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Advances in Applied Science Research, 2011, 2 (3):20-29



# Study of the physical properties with compositional dependence in $(Se_{70}Ge_{30})_{100-x}Bi_x$ (0<x< 8) glassy semiconductors

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# ABSTRACT

In the present paper we have theoretically predicted the physical parameters viz. coordination number, constraints, glass transition temperature, fraction of floppy modes, number of lone pair electrons, bond energy, cohesive energy, heat of atomization, ionicity, metallicity and mean bond energy for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0 < x < 8) glassy alloys. It has been found that average heat of atomization and cohesive energy decreases with Bi content. The glass transition temperature and mean bond energy increases with Bi content up to x=2, further addition of Bi lead to decrease in there values. An attempt has been made to explain the varying trend of various parameters with increasing Bi content. A ternary phase diagram has also been reported to explain the structure of  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0 < x < 8) glassy semiconductors.

**Keywords**: Chalcogenide glasses, molar volume, cohesive energy, mean bond energy, Se-Ge-Bi glass.

# **INTRODUCTION**

Chalcogenide glasses are interesting candidates for reversible phase change optical recording devices [1–3]. Selenium exhibits the unique property of reversible phase transformation [4] and it having various device applications like rectifiers, photocells, xerography, switching and memory etc. which made it attractive, but pure selenium has disadvantages like short lifetime and low photo-sensitivity. This problem can be overcome by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, Sb and As etc), which gives higher sensitivity, higher crystallization temperature and smaller ageing effects. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Se chain structure, thereby increasing the glass transition temperature and resistivity [5]. Several researchers have studied the effect of bismuth (Bi) on the optical and electrical properties of chalcogenide materials [6–8]. Addition of the third element like Bi will expand the glass forming area and also create compositional and configurational disorder in the system and has large effect on their structural, physical, optical, electronic and thermal properties [9]. The Ge-Se-Bi system has attracted the attention of various researchers because the density of states in conduction band as well as in the valence band in amorphous

 $Ge_{20}Se_{80-x}Bi_x$  thin films has been investigated by the inverse photoemission and ultraviolet photoemission spectroscopies [10]. The composition dependence of thermal properties on the  $Ge_{20}Se_{80-x}Bi_x$  system was studied by Thomas and Philpis [11]. The present paper is concerned with the theoretical prediction of the physical parameters related to composition, viz: coordination number, constraints, glass transition temperature, fraction of floppy modes, number of lone pair electrons, bond energy, cohesive energy, heat of atomization ionicity, metallicity and mean bond energy for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0<x< 8) glassy system.

# Theory

The optical band gap is predicted by using the Shimakawa relation, whereas the prediction and the correlation between glass transition temperature and mean bond energy has been done by using the Tichy and Ticha relation. Cohesive energy for the investigated samples has been calculated with the help of Chemical bond approach method. Ionicity and metallicity of the samples have been calculated by the Chlikowsky and Phillips relation. The ternary phase diagram is proposed for two fold coordination of Se.

# **RESULTS AND DISCUSSION**

#### 3.1 Coordination number and constraints

In a glassy system covalent networks are influenced by mechanical constraints (N<sub>con</sub>) associated with the atomic bonding and an average effective coordination number <  $r_{eff}$  >. The atomic species with coordination number r having the number of constraints per atom arising from bond bending N<sub>β</sub> = 2r - 3 and from bond stretching N<sub>α</sub> = r/2. Knowing the average number of constraints N<sub>con</sub> = N<sub>α</sub> + N<sub>β</sub> and the average coordination number r for different composition of (Se<sub>70</sub>Ge<sub>30</sub>)<sub>100-x</sub>Bi<sub>x</sub> (0<x< 8) glassy system, the effective average coordination number <  $r_{eff}$  > can be calculated [12] by using the formula

$$\left\langle r_{eff} \right\rangle = \frac{2}{5} \left( N_{con} + 3 \right) \tag{1}$$

Table 1 shows the values of  $N_{\alpha}$ ,  $N_{\beta}$  and  $N_{con}$  along with  $\langle r_{eff} \rangle$  for the  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0 $\langle x \langle 8 \rangle$ ) glassy system. From the Table 1 we observed that the value of the coordination number and the constraints increase with the addition of Bi. The cross linking density (*X*) is equal to the average coordination number of cross-linked chain less the coordination number of the initial chain [13].

$$X = N_{\text{con}} - 2 \tag{2}$$

The value of cross linking density (X) and molecular weight (M) is shown in Table 1. where N<sub>con</sub> indicate the average number of bonds per atom which must be broken in order to obtain fluidity [13]. From the Table 1 we observed that the value of N<sub>con</sub> and cross linking density (X) increase with increase in Bi content. According to M.F. Thorpe [14], the uncoordinated networks having finite fraction of zero frequency normal vibration modes termed as floppy modes in absence of weak long range forces. The fraction f of zero frequency modes is given by

$$f = 2 - \frac{5}{6} \langle r \rangle \tag{3}$$

*f* is calculated for varying composition of Bi and is listed in Table 1. It has been observed that with increase in Bi content in the system the value of fraction of floppy modes becomes more and more negative, this shows that the system becomes more and more rigid.

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# **3.2 Role of lone pair electrons**

Chalcogenide glasses are also called lone pair semiconductors. According to Zhenhua the lone pair electrons in the structure of a system are a necessary condition for obtaining the system in vitreous state. The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation [15]

$$\mathbf{L} = \mathbf{V} - \mathbf{r} \tag{4}$$

where L and V are the lone pair electrons and valence electrons, respectively. The number of lone pair electrons obtained by using equation (4) is listed in Table 1. According to the Pauling [16], lone-pair electrons containing chemical bonds are characterized by the flexibility. Thus it is easier to deform a bond with lone pair electrons than a bond with no unshared electrons Structures with large number of lone-pair electrons favour glass formation [17]. It is clear from Table 1 that the lone pair electrons, L, decrease continuously with addition of Bi. Thus we conclude that the bond deformation decreased with increase in Bi content leading to decrease in the flexibility of the system. The lone pair electrons of  $(Se_{70}Ge_{30})_{100-x}Bi_x$  system are between 2.72 and 2.83. This leads them to indicate that this system can form glass at ordinary rate [18]. For a binary system the value of L must be larger than 2.6 and for a ternary system it must be larger than 1 [19].

#### 3.3 Correlation between mean bond energy and glass transition temperature

The parameter R which determines the deviation of stoichiometry can be expressed by the ratio of the covalent bonding possibilities of chalcogen atoms to that of non- chalcogen atoms. It is calculated using the following relation [20, 21].

$$R = \frac{zCN(Se)}{xCN(Ge) + yCN(Bi)}$$
(5)

The value of the R is shown in Table 2. The properties of chalcogenide glasses are related to overall mean bond energy  $\langle E \rangle$ , which is a function of average coordination number r, the type of bonds and the bond energy. Using the correlation proposed by Tichy [22]. The overall mean bond energy for the Se<sub>y</sub>Ge<sub>x</sub>Bi<sub>z</sub> system is given by

$$\langle E \rangle = E_c + E_m \tag{6}$$

Where  $E_c$  is the overall contribution towards bond energy arising from strong heteropolar bonds,  $E_{rm}$  is the contribution arising from the weaker bonds that remain after the strong bonds have been maximized i.e average bond energy per atom of the 'remaining matrix'. For chalcogen rich systems for R > 1 where there are heteropolar bonds and chalcogen–chalcogen bonds.

$$E_c = 4xE_{Ge-Se} + 3zE_{Se-Bi} \tag{7}$$

and

$$E_{rm} = \left[\frac{2y - 4x - 3z}{\langle r \rangle}\right] E_{Se-Se}$$
(8)

In the selenium poor region (R<1), there are heteropolar and metal-metal bonds present

$$E_{c} = \frac{2y(4xE_{Ge-Se} + 3zE_{Se-Bi})}{4x + 3z}$$
(9)

and

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(10)

$$E_{rm} = \frac{(4x + 3z - 2y)}{\langle r \rangle} E_{\diamond}$$
(10)

where

$$E_{\Rightarrow} = \frac{1}{3[E_{Ge-Ge} + E_{Bi-Bi} + E_{Bi-Bi}]}$$
(11)

Here,  $E_{Ge-Se}$  and  $E_{Se-Bi}$  are the heteropolar bond energies of Ge–Se and Se–Bi, respectively and are estimated by applying Pauling's [16] relation

$$E_{AB} = 0.5(E_{AA} + E_{BB}) + 23(\chi_A - \chi_B)^2$$
(12)

Finally, the overall mean bond energy  $E_{rm}$  is given by

$$E_{rm} = E_C + E_{rm} \tag{13}$$

The properties of chalcogenide glasses are related to overall mean bond energy  $\langle E \rangle$ , which is a function of the average coordination number 'r', the type of bonds, the degree of cross-linking  $E_c$ , and the bond energy forming a network. For all glasses, we calculated the values of the overall mean bond energy and are tabulated in Table 2. The glass transition temperature for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0 < x < 8) glassy alloys is predicted theoretically by Tichy and Ticha [20, 21].

$$T_g = 311[< E > -0.9] \tag{14}$$

where  $\langle E \rangle$  is the mean bond energy of the system. The value of T<sub>g</sub> is computed by Tichy and Ticha relation and is tabulated in Table 2 along with  $dT_g/dE_{04}$ . The variation of T<sub>g</sub> with the Bi content is shown in Fig. 1.

#### 3.4 Bond energy and cohesive energy

The possible bonds in for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0<x< 8) system are Ge-Se, Se-Se, Se-Bi and Bi-Bi. The CON [23] model suggests that heteropolar bonds are favored over homopolar bonds and they are formed in the sequence of their decreasing bond energy. The bond energy of heteropolar bonds is estimated by the method by using the bond energy of homopolar bonds and the electronegativity of the atoms involved [24]. Following expression is used to calculate the bond energy of heteronuclear bonds.

$$D (A-B) = [D(A-A) D(B-B)]^{1/2} + 30 (X_A - X_B)^2$$
(15)

Where D (A-B) = bond energy of heteronuclear bond, D (A-A) and D (B-B) is the bond energy of homonuclear bonds.  $X_A$  and  $X_B$  are the electronegativity values of A and B, respectively. Cohesive energy is the stabilization energy of an infinitely large cluster of material per atom and also reflects the average bond strength. Cohesive energy for the investigated samples has been calculated with the help of Chemical bond approach method [25]. According to CBA the bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied and the bond energies are assumed to be additive. Therefore the cohesive energy was calculated by summing the bond energies over all bonds expected in the material. The values of

cohesive energy along with the chemical bond distribution for all the composition are tabulated in Table 3. The variation of cohesive energy with Bi content is shown in Fig. 2. It has been observed that the variation in the values of theoretical band gap ( $E_g$ ) with composition can be described by the following relation [26]:

$$E_g(ABC) = aE_g(A) + bE_g(B) + cE_g(C)$$
(16)

where a, b, and c are the volume fractions and  $E_g(A)$ ,  $E_g(B)$  and  $E_g(C)$  are the optical gaps of elements A, B and C respectively. The values of theoretical band gap  $(E_g)$  and optical band gap  $(E^{opt})$  for all the compositions are given in Table 3. From Table 2 it has been found that  $\langle E \rangle$  and  $T_{\sigma}$  increases up to x=2 and then decrease with increasing Bi content. The value of the mean bond energy is maximum at x=2 shows that the chemical threshold occurs at this composition. However, the overall compositional trend seems to be influenced mainly by the chemical bond arrangement. From Table 3, it can be seen that the C.E decrease with increase in Bi. The decrease of CE implies lower bonding strength; i.e. higher defect bonds. It can be concluded that decrease of band gap,  $E_g$  and  $E^{opt}$  with increasing Bi content is most probably due to a decrease of average stabilization energy and decrease of electronegativity ( $\chi$ ) of the system calculated from Sanderson's principle [27]. According to this principle, the electronegativity of an alloy is the geometric mean of electronegativity of its constituent elements. It is evident from the Table 3 that electronegativity decreases as the optical band gap decreases. It has been also observed that Se atoms bond strongly to Te thus they fill the available valences of the Bi 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. The numbers of excess bonds of  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0<x< 8) glassy system are listed in Table 3.

# 3.5 Relation between $E_{04}$ , $H_s$ and r

Where  $E_{04}$  is arbitrary quantity defined as photon energy, at which optical absorption coefficient has the value of  $10^4$  cm<sup>-1</sup>. The photon energy at  $\alpha = 10^4$  cm<sup>-1</sup> is about 0.2eV larger than the optical band gap  $E^{opt}$ . The value of the  $E_{04}$  for all the compositions is tabulated in Table 3.

# 3.5.1 Average heat of atomization

According to Pauling [28, 16] 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  $\Delta H$  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 [29]

$$H_{s}(A-B) = \Delta H + \frac{1}{2} (H_{s}^{A} + H_{s}^{B})$$
(17)

The first term in equation (17) is proportional to the square of the difference  $\chi_A$  and  $\chi_B$  of the two atoms.

$$\Delta H \Box (\chi_{A} - \chi_{B})^{2}$$
(18)

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

$$H_{s}(A-B) = \frac{1}{2}(H_{s}^{A} + H_{s}^{B})$$
 (19)

The results of  $H_s$  for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0<x< 8) using the values of  $H_s$  for Se, Ge and Bi are 226.4 for Se, 373.8 for Ge and 207.36KJ/mol for Bi are listed in Table 2. From Table 2, we

found that the value of average heat of atomization ( $H_s$ ) and average single bond energy ( $H_s/r$ ) decreases with the addition of Bi.

In chalcogenide glasses containing a high concentration of a group VI element the lone pair electrons form the top of valence band and antibonding band forms the conduction band [30, 31]. Therefore it is interesting to relate the optical gap with chemical bond energy. The relation between the energy gap and the average heat of atomization was discussed by Aigrain et al [32]. According to them there exists a linear correlation that can be expressed for the semiconductors of the diamond and Zinc-blende structure by

$$\Delta E = a(H_s - b)$$
 (20)

Where a and b are characteristics constants. It is suggested from the above equation that the average heat of the atomization are a measure of cohesive energy and represents the relative bond strength, that is correlated with the properties such as energy gap of isostructural semiconductors. The variation of  $E_{04}$  and  $H_s/r$  with Bi for all the composition of the  $(Se_{70}Ge_{30})_{100-x}Bi_x$  (0<x< 8) glassy system is represented by Fig. 3. From the Fig. 3 we observed that there is decrease in  $E_{04}$  and  $H_s/r$  with the addition of Bi. For over-constrained materials with higher connectivity (i.e.  $3 \le r \le 4$ ),  $E_{04}$  depends more strongly on  $H_s$  than for glasses with lower connectivity,  $2 \le r \le 3$  [33, 18]. In our case, the value of  $<r_{eff}>$  varies from 2.600 to 2.632, which can be correlated with low connectivity glasses. This further suggests that the parameter  $H_s/r$  have a very negligible effect on  $E_{04}$ . Similar results have also been reported for Te–As–Ge–Si and As–Sb–Se–Te systems [34, 35].

# 3.6 Ionicity and metallicity

According to the Chlikowsky and Phillips [33]  $r_s$  and  $r_p$  corresponds to the orbitally dependent ionic radii of S-orbital and P-orbital respectively derived from the Pauli force model potential. The R  $_{\sigma}$  <sup>AB</sup> and R  $_{\tau}$  <sup>AB</sup> scales correspond to the ionicity and metallicity of an A-B bond respectively and are defined as [33]

$$\mathbf{R}_{\sigma}^{AB} = (r_s^A + r_p^A) - (r_s^B + r_p^B)$$
(21)

$$R_{\tau}^{AB} = (r_s^A - r_p^A) + (r_s^B - r_p^B)$$
(22)

The value of R  $_{\sigma}$  <sup>AB</sup> and R  $_{\tau}$  <sup>AB</sup> has been tabulated in Table 4. The relative probability of chemical bonds formation can be calculated by the Boltzmann factors exp (-E/RT) = exp (D/RT), where D is the bond energy, R the gas constant and T the reaction temperature at which the samples were prepared during their synthesis in Kelvins (1173.15°K). The orders of bond energies and the relative probabilities listed in Table 4 indicate that the stronger the chemical bond is, the larger is its forming probability. According to the Ordered Bond Network Model, the chemical bonds in the (Se<sub>70</sub>Ge<sub>30</sub>)<sub>100-x</sub>Bi<sub>x</sub> (0<x< 8) glasses must be formed in the order of Ge-Se > Bi-Se.

# 3.7 Structure of Se-Ge-Bi

The ternary phase diagram for Se-Ge-Bi system is shown in Fig. 4. In the figure, two pseudo binary compositions lines are indicated, the bold line represents the  $Bi_2Se_3$ -GeSe composition whereas the dashed line represents the  $Bi_2Se_3$ -GeSe\_2 composition. If the Se is always two fold coordinated then there are only Ge-Se and Bi-Se bonds but there may be also the existence of the Ge-Ge, Bi-Bi and Se-Se bonds.

Composition	< r <sub>eff</sub> >	Nα	Nβ	N <sub>conc</sub>	X	Μ	f	V	L= V-< r >
a-Se <sub>70</sub> Ge <sub>30</sub>	2.600	1.300	2.20	3.50	1.50	77.159	-0.1666	5.43	2.83
$(Se_{70}Ge_{30})_{98}Bi_2$	2.608	1.304	2.216	3.52	1.52	84.073	-0.1733	5.41	2.80
(Se70Ge30)96Bi4	2.616	1.308	2.232	3.54	1.54	90.544	-0.1800	5.39	2.77
(Se <sub>70</sub> Ge <sub>30</sub> ) <sub>94</sub> Bi <sub>6</sub>	2.624	1.312	2.248	3.56	1.56	96.613	-0.1866	5.37	2.74
(Se <sub>70</sub> Ge <sub>30</sub> ) <sub>92</sub> Bi <sub>8</sub>	2.632	1.316	2.264	3.58	1.58	102.316	-0.1933	5.35	2.72

Table 2 Values of H<sub>s</sub>, H<sub>s</sub>/r, R, < E > and T<sub>g</sub> obtained by Tichy and Ticha along with  $dT_g/dE_{04}$  for  $(Se_{70}Ge_{30})_{100}$ . xBi<sub>x</sub> glassy system

a	H <sub>s</sub>	$H_s/< r >$	< E >	D	<b>T</b> ( <b>T T</b> )	$\partial T_{g}$
Composition	(KJmol <sup>-1</sup> )	(KJmol <sup>-1</sup> )	(eV/atom)	к	$T_{g}(1.1)$	$/ \partial E_{04}$
a-Se <sub>70</sub> Ge <sub>30</sub>	268.06	103.10	2.63	1.27	538.02	284.66
(Se <sub>70</sub> Ge <sub>30</sub> ) <sub>98</sub> Bi <sub>2</sub>	264.87	101.56	2.65	1.10	545.48	304.73
(Se <sub>70</sub> Ge <sub>30</sub> ) <sub>96</sub> Bi <sub>4</sub>	261.89	100.11	2.63	0.97	539.86	319.44
(Se <sub>70</sub> Ge <sub>30</sub> ) <sub>94</sub> Bi <sub>6</sub>	259.10	98.74	2.46	0.87	486.21	301.99
$(Se_{70}Ge_{30})_{92}Bi_8$	256.47	97.44	2.31	0.78	438.10	284.48

Table 3 The electronegtivity, type of bonds formed with corresponding cohesive energy (C.E), excess of Se-Se bonds, theoretical band gap ( $E_g$ ), optical band gap ( $E^{opt}$ ) and photon energy ( $E_{04}$ ) for (Se<sub>70</sub>Ge<sub>30</sub>)<sub>100-x</sub>Bi<sub>x</sub> glassy system

Composition	χ	Distril	oution of	chemical	bonds	C.E	Excess of	Eg	Eopt	E <sub>04</sub>
		Ge-Se	Se-Bi	Se-Se	Bi-Bi	(Kcalmol <sup>-1</sup> )	Se-Se	(eV	(eV)	(eV)
							bonds			
a-Se <sub>70</sub> Ge <sub>30</sub>	2.397	0.8571	-	0.1428	-	48.371	113.055	1.69	2.60	2.90
$(Se_{70}Ge_{30})_{98}Bi_2$	2.377	0.7879	0.1157	0.0962	-	47.636	80.900	1.59	2.52	2.72
$(Se_{70}Ge_{30})_{96}Bi_4$	2.359	0.7692	0.2069	-	0.0237	46.789	50.807	1.49	2.44	2.64
$(Se_{70}Ge_{30})_{94}Bi_6$	2.341	0.6852	0.1843	-	0.1304	44.407	22.582	1.41	2.37	2.57
$(Se_{70}Ge_{30})_{92}Bi_8$	2.325	0.6150	0.1654	-	0.2194	42.421	-	1.34	2.30	2.50

Table 4 Relative probability, ionic character and metallicity of different bonds

Bond	Bond energy (KJ/mol)	Relative Probability	$R_{\sigma}^{AB}$ (a.u)	$R_{\tau}^{\ AB}(a.u)$	
Ge-Se	206.91	$1.566 \times 10^9 = 1$	0.21	-0.45	
Se-Bi	170.126	0.024024	0.39	0.13	



Fig. 1 Plot of  $T_g$  with Bi content for  $(Se_{70}Ge_{30})_{100\mathchar`s}Bi_x$  glassy system



Fig. 2 Plot of cohesive energy with Bi content for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  glassy system



Fig.3 Plot of  $E_{04}$  and  $H_s/\langle r \rangle$  with Bi content for  $(Se_{70}Ge_{30})_{100-x}Bi_x$  glassy system





# CONCLUSION

The addition of Bi to  $Se_{70}Ge_{30}$  glassy alloy leads to change in the physical properties. The average coordination number increase with increase in Bi content which gives an indication that the number of constraints increases hence the value of optical band gap will strongly depends upon H<sub>s</sub>. Due to decrease in average stabilization energy the average heat of atomization (H<sub>s</sub>) and cohesive energy decrease with increase in Bi content. The mean bond energy < E > and glass transition temperature (T<sub>g</sub>) increases with Bi content up to x=2, further addition of Bi lead to decrease in there values. The overall compositional trend seems to be influenced mainly by the

chemical bond arrangement. The value of the theoretical band gap  $(E_g)$ , optical band gap  $(E^{opt})$  and the photon energy  $(E_{04})$  has been decreased with increase in Bi content. This is due to decrease in the cohesive energy and the electronegtivity of the system because optical band gap is a bond sensitive property. It can also be observed that the Ge-Se bond having more probability of formation than the Se-Bi bond.

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