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The Study of the theoretical parameters of Ge Sn substituted Pb based quaternary chalcogenide glasses at their rigidity percolation threshold

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In the present paper we have theoretically studied the quaternary chalcogenide glass system $Pb_9Se_{71}Ge_{20-x}Sn_x$ (where x = 8, 9,10,11,12 at.%) at rigidity percolation threshold(RPT) .At the RPT the effect of variation of at. wt .% of Sn and Ge on cohesive energy, heat of atomization and mean bond energy and glass transition have been studied. The mean bond energy <E> and the glass transition temperature (Tg) are calculated by using the Tichy-Ticha approach. It has been found that cohesive energy (calculated using a chemical-bond approach), heat of atomization , mean bond energy and glass transition temperature decrease with increase in at.wt.% of the Sn (or with decrease in at.wt.% of Ge),this is due to increase in the concentration of the weaker Sn-Se and Pb-Se bonds as compare to stronger Ge-Se bonds.

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1. Introduction

In the present era of modern technology ,chalcogenide glasses are used in infrared detectors, mouldable infrared optics such as lenses, and infrared optical fibers, They may be useful for new infrared (IR) applications such as CO_2 laser (10.6 μm) power delivery, thermal imaging bundles and IR remote chemical or temperature sensors. The main advantage of these materials is that these can transmit across a wide range of the infrared electromagnetic spectrum. The physical properties of chalcogenide glasses (high refractive index, low phonon energy, high nonlinearity) also make them ideal for incorporation into lasers and other active devices. Some chalcogenide materials experience thermally driven amorphous crystalline phase changes, enabling the encoding of binary information on thin films of chalcogenides, forming the basis of rewritable optical discs and non-volatile memory devices.Chalcogenide glasses are the most promising materials for a wider range of wavelengths, near and mid-infrared.In general, there are two main sources of infrared absorption in chalcogenide glasses, affecting the transmittance near 10.6μ*m* wavelength. They are (1) impurity absorption (usually the major impurity is oxygen) and (2) molecular vibration of constituent elements which arises from excitation of phonon modes in the glass. In particular, glasses made from Ge-Se have an absorption peak due to the Ge-O bond at about 13μm, and have high absorption in the multiphonon region (from~13.6μ m), with two-phonon absorption peaks at17.8 μm due to Ge-Se bonds. These two types of absorptions affect the transmittance also at 10.6 μm, particularly when the glass is drawn into fibers. If Ge and Se atoms are replaced in the glass system Ge-Se, with heavier atoms of Sn Introducing Sn and Pb atoms is accompanied by formation of bonds like Sn-Se and Pb-Se for which absorptions due to vibration should occur at longer wavelength than those of Ge-Se bonds in accordance to the relation:

$$\lambda \sim \sqrt{\frac{\mu}{k}} \tag{1}$$

where λ is the wavelength at which absorption occurs due to the vibration; μ is the reduced mass, $\mu = \frac{M_1 \times M_2}{M_1 + M_2}$ when M_l and M_2 are the atomic masses of the participating (bond forming) atoms; *k* is the force constant which depends on the nature and strength of the bond. Based on the thermodynamic stability of the oxides in the melt at the reaction temperature and the relative ratio between the elements, the Ge-O peak of contamination might be replaced by Sn-O[1].The infrared transmission spectra of glassy alloy system GeSnSe have been observed in the spectral range 200–500 cm^{-1} at room temperature.There are the formation of the strong bands around 231, 284 and 311 cm^{-1} which were assigned to GeSe, SeSn, Se–Se as reported by S.A Fayek [2].

Some charged additives like Pb, Bi which changes the ratio of valence-alternation pairs to such an extent that the Fermi energy could become unpinned. When the concentration of charged additives exceeds that of valence-alternation pairs, the chalcogenide glasses can exhibit carrier-type reversal. *p-n* transition as has been observed in Ge-Se and In-Se glasses, with the addition of Bi and Pb. Carrier-type reversal (*p* to *n*) has been observed, in $Pb_xGe_{42-x}Se_{48}Te_{10}$ glasses ($0 \leq x \leq 20$) at 8 at. % of Pb [3]. In the chalcogenide glasses there are two significant coordination numbers 2.4 and 2.7 which characterize two topological thresholds. This was introduced by Phillips and later refined by Thorpe and Tanaka in their constraint theories. A transformation from floppy to a rigid network structure (rigidity percolation) occurs at coordination number 2.4 at which the mechanical stability of the glass is optimized. The glass forming ability of many alloys is generally found to be good at this composition (corresponding to 2.4) at which the rigidity percolation occurs. In addition a chemical ordering occurs in chalcogenide glasses, at higher coordination numbers. This happens at Tanaka's threshold 2.67. At this threshold the structural network is maximally ordered. These chemically ordered networks have a maximum atomic volume which indicates that they are closest to crystalline state. The glass forming ability of the chalcogenide glasses is found to be poor at compositions corresponding to the chemically ordered networks as they attain the crystalline state easily [4]. The main motivation behind these studies is to explore the possibility of variation in properties of material at RPT on varying the concentration of Sn and Ge in Pb-Se system.

2. Experimental details

Bulk chalcogenide $Pb_9Se_{71}Ge_{20-x}Sn_x$ alloys (where x = 8, 9,10,11,12 at.%) are prepared by the melt quenching technique. Granules of Pb, and powder of Sn ,Ge and Se having 99.999% purity are used. The materials are weighed according to their atomic percentages and sealed in quartz ampoules in a vacuum of 10^{-6} pascal. The sealed ampoules are kept inside a furnace where the temperature is increased up to 1000^oC at a heating rate of $2–3^oC$/min. It is recognized that selenium has a high vapor pressure and a strong tendency to react with oxygen. Thus, care and precaution are taken to avoid any explosion during the heating of the ampoule. The ampoules are inverted at regular intervals of 1 hour for 12 hours at the higher temperature to ensure homogeneous mixing of the constituents. After that quenching is done in ice cold water. The vitreous natures of the samples are confirmed by x-ray diffraction using a Philips X'pert MRD diffractometer. The diffraction patterns are obtained using Cu-Kα radiation (λ = 1.54837 Å) as shown in Fig. 1.From figure it is clear that there is no sharp peak in any of the diffractrograms.This shows the amorphous glassy nature of the material.

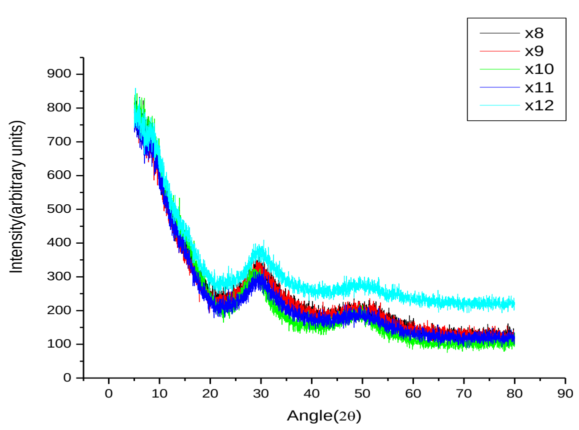

Fig. 1 X- Ray Diffactogram of the chalcogenide compositions $Pb_9Se_{71}Ge_{20-x}Sn_x$(where x= 8,9,10,11,12)

3. Theoretical study and discussion

The different parameters viz. bonding constraints, coordination number, fraction of the floppy modes, lone pairs, bond energy, cohesive energy, heat of atomization and mean bonding energy are calculated for our Se-Sn-Pb-Ge quaternary chalcogenide glassy systems.

3.1 Bonding constraints and coordination number

J.C.Phillips had given the mechanical-constraint counting algorithms to explain glass forming tendencies. The strongest covalent forces between nearest neighbors serve as Lagrangian (mechanical) constraints defining the elements of local structure (building blocks). Constraints associated with the weaker forces of more distant neighbors must be intrinsically broken leading to the absence of long-range order. Phillips–Thorpe approach is based on comparing the number of atomic degrees of freedom with the number of interatomic force field constraints. If the number of degrees of freedom is greater than the number of constraints, the network is "floppy;" conversely, if the network becomes overconstrained, stressed-rigid structures will percolate throughout the entire network. According to Phillips the tendency of glass formation would be maxim when the number of degrees of freedom exactly equals the number of constraints (i.e N_d=N_c).In covalent solids, there are two types of near-neighbor bonding forces; bond-stretching (α-forces) and bond-bending (β- forces). The number of Lagrangian bond-stretching constraints per atom is $N_\alpha = r/2$, and of bond-bending constraints is $N_\beta = 2r-3$. For the case when all α and β constraints are intact and no dangling ends exist in the network, equation implies that the optimum mean coordination number is r = 2.40 which is known as the regiditty percolation threshold. Highly overcoordinated or undercoordinated structures are not conducive to glass formation and, upon cooling, lead to crystalline solids.In 1983, M. F. Thorpe pointed out that the number of floppy modes per atom, f, is rather accurately described by the mean-field constraint count according to the relation,

$$F = 3 - N_c \tag{2}$$

This led to the realization that a glass network will become spontaneously rigid when f → 0, defining a *floppy* to *rigid phase transition*[5-6].

3.1.1 Nearest neighbor coordination and floppy modes

In our quarternary chalcogenide system of Ge ,Se Sn and,Pb, the Coordination numbers are $Z_{Se}=2$,$Z_{Sn}=4$,$Z_{Ge}=4$,$Z_{Pb}=2$.The average coordination number <r> of our glassy system is given by

$$\langle r\rangle = \frac{aZ_{Se}+bZ_{Ge}+cZ_{Sn}+dZ_{Pb}}{a+b+c+d} \tag{3}$$

where a,b,c and d are the atomic weight percentage of the Se ,Ge , Sn and Pb.

The Calculated value of coordination number for each sample in our series is 2.4. Constraints produce floppy modes in the network, which have zero frequency. In this quarternary chalcogenide system the number of the bond stretching constraints are

$$N\alpha = \frac{r}{2} = \frac{2.4}{2} = 1.2 \tag{4}$$

and bond bending constraints are

$$N_\beta=2r-3=1.8 \tag{5}$$

Then the total number of the constraints are given by

$$N_c= N\alpha+ N_\beta \tag{6}$$

which comes out to be 3 which show our critical composition at which the number of constraints Nc (bond bending and bond stretching forces) acting on the network are balanced by the number of degrees of freedom N_d available for the atoms in the network

This means that network is *isostatically rigid*, where no stress is present, it means at Nc=Nd. Stresses are said to exist when already present bond lengths and/or angles changes on the addition of more atoms to the structure The stability of the network at this threshold is associated with atomic arrangements that become more tightly bound with shorter bond lengths. This results in the minimum atomic volume and consequently maximum in the atomic density of the glass.

It can be shown that the fraction of floppy modes available in a network is

$$f = 2 - \frac{5}{6} < r > \tag{7}$$

Where <r> is the average coordination number. In the present chalcogenide systems the number of floppy modes is zero. This point was recognized by Thorpe to be a ‘‘rigidity transition,’’ between a floppy network and a rigid one; it corresponds to a strong tendency for making glass [7].

3.1.2 Lone pair electrons

The number of lone pairs electrons in a chalcogenide glass system are calculated by using the formula [8-9]

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

Where L and V are the number of lone pairs and valence electrons respectively. The numbers of lone pair electrons obtained by using this equation are 3.02 for each sample in the series. According to the Ovshinsky, interaction between lone pair electrons on different atoms and the interaction with the local environment result in localized states in gap of chalcogenide glasses. The specific interactions between non bonding orbital give rise to unusual bonding configurations which we call valence alternation pairs (VAP’s) The creation of such VAP require relatively small energy , which increase density of VAP’s in glasses. These VAP’s when photo exited play important role in processes such as photo induced diffusion, crystallization, phase separation and decomposition.

3.2 Deviation from the stoichiometry of composition

R is a parameter that determines the deviation from stoichiometry and is expressed by the ratio of covalent bonding possibilities of chalcogen atom to non-chalcogen atom. For the $Se_aGe_bSn_cPb_d$ system, the quantity R is defined by [10,11]

$$R = \frac{aZ_{Se}}{bZ_{Ge}+cZ_{Sn}+dZ_{Pb}} \tag{9}$$

where a,b,c and d are the atomic fractions of Se,Ge, Sn and Pb respectively. The threshold at R=1 (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor. For the composition $Pb_9Se_{71}Ge_{20-x}Sn_x$ the deviation from the stoichimetry is

$$R=1.44 \tag{10}$$

So it is clear that our quaternary system is chalcogen rich.The major limitation of this approach is that it does not account for molecular interactions, which play a vital role in the relaxation process in the glass transition region.

3.3 Heat of atomization

The enthalpy change of atomization (Hs) is the enthalpy change that accompanies the total separation of all atoms in a chemical substance (either a chemical element or a chemical compound). According to Pauling, 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 heats of formation ΔH and the average of the heats of atomization of H_S^A and H_S^B that corresponds to the average non-polar bond energy of the two atoms [11-13]

$$H_S(A-B) = \Delta H + \frac{1}{2}\left(H_S^A + H_S^B\right) \qquad (11)$$

ΔH is proportional to the square of the difference between the electronegativities χ_A and χ_B of the two atoms:

$$\Delta H \;\alpha\; (\chi_A - \chi_B)^2 \qquad (12)$$

In the case of ternary and higher order semiconductor compounds, the average heat of atomization is defined for quaternary compound $A_aB_bC_cD_d$ as [14]

$$H_S = \frac{aH_S^A + bH_S^B + cH_S^C + dH_S^D}{a+b+c+d} \qquad (13)$$

Where a, b, c and d are the atomic percentages of A, B,C and D respectively. In the few materials for which it is known, the heat of formation ΔH is about 10% of the heat of atomization and, therefore, can be neglected. H_s(Pb) = 195 KJ/mol, H_s(Sn) = 302 KJ/mol, H_s(Se) = 227KJ/mol, H_s(Ge) = 377 KJ/mol [15-17]. The values of Hs for $Pb_9Se_{71}Ge_{20-x}Sn_x$ Chalcogenide glass are obtained by using the values of H_s of Sn, Ge, Se and Pb given in table 3.3.

Table 1 The Heat of atomization of compositions

S.No.	Composition	Heat of the atomization (KJ/mol)
I.	$Pb_9Se_{71}Ge_{12}Sn_8$	248.12
II.	$Pb_9Se_{71}Ge_{11}Sn_9$	247.37
III.	$Pb_9Se_{71}Ge_{10}Sn_{10}$	246.62
IV.	$Pb_9Se_{71}Ge_9Sn_{11}$	245.87
V.	$Pb_9Se_{71}Ge_8Sn_{12}$	245.12

The variation of the heat of the atomization with increasing the Sn content is shown in Fig. 3.3. It is evident from the figure that with increase in the at % of the Sn (or decrease in at % the Ge) content there is the decrease in the heat of the atomization, this is due to the fact that on increasing the Sn content the number of the Sn-Se bonds increase and Ge–Se bonds decrease. The bond energy of the Ge-Se bond is more than the Se-Sn bond and Ge-Se bonds are stronger than the Se-Sn bond that is why there is the decrease in the heat of the atomization of the material on increasing the Sn content.

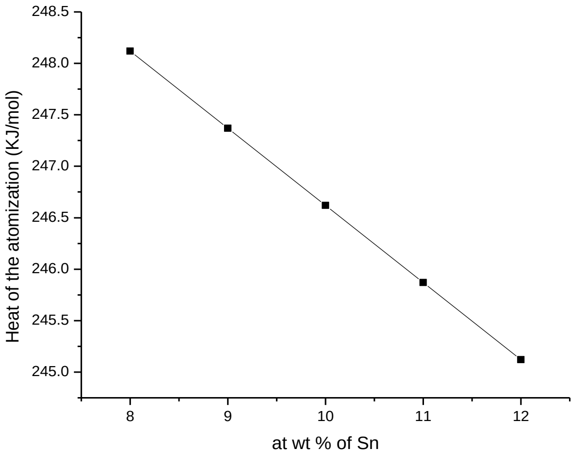

Fig. 2. The variation of the heat of atomization with increasing Sn content.

3.4 Bond energy and cohesive energy

In our quarternary chalcogenide system of Se-Ge-Pb-Sn, there are the formation of the Ge-Se, Se-Se, Se-Sn and Pb-Se bonds. The chemically ordered network (CON) [18] model suggests that heteropolar bonds are preferred over homopolar bonds and they are formed in the order of their decreasing bond energy. The Ge-Se glassy system is a covalent chalcogenide system. From Raman scattering studies, it has been realized that the local structure of Ge-Se glasses consists of chain segments of *edge-sharing* $GeSe_2$ and *corner-sharing* $GeSe_4$ tetrahedral. The properties of Ge-Se glassy system can be modified by the addition of metallic impurities which has a pronounced effect on the structure of Ge-Se network. In selenium based chalcogenide glasses the metallic atoms play a dual role as network modifiers in Se rich side and network formers in Se deficient side and changes the properties considerably [19].

The bond energy of heteropolar bonds can be calculated by the method suggested by Pauling using the bond energy of homopolar bonds and the electronegativity of the atoms involved .The bond energy of heteronuclear bond is given by

$$D(A\text{-}B) = [D(A\text{-}A)\, D(B\text{-}B)]^{½} + 30\,(X_A - X_B)^2 \qquad (14)$$

where D(A-B) = bond energy of heteronuclear bond, D(A-A) and D(B-B) are the bond energies of homonuclear bonds. X_A and X_B are the electronegativity values of A and B, respectively. The electronegativity for Se, Ge, Sn and Pb are 2.55, 2.01, 1.96 and 2.33 respectively [20-21]. The bond energy of the homopolar and hetropolar bonds are given in Table 2(a)

In the present Ge-Pb-Sn-Se system, Sn atoms have only a medium range interaction with the Ge atoms in the liquid state, and take the fourfold coordination in the glassy state to form $SnSe_{4/2}$ tetrahedra units. There is an isomorphous replacement of Ge atoms by Sn atoms (in contrast to phase separation) in the glasses network; thus Sn atoms are incorporated into the clusters of Ge- Se alloys. The tetravalent Sn, which combines only with Se, has a covalent radius of 1.41Ǻ, 15% larger than the covalent radius of Ge of 1.22Ǻ.So it is evident that Sn-Se bond has a larger conicity than the Ge-Se bond, which causes lack of flexibility of the bond angle between Se and Sn atoms. Thus, addition of Sn introduces strain to the network and leads to a considerable weakening of the Ge-Se network structure [1]. The substitution of Ge with Pb atom results in the reduction of Ge–Se bonds and an increase in Pb–Se bonds. Since Pb–Se bonds have a lower energy than Ge–Se bonds, so addition of Pb results in a reduction in the average bond energy of $Pb_9Se_{71}Ge_{20-x}Sn_x$ glasses (where x = 8, 9,10,11,12 at.%)

Table 2(a) The bond energy of homopolar and hetropolar bonds of chalcogenide system

Bond	Bond Energy(Kcal/mol)	Bond	Bond Energy(Kcal/mol)
Se-Se	44.00	Se-Ge	49.41
Ge-Ge	37.60	Se-Sn	49.23
Sn-Sn	34.20	Se-Pb	31.47
Pb-Pb	20.48		

The cohesive energy of the system is the measure of the strength of a chemical bond and is defined as the stabilization energy of an infinitely large cluster of material per atom which allows determination of the number of possible bonds. According to covalent bond approach, atoms combine more easily with atoms of different type rather than the same type and in the bond formation heteropolar bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied, also each constituent atom is coordinated by 8–N atoms, where N is the number of outer shell electrons In this approach van der Waals interactions are neglected, which can provide a means for further stabilization by the formation of much weaker links than covalent bonds. So according to this model the bond energies are assumed to be additive. Thus, the cohesive energies is calculated by summing the bond energies over all bonds expected in the material

$$CE = \sum \frac{C_i D_i}{100} \tag{15}$$

where the C_i and D_i are the bond probabilities and D_i is the corresponding bond energy of the occurring bonds in glassy systems.

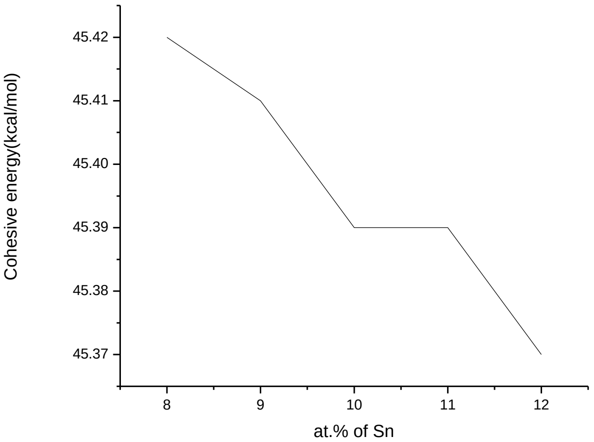

Fig. 3 Variation of cohesive energy with at. % of Sn.

In our a-Se-Ge-Sn-Pb system, the Ge–Se bonds with highest possible energy are expected to occur first, followed by Se-Sn, Se–Pb. Calculated values of CE along with chemical bond distribution for all compositions are tabulated in Table 2(b).

Table 2(b) The cohesive energy, electronegativity, and distributions of chemical bonds in the chalcogenide systems

Compositions $Pb_9Se_{71}Ge_{20-x}Sn_x$	Electronegativity (χ)	Distribution of the chemical bonds				Cohesive energy (kcal/mol)
		Ge-Se	Sn-Se	Pb-Se	Se-Se	$CE = \sum \frac{C_i D_i}{100}$
X=8	2.418	0.3380	0.2253	0.1268	0.3099	45.42
X=9	2.417	0.3098	0.2535	0.1268	0.3099	45.41
X=10	2.417	0.2816	0.2816	0.1268	0.3100	45.39
X=11	2.416	0.2535	0.3098	0.1268	0.3099	45.39
X=12	2.416	0.2253	0.3380	0.1268	0.3099	45.37

From the data it is clear that the bonding probability of Pb-Se in every composition is almost constant this means that in every composition Ge-Se bonds are approximately replaced in the equal proportion by Pb-Se bonds. Here is the continous decrease in the cohesive energy as the concentration of the Sn is increasing. The decrease in the cohesive energy is due to the fact that with increase in the Sn concentration there is a increase in the weaker Sn-Se bonds and a decrease in the stronger Se-Ge bonds. The formation of the Pb-Se bonds also lower the cohesive energy because the Pb-Se has the lesser bond energy than others.Here in our chalcogenide system there is slight decrease in the electronegativity of chalcgenide material with increase in Sn at % because its electronegativity is slightly less(0.5) than Ge. The results indicate that the CE decreases with the addition of Sn, which means that the average stabilization energy decreases. The decrease in the CE tends to decrease the energy of the conduction band edge, causing a decrease in the gap between bonding and antibonding orbitals and thus a decrease in the optical energy gap.

As the material is chalcogen rich and so having the high energy lone pair electrons (Kastner1972) leads to qualitative different electronic densities of states. The valence band is then non bonding and does not significantly contribute to the cohesive energy [22].

3.5 Mean bond energy and glass transition temperature

Many properties of chalcogenide glasses are related to overall mean bond energy <*E*>, which is a function of average coordination number <r> , the type of bonds and the bond energy. Using the correlation proposed by Tichy for a chalcogenide rich system we can determine the value of <*E*> **.** The overall mean bond energy for the system $Se_aGe_bSn_cPb_d$ is given by

$$\langle E \rangle = E_{cl} + E_{rm} \tag{16}$$

where E_{cl} is the mean bond energy of average cross linking per atom and is given by

$$E_{cl} = P_r D_{hb} \tag{17}$$

here P_r is the degree of cross linking and D_{hb} is the average heteropolar bond energy "E_{rm}" is the average bond energy per atom of the remaining matrix of bonds using a set of 186 glasses, Tichy and Ticha illustrated an impressive correlation of T_g with mean bond energy in the form

$$Tg = 311[<E>-0.9] \tag{18}$$

In particular, the compositional dependence of Tg in many glassy systems presents maximum value near to the chemical threshold (i.e. R=1) because the chemical bond energies are maximized at this composition. The variation of the Tg and mean bond energies of the chalcogenide glasses are shown in Table 3.

Table 3. The variation of the Tg and mean bond energy of chalcogenide glasses

Compositions	Mean bond energy(<E>) Kcal/mol	Tg (kelvin)
$Pb_9Se_{71}Ge_{12}Sn_8$	53.21	438.51
$Pb_9Se_{71}Ge_{11}Sn_9$	53.20	437.83
$Pb_9Se_{71}Ge_{10}Sn_{10}$	53.19	437.58
$Pb_9Se_{71}Ge_9Sn_{11}$	53.18	437.26
$Pb_9Se_{71}Ge_8Sn_{12}$	53.17	436.95

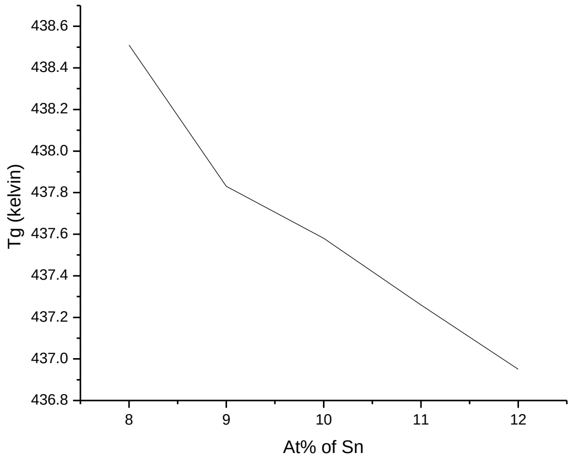

Fig. 4. The variation of the glass transition temperature with at.% of Sn

The Fig. 4 is clearly depicting the fall of glass transition temperature with increasing at % of Sn due to the fall in cohesive energy and mean bond energy of the glassy systems.

4. Conclusion

In the theoretical study of physical parameters of quaternary Se-Ge-Sn-Pb glassy system ,we have concluded that our material is stress free ,amorphous and network is *isostatically rigid* having optimum mean coordination number *r* = 2.40 which is known as the rigidity percolation threshold. The results indicate that there is decrease in the heat of the atomization, cohesive energy, mean bond energy and Tg of the material with the addition of Sn, due to replacement of stronger Ge-Se bonds with Se-Sn and Pb-Se bonds. The decrease in the CE tends to decrease the energy of the conduction band edge, causing a decrease in the gap between bonding and antibonding orbitals. In these glasses, Sn atoms have only a medium range interaction with the Ge atoms in the liquid state, and take the fourfold coordination in the glassy state to form $SnSe_{4/2}$ tetrahedra units. The tetravalent Sn, which combines only with Se, has a covalent radius larger than the covalent radius of Ge .Hence Sn-Se bond has larger ionicity than the Ge-Se bond, which causes lack of flexibility of the bond angle between Se and Sn atoms. Thus, addition of Sn produces strains in the network which causes considerable weakening of the Ge-Se network and which is reflected by the decrease of H_s and T_g with increasing Sn content.

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