The Study of Physical Parameters of Pb Modified Germanate Chalcogenide Glass

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In the present paper we have studied the physical properties of Se-Sn-Pb chalcogenide material. The necessary physical parameters which have important role in determining the structure and strength of the material viz. constraints, coordination number, glass transition temperature etc. has been calculated. The decreasing trend has been found in cohesive energy, heat of atomization and mean bond energy. The glass transition has been studied using the Tichy-Ticha approach which also decreases. The decrease in these physical parameters is due to the increase of ionic character in the material.

Keywords: Ternary chalcogenide glasses, Heat of atomisation, Mean bond energy, Glass transition temperature SEM.

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1. INTRODUCTION

Materials science is an interdisciplinary field applied for properties of matter to various areas of science and engineering. This scientific field investigates the relationship between the structure of materials at atomic or molecular scales and their macroscopic properties. It incorporates elements of applied physics and chemistry. Materials science encompasses various classes of materials, each of which may constitute a separate field. There are several ways to classify materials. The traditional groups are ceramics, metals and polymers based on atomic structure and chemical composition.

Chalcogenide glasses are used in infrared optical transmitting materials, fibre optics and memory devices because of their remarkable optical properties [1-4]. Amorphous chalcogenides are generally insensitive to doping, because of the pinning of the Fermi level at midgap by the valence-alternation pairs [5]. However it has been realized by Mott [6] that charged additives could change the ratio of valence-alternation pairs to such an extent that the Fermi energy could become unpinned. The physical properties of amorphous chalcogenides can be easily varied by the addition of some metals or semimetals that enable an extension of the application field. The absence of long-range order of chalcogenide glassy semiconductors allows the modification of their optical properties to a specific technological application by tailoring their chemical composition. Hence, the study of the dependence of the physical properties on composition is important to improve technological applications. The introduction of Bi or Pb into Ge-Se glass induces a change of electrical conduction from p to n type because of change in the concentration of valence-alternation Pairs, altering the concentration of valence-alternation Pairs When the concentration of charged additives exceeds that of valence-alternation pairs [7] .The chalcogenide glasses can exhibit carrier-type reversal in Ge-Se and In-Se glasses, with the addition of Bi or Pb.[8-9]. In Se-Ge-Pb chalcogenide glassy semiconductors, the physical properties are strongly dependent on composition [10-13].

2. EXPERIMENTAL WORK
2.1 Material Preparation and Synthesis

The chalcogenide glasses $Se_{82}Ge_{18-x}Pb_x$ (x = 7, 8, 9, 10, 11 at %) are prepared by using melt quenching technique.

The amorphous nature of chalcogenide glasses are confirmed by X-ray diffraction technique and particle size of structural in homogeneity studies by the SEM. Chalcogenide $Se_{82}Ge_{18-x}Pb_x$ (where x = 7, 8, 9, 10, 11 at %) glasses are prepared by ice cool melt quenching technique. High purity (99.999 %) elemental substances are weighed using an electronic balance, with a least count of 10^{-4} gm, according to their atomic percentage and sealed in quartz ampoule in an vacuum of 10^{-6} Pascal. The sealed ampoules are then kept inside a furnace where the temperature is increased up to 1000° C at a heating rate of 3-4° C/ min. The ampoules are rocked frequently during heating in order to ensure homogenization of the melt. The ampoules are then quenched in ice cooled water to obtain glassy alloy.

2.2 Material Characterization

The amorphous nature of the material prepared is confirmed by the XRD. The powder method was used to check the amorphous nature of the bulk samples. The bulk samples were crushed to fine powder with a pestle and mortar and then this powder was used for taking XRD pattern. Philips PW 1710 X-Ray difractometer Cu-kα radiation, λ = 1.540598 Å, 40KV and 25 mA was used to take the XRD patterns of the samples. Data acquisition was made in the 2θ range from 10° to 70°. Step size 0.034° was employed. The absence of any sharp peak in XRD of bulk confirms amorphous nature.

2.3 Scanning Electron Microscope

Scanning electron microscope is used to study the inhomogenity in the sample and particle or grain size of the material formed in the sample. There is the indi indication of the phase separation in the material due to inhomogenity in the sample. Which is clear from the SEM images and formation of two halos in the XRD diffractograms

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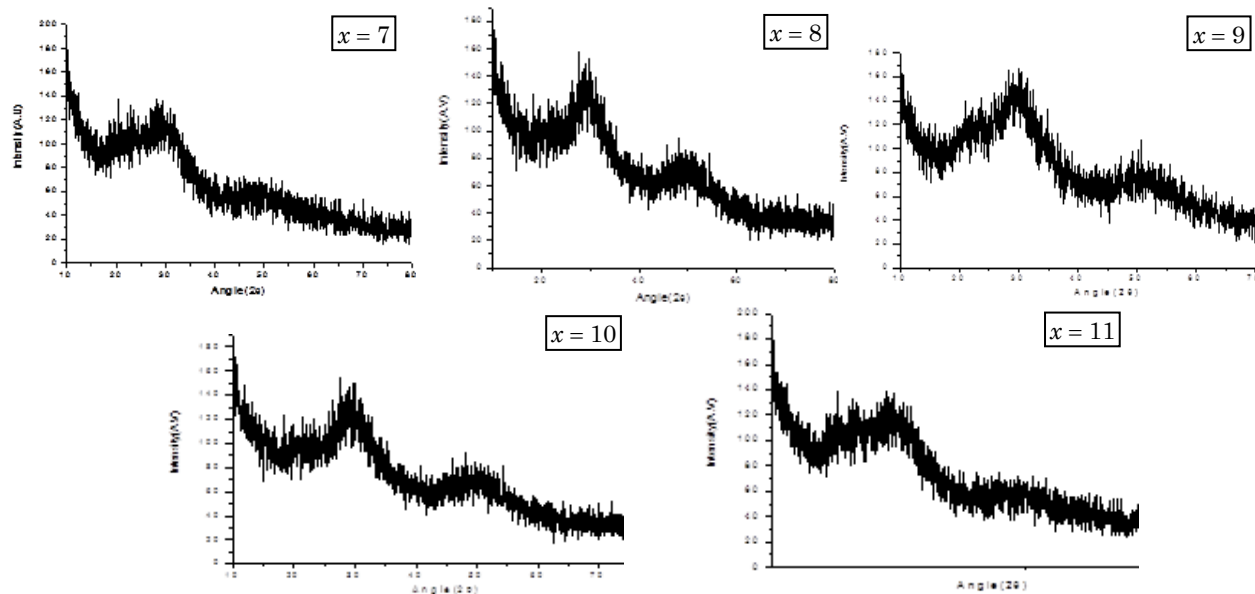* prashantshrm5@gmail.com
† vivekmodgilphycics.hpu@gmail.com

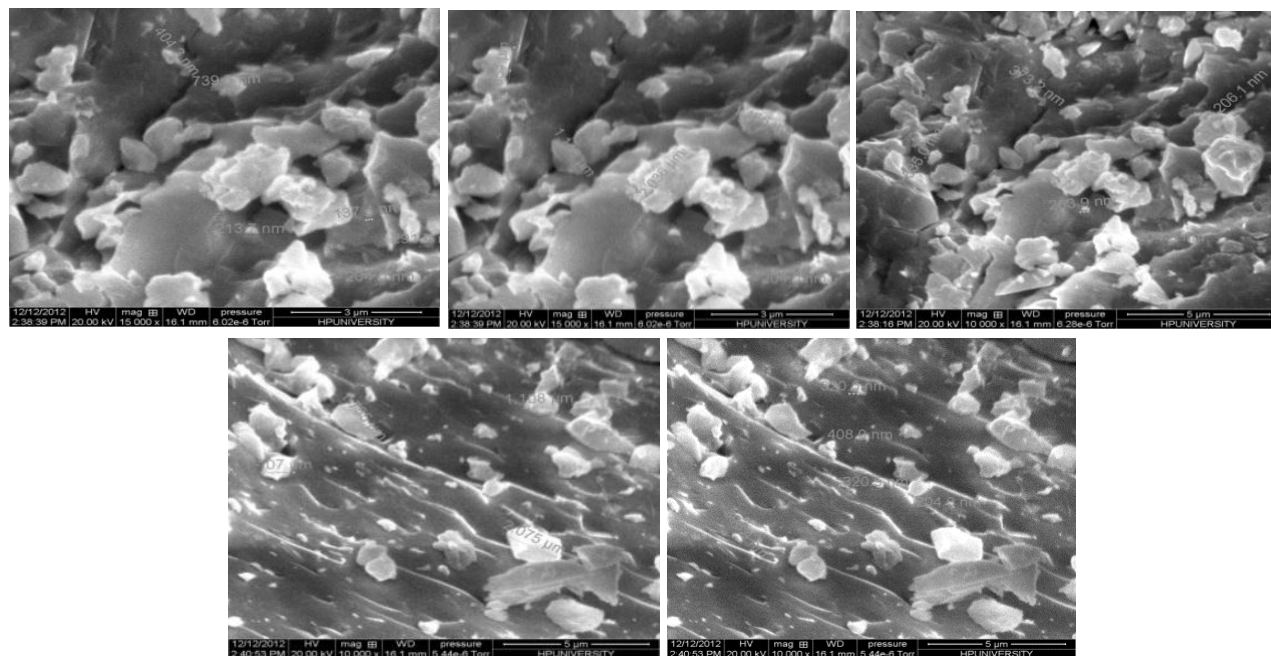**Fig. 1** – X-ray Diffactogram of Chalcogenide composition

Fig. 2 – SEM micrographs of chalcogenide composition

3. DETERMINATION OF PHYSICAL PARAMETERS

The various parameters viz. coordination number, fraction of floppy modes, loan pairs, heat of atomization, bond energy, cohesive energy, transition temperature are calculated for our Se-Ge-Pb ternary chalcogenide glassy system.

3.1 Coordination Number and Constraints

In our ternary chalcogenide system $Se_{82}Ge_{18-x}Pb_x$, coordination numbers of Se, Ge and Pb are 2, 4 and 2 respectively. The average coordination number $\langle r \rangle$ of our glassy system is given by the formula

$$\langle r \rangle = \frac{\alpha Z(\mathrm{Se}) + \beta Z(\mathrm{Ge}) + \gamma Z(\mathrm{Pb})}{\alpha + \beta + \gamma}, \qquad (1)$$

Table 1 – Values of average coordination number ($\langle r \rangle$), bond stretching constraints (N_a), bond bending constraints (N_β), average number of constraints (N_c) and floppy modes for $Se_{82}Ge_{18-x}Pb_x$ (x = 7, 8, 9, 10, 11 at. %) glassy alloys

x	$\langle r \rangle$	N_a	N_β	N_c	Fraction of floppy modes
$x = 7$	2.22	1.11	1.44	2.55	0.151
$x = 8$	2.2	1.1	1.4	2.5	0.167
$x = 9$	2.18	1.09	1.36	2.45	0.184
$x = 10$	2.16	1.08	1.32	2.4	0.201
$x = 11$	2.14	1.07	1.28	2.35	0.217

where α, β and γ are the atomic weight percentage of the Se, Ge, and Pb respectively and $Z(\mathrm{Se})$, $Z(\mathrm{Ge})$, and $Z(\mathrm{Pb})$ are their respective coordination numbers. The calculated value of coordination numbers $\langle r \rangle$ lie in the range

$2.14 \leq r \leq 2.22$. The glasses with a low average coordination number ($r < 2.4$) exhibit a large number of floppy mode. Constraints produce floppy modes in the network, which have zero frequency. In chalcogenide system the number of the bond stretching constraints are given by $N_a = r/2$ and bond bending constraints are $N_\beta = 2r - 3$.

Then the total number of the constraints is given by

$$N_c = N_\alpha + N_\beta \qquad (2)$$

Stresses are said to exist when already present bond lengths and angles changes on the addition of some more atoms in the structure The stability of the network is associated with atomic arrangements that becomes more tightly bound with shorter bond lengths. This results in the minimum atomic volume and consequently a maximum in the atomic density of the glass by considering a Kirk-Keating type of potential. It can be shown that fraction of floppy modes available in the network

$$f = 2 - \frac{5}{6}\langle r \rangle \qquad (3)$$

Here $\langle r \rangle$ is the average coordination number. The average coordination number decreases with increasing Pb concentration, because with increasing Pb concentration average degree of cross-linking decreases and material becomes soft fragile.

The values of average coordination number ($\langle r \rangle$), bond stretching constraints (N_a), bond bending constraints (N_β), average number of constraints (N_c) and floppy modes for Se$_{82}$Ge$_{18-x}$Pb$_x$ ($x = 7, 8, 9, 10, 11$ at.%) glassy alloys are listed in table 1
A graphical representation of fraction of floppy modes (f), and mean coordination number $\langle r \rangle$ is also given in figure 3.
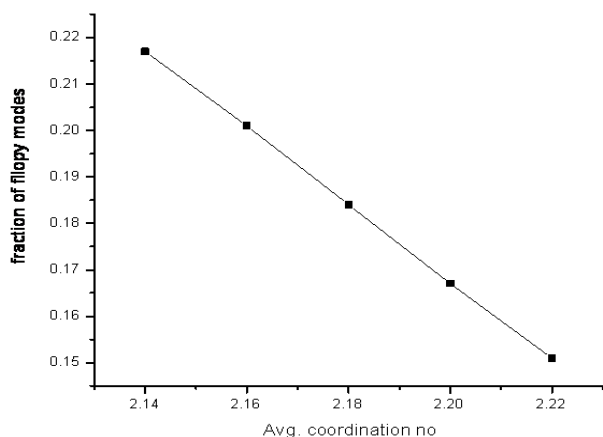

Fig. 3 – Variation of floppy modes with Average Co-ordination No

3.2 Lone Pair Electrons

The number of lone pair electrons in a chalcogenide glassy system are calculated by using the formula (4)

$$L = V - \langle r \rangle \qquad (4)$$

where L and V are the number of lone pairs and valence electrons respectively. The number of lone pair electrons obtained by using equation (4) is listed in Table 2.

According to the Ovshinsky, interaction between lone pair electrons on different atoms and their interaction

with the local environment result in localized states in gap of chalcogenide glasses. The specific interactions between nonbonding orbital give rise to unusual bonding

Table 2 – The number of lone pair electrons obtained by using equation (4)

x	$\langle r \rangle$	V	$L = V - \langle r \rangle$
$x = 7$	2.22	5.64	3.42
$x = 8$	2.20	5.64	3.44
$x = 9$	2.18	5.64	3.46
$x = 10$	2.16	5.64	3.48
$x = 11$	2.14	5.64	3.50

configurations which we call valence alternation pairs (VAP's). The creation of such VAP requires relatively small energy, which increases the 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.
A graphical representation of variation of lone pair with lead content is given in figure 4.
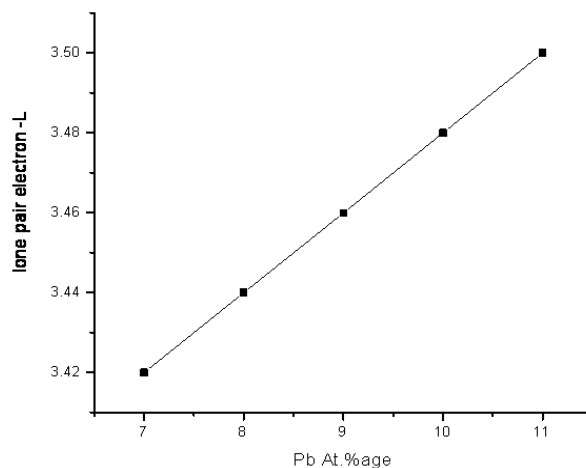

Fig. 4 – The number of lone pair electrons as a function of Lead content

It is clear from Fig. 4 that the lone pair electrons, L increase continuously with the increase in Pb content. We can conclude from these results that some lone pair electrons in the structure of a system are a necessary condition for obtaining the system in vitreous state. For a binary system the value of L must be larger than 2.6 and for a ternary system it must be larger than 1 [15].

3.3 Deviation from the Stoichiometry of Composition

The parameter (R) which determines the deviation from stoichiometry is expressed by the ratio of covalent bonding possibilities of chalcogen atom to that of nonchalcogen atom. For the Se$_a$Ge$_\beta$Pb$_y$ system, the quantity R is defined by [16-17]

$$R = \frac{\alpha Z(Se)}{\beta Z(Ge) + \gamma Z(Pb)} \qquad (5)$$

where α, β, and γ are the atomic fractions of Se, Ge, and Pb respectively. The threshold at $R = 1$ (the point of existence of only heteropolar bonds) marks the mini-

mum 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 our composition the deviation from the stoichimetry is $R > 1$ hence system is chalcogen rich.

3.4 Bond Energy and Cohesive Energy

In chalcogenide system $Se_{82}Ge_{18-x}Pb_x$ there is comparatively more probability of Se-Ge, and Pb-Se bonds formation as compare to homopolar bonds. The chemically ordered network (CON) model [18] 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

$$D(A - B) = [D(A - A)D(B - B)]^{1/2} + 30(X_A - X_B)^2 \quad (6)$$

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, and Pb are 2.55, 2.01, and 2.33 respectively [20-21]. In the present Se-Ge-Pb system, 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 decrease in the cohesive energy of $Se_{82}Ge_{18-x}Pb_x$ glasses ($x = 7, 8, 9, 10, 11$).

Table 3 – The bonds probabilities in chalcogen glass and cohesive energy

x	Bonds formed			Cohesive energy, (eV/atom)
	Se-Pb	Se-Ge	Se-Se	
$x = 7$	0.08536	0.2682	0.6464	44.37
$x = 8$	0.09756	0.2439	0.6585	44.09
$x = 9$	0.10970	0.2195	0.6707	43.81
$x = 10$	0.12190	0.1951	0.6830	43.53
$x = 11$	0.13410	0.1707	0.6953	43.24

3.5 Heat of Atomization

The enthalpy change of atomization (H_s) is the enthalpy change that accompanies the total separation of all atoms in a chemical substance (either a chemical element or a chemical compound). Heat of atomization H_s(A–B) at standard temperature and pressure of a binary semiconductor formed from atoms *A* and *B*, as proposed by Pauling [22], is the sum of the heat of formation, ΔH, and the average of heat of atomization H_s^A and H_s^B, that corresponds to the average non polar bond energy of two atoms.

$$H_s(A - B) = \Delta H + \frac{1}{2}(H_S^A + H_S^B) \quad (7)$$

The first term in equation (6) is proportional to the square of the electro negativity difference of two atoms involved i.e.

$$\Delta H \sim (X_A - X_B)^2 \quad (8)$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization H_s is defined for the compounds $A_\alpha B_\beta C_\gamma$ as a direct measure of cohesive energy and the average bond strength is given by

$$H_S = \frac{\alpha H_S^A + \beta H_S^B + \gamma H_S^C}{\alpha + \beta + \gamma} \quad (9)$$

The values of H_s (Average Heat of atomization) obtained by using the value of Hs for Se, Ge, Pb (Hs values in units kJ / mol are Se-227, Ge-377 and Pb-195).

Table 4 – Average Heat of atomization of $Se_{82}Ge_{18-x}Pb$

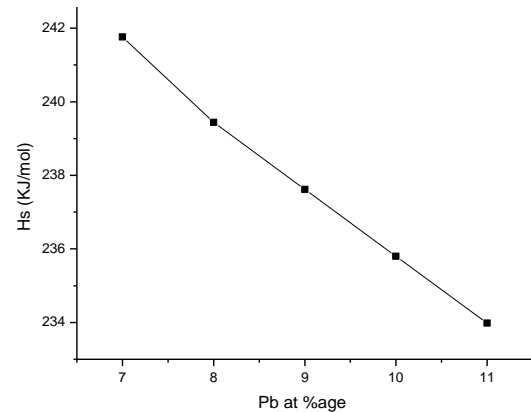| Composition $Se_{82}Ge_{18-x}Pb_x$	H_s(kJ/mol)
$x = 7$	241.76
$x = 8$	239.44
$x = 9$	237.62
$x = 10$	235.80
$x = 11$	233.98

Fig. 5 – Variation of Average Heat of atomization (H_s) with Pb at. %

3.6 Mean Bond Energy and glass Transition Temperature

The properties of chalcogenide glasses are related to overall mean bond energy E, which is a function of average coordination number $\langle r \rangle$, 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 [23] and is given by

$$\langle E \rangle = E_{cl} - E_{rm}, \quad (10)$$

where E_{cl} The overall contribution towards mean bond energy arising from strong hetropolor bonds and is given by

$$E_{cl} = P_r D_{hb} \qquad (11)$$

Here P_r is the degree of cross linking given

$$P_r = \frac{\beta Z(Ge) + \gamma Z(Pb)}{\alpha + \beta + \gamma}. \qquad (12)$$

D_{hb} is the average heteropolar bond energy and is suggested to be

$$D_{hb} = \frac{\gamma Z(Pb)D(Se-Pb) + \beta Z(Ge)D(Ge-Se)}{\beta Z(Ge) + \gamma Z(Pb)}. \qquad (13)$$

The average bond energy per atom of the "remaining matrix" E_{rm} is given by

$$E_{rm} = \frac{2D(Se-Se)[0.5\langle r \rangle - P_r]}{\langle r \rangle} \qquad (14)$$

Tichy and Ticha illustrated an impressive correlation of T_g with mean bond energy in the form

$$T_g = 311[\langle E \rangle - 0.9] \qquad (15)$$

In particular, the compositional dependence of T_g 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 T_g and mean bond energies of the chalcogenide glasses are shown in Table 5.
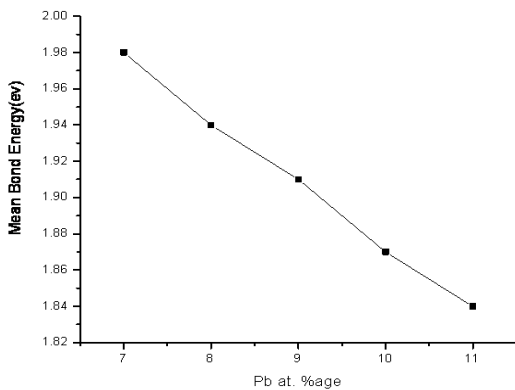

Fig. 6 – Variation Mean Bond Energy with Pb at. %

The incorporation of the Pb atoms in the clusters of Ge-Se alloys results in weakening of the network. The Pb atoms has a covalent radius of 1.46 Å, which is greater than the covalent radius of Ge (1.22 Å). So it is evident that Pb-Se bond has a larger iconicity than the Ge-Se bond, which causes lack of flexibility of the bond angle between Se and Pb atoms. Thus, addition of Pb introduces strain to the network and weaken the Ge-Se network structure. As according to Random Covalent Network Model hetropolar bonds are favored over the homopolar bonds. In this chalcogenide system Pb-Se bonds are increasing and replacing the Ge-Se bonds.

The bond energy of Pb-Se bond is less as compare to the Ge-Se bond. As a result of which the mean bond energy, heat of atomization and hence the glass transition temperature T_g also falls with increase of Pb concentration.
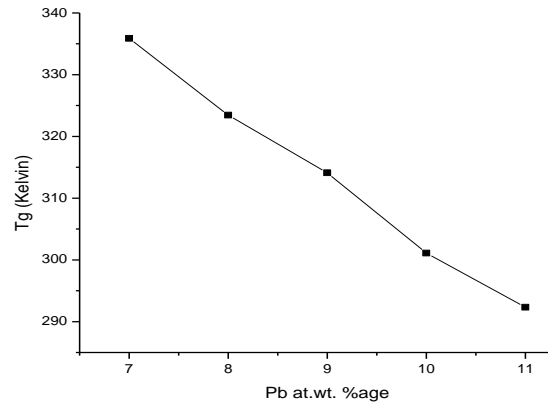

Fig. 7 – Variation of glass transition temperature T_g with Pb at. %

Table 5 – The variation of Tg and mean bond energy of chalcogenide glasses

Composition $Se_{82}Ge_{18-x}Pb_x$	Mean Bond Energy $\langle E \rangle$, (eV)	T_g, (Kelvin)
$x = 7$	1.978	335.88
$x = 8$	1.942	323.44
$x = 9$	1.909	314.11
$x = 10$	1.870	301.11
$x = 11$	1.840	292.34

4. CONCLUSION

The chalcogenide glasses are prepared by melt quenching technique. The material so formed is amorphous in nature as there are no prominent sharp peaks in the XRD diffractograms of the material. There are some structural inhomogenities in the material which are predicted in XRD and SEM of the samples. The various physical parameters like, mean bond energy, cohesive energy, heat of atomization and glass transition temperature etc are calculated for $Se_{82}Ge_{18-x}Pb_x$ ($x = 7, 8, 9, 10, 11$) system. The fragility in the material increases because glass is under constraint and average coordination number varies from 2.22 to 2.14. The cohesive energy of the investigated samples has been calculated by using chemical bond approach and has been found to decrease with increase in Pb content. The heat of atomization, the mean bond energy and the glass transition temperature are found to decrease with increasing Pb content in the Se-Ge system. So this decrease in heat of atomization (H_s) and mean bond energy $\langle E \rangle$ is due to the fact that Pb-Se bonds in the material increase by replacing Ge-Se bonds. Pb-Se bond has comparative low bond energy than Ge-Se bonds. Moreover the size effect of the Pb also contributes to weaken the network structure. So these factors causes the decrease in heat of atomization Hs and mean bond energy and hence is the glass transition temperature T_g. Because T_g is dependent on mean bond energy.

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