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THEORETICAL PREDICTION OF PHYSICAL PARAMETERS OF Ge-Te-Bi GLASSY ALLOYS (PART II)

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In the present paper we have theoretically predicted the composition dependent physical parameters of Ge-Te-Bi glassy alloys viz: interplanner spacing, optical energy gap and glass transition temperature. It has been found that interplanner spacing and band gap decreases whereas glass transition temperature increases with increasing Bi content. An attempt has been made to explain this increasing or decreasing trend of various parameters with increasing Bi concentration. A ternary diagram has also been proposed to explain the structure of Ge-Te-Bi glassy alloy.

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1. Introduction

The chalcogenide glasses have recently attracted the attention because of their use in various solid state devices. The structural study of these materials is very important for better understanding of transport mechanism in them. The chalcogenide materials are also studied extensively because their electronic and optical properties are quite different from those of crystalline semiconductors. The addition of impurity has a pronounced effect on the conduction mechanism and the structure of amorphous glass and this effect can be widely different for different impurities. These materials show interesting physical properties like threshold and memory switching. An optical storage [1] system is particularly attractive component of this hierarchy because it provides data access times that are intermediate solution between a hard disk drive and a tape drive. A glass upon heating softens at a characteristic temperature, known as glass transition temperature, T_g, where molar volume (V) and enthalpy (H) undergo a qualitative change [2]. The present paper is a theoretical prediction of various physical parameters of Ge-Te-Bi glassy alloys viz: interplanner spacing, glass transition temperature, and band gap. A ternary phase diagram is also proposed to study the structure of Ge-Te-Bi glassy alloys.

2. Theory

Interplanner spacing is predicted theoretically from the microscopic model for glass transition temperature. The optical band gap is predicted by using Shimakawa relation, whereas glass transition temperature is predicted by using Gibbs Di-Marzio law in which the effect of chemical ordering is taken into account. A ternary diagram representation is proposed for two fold coordination of Te.

3. Results and discussion

3.1 Interplanner Spacing

From the microscopic model for glass transition [3], the glass transition temperature for higher coordination number, interplanner spacing and molar volume are related as

$$kTg \sim \frac{1}{d^4} \sim \frac{(N)^{4/3}}{(V)^{4/3}} \tag{1}$$

Where kT_g is the thermal energy at glass transition temperature T_g, d is the interplanner spacing, N is the Avogadro number and V_m is the molar volume. Here molar volume is calculated on the basis that fractional molar volumes for different molecules are additive. The theoretically calculated values of interplanner spacing (d), for varying composition of Bi are tabulated in table 1. A graphical representation of coordination number $\langle r \rangle$ and interplanner spacing (d) is also given in Fig. 1.

Table 1.

Composition	Interplanner Spacing (d) Å	Optical Energy Gap (E_g) eV
$Ge_{20}Te_{80}$	2.961	1.20
$Ge_{20}Te_{75}Bi_5$	2.929	0.55
$Ge_{20}Te_{70}Bi_{10}$	2.902	0.37
$Ge_{20}Te_{65}Bi_{15}$	2.876	0.20
$Ge_{20}Te_{60}Bi_{20}$	2.851	0.04

From table 1 and figure 1, it is well understood that

(a) With the increase of coordination number $\langle r \rangle$, the interplanner spacing (d) decreases, indicating that the partial substitution of Bi for Te leads to the densification of structure system. Same phenomenon is observed in Ge-Se-Bi glassy alloys in which Bi replaces Se [4].

(b) Around the coordination number $\langle r \rangle$ = 2.47, a change in slope was observed. The change in slope at this coordination number is explained on the basis that at this coordination number, system gets a transition from two dimensional planner chains to three dimensional covalent network structures. This phenomenon predicts our percolation threshold around the coordination number $\langle r \rangle$ = 2.47, with interplanner spacing (d) = 2.914 Å, where the rigidity of the network percolates. The network is floppy below $\langle r \rangle$ = 2.47 and rigid above $\langle r \rangle$ = 2.47. The applicability of the ideas of rigidity percolation was verified in many binary and ternary glasses [5-8]. The phenomenon of rigidity percolation has been reported to occur at $\langle r \rangle$ = 2.4 or near $\langle r \rangle$ = 2.67 in various glasses. In binary glasses such as As-Se the threshold percolation occurs at $\langle r \rangle$ = 2.4 (the threshold proposed by Phillips and Thorpe [9]), whereas Tanaka threshold value occur at $\langle r \rangle$ = 2.67).

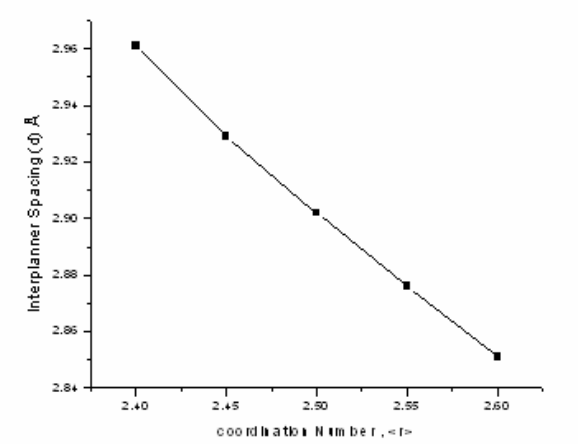

Fig. 1. The plot of the interplanner spacing (d) as a function of the coordination number $\langle r \rangle$.

3.2 Theoretical Prediction of Band Gap (E_g)

According to Kastner, the valence band in chalcogenide glasses is constituted by lone pair band whereas the conduction band arises from the antibonding band. In a multicomponent glass like Ge-Te-Bi, the position of the conduction band and valence band edges and thus the energy gap largely depends upon the relative number of various possible bonds and thus the average bond energy. The band gap for Ge-Te-Bi system can be calculated by using Shimakawa relation.

$$E_g(AB) = YE_g(A) + (1\text{-}Y)\,E_g(B) \qquad (2)$$

Where Y is the volume fraction of element A, E_g (A) and E_g (B) are the band gaps for A and B respectively. A theoretical prediction of band gap for Ge-Te-Bi glassy alloy is given in table1. A graphical representation of energy gap with coordination number is given in figure 2. It is clear from figure 2 that initially the optical energy gap decreases rapidly with the addition of Bi content. However at the higher Bi concentration E_g decreases but at a slower rate. This trend can be associated with the fact that at a lower Bi concentration localized states are developed in the gap. At a higher Bi concentration alloying effects may dominate, which produce a modified semiconductor [10]. Another explanation for the decrease of band gap may be attributed on the basis that, when Bi is added to Ge-Te binary alloy, Te-Bi bond formation takes place. Since bonds are formed in sequence of decreasing bond energy and the bond energy of Te- Bi bond is less than that of Ge-Te, Te-Bi bonds systematically replaces the Ge-Te bonds. Thus the average bond energy of the system decreases as the Bi concentration is increased. Since optical band gap is a bond sensitive property, a decrease in average bond energy results in the decrease in optical band gap.

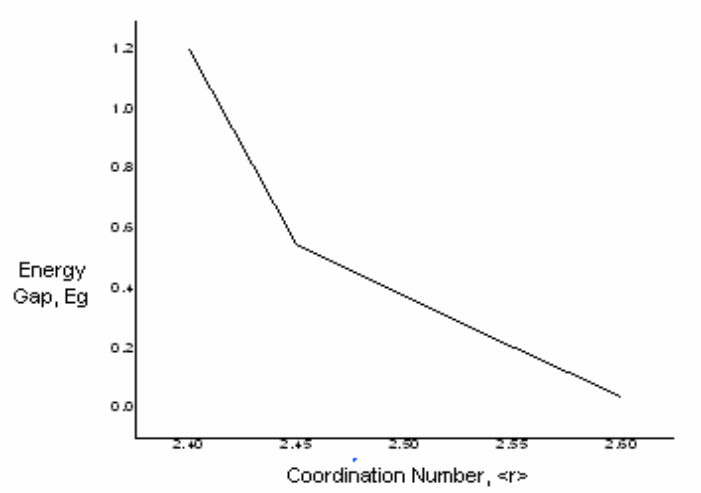

Fig. 2. The plot of the energy gap as a function of the coordination number.

3.3 Glass Transition Temperature

The glass transition temperature for Ge-Te-Bi glassy alloys is predicted theoretically by using modified Gibbs-Di Marzio law in which the effect of chemical ordering is considered [11]. In most of the chalcogenide systems the chemical ordering occurs for $\langle r \rangle \geq 2.4$. Above this coordination number the stochastic description fails and the network can be thought as a set of compound clusters inside a random network. When the effect of chemical ordering is considered the effective coordination number of the system is given by

$$r_{eff} = r_A + \frac{y(r_C - r_A)}{1 - x\dfrac{(r_A + r_B)}{r_A}} \tag{3}$$

Where r_A, r_B and r_C are the coordination numbers for Te, Ge and Bi respectively. The parameter β in this case is given by

$$\beta^{-1} = (r_C - r_A)\ln\left[\frac{r_C}{r_A}\right] \tag{4}$$

The glass transition temperature T_g is then calculated by using the relation

$$T_g = \frac{T_0}{1 - \beta(r_{eff} - 2)} \tag{5}$$

Here T_0 is the glass transition temperature of chalcogen (here T_0 is the glass transition temperature of Te = 343 K). Glass transition temperature is also computed by using the relation given by Tichy and Ticha [12, 13].

$$T_g = 311\left[\langle E\rangle - 0.9\right] \tag{6}$$

Where <E> is the mean bond energy of the system and is already been computed in [14]. The value of T_g is computed by both the approaches and is tabulated in table 2.

Table 2.

Composition	Gibbs-Di Marzio Law	Tichy and Ticha
$Ge_{20}Te_{80}$	343.00 K	354.54 K
$Ge_{20}Te_{75}Bi_5$	361.11 K	360.76 K
$Ge_{20}Te_{70}Bi_{10}$	381.00 K	373.20 K
$Ge_{20}Te_{65}Bi_{15}$	408.30 K	385.64 K
$Ge_{20}Te_{60}Bi_{20}$	428.80 K	401.19 K

3.4 Structure of Ge-Te-Bi Glassy Alloy

Fig. 3 is the proposed ternary phase diagram for Ge-Te-Bi system with three pseudo binary composition lines indicated. The bold line GeTe-Bi_2Te_3 contains the $Ge_2Bi_2Te_5$ composition (2 GeTe-Bi_2Te_3). This line is technologically useful as this composition is used in commercial rewritable digital versatile disks (DVD's). Along the line $GeTe_2$-Bi_2Te_3, if Te is always two fold coordinated then there are only Ge-Te and Te-Bi bonds. But along the line GeTe-Bi_2Te_3 as it contains insufficient Te to satisfy the constraints of only Ge-Te and Te-Bi bonds, there must be some additional bonds like Ge-Ge, Bi-Bi (or Ge-Bi may be). The vertical dashed line represents the composition for which the average coordination number is the same as it is for $Ge_2Bi_2Te_5$. This line is important because in some glassy systems many properties depend only on the average coordination number and not on the exact composition. This phenomenon is sometimes known as isocoordination rule [15].

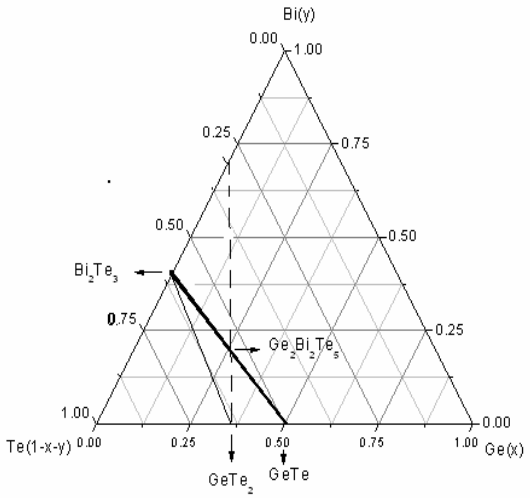

Fig. 3. The ternary phase diagram for Ge-Te-Bi system with the indication of the three pseudo binary composition lines.

4. Conclusion

From the above theoretically analyzed parameters we can conclude that as the coordination number increases the interplanner spacing decreases indicating that the structure system gets densified with the addition of Bi content. A change in slope near $\langle r \rangle$ = 2.47 predicts the percolation threshold at this coordination number. It has been seen that band gap also decreases whereas glass transition temperature increases with increasing Bi concentration. From the ternary diagram representation for

Ge-Te-Bi glassy alloys it can be concluded that if Te is two fold coordinated there should some additional bonds like Ge-Ge, Bi-Bi or perhaps Ge-Bi.

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