Theoretical Predictions of $Ge_{14}Bi_xSe_{76-x}In_{10}$ Chalcogenide Glasses

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Abstract: Chalcogenide glasses have attracted much attention in recent past as physical properties of chalcogenide glasses make them ideal for incorporation into lasers and other active devices. In the present work, the effect on the physical properties of $Ge_{14}Bi_xSe_{76-x}In_{10}$ (x = 2, 4, 6, 8, 10 at. %) chalcogenide glasses with the variation in bismuth content has been studied theoretically. All the parameters, studied here, have been found to vary linearly with change in Bi concentration which indicates this system suitable for phase change optical recording and find applications in rewritable optical recording.

Keywords: Chalcogenide Glasses**,** Average Coordination Number, Glass Transition Temperature, Cohesive Energy.

1. Introduction

Chalcogenide glasses, based on the chalcogen elements S, Se, and Te, have attracted much attention amongst researchers due to their vast applications. The chalcogenide glasses are disordered non crystalline materials which have pronounced tendency to link their atoms together to form link chain. Chalcogenide glasses can be obtained by mixing the chalcogen elements, viz, S, Se and Te with elements of the periodic table such as Ge, Bi, Ga,In, Sn, Si, Ag, As, Sb, Zn and Cd etc. The chalcogenide glasses are used in various optoelectronics applications, but still have plenty of room for their applications in a number of areas which have either less studied or undiscovered. These glasses are generally optically highly nonlinear and could therefore be useful for almost all-optical switching (AOS) devices. These glasses find potential applications in optical memory/switching devices, solar cells, infrared sensors, xerography, optoelectronic, microelectronic applications etc. One of the recent applications of chalcogenide alloys, containing at least one of the chalcogen elements like S, Se or Te, is in rewritable optical data recording i.e. phase change recording. This technology is based on reversible phase transition between amorphous and crystalline state [1–4].

The compositional dependence studies on glassy alloys were reported for the alloys based on the materials like Ge, Se, Te, Sb, Sn, Bi, Ag, As, Pb, Ga etc. Chalcogenide glasses in Ge–Se system are very often used as switching, memory elements and optoelectronic devices and are interesting material for infrared optics too. It has been established that physical properties in this system are highly composition dependent [5 –8]. It is worth to add more than two components into selenium matrix to produce considerable changes in the properties of complex glasses. Addition of an element like Bi to Ge-Se-In system expands the glass forming region and also creates compositional and configurational disorder in the system as well as induce large effect on their structural, physical, optical, electronic and thermal properties [9–11].

In the present work, we have taken a quaternary alloy comprising of Ge-Bi-Se-In i.e., $Ge_{14}Bi_xSe_{76-x}In_{10}$. Here we have fixed the concentration of Ge

at 14 at.% and In at 10 at.%, and then studied the variation of various important parameters by varying the concentration of Bi from 2 – 10 at.%. The variation in concentration of Bi element used to create compositional and configurational disorder in the material with respect to the quaternary alloys. The $Ge_{14}Bi_xSe_{76-x}In_{10}$ glass system seems to be of special interest as it forms glasses over a wide domain of compositions. The present article is concerned with the theoretical prediction of some important physical parameters related to composition, viz. average coordination number, lone pair, heat of atomization, cohesive energy, etc. for $Ge_{14}Bi_xSe_{76-x}In_{10}$ (x = 2, 4, 6, 8, 10 at. %) glassy alloys.

2. Theoretical Studies and Discussion

2.1 Ionic Character of Covalent Bond

According to Philips – Thorpe bond constraint theory for coordination number Z = 2.4 all bonds are absolutely covalent. But for any other value of Z the covalent bonds have some ionic character, i.e., molecule becomes polar. The percent ionic character or ionicity introduces a tendency towards ordering because of the non-directional character. Using the Pauling formula, the percent ionic character of a bond may be calculated [12].

Percent ionic character =

$$\left[1-e^{-\left[\frac{(\chi_A-\chi_B)^2}{4}\right]}\right]x100$$

where (χ_A-χ_B) is the difference in the electro negativities of atoms A and B. That, there should be a direct connection between bond strength and the glass formations was recognized by a number of investigators [13, 14]. High value of bond strength increases the glass forming tendency. The amount of covalent character or degree of covalency in the bond of amorphous glass under investigation can be calculated by using the Pauling formula as

Amount of covalent character =

$$\left[e^{-\left[\frac{(\chi_A-\chi_B)^2}{4}\right]}\right]x100$$

Elements with more than 85% covalent character are more promising for glass formation.

2.2 Bonding Constraints & Average Coordination Number

Phillips [15, 16] suggested the mechanical-constraint counting algorithms to explain glass forming tendencies. The strongest covalent forces between nearest neighbours serve as Lagrangian (mechanical) constraints defining the elements of local structure (building blocks). Constraints associated with the weaker forces of more distant neighbours must be intrinsically broken leading to the absence of long-range order. According to Phillips, the tendency of glass formation would be maximum when the number of degrees of freedom exactly equals the number of constraints.

The average coordination number (Z) was calculated using standard method [8] for the composition $Ge_{14}Bi_xSe_{76-x}In_{10,}$ Z is given by

$$Z=\frac{\alpha CN_{Ge}+\beta CN_{Bi}+\gamma CN_{Se}+\delta CN_{In}}{\alpha+\beta+\gamma+\delta}$$

where α, β, γ and δ are the at.% of Ge, Bi, Se and In respectively and $CN_{Ge}(4)$, $CN_{Bi}(3)$, $CN_{Se}(2)$, $CN_{In}(4)$ are their respective coordination number [17].

2.3 Role of Lone Pair Electrons

It is well established fact that an increase in the number of lone-pair electrons decreases the strain energy in the system and structures with large number of lone-pair electrons favours glass formation [12]. The numbers of lone-pair electrons are calculated by using the relation

$$L = V - Z$$

where L is the number of lone-pair electrons, V is the valance electrons and Z is the average coordination number. Zhenhua [18] proposed a simple criterion for a binary system and a ternary system, i.e., for a binary system the number of lone-pair electrons must be greater than 2.6 while for a ternary system it must be greater than 1.0 .

2.4 Deviation from the stoichiometry of composition

The parameter R that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For the present $Ge_{14}Bi_xSe_{76-x}In_{10}$ system, the parameter R is given by [19]

$$R = \frac{\gamma CN(Se)}{\alpha CN(Ge) + \beta CN(Bi) + \delta CN(In)}$$

where α, β, γ and δ are atomic frictions of Ge, Bi, Se and In respectively.

The parameter R, also play an important role in the analysis of the results. Depending on R values, the chalcogenide systems can be organized into three different categories. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor [19].

2.5 Mean Bond Energy and Glass Transition Temperature

According to Tichy and Ticha [20, 21], the value of glass transition temperature should not only be related to connectedness of the network which is related to Z, but should also be related to the quality of connections, i.e., the mean bond energy between the atoms of the network. The overall mean bond energy for the $Ge_{14}Bi_xSe_{76-x}In_{10}$ system is given by

$$< E >= E_c + E_{rm}$$

where E_c is overall contribution towards bond energy arising from strong heteropolar bonds and E_{rm} is contribution arising from weaker bonds that remains after the strong bonds have been maximized. For $Ge_\alpha Bi_\beta Se_\gamma Te_\delta$ system, where (α + β + γ + δ) = 1, in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4\alpha E_{Ge-Se} + 3\beta E_{Bi-Se} + 4\delta E_{In-Se}$$

and

$$E_{rm} = \left[\frac{2\gamma - 4\alpha - 3\beta - 4\delta}{Z}\right] E_{Se-Se}$$

denotes the average homo-polar bonding energy.

An impressive correlation of mean bond energy with glass transition temperature T_g was illustrated by the relation given by Tichy and Ticha [20, 21]

$$T_g = 311[< E > -0.9]$$

2.6 Average Heat of Atomization

The average heat of atomization H_s for a compound like $Ge_\alpha Bi_\beta Se_\gamma In_\delta$ is considered as a direct measure of the cohesive energy and thus average bond strength, as [22]

$$H_s = \frac{\alpha H_s^{Ge} + \beta H_s^{Bi} + \gamma H_s^{Se} + \delta H_s^{In}}{\alpha + \beta + \gamma + \delta}$$

where α, β, γ and δ are the ratios of Ge, Bi, Se and In respectively.

2.7 Cohesive Energy

Cohesive energy measures the average bond strength of the system. By using the chemical bond approach (CBA) method, the bond energies

are assumed to be additive. The cohesive energy for investigated samples has been calculated [8]. The cohesive energy for the Ge-Bi-Se-In system is calculated by summing the bond energies over all bonds expected in the system by using the relation:

$$CE = \sum C_i D_i$$

where C_i and D_i are the number of expected chemical bonds and energy of each bond respectively.

3. Results and Discussions

From the calculated values of average coordination number, as shown in fig. 1, the values of Z increase from 2.50 to 2.58 with increase in concentration of Bi from 2 to 10 using the calculated values of average coordination number for $Ge_{14}Bi_xSe_{76-x}In_{10}$ system. It is observed that for the glassy system $Ge_{14}Bi_xSe_{76-x}In_{10}$, that on increasing the Bi content, the number of lone-pair electrons goes on decreasing. This may be due to the interaction between Bi ion and lone-pair of electrons of bridging Se atom. In our system $Ge_{14}Bi_xSe_{76-x}In_{10}$, the values of lone-pair of electrons are found to be far greater than 1.00, however, it is found to be decreasing from 3.00 to 2.84 with the increase in Bi content from 2 to 10 at % as depicted in fig. 2.

It may be concluded that the present system under investigation can be obtained in amorphous glassy state. A system with large number of lone-pair electrons constitutes a stable state. Chalcogenides with lone-pair electrons are also characterized by flexibility. This flexibility of bonds causes these atoms to readily form amorphous network.

From fig. 3, it is clear that present system is within limit to be chalcogen rich but turning towards less chalcogen rich with the increase in Bismuth concentration in the system, and beyond 10 at % concentration, it becomes chalcogen poor. As the material is chalcogen rich up to 10 at % of bismuth and so having the high energy lone pair electrons leads to qualitative different electronic densities of state. The valence band is then non bonding and does not significantly contribute to the cohesive energy.

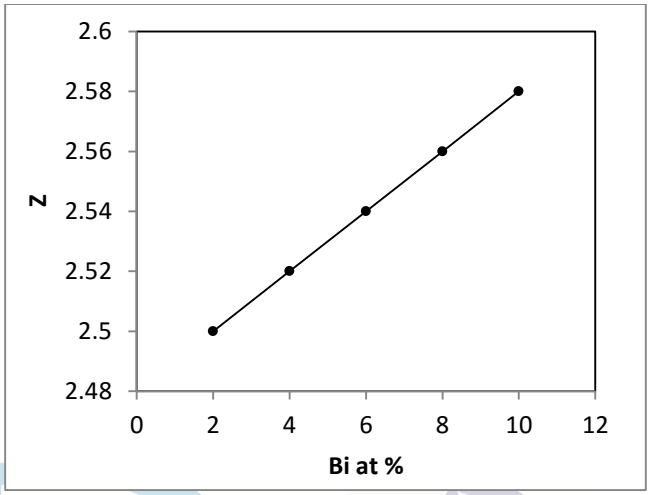

Fig 1: *Variation of Average Coordination Number with Bi content*

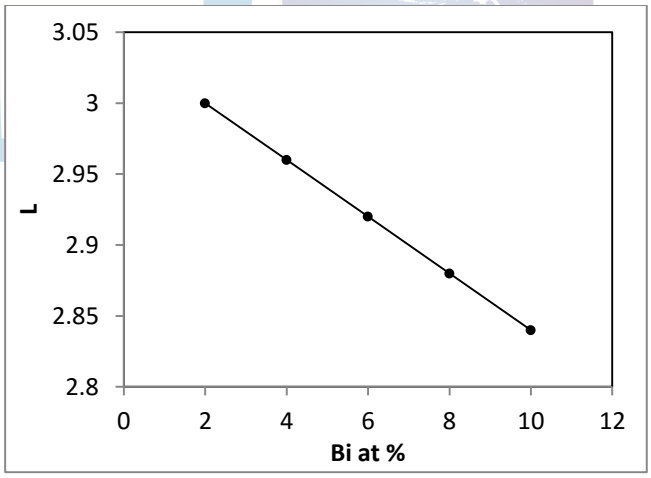

Fig 2: *Variation of Lone Pair Electron with Bi content*

It is clear from fig. 4 that <E> increases from 2.52 to 2.64 with increase in concentration of Bi from 2 to 10 at % i.e., selenium rich region. The variation of T_g with Bi content is shown in fig. 5, which is clearly depicting the rise in glass transition temperature from 505.49 to 541.61 with increasing the content of Bi from 2 to 10 at % due to rise in mean bond energy of the glassy system.

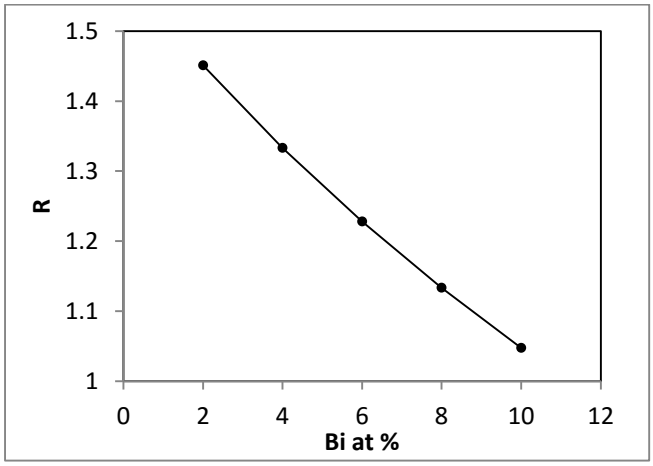

Fig 3: *Variation of parameter R with Bi content*

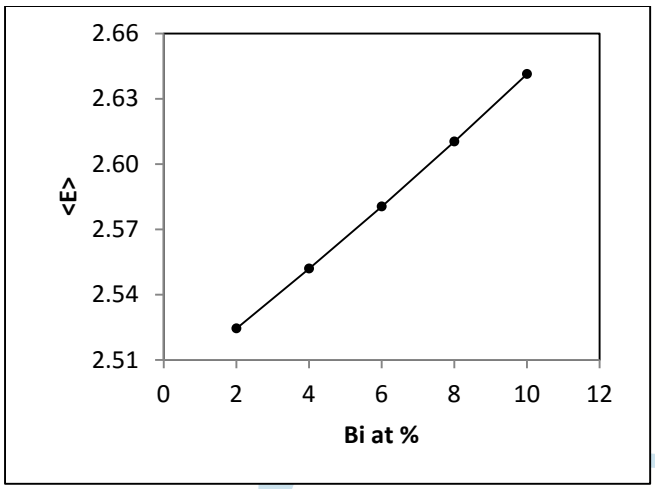

Fig 4: *Variation of overall mean bond energy with Bi content*

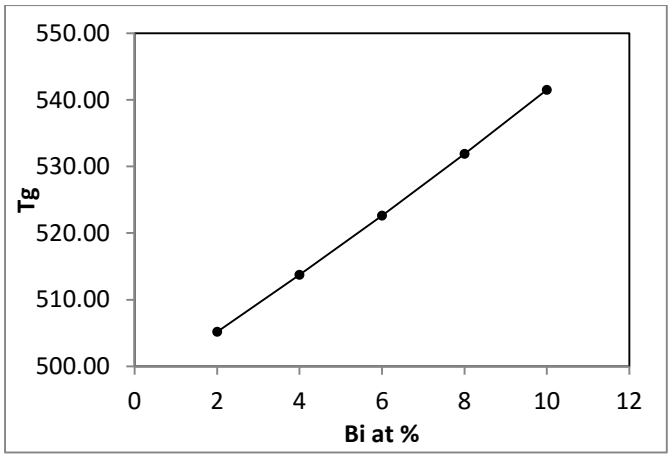

Fig 5: *Variation of glass transition temperature T_g with Bi content*

The values of average heat of atomization of Ge-Bi-Se-In quaternary system is calculated by using the above discussed relation Average single bond energy H_s which is a measure of cohesive energy, decreases with increase in Bi content from 2 to 10 at % for all the this composition, resulting in increase of optical band gap. A graphical representation of average heat of atomization per single bond H_s with the variation in Bi content is given in fig. 6.

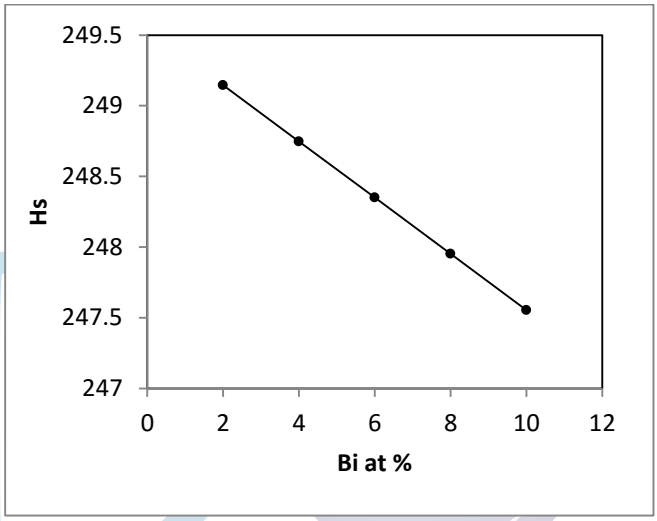

Fig 6: *Variation of average heat of atomization per single bond H_s with Bi content*

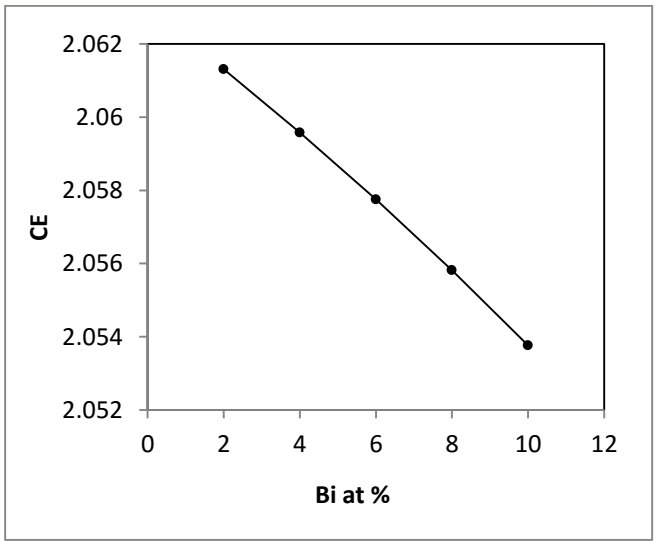

Fig 7: *Variation of cohesive energy with Bi content*

The variation of cohesive energy with Bi content is shown in fig. 7 which indicates a decrease in cohesive energy with increase in Bi content from 2 to 10 at % for this composition.

4. CONCLUSIONS

In the present work, we had considered a quaternary alloy $Ge_{14}Bi_xSe_{76-x}In_{10}$ (x = 2, 4, 6, 8, 10 at. %). The $Ge_{14}Bi_xSe_{76-x}In_{10}$ glass system is of special interest as it forms glasses over a wide domain of compositions. Various physical parameters properties have been calculated theoretically for $Ge_{14}Bi_xSe_{76-x}In_{10}$ system. The present system is in accordance with the earlier works according to which system with large number of lone-pair electrons constitutes a stable state. It is clear from various figures given above that almost all the parameters vary linearly with the change in Bi concentration from 2 to 10 at % in $Ge_{14}Bi_xSe_{76-x}In_{10}$ system and subsequently making this present system suitable for phase change optical recording.

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