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BASIC PHYSICAL ANALYSIS OF NEW *Sb-Se-Ge-In* CHALCOGENIDE GLASSY ALLOYS BY PREDICTING STRUCTURAL UNITS: A THEORETICAL APPROACH

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Indium based chalcogenides have an adequate potential in nonlinear and optoelectronic applications. $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15) system has been studied theoretically for physical parameters. The connectivity of the system has been discussed in terms of average coordination number and total number of constraints which also influence the mean bond energy and cohesive energy of the system. Energy band gap has been correlated to average single bond energy and electronegativity.

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1. Introduction

Low transmission losses, semiconducting and phase change properties of chalcogenides make them attractive candidates to be used in all-optical devices [1], conducting chalcogenide glass sensors [2] and phase change memory devices [3] etc. *SbSeGe* glasses have possible applications in IR optical fibers because of their large bandgap, low material dispersion, low light scattering and long wavelength multiphonon edge [4, 5]. For 25 at. % of *Ge* alloying in $Sb_{10}Se_{90-x}Ge_x$ glass alloys a more rigid composition is obtained [6, 7]. This composition contains only heteropolar *Ge-Se* and *Sb-Se* bonds. $Sb_{10}Se_{65}Ge_{25}$ has been alloyed with *In* to investigate $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15) system *via* different physical parameters. Sharma *et al.* have reported that *In* addition increases the dark conductivity due to an increase in the number of defect states [8]. It has also been reported that *In* alloying decreases the optical energy band gap [9], suitable to explore the system for optoelectronic devices, and thermal activation energy [10] of the systems. These results motivate us to study the *In* alloying on $Sb_{10}Se_{65}Ge_{25}$ glass alloy. Due to large electronegativity difference between *Ge* and *In*, there is a possibility of increase in the glass forming region and *In* may also bring configurational and conformal changes in the base system.

The aim of present work is to study the effect of *In* on the theoretically calculated parameters of $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15). Average coordination number (m), total number of constraints per atom (N_t), Parameter R and mean bond energy ($<E>$) have been evaluated. Energy gap (E_g) has been correlated to the cohesive energy, average single bond energy (H_s/m) and electronegativity (χ). The density (ρ) and compactness (δ) have also been calculated.

2. Experimental details

The Thermo Gravimetric measurements for $Sb_{10}Se_{90-x}Ge_x$ (x = 0, 19, 21, 23, 25, 27) alloys were carried out using EXSTAR TG/DTA 6300. Bulk samples of $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9,

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12, 15) were prepared using melt quenching technique. High purity elements *Sb*, *Se*, *Ge* and *In*, in appropriate weight proportions, were vacuum (10^{-4} Pa) sealed in quartz ampoules. The sealed ampoules were then heated upto 1000 ^{0}C with a heating rate of 3-4 ^{0}C and frequently rocked to make the melt homogeneous. The quenching was done in ice cold water immediately after taking out the ampoules from the furnace. The ingots of the glassy system were obtained by breaking the ampoules. The amorphous nature of the alloys was confirmed by the absence of sharp peaks in the X-ray diffraction peaks (spectrum not shown here).

3. Results and discussion

Figure 1 shows the Thermo Gravimetric (TG) percentage variation with temperature for $Sb_{10}Se_{65}Ge_{25}$ at a heating rate of 10 ^{0}C/min. The composition is stable against decomposition at higher temperatures. Thus, the effect of *In* alloying has been studied on $Sb_{10}Se_{65}Ge_{25}$ by calculating the physical parameters.

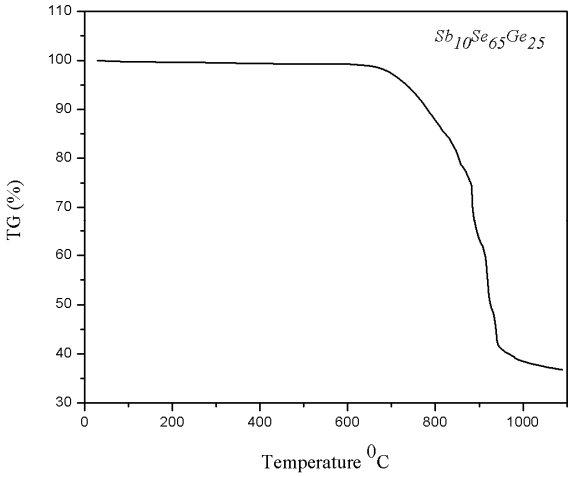

Fig. 1: Thermo Gravimetric (TG) %age variation with temperature for $Sb_{10}Se_{65}Ge_{25}$ at heating rate of 10 ^{0}C/min.

3.1 Average Coordination Number and Constraints

The average coordination number signifies the crosslinking in a covalent bonded glass system and has been calculated for $Sb_\alpha Se_\beta Ge_\gamma In_\lambda$ using the relation [11],

$$m = \frac{\alpha N_{Sb} + \beta N_{Se} + \gamma N_{Ge} + \lambda N_{In}}{\alpha + \beta + \gamma + \lambda} \quad (1)$$

where α, β, γ and λ are the atomic percentages and N_{Sb}, N_{Se}, N_{Ge} and N_{In} are the coordination numbers of *Sb*, *Se*, *Ge* and *In* respectively. Determination of *m* allows the calculation of the total number of constraints, $N_t = N_{bs} + N_{bb}$.

$N_{bs} = m/2$ is the number of bond stretching constraints and $N_{bb} = 2m - 3$ is the number of bond bending constraints. For $y = 0$, $m = 2.60$ and $N_t = 3.50$ indicates that the system is stressed rigid and over constrained. But, with increasing *In* concentration value of *m* decreases to 2.45 and that of N_t decreases to 3.125 for $y = 15$. So, there is a decrease in the connectivity of the system making the system less constrained which is due to the fact that more threefold coordinated *In* atoms are replacing fourfold coordinated *Ge* atoms as the *In* concentration increases.

3.2 Parameter R and Mean Bond Energy

Parameter *R* indicates the deviation of the glassy system from stoichiometry and is expressed as the ratio of covalent bonding possibilities of chalcogen atom to the non-chalcogen atoms [12],

$$R = \frac{bN_{Se}}{aN_{Sb}+cN_{Ge}+dN_{In}} \tag{2}$$

where *a*, *b*, *c* and *d* are atomic fractions of *Sb*, *Se*, *Ge* and *In* respectively. $R > 1$ signifies that the system is chalcogen rich and $R < 1$ indicates chalcogen poor material. The glass transition temperature T_g, below which supercooled liquid becomes glass, depends on overall mean bond energy, degree of crosslinking, '*m*', types of bonds and bond energy of network formation [12]. Mean bond energy of the system $Sb_aSe_bGe_cIn_d$ has been calculated using the relation [12],

$$<E> = E_c + E_{rm} \tag{3}$$

where E_c is the mean bond energy of the average cross linking per atom and E_{rm} is the average bond energy per atom of remaining matrix. For $R > 1$,

$$E_c = 4cE_{Ge\text{-}Se} + 3dE_{In\text{-}Se} + 3aE_{Sb\text{-}Se} \tag{4}$$

$$E_{rm} = \frac{(2b-3a-4c-3d)}{m} E_{Se-Se} \tag{5}$$

R and <*E*> have been plotted against *In* concentration in Figure 2. It can be observed that for $y = 0$, $R = 1$, which indicates that the system contains only trigonal Sb_2Se_3 and tetrahedral $(GeSe_{1/2})_4$ units. This signifies that a full 3D network between the two structural units has been attained. The $Sb_{10}Se_{65}Ge_{25}$ system can now be written as $(GeSe_2)_{25}(Sb_2Se_3)_5$. With increase in *In* at. %, *R* increases with values greater than 1 and <*E*> decreases. From the obtained values of *R*, it can be deduced that with *In* addition the system becomes chalcogen rich. For $R > 1$ the system also contains *Se-Se* homopolar bonds. <*E*> decreases with *In* introduction into the ternary glass matrix. This may be due to the fact that for $y = 0$ only heteropolar *Ge-Se* and *Sb-Se* bonds with structural units $Ge(Se_{1/2})_4$ and Sb_2Se_3 exists. But, with *In* addition *Ge* content decreases and hence the *Ge-Se* bonds. The lower energy *In-Se* bonds formation takes place and increases with *In* content. This decreases the values of <*E*> with *In* alloying.

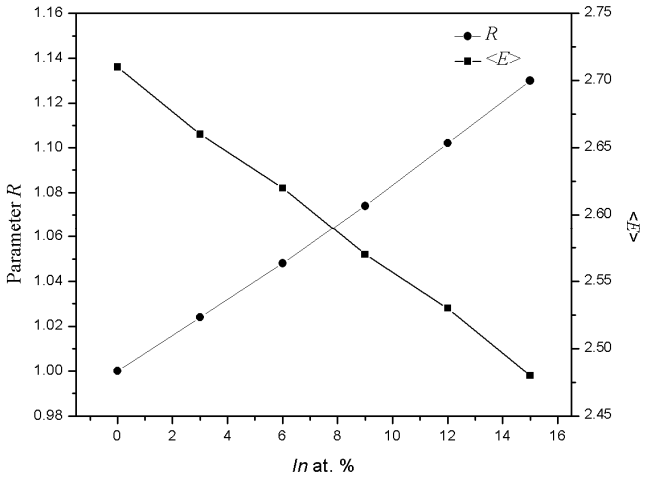

Fig. 2: Variation of Parameter R and mean bond energy (<E>) with increasing In content in $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15) glass system.

3.3 Cohesive Energy, Average Heat of Atomization, Energy Gap and Electronegativity

The cohesive energy of the system, defined as the stabilization energy of an infinitely large cluster of material per atom, has been calculated using the Chemical Bond Approach (CBA) [13]. According to CBA, atoms combine more favourably with atoms of different kind until all the available valences of the atom are filled. Bonds are always formed in the sequence of decreasing bond energies, which are assumed to be additive in nature. The heteropolar bond energies can be calculated as [13],

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2 \quad (6)$$

where E_{A-A} and E_{B-B} are the homopolar bond energies and χ_A and χ_B are corresponding electronegativities. The degree of covalency (C_c) of these bonds can be expressed as [14],

$$C_c = 100\ exp[-(\chi_A - \chi_B)^2/4] \quad (7)$$

C_c varies with the electronegativity difference between the two atoms and increases for *In* bonds with the decrease in bond energy (Table 2). The cohesive energy can be calculated using the relation [13],

$$CE = \sum_i C_i E_i \quad (8)$$

where C_i is the distribution of the chemical bonds and E_i is the energy associated with the corresponding bonds. Bond energies, distribution of chemical bonds and corresponding cohesive energies are given in Table 1. From Table 1 it is evident that *CE* decreases with increase in *In* at. % from 3 to 15. *Se* atoms are strongly bonded to the *Ge* atoms and fill the available valences of the *In* and *Sb* atoms respectively. But, still there are unsaturated *Se* atoms which appear as excess *Se-Se* bonds in the system. With increase in *In* content, *Ge-Se* bonds concentration decreases having bond energy 49.42 kcal/mol and *In-Se* bonds concentration increases having energy 48.20 kcal/mol. Thus, the overall bond energy of the system decreases and hence the value of *CE* .

Table 1: Values of average coordination number (m), bond stretching constraint (N_{bs}), bond bending constraint (N_{bb}), total number of constraints per atom (N_t), distribution of bonds, cohesive energies (CE) and electronegativity (χ)for $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15) glass system.

					Bond Distribution					
y	***m***	N_{bs}	N_{bb}	N_t	***Ge-Se***	***Sb-Se***	***In-Se***	***Se-Se***	***CE*** **(kcal/mol)**	**χ**
0	2.60	1.30	2.20	3.50	0.7692	0.2308	0	0	48.16	2.35
3	2.57	1.285	2.14	3.425	0.6769	0.2308	0.0692	0.0231	47.95	2.34
6	2.54	1.27	2.08	3.35	0.5846	0.2308	0.1385	0.0461	47.74	2.33
9	2.51	1.255	2.02	3.275	0.4923	0.2308	0.2077	0.0692	47.53	2.32
12	2.48	1.24	1.96	3.20	0.4000	0.2308	0.2769	0.0923	47.32	2.31
15	2.45	1.225	1.90	3.125	0.3077	0.2308	0.3462	0.1153	47.11	2.30

The average heat of atomization, H_s, is defined as a direct measure of cohesive energy and can be calculated, in kcal/g/atom, for the quaternary system ($Sb_\alpha Se_\beta Ge_\gamma In_\delta$) using [15],

$$H_s = \frac{\alpha H_S^{Sb} + \beta H_S^{Se} + \gamma H_S^{Ge} + \lambda H_S^{In}}{\alpha + \beta + \gamma + \lambda} \tag{9}$$

where α, β, γ, λ are the atomic % of *Sb*, *Se*, *Ge* and *In*. H_s values for *Sb*, *Se Ge* and *In* are 62, 49.4, 90 and 58 Kcal/g/atom respectively [6, 16]. The band gap values may be correlated to the bond strength of the system. Average single bond energy (H_s/m) specifies the bond strength and it decreases with an increase in the *In* at. % (Figure 3). This decreases the bond strength of the system and hence, the E_g values with *In* addition. The band gap values have been calculated using Shimakawa's relation as [17],

$$E_g(Sb - Se - Ge - In) = AE_g(Sb) + BE_g(Se) + CE_g(Ge) + DE_g(In) \tag{10}$$

where *A*, *B*, *C*, *D* are the volume fractions and E_g (*Sb*) = 0.101 eV, E_g (*Se*) = 1.95, E_g (*Ge*) = 0.95 eV and E_g (*In*) = 0 eV are the energy gaps of *Sb*, *Se*, *Ge* and *In* respectively. The variation of E_g with *In* at. % in Figure 3 follows from the above discussion. E_g may also be correlated to χ which gives an idea about the ionicity of the system. χ has been calculated using Sanderson's principle. In chalcogenide glasses, the lone pair of *Se* atom forms the top of the valence band and antibonding band forms the bottom of conduction band [6]. The lone pair of *Se* atom has energy higher than the electronegative *Se* atom. When electronegative *Ge* atom (χ = 2.01) is replaced by electropositive *In* atom (χ = 1.78), the energy of the lone pair gets enhanced and the valence band moves toward the energy gap [6]. This leads to a decrease in the energy gap. This is also evident from Table 1 with decreasing electronegativity values.

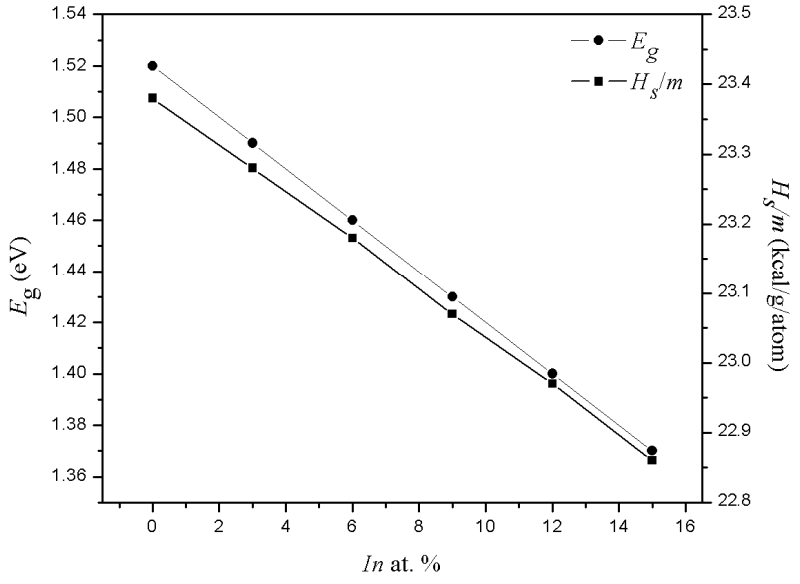

Fig. 3: Plot of E_g and H_s/m against increasing In at. % in $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15) glass system.

3.4 Density, Molar Volume, Packing Density and Compactness

The density (ρ) for the $Sb_{10}Se_{65}Ge_{25-x}In_x$ glass system has been calculated using the relation,

$$\rho = \left(\sum_i \frac{m_i}{d_i}\right)^{-1} \quad (11)$$

where m_i is the fraction of mass and d_i is the density of i^{th} structural unit. The density of the system increases on *Ge* substitution by *In* atoms (Table 2). As the structural modifications take place, higher density *In* atoms replace low density *Ge* atoms. Thus, the density of the system increases for each composition with increase in *In* at. %. The molar volume of the glassy system has been calculated as,

$$V_m = \frac{\sum X_i M_i}{\rho} \quad (12)$$

where X_i is the atomic fraction of i^{th} element and M_i is the molecular weight of the i^{th} component in the sample. The values of V_m (Table 2) increases with *In* content from $y = 0$ to $y = 15$. This may be attributed to the fact that *Ge* is substituted by larger *In* atoms leading to an increase in V_m with *In* content. The packing density of the system depends upon the mass and atomic radius of the constituting elements and can be calculated using,

$$Packing\ Density = \frac{N \times \rho}{M} \quad (13)$$

where N is Avogadro's number, ρ is density of the system as calculated above and M is the molecular weight. Packing density decreases (Table 2) with increase in *In* at. % as it has larger mass and atomic radius in comparison to the substituted *Ge* atoms.

Compactness (δ) measures the normalized change of the mean atomic volume on chemical interaction with the elements forming the network of a given solid [14]. δ has been calculated using the relation [14],

$$\delta = \frac{\sum_i \frac{c_i w_i}{\rho_i} - \sum_i \frac{c_i \rho_i}{\rho}}{\sum_i \frac{c_i \rho_i}{\rho}} \quad (14)$$

where c_i is the atomic fraction, w_i is the atomic weight and ρ_i is the atomic density of the i^{th} element of the glass. The compactness for the system increases with the *In* addition (Table 2). The density of the system increases with increasing *In* content. This leads to an increase in the compactness of the system.

Table 2: Values of degree of covalency (C_c), density (ρ), molar volume (V_m), molecular weight (M), Packing Density and compactness (δ) for $Sb_{10}Se_{65}Ge_{25-y}In_y$ (y = 0, 3, 6, 9, 12, 15) glass system.

y	**Bonds**	***C_c* (%)**	***ρ*** **(g/cm^3)**	***V_m*** **(cm^{3}mol^{-1})**	***M*** **(g mole)**	***Packing Density*** **(× 10^{22} atom/cm^3)**	***δ***
0	*Ge-Se*	92.96	5.11	15.97	81.66	3.76	-0.001505
3	*In-Se*	86.22	5.17	16.03	82.92	3.75	-0.001421
6	*Sb-Se*	93.94	5.23	16.09	84.19	3.74	-0.001252
9	*Ge-Sb*	99.96	5.29	16.14	85.45	3.72	-0.001002
12	*Ge-In*	98.68	5.35	16.20	86.72	3.71	-0.000674
15	*Sb-In*	98.19	5.41	16.26	87.98	3.70	-0.000272

The system has become less rigid due to decrease in connectivity of the system on *In* addition. This structural deformation also leads to a decrease in mean bond energy and band gap of the system.

4. Conclusion

In addition to $Sb_{10}Se_{65}Ge_{25}$ decreases the connectivity of the system. *In-Se* bonds, with lesser energy are formed at the cost of higher energy *Ge-Se* bonds and the system becomes chalcogen rich ($R > 1$) with increasing *In* at. %. There is decrease of mean bond energy and cohesive energy on *In* addition. Band gap decreases with increase in *In* concentration due to the decreasing values of average single bond energy and electronegativity. The system becomes denser with increase in *In* at. % which leads to increased compactness and decreased packing density of the system.

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