THEORETICAL INVESTIGATION OF THE OPTICAL PROPERTIES OF $Ge_{20}Se_{80-x}Bi_X$ THIN FILMS

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The structure of the glassy $Ge_{20}Se_{80-x}Bi_x$ glassy alloys has been examined theoretically. The experimentally observed and the theoretically calculated optical band gap E_g in the amorphous $Ge_{20}Se_{80-x}Bi_x$ system prepared in vacuum with x = 0, 4, 6, 8, 10, 12. were found to be in good agreement. Besides all these a relationship between the glass transition temperature and E_g has been established. The effective coordination number, number of constraints, number of excess Se-Se bonds , the cohesive energies of the bonds, average heat of atomization, theoretical optical band gap and the band gap and dispersion energy based on WDD model has been calculated for the $Ge_{20}Se_{80-x}Bi_x$ system.

1. Introduction

Chalcogenide glasses have been recognized as promising materials for infrared optical elements [1], infrared optical fibres [2], and for the transfer of information [3]. They have also found applications in xerography [4], switching and memory devices [5], photolithography [6], and in the fabrication of inexpensive solar cells [7] and, more recently for reversible phase change optical records [8]. The addition of an impurity has a pronounced effect on the conduction mechanism and the structure of the amorphous glass and this effect can be widely different for different impurities. It was believed that impurity has very little effect on the properties of amorphous semiconductors as each impurity can satisfy its valence requirements by adjusting its nearest neighbour environment [8]. However, it was shown that the effect of charged additivons in lone-pair semiconductors depend on whether the charged additivons equilibrate or not with valence-alternation defects [9].

The optical properties of amorphous semiconductors have been extensively studied in recent decades because of their wide range of applications and strong dependence on composition. In the present paper the effective coordination number, number of constraints, number of excess Se-Se bonds, the cohesive energies of the bonds, average heat of atomisation, optical band gap predicted theoretically; the band gap and dispersion energy based on WDD model has been calculated for the $Ge_{20}Se_{80-x}Bi_x$ system. From the chemical bond approach, interesting relationships between the average heat of atomisation, glass transition temperature, chemical bonds and the optical band gap has been reported.

2. Experimental

Bulk $Ge_{20}Se_{80-x}Bi_x$ materials (x = 0, 4, 6, 8, 10, 12) were prepared by the conventional melt quenching technique. Thin films of $Ge_{20}Se_{80-x}Bi_x$ were prepared at room temperature at 10^{-5} Torr

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vacuum using flash evaporation technique on a glass substrate of 1cm ×1cm size. The film thickness were monitored and measured by quartz crystal digital thickness monitor DTM –101 model and the film thickness was kept around 2000A°. The spectral transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were measured at normal incidence in the wavelength range 200 nm – 840 nm by means of a Hitachi double monochromator spectrophotometer model 330.

3. Results and discussion

The values of direct and indirect band gaps were calculated from the graphs of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs. $h\nu$, respectively. For indirect and direct allowed transitions the energy gaps were determined by the intercept of the extrapolations to zero absorption with the photon energy axis are taken as the values of the indirect and direct energy gaps E_g^i and E_g^d respectively. Both direct and indirect band gaps decrease with increasing bismuth content. The indirect band gap decreased from 1.48 to 1.16 eV and the direct band gap decreases from 2.14 to 1.68 eV when Bi content is increased from x = 0 to x = 12 [29].

3.1. The effective coordination number and number of constraints

The glassy networks are influenced by mechanical constraints (N_{con}) associated with the atomic bonding, and an average effective coordination number $< r_{eff} >$ which is also related to N_{con}. In a covalently bonded glassy network two types of constraints, bond-bending N^β and bond stretching N^α need to be counted [10]. For an atomic species with coordination number r, the number of constraints per atom arising from bond bending $N^\beta = 2r - 3$ and from bond stretching $N^\alpha = r/2$. Knowing the average number of constraints $N_{con} = N^\alpha + N^\beta$ and the average coordination number r for different composition of $Ge_{20}Se_{80-x}Bi_x$ (x = 0,2,4,6,8,10,12) glassy system, the effective average coordination number $< r_{eff} >$ can be calculated [11]using the formula

$$< r_{eff} > = (2/5)(N_{con} + 3) \qquad (1)$$

Table 1 shows the values of N^α, N^β, N_{con} along with $< r_{eff} >$ for the $Ge_{20}Se_{80-x}Bi_x$ glassy system. In our system the average number of constraints per atom N_{con} exceeds the number of degrees of freedom $N_d = 3$, the heteropolar- bonded Bi concentration is found to be less than one. Thus the non-monotonic behaviour of various properties observed in these glasses is explained in terms of an interplay between "mechanical" and "chemical" forces which affect the structure of the glass as a function of $< r_{eff} >$.

According to Thorpe [12] in the range of the glass-forming compositions, the system should contain rigid and floppy regions. The $Ge_{20}Se_{80}$ composition corresponding to an average coordination of m = 2.4 is a percolation threshold at which a transition from floppy glass to a rigid glass take place. This means when m= 2.4 corresponding to the mechanical percolation threshold.

According to Zachariasen [13], atoms combine more with atoms of different kinds than with the same kind. This condition is equivalent to assuming the maximum amount of chemical ordering possible. This means that bonds between like atoms will only occur if there is an excess of a certain type of atom, so that it is not possible to satisfy its valence requirements by bonding it to atoms of different kinds alone, so bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated.

3.2. Chemical bond determination

The possible bond distribution at various compositions using chemically ordered network (CON) model [14]. The model assumes that: (a) atoms combine more favourably with atoms of different kinds than with the same and (b) bonds are formed in the sequence of bond energies (Table 1) [15].

Table 1.

Composition	N^α	N^β	N_{con}	$<r_{eff}>$
$Ge_{20}Se_{80}$	1.2	1.8	3	2.4
$Ge_{20}Se_{76}Bi_4$	1.22	1.88	3.1	2.44
$Ge_{20}Se_{74}Bi_6$	1.23	1.92	3.15	2.46
$Ge_{20}Se_{72}Bi_8$	1.24	1.96	3.2	2.48
$Ge_{20}Se_{70}Bi_{10}$	1.25	2.0	3.25	2.5
$Ge_{20}Se_{68}Bi_{12}$	1.26	2.04	3.3	2.52

Also, we apply the well known 8-N rule to all the chemical species. As Bi replaces Se, the number of Bi-Se bonds increase at the expense of Se-Se. The bond energies D(A-B) for heteronuclear bonds have been calculated by using the relation [16].

$$D(A-B) = [D(A-A)\ D(B-B)]^{1/2} + 30(\chi_a - \chi_b)^2 \qquad (2)$$

where, D(A-A) and D(B-B) are the energies of the homonuclear bonds and χ_a and χ_b are the electronegativity values of the atoms involved. The bonds formed in $Ge_{20}Se_{80-x}Bi_x$ system and their energies are given in Table 2 and electronegativity for Bi = 2.0, Se = 2.55 and of Ge = 2.01. The assumption mentioned above can be applied in its simplest form to memory materials, where there is no ambiguity about the formal order in which the bonds are formed [17]. The Bi atoms bond strongly to Se, the Se atoms also fill the available valences of the Ge atoms. After all these bonds are formed, there are still unsatisfied Se valences "excess bonds" which must be satisfied by the formation of Se-Se bonds. If we further assume that, the bond energies are additive, we can estimate the cohesive energy (C.E), i.e., the stabilization energy per atom for an infinitely large cluster of the material. The number of excess bonds and the C.E. of $Ge_{20}Se_{80-x}Bi_x$ system are listed in Table 2.

Table 2.

Composition	Excess of Se-Se bonds	Cohesive energy(eV/atom)	Bond	Bond energy (kcal/mol)
$Ge_{20}Se_{80}$	80	2.489	Ge-Se	49.5
$Ge_{20}Se_{76}Bi_4$	60	2.510	Se-Se	44
$Ge_{20}Se_{74}Bi_6$	50	2.521	Se-Bi	40.7
$Ge_{20}Se_{72}Bi_8$	40	2.532		
$Ge_{20}Se_{70}Bi_{10}$	30	2.542		
$Ge_{20}Se_{68}Bi_{12}$	20	2.553		

It is found that the density of Ge-Se-Bi system is higher than that of $Ge_{20}Se_{80}$ and that the partial substitution of Bi atoms for Se atoms leads to a "densification" of the structure system as indicated in Table 3. Moreover it seems that this is also connected with a "compositional shift towards the Se rich region".

3.3. The correlation between glass transition temperature T_g and band gap E_g

The T_g-band gap correlation is an essential feature of any comprehensive theory relating structure and properties for amorphous materials [18]. The origins of the T_g vs. E_g

Correlation are based only upon a knowledge of E_g and coordination number r. For E_g we have used the quantity E_{04}, defined as the photon energy at which the optical absorption coefficient has a value of 10^4 cm^{-1}. The obtained values of E_{04} are listed in Table 3 in comparison with T_g for the $Ge_{20}Se_{80-x}Bi_x$ system.

Table 3.

Composition	T_g (K)	density(gmcm^{-3})	E_{04} (eV)
$Ge_{20}Se_{80}$	429.1	4.912	1.96
$Ge_{20}Se_{76}Bi_4$	473.2	5.1116	1.79
$Ge_{20}Se_{74}Bi_6$	488.9	5.2114	1.77
$Ge_{20}Se_{72}Bi_8$	489.5	5.3112	1.74
$Ge_{20}Se_{70}Bi_{10}$	490.9	5.411	1.65
$Ge_{20}Se_{68}Bi_{12}$	471.4	5.5108	1.61

Table 4.

Element	Bi	Se	Ge
Eg (eV)	0.2275	1.95	0.95
Density (g/cm^{-3})	9.8	4.79	5.0
m	3	2	4
H_s (kJ/mol)	207.36	226.4	373.8
Electronegativity	2.02	2.55	2.01

3.4. Theoretical prediction of the band gap

It is found that the variation of energy gap with composition in amorphous alloys can be described by assuming random band network using the Shimakawa relation

$$E_{g(AB)}(Y) = YE_{g(A)} + (1-Y)E_{g(B)} \tag{3}$$

where Y is the volume fraction of element A, $E_{g(A)}$ and $E_{g(B)}$ are the optical gaps for A and B elements, respectively. The conversion from atomic composition (at%) or molecular composition (mol %) to volume fraction Y is made using atomic or molecular mass and density of both Bi and Se. Calculation based on a random network with experimental results for optical gap for $Ge_{20}Se_{80-x}Bi_x$ films are shown in Table 5. In conclusion the optical gap E_o for $Ge_{20}Se_{80-x}Bi_x$ determined by volume fraction and the optical gap E_g calculated using the experimental data, lead to the conjecture that a modified virtual crystal approach for mixed crystals is acceptable for an amorphous system.

Table 5.

Composition	H_s (KJ/mol)	r	H_s/r	$E_{g, th}$ (eV)
$Ge_{20}Se_{80}$	255.88	2.4	106.616	1.769
$Ge_{20}Se_{76}Bi_4$	255.48	2.44	104.706	1.68
$Ge_{20}Se_{74}Bi_6$	254.74	2.46	103.5516	1.64
$Ge_{20}Se_{72}Bi_8$	254.36	2.48	102.563	1.59
$Ge_{20}Se_{70}Bi_{10}$	253.97	2.5	101.5904	1.55
$Ge_{20}Se_{68}Bi_{12}$	253.95	2.52	100.7746	1.51

The experimentally obtained optical band gap [29] and the theoretically calculated values for $Ge_{20}Se_{80-x}Bi_x$ both were found to decrease with increasing Bi content. Since optical absorption depends on short range order in the amorphous state and defects associated with it, the decrease in optical gap may be explained on the basis of the "density of states" model in amorphous solids proposed by Davis and Mott. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous state [19].

3.5. The average heat of atomization

According to Pauling [20] the heat of atomization H_s(A-B) at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of the heat of formation ΔH and the average of the atomization H_s^A and H_s^B that corresponds to the average non-polar bond energy of the two atoms [21]

$$H_s(A\text{-}B) = \Delta H + \tfrac{1}{2}(H_s^A + H_s^B) \tag{4}$$

The first term in equation (4) is proportional to the square of the difference χ_A and χ_B of the two atoms.

$$\Delta H \propto (\chi_A - \chi_B)^2 \tag{5}$$

In the few materials for which it is known, the amount of heat of formation ΔH is about 10% of the heat of atomization and is therefore neglected. Hence

$$H_s(A\text{-}B) = \tfrac{1}{2}(H_s^A + H_s^B) \tag{6}$$

The results of H_s for $Ge_{20}Se_{80-x}Bi_x$ films using the values of H_s for Ge, Se, Bi (given in Table 4) are listed in Table 5. In order to correlate H_s with E_g in non-crystalline solids, it is reasonable to use the average coordination number r instead of the isostructure of crystalline semiconductors.

The data listed in Table 5 reveal that the addition of Bi leads to a change in the considered properties. The increase of Bi leads to the decrease of $E_{g,th}$ and H_s/r whereas r increases. The various bond energies of the expected bonds in the system are listed in Table 2. If there is a linear dependence between the bond strength and the average band gap, and if one allows their superposition to describe the compounds, then the addition of Bi to $Ge_{20}Se_{80}$ matrix will affect the average band gap. By adding Bi to $Ge_{20}Se_{80}$ the average band strength of the compound decreases, and hence E_g will decrease. In order to emphasize the relationship between E_g and the average band strength more clearly, E_g is compared with H_s/r which is the average single- bond energy in the alloy. One observes that E_g as well as H_s/r decreases with increasing Bi content, which suggests that one of the main factors determining E_g is the average single bond in the alloy [22].

3.6. Average energy gap and dispersion energy from WDD model

According to the single oscillator model proposed by Wemple and DiDomenico [23] and Wemple [24] the optical data could be described to a very good approximation by the following formula

$$n^2 = (E_d E_o)/(E_o^2 - E^2) \tag{7}$$

where, n is the refractive index, E_o is the average energy gap, E is the photon energy and E_d is the so – called dispersion energy. The latter quantity measures the average strength of the interband optical transitions. Plotting $(n^2 - 1)^{-1}$ against $(h\nu)^2$ allows the determination of the oscillator parameters by fitting a straight line to the points. The value of E_o and E_d can be directly determined from the slope $(E_o E_d)^{-1}$ and the intercept on the vertical axis, (E_d / E_o). The values obtained for the dispersion parameters, E_o and E_d are tabulated in Table 6. As it was found by Tanaka [25], the first approximate value of the optical band gap, E_g, is also derived from the Wemple – DiDomenico dispersion relationship, according to the expression $E_{gopt} \cong E_o / 2$. The values so obtained from this equation are in almost agreement with the values obtained from the Tauc's extrapolation using the value of the absorption coefficient from the T and R measurements.

Table 6.

Composition	E_o	E_d
$Ge_{20}Se_{76}Bi_4$	1.54	36.47
$Ge_{20}Se_{74}Bi_6$	3.45	8.52
$Ge_{20}Se_{72}Bi_8$	3.64	4.62
$Ge_{20}Se_{70}Bi_{10}$	4.62	4.25
$Ge_{20}Se_{68}Bi_{12}$	5.17	4.19

On the other hand, an important achievement of the WDD model is that it relates the dispersion energy E_d to other physical parameters of the material through the following empirical relationship.

$$E_d = \beta N_c Z_a N_e \qquad (8)$$

where N_e is the effective No. of valence electrons per anion, N_c is the effective coordination No. of the cation nearest neighbour to the anion, Z_a is the formal chemical valency of the anion, β is a two valued constant with either an ionic or a constant value ($\beta_i = 0.26 \pm 0.03$ eV and $\beta_c = 0.37 \pm 0.04$ eV) [26]. It is observed that the variation in the transition strength E_d results primarily from changes in the average nearest neighbour coordination number. It is proposed that the layer – layer and chain-chain bonding, increase the effective coordination number. The primary optical effect is a reduction in the oscillator strength of the lone-pair to conduction band transitions causing a corresponding decrease in E_d. It is observed here that the increase in Bi content increases the coordination number and decreases the energy gap E_g. According to the WDD model the refractive index becomes dependent on the dispersion energy E_d as the photon energy approaches zero. In this case E_d is mainly affected by the nearest neighbours, i.e. by the short range order and remains unaffected by medium range order. At wavelengths in near infrared region (toward $\lambda = 820$ nm) the short range order is dominant and therefore, no feature related to the medium range order is developed in the compositional dependence of n [27]. Shifting to shorter wavelengths the medium range order in the glasses becomes a decisive factor, which can affect the shape of refractive index n and the dependence of extinction coefficient on $<r_{eff}>$.

4. Conclusions

The optical gap reflects the separation of the top of the filled lone pair p-states of the valence band from the bottom of the antibonding states in the conduction band. It is, therefore, interesting to relate the optical band gap with the chemical bond energy. For this purpose we used two parameters that specify the bonding, the average heat of atomization and the average coordination number. Following conclusions were drawn from the present analysis:

- The optical band gap was found to decrease with the increasing Bi content.
- The average coordination number r, increases with increase of Bi content which gives an indication that the number of constraints increases, hence the value of optical band gap will strongly depend on H_s
- The density of $Ge_{20}Se_{80-x}Bi_x$ system is higher than that of $Ge_{20}Se_{80}$ and increases with increase in x thus leading to the densification of the system.
- E_{04} defined as photon energy at which optical absorption coefficient has a value of 10^4 cm^{-1} is found to decrease with increase in x and increase in the value of T_g.
- The increase of Bi content leads to decrease of E_g and H_s/r. The average heat of atomization H_s which is a measure of the cohesive energy and represents the relative bond strength. Considering a linear dependence between the bond strength and the average band gap, we conclude that the Bi addition to the $Ge_{20}Se_{80}$ causes a decrease in the average bond strength thereby reducing the optical band gap.

It is observed that the variation in the transition strength E_d results from the change in the average nearest neighbour coordination number. The layer-layer and chain-chain bonding increase the effective coordination number r. The primary optical effect is the reduction in the oscillator strength of the lone-pair to conduction band transitions causing the decrease in E_d. Thus the increase in Bi content leads to the increase in r and decrease in E_g [28].

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