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A study of physical properties of Ge-Se-In glassy semiconductors

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In the present paper we have calculated the number of constraints, effective coordination number, theoretical band gap, average heat of atomization, average single bond energy, lone pair electrons, bond energy of different bonds, glass transition temperature and mean bond energy for $Ge_{17}Se_{83-x}In_x$ (x = 0, 3, 6, 9, 12, 15) alloys. Alloys were prepared using melt quenching technique. It has been observed that theoretical band gap decreases with the increase of In content. This decrease may be explained on the basis of increase in heat of atomization with the increase of In content. From the mean bond energy calculations it has been found that there is a change in trend at $<r> = 2.43$.

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1. Introduction

Chalcogenide glasses have drawn prodigious attention because of their potential use in photoresist, microelectronic, optoelectronic, holographic applications and especially their ability to transmit light in the mid to far-infrared region [1-6]. Impurity effects in chalcogenide glasses may have importance in fabricating glassy semiconductors. The infrared transparency of chalcogenide glasses allows their use in optical fibers for transmission of light generated by CO and CO_2 lasers operating in infrared region and such fibers are applied towards high-precision tools in surgery, industrial cutting and welding etc.

Ge–Se system is a widely studied system [7-10] and glass formation in this system occurs predominantly in alloys enriched with Se and containing 0–25 at% of Ge [11]. In the present work, we have incorporated indium (In) in the Ge-Se alloy. The addition of third element will create compositional and configurational disorder in the material with respect to the binary alloys [10]. Chalcogenide glasses in Ge–Se system are 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 [12,13].

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 [14]. Therefore, it is a suitable system for the investigation of the variation of certain physical properties.

In present paper a study has been conducted on the physical properties viz. number of constraints, effective coordination number, theoretical band gap, average heat of atomization, average single bond energy, lone pair electrons, bond energy of different bonds, glass transition temperature and mean bond energy for $Ge_{17}Se_{83-x}In_x$ (x = 0, 3, 6, 9, 12, 15) alloys. The variation of properties has been discussed on the basis their compositions.

2. Experimental details

Bulk sample of $Ge_{17}Se_{83-x}In_x$ (x = 0, 3, 6, 9, 12, 15) were prepared using melt quench technique. Materials (99.999% purity) were weighed according to their atomic percentages and sealed in quartz ampoules in a vacuum ~ 10^{-4} Pa. The sealed ampoules were heated up to 950 ^{0}C at a rate of 2-3 ^{0}C/min and rocked for 12 hours at the highest temperature to make the melt homogeneous. The quenching was done in ice-cold water immediately after taking out the ampoules from the furnace. The amorphous nature of bulk samples has been confirmed by X-ray diffraction studies as no sharp peak is observed.

3. Results and discussion

3.1 Number of constraints and the effective coordination number for the system

The glassy networks are influenced by mechanical constraints (N_c) associated with the atomic bonding and an average effective coordination number $< m_{eff} >$ which is also related to N_c. In a covalently bonded glassy network two types of constraints, bond stretching N^{α} and bond-bending N^{β} need to be counted [15]. For atomic species with coordination number *(m)*, the number of constraints per atom arising from bond bending $N_b = 2m - 3$ and from bond stretching $N_a = m/2$. Knowing the average number of constraints $N_c = N_a + N_b$ and the average coordination number m for different composition of *a*- $Ge_{17}Se_{83-x}In_x$

glassy system, the effective average coordination number $< m_{\text{eff}} >$ can be calculated [16] using the formula

$$< m_{\text{eff}} > = (2/5)(N_c + 3) \tag{1}$$

The values of N^{α}, N^{β}, N_c along with $< m_{\text{eff}} >$ for the *a*-$Ge_{17}Se_{83\text{-}x}In_x$ glassy system are given in Table 1. In our system the average number of constraints per atom N_c exceeds the number of degrees of freedom $N_d = 3$ for the compositions x = 9, 12 and 15. 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 $< m_{\text{eff}} >$. According to Thorpe [17] in the range of the glass-forming compositions, the system should contain rigid and floppy regions. In the *a*- $Ge_{17}Se_{83\text{-}x}In_x$ compositions the average coordination number varies from 2.34 to 2.49. The transition from floppy mode to rigid mode [17] takes place for the composition $Ge_{17}Se_{77}In_6$. This means m = 2.4 corresponds to the mechanical percolation threshold. According to Zachariasen [18], atoms combine more with atoms of different kinds than with the same kind. This condition is equivalent to assuming the maximum amount of chemical ordering possible. This means that bonds between like atoms will only occur if there is an excess of a certain type of atom, so that it is not possible to satisfy its valence requirements by bonding it to atoms of different kinds alone, so bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated.

Table 1. Values of average coordination number <r>, number of constraints arising from bond stretching (N^{α}), number of constraints arising from bond bending (N^{β}), average number of constraints (N_c), and effective coordination number (<r_{eff}> for a-$Ge_{17}Se_{83\text{-}x}In_x$ (x=0, 3,6,9,12,15).

Composition	<r>	N_α	N_β	N_c	<r_{eff}>
$Ge_{17}Se_{83}$	2.34	1.17	1.68	2.85	2.34
$Ge_{17}Se_{80}In_3$	2.37	1.185	1.74	2.925	2.37
$Ge_{17}Se_{77}In_6$	2.4	1.2	1.8	3	2.4
$Ge_{17}Se_{74}In_9$	2.43	1.215	1.86	3.075	2.43
$Ge_{17}Se_{71}In_{12}$	2.46	1.23	1.92	3.15	2.46
$Ge_{17}Se_{68}In_{15}$	2.49	1.245	1.98	3.225	2.49

The possible bond distribution at various compositions using chemically ordered network (CON) model [19]. The model assumes that atoms combine more favourably with atoms of different kinds than with the same and bonds are formed in the sequence of bond energies [19]. As In replaces Se the number of In-Se bonds increase at the expense of Se-Se. The bond energies E_{AB} for heteronuclear bonds have been calculated by using the relation [20]

$$E_{AB} = (E_{AA} + E_{BB})/2 + 23(\chi_A - \chi_B)^2 \tag{2}$$

where E_{AA} and E_{BB} are the energies of the homonuclear bonds and χ_A and χ_B are the electronegativies of the atoms involved. The bonds formed in *a-$Ge_{17}Se_{83\text{-}x}In_x$* system and their energies are given in Table 2 and electronegativity for Ge = 2.01, Se = 2.55 and In = 1.78. The assumption mentioned above can be applied in its simplest form to memory materials, where there is no ambiguity about the formal order in which the bonds are formed [21].

Table 2. Values of average heat of atomization (H_s) (kcal/g-atom), average single bond energy (H_s/m), valence electrons (V) and lone pair electron (L) in a-$Ge_{17}Se_{83\text{-}x}In_x$ (x=0, 3,6,9,12,15).

Composition	H_s	H_s/<r>	V	L
$Ge_{17}Se_{83}$	56.302	24.06068	5.66	3.32
$Ge_{17}Se_{80}In_3$	56.56	23.86498	5.63	3.26
$Ge_{17}Se_{77}In_6$	56.818	23.67417	5.6	3.2
$Ge_{17}Se_{74}In_9$	57.076	23.48807	5.57	3.14
$Ge_{17}Se_{71}In_{12}$	57.334	23.3065	5.54	3.08
$Ge_{17}Se_{68}In_{15}$	57.592	23.12932	5.51	3.02

3.2 Theoretical energy gap

It is found that the variation of energy gap with composition in amorphous alloys can be described by assuming random network using relation [22]

$$E_g(AB)(Y) = YE_g(A) + (1 - Y)E_g(B) \tag{3}$$

where Y is the volume fraction of element A, $E_g(A)$ and $E_g(B)$ are the optical gaps for A and B elements, respectively. The conversion from atomic composition (at%) or molecular composition (mol %) to volume fraction Y is made using atomic or molecular mass and density of both In and Se.

3.3 The average heat of atomization

It is interesting to relate the band gap with the chemical bond energy. For this purpose we calculate the heat of atomization. According to Pauling [23], the heat of atomization $H_s(A-B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of heat of formation ΔH and the average heats of atomization H_s^A and H_s^B that corresponds to the average non-polar bond energy of the two atoms

$$H_s(A-B) = \Delta H + \frac{1}{2}\left(H_s^A + H_s^B\right) \tag{4}$$

The first term in above equation is proportional to the square of the difference between the electronegativities χ_A and χ_B of the two atoms:

$$\Delta H \quad \alpha \quad \left(\chi_A - \chi_B\right)^2 \tag{5}$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization $\overline{H}_s$ (in kcal per gram-atom) is defined for a compound $A_\alpha B_\beta C_\gamma$ as a direct measure of the cohesive energy and thus of average bond strength, as

$$\overline{H}_s = \frac{\alpha H_s^A + \beta H_s^B + \gamma H_s^C}{\alpha + \beta + \gamma} \tag{6}$$

Obviously the $\overline{H}_s$ values do not contain the heat of formation (ΔH) as part of cohesive energy, however $\overline{H}_s$ is useful parameter for correlating the physical properties of semiconducting compounds. In case of chalcogenide glasses the heat of formation contributes very little towards the average heat of atomization because the electronegativities of the constituent elements *i.e.* Ge, Se and In are very similar and in most of the cases of chalcogenide glasses the heat of formation is unknown. In few materials for which heat of formation is known it accounts only 10% of the heat of atomization and is therefore neglected. Hence for binary chalcogenide glasses $H_s(A-B)$ is given by

$$H_s(A-B) = \frac{1}{2}\left(H_s^A + H_s^B\right) \tag{7}$$

whereas for ternary and higher order compounds, $\overline{H}_s$ is given by the equation (7) is applicable. The heat of atomization for Ge, Se, In elements [24] and average heat of atomization $\overline{H}_s$ (kcal/g-atom) and average single bond energy $\left(\overline{H}_s / m\right)$ are given in Table 4, where *m* is the average coordination number. The average coordination number *(m)* was calculated using the standard method [8]. For the composition $Ge_aSe_bIn_c$ is given by,

$$< r > = \frac{aN_{Ge}bN_{Se}cN_{In}}{a+b+c} \tag{8}$$

where $N_{Ge}=4$, $N_{Se}=2$ and $N_{In}=3$, a, b and c are the ratios of Ge, Se and In, respectively. From the Table 3 it is found that the heat of atomization decreases with the increase of In content *i.e.* the average single bond energy decreases. This decrease in the average single bond energy with the increase of In content may causes the decrease of band gap.

Table 3. Values of theoretical energy gap, mean bond energy (<E>), glass transition temperature (T_g) and bond energies of various possible bonds in a-$Ge_{17}Se_{83-x}In_x$ (x=0, 3,6,9,12,15).

Composition	Eg (Theoretical)	<E> kcal/mol	Tg (K)	Bonds	Bond Energy
$Ge_{17}Se_{83}$	1.804765075	51.81535043	422.4215	Ge-Se	49.1
$Ge_{17}Se_{80}In_3$	1.756705194	77.13930802	765.6703	Se-Se	44
$Ge_{17}Se_{77}In_6$	1.708510853	102.9146667	1115.038	Se-In	48.2
$Ge_{17}Se_{74}In_9$	1.660181487	129.1247078	1470.297	Ge-Ge	37.6
$Ge_{17}Se_{71}In_{12}$	1.611716528	57.53674797	499.9711	In-In	29.83
$Ge_{17}Se_{68}In_{15}$	1.563115404	59.14225703	521.7327	Ge-In	33.72

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 [25], 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 formation. The lone pair of electrons are calculated by equation 8.

$$L = V - < r > \tag{9}$$

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.

Fig. 3 shows the variation of lone pair electrons with In content. It is seen from Fig. 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. Liang [26] 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.

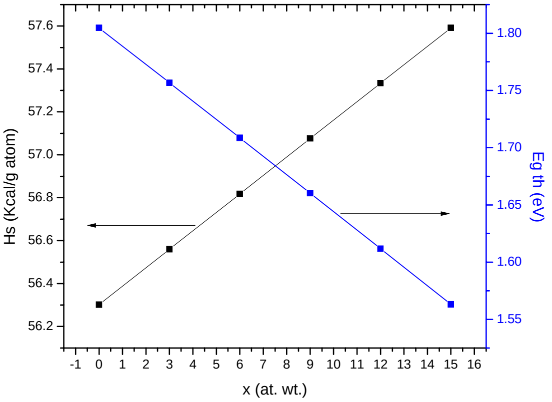

Fig. 1. Variation of theoretical energy gap and average heat of atomization with In content.

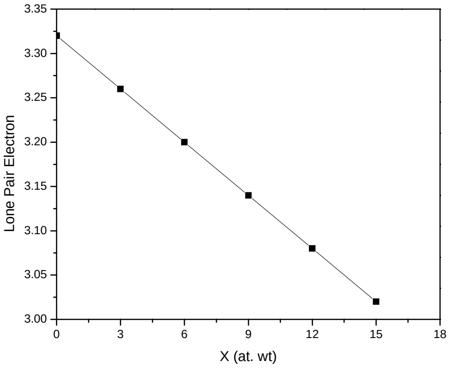

Fig. 2. Variation of lone pair electron with In content.

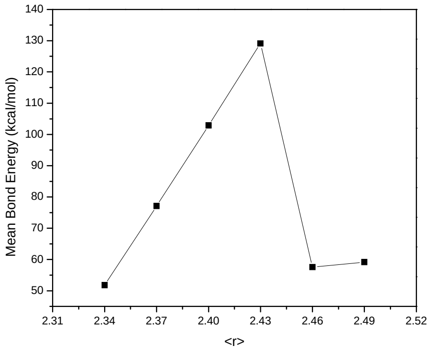

Fig. 3. Variation of mean bond energy with average coordination number for.

3.5 Determination of R

It is the parameter which determines the deviation of stoichiometry and is expressed by the ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom. Values of R were found to be larger than unity for such glasses which indicate chalcogen-rich materials and less than unity for the glass which shows chalcogen poor material. For $Ge_xSe_yIn_z$ system, the quantity $'R'$ is defined by [27,28]

$$R = \frac{yCN(Se)}{xCN(Ge) + zCN(In)} \tag{10}$$

where x, y and z are respectively the atomic fractions of *Ge, Se* and *In*.

However the calculation of $'R'$ also requires the knowledge of coordination number (CN) of all the constituents of glassy alloys. For the investigating system, the $CN(Ge)$ and $CN(Se)$ respect the Mott $"8 - N"$ rule [20], where N is the number of outer shell electrons and coordination number of In in $Ge_xSe_yIn_z$ system has been discussed by Saiter et al. [29,30]

3.6 Mean bond energy $(< E >)$ and glass transition temperature (T_g)

Tichy and Ticha [28] were the first to point out that the value of glass transition temperature should not be only related to connectedness of the network (which is related to $< r >$, the average coordination number) but should also be related to the quality of connections, i.e. the mean bond energy between the atoms of the network.

Mean bond energy is given by

$$< E > = E_c + E_{rm} \tag{11}$$

where,

E_c = overall contribution towards bond energy arising from strong bonds.

E_{rm} = contribution arising from weaker bonds that remains after the strong bonds have been maximized.

For $Ge_xSe_yIn_z$ system (where $x + y + z = 1$),

Case 1. In the selenium rich region $(R > 1)$,

$$E_c = 4xE_{Ge-Se} + 3zE_{In-Se} \tag{12}$$

and

$$E_{rm} = \frac{[2y - 4x - 3z]}{< r >} E_{Se-Se} \tag{13}$$

Case 11. In the selenium poor region $(R < 1)$,

$$E_c = \frac{2y(4xE_{Ge-Se} + 3zE_{Se-In})}{4x + 3z} \tag{14}$$

and

$$E_{rm} = \frac{(4x + 3z - 2y)}{< r >} E_{<>} \tag{15}$$

where,

$$E_{<>} = \frac{1}{3}[E_{Ge-Ge} + E_{Se-Se} + E_{Ge-Se}] \tag{16}$$

denotes the average homopolar bonding energy. The homopolar and heteropolar bond energies are given in Table 1.

4. Conclusions

The average coordination number increases with the increase of In content which gives an indication that the value of optical gap will strongly depend on the heat of atomization as with the increase of In content the heat of atomization decreases leading to decrease of the average single bond energy and this reflects the cause of decrease in optical band gap. This decrease in band gap is confirmed from the theoretical calculations of E_g. Number of lone pair electrons is found to be greater than 1 confirming possibilities of good glass formation. Mean bond energy and glass transition temperature is found to increase upto x = 9 and thereafter decreases.

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