Theoretical analysis of physical parameters of group VI amorphous semiconductors

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Physical properties and their correlation with optical parameters for *a*-$Ga_{20}Se_{80-x}Bi_x$ (x = 0, 5, 10, 15, 20) glassy alloys were discussed. It was found that increase in density accounts for the concurrent increase in refractive index values with addition of Bi. Number of atoms per unit volume (N) was calculated and was found to increase with Bi concentration. This increase in *N* accounts for the subsequent decrease in optical band gap. A linear relation was found between cohesive energy and optical band gap (calculated experimentally and theoretically). Decrease of electro-negativity also supported the decrease of optical band gap. The relationship between the optical band gap and chemical composition in *a*-Ga-Se-Bi glasses was also examined. Mean bond energy and glass transition temperature exhibited relatively sharp maxima at chemical threshold and thereby shows the stability of the system.

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1. Introduction

The investigation of chalcogenide glasses has aroused enormous interest in last few decades because of both fundamental interest and manifold potential applications. These materials are good candidates for functional nano devices and solid state devices [1-6].

Besides the wide commercial and device applications in switching, memory, solar technologies, xerography etc., selenium (Se) also exhibits a unique property of reversible transformation [7]. This property makes it very useful in optical memory devices. But in pure state, Se has disadvantage of its short lifetime and low sensitivity. Certain additives like gallium (Ga) may be used to overcome this problem. Pure amorphous selenium films also exhibit optical absorption and photosensitivity in the visible range, while it's alloys exhibit the same properties over a larger wavelength range [8]. For example, Ga-Se has become an attractive material as a substrate because of its good lattice matching with the solid solutions of the III-VI compound semiconductors, very useful for the fabrication of solid-state devices [9]. Moreover, gallium readily alloys with many metals and has been used as a component of low-melting-point alloys.

The addition of a third element is quite useful to understand the transport mechanism in chalcogenide glasses. Bi addition to Ga-Se system increases the chemical durability and leads the system towards the intermediate region [10]. The replacement of Se with Bi in host matrix leads to a decrease in optical band gap and increased transparency in NIR region. Earlier experiments have shown that the addition of Bi in Se system decreases the optical band gap for n-type conducting samples, resulting in an enhancement of photoconduction for n-type samples [11-12].

Optical parameters of $Ga_{20}Se_{80-x}Bi_x$ (x = 0, 5, 10, 15, 20) have already been discussed in detail [13]. In the present manuscript correlation between physical parameters *viz.* density, compactness, molar volume, cohesive energy, average heat of atomization and optical parameters (refractive index and optical band gap) were investigated for $Ga_{20}Se_{80-x}Bi_x$ glassy alloys. The variations of these parameters were shown in terms of composition or equivalently with average coordination number ($< r >$). Correlation between glass transition temperature and mean bond energy was studied by using Tichy – Ticha approach [14, 15].

2. Experimental details

Bulk samples of the $Ga_{20}Se_{80-x}Bi_x$ (x = 0, 5, 10, 15, 20) chalcogenide system were prepared using melt quench technique. The materials (Ga, Se and Bi) (5N pure) were crushed to powder form and then sealed in evacuated (~ 10^{-4} Pa) quartz ampoules, each of 4g batch, weighed according to their atomic weight percentage. The sealed ampoules were kept inside a furnace where the temperature was increased up to 1000 ^{o}C gradually at a heating rate of 2-3 ^{o}C/min. The ampoules were rocked for 24 hours at the highest temperature to make the melt homogeneous. The quenching was done in ice cold water. The thin films of $Ga_{20}Se_{80-x}Bi_x$ glassy alloys were prepared by thermal evaporation technique (Vacuum coating unit HINDHIVAC 12A4D Model), keeping the substrate at room temperature, and at a base pressure of 10^{-3} mbar. Amorphous nature of the bulk samples and thin films was confirmed by XRD technique. No prominent peak was observed in the bulk as well as in thin films.

3. Result and discussion

3.1 Nearest neighbor coordination

The average coordination number $(< r >)$ in ternary system, using the concept of nearest-neighbor coordination [16], is defined as

$$< r > = \frac{aX + bY + cZ}{a + b + c} \qquad (1)$$

where, in our investigating system, a, b *and* c are the % at. wt. of Ga, Se and Bi respectively and $X = 3$, $Y = 2$ and $Z = 3$ are their respective coordination numbers. The calculated values of $< r >$ for $Ga_{20}Se_{80-x}Bi_x$ are listed in table 1. In chalcogenide glasses covalent network constrained by bond bending and bond stretching forces possesses a critical connectivity threshold at $< r > = 2.4$. According to constraint model and development theories [17-18], equating the number of operative constraints to the number of degree of freedom, $< r >$ of the most stable glass is ≈ 2.4. From table 1, it is clear that with $< r > = 2.4$, $Ga_{20}Se_{60}Bi_{20}$ composition glass network lies at the threshold of the mode change *i.e.* floppy ↔ intermediate region and therefore, it is theoretically the most stable composition among all the compositions under investigation.

3.2 Density, compactness and molar volume

For the system under investigation, density was measured by the Archimedes method using double distilled water as a reference liquid, which has a density of 1.0 g/cc at 20 °C. The density was calculated from the formula

$$\rho = \left[\frac{w_1}{w_1 - w_2} \right] \rho_{water} \qquad (2)$$

where w_1 and w_2 are the weights of the sample in air and in the reference liquid respectively. Theoretically, density was also deduced by Fayek *et.al* [19]

$$\rho = (\sum x_i d_i)^{-1} \qquad (3)$$

where x_i is the fraction of weight and d_i is the density of the i^{th} structural unit. Experimentally and theoretically calculated density values are reported in table 1. It is clear from the table that measured density increases with the addition of Bi content to the *a*-Ga-Se alloy. This increase in physical density of the system also attributes to the increase in refractive index of these thin films (table 1). This increase in refractive index is due to the increase in polarizability associated with the larger Bi atom. Larger the atomic radius of the atom, larger will be its polarizability and consequently, according to Lorentz-Lorentz relation, $\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\varepsilon_0} \sum_i N_i \alpha_{pi}$, larger will be the refractive index [20], where ε_0 is the vacuum permittivity, N_i is the number of polarizable units of type i per unit volume with polarizability α_{pi}. The atomic radius of Se is 1.16 Å and Bi is 1.46 Å.

The compactness (δ) was calculated from the relation [21]

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}} \qquad (4)$$

where c_i is the atomic fraction, A_i is the atomic weight, ρ_i is the atomic density of the i^{th} element of the glass and ρ is the measured density of the glass. Thus, δ is a measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of a given solid [15]. Consequently, it is more sensitive to changes in the structure of the glass network as compared to mean atomic volume. Table 1 summarizes the density of the investigated compositions and corresponding compactness.

With the addition of Bi to Ga-Se alloy, compactness decreases. It can be associated with atomic arrangements that become less tightly bound with comparatively longer bond lengths. When Bi enters in Ga-Se system, it makes bond with Se, new bonds are formed with longer bond length. Since, the bond length of Ga-Se is 2.324 Å and those of Bi-Se is 2.704 Å, this further result in increase in mean atomic volume of the network and hence decrease in compactness value.

The molar volume (V_m) was determined from the density data by the equation

$$V_m = \frac{1}{\rho} \sum_i x_i M_i \qquad (5)$$

where M_i is the molecular weight of the i^{th} component and x_i is the atomic percentage of the same element in the sample. The variation of molar volume with composition is also tabulated in table 1. In chalcogenide glasses, the valence band originates from lone pair electron states whereas the conduction band arises from anti-bonding states. The energy of the conduction band edge is determined by the number of atoms per unit volume (N) and is given by,

$$N = < r > (\frac{N_A}{V_m}) \qquad (6)$$

where, N_A is the Avogadro's number and V_m is the molar volume [19]. An increase in N, leads to decrease in the energy of conduction band edge which corresponds to decrease in optical gap subsequently [22]. The variation of optical band gap also follows the same trend with Bi concentration [13]. This variation of N is given in table 1 and is also plotted in Fig. 1 against the optical band gap.

Table 1. Average coordination number $(< r >)$*, density* (ρ)*, refractive index (n), molar mass (M), molar volume* (V_m)*, No. of atoms per unit volume* (N)*, compactness* (δ) *for* $Ga_{20}Se_{80-x}Bi_x$ *(x = 0, 5, 10, 15, 20) system.*

x	$< r >$	ρ_{th}, ρ_{exp} (g/cm^3)	n	M (g/mol)	V_m (cm^3/mol)	N x10^{23} (cm^{-3})	δ
0	2.2	5.08, 5.07	1.6	77.11	15.2	0.871	0.0171
5	2.25	5.22, 5.39	1.67	83.61	15.51	0.873	0.0116
10	2.3	5.37, 5.69	1.68	90.11	15.83	0.875	0.0083
15	2.35	5.52, 6.00	1.74	96.61	16.01	0.878	0.0050
20	2.4	5.68, 6.28	2.33	103.11	16.42	0.880	0.0010

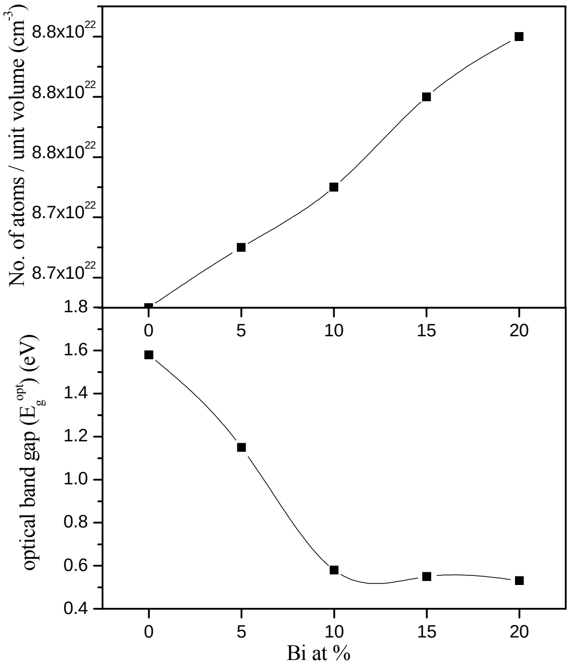

Fig. 1. Variation of number of atoms per unit volume (N) and optical band gap (E_g^{opt}) *with Bi at % for* $Ga_{20}Se_{80-x}Bi_x$ *(x = 0, 5, 10, 15, 20) system.*

3.3 Relation between glass forming ability and lone pair electrons of the structure

Most of the substances which can solidify in the vitreous state are found to possess structural 'bridges', that give rise to tri-dimensional, bi-dimensional or linear heteropolymeric formations. In most glasses, the bridges are form by elements of group VI and VII. Se atoms in glass structures have two pairs of lone-pair electrons. The existence of bridging atoms with lone-pair electrons can decrease the strain forces caused by the formation of amorphous materials. This can be further understood in terms of the view point proposed by Pauling [23], that the chemical bonds, with lone-pair electrons, have a character of flexibility. Thus, increasing the number of lone-pair electrons decreases the strain energy in a system. Hence, structures with large numbers of lone-pair electrons favor glass formation. The lone pairs of electrons are calculated by

$$L = V - < r > \qquad (7)$$

where, V is the number of valance electrons which is equal to unshared lone-pair electrons, $< r >$ is the coordination number and L is the number of lone pair electrons. The results are listed in table 2.

Table 2. Average coordination number $(< r >)$*, Valence electrons (V) and lone pair (L) electrons with Bi at. % for* $Ga_{20}Se_{80-x}Bi_x$ *(x = 0, 5, 10, 15, 20) system.*

x	$< r >$	V	$L = V - < r >$
0	2.2	5.4	3.2
5	2.25	5.35	3.1
10	2.3	5.3	3.0
15	2.35	5.25	2.9
20	2.4	5.20	2.8

It is seen from Table 2 that the number of lone-pair electrons decreases continuously with the increase of Bi content in the system. This is caused by the interaction between the Bi and the lone pair electrons of a bridging Se atom. Liang [24] correlated the ability of a chalcogenide system to retain its vitreous state, with the number of lone pair electrons. For a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1. So, looking at the tabulated values, it can be said that our system is in well defined range, as required for vitreous state according to Liang's theory.

3.4 Correlation between cohesive energy (CE) and optical gap (E_g^{opt})

Explanation of optical behavior of *a*-Ga-Se-Bi glasses is given in terms of cohesive energy using the chemical bond approach (CBA) method [25]. The cohesive energy is the stabilization energy of an infinitely large cluster of material per atom and also reflects the average bond strength. At the same time it also allows to determine the number of possible bonds and their type *i.e.* heteropolar or homopolar. According to CBA, (*i*) atom combine more easily with atoms of different type rather than the same type, (*ii*) the heteropolar bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied, (*iii*) each constituent atom is coordinated by 8-*N* atoms, where *N* is the number of outer shell electrons. In CBA, dangling bonds and other valence defects are neglected. Also vander Waals interactions are neglected, which can provide a means for further stabilization by the formation of much weaker links than regular covalent bonds. Based on CBA, the bond energies are assumed to be additive. Thus the cohesive energies were calculated by summing the bond energies over all bonds expected in the material. In *a*-Ga-Se-Bi system, amount of Ga is fixed, as metallic heteropolar bonds are not formed in amorphous system. Hence, number of the Ga-Se bond, with highest bond energy, will be fixed. As such the decrease in the average bond energy, with the increase in Bi content, can be attributed to the numbers of heteropolar Bi-Se and homopolar Se-Se bonds. Also the decrease in band gap can be attributed to the formation of heteropolar Bi-Se bonds (bond energy = 40.7 kcal/mole) at the expense of homopolar Se-Se bonds (bond energy = 44 kcal/mole) which results in the overall decrease in cohesive energy of the system.

The Ga-Se and Se-Bi bond energies are calculated by the formulation proposed by Pauling [23],

$$D(A-B)=[D(A-A).D(B-B)]^{1/2}+30(\chi_A-\chi_B)^2 \tag{8}$$

where, $D(A-A)$ and $D(B-B)$ are the homonuclear bond energies of atoms *A* and *B* respectively and χ_A and χ_B are their respective electronegativities. Homonuclear bond energies used to calculate heteronuclear energies are tabulated in table 4. Electronegativity values are taken from Pauling scale *i.e.* $\chi_{Ga}=1.81$, $\chi_{Se}=2.55$ and $\chi_{Bi}=2.02$ [23]. Calculated values of *CE* along with chemical bond distribution for all compositions are tabulated in table 3.

Table 3. Values of electronegativity (χ), theoretical band gap (E_g^{th}), distribution of chemical bonds, cohesive energy and optical band gap (E_g^{opt}) for $Ga_{20}Se_{80-x}Bi_x$ (x = 0, 5, 10, 15, 20) system.

X	χ	E_g^{th} (eV)	Distribution of chemical bonds			Cohesive Energy (kcal/mol)	E_g^{opt} (eV)
			$Ga-Se$	$Bi-Se$	$Se-Se$		
0	2.38	1.97	0.375	-	0.625	46.56	1.58
5	2.35	1.86	0.4	0.1	0.5	46.40	1.15
10	2.32	1.75	0.43	0.21	0.36	46.22	0.58
15	2.29	1.64	0.461	0.346	0.193	45.96	0.55
20	2.27	1.53	0.5	0.5	-	45.76	0.53

From Table 3, this is found that *CE* of these glassy alloys decreases with increasing Bi content. Therefore, it can be concluded that the decrease of optical band gap with increasing Bi content may also be due to reduction of average stabilization energy with addition of Bi content. The decrease of *CE* implies lower bonding strength. The optical band gap is a bond sensitive property [26]. So the decrease of *CE* accounts for the gradual decrease of optical band gap with the addition of Bi at the expense of Se. This behavior is also consistent with theoretical band gap.

It was found that the variation in the theoretical values of the energy gap (E_g^{th}) with composition for ternary alloys can be described by the following relation [27],

$$E_g^{th}(ABC)=aE_g(A)+bE_g(B)+cE_g(C) \tag{9}$$

where *a*, *b* and *c* are the volume fraction and $E_g(A)$, $E_g(B)$ and $E_g(C)$ are optical gaps of *A*, *B* and *C* elements respectively. The conversion from volume fraction to atomic percentage is made by using atomic weights and densities. The values of E_g^{th} for all the compositions are also tabulated in table 3 and are plotted in Fig. 2, as a function of Bi at. % and also in comparison with E_g^{opt}. It can be concluded that decrease of E_g^{th} and E_g^{opt} with increasing Bi content may be due to decrease of average stabilization energy and decrease of electronegativity of the system, calculated from Sanderson's principle [28]; $S_E = [\Pi S_{E,Z}^{x}]^{(\Sigma x)^{-1}}$, where x is at. % and $S_{E,Z}$ is the electronegativity of individual atom. According to this principle, electronegativity of the alloy is the geometric mean of electronegativity of its constituent elements. It is evident from the table 3 and inset of Fig. 2 that the electronegativity decreases as the optical band gap decreases.

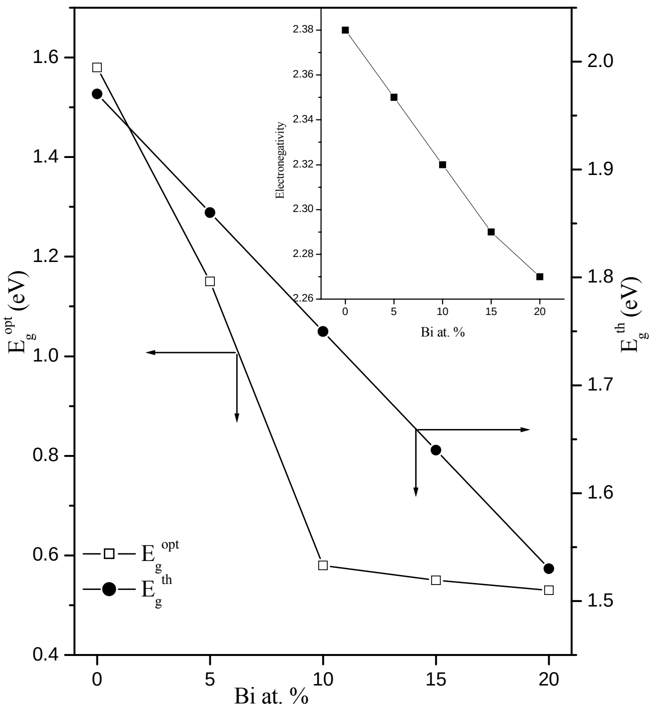

Fig. 2. Variation of E_g^{opt} and E_g^{th} with Bi at. %. Inset of figure shows the variation of electronegativity with Bi at % for Ga$_{20}$Se$_{80\text{-}x}$Bi$_x$ (x = 0, 5, 10, 15, 20) system.

3.5 Relation between E_{04}, $\overline{H_s}$ and $< r >$

E_{04} is an arbitrary quantity defined as photon energy at which optical absorption coefficient has the value of 10^4 cm^{-1}. The photon energy at $\alpha = 10^4$ cm^{-1} is about 0.2 eV larger than the optical band gap (E_g^{opt}) [29]. The obtained E_{04} values are given in table 4. It is interesting to relate E_{04} with average single bond energy, ($\overline{H_s}/< r >$). To correlate these values with average single bond energy for Ga$_{20}$Se$_{80\text{-}x}$Bi$_x$ system, average heat of atomization was calculated.

According to Pauling [23], the heat of atomization $\overline{H_s}(A-B)$ at standard temperature and pressure for a binary semiconductor formed from atoms A and B is given as

$$\overline{H_s}(A-B) = \Delta H + \frac{1}{2}\left(\overline{H_s^A} + \overline{H_s^B}\right) \tag{10}$$

where, $\Delta H \;\alpha\; (\chi_A - \chi_B)^2$ and χ_A and χ_B are their respective electronegativities. To extend this idea for ternary and higher order semiconductor compounds [27], the average heat of atomization $\overline{H}_s$ (kcal/g-atom) for $A_\alpha B_\beta C_\gamma$ compound is given by

$$\overline{H}_s = \frac{\alpha H_s^A + \beta H_s^B + \gamma H_s^C}{\alpha + \beta + \gamma} \tag{11}$$

where α, β and γ are the ratios of A, B and C respectively. In the present ternary glassy system, the average heat of atomization is calculated by equation (11) using the values of heat of atomization, 66.05, 49.4 and 49.1 in kcal/g-atom for Ga, Se and Bi respectively. Average heat of atomization (kcal/g-atom) and average single bond energy are given in table 4.

In chalcogenide glasses containing a high concentration of a group VI element (Se), the valance band $(\sigma - bonding)$ originates from lone pair (LP) electron states whereas the conduction band arises from antibonding (σ^*) states [30]. It is therefore interesting to relate the optical gap with the average single bond energy. According to Aigrain *et.al.* [31], there exists a linear correlation between the energy gap and the average heat of atomization, and can be expressed by $\Delta E = a(H - b)$, where a and b are the characteristic constants. It is suggested that the average heat of atomization is a measure of the cohesive energy and represents the relative bond strength, which in turn are correlated with the energy gap of semiconductors. Decrease in bond strength causes a less splitting between σ and σ^* which results in decrease in band gap.

Table 4. Values of R, $<E>$, T_g, $\overline{H_s}$, $\overline{H_s}/<r>$ *and* E_{04} *for* $Ga_{20}Se_{80-x}Bi_x$ *(x = 0, 5, 10, 15, 20) system and bond energies of their respective bonds.*

x	R	$<E>$ (kcal/mol)	T_g (K)	$\overline{H_s}$ (kcal/g-atom)	$\overline{Hs}/<r>$ (kcal/g-atom)	E_{04} (eV)	*Bonds*	*Bond Energy* (kcal/mol) (* from ref.[37])
0	2.27	2.20	405.5	52.73	23.96	1.78	$Ga-Ga^*$	26.9
5	2.00	2.23	413.6	52.71	23.42	1.35	$Se-Se^*$	44.00
10	1.55	2.26	422.9	52.70	22.91	0.78	$Bi-Bi^*$	25.0
15	1.24	2.32	441.6	52.68	22.41	0.75	$Se-Bi$	40.7
20	1	2.38	460.9	52.67	21.94	0.73	$Ga-Se$	50.83

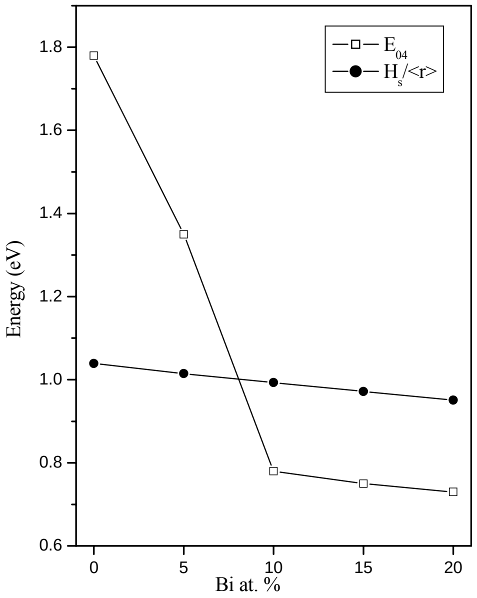

Fig. 3. Variation of E_{04} *and* $\overline{H_s}/<r>$ *with composition in Ga-Se-Bi glassy system.*

Fig. 3 represents the variation of E_{04} and $\overline{H_s}/<r>$ with composition in Ga-Se-Bi glassy system. It is clear from the figure that there is decrease in E_{04} with the addition of Bi. However, the average heat of atomization shows negligible deceases with Bi addition. For over constrained materials, with higher connectivity *i.e.* $3 \le <r> \le 4$, E_{04} depends more strongly on $\overline{H}_s$ than for glasses with lower connectivity, *i.e.* $2 \le <r> \le 3$ [30]. In our case, the value of $<r>$ varies from $2.2-2.4$, which can be correlated with low connectivity glasses. This further suggests that the parameter $\overline{H}_s/<r>$ is almost constant with composition and has a very negligible effect on E_{04}. Similar results have also been reported for Te-As-Ge-Si and As-Sb-Se-Te systems [32, 33].

3.6 Correlation between mean bond energy and glass transition temperature

Glass transition temperature represents the temperature, above which an amorphous matrix can attain various structural configurations and below which the matrix is frozen into a structure which cannot easily change to another structure. Significant attention has been devoted to predict T_g of chalcogenide based glasses. Tichy and Ticha [34] firstly recognize that in chemically ordered system, glass transition temperature should not be only related to connectedness of the network ($<r>$) but there should also be an excellent empirical correlation between the T_g and overall mean bond energy. In *a*-Ga-Se-Bi system, there is a significant difference in the bonding energies of heteropolar bonds *i.e.* Ga-Se and Bi-Se and homopolar bonds *i.e.* Se-Se bonds. Thus a chemical ordered network is expected.

Therefore, it is reasonable to assume that T_g must be related to the magnitude of the cohesive forces within the network, since these forces must overcome to allow the atom movement. It is thus not surprising that predictions of T_g are generally based on simple models in which it is assumed that T_g is proportional to another material parameter (such as mean bond energy) which strongly depends on the cohesive forces or rigidity of the network (here chemical bond ordering model is assumed). Based on this assumption, mean bond energy is given by

$$<E> = E_c + E_{rm} \tag{12}$$

where,

E_c = overall contribution towards bond energy arising from strong heteropolar bonds.

E_{rm} = contribution arising from weaker bonds that remain after the strong bonds have been maximized *i.e.* the average bond energy per atom of the ‘remaining matrix’.

Values of E_c and E_{rm} will further depend on a parameter which determines the deviation of stoichiometry (R).

3.6.1 Determination of R

It is expressed by the ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom.

$R > 1$, indicate chalcogen-rich materials and

$R < 1$ show chalcogen poor materials.

For $Ga_xSe_yBi_z$ system, the quantity $'R'$ is defined by

$$R = \frac{yCN(Se)}{xCN(Ga) + zCN(Bi)} \tag{13}$$

where, x, y and z are respective atomic fractions of Ga, Se and Bi. The calculation of $'R'$ also requires the knowledge of coordination number (*CN*) of all the constituents of glassy alloys, which have been discussed earlier in section 3.1. Values of *R* are also tabulated in table 4. Since, minimum value of *R* is 1, so there are no signs of chalcogen poor region.

3.6.2 Determination of mean bond energy for $Ga_xSe_yBi_z$ system (where $x + y + z = 1$);

Case I. In the selenium rich region $(R > 1)$, there are heteropolar bonds and chalcogenide – chalcogenide bonds.

$$E_c = 4xE_{Ga-Se} + 3zE_{Bi-Se} \tag{14}$$

and

$$E_{rm} = \frac{[2y - 3x - 3z]}{<r>} E_{Se-Se} \tag{15}$$

where, E_{Se-Se} is the homopolar bond energy of Se-Se bonds.

Case II. In the selenium poor region $(R < 1)$, there are heteropolar and metal – metal bonds present

$$E_c = \frac{2y(3xE_{Ga-Se} + 3zE_{Se-Bi})}{3x + 3z} \tag{16}$$

and

$$E_{rm} = \frac{(3x + 3z - 2y)}{<r>} E_{<>},$$

where

$$E_{<>} = \frac{1}{2}[E_{Ga-Ga} + E_{Bi-Bi}] \tag{17}$$

denotes the average bond energy of metal - metal bond for $R < 1$.

Using a set of 186 glasses, Tichy and Ticha illustrated an impressive correlation of T_g with mean bond energy in the form;

$$T_g = 311[<E> -0.9] \tag{18}$$

In particular, the compositional dependence of T_g in numerous glassy system presents maximum value near to the chemical threshold *i.e.* $R = 1$, because the chemical bond energies are maximized at this composition [14,15]. From figure 4, same trend is observed for our investigated system also. The threshold at $R = 1$ shows the point of existence of only heteropolar bonds and is also evident from chemical bond distribution given in table 3. For $R > 1$, the system is chalcogen rich and for $R < 1$, the system is chalcogen poor. The values of R along with $<E>$ and predicted T_g values are tabulated in table 4. It is clear that with the increase in Bi content in Ga-Se-Bi glassy alloy, both mean bond energy and glass transition temperature increases and reach its maximum at $R = 1$ (figure 4). This marks the minimum selenium content at which chemically ordered network is possible without metal-metal bond formation.

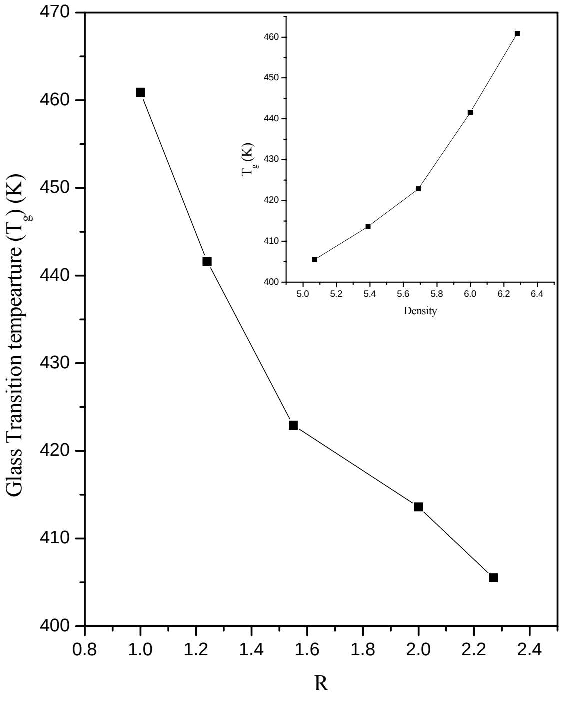

Fig. 4. Variation of glass transition temperature (in K) with R. Inset of figure shows the variation of glass transition temperature (T_g) (in K) with density (ρ) for $Ga_{20}Se_{80-x}Bi_x$ (x = 0, 5, 10, 15, 20) system.

A linear agreement is found between the density and glass transition temperature (inset of Fig. 4) as experimentally proven by various workers [35, 36]. This further confirms that greater the T_g, greater is the rigidity of the system. Maximum T_g is found for $Ga_{20}Se_{60}Bi_{20}$ alloy with $<r> = 2.4$ which is also the most stable composition among the investigated system. An account of these features is given by the existing Phillips model and the chemically ordered network model. Major limitation of the model is that, it does not account for the molecular interaction, which plays a vital role in the relaxation process in glass transition region.

4. Conclusion

In the present work, we observe that the physical properties of a-Ga$_{20}$Se$_{80\text{-x}}$Bi$_\text{x}$ (x = 0, 5, 10, 15, 20) glassy alloys are in consistence with optical properties. Density is found to increase which accounts for the increase of refractive index with Bi content. Molar volume also increases with addition of Bi. Number of atoms per unit volume decreases and also accounts for the decrease in optical band gap. Compactness of the system and lone pair electrons decreases with increase in Bi content. Cohesive energy of the composition is calculated using CBA and decreases with increase in Bi content. This change is in the same fashion to that of optical band gap calculated theoretically and experimentally. Electronegativity also decreases with Bi content. No correlation between photon energy and average single bond energy is found for low connectivity glasses. Average single bond energy shows almost constant trend whereas, a decrease in photon energy with composition is observed. Mean bond energy and glass transition temperature increases in chalcogen rich region and shows a maxima at $< r >= 2.4$ and R=1, which further corresponds to the most stable composition.

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