and 3,  $E_g^T$  denotes the band gap obtained by Tauc's method and  $E_g^S$  denotes the band gap calculated from Shimakawa's relation. From Tables 2 and 3 it is inferred that both  $E_g^S$  and  $E_g^T$  increase with an increase in Ag content which shows that  $E_g^S$  and  $E_g^T$  are qualitatively in agreement.

## 5. Conclusions

The optical parameters of  $\text{Se}_{80.5}\text{Bi}_{1.5}\text{Te}_{18-y}\text{Ag}_y$  ( $y=0, 1.0, 1.5$  and  $2.0$ ) thin films have been studied using normal incidence transmission spectra in the spectral range 500 nm–2500 nm. The optical parameters are determined by using Swanepoel's envelope method based upon Manifacier's idea. Present results show that the refractive index ( $n$ ) increases, over the entire spectral range, with increasing Ag content. This increase in the refractive index may be interpreted in terms of the increased density and polarizability of larger Ag atomic radius (153 pm) as compared to the Te atomic radius (135 pm). The optical band gap  $E_g$  has been estimated by using Tauc's nondirect transition model and is seen to increase with an increase in Ag concentration. Increase in the optical band gap is explained in terms of increase in cohesive energy and decrease in density of defect states which results in reduction of tailing bands. The increase in the cohesive energy of films with increasing Ag concentration is due to the formation of cross-linked structures in the chalcogenide matrix. The optical band gap is also determined, theoretically, by using Shimakawa's relation. The calculated values of optical band gap by Shimakawa's relation are in qualitative agreement with the values obtained experimentally from Tauc's method. The real and imaginary part of the dielectric constant  $\epsilon$  and optical conductivity  $\sigma$  are also seen to increase with the increasing concentration of Ag.

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