

THE FAR-INFRARED STUDY OF Ge MODIFIED Sn–Se–Pb CHALCOGENIDE GLASSES

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The study of bonding arrangements and glassy nature of the chalcogenide alloys help us to detect the material's utility in particular technological application. The vitreous and glassy nature of the alloy is confirmed through XRD and DSC respectively. The glass so formed exhibit high value of T_g and thermal stability. The bond arrangements are studied by using far infrared spectra of the material and explained on the basis of CONM bond approach. With the varying Ge content the rigidity and cross-linking increases in the glassy matrix. The rising T_g is due to the increase in Ge-Se bonds which is also evident from our far-infrared results.

(Received February 25, 2014; Accepted April 11, 2014)

Keywords: Far-infrared spectra, glass transition temperature, Bonding arrangement, differential scanning calorimetry.

1. Introduction

The group VI chalcogen elements (S,Se,Te) of periodic table form a wide range of alloys and compounds, which exhibit their own remarkable role in material science and technological applications. Among amorphous semiconductors, chalcogenide glasses have received major attention in recent years for applications in microphotonic devices due to their unique properties such as high infrared transparency, photosensitivity and large optical nonlinearity [1]. Amorphous chalcogenides are covalent semiconductors having indirect bandgap that can be tuned from visible to infrared region [2]. In order to tune the band gap from visible to IR, we can replace S by Se in chalcogenide glasses. The addition of Ge to chalcogenide glasses produces a more 3-D glass network that increases glass transition temperature (T_g) [1,3].

An understanding of the structure of an amorphous material is essential to understand its physical properties. In the chalcogenide glasses a great attention has been focused on Ge-Se glasses due to their interesting physical properties such as glass formation ability and rigidity. The variation in optical and electrical properties of chalcogenide glasses is mostly related to their structural behavior. So, it becomes essential for us to understand the details of short-range structural order of chalcogenide glasses in order to explore structure-properties correlations [4].

The structure of germanium selenides has been studied by many authors using Raman and FTIR spectroscopy. The discovery of Carrier Type Reversal in Ge-Se-Pb type glasses has led to extensive research on these materials and role of substituents in these glasses. The Raman and FTIR investigations of stoichiometric GeSe_2 are reported by Lucovsky et al. [5] and Wang et al. [6]. There are many more reviewers who have worked on the structure of $\text{Ge}_x\text{Se}_{1-x}$ glasses [7,8]. The role of Pb modifier in the form of n type conduction in Se-Ge glasses were pointed by Tohge et al. [9] The effect of chemical bonding on the physical properties of Se-Ge system has been investigated by Fouad et al.[10]. The additives such as Sn and Pb to the material improve the phase change characteristics and device performance as evidenced from the literature [11-14]. The

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properties of Se-Ge system thus have been studied in detail and it has been found that their physical properties are highly compositional dependant.

We have studied the basic boundary arrangement and confirmed the structural and glassy behavior of $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x = 7, 8, 9, 10, 11$ at. %) glasses. These studies are quite important as they lead to an insight into the molecular structure and to understand and explore the physical properties of these glasses.

2. Experimental procedure:

The chalcogenide materials $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x = 7 \leq x \leq 11$) are prepared by the melt quenching technique. The high purity elements (99.999%) in appropriate atomic percentage are weighed and mixed in evacuated ($\sim 10^{-6}$ Torr) quartz ampoule. The ampoules containing material are heated up to 980°C and held at that temperature for 8 hours. The temperature of the furnace is raised slowly at a rate of $3 - 4^{\circ}\text{C}$ per minute. After heating for about 8 hours, the obtained melt is quenched in ice cool water. The quenched sample is then taken out by breaking the quartz ampoule and grinded to the fine powder. The amorphous nature is confirmed through the XRD by using an X-ray diffractometer Panalytical X'pert Pro (PW 3050/60).

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by scientists. It is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The far-infrared absorption spectra of different glassy alloys are recorded in the spectral range of $30\text{cm}^{-1} - 600\text{cm}^{-1}$ at room temperature using Perkin Elmer 1600 FT-IR Spectrometer with a resolution of 2 cm^{-1} . All the measurements were carried out using polythene pallet method. Powdered samples of 5 mg are thoroughly mixed and grinded with polythene after which the mixtures are pressed at 12 tons cm^{-2} for 5 minute in vacuum. To confirm the glassy nature Differential Scanning Calorimeter (Mettler Star modal SW 9.010DSC) has been carried out to find the glass transition temperature at heating rate of $10^{\circ}\text{K}/\text{minute}$.

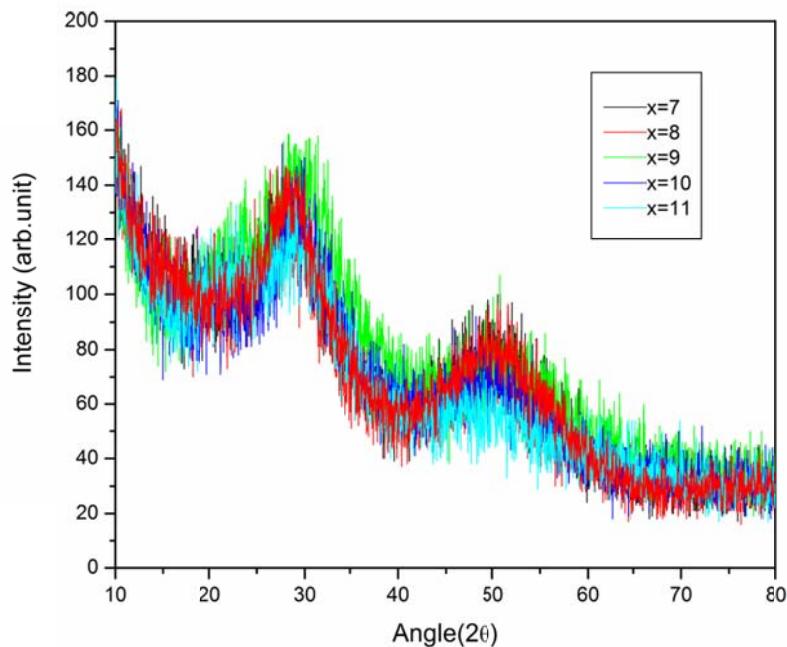


Fig.2.1. X- Ray Diffractogram of the chalcogenide compositions $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x = 7, 8, 9, 10, 11$)

3. Results and discussions

3.1 Justification of glassy nature and basic thermal parameters:

In chalcogenide alloys it is important to know the amorphous and glassy nature of the material. The glassy nature of the material is confirmed by DSC analysis. The variation of glass transition temperature, crystallization temperature and melting point with the addition of Ge concentration has been studied by

Table 3.1 Glass Transition Temperature, Peak Crystallization Temperature, Melting Temperature and thermal stability parameters of $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x = 7, 8, 9, 10, 11$).

x	Temperatures (°C)				Hurby Parameter H _r	Stability Parameter (T _c - T _g)	Mean Bond Energy <E> Kcal/mol (Theoretical)
	Glass Transition T _g	Peak Crystallization T _p	Melting T _m	Reduced Glass Transition T _{rg}			
7	135.36	262.19	425.08	0.585	0.779	126.83	49.13
8	141.68	268.69	438.95	0.583	0.746	127.01	49.69
9	143.32	272.76	440.52	0.584	0.772	129.44	50.87
10	146.30	276.60	442.41	0.587	0.786	130.30	51.74
11	159.14	281.46	450.31	0.598	0.724	122.32	52.62

comparing the DSC thermo grams of all samples at same heating rate of 10 K minute⁻¹ fig.3.2 and table 3.1 shows the DSC thermo grams and the values of glass transition temperature (T_g), peak crystallization temperature (T_p), thermal stability, Hurby parameters ($Hr = \frac{T_m - T_c}{T_c - T_g}$) for $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x=7, 8, 9, 10, 11$) glassy materials respectively. It has been suggested by many researchers that the temperature difference $\Delta T = T_c - T_g$ is a good indication of thermal stability. A higher difference in the value of ΔT indicates a good thermal stability. Compositional analysis using DSC has shown that with the addition of Ge to Sn-Se-Pb glasses the thermal stability has improved.

Glass forming ability ($T_{rg} = T_g/T_m$) [15] of glassy material is the ease with which melt can be cooled escaping the nucleation [16]. This may be due to the increase in the effective bond energy (Ge-Se have larger bond energy than Se-Pb) of the system which increases with the increased degree of cross linking and considerable strengthening of network structure with the increase in Ge at %. The T_g is a dependant variable of mean bond energy <E> given by Tichy and Ticha and of H_s according to Lanhkhost, as theoretical mean bond energy, heat of atomization increases with addition of Ge in material. This has also been reported earlier in our previous work of theoretical study of physical parameters [17].

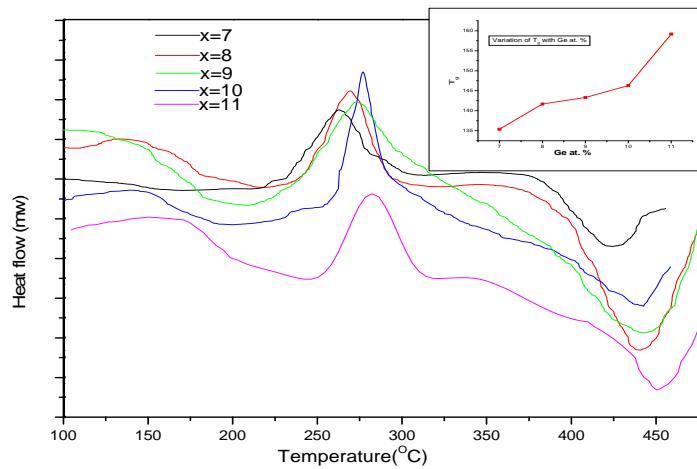


Fig.3.2. DSC thermograms of the samples and variation of the T_g with Ge concentration.

3.2 Bond energy and relative bond formation probabilities

The addition of Ge in the Sn-Se-Pb system plays a key role in deciding the structural properties of the material. According to CONM model the probabilities of heteropolar bonds formation are greater as compared to homopolar bonds. These heteropolar bonds are formed in order of their decreasing bond energy as is evident from the bond probability calculations. 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. Bond energies of heteronuclear bonds are given by

$$D_{(A-B)} = [D_{(A-A)} D_{(B-B)}]^{1/2} + 30 (\chi_A - \chi_B)^2 \quad (1)$$

Where $D_{(A-B)}$ = bond energy of heteronuclear bond, $D_{(A-A)}$ and $D_{(B-B)}$ are the bond energies of homonuclear bonds. χ_A and χ_B are the electronegativity values of A and B respectively. The electronegativities for Se, Ge, Sn and Pb according to pauling scale are 2.55, 2.01, 1.96 and 2.33 respectively [18-19]. The bond energies of the homopolar and heteropolar bonds and relative probabilities of different bonds are given in Table 3.1(a). Probabilities are calculated by using the probability function $e^{D/k_B T}$ at room temperature as well as at 980°C, which is sample preparation temperature, where D is the bond energy, k_B is the Boltzmann constant and T is temperature [20].

Table 3.2 Bond energies and relative probabilities of bonds formation of possible bonds in material.

Bond	Bond Energy K cal /mol	Rel. Bond Probability	
		at 298.15K	at 1253.15K
Se-Ge	49.41	1	1
Se-Sn	49.23	7.4×10^{-1}	9.3×10^{-1}
Se-Se	44.00	1.1×10^{-4}	1.1×10^{-1}
Ge-Ge	37.60	2.2×10^{-9}	8.7×10^{-3}
Se-Pb	31.47	7.1×10^{-14}	7.5×10^{-4}
Pb-Pb	20.48	6.3×10^{-22}	9.02×10^{-6}

3.3 Infrared spectroscopy

3.3.1 Qualitative justification of some absorption bands:

The absorption bands in the present chalcogenide glasses are appearing in the far infrared region 30-600 cm⁻¹. The far infra-red transmission measurement of the Sn₈Se₇₄Pb_{18-x}Ge_x(x = 7,8,9,10,11 at. %) materials are discussed under the following assumptions: (i) ‘valence force field model’ (VFF) [21] and (ii) the position of the intrinsic IR features is influenced mainly by stretching force constants of corresponding bonds formed in the material. The wavenumbers of the vibration modes in the far infrared region is determined by the reduced mass of the atoms and the interatomic force within the group of the atoms comprising the amorphous network. The wavenumber ν is given by the following formula

$$\nu = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2} \quad (2)$$

Where k is the stretching force constant of the bond, c is the speed of light and μ is the reduced mass of the molecule/bond which is given by

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (3)$$

were M_1 and M_2 are the atomic masses of the two atoms. The force constant which gives the measure of strength of bond can be calculated using the relation given by Gordy [22]

$$K_r = aN \left(\frac{\epsilon_a \epsilon_b}{d^2} \right)^{3/4} + b \quad (4)$$

This relation holds accurately for a large number of diatomic and simple polyatomic molecules in their ground states. Here, a and b are constants which depend on the structural unit type, d is the bond length, ϵ_a and ϵ_b are the electronegativities in the Pauling scale and N is the bond order, which can be determined from the expression

$$N = \frac{d+2r_1-3r_2}{2d+r_1-3r_2} \quad (5)$$

where r_1 and r_2 are the covalent radii for the single and double bond, respectively. Secondly Somayayulu [23] has developed a method for predicting the polyatomic force constants by using the elemental covalent force constants and electronegativities as

$$K_{AB} = (K_{AA} K_{BB})^{1/2} + (\chi_A - \chi_B)^2 \quad (6)$$

Here K_{AB} is the force constant between the elements A and B, and k_{AA} and k_{BB} are the force constants for bonds A–A and B–B, respectively, the values of which are (10^5 dyne cm⁻¹) 1.29 for Ge–Ge, 1.21 for Sn–Sn, 0.8 for Pb–Pb [24] and 1.91 for Se–Se. Bond-stretching forces acting as mechanical constraints are present in Ge, Se, Pb and Sn. The bond bending constraints are important in Ge and Se but may be ignored in Sn and Pb because of larger covalent radii and the corresponding force constant in Sn and Pb are weak compared to Ge and Se. The force constants, bond length, reduced mass of all possible bonds are shown in Table 3.3

Table 3.3 Various bonds possible in material with their reduced mass, bond length, and force constants.

Bond	Reduced mass 10^{-26} $\text{KgU}^{-1})(\mu)$	Bond length (nm)(d)	Force Constant $K_{AB}(\text{ev})$
Ge-Ge	6.06	0.245	1.29
Ge-Sn	7.513	0.262	1.25
Ge-Pb	8.92	0.298	1.02
Ge-Se	6.301	0.239	1.93
Pb-Se	8.82	0.291	1.24
Pb-Sn	12.53	0.315	0.99
Pb-Pb	17.2	0.35	0.8
Sn-Se	7.884	0.257	1.52
Sn-Sn	9.882	0.28	1.21
Se-Se	6.559	0.232	1.91

The basic information about the atomic configuration of the glasses in amorphous state can be obtained from comparing the IR spectra of the amorphous state of the glasses with their crystalline analogues. On comparing the IR spectra of both states it is found that the basic structural units in the glasses are essentially the same as those in the corresponding crystalline material.

3.3.2:- Quantitative justification of some absorption bands

The physical properties of chalcogenide glasses has been explained on the basics three models. (i) Chain crossing model (CCM) of Tronc et al [25], (ii) the random covalent network model (RCNM) of Lecovsky et al [26], (iii) chemically ordered network model (CONM) [27]. According to CONM priorities of heteropolar bonds formation are greater over the homopolar bonds and the bonds are formed in order of their decreasing bond energy until all the available valencies of participating atoms are satisfied. A lot of work has been done to understand the glassy structure of selenium. The studies have revealed that Se consists of Se_8 rings and Se_n spiral chains, and in case of binary Ge-Se chalcogenide glasses $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedral, $\text{Ge}_2(\text{Se}_{1/2})_6$ ethane like and $\text{Ge}(\text{Se}_{1/2})_2$ structural units were formed [28]. In the present chalcogenide glassy system various absorption bands are appearing in the far infrared region $30\text{-}600 \text{ cm}^{-1}$ as shown in the Fig. 3.3(a),(b) and tabulated in the Table 3.4. We have observed all possible heteropolar bonds of Pb, Sn and Ge with Se in the FTIR spectrum.

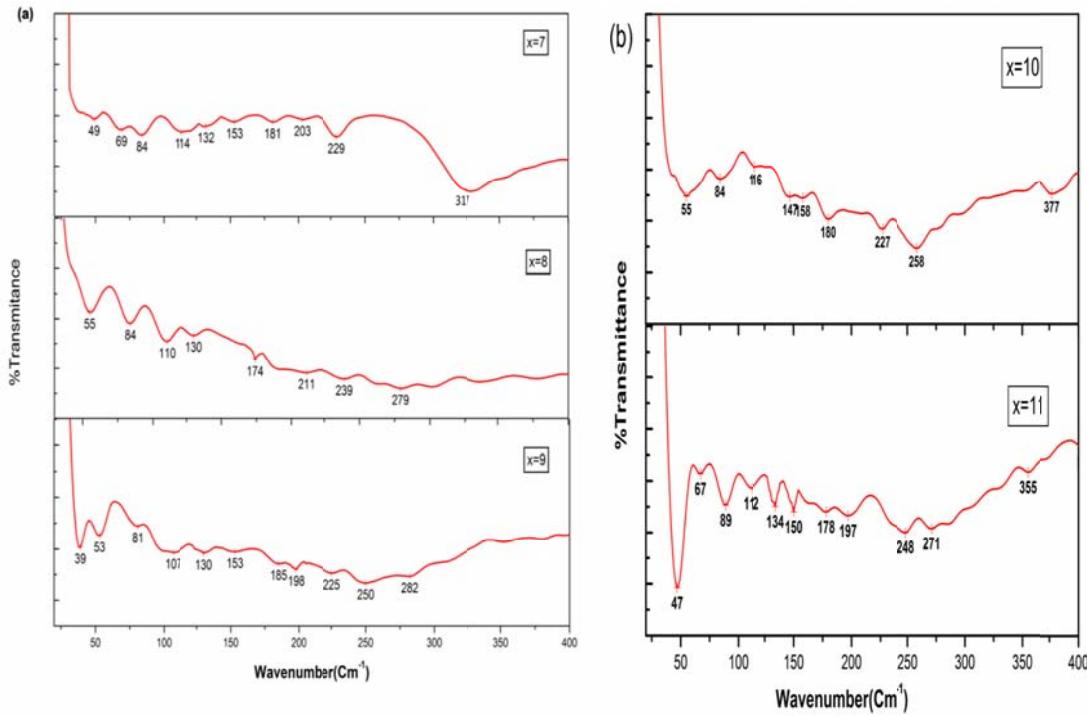


Fig. 3.3 FTIR spectrum of $Se_{74}Sn_8Pb_{18-x}Ge_x$ at (a) $x=7,8,9$ (b) $x=10,11$

The absorption bands from 39cm^{-1} to 84 cm^{-1} are due to the Se_8 (E2 mode)[29] observed in all samples while the bands 107 cm^{-1} at $x=9$ has been assigned to infrared active A2 mode[30] of trigonal Selenium, which is infrared active. According to Zhenhua[31] the absorption peaks 225 cm^{-1} - 239 cm^{-1} for $x=7$ to $x=10$ are assigned to Se_8 ring modes and Se polymeric chain. The bands at 114 cm^{-1} , 110 cm^{-1} , 116 cm^{-1} , 112 cm^{-1} and 153 cm^{-1} , 158 cm^{-1} for $x=7$ to 11 are due to $Sn(Se_{1/2})_4$. The absorption bands 110 - 116 cm^{-1} due to $Sn(Se_{1/2})_4$ appears at $x=7,8,10,11$, but we also see that there is a fall in absorption intensity as we go from $x=7$ to $x=11$. The higher wave number of $Sn(Se_{1/2})_4$ has also been observed in 150 - 158 cm^{-1} absorption band and similar variation in their intensity has also been observed. This confirms the decreasing concentration of Sn-Se bonds in glassy network [32,33]. The are absorption bands at 377 cm^{-1} , 355 cm^{-1} which are due to $Sn(Se_{1/2})_4$ [34]. The absorption peaks 174 cm^{-1} , 178 cm^{-1} , 181 cm^{-1} , 185 cm^{-1} , observed at $x=7,8,9,11$ are due to $GeSe_2$ bond[18,35]. With increasing Ge content in the material these absorption peaks shifts to higher wave number and increase in absorption intensity has been observed. The absorption peaks around 203 cm^{-1} and 211 cm^{-1} at $x=7, 8$ are due to bending mode associated with Ge-Ge-Ge type links. Also the absorption bands at 130 cm^{-1} , 132 cm^{-1} , 134 cm^{-1} are associated with vibrational mode of $[Pb-Se_6]$ distorted octahedra. The peaks at 250 cm^{-1} , 258 cm^{-1} , 248 cm^{-1} are attributed to the vibrations of tetrahedrally coordinated Ge, which are only formed in Pb containing glasses .The peaks at 174 cm^{-1} and 198 cm^{-1} are associated with Ge in tetrahedral position observed at $x=8,9,10,11$ respectively. The peak at 174 cm^{-1} is called as ethane like mode $Ge_2(Se_{1/2})_6$. The peaks at 279 cm^{-1} , 282 cm^{-1} are associated with Ge-Ge phonon mode in glasses [25,37].

Table 3.4 FTIR spectrum peak assignment to various possible bands in $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x=7,8,9,10,11$ at.%)

Sr.no.	x=7	x=8	x=9	x=10	x=11	Assignment
1	49,69	55	39,53	55	47,67	Se_8 (E ₂ Mode)
2	84	84	81	84	89	Se_8 (E ₂ Mode)
3	-	-	107	-	-	Trigonal Se(A ₂ Mode)
4	114	110	-	116	112	$\text{Sn}(\text{Se}_{1/2})_4$
5	132	130	130	-	134	Pb-Se
6	153	-	153	158	150	$\text{Sn}(\text{Se}_{1/2})_4$
7	181	174	185	-	178	GeSe_2
8	-	-	198	198	197	GeSe_4 (RamanMode)
9	203	211	-	-	-	$\text{Ge}(\text{Se}_{1/2})_4$
10	229	239	225	227	-	Se_8 (A ₁ ,E Modes)
11	317	279	250,282	258	248,271	$\text{Ge}(\text{Se}_{1/2})_4$
12	-			377	355	$\text{Sn}(\text{Se}_{1/2})_4$

In $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ Ge atoms are supposed to replace the Pb atoms in the ‘outrigger’ sites. Different studies have revealed that the Pb is present in Pb^{+2} state and forms ion covalent bonds with two non bridging negatively charged chalcogen atoms, which in turn form separate covalent bond with one Ge atom to yield $\text{GeSe}_{4/2}$ tetrahedral units. In $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ glasses, the substitution of Pb atoms by Ge atoms takes place up to $x = 11$. As Ge is increased the concentration of Ge-Se bonds increases and the system contains mostly hetropolar Ge-Se bonds in chemical ordered network stage and the number of the Pb-Se bonds decreases. Also the additional peaks at higher wave number are due to the vibrational mode of $\text{Sn}(\text{Se}_{1/2})_4$ tetrahedron as reported by Mikrut et al [38]. These peaks results from Sn substitution for Ge, it will prefer to enter the “outrigger” tetrahedral site. As Sn (1.41Å) has large covalent radius than Ge (1.22Å) so it is likely to enter “outrigger” sites located at edges of molecular clusters where it would cause the greatest reduction in stress [34]. According to CONM and calculated relative probability of bond formation shows the least existence of homopolar bonds which is in good agreement with the Far-infrared spectra results. There is a replacement of Pb atoms by Ge atoms in the glasses network, thus Ge atoms are incorporated into the clusters of Pb-Se alloys. Thus, addition of Ge introduces strength to the network and leads to a considerable strengthening of the Ge-Se network structure. The consequences of this addition are increase in mean bond energy and T_g . with increasing Ge concentration.

4. Conclusions

A thermal analysis to know glassy nature and FTIR to study structure and bonding arrangements has been carried out on $\text{Sn}_8\text{Se}_{74}\text{Pb}_{18-x}\text{Ge}_x$ ($x=7,8,9,10,11$) systems. The results are interpreted in terms of the vibrations of the isolated molecular units in such a way as to preserve fourfold and twofold coordination for germanium, tin and chalcogen atoms respectively. The theoretically calculated mean bond energy and experimental analysis of far-infrared spectrum agree with the CONM and chemical bond approach model. On the basics of vibrational spectra we assume that Ge is always tetrahedrally coordinated and Pb octahedrally coordinated in the present glass system. We see the absorption bands due to Se rings, Sn-Se, Ge-Se and Pb-Se bonds in our FIR spectra. The effect of increasing concentration of Ge-Se bonds enhances the strength of glassy network hence rises the glass transition temperature.

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