Effect of composition on optical properties of $\text{GeSe}_3\text{--Sb}_2\text{Se}_3\text{--ZnSe}$ thin films

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Abstract. Optical properties of the chalcogenides GeSe_3 , Sb_2Se_3 , ZnSe , $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ and $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ thin films are investigated. Incorporation of ZnSe into both GeSe_3 , Sb_2Se_3 results in amorphous $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ composition. The estimated optical energy gap, E_g , is found to decrease from 3.06 eV for ZnSe to 1.81 eV for $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$. While, the band tail width, E_c , exhibits an opposite trend. The E_g behaviour is believed to be associated with cohesive energy, CE, as the incorporation of ZnSe lowers its value. The calculated number of the excess of Se–Se homopolar bonds is found to affect mainly the E_c values. The refractive index, n , is discussed in terms of Wemple–DiDomenico single oscillator dispersion model in the normal dispersion region. The oscillator energy, E_o , and the dispersion energy, E_d , are determined for films under investigation.

Keywords. Amorphous semiconductors; chalcogenide glasses; optical properties.

1. Introduction

Chalcogenide glasses have exhibited promising phenomena applicable for various purposes, especially the optical one such as optical lenses for infrared transmission (Zhang *et al* 2003). Optically, ZnSe which belongs to II–VI semiconductors, with band gap of about 2.82 eV, finds many applications in direct optical transition devices like blue-green semiconductor lasers when prepared in layered structure by the molecular beam epitaxy (MBE) and also can be used for optical windows in the infrared applications at the transmission range from 0.5 to 22 μm used for high-power CO_2 laser optics at 10.6 μm (Zhang *et al* 2003). Because of its crystalline nature, it is not possible to produce optical fibres with useful length from this material (Zhang *et al* 2003). On the other hand, chalcogenide glasses are transparent from 2 μm region up to 16 μm (Mehra *et al* 1988).

The main advantage of these glasses, compared to ZnSe is the possibility of obtaining glass fibres and complex optical components like optical lenses for infrared transmission (Zhang *et al* 2003).

Studying the glass-forming ability of $\text{GeSe}_3\text{--Sb}_2\text{Se}_3\text{--ZnSe}$ system with certain proportions has been under investigation (Vassilev *et al* 1998; Vassilev 2006), where combination of them could yield homogeneous single-phase compositions in the amorphous form determined by

Gibbs triangle mol% of GeSe_3 , Sb_2Se_3 and ZnSe independently. Of these, the pseudo-binary $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ and the pseudo-ternary $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ compositions are found to be fairly homogeneous and amorphous in their bulk form.

This paper focusses on ZnSe composition as a modifier to the optical properties of $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ glass system, when partially incorporated with both GeSe_3 and Sb_2Se_3 to form $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ glass composition. The expected advantages obtained from modification by ZnSe incorporation is manifested in obtaining an amorphous system with different parameters for optical transmission. The interrelation of features between these optical parameters and the chemical composition could be interpreted using chemical bonding aspects, namely, the cohesive energy (CE) and the average coordination number $\langle r \rangle$.

2. Experimental

Optical study of the binaries, namely GeSe_3 , Sb_2Se_3 , ZnSe and their combinations $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ and $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$, require thin films preparation from their bulk compositions in homogeneous form. Bulk glasses of the compositions GeSe_3 and Sb_2Se_3 were prepared from high purity (99.999%) Ge, Se and Sb using the quenching technique. The constituent elements for a particular composition were sealed in well-cleaned silica ampoules under vacuum of about 1.3×10^{-4} mbar. The sealed ampoules were heated up to 900 °C in an electric

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furnace for 24 h. Through heating, ampoules were regularly shaken several times to ensure homogeneity of the compositions, then, quenched in ice water to form the bulk compositions. ZnSe composition by Aldrich Chemical Company in powder form with purity (99.99%) was taken as the raw material in preparing the pseudo-ternary composition.

The source composition of pseudo-binary $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ and pseudo-ternary $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ sample, were prepared in bulk form from the base binaries GeSe_3 – Sb_2Se_3 and GeSe_3 – Sb_2Se_3 – ZnSe , respectively. Then, the same steps of preparation mentioned above (for binary samples) were performed, except that for the ultimate reached temperature, where the samples were heated up to 1050 °C for 24 h before quenching process. Thin films of ZnSe, GeSe_3 , Sb_2Se_3 , $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ and $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ with average thickness of 500 nm were prepared on glass substrates using a single source thermal evaporator (Edwards-306E). Thermal evaporation of the bulk samples was carried out under a vacuum of 5.3×10^{-3} Pa and the substrate temperature was held constant at room temperature ≈ 298 K during the deposition process of ZnSe, GeSe_3 , Sb_2Se_3 and $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ compositions. While, thin film of $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ composition was prepared successfully by raising up the substrate temperature to about 345 K using an electrical heater during the thermal evaporation process. The prepared samples were checked out compositionally in both bulk and thin film forms using the energy dispersive X-ray (EDX) analyser attached to a scanning electron microscope (JEOL-JSM-5400) with an EDX detector of OXFORD Link ISIS. Structural phase of the prepared films were investigated using the X-ray diffraction (XRD) analysis with equipment of Bruker-D8 computerized X-ray diffractometer. The X-ray tube was operated at 45 kV and 9 mA. The diffraction patterns were collected using $\theta-2\theta$ configuration in the angle inverted $5^\circ \leq 2\theta \leq 90^\circ$ with steps of size $\Delta(2\theta) = 0.05^\circ$. Optical transmittance of thin films was measured at room temperature in the wavelength range from 200 to 1100 nm using a double beam Shimadzu UV-Vis spectrophotometer model UV-160A.

3. Results

3.1 X-ray diffraction (XRD)

X-ray diffractograms of the prepared films are shown in figure 1. For ZnSe film the diffractograms exhibit a sharp line at $2\theta = 27^\circ$, which corresponds to the ZnSe crystalline origin according to the ICDD card no. 37-1463 (cubic system). The lattice parameters of this phase are $a = b = c = 5.67$ Å and $\alpha = \beta = \gamma = 90^\circ$. This peak is surmounted on a broad hump indicating that there is a crystalline centre, i.e. the sample is a mixture of amorphous and

Figure 1. X-ray diffraction patterns for (a) ZnSe, GeSe_3 , Sb_2Se_3 and (b) $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$, $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ thin films.

minority crystalline phase, which may be attributed to the preparation from a high pure crystalline powder source. On the other hand, pure amorphous nature is observed for GeSe_3 , Sb_2Se_3 , $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ and $(\text{GeSe}_3)_{70}(\text{Sb}_2\text{Se}_3)_{10}(\text{ZnSe})_{20}$ films due to the high degree of amorphicity in the source materials as well as precise control of the substrate temperature employed during the thermal evaporation.

3.2 Determination of the optical constants

Optical transmittance, T , of the prepared films is measured in the wavelength range from 200 to 1100 nm. Figure 2 shows the spectral distribution of $T(\lambda)$ for GeSe_3 as a representative example of those under study. In this figure, the oscillating part of the curve is due to interference effect of the multiple reflections, in the film transparent region, of the incident beam inside the film, while the interference-free part or the curve tail is due to the film optical absorption. In order to determine the optical

Figure 2. Transmission spectrum, $T(\lambda)$, of GeSe₃ thin film.

constants represented by the refractive index, n , and the extinction coefficient, κ , as a function of wavelength λ ; several methods (Manifacier *et al* 1976; Swanepoel 1983; Demiryont *et al* 1986) have been developed based on creating upper and lower envelopes, T_M and T_m , respectively, of the transmission spectrum. In this work, the method proposed by Swanepoel (1983) is effectively used.

In this method, the optical constants are deduced from the fringes pattern in the transparent region, where the absorption coefficient $\alpha \cong 0$. Accordingly, the refractive index, n , is given by

$$n = [H + (H^2 - n_s^2)^{0.5}]^{0.5}, \quad (1)$$

where

$$H = \frac{4n_s^2}{(n_s^2 + 1)T_\alpha^2} - \frac{n_s^2 + 1}{2}, \quad (2)$$

n_s is the refractive index of the glass substrate ($n_s = 1.5$) and $T_\alpha = (T_M \times T_m)^{1/2}$. In the absorption region, where $\alpha \neq 0$, the value of $n(\lambda)$ is estimated by using Cauchy's formula (Jenkins and White 1985)

$$n = C + \frac{D}{\lambda^2}, \quad (3)$$

where C and D are the constants. Besides, knowing the film thickness, t , and the values of $n(\lambda)$, the corresponding absorption coefficient, $\alpha(\lambda)$, can be determined using the formula

$$X = \exp(-\alpha t), \quad (4)$$

where X is the absorbance extracted from the part of the transmission spectrum at high energy region or the interference-free part and is calculated by

$$X = \{P + [P^2 + 2QT_\alpha(1 - R_2R_3)]^{0.5}\} / Q, \quad (5)$$

Figure 3. Refractive index, n as a function of wavelength, λ for (a) ZnSe, GeSe₃, Sb₂Se₃ and (b) (GeSe₃)₈₀(Sb₂Se₃)₂₀, (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ thin films.

where

$$Q = 2T_\alpha(R_1R_2 + R_1R_3 - 2R_1R_2R_3), \quad (6)$$

$$P = (R_1 - 1)(R_2 - 1)(R_3 - 1), \quad (7)$$

$$R_1 = [(1 - n)/(1 + n)]^2, \quad (8)$$

$$R_2 = [(n - n_s)/(n + n_s)]^2, \quad (9)$$

$$R_3 = [(n_s - 1)/(n_s + 1)]^2, \quad (10)$$

and the corresponding extinction coefficient κ is given by

$$\kappa = \frac{\lambda \alpha}{4\pi}. \quad (11)$$

Now, both n and k are fully determined as a function of λ over the spectral range from 200 to 1100 nm using the above mentioned method and their spectral behaviour is shown in figures (3) and (4) for the studied films. From figure 3, it is clear that the refractive index of each composition has the tendency to increase towards lower wavelength values (higher frequencies) which is consistent with normal dispersion of matter. At higher wavelength values (lower frequencies), the refractive index tends to be a constant or static value for each

Figure 4. Extinction coefficient, κ as a function of wavelength, λ for (a) ZnSe, GeSe₃, Sb₂Se₃ and (b) (GeSe₃)₈₀(Sb₂Se₃)₂₀, (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ thin films.

composition, i.e. the films become non-dispersive at high wavelengths. Also, from figure 4, the extinction coefficient for each composition has the tendency to increase towards lower wavelengths corresponding to strong electronic absorption between valence and conduction band and tends to be a zero at longer wavelengths, where the absorption coefficient is nearly zero.

3.3 Determination of the dispersion parameters

In the normal dispersion region, the refractive index values of the films are obtained from Cauchy's formula can be fit to the Wemple–DiDomenico single oscillator dispersion model (Wemple and DiDomenico 1971; Wemple 1973)

$$n^2(h\nu) = 1 + \frac{E_d E_o}{[E_o^2 - (h\nu)^2]}, \quad (12)$$

where E_o is the oscillator energy and E_d the dispersion energy. Representing $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ and performing a

Figure 5. Linearization of the Wemple–Di Domenico model for (a) Sb₂Se₃, GeSe₃, ZnSe and (b) (GeSe₃)₈₀(Sb₂Se₃)₂₀, (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ thin films.

linear fit, the values of E_o and E_d can be found from both the slope $(E_d E_o)^{-1}$, and the intercept on the vertical axis, E_o/E_d , as shown in figure 5.

Extrapolating the linear part to intercept the ordinates gives $n_\infty^2 = 1 + (E_d / E_o)$ and hence, $n_\infty^2 = \xi_\infty$, where ξ_∞ is the dielectric constant at infinite wavelength or the static dielectric constant. The values of E_o , E_d and ξ_∞ are given

Table 1. Values of the single-oscillator energy, E_o , dispersion energy, E_d , dielectric constant at infinite wavelength, ξ_∞ , lattice dielectric constant, ξ_L , and moments, M_{-1} and M_{-3} .

Composition	E_o (eV)	E_d (eV)	ξ_∞	ξ_L	$N/m^* \times 10^{44}$ (g ⁻¹ cm ⁻³)	M_{-1}	M_{-3}
ZnSe	3.329	5.352	2.608	3.328	0.707	1.608	0.145
GeSe ₃	4.058	13.241	4.263	5.222	0.787	3.263	0.198
Sb ₂ Se ₃	3.013	23.115	8.672	12.771	3.760	7.672	0.845
(GeSe ₃) ₈₀ (Sb ₂ Se ₃) ₂₀	5.090	18.255	4.586	5.072	0.322	3.586	0.138
(GeSe ₃) ₇₀ (Sb ₂ Se ₃) ₁₀ (ZnSe) ₂₀	3.161	11.762	4.722	6.127	1.172	3.721	0.372

Figure 6. Dispersion of the refractive index, n , in the form of n^2 against the wavelength square λ^2 for (a) Sb₂Se₃, GeSe₃, ZnSe and (b) (GeSe₃)₈₀(Sb₂Se₃)₂₀, (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ thin films.

in table 1. The relation between the refractive index, n , and wavelength, λ , is given by (Kumar *et al* 2000)

$$n^2 = \xi_L - \left(\frac{e^2 N}{\pi c^2 m^*} \right) \lambda^2, \quad (13)$$

where ξ_L is the lattice high-frequency dielectric constant and N/m^* the ratio of the free carrier concentration to the electron effective mass. The dependence of n^2 on λ^2 is linear at longer wavelength as shown in figure 6. For the compositions under investigation, the lattice dielectric constant, ξ_L , can be obtained from the intercept of the extrapolation of the straight line to n^2 axis. The dispersion parameters value of ξ_L and N/m^* are also summarized in table 1.

On the basis of the single oscillator model mentioned above, the parameters, E_o and E_d are interrelated to the imaginary part of the complex dielectric constant, ξ_i , through the relation $\xi_i = 2n\kappa$. The moments, M_{-1} and M_{-3} , of the $\xi_i(h\nu)$ optical spectrum (Jenkins and White 1985)

can be derived from the relations

$$E_o^2 = M_{-1}/M_{-3}, \quad E_d^2 = M_{-1}^3/M_{-3}, \quad (14)$$

where their values are given in table 1.

3.4 Absorption coefficient

Owing to the value of the absorption coefficient, α , in the absorption region, two important parameters can be evaluated, namely, the band tail width, E_e , and the optical energy gap, E_g . In the region, where $1 \text{ cm}^{-1} < \alpha < 10^4 \text{ cm}^{-1}$, absorption takes place between valence band tail and conduction extended states and the absorption coefficient depends exponentially on the photon energy as given by the empirical relation (Urbach 1953)

$$\ln \alpha = \ln B + \left(\frac{h\nu}{E_e} \right), \quad (15)$$

Table 2. Values of the band tail width, E_e , and optical energy gap, E_g , for the prepared thin film compositions.

Composition	E_e (eV)	E_g (eV)
ZnSe	0.063 ± 0.004	3.06 ± 0.04
GeSe ₃	0.133 ± 0.001	2.05 ± 0.02
Sb ₂ Se ₃	0.068 ± 0.002	1.33 ± 0.01
(GeSe ₃) ₈₀ (Sb ₂ Se ₃) ₂₀	0.129 ± 0.002	1.87 ± 0.02
(GeSe ₃) ₇₀ (Sb ₂ Se ₃) ₁₀ (ZnSe) ₂₀	0.123 ± 0.001	1.81 ± 0.01

Figure 7. Linear dependence of $\ln \alpha$ on photon energy, $h\nu$ for (a) (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (b) (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ thin films.

where B is a constant and E_e the band tail width corresponding to the width of tails of localized states at the band edges into the energy gap and generally E_e represents the degree of disorder in an amorphous semiconductor (Olley 1973). The value of E_e is determined from the reciprocal of the slope of the relation between $\ln \alpha$ and $h\nu$ as given in figure 7 for (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ films as representative examples. The values of E_e for different film compositions are given in table 2.

For $\alpha > 10^4 \text{ cm}^{-1}$, the absorption takes place between valence and conduction band extended states and has the form (Tauc *et al* 1966; Davis and Mott 1970)

$$(\alpha h\nu)^r = A(h\nu - E_g), \quad (16)$$

where A is a constant, E_g the optical energy gap corresponding to the energy difference between the lowest energy of the conduction band and the highest energy of the valence band and r takes the values 1/2, 2, 1/3 or 2/3 for indirect allowed-, direct allowed-, indirect-forbidden and direct forbidden-transitions, respectively.

For the studied compositions, ZnSe is found to follow the variation of $(\alpha h\nu)^2$ vs $h\nu$ as observed in figure 8, showing a direct allowed band gap transition in ZnSe film. On the other hand, GeSe₃, Sb₂Se₃, (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ compositions

Figure 8. Plot of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ for ZnSe thin film. **Figure 9.** Plot of $(\alpha h\nu)^{1/2}$ as a function of the photon energy $h\nu$ for (a) GeSe₃, (b) Sb₂Se₃, (c) (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (d) (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ thin films.

are found to follow the variation of the plots $(\alpha h\nu)^{1/2}$ vs $h\nu$ as observed from figure 9, owing to indirect allowed transition. The E_g values for the studied films given in table 2 are obtained by extrapolating the straight line portion of the plot $(\alpha h\nu)^r$ vs $h\nu$ to zero absorption coefficient.

Table 3. Average coordination number, $\langle r \rangle$, cohesive energy, CE and excess of Se–Se bonds for the studied compositions.

Composition	$\langle r \rangle$ (atom ⁻¹)	CE (eV/atom)	Excess of Se–Se bonds
ZnSe	2.00	1.79	–
GeSe ₃	2.50	2.59	50
Sb ₂ Se ₃	2.40	2.26	–
(GeSe ₃) ₈₀ (Sb ₂ Se ₃) ₂₀	2.48	2.55	40
(GeSe ₃) ₇₀ (Sb ₂ Se ₃) ₁₀ (ZnSe) ₂₀	2.39	2.39	35

3.5 Average coordination number and cohesive energy

For most atoms, the coordination number, N_C , is a bonding character in the nearest neighbour region, characterizing the electronic properties of the semiconducting materials, where it follows the simple 8- N rule, where N is the number of valence electrons. For molecular glasses, the average coordination number $\langle r \rangle$, which designates the average number of covalent bonds per atom in the glassy system, can be calculated as follows, for binary alloys A_xB_{1-x} , the average coordination number is

$$\langle r \rangle = xN_A + (1-x)N_B,$$

where N_A and N_B are the coordination numbers of elements A and B, respectively. In ternary compounds, $A_\alpha B_\beta C_\gamma$, the average coordination number is (Yamaguchi 1985)

$$\langle r \rangle = \frac{\alpha N_A + \beta N_B + \gamma N_C}{\alpha + \beta + \gamma}, \quad (17)$$

where N_A , N_B and N_C are the coordination numbers of elements A, B and C, respectively and $\alpha + \beta + \gamma = 100$. The former formula can be generalized for compounds with any number of elements.

The values of average coordination number for different compositions of ZnSe, GeSe₃, Sb₂Se₃, (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ are listed in table 3. For binary compositions, the $\langle r \rangle$ value of GeSe₃ is greater than that of Sb₂Se₃, which in turn is greater than that of ZnSe. This decrease in values of $\langle r \rangle$ is attributed to the fact that the Ge atom has a coordination number ($N_C = 4$) greater than that of Sb ($N_C = 3$) and followed by Zn ($N_C = 2$). Therefore, when Se ($N_C = 2$) atom is bonded to either Ge, Sb or Zn atom, the $\langle r \rangle$ values of the resulting compositions will follow the sequence of the coordination number N_C of Ge, Sb and Zn atoms as listed in table 3. For pseudo-binary composition, (GeSe₃)₈₀(Sb₂Se₃)₂₀, it is obvious that the value of $\langle r \rangle$ lies between that of GeSe₃ and Sb₂Se₃. This decrease in the $\langle r \rangle$ value of (GeSe₃)₈₀(Sb₂Se₃)₂₀ composition as compared to that of GeSe₃, when Sb₂Se₃ is incorporated, is attributed to the presence of Sb–Se bonds coexisting with Ge–Se bonds, and since Sb atom has a coordination number ($N_C = 3$) less than that of Ge atom ($N_C = 4$), therefore, $\langle r \rangle$ is expected to decrease

for (GeSe₃)₈₀(Sb₂Se₃)₂₀ as compared to GeSe₃. For pseudo-ternary composition, (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀, the value of $\langle r \rangle$ decreases as compared to that of (GeSe₃)₈₀(Sb₂Se₃)₂₀. The incorporation of ZnSe partially at the expense of both GeSe₃ and Sb₂Se₃ results in a decreasing $\langle r \rangle$ and this is attributed to the low value of $\langle r \rangle$ for ZnSe as compared to that for GeSe₃ and Sb₂Se₃, also the coordination number of Zn ($N_C = 2$) is lower than that of Ge and Sb, therefore, $\langle r \rangle$ is expected to decrease for (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ as compared to (GeSe₃)₈₀(Sb₂Se₃)₂₀ composition.

The cohesive energy, CE, which is the average bond energy per atom of the covalently bonded amorphous composition, can be calculated using the chemical bond approach method (Fouad 1995), which assumes that the bonds are formed in sequence of decreasing heteropolar bond energies until all available covalent bonds of atoms are saturated. The bond energies $D(A-B)$ for heteronuclear bonds is calculated by using the relation

$$D(A-B) = [D(A-A)D(B-B)]^{1/2} + 1.29(\chi_A - \chi_B)^2, \quad (18)$$

proposed by Pauling (1960), where $D(A-A)$ and $D(B-B)$ are the energies of the homonuclear bonds. The $D(A-A)$ values used, in units of eV, are 1.62 for Ge, 1.29 for Sb, 1.89 for Se and 0.30 for Zn, respectively. While, the values of the electronegativities, χ , of the atoms involved are 2.01 for Ge, 2.05 for Sb, 2.55 for Se and 1.65 for Zn, respectively, and the cohesive energy, CE, values for the studied compositions are given in table 3.

For binary compositions, ZnSe, GeSe₃ and Sb₂Se₃, it is obvious that, the highest value of CE corresponds to GeSe₃ composition and the lowest one corresponds to ZnSe. This is attributed to the fact that Ge–Se bond energy value is the highest (2.12 eV), followed by the bond energy value of Sb–Se (1.88 eV) and finally the bond energy of Zn–Se (1.79 eV).

4. Discussion

In order to explain the previously obtained results of the prepared samples, one has to start with the CE values given in table 3. For the pseudo-binary composition (GeSe₃)₈₀(Sb₂Se₃)₂₀, where the Sb₂Se₃ is partially

incorporated with pure GeSe₃, it is expected that the Se atoms will saturate all available valence of Ge, owing to the highest value of Ge–Se bond energy, then followed by Sb–Se bonds and finally, the excess Se bonds are satisfied by Se–Se homopolar bonds. Therefore, the presence of Sb–Se after all Ge–Se bonds are satisfied would result in a decreasing CE value of (GeSe₃)₈₀(Sb₂Se₃)₂₀ as compared to that of GeSe₃. Similarly, for the pseudo-ternary composition (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀, as ZnSe is partially incorporated at the expense of both GeSe₃ and Sb₂Se₃, the highest value of Ge–Se bond energy are expected to saturate all available valence of Ge, followed by Sb–Se, then followed by Zn–Se and finally, the unsatisfied Se bonds must be satisfied by Se–Se homopolar bonds. Hence, the presence of Zn–Se after all Ge–Se and Sb–Se bonds are satisfied would result in a decreasing CE value of (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ as compared to that of (GeSe₃)₈₀(Sb₂Se₃)₂₀.

On the basis of the values of CE and excess of Se–Se bonds listed in table 3, the behaviour of both E_g and E_e are listed in table 2 can be interpreted for films under investigation. For films following the indirect allowed transition, it can be observed that the values of E_g decrease as the cohesive energy (low bond strength) of the film composition decreases, i.e. the conduction band edge becomes closer to the valence band and so, E_g becomes narrower as the CE decreases (Pamukchieva *et al* 1998a). For ZnSe film, the value of E_g is the highest one, although the CE value is the smallest. This could be attributed to the transition behaviour between valence and conduction bands, which follows the direct allowed transition. For the values of E_e listed in table 2, it can be observed that its values increase as the number of excess Se–Se homopolar bonds increases in the compositions. This behaviour could be attributed to the notion that as the number of excess Se–Se homopolar bond increases, isolated centres of these defects can only introduce states at or near the band edges (O'Reilly and Robertson 1986), leading to an increase in the band tail width values which is verified for GeSe₃ composition with the largest value of excess Se–Se homopolar bond and consequently, it has the largest E_e value followed by (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ in sequence. Moreover, the process by which films are deposited onto the substrate may cause formation of some structural defects, like unsatisfied bonds or probably defect homopolar bonds between the same atoms (Pamukchieva *et al* 1998b) and thus, may have some effect on the values of E_e , especially, for the stoichiometric compositions Sb₂Se₃ and ZnSe, where E_e values may be originated from the unsatisfied bonds or defect homopolar bonds between the same atoms during film deposition. Besides, comparing the values of E_e for the studied compositions, it can be seen that the E_e values for the stoichiometric compositions, Sb₂Se₃ and ZnSe are considerably smaller than that of the rest of the film compositions confirming that the E_e

values are greatly affected by the excess of Se–Se bonds as one of many reasons forming the defect states.

Finally, the behaviour of both n and κ , as shown in figures 3 and 4, can be correlated to the values of E_g given in table 2, where it can be observed that both n and κ increase as the E_g value of the film composition becomes smaller, which is in agreement with Penn's relation applicable to chalcogenide semiconductors given as (Abdel-Aziz *et al* 2001)

$$n^2 = 1 + \left(\frac{\hbar \omega_p}{E_g} \right)^2, \quad (19)$$

where ω_p is the plasma frequency determined by the ratio

$$\omega_p^2 = \frac{4\pi e^2 N}{m^*}, \quad (20)$$

where N is the free charge-carrier concentration and m^* the effective mass of the carrier. From (19) and (20), it can be seen that there are two competing values affecting the behaviour of n^2 , namely N/m^* value represented in numerator and the E_g^2 value in denominator. For binary compositions, it is clear that as the E_g value decreases, the ratio $(N/m^*)/E_g^2$ increases and consequently n^2 increases as predicted by (19). Therefore, as the E_g value of the studied composition decreases, n increases and this is exactly verified experimentally in figure 3(a). Similarly, for pseudo-binary and ternary compositions, the same behaviour applies and verified in figure 3(b).

The extinction coefficient, κ , behaviour shown in figure 4 can also be attributed to the E_g value, in a manner that the lower the E_g value, the larger the number of carriers absorbing photon energy to jump from valence to conduction band, leading to an increase in the absorption coefficient, α , and hence, κ increases as E_g of the composition decreases.

5. Conclusions

Estimation of the optical properties in the spectral range from 200 to 1100 nm of the as-deposited film compositions (GeSe₃)₈₀(Sb₂Se₃)₂₀ and (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ reveals a significant difference in their optical parameters due to ZnSe partial incorporation with the glass system (GeSe₃)₈₀(Sb₂Se₃)₂₀. The main difference in their optical parameters is observed in the optical energy gap, E_g , values where it shows a decrease in its value for (GeSe₃)₇₀(Sb₂Se₃)₁₀(ZnSe)₂₀ composition as compared with (GeSe₃)₈₀(Sb₂Se₃)₂₀ and this behaviour follows the same trend as that for the cohesive energy (CE) of the compositions, where ZnSe incorporation results in average bond strength weakening of the resulting composition. Another important parameter termed as the band tail width, E_e , which corresponds to localized states depth in the band gap, is found to decrease for (GeSe₃)₇₀(Sb₂Se₃)₁₀

$(\text{ZnSe})_{20}$ as compared with $(\text{GeSe}_3)_{80}(\text{Sb}_2\text{Se}_3)_{20}$ composition due to the decrease in the homopolar bonds, especially the excess of Se–Se bond. In other words, the smaller the number of the excess of Se–Se bonds of the composition, the smaller the value of E_g . Spectral behaviour, in the studied region, of both the refractive index, n , and the extinction coefficient, k , of the prepared films, exhibits an increase in their values as E_g of the sample decreases.

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