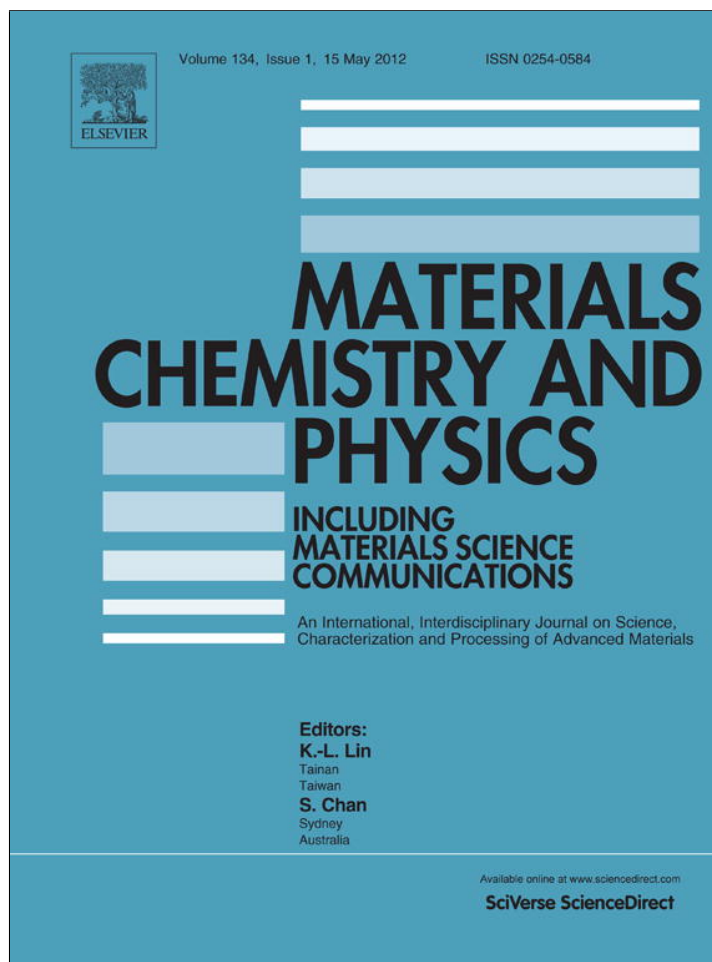


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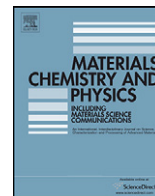
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Band gap and dispersive behavior of Ge alloyed *a*-SbSe thin films using single transmission spectrum

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ABSTRACT

The transparency of *SbSeGe* glasses in the IR region makes them attractive candidates for low transmission loss applications. The samples of $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) glasses have been prepared by melt quench technique. The thin films of these glasses have been deposited by vacuum evaporation technique. The optical study of thin films has been carried out. The refractive index, oscillator parameters, optical band gap and dielectric parameters have been calculated from optical measurements. The optical study reveals that the variation in the density of localized defect states on *Ge* addition affects the optical parameters of the system. The variation in concentration of localized defect states has been interpreted in terms of the change in structural network of the system.

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1. Introduction

Various optical properties of chalcogenide glasses such as transparency to IR radiation in the wavelength range 3–5 μm and 8–14 μm , high refractive index, low optical losses and phonon energies make them efficient materials for switching devices, IR optical fibers and AR coatings [1–3]. Amorphous *Se* has a unique property of reversible transformation [4] making its glasses useful for optical memory devices [5]. Its disadvantages like low sensitivity and ageing effects can be overcome by alloying *a*-*Se* with *Sb* [6]. The addition of *Sb* to *a*-*Se* breaks the ring structure of *a*-*Se* increasing the localized states and hopping conduction, leading to a reduction in the optical band gap of the system [7,8]. *SbSe* system, due to its higher photosensitivity has applications in photoconductive devices [9]. But, these are limited due to greater crystallization tendency of *Sb*. Moreover, eutectic *a*-*SbSe* system is less stable [10]. The variation in the photoconductive and elastic properties of *Ge*–*Sb*–*Se* has been reported by Mathew et al. [11] and Mahadevan et al. [12] respectively. With the addition of *Ge* to $Sb_{10}Se_{90}$, structural and configurational changes have been reported by Sharda et al. [13]. This strongly underlines the requirement for the study of band gap and dispersive parameters of $Sb_{10}Se_{90-x}Ge_x$ system. The transmission spectra of the films $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) have been used for the said investigation. Swanepoel method has been employed to calculate refractive index (*n*) and thickness

(*d*) of the films [14–16]. Optical band gap E_g^{opt} has been estimated using Tauc's [17] extrapolation method. The dispersion of refractive index has been studied in terms of Wemple–DiDomenico single oscillator model [18]. Dielectric constant, loss factor and optical conductivity have also been determined.

2. Experimental details

Bulk samples of the glass $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) were prepared using the melt quenching technique. High purity elements *Sb*, *Se* and *Ge* were appropriately weighed in the atomic weight percentage and vacuum sealed in quartz ampoules (10^{-4} Pa). The sealed ampoules were kept in a furnace and heated up to 1000 °C under continuous rocking at a heating rate of 3–4 °C min⁻¹. The quenching was done in ice cold water. The glass thin films were deposited using vacuum evaporation technique onto well cleaned glass substrates and kept in the deposition chamber for 24 hr to attain thermodynamic equilibrium. The thin films were characterized by X-ray diffractometer ($2\theta=10$ –80°) using PANalytical's X'Pert PRO. The composition of evaporated samples has been verified by EMPA (JEOL 8600 MX) on the different spots (size ≈ 2 μm) for the composition analysis. The compositional elements (*Sb*, *Se* and *Ge*) and the quenched samples were taken as reference. The composition of all thin films (2 cm \times 2 cm) has been found to be uniform within an accuracy of about ± 1 –1.5%. The transmission spectra of the deposited films in the spectral range 400–2600 nm were obtained using double beam UV–Vis–NIR (Perkin Elmer Lambda 750) at room temperature (300 K). The spectrophotometer was set with a slit width of 1 nm.

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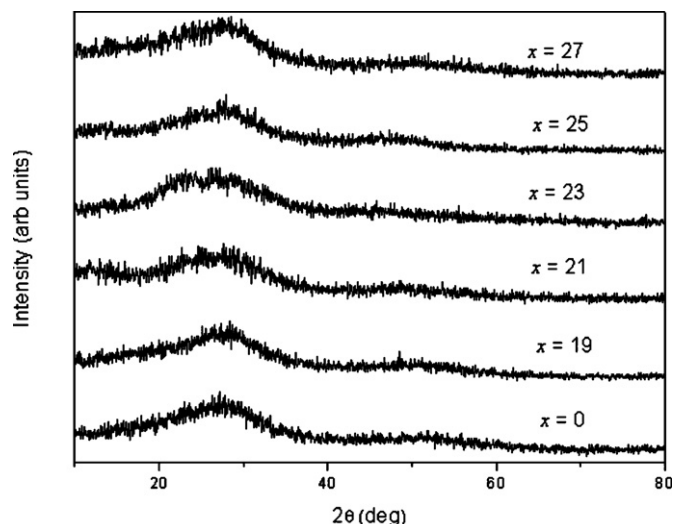


Fig. 1. XRD spectra of $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

3. Results

The spectra in Fig. 1 show no sharp peak thereby confirming the amorphous nature of the thin films. The variation of transmittance with the wavelength in Fig. 2 shows that the interference fringes are formed with alternate maxima and minima.

3.1. Refractive index and film thickness

A first approximation of the refractive index (n_1) in the region of weak and medium absorption has been made by Swanepoel method [14] based on the idea of Manifacier et al. [15] of creating upper and lower envelopes of the interference maxima and minima.

$$n_1 = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (1)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \quad (2)$$

Here T_M and T_m are the transmission maximum and corresponding minimum respectively at a certain wavelength and s is the

Table 1

Values of d , α , E_0 , E_d and n_0 for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

x	d (nm)	α (cm^{-1})	E_0 (eV)	E_d (eV)	n_0
0	254	0.76×10^4	4.51	34.30	2.93
19	404	0.42×10^4	4.77	35.21	2.89
21	311	0.41×10^4	4.87	34.26	2.83
23	298	0.36×10^4	5.31	36.23	2.80
25	413	0.23×10^4	5.66	37.28	2.75
27	373	0.31×10^4	5.95	38.29	2.73

refractive index of the substrate. If n_{e1} and n_{e2} are the refractive indices of the two adjacent maxima at wavelengths λ_{e1} and λ_{e1} , then the thickness of the thin films can be calculated as,

$$d = \frac{\lambda_{e1}\lambda_{e2}}{2(\lambda_{e1}n_{e2} - \lambda_{e2}n_{e1})} \quad (3)$$

The mean d and n_1 are used to accurately calculate the order number m (integer for maximum and half integer for minimum) in the interference equation, $2nd = m\lambda$. The corrected values of d (Table 1) have been used for the calculation of optical parameters. The values of n can be fitted to a two term Cauchy dispersion relation [16] $n = A + B/\lambda^2$ and extrapolated to all wavelengths. Fig. 3 indicates that for shorter wavelengths the refractive index decreases but becomes almost constant at higher wavelengths. The refractive index decreases with an increase in Ge.

3.2. Absorption coefficient and extinction coefficient

Using the values of refractive index calculated from Cauchy dispersion relation and thickness, the absorption coefficient (α), signifying the number of absorbed photons per incident photon, can be calculated using the relation [14],

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{x} \right) \quad (4)$$

where x is the absorbance [14]. The extinction coefficient (k), an imaginary part of the complex refractive index ($n^* = n - ik$) is a measure of the fraction of light lost due to scattering and can be expressed as, $k = \alpha\lambda/4\pi$. The value of k decreases with the increase in wavelength as shown in Fig. 4. This indicates a decrease in the fraction of light scattered and an increase in the transmission with increasing wavelength (Fig. 2). This loss decreases to a minimum for 25 at.% of Ge addition to a - $SbSe$.

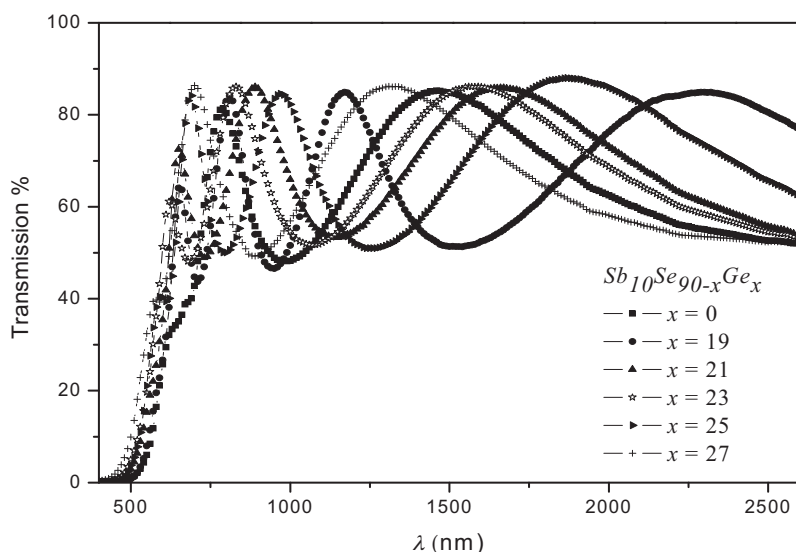


Fig. 2. Transmission spectra of $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

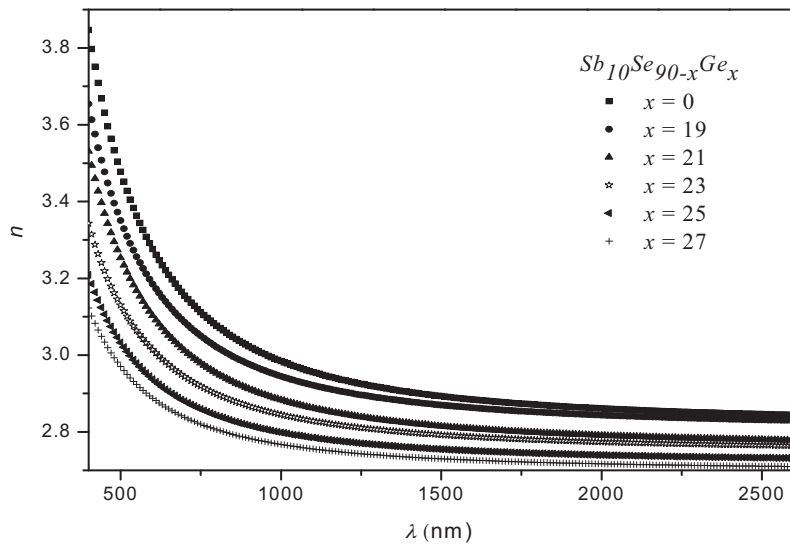


Fig. 3. Plot of n vs. λ for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

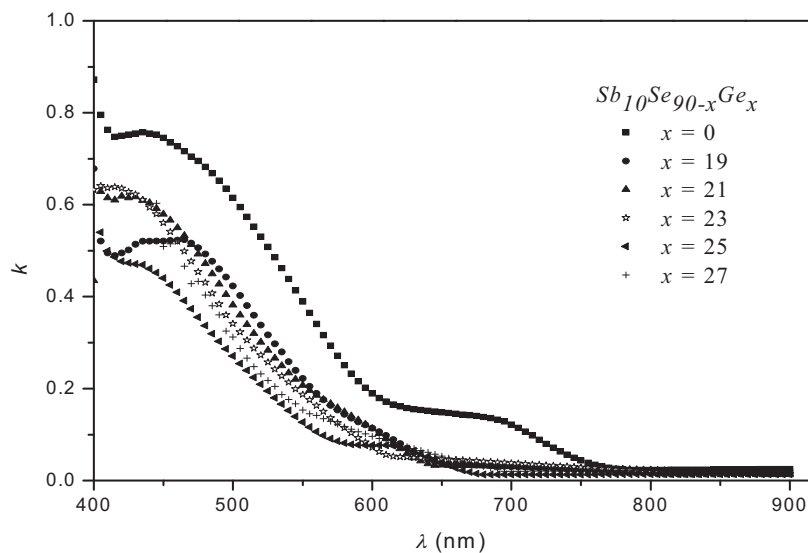


Fig. 4. Plot of k vs. λ for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

3.3. Optical gap and Wemple–DiDomenico model

For high absorption region ($\alpha \geq 10^4 \text{ cm}^{-1}$), corresponding to the transitions between extended states in both valence and conduction bands, the value of α is given by Tauc's relation [17],

$$\alpha h\nu = B(h\nu - E_g^{opt})^p \quad (5)$$

where B is a constant, which depends on the electronic transition probability and E_g^{opt} is the optical band gap. Parameter p characterizes the type of optical transition process, $p = 1/2$ for direct and $p = 2$ for indirect allowed transitions. A linear graph between $(\alpha h\nu)^{1/2}$ and $h\nu$ confirms the indirect nature of the transitions as shown in Fig. 5. The intercepts on extrapolation with the energy axis give the values of optical band gap. The E_g^{opt} increases with increasing Ge incorporation attaining a maximum for $x=25$ and then decreases for $x=27$.

The spectral dependence of the refractive index has been fitted to the single oscillator, i.e. Wemple–DiDomenico model [18]. It

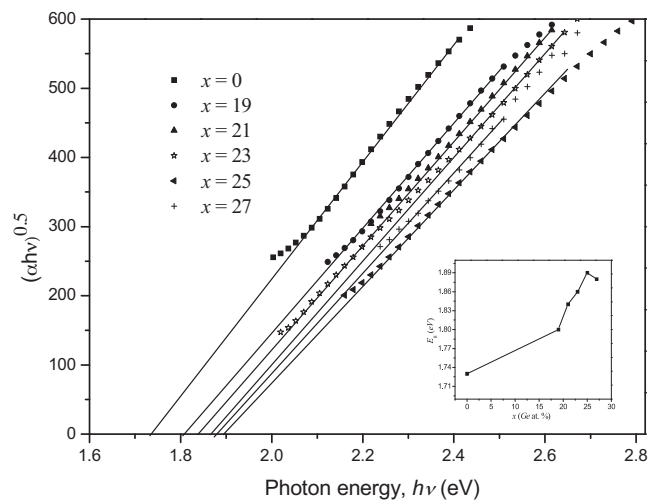


Fig. 5. Plot of $(\alpha h\nu)^{0.5}$ vs. $h\nu$ wavelength for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films. Inset shows the variation of E_g^{opt} with Ge at.%.

Table 2

Values of E_g^{opt} , ε_r , ε_i , $\tan \delta$ and theoretically calculated E_d for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

x	E_g^{opt} (eV)	ε_r	ε_i	$\tan \delta$	E_d (eV)
0	1.73	11.06	2.27	0.2201	15.73
19	1.80	10.46	1.22	0.1266	22.73
21	1.84	9.90	1.16	0.1243	23.36
23	1.86	9.29	0.99	0.1150	24.01
25	1.89	8.80	0.63	0.0781	24.68
27	1.88	8.48	0.82	0.0996	25.38

suggests a relation between refractive index and single oscillator strength, below the fundamental absorption edge,

$$n^2(h\nu) = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad (6)$$

where E_0 , oscillator energy, is the mean transition energy and E_d , the oscillator strength is a measure of the interband optical transitions. The values of E_0 and E_d can be determined from the intercept E_0/E_d and slope $(E_0 E_d)^{-1}$ of the fitted straight lines in Fig. 6 and are given in Table 1. The values of static refractive index (n_0), i.e. refractive index when $h\nu \rightarrow 0$, can be calculated from E_0 and E_d values (Table 1). n_0 is the lower limit of the refractive index and represents the response of the material to the DC electric field. The E_0 and E_d values increase, while n_0 decreases as the Ge alloying increases in the base system.

3.4. Dielectric constant and optical conductivity

The refractive index and oscillator parameter variation with Ge addition can be further analyzed by considering the dielectric behavior of the SbSeGe system. The complex dielectric constant; $\varepsilon = \varepsilon_r + i\varepsilon_i$ where ε_r is the real part representing the dielectric constant or relative permittivity and is a measure of polarizability of a material. ε_i is the imaginary part of the dielectric constant indicating the energy loss, i.e. the energy lost in aligning the dipoles. The loss tangent $\tan \delta = \varepsilon_i/\varepsilon_r$, measures the inherent dissipation of energy of a dielectric material. Since, ε_r and ε_i are both frequency dependent, so is δ . ε_r and ε_i have been calculated [6] and their values are given in Table 2. The values of ε_r decrease for $x=0$ to $x=27$ whereas ε_i and $\tan \delta$ decrease to a minimum for $x=25$ and increases for $x=27$.

To get a better idea of the effect of Ge addition to SbSe on the dielectric loss, the optical conductivity (σ) has been calculated. σ is directly related to the ε_i ($\varepsilon_i = \sigma(\omega)/\omega\varepsilon_0$) and tells about the

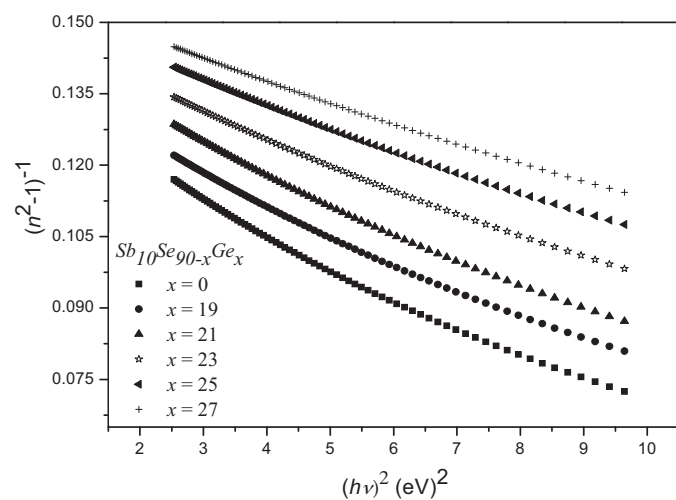


Fig. 6. Plot of $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

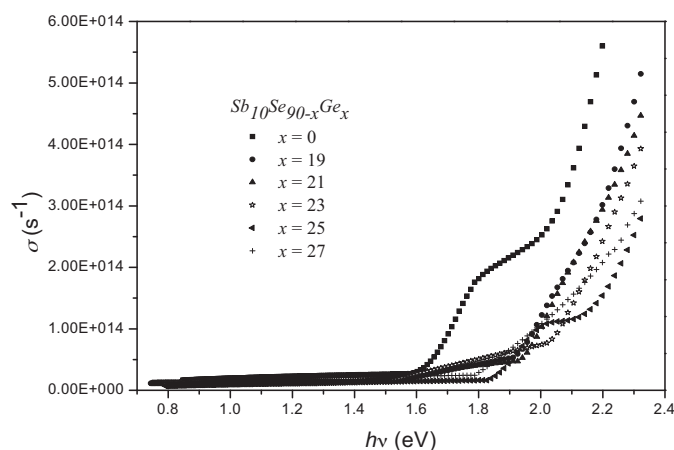


Fig. 7. Plot of σ vs. $h\nu$ for $Sb_{10}Se_{90-x}Ge_x$ ($x=0, 19, 21, 23, 25, 27$) thin films.

electronic structure of a system. The optical conductivity of the present system has been calculated using the relation [19],

$$\sigma = \frac{\alpha n c}{4\pi} \quad (7)$$

where c is the velocity of light and α and n are the absorption coefficient and refractive index respectively. Fig. 7 shows that the optical conductivity shifts towards lower photon energy with a minimum at $x=25$ followed by an increase for $x=27$.

4. Discussion

With the addition of Ge to the base composition, the transmission fringes show a blue shift, i.e. a shift towards the smaller wavelength indicating an increase in the transmission of light through the medium as Ge concentration increases. The refractive index $n = c/v$ increases with the decrease in the velocity of light in the medium due to oscillation of negative electron cloud stimulated by the incident electromagnetic radiation [20]. Conversely, n decreases with increasing wavelength for the system under study (Fig. 3). The n values also decrease with the addition of Ge to the $Sb_{10}Se_{90}$ system. On substituting Ge at the cost of Se atoms, the density to atomic radius ratio decreases from $x=19$ to 27 at.% Ge. This drop in the ratio indicates a decrease in the polarizability of the system. The refractive index being proportional to the atomic polarizability leads to a decrease in the refractive index with decreasing polarizability of the system [21].

The oscillator energy E_0 corresponds to the distance between the 'centers of gravity' of the valence and conduction bands. It is the 'average' energy gap and approximately scales with Tauc's gap, E_g^{opt} , i.e. $E_0 \approx 2E_g^{opt}$ [22]. Therefore, E_0 can be related to the bond energies of the different chemical bonds present in the system, as the optical band gap is a bond sensitive property. E_0 increases as Ge at.% increases from $x=19$ to 27 at.% in consistency with Tanaka's relation [22]. The dispersion energy or oscillator strength, E_d , also follows a simple empirical relation, $E_d = \beta N_c Z_a N_e$; where β is a two valued constant. According to Wemple, for the covalent crystalline and amorphous materials, β has a value of 0.37 ± 0.04 eV and 0.26 ± 0.03 eV for the ionic materials. N_c is the coordination number of the cation nearest neighbor to the anion, $Z_a=2$ is the formal chemical valency of the anion and N_e is the total number of valence electrons per anion. The total number of valence electrons per anion, for the $Sb_{10}Se_{90}$ binary system is, $N_e = (5 \times 10 + 6 \times 90)/90 \approx 6.556$. The base composition can be written as $(Sb_1Ge_0)_{10}Se_{90}$. Considering a hypothetical cation Sb_1Ge_0 , N_c can now be calculated as, $N_c = (3 \times 1 + 4 \times 0) = 3$ Similarly, for $Sb_{10}Se_{71}Ge_{19}$ composition, $N_e = (5 \times 10 + 6 \times 71 + 4 \times$

19)/71 \approx 7.775. Rewriting the $Sb_{10}Se_{71}Ge_{19}$ composition in the form $(Sb_{0.345}Ge_{0.655})_{29}Se_{71}$, the hypothetical cation is $Sb_{0.345}Ge_{0.655}$. Therefore, $N_c = (3 \times 0.345 + 4 \times 0.655) \approx 3.655$.

The incorporation of *Ge* to the $Sb_{10}Se_{90-x}Ge_x$ glass system increases the oscillator strength (E_d) indicating that one of the parameter (N_c) in the empirical relation is increasing. The *Ge* addition may change the nature of chemical bonding to more ionic. But, this cannot be attributed to the increase in E_d , since this leads to decrease in β . In WDD model [18], β is assumed to be a constant. The cation coordination number and the total number of valence electrons per anion are increasing with *Ge* incorporation in the base system. The cation coordination number, N_c , can be reasonably assumed to affect the oscillator strength with an increase in *Ge* concentration. The overall increase observed in the values of E_d and consequently in N_c suggests a greater interaction between the structural layers [21], which is consistent with the increase in the theoretically calculated structural compactness of $Sb_{10}Se_{90-x}Ge_x$ system [13]. *Ge* breaks the polymeric structure of the $Sb_{10}Se_{90}$ system forming tetrahedral $Ge(Se_{1/2})_4$ units, leading to an increase in the rigidity of the system and hence, the compactness. The decrease in n_o on increasing the *Ge* content may be explained using the fundamental Kramer–Kronig [23] relationship. Accordingly, the relation, $(n(0) - 1) = (1/2\pi^2) \int_0^\infty \alpha d\lambda$, predicts a blue shift in the absorption spectrum leading to a decrease in the refractive index.

The optical band gap increases to a maximum for 25 at.% *Ge* and then, decreases on further *Ge* addition. This observed change can be explained on the basis of the structural changes in the glassy network. $Sb_{10}Se_{90}$ contains only the Sb_2Se_3 structural units which have weak *Sb–Se* bonds. But, with the addition of *Ge*, *Sb–Se* bonds are replaced by stronger *Ge–Se* bonds forming tetrahedral $Ge(Se_{1/2})_4$ units. At $x=25$, the stoichiometric composition is obtained containing only the *Sb–Se* and *Ge–Se* heteropolar bonds. The cohesive energy of the system is maximum at $x=25$ and decreases above and below this composition due to the replacement of Sb_2Se_3 and $Ge(Se_{1/2})_4$ units by the weaker *Se–Se* and *Ge–Ge* bonds respectively [13]. Thus, the defect state concentration increases above and below $x=25$. This results in maximum E_g^{opt} for $x=25$ at.% of *Ge* alloying. The value of α can be correlated to E_g^{opt} on the basis of density of defect states, as α follows the Tauc relation with $p=2$, a characteristic of indirect band gap. Therefore, α decreases till $x=25$ and then increases for $x=27$ due to the variation in the bonding arrangements and hence, in the defect states.

The dielectric dispersion gives an idea about the dielectric losses which in turn are useful in the determination of electronic structure or defects in the system. The electron transfer, in the chalcogenide glasses, from one chain to another form dangling bonds, i.e. the paired D^- and D^+ defect states [24]. *Ge* alloying in the *SbSe* system reduces the charge defects and hence, the number of dipoles to a minimum for 25 at.% leading to a decrease in the dielectric parameters. The addition of *Ge* in excess of 25 at.% increases the charged

defects and hence, the dielectric parameters. The optical conductivity is related to absorption coefficient of the system. So, σ varies in accordance with α as the *Ge* alloying concentration increases in the base system on an account of change in density of defect states in the forbidden gap of the system.

5. Conclusion

The band gap and dispersive behavior of $Sb_{10}Se_{90-x}Ge_x$ have been studied on the basis of the transmission measurements. The oscillator strength increases with the *Ge* addition. The decrease in the *Se–Se* bonds till $x=25$ and the predominant formation of *Ge–Ge* bonds at $x=27$ changes the structure of the glassy alloys. This affects the structural network and the density of defect states which play a significant role in the variation of the band gap and dielectric parameters of the system. The defect states density decreases to a minimum for the stoichiometric composition $Sb_{10}Se_{65}Ge_{25}$ with maximum E_g^{opt} . This results in a minimum for α , $\tan \delta$ and σ at $x=25$ at.% of *Ge* addition. The study reveals that *SbSeGe* system can be explored for IR applications.

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