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Effect of indium incorporation on the physical parameters of Ge-Se glassy alloy

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Chalcogenide bulk glasses from $Ge_{20}Se_{80-x}In_x$ system, with $x = 0, 5, 10, 15, 20$ at. % has been prepared from high purity Ge, Se and In. Some physical parameters of these glassy alloys have also been examined theoretically. Nearest neighbor co-ordination number $< r >$, number of constraints per atom (N_{con}) as a function of $< r >$ is also calculated. It has been observed that N_{con} exceeds the number of degree of freedom (N_d) with increasing In content and shows non monotonic behavior. The compactness, as calculated from measured density of glassy system were examined in order to display the chemical threshold in the system using Phillips – Thorpe topological models proposed for the structure of these covalently bonded solids. Maximum of the compactness is observed at $< r >= 2.4$ for $Ge_{20}Se_{80}$ system is attributed to floppy to rigid transition occurring in networks. Lone pair of the system is also calculated and is found to decrease with increasing In content. This is due to the interaction between In atom and lone pair of bridging Se atoms, as interaction decreases the role of lone pair electron in glass formation.

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1. Introduction

Due to extensive applications from the view point of basic physics as well as device technology [1-6], chalcogenide glasses have received much attention in recent years. Se rich chalcogenide glasses exhibit high resistivity values implying certain limitations in their applications so in order to produce changes in the properties of new complex glass, it is worth to add more than one component into selenium matrix

Ge-Se system is a widely studied system and it has been established that physical properties in this system are highly composition dependent [7, 8]. Chalcogenide glasses in Ge-Se system are used as switching, memory elements and optoelectronic devices and are interesting material for infrared optics too [9]. They have a large range of transparency and many good mechanical properties like low internal stress, adhesion, hardness etc. The addition of third element in Ge-Se tetrahedral glassy network makes the glass an interesting material and new properties are expected since $Ge_{20}Se_{80}$ glassy alloy lies at the threshold of the mode change i.e. floppy ↔ intermediate region [10]. The addition of indium to $Ge_{20}Se_{80}$ system in an effective way control it's electrical, optical and physical properties as this will lead the system towards intermediate region.

The Ge-Se-In system is of special interest in view of the fact that it forms glasses over a wide domain of compositions. The glass forming region in the ternary Ge-Se-In system extends to about 20 at. % In and about 60-90 at % Se, with the rest being Ge [11]. Therefore, it is a suitable model system for the investigation of the variation of a certain physical property with composition or equivalently with the average coordination number, $< r >$. However the calculation of $< r >$ requires the knowledge of coordination numbers (CN) of all the constituents of glassy alloys. For the investigating system the $CN(Ge)$ and $CN(Se)$ respects the Mott $"8-N"$ rule [12], where N is the number of outer shell electrons and coordination number for In in Ge-Se-In system has been discussed by Saiter et al. [13, 14]. In the present paper, bond bending, bond stretching, number of constraints per atom (N_{con}), average effective coordination number $< r_{eff} >$, results of the compactness of the structure of these glasses as a function of $< r >$ and correlation between molar volume and optical band gap has been discussed. Influence of In variation on the lone pair electrons is also discussed in the paper.

2. Experimental details

Bulk samples $Ge_{20}Se_{80-x}In_x$ ($x = 0, 5, 10, 15, 20$) were prepared by melt quenching technique. High purity $(5N)$ elements Ge, Se and In, in the appropriate weight proportion, were vacuum sealed (10^{-6} mbar) in quartz ampoules and heated upto 1000 ^{0}C in a rocking furnace at a heating rate of 3-4 ^{0}C/min. The ampoules were frequently rocked at the highest temperature for 10 hours to maintain the homogeneity in the sample. The quenching was done in ice cold water immediately after taking out the ampoules from the furnace. The amorphous nature of the bulk samples was confirmed by the X-ray diffraction technique as no sharp peak was observed in spectra. The density of the glasses was measured by the Archimedes method.

3. Result and Discussion

3.1 Coordination no. of the system

Nearest-neighbor coordination in a ternary system is particularly suitable for testing the validity of these topological concepts [15, 16], because of its large glass forming region. The average coordination number $<r>$ in our system is defined by

$$<r> = \frac{aX + bY + cZ}{a + b + c} \tag{1}$$

where X, Y, Z are the percentage atomic weight of Ge, Se and In respectively and $a = 4$, $b = 2, c = 3$ are their respective coordination numbers. The obtained values of $<r>$ for the five compositions of $Ge_{20}Se_{80-x}In_x$ with x = *0*, *5*, *10*, *15* and *20* are listed in table 1.

3.2 Rigidity percolation in covalent networks and number of constraints

The idea of rigidity percolation was introduced by Phillips [17-19], and subsequently modified in detail by Thorpe [20]. Consider a network consisting of $N = \sum_i n_i$ atoms. If no bonds are formed there are $3N$ translational degrees of freedom. However, the translational mobility is reduced by the formation of covalent bonds among these atoms. The glassy networks are influenced by mechanical constraints (N_{con}), due to bond stretching forces $'\alpha'$ and bond bending force $'\beta'$. The residual mobility can be expressed by the number of zero frequency modes M_0, normalized by $3N$, according to

$$M_0 = (3N - N_{con}) / 3N \tag{2}$$

The total number of bond stretching and bond bending constraint are calculated according to

$$N^{\alpha} = \sum_i n_i r_i / 2 \quad \text{and} \quad N^{\beta} = \sum_i n_i (2r_i - 3) \tag{3}$$

Knowing the average number of constraints (per atom), $N_{con} = N^{\alpha} + N^{\beta}$ and the average coordination number $<r>$ for different composition of *a*-glassy system, the effective average coordination number $<r_{eff}>$ can be calculated [21] using the formula

$$<r_{eff}> = (2/5)(N_{con} + 3) \tag{4}$$

The values of $N^{\alpha}, N^{\beta}, N_{con}$ along with $<r_{eff}>$ for the $a\text{-}Ge_{20}Se_{80-x}In_x$ glassy system are given in table 1. In our system the average number of constraints per atom N_{con} exceeds the number of degrees of freedom $N_d = 3$ for all compositions. This is attributed to non-monotonic behaviour which revealed the presence of concentration dependent intrinsic homopolar bond defects. Thus the non-monotonic behaviour of various properties observed in these glasses is explained in terms of interplay between "mechanical" and "chemical" forces which affect the structure of the glass as a function of $<r_{eff}>$. According to Thorpe [20]; in the range of the glass-forming compositions, the system should contain rigid and floppy regions. In the $a\text{-}Ge_{20}Se_{80-x}In_x$ compositions the average coordination number varies from 2.4 to 2.6. Here $<r> = 2.4$ corresponds to the mechanical percolation threshold where number of floppy modes goes to zero and an abrupt transition from a deformable network to a rigid glass takes place.

Table 1.

Composition	$<r>$	N^{α}	N^{β}	N_{con}	$<r_{eff}>$
$Ge_{20}Se_{80}$	2.4	1.2	1.8	3	2.4
$Ge_{20}Se_{75}In_{05}$	2.45	1.225	1.9	3.125	2.45
$Ge_{20}Se_{70}In_{10}$	2.5	1.25	2	3.25	2.5
$Ge_{20}Se_{65}In_{15}$	2.55	1.275	2.1	3.375	2.55
$Ge_{20}Se_{60}In_{20}$	2.6	1.3	2.2	3.5	2.6

3.3 Compactness of the system

The density of the glasses was measured by the Archimedes method using double distilled water as a reference liquid, which has a density of 1.0 g/cc at 20°C. The density was calculated from the formula

$$\rho = \left[\frac{w_1}{w_1 - w_2} \right] \rho_{water} \tag{5}$$

where w_1 and w_2 are the weight of the sample in air and the weight of the sample in the reference liquid respectively. The calculated density values are reported in table 2. The error in the density measurement and consequently in δ, obtained by measuring the densities of some pure elements was estimated to be less than $\pm 1\%$. The compactness δ was calculated by the formula [22-24]

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}} \qquad (6)$$

where c_i is the atomic fraction, A_i is the atomic weight, ρ_i is the atomic density of the i^{th} element of the glass and ρ is the measured density of the glass. Thus, δ is a measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of a given solid [25]. Consequently, it is more sensitive to changes in the structure of the glass network as compared to the mean atomic volume.

The molar volume (V_m) was determined from the density data by the equation

$$V_m = \frac{1}{\rho}\sum_i x_i M_i \qquad (7)$$

where M_i is the molecular weight of the i^{th} component and x_i is the atomic percentage of the same element in the sample.

Table2.

Composition	$\rho(g/cc)$	$M(g/mole)$	$V_m(cc/mole)$	δ	$E_g^{opt}(eV)$
$Ge_{20}Se_{80}$	4.268	77.696	18.20	-0.13002	1.69
$Ge_{20}Se_{75}In_{05}$	4.2258	79.489	18.81	-0.15985	1.72
$Ge_{20}Se_{70}In_{10}$	4.2	81.282	19.35	-0.18515	1.75
$Ge_{20}Se_{65}In_{15}$	4.38	83.075	18.97	-0.17036	1.67
$Ge_{20}Se_{60}In_{20}$	4.64	84.867	18.29	-0.14153	1.51

Table 2 summarizes the densities of the investigated compositions, their corresponding compactness and molar volume. The compositional variation of compactness, characterized by $< r >$ of the investigated glassy alloys is shown in figure 1. From the figure, it is evident that maxima of the compactness occurs at the $< r >= 2.4$, which can be well understood in light of constraint theory and rigidity percolation concept [17, 19, 20, 26]. The stability of the network with $< r >= 2.4$, where the floppy-to-rigid transition takes place can be associated with atomic arrangements that become more tightly bound with shorter bond lengths resulting to smallest mean atomic volume of the network and hence compactness rises to the maximum. Thus, this maximum observed compactness at $< r >= 2.4$ for $Ge_{20}Se_{80}$ glassy alloy, is attributed to the floppy-to-rigid transition occurring in these networks.

The variation of molar volume (V_m) with composition (x at. %) is shown in figure 2. From the figure, it is clear that molar volume first increases up to 10 at. % In concentration and then decreases with further In addition. The variation of optical band gap (E_g) also follows the same trend with In concentration [27]. In chalcogenide glasses, the valance band $(\sigma - bonding)$ originates from lone pair (LP) electron states whereas the conduction band arises from antibonding $(\sigma *)$ states [28]. The energy of the conduction band edge is decided by number of atoms per unit volume (N). A decrease in N leads to an increase in the energy of conduction band edge hence increase optical band gap. From figure 2, N decreases up to 10 at. % In, corresponds to increase in optical band gap and with more In addition, N increases and subsequent decrease in optical band gap.

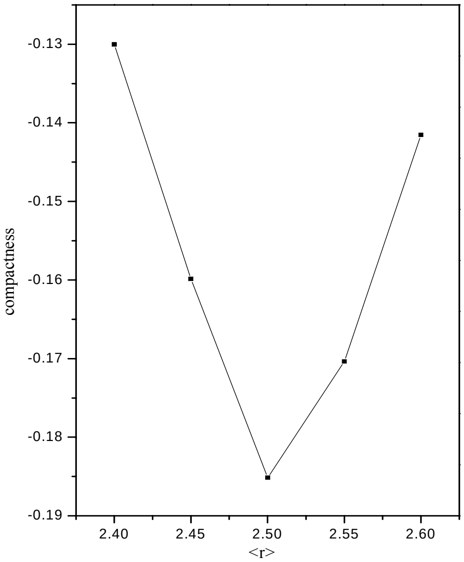

Fig. 1. Variation of compactness with average coordination number <r>

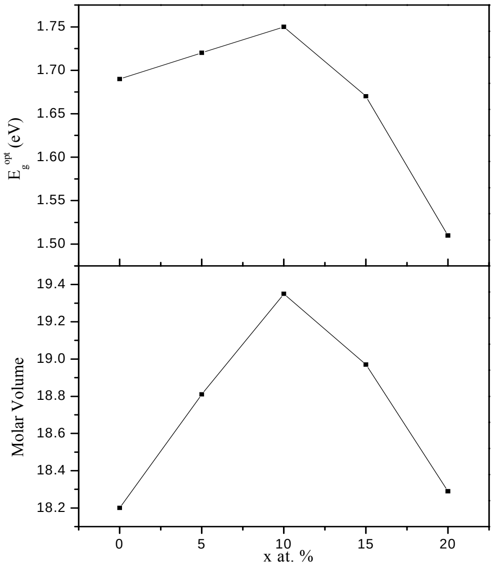

Fig. 2. Variation of molar volume and optical band gap (E_g^{org}) *with x at.%*

3.4 Relation between glass forming ability and lone pair electrons of structure

Most of the substances which can solidify in the vitreous state are found to possess structural 'bridges', that give rise to tri-dimensional, bi-dimensional or linear heteropolymeric formation. In most glasses, the bridges are formed of elements of group VI and VII .The Se atoms in glass structures have two pairs of lone-pair electrons. The existence of bridging atoms with lone-pair electrons can eliminate the strain force caused by the formation of amorphous materials. In terms of the viewpoint proposed by Pauling [29], the chemical bonds with lone-pair electrons have a character of flexibility. Increasing the number of lone-pair electrons decreases the strain energy in a system, and structures with large numbers of lone-pair electrons favor glass.

Table 3.

x	$< r >$	V	$L = V - < r$
0	2.4	5.6	3.2
5	2.45	5.45	3.0
10	2.5	5.30	2.8
15	2.55	5.15	2.6
20	2.6	5.00	2.4

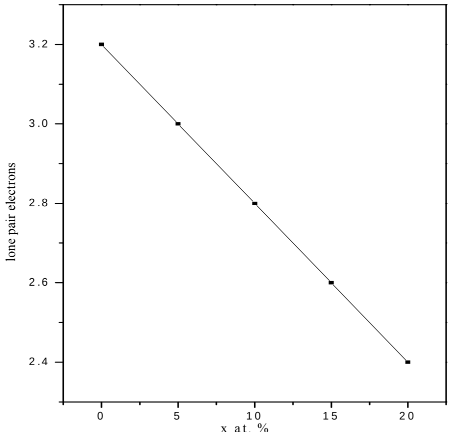

Fig. 3. Variation of lone pair electrons with Indium content (xa.%).

formation. The lone pair of electrons are calculated by the following equation:

$$L = V - < r > \tag{8}$$

where L is the number of lone pair electrons, V is the valance electron which is equal to unshared lone-pair electrons and $< r >$ is the coordination number and the results are listed in table 3.

Figure 3 shows the variation of lone pair electrons with In content. It is seen from figure 3 that the number of lone-pair electrons decreases continuously with the increase of the content of In in the system. This result is caused by the interaction between the In ion and the lone pair electrons of a bridging Se atom. The interaction decreases the role of lone-pair electrons in the glass formation. Zhenhua [30] introduced a simple criterion for computing the ability of a chalcogenide system to retain its vitreous state, the criterion contains the number of lone-pair electrons which is necessary for obtaining the system in its vitreous state. For a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1.

4. Conclusion

The influence of In content on the physical parameters of Ge-Se glassy alloy is investigated. With the addition of In, Ge-Se system changes from floppy to intermediate or rigid region. Average Number of constraints per atom $\left(N_{con}\right)$ exceeds the number of degree of freedom $\left(N_d\right)$ for all compositions and shows non monotonic behavior. The density, the compactness varies due to the variation of In content. Compactness (δ) as a function of average coordination number $< r >$ has been investigated. The observed maxima at $< r >= 2.4$ is caused by Phillip's – Thorpe floppy to rigid transformation. Molar volume first increases to its maximum value up to 10 at. % of In content and then decreases with further In addition to Ge-Se alloy. With addition of In, number of lone pair decreases continuously which is caused by the interaction between the In ion and lone pair electrons of bridge Se atoms.

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