THEORETICAL PREDICTION OF PHYSICAL PARAMETERS OF Ge-Te-Bi GLASSY ALLOYS

Ambika, P. B. Barman

Department of Physics, Jaypee University of Information Technology,
Waknaghat, Solan 173215, (H.P.), India

In the present paper we have theoretically predicted the physical parameters *viz.* coordination number, constraints, molar volume, fraction of floppy modes, number of lone pair electrons, bond energy, cohesive energy, heat of atomization and mean bond energy for $Ge_{20}Te_{80-x}Bi_x$ (x = 0, 5, 10, 15, 20, 25) glassy alloys. It has been found that average number of constraints, cohesive energy and mean bond energy increases whereas, all other parameters decrease with the increasing Bi content. The mean bond energy is calculated using the chemical bond approach of Tichy and Ticha and it was found to be proportional to the average coordination number $\langle r \rangle$ and number of lone pair electrons of the system.

1. Introduction

Chalcogenide glasses have been investigated intensively as they exhibit electrical and optical properties which make them useful for several potential applications. They are used in memory devices and fiber optics [1, 2] as they exhibit the threshold and memory switching behavior as well as infrared transmission. They have been, also, applied in xerography [3], photolithography [4], and in the fabrication of inexpensive solar cells [5]. Multicomponent glasses were found to be more useful for many of these applications [6, 7]. Depending upon the composition, the chalcogenide glasses are stable against crystallization and are chemically inert. They have excellent thermal stability and are relatively easy to fabricate. The present paper is concerned with the theoretical prediction of the physical parameters related to composition, *viz*: coordination number, constraints, molar volume, fraction of floppy modes, number of lone pair electrons, bond energy, cohesive energy, heat of atomization and mean bond energy for Ge-Te-Bi glassy system. It has been observed that partial substitution of Bi for Te leads to the densification of the system.

Chalcogenide glasses are often called lone pair semiconductors. The chemical bonds with lone pair electrons are characterized by flexibility. It is easier to distort a bond with lone pair electrons than a bond with no unshared electrons. By increasing the number of lone pair electrons, the strain energy in a system decreases. The structure with large number of lone pair electrons favor the glass formation.

2. Analysis of various theoretical parameters

Various parameters *viz.* coordination number and constrains, molar volume and fraction of floppy modes, number of lone pair electrons, bond energy and cohesive energy, heat of atomization and mean bond energy has been theoretically predicted for Ge-Te-Bi glassy system.

2.1 Coordination Number and Constraints

The average coordination number $\langle r \rangle$, for the system is calculated using the   expression,

$$\langle r \rangle = (X)\, Z_{Ge} + (Y)Z_{Te} + (1\text{-}X\text{-}Y)Z_{Bi} \tag{1}$$

where $Z_{Ge} = 4$, $Z_{Te} = 2$, $Z_{Bi} = 3$, are the coordination numbers for Ge, Te, and Bi, respectively, the average coordination number being situated in the range $2.40 \leq \langle r \rangle \geq 2.65$. In a glassy system covalent networks can be mechanically constrained by interatomic valence forces such as bond stretching and bond bending. Optimal glass formation is attained when the network is at a mechanically critical point. This point is reached when the number of constraints (N_{con}) per atom is equal to the degrees of freedom (N_d) per atom i.e. for ideal glass $N_{con} = N_d$. The enumeration of mechanical constraints in this system gives $\langle r \rangle / 2$ bond stretching constraints (N^{α}) and $2\langle r \rangle - 3$ bond bending constraints (N^{β}) [8]. The average coordination number $\langle r \rangle$ and the average number of constraints, given by $N_{con} = N^{\alpha} + N^{\beta}$ for various compositions with Bi are listed in table 1.

Table 1 The average coordination number $\langle r \rangle$ and the average number of constraints, given by $N_{con} = N^{\alpha} + N^{\beta}$ for various compositions with Bi

Composition	<r>	N^{α}	N^{β}	N_{con}
$Ge_{20}Te_{80}$	2.40	1.200	1.80	3.000
$Ge_{20}Te_{75}Bi_5$	2.45	1.225	1.90	3.125
$Ge_{20}Te_{70}Bi_{10}$	2.50	1.250	2.00	3.250
$Ge_{20}Te_{65}Bi_{15}$	2.55	1.275	2.10	3.375
$Ge_{20}Te_{60}Bi_{20}$	2.60	1.300	2.20	3.500
$Ge_{20}Te_{55}Bi_{25}$	2.65	1.325	2.30	3.625

2.2 Molar Volume and Fraction of Floppy Modes

Molar volume for Ge-Te-Bi glassy alloys is calculated on the basis that fractional molar volumes for different molecules are additive. The conversion from atomic composition (at. %) or molecular composition (mol. %) to the volume fraction is made using atomic or molecular mass and density of Ge, Te and Bi. The theoretically calculated values of molar volume (V_m) for various content of Bi are tabulated in Table 2. From Table 2 it is clear that with the increase of coordination number $\langle r \rangle$, the molar volume (V_m) decreases indicating that the partial substitution of Bi for Te leads to the densification of structure system.

M. F. Thorpe [9] pointed out that undercoordinated networks would posses in the absence of the weaker longer range forces, a finite fraction of zero frequency normal vibrational modes, floppy modes. The fraction, f of zero frequency modes is given by

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

f is calculated for varying composition of Bi and is listed in Table 2. A graphical representation of fraction of floppy modes, f, and mean coordination number $\langle r \rangle$ is also given in figure1. It is clear from Fig. 1 that for coordination number $\langle r \rangle = 2.40$, $f = 0$, i.e. the system suffered a phase transition from floppy to rigid one. Initially, in the absence of Bi content, the whole network is isostatically rigid and therefore rigidity percolates. By the term isostatic we mean that the system is unstressed i.e. each bond

length can have its natural length without being forced to adjust by the surrounding environment [10]. As Bi content is increased in the system the fraction of floppy modes goes to more and more negative because with the addition of Bi content the rigidity of the system increases.

Table 2 The theoretically calculated values of molar volume (V_m) for various content of bismuth.

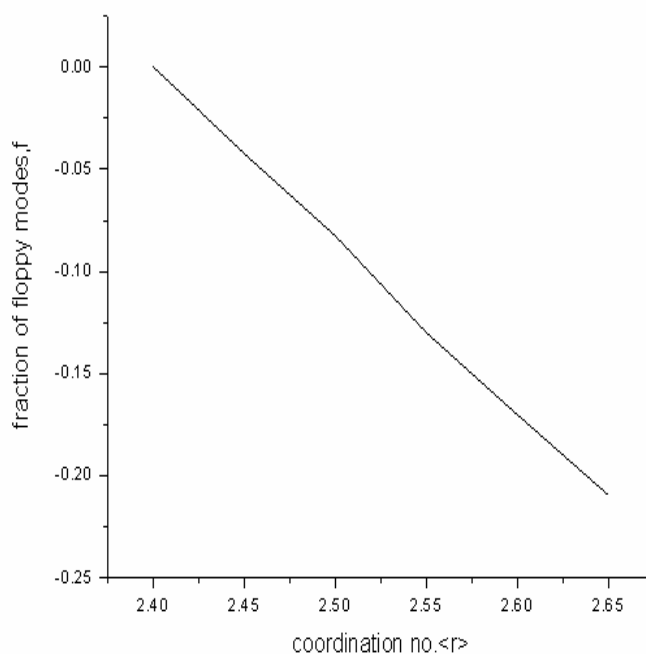| Mean coordination number $\langle r \rangle$	Molar volume (V_m) (m^3)	Fraction of floppy modes , f
2.40	15.6330×10^{-6}	0
2.45	15.1365×10^{-6}	-0.042
2.50	14.7187×10^{-6}	- 0.083
2.55	14.3208×10^{-6}	-0.13
2.60	13.9558×10^{-6}	- 0.17
2.65	13.6039×10^{-6}	-0.21

Fig. 1. The fraction of floppy modes versus the average coordination number in the system.

2.3 Role of lone pair electrons

The number of lone pair electrons in a chalcogenide glass system can be calculated by using the relation [11]

$$L = V - \langle r \rangle \tag{3}$$

where L and V are the lone pair electrons and valence electrons, respectively. The number of lone pair electrons obtained by using equation (3) is listed in Table 3. A graphical representation of L and Bi composition is given in figure 2. It is clear from Fig. 2 that the lone pair electrons, L, decrease continuously with the increase in Bi content. We can conclude from these results that some lone pair electrons in the structure of a system are a necessary condition for obtaining the system in vitreous state. 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 [12].

Table 3. The number of lone pair electrons obtained by using equation (3).

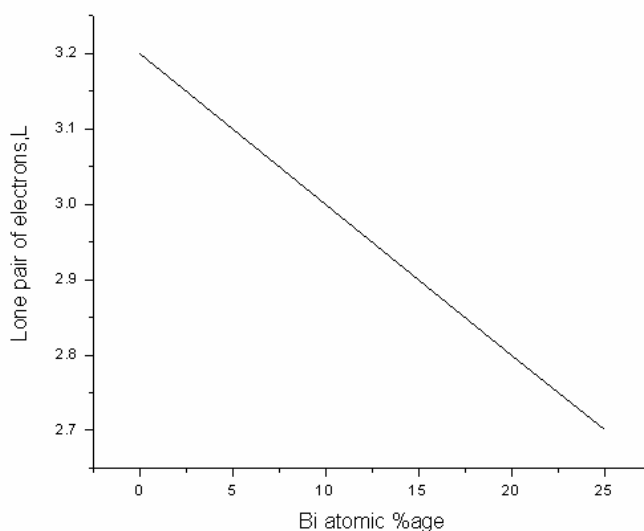| Composition $Ge_{20}Te_{80-X}Bi_X$	$\langle r \rangle$	V	L = V - Z
x = 0	2.40	5.60	3.2
x= 5	2.45	5.55	3.1
x=10	2.50	5.50	3.0
x=15	2.55	5.45	2.9
x=20	2.60	5.40	2.8
x=25	2.65	5.35	2.7

Fig. 2 The number of lone pair electrons as a function of bismuth content.

2.4 Bond Energy and Cohesive Energy

The possible bonds in Ge-Te-Bi system are Ge-Te, Te-Te and Te-Bi. The CON [13] model suggests that heteropolar bonds are favored over homopolar bonds and they are formed in the sequence of their decreasing bond energy. The binary alloy composition $Ge_{20}Te_{80}$ is just at the stiffness threshold. As Bi concentration is increased in the binary alloy $Ge_{20}Te_{80}$ the Bi_2Te_3 clusters having tetradymite structure find themselves embedded in the background matrix of $GeTe_2$ and Te chains or layers [14]. At lower concentrations of Bi the mechanical misfit between Bi_2Te_3 and $GeTe_2$ clusters is relieved by distortion of Te chains or layers. However as the Bi concentration is increased the rigidity of combined elastic medium Te and $GeTe_2$ increases steadily. The bond energy of heteropolar bonds is estimated by the method suggested by using the bond energy of homopolar bonds and the electronegativity of the atoms involved [15].
Following expression is used to calculate the bond energy of heteronuclear bonds.

$$D(A\text{-}B) = [D(A\text{-}A)\, D(B\text{-}B)]^{1/2} + 30\,(X_A - X_B)^2. \tag{5}$$

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. The electronegativity for Ge, Te and Bi are 2.01, 2.1 and 2.0, respectively. The cohesive energy of the system is the measure of the strength of a chemical bond and is defined as the stabilization energy per

atom. Different types of bonds formed with their bond energy and corresponding   cohesive energy are listed in Table 4.

Table 4 The types of bonds formed with their bond energy and corresponding cohesive energy.

Composition	Cohesive energy (eV/atom)	Bonds formed	Bond energy (kcal/mole)
$Ge_{20}Te_{80}$	2.17	Ge-Te	37.22
$Ge_{20}Te_{75}Bi_5$	2.28	Te-Te	33.00
$Ge_{20}Te_{70}Bi_{10}$	2.40	Te-Bi	27.69
$Ge_{20}Te_{65}Bi_{15}$	2.55		
$Ge_{20}Te_{60}Bi_{20}$	2.72		
$Ge_{20}Te_{55}Bi_{25}$	2.92		

Table 4

2.5 Heat of Atomization and Mean Bond Energy

Heat of atomization $H_S(A\text{-}B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B, as proposed by Pauling [16], is the sum of the heat of formation, $\Delta H,$ and the average of heat of atomization H_S^A and H_S^B, that corresponds to the average non polar bond energy of two atoms.

$$H_S(A-B) = \Delta H + \frac{1}{2}\left(H_S^A + H_S^B\right) \tag{4}$$

The first term in equation (4) is proportional to the square of the electronegativity difference of two atoms involved i.e.

$$\Delta H \propto \left(X_A - X_B\right)^2 \tag{5}$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization H_S is defined for the compounds $A_\alpha B_\beta C_\gamma$ as a direct measure of cohesive energy and the average bond strength is given by

$$H_S = \frac{\left(\alpha H_S^A + \beta H_S^B + \gamma H_S^C\right)}{\left(\alpha + \beta + \gamma\right)} \tag{6}$$

Table 5. The value of H_S obtained by using the values of H_S for Ge, Te, and Bi (the H_S values in units of Kcal / mol are 77.71 for Ge, 46 for Te and 43.11 for Bi); Last columns gives the values of the overall mean bond energy for the glassy alloy $Ge_{20}Te_{80-x}Bi_x$.

Coordination Number $\langle r \rangle$	H_S (Kcal / mol)	$\langle E \rangle$ (eV)
2.40	52.34	2.04
2.45	52.19	2.06
2.50	52.05	2.10
2.55	51.91	2.14
2.60	51.77	2.19
2.65	51.62	2.24

Equation (6) is applicable to this ternary system. The value of H_S obtained by using the values of H_S for Ge, Te, and Bi (the H_S values in units of kcal / mol are 77.71 for Ge, 46 for Te and 43.11 for Bi) are listed in Table 5. It is clear that value of H_S decreases with the partial substitution of Bi for Te.

The properties of chalcogenide glasses are related to overall mean bond energy $\langle E \rangle$, which is a function of average coordination number $\langle r \rangle$, the type of bonds and the bond energy. Using the correlation proposed by Tichy [17], for a chalcogenide rich system we can determine the value of $\langle E \rangle$. The overall mean bond energy for the system $Ge_a Te_b Bi_c$ is given by

$$\langle E \rangle = E_{cl} + E_{rm} \tag{7}$$

where E_{cl} is the mean bond energy of average cross linking per atom and is given by

$$E_{cl} = P_r D_{hb} \tag{8}$$

Here P_r is the degree of cross linking given by

$$P_r = \frac{(aZ_{Ge} + cZ_{Bi})}{(a+b+c)} \tag{9}$$

D_{hb} is the average heteropolar bond energy and is suggested to be

$$D_{hb} = \frac{[aZ_{Ge} D_{Ge-Te} + cZ_{Bi} D_{Bi-Te}]}{[aZ_{Ge} + cZ_{Bi}]} \tag{10}$$

The average bond energy per atom of the "remaining matrix" E_{rm} is given by

$$E_{rm} = \frac{2D_{Te-Te}(0.5\langle r \rangle - P_r)}{\langle r \rangle} \tag{11}$$

The values of the overall mean bond energy for the glassy alloy $Ge_{20}Te_{80-x}Bi_x$ are listed in Table 5 and are found to increase with increasing Bi content. A graphical representation of $\langle E \rangle$ with increasing Bi content is given in Fig. 3.
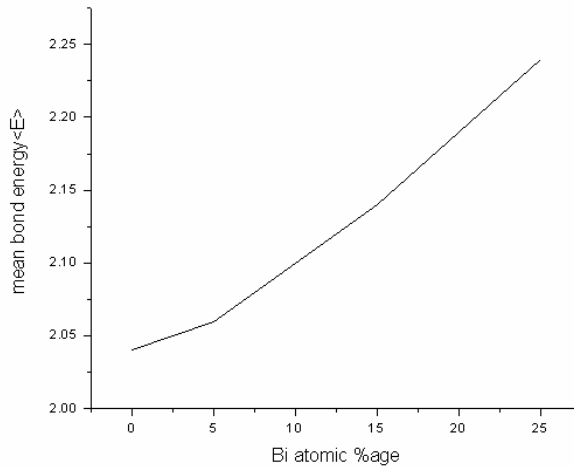
Fig. 3

3. Conclusion

From above theoretically analyzed physical parameters of Ge-Te-Bi glassy system the following conclusions were drawn.

It has been seen that average coordination number, constraints, cohesive energy and mean bond energy increases with increasing Bi content or decreasing Te content in Ge-Te-Bi glassy system. This behavior is due to the increase of average binding strength. Molar volume and number of lone pair electrons are found to decrease with increasing Bi content and the same behavior is exhibited by the heat of atomization.

References

[1] D. Adler, Sci Amer **36**, 236 (1977).
[2] J. A Savage, P.J. Webber and A. M Pitt, IR Phys, **20**, 313 (1980).
[3] J.H Dessaur, H. E. Clarke, xerography and related processes, Local London, (1965).
[4] D. E. Carlson, C.R Wronski, App. Phys Lett **28**, 671 (1976)
[5] J. Fusong, M. Okuda, Jpn, J. Appl. Phys **30**, 97(1991)
[6] H. Feritsche, In: Amorphous and Liquid Semiconductors, Ed. J. Tauc, Plenum Press, New York p. 313, (1974).
[7] I. Haruvi - Bushnach, J. Dror, and N. J. Croituro, Mater. Res. **5**, 1215 (1990)
[8] S.A. Fayek, A.F. Maged, M.R.Balboul Vacuum **53**, 447 (1999).
[9] M.F.Thorpe, J.of Non Cryst. Solids **57**, 355 (1983).
[10] M.V.Chubynsky, M.F. Thorpe, current opinion in solid state and materials science **5**, 525 (2001).
[11] Achamma George, D.Sushamma, P. Predeep, Chalcogenide Letters **3**(4), 33 (2006).
[12] Liang Zhenhua, J. Non Cryst. Solids **127**, 298 (1991).
[13] S. R Elliot, Physics of Amorphous Solids, Longman Inc, New York, 134 (1984).
[14] K.L. Bhatia, G.Parthasarthy, Ashwani Sharma, E. S.R. Gopal Physical Review B **38**(9), (1988).
[15] K.Sedeek, M. Fadel, Thin Solid Films **229**, 223 (1993).
[16] L.Pauling, J.Phys.Chem. **58**, 662 (1954).
[17] L.Tichy, L.Ticha, J. Non Cryst. Solids, **189**, 141 (1995).