Compositional dependence of physical parameters in Ge17Se83–xSbx (x = 0, 3, 6, 9, 12, 15) glassy semiconductors

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Compositional dependence of physical parameters in Ge$_{17}$Se$_{83-x}$Sb$_x$ (x = 0, 3, 6, 9, 12, 15) glassy semiconductors

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Glasses of $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) have been synthesized by melt quenching technique. Various physical parameters viz. coordination number, lone pair of electrons, number of constraints, bond energy, heat of atomization, glass transition temperature and mean bond energy, for glassy alloys have been calculated. It is inferred that on increasing the Sb content average number of constraints, average heat of atomization, mean bond energy and glass transition temperature increases whereas number of lone pair of electrons calculated here decreases. The increase in glass transition temperature has been explained on the basis of accumulation of Sb atoms in Se-chain.

1. Introduction

Prior investigative studies of physical properties in chalcogenide glasses have gained immense importance in technological [1] and commercial field [2]. Chalcogenide glasses are considered as promising materials for infrared optical elements, infrared optical fibres, information transfer, xerography, switching and memory devices, photolithography, fabrication of inexpensive solar cells and for reversible phase change optical records [3-11]. The Ge_xSe_{1-x} system is of special interest in view of the fact that it forms glasses over a wide domain of composition [12,13]. Addition of third element like As, Sb, Te, In etc. increases the glass forming region as well as creates the compositional and configurational disorder in the system. Since, each impurity may satisfy its valence requirements by adjusting its nearest neighbour's environment, so it was believed that properties of amorphous semiconductors are weakly affected by the addition of impurities [14], but recently this has been reported that the addition of metal impurities [15] increases the refractive index and lowers the optical band gap significantly. The addition of Sb in the Ge-Se system may change its optical and electrical properties significantly. This stimulated to us to study the Ge-Se-Sb system which varies from floppy mode to rigid mode.

The aim of the present work is to examine the system $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) theoretically for various physical parameters. The physical parameters viz. coordination number, number of constraints, number of lone pair electrons, bond energies of the different bonds formed in the system, heat of atomization, average single bond energy (which is a measure of cohesive energy [16]), mean bond energy and glass transition temperature. The glass transition temperature has been theoretically investigated using the model proposed by Tichy and Ticha [17,18].

2. Experimental details

Bulk samples Ge$_{17}$Se$_{83-x}$Sb$_x$ (x = 0, 3, 6, 9, 12, 15) were prepared by conventional melt quenching technique. High purity (99.999%) elements Ge, Se and Sb in the appropriate weight proportion, were vacuum sealed (10-4 Pa) in quartz ampoules and heated upto 950 °C in a rocking furnace at a heating rate of 3-4 °C/min, the ampoules were frequently rocked at the highest temperature for 8 hrs. The quenching was done in ice-cold water immediately after taking out the ampoules from the furnace. The detailed experimental technique has been given elsewhere [19]. The amorphous nature of the bulk samples was confirmed by the X-ray diffraction technique as no sharp peak was observed in spectra.

3. Results and discussion

3.1 Calculation of coordination number (*m*) and number of constraints in glassy network

Nearest neighbour coordination number (m) in the ternary system $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) is suitable for testing the validity of topological concepts [20,21] because of its large glass forming domain. The average coordination number in our system has been calculated using the relation

$$m = \frac{\alpha N_{Ge} + \beta N_{Se} + \gamma N_{Sb}}{100} \quad (1)$$

where α, β and γ are the at.% of Ge, Se and Sb respectively and N_{Ge}, N_{Se} and N_{Sb} are their respective coordination numbers. The calculated coordination numbers (m) lie in the range $2.34 \leq m \leq 2.49$ and are given in Table 1.

The covalent bonded glassy networks are influenced by mechanical constraints (N_c) i.e. bond stretching (N_a) and bond bending (N_b) which are associated with atomic bonding and effective coordination number $<m_{eff}>$. The number of constraints per atom arising from bond bending can be calculated by $N_b = 2m - 3$ and from bond stretching by $N_a = m/2$ for the atomic species having coordination number (m). For different compositions of the glassy system $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15), knowing the average number of constraints i.e. $N_c = N_a + N_b$ and the average coordination number (m), the effective coordination number $<m_{eff}>$ can be calculated

$$<m_{eff}> = \frac{2}{5}(N_C + 3) \quad (2)$$

The calculated values of N_a, N_b, N_c and $<m_{eff}>$ for the glassy system $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) are listed in Table 1. The average number of constraints per atom N_c exceeds the number of degrees of freedom $N_d = 3$ after 6 at.% of Sb content in $Ge_{17}Se_{83-x}Sb_x$ glassy alloy. This is attributed to non-monotonic behaviour which reveals 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 $<m_{eff}>$. According to Thorpe [21], in the range of the glass-forming compositions, the system should contain floppy and rigid regions. In a-$Ge_{17}Se_{83-x}Sb_x$ compositions the average coordination number varies from 2.34 to 2.49. Here for 6 at.% of Sb content $m = 2.4$ corresponds to the mechanical percolation threshold where the number of

floppy modes goes to zero and an abrupt transition from a deformable network to a rigid glass takes place.

Table 1. Values of the average coordination number (m), number of constraints arising from bond stretching (N_a), number of constraints arising from bond bending (N_b), average number of constraints (N_c), effective coordination number $<m_{eff}>$ for $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) glassy alloys.

Composition	m	N_a	N_b	N_c	$<m_{eff}>$
$Ge_{17}Se_{83}$	2.34	1.17	1.68	2.85	2.34
$Ge_{17}Se_{80}Sb_3$	2.37	1.185	1.74	2.925	2.37
$Ge_{17}Se_{77}Sb_6$	2.40	1.20	1.80	3.0	2.40
$Ge_{17}Se_{74}Sb_9$	2.43	1.215	1.86	3.075	2.43
$Ge_{17}Se_{71}Sb_{12}$	2.46	1.23	1.92	3.15	2.46
$Ge_{17}Se_{68}Sb_{15}$	2.49	1.245	1.98	3.225	2.49

According to Zachariasen [22] heteropolar bonds have supremacy over the formation of homopolar bonds. 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. The possible bond distribution at various compositions is expressed using chemically ordered network (CON) model by Ovshinsky et al [23]. The model assumes that (a) atoms combine more favorably with atoms of different kinds than with the same and (b) bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated. The bond energies EA-B for heteronuclear bonds have been calculated by using the relation [24]

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2 \quad (3)$$

where E_{A-A} and E_{B-B} are the bond energies of the homonuclear bonds and χ_A and χ_B are the electronegativities of the atoms involved. The values of the electronegativities of Ge, Se and Sb are 2.01, 2.55 and 2.05 respectively. The calculated values for different bonds are given in Table 2.

Table 2. The number of lone pair electrons and bond energies of different bonds possible in $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) glassy alloys.

Composition	m	V	$L = V - m$	Bonds	Bond energy (eV/bond)
$Ge_{17}Se_{83}$	2.34	5.66	3.32	Ge-Se	2.144
$Ge_{17}Se_{80}Sb_3$	2.37	5.63	3.26	Se-Se	1.908
$Ge_{17}Se_{77}Sb_6$	2.40	5.60	3.20	Se-Sb	1.906
$Ge_{17}Se_{74}Sb_9$	2.43	5.57	3.14	Ge-Sb	1.724
$Ge_{17}Se_{71}Sb_{12}$	2.46	5.54	3.08	Ge-Ge	1.631
$Ge_{17}Se_{68}Sb_{15}$	2.49	5.51	3.02	Sb-Sb	1.309

3.2 Role of lone pair electrons in the glass forming ability

The introduction of average coordination number proposed by Phillips [20] leads to the calculation of the number of lone pairs of a chalcogenide glass system. The number of lone pair electrons is equal to the difference of all the valence electrons of the system and the shared electrons i.e.

$$L = V - m \qquad (4)$$

where L and V are lone pair electrons and valence electrons respectively. For the glassy system $Ge_{17}Se_{83-x}Sb_x$ the number of lone pair electrons is obtained by using equation (4) and are listed in Table 2. It is inferred from the above table and from Fig. 1 that with the increase in content of Sb the number of lone pair of electrons decreases continuously for $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) glassy system. This result is caused by the interaction between the Sb ion and the lone pair electrons of a bridging Se atom. The interaction decreases the role played by the lone-pair electrons in the glass formation. Zhenhua [25] 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. In our case the values of lone pair electrons lie in the range $3.02 \leq L \leq 3.32$. This explains the fact that the system can be obtained in glassy state.
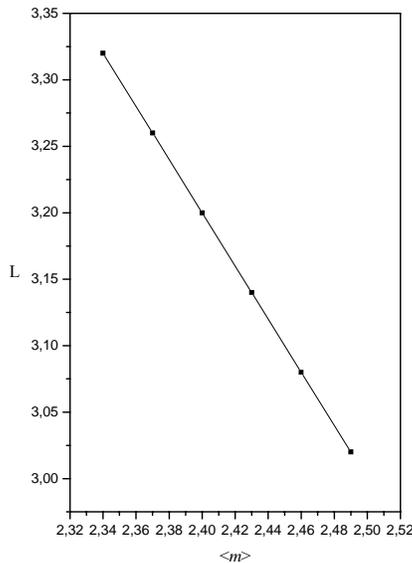
Fig. 1. Variation of lone pair of electrons (L) with average coordination number <m> for the glassy alloys $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15).

3.3 Average heat of atomization

In chalcogenide glasses containing a high concentration of group VI element the lone-pair form the top of the valence band and the antibonding band forms the bottom conduction band [26]. The optical gap corresponds closely to the energy difference between the top of the valence band and the bottom of the conduction band. Metal atoms can form a dative bond with group VI atoms (lone pair with empty orbital) without any cost of energy, due to the presence of high-energy lone pair on the latter. Dative bonds correspond to (empty) antibonding levels which give localized acceptors states in the gap [27].

It is interesting to relate the optical band gap with the chemical bond energy. According to Pauling [28] 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 the heat of formation ΔH and the average of the atomization H_S^A and H_S^B that corresponds to the average non polar bond energy of the two atoms

$$H_S(A-B) = \Delta H + \frac{1}{2}\left(H_S^{\,A} + H_S^{\,B}\right) \qquad (5)$$

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

$$\Delta H \propto \left(\chi_A - \chi_B\right)^2 \qquad (6)$$

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

$$\overline{H_s} = \frac{\alpha H_s^{\,A} + \beta H_s^{\,B} + \gamma H_s^{\,C}}{\alpha + \beta + \gamma} \qquad (7)$$

Obviously the $\overline{H_s}$ values do not contain the heat of formation (ΔH) as part of cohesive energy; however $\overline{H_s}$ is a 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, Sb are very similar and in most of the cases of chalcogenide glasses the heat of formation is unknown. In the few materials for which heat of formation is known it accounts only 10% for the heat of atomization and is therefore neglected. Hence for binary chalcogenide glasses $H_S(A-B)$ is given by

$$H_S(A-B) = \frac{1}{2}\left(H_S{}^A + H_S{}^B\right) \qquad (8)$$

whereas for ternary and higher order compounds, $\overline{H_s}$ is given by equation (7). The values of heat of atomization for Ge, Se and Sb elements are 373.8 kJ/mol, 226.0 kJ/mol and 262.04 kJ/mol, respectively, and the calculated average heat of atomization $\overline{H_s}$ and average single bond energy $\left(\overline{H_S}/m\right)$ are given in Table 3, where m is the average coordination number. From Table 3 it is found that heat of atomization increases with the increase of Sb content while the average single bond energy $\left(\overline{H_S}/m\right)$ which is a measure of cohesive energy decreases with the increase of Sb content. This decrease in the average single bond energy with the increase of Sb content may cause the decrease of optical band gap [16].

Table 3. Values of average heat of atomization $(\overline{H_s})$, average single bond energy $(\overline{H_s}/m)$, mean bond energy $< E >$ and glass transition temperature T_g (K) for $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) glassy alloys.

Composition	$\overline{H_s}$ (eV/bond)	$\overline{H_s}/m$ (eV/bond)	$< E >$	T_g (K)
$Ge_{17}Se_{83}$	2.61	1.115	2.257	422.03
$Ge_{17}Se_{80}Sb_3$	2.62	1.105	2.297	434.68
$Ge_{17}Se_{77}Sb_6$	2.63	1.095	2.341	448.35
$Ge_{17}Se_{74}Sb_9$	2.64	1.086	2.388	462.99
$Ge_{17}Se_{71}Sb_{12}$	2.65	1.077	2.438	478.59
$Ge_{17}Se_{68}Sb_{15}$	2.66	1.068	2.491	495.09

3.4 Mean bond energy and glass transition temperature

The covalent bond approach of Tichy and Ticha [17,18] may be considered as a first approximation in the case of chalcogenide glasses. The glass transition temperature is considered to be proportional to the mean bond energy <E>, which depends on factors like average coordination number, degree of cross linking, bond energy and the nature of the bonds. Taking account of all these factors, they have examined 186 chalcogenide glasses with Tg ranging from 320 to 760 K, and obtained a good correlation between Tg and <E> in the form

$$T_g = 311\left[\langle E \rangle - 0.9\right] \qquad (9)$$

which satisfies the Arrhenius relation for viscosity. The mean bond energy of the system may be calculated using the relation

$$< E > = E_c + E_{rm} \qquad (10)$$

where E_c is the overall contribution towards bond energy arising from strong bonds and E_{rm} is the contribution

arised from weaker bonds that remain after the number of strong bonds will become maximum. For $Ge_xSe_ySb_z$ system (where $x + y + z = 1$),

In the selenium rich region,

$$E_c = 4xE_{Ge-Se} + 3zE_{Sb-Se} \qquad (11)$$

and

$$E_{rm} = \frac{[2y - 4x - 3z]}{<r>}E_{Se-Se} \qquad (12)$$

The calculated values of the mean bond energy are given in Table 3. This is clear from mean bond energy data that when Sb content increases, the mean bond energy of the system increases. Fig. 2 shows the variation of glass transition temperature with mean bond energy. The glass transition temperature increases with the increase of mean bond energy. The glass transition temperature for the various compositions of the system $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) have been calculated using equation (9) and is listed in Table 3. The glass transition temperature of the system under consideration shows that it increases with the increase of the Sb content. This increase in the value of the glass transition temperature with increasing Sb content in glass forming alloys may be due to the accumulation in them of three dimensional structural units $SbSe_{3/2}$ and $GeSe_{4/2}$, and to the decrease of the content of chain like formation of excess Se.
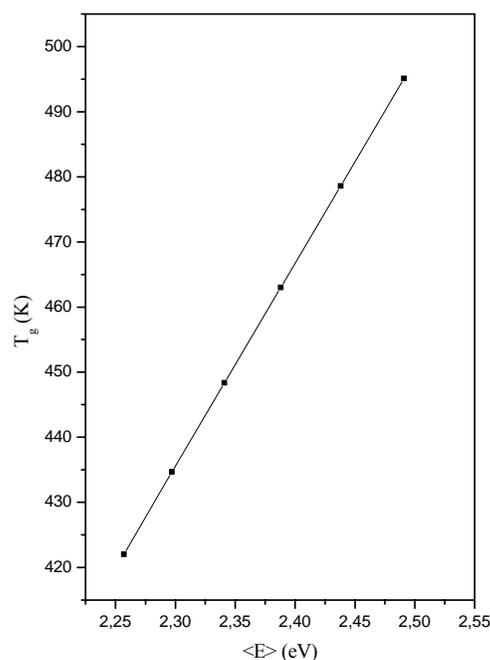
Fig. 2. Variation of glass transition temperature (T_g) with mean bond energy (<E>) in $Ge_{17}Se_{83-x}Sb_x$ (x = 0, 3, 6, 9, 12, 15) glassy alloys.

4. Conclusions

The theoretical investigation of various physical parameters for $Ge_{17}Se_{83-x}Sb_x$ (x =0, 3, 6, 9, 12, 15) glassy system leads to the conclusion that the average coordination number, number of constraints, average heat of atomization, mean bond energy and glass transition temperature increases with the increase of Sb content while the number of lone pair of electrons decreases. The increase of glass transition has been explained on the basis of accumulation of Sb in Se-chain.

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