EFFECT OF COMPOSITIONAL VARIATION OF THE PHYSICAL PARAMETERS OF Ge-Se-In GLASS SYSTEM

By

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ABSTRACT

In this paper an attempt has been made to theoretically find the variation of some important parameters of one of the arsenic fre Ge-Se glass system by the addition of In content. Various parameters like co-ordination number, floppy modes, bond energy, electro negativity, heat of atomization, cohesive energy and glass transition temperature have been calculated for $Ge_{16}Se_{84-x}In_x$ (x=0,1,2,3,4,5,6) glass system. Glass transition temperature (Tg) is calculated by using two approaches i.e. Tichy-Ticha and Lankhorst approaches. Tg seems to be increasing in theoretical calculations while average single bond energy is decreasing with the increase in the content of In.

Keywords: Chalcogenide, Cohesive Energy, Glass transition temperature, Lone pair electrons, Heat of Atomization.

INTRODUCTION

Chalcogenide Glasses (C.G) have recently attracted the attention of various researchers due to their wide applications in electronics and optical devices. Among these, due to the reversible phase transformation property, high transparencies in low and middle IR region, Selenium (Se) finds numerous applications in photocells, rectifiers, switching, memory etc. [1]. But Se also finds some disadvantages like short life time, aging and low sensitivity [2-4]. To improve its properties, it is alloyed with the elements of 3rd, 4th and 5th group of periodic table. The second element makes bonds with Se chain and thus strengthens the average bond and thereby increases the glass transition temperature. Ge-Se system is found to have wide glass forming ability. Whereas third element like In added to Ge-Se host structure in turn disturbs the long Se chains and results in short range ordering and increases defect concentration which helps in the network flexibility and thereby widens the glass forming region. So, in this paper, an attempt has been made to theoretically study the effect of partial replacement of Se by In on the physical parameters (i.e. co-ordination number, floppy modes, bond energy, electro negativity, heat of atomization, cohesive energy and glass transition temperature) of $Ge_{16}In_xSe_{84-x}$ (x=0,1,2,3,4,5,6) system.

1. Theoretical Methodology

Co-ordination number is an important parameter in describing the geometrical arrangement of particles in a unit cell of a crystal and is helpful in explaining some structural properties. In multi component glasses, the average co-ordination number describes the cross linking in the covalently bonded solids. Higher the co-ordination number is, stronger is the bonding between the atoms. Average Co-ordination number <r> has been calculated by the standard result [5-6]. Average Co-Coordination number <r> for the composition $Ge_{16}In_xSe_{84-x}$ (x=0, 1, 2, 3, 4, 5, 6) is given by

$$\langle r \rangle = \frac{aN_{Ge}+bN_{In}+cN_{Se}}{a+b+c} \qquad (1)$$

where a,b,c are concentrations (in %) of Ge, In, Se respectively and N_{Ge} = 4, N_{In}=4, N_{Se} = 2 are their respective co-ordination numbers.

Mechanical constraint theory proposed by Philips and Thorpe [5-6] explains the glass formation tendencies of the material structure. These constraints are associated with the breaking of long rage ordering and resulting into short range order which provides the flexibility required for the formation of glass. Philips and Thorpe approach compares the degree of freedom per atom and degree of

constraints acting on it. Number of constraints in an atomic species with average co-ordination <r> arises from Bond Bending N_B (angular) and Bond Stretching Ns (linear).

Bond Bending per atom is given by:

$$N_B = 2<r>-3 \quad (2)$$

Bond stretching per atom Ns is given by

$$N_S = <r>/2 \quad (3)$$

Total number of constraints is given by

$$N_T = N_B + N_S. \quad (4)$$

It has been further suggested that the composition at which the covalently bonded glassy system shows a sudden change from floppy (polymeric) state to rigid or stressed state is referred to as the Rigid Percolation Threshold (RPT) or Mechanical Threshold [6]. For covalently bonded network, rigid percolation occurs at <r> = 2.4 and at this point, the degree of freedom per atom and total number of constraints become equal. At this composition, glass forming ability of alloys is maximum. For <r>>2.4, the system is said to be over-stressed or rigid and for <r>< 2.4, the system is said to be under coordinated or floppy.

The effective co-ordination number $<r_{eff}>$ is also related with the total number of constraints

$$<r_{eff}> = 2(<r> +3)/5 \quad (5)$$

Number of floppy modes signifies the degree of cross-linking and is the function of average co-ordination number. The number of floppy modes can be determined by the following relation

$$f = 2-\frac{5}{6}<r> \quad (6)$$

Number of lone pairs can be calculated by using the following formula

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

Where L is the number of lone pairs and V is the number of valence electrons [7]. Number of lone pairs signifies the degree of flexibility. More the number of lone pairs, more is the possibility of the formation of amorphous network which enhances the glass formation ability. Thus lone pair electrons in the structure of a system are a necessary condition for obtaining the system in vitreous state [8].

Heat of atomization (H_s) is the energy required to dissociate the molecule into individual atoms. In case of the ternary compounds, the relation is given as

$$Hs = \frac{(aHs_{Ge} + bHs_{In} + cHs_{Se})}{a+b+c} \quad (8)$$

Where Hs_{Ge}, Hs_{In}, Hs_{Se} are heat of atomization of G_e, I_n, S_e. Average single bond energy which is a measure of bond strength can be calculated by heat of atomization as Hs/<r>. For ternary compounds, energy can be estimated using the relation [10]

$$Eg = aEg_{Ge} + bEg_{In} + cEg_{Se} \quad (9)$$

In $Ge_{16}In_xSe_{84-x}$ system, there is relatively more probability of the formation of Ge-Se, Se-In, Ge-In bonds, then homopolar bonds Se-Se. According to Chemically Ordered Network model, formation of hetropolar bonds dominates over homopolar bonds and the formation of bonds is in the decreasing order of their bond energy [9]. The energies of their hetropolar bonds is given by

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{1/2} + 30(x_A - x_B)^2 \quad (10)$$

where E_{A-A} , E_{B-B} are homopolar bond energies and x_A, x_B are corresponding electro-negativities.

Cohesive Energy of the system is the stabilization energy per atom of the large cluster. It is the amount of energy released when the crystalline structure is formed or amount of heat absorbed when crystalline structure is broken into individual atoms. Cohesive energy can be calculated by using the relation

$$C_E = \Sigma P_i E_i \quad (11)$$

where Pi is the number of bonds expected and Ei is the energy of corresponding bonds.

Various properties of C.G depends on mean bond energy E of the system which is the function of degree of cross linking, average co-ordination number and bond energy. Mean bond energy as proposed by Tichy-Ticha [11-12], is a combination of two factors, contribution to the bond energy by hetropolar bonds E_c and contribution by the remaining matrix E_{rm}. Thus mean bond energy can be given as

$$E = Ec + E_{rm} \quad (12)$$

E_c and E_{rm} can be calculated by using the following relations:

$$Ec = aE_{Ge\text{-}Se}r_{Ge} + bE_{Se\text{-}In}r_{In} \quad (13)$$

and

$$E_{rm} = \frac{(cN_{Se} - aN_{Ge} - bN_{In}) \times E_{se\text{-}se}}{\langle r \rangle} \quad (14)$$

Where N_{Ge}, N_{Se}, N_{In} are coordination numbers and a, b, c are concentration (in %) of Ge, Se, In respectively.

Parameter R is the ratio of covalent bonding of chalcogen atoms to non-chalcogen bonds. Parameter R indicates the deviation which represents that either chalcogen or metal bonds dominates the structure.

$$R = \frac{cN_{Se}}{(a N_{Ge} + b N_{In})} \quad (15)$$

where a,b,c are concentrations (in %) of Ge, In, Se respectively. R>1 signifies that the system is chalcogen rich and R<1 indicates chalcogen poor material i.e. metal-metal bonds dominates the structure.

Another parameter which can be determined is the glass transition temperature Tg. Glass transition temperature Tg is the transition from a pliable or "rubbery" state to more viscous, hard or rigid state. Or in other words, below Tg the material is rigid or glassy and above Tg the material is first super cooled liquid and then finally a liquid. Decrease in temperature hinders the mobility of molecular chains [13]. Tg is the function of overall mean bond energy, degree of cross linking, types of bonds and bond energy of network formation [14].

According to Tichy-Ticha, bond energy of the system also influences glass transition temperature [12]. They proposed an empirical relation between the mean bond energy and glass transition temperature which is given as

$$T_{gT} = 311\,(E\text{-}0.9) \quad (16)$$

Glass transition temperature is also related to the heat of atomization by a relation given by Lankhorst [15]. This is expressed by the relation,

$$T_{gL} = 3.44\,Hs - 488 \quad (17)$$

Results and Discussion

The values of average coordination number, constraints, floppy modes and lone pairs electrons calculated for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2, 3, 4, 5, 6) are shown in Table 1. From the table it is inferred that average coordination number, number of constraints and hence effective coordination number increases with the increasing concentration of In.

For x = 0, 1, 2, 3, 4, 5, 6 $Ge_{16}In_xSe_{84-x}$, average co-ordination number is first $\langle r \rangle < 2.4$, then becomes equal to 2.4 and finally $\langle r \rangle > 2.4$ and similarly total number of constraints range between $0 \geq N_t \geq 3$. Thus the system is showing transition from under stressed or floppy to stressed, rigid and over coordinated glass. Number of floppy modes and lone pair electrons decreases with the increasing concentration of In, indicating that the system is getting more and more rigid. Variation of effective coordination number, number of constraints, floppy modes and lone pair electrons with In concentrations is shown in Figure 1.

	<r>	N_α	N_s	N_t	r_{eff}	f	L
$Ge_{16}In_0Se_{84}$	2.32	1.64	1.16	2.8	2.128	0.066666667	3.36
$Ge_{16}In_1Se_{83}$	2.34	1.68	1.17	2.85	2.136	0.05	3.31
$Ge_{16}In_2Se_{82}$	2.36	1.72	1.18	2.9	2.144	0.033333333	3.26
$Ge_{16}In_3Se_{81}$	2.38	1.76	1.19	2.95	2.152	0.016666667	3.21
$Ge_{16}In_4Se_{80}$	2.4	1.8	1.2	3	2.16	0	3.16
$Ge_{16}In_5Se_{79}$	2.42	1.84	1.21	3.05	2.168	-0.01666667	3.11
$Ge_{16}In_6Se_{78}$	2.44	1.88	1.22	3.1	2.176	-0.03333333	3.06

Table 1. Values of Average Coordination No. (<r>), Constraints Bond bending (N_α), Bond Stretching (N_s) and Total (N), Effective Coordination Number, Floppy Modes (f) lone pairs of electrons(L) for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2,3, 4, 5, 6).

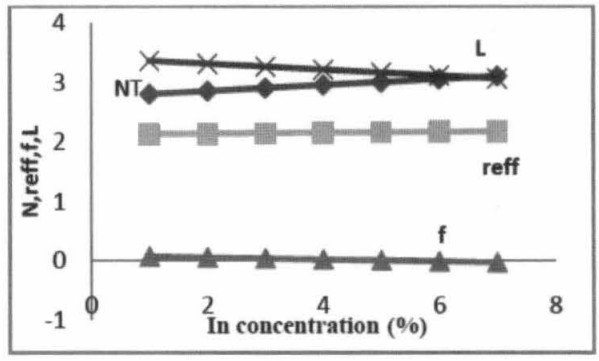

Figure 1. shows the variation of Number of constraints (N), Effective Coordination number (r_{eff}), number of floppy modes (f) and lone pair electrons (L) with In concentration for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2,3, 4,5, 6).

	H_s (kcal/g-atom)	$H_s/\langle r \rangle$	T_{gL} (K)	E_g (eV)
$Ge_{16}In_0Se_{84}$	55.89	24.09051724	316.96	1.79
$Ge_{16}In_1Se_{83}$	55.98	23.92307692	317.7168	1.77
$Ge_{16}In_2Se_{82}$	56.07	23.75847458	319.55333	1.75
$Ge_{16}In_3Se_{81}$	56.15	23.59243697	320.16608	1.73
$Ge_{16}In_4Se_{80}$	56.24	23.43333333	322.00304	1.71
$Ge_{16}In_5Se_{79}$	56.32	23.27272727	322.61192	1.69
$Ge_{16}In_6Se_{78}$	56.41	23.11885246	324.44888	1.67

Table 2. Values of Heat of Atomisation (H_s), Average Single Bond Energy ($H_s/\langle r \rangle$), Glass Transition Temperature (T_{gL}(Lankhorst)), Band Gap (Eg)for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2,3, 4, 5, 6).

Table 2 is showing the variation of heat of atomization, average single bond energy, glass transition temperature with x = 0, 1, 2, 3, 4, 5 ,6.

Values of glass transition temperature are calculated using Lankhorst relation for $Ge_{16}In_xSe_{84-x}$system.

Heat of Atomization of the system increases with In content, while average single bond energy decreases with the increasing content of In. In chalcogenide glasses, the lone pair of Se atom forms the top of the valence band. The lone pair of Se atoms has energy higher than the electronegativity of Se atoms. When electronegative Se atom (χ=2.55) is replaced by electropositive In (χ = 1.78), the energy of lone pair gets enhanced and valence band moves towards the energy gap. Thus, Energy gap decreases (E_g). Table 3 shows the variation of electro negativity, deviation of stoichiometry (R), distribution of bonds and cohesive Energy for $Ge_{16}In_xSe_{84-x}$system.

From Table 3, it can be observed that electro negativity is decreasing with electropositive content of In. Decrease of parameter R factor shows that the system is becoming chalcogen poor which implies that hetropolar bonds are increasing over homopolar bonds. Variation of number of bonds of Ge-Se, Se-In, Ge-In and Se-Se with the increasing content of In is also shown in Table 3. Since bond energy of Se-In bonds is highest among the bonds for the present system and number of Se-In bonds is increasing at a faster rate than Se-Se, Ge-In bonds, it leads to the increase in glass transition temperature. Cohesive energy is also increasing due to the increase in Ge-Se, Se-In content. This reflects that stabilization energy per atom increases with increasing In concentration. Variation of heat of atomization, cohesive energy and mean bond energy with In concentration is shown in Figure 2.

	c	R	Distribution of Bonds				CE
			Se-Ge	Se-In	Ge-In	Se-Se	(Kcal/mol)
$Ge_{16}In_0Se_{84}$	2.46	2.63	0.38	-	-	0.62	46.0596
$Ge_{16}In_1Se_{83}$	2.456	2.44	0.385	0.0481	0.24	0.54	46.3494
$Ge_{16}In_2Se_{82}$	2.45	2.28	0.39	0.09756	0.04878	0.4637	46.6574
$Ge_{16}In_3Se_{81}$	2.44	2.13	0.395	0.1481	0.0741	0.383	46.9576
$Ge_{16}In_4Se_{80}$	2.43	2	0.4	0.2	0.1	0.3	47.2789
$Ge_{16}In_5Se_{79}$	2.425	1.88	0.40506	0.253	0.1265	0.2152	47.5979
$Ge_{16}In_6Se_{78}$	2.41	1.77	0.41	0.31	0.1538	0.1282	48.0425

Table 3. Values of Electronegativity (χ), Deviation from Stoichiometry (R), Distribution of Bonds, Cohesive Energy(CE), for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2, 3, 4,5, 6)

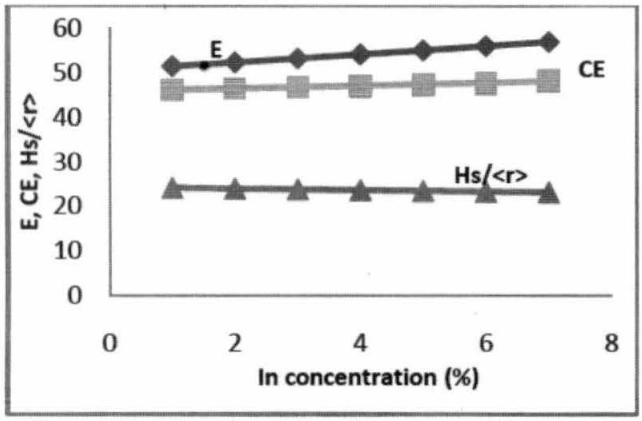

Figure 2. Variation of mean bond energy, cohesive energy, average single bond energy with In concentration for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2,3, 4,5, 6).

Table 4 shows the variation of mean bond energy with x = 0,1,2,3,4,5,6. As In increases, it is observed from Table 4 that hetero-polar bonds are increasing and thus E_c is increasing at the cost of weaker bonds resulting in the decrease of E_{rm}. Values of glass transition temperature are

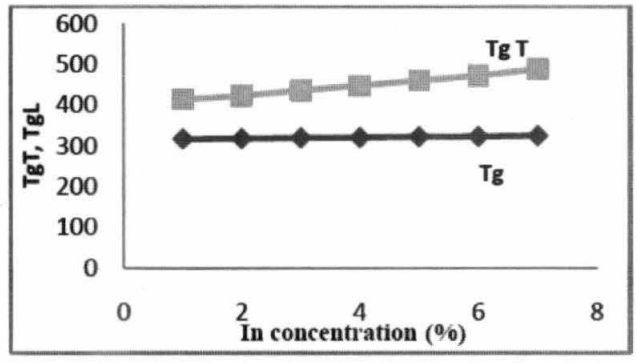

Figure 3.Variation of glass transition temperature (Tg) with In concentration for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2,3, 4,5, 6).

	Ec	Erm	E (Kcal/mol)	T_{gT} (K)
Ge16In0Se84	31.63	19.72	51.35	413.63
Ge16In1Se83	33.79	18.427	52.217	422.96
Ge16In2Se82	35.95	17.15	53.1	436.2086
Ge16In3Se81	38.11	15.899	54.009	447.84
Ge16In4Se80	40.27	14.66	54.93	460.28
Ge16In5Se79	42.43	13.455	55.885	472.72
Ge16In6Se78	44.59	12.26	56.85	488.27

Table 4. Values of Mean Bond Energy (E), Glass Transition Temperature (T_{gT} (Tichy-Ticha)), for $Ge_{16}In_xSe_{84-x}$ (x = 0, 1, 2, 3, 4, 5, 6)

Bonds	Bond Energy (Kcal/mol)
Ge-Se	49.42
In-Se	54.02
Ge-In	35.0774
Se-Se	44

Table 5. Values of Bond Energy for Ge-In-Se System.

also calculated from Tichy-Ticha formula.

Variation of glass transition temperature with Se concentration by using Lankhorst and Tichy-Ticha approach is shown in Figure 3. Bond energies of Ge-Se, Se-In, Ge-In, Se-Se are also shown in the Table 5.

Conclusion

Increasing concentration of In increases the number of hetero-polar bonds in the system and the system becomes more and more rigid. It is seen that average coordination number, number of constraints, cohesive energy is also increasing with the increase in the concentration of In or decrease in concentration of Se, whereas number of lone pairs and bond energy is decreasing with the increase in In content. Mean bond energy and heat of atomization increases with increase in In concentration leading to increase in glass transition temperature.

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