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EFFECT OF PARTIAL REPLACEMENT OF Se BY Ge ON THE PHYSICAL PARAMETERS OF Ge-Sn-Se GLASS SYSTEM

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Ge-Sn-Se is one of the important arsenic free chalcogenide system. We have attempted to analyse effect of partial replacement of Se by Ge on the physical parameters such as coordination number, lone pair electrons, floppy modes, bond energy and glass transition temperature of $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20). Heat of atomization and cohesive energy of the system has been also evaluated. Average single bond energy decreases with increasing concentration of Ge while glass transition temperature increases. Number of lone pair electrons decreased with the addition of Ge, leading to the decrease in flexibility of the system.

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1. Introduction

Chalcogenides glasses are materials of interest due to their applications in diverse fields such as memory devices, optical switching, optical fibers for laser power delivery, xerography etc. [1-4]. Generally containing atleast one chalcogen element (S, Se, Te), these glasses have the advantage that they are highly transparent in IR region having high refractive index and low phonon energy [5]. Properties of these glasses are composition dependent and can be changed by continuously varying the concentration of impurity element [6-7]. Chemical bond approach is an important tool to analyse chalcogenide glasses as properties of these glasses strongly depend on the type of chemical bonds present in the system [8]. Ge-Se is one of the most studied system because of its wide glass forming ability. Various studies has been performed on the effect of different impurities such as Sn, Sb, Tl, Bi etc in Ge-Se system. It has been reported that glass transition temperature decreases with the increasing Sn concentration [9-12]. Ge Sn Se is an important glass system having application in CO_2 laser power delivery. In the present study, we have tried to analyse the effect of partially replacing Se by Ge for fixed concentration of Sn, by calculating system parameters such average coordination number, number of floppy modes, distribution of bonds, cohesive energy and glass transition temperature.

2. Theoretical Methodology

Constraints theory of Philip & Thorpe [13-14], for covalent bonded glasses, proposes that mechanical constraints play an important role structure formation of a network. According to this theory, if long range order is neglected, then two types of constraints i.e. bond bending N_B and

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bond stretching N_S, need to be counted. For an atom with coordination number r, bond bending constraints per atom are given by

$$N_B = 2r-3$$

while the bond stretching constraints per atom are given by

$$N_S = r/2.$$

For multicomponent glasses, average coordination number <r> is taken which can be calculated as

$$<r> = (ar_A+br_B+cr_C)/a+b+c$$

where a,b,c are atomic percentages and r_A, r_B, r_C are coordination numbers, of constituents elements. Total number of constraints are given by

$$N = N_S+N_B.$$

The effective coordination $<r_{eff}>$ is related to total number of constraints by the relation

$$<r_{eff}> = 2(N+3)/5.$$

Constraints theory further proposes rigidity percolation or mechanical threshold when total number of constraints equal the number of degrees of freedom of system, which is obtained for <r> = 2.4. For <r> <2.4 the system is said to be under coordinated or floppy and for <r> >2.4, system is over coordinated or rigid. Number of floppy modes in the system is related to degree of cross linking, which is a function of average coordination number. The number of floppy modes in the system is calculated by the relation

$$f = 2-5/6<r>.$$

Number of lone pair electrons in the system influences the glass formation ability of the system. More the number of lone pair electrons in the system, more is the glass formation ability of the system. Lone pair electrons decreases the strain energy in the system. Presence of lone pair electrons in the bonding atoms provide a character of flexibility to the bond, which allows it to form amorphous network easily. The number of lone pair electrons in any system can be calculated by the relation [15]

$L = V - <r>$, where V is average number of valance electrons and <r> is average coordination number.

Heat of atomization is the enthalpy change required to break all bonds dissociate the material to individual atoms. It is a measure of cohesive energy and average bond strength of the system, and for ternary and higher order compounds can be calculated using the formula [16]

$$H_s = (aH_S^A+bH_S^B+cH_S^C)/a+b+c$$

where H_S^A, H_S^B, H_S^C are heats of atomization for elements A, B, C.
For a ternary compound, energy can be estimated using the relation [17]

$$E_g = aE_g^A+bE_g^B+cE_g^C$$

where a, b,c are volume fractions of constituent elements A, B,C and E_g^A, bE_g^B, cE_g^C are corresponding energy gaps. From average heat of atomization, a parameter, H_S/<r>, called average single bond energy can be calculated, which can be related with the energy gap by a relation given as [18]

$Eg = x(H_S-y)$, where x and y are characteristic constants of system.

Since the properties of glassy semiconductors are influenced by the chemical bonding present in the system, study of distribution of bonds in the system is of utmost importance. The chemically Ordered Network model proposes that heteropolar bonds are preferred by the system over the homopolar bonds and the bonds are formed in the decreasing order of their bond energy [19]. The energies of heteropolar bonds can be calculated using the Pauling relation [20]

$$E_{AB} = (E_{AA} \text{ x } E_{BB})^{1/2} + 30\ (\chi_A - \chi_B)^2$$

where E_{AA} & E_{BB} are the energies of homopolar bonds and χ_A& χ_B are electronegativities of elements A & B. Further considering that bond energies are additive, cohesive energy of the system i.e., stabilization energy per atom for a large cluster material can be calculate using the formula [21]

$$C_E = \Sigma\ P_i\ E_i$$

where P_i is the number of bonds expected and E_i is the energy of the corresponding bond.

Another important parameters for chalcogenide glasses in the mean bond energy, which has major influence on glass transistion temperature of the system. It is a function of coordination number, degree of cross linking, type of bonds and bond energies. Mean bond energy of the system, as proposed by Tichy & Techa, is a combination of two contributing factors E_c and E_{rm}. E_c is the contribution to bond energy by heteropolar bonds and E_{rm} is the contribution by the remaining matrix. So mean bond energy can be written as

$E = E_c + E_{rm}$ where E_c and E_{rm} for Ge Sn Se system are given by

$$E_c = a\ E_{Ge\text{-}Se}\ r_{Ge} + b\ E_{Sn\text{-}Se}\ r_{sn}$$

$$E_{rm} = (\ b\ r_{Se} - a\ r_{Ge} - c\ r_{Sn}) \text{ x } E_{Se\text{-}Se} / <r>$$

Where a, b, c are atomic percentages and r_{Ge}, r_{Se}, r_{Sn} are coordination numbers of Ge, Se and Sn respectively.

Parameter R, which determines the deviation from stoichiometry is calculated using the formula

$R = b\ r_{Se}/ (\ a\ r_{Ge} + c\ r_{Sn})$.

Glass transition temperature is another important parameter for characterization of the glassy state. There have been many attempts to relate the glass transition temperature to rigidity of the network which is represented by the coordination number. Tichy and Techa proposed that it is not only the connectedness of the network but also the quality of the connection i.e. bond energy of the system that influences the glass transition temperature [22]. They proposed an empirical relation between the mean bond energy and glass transition temperature given as

$$T_g = 311\ (\ E - 0.9\ ).$$

Glass transition temperature can also be related to heat of atomization by a relation given by Lankhorst [23]. This is given as

$$T_g = 3.44\ H_S - 488.$$

Probability of bond formation and can be calculated using the probability function exp (D/RT) where D is bond energy, R is gas constant and T is absolute temperature [24].

3. Results and dfiscussion

The values of average coordination number, constraints, floppy modes and lone pair electrons calculated for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20) are shown in table 1. Average coordination number, number of constraints and hence effective coordination number increases with the increasing concentration of Ge. Number of floppy modes and lone pair electrons decreases with increasing concentration of Ge, indicating that the system is getting more and more rigid with the addition of Ge. Variation of effective coordination number, number of constraints, floppy modes and lone pair electrons with Ge concentration is shown in figure 1. Values of heat of atomization, average single bond energy, glass transition temperature, calculated using Lankhorst formula based on heat of atomisation and band gap calculated for the $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20) are shown in table 2. Heat of atomization of the system increases with Ge content while average single bond energy decreases with increasing Ge content. Variation of average single bond energy, cohesive energy and mean bond energy with Ge concentration is shown in figure 2. Glass transition temperature increases with increasing Ge content while the band gap decreases. Variation of Glass transition temperature with Ge concentration is shown in figure 3.

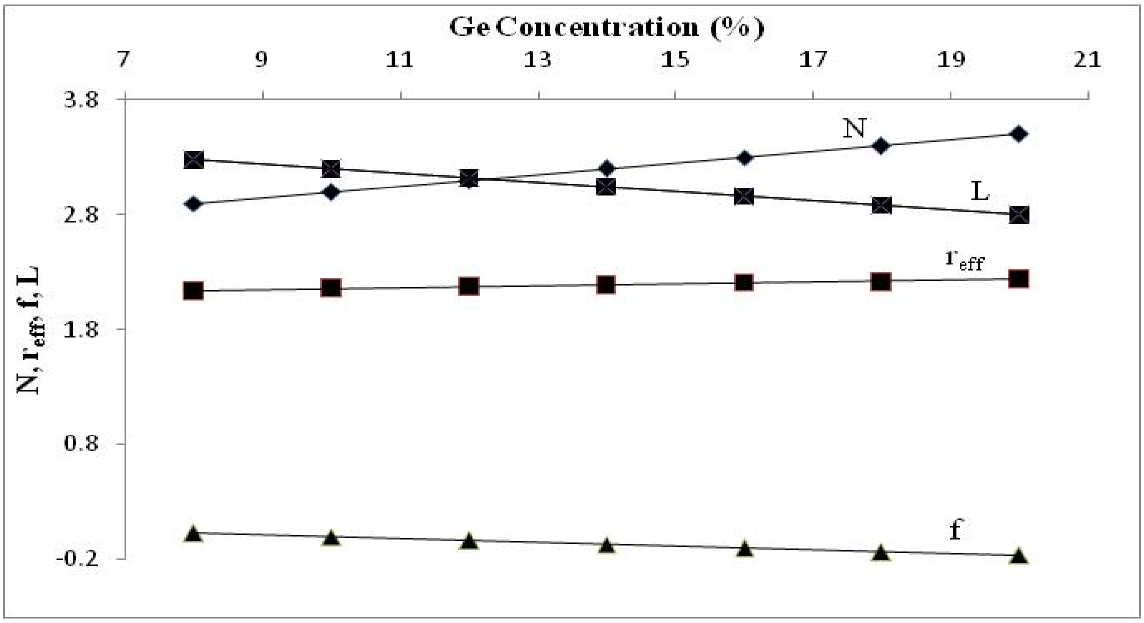

Fig.1. Variation of Number of constraints (N) Effective coordination number (r_{eff}), Number of floppy modes (f) and Lone pair electrons (L) with Ge concentration for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

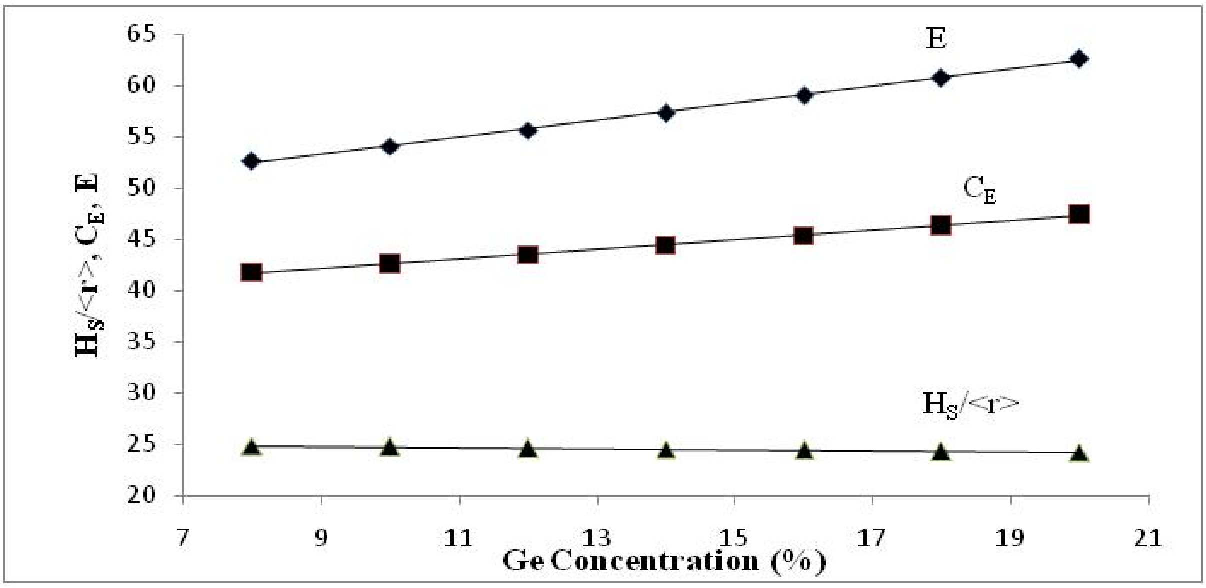

Fig.2. Variation of Average single bond energy (H_s/<r>), Cohesive energy (C_E) and Mean bond energy (E) with Ge concentration for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

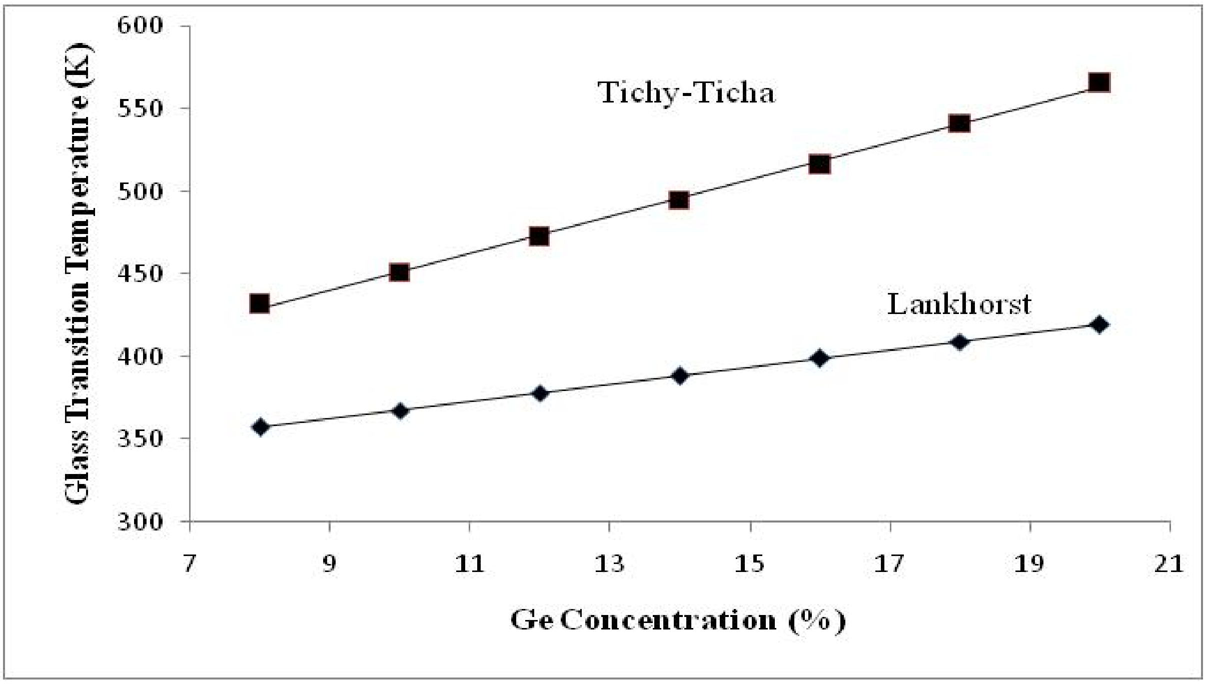

Fig.3. Variation of Glass transition temperature (T_g) with Ge concentration for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

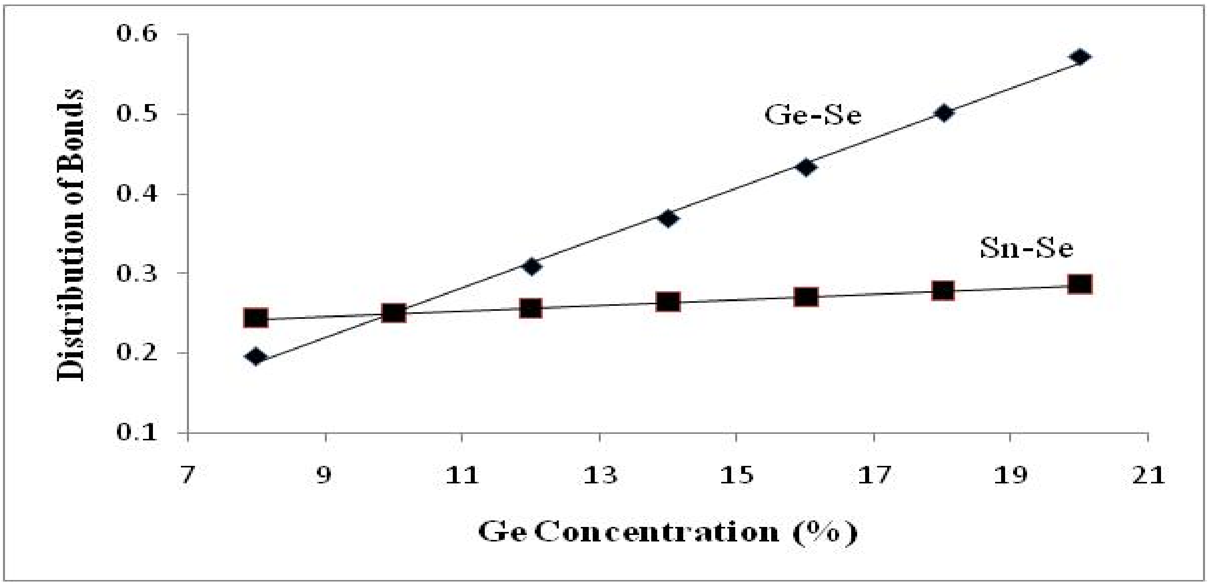

Fig.4. Distribution of bonds with Ge concentration for$Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

Variation in glass transition temperature can be understood in terms of structure of glass system. We know that when Sn is added in the Ge-Se system, it isomorphously replaces Ge and combines with Se, introducing Sn-Se bonds in the system. Since the iconicity of Sn-Se is larger than Ge-Se, it introduces strain in the system and weakens the Ge-Se structure, leading to a decrease in glass transition temperature. However with the increase in concentration of Ge, number of Ge-Se and Sn-Se bonds in the system increases. Variation of number of Ge-Se and Se-Sn bonds with Ge concentration is shown in the figure 4. Since the energy of the Ge-Se bonds is highest among the bonds for the present system, number of Ge-Se bonds increase at much faster rate than Sn-Se bonds, as is also evident from the figure 4, offsetting the effect of Sn-Se bonds and leading to increase in glass transition temperature. Values of Electronegativity, Deviation from Stoichiometry, Distribution of Bonds and Cohesive Energy for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20) are given in table 3. Electronegativity of the system and deviation from stoichiometry decreases with increasing Ge concentration, but for all compositions, system is chalcogen rich. Increasing concentration of Ge leads to an increase in number of Se-Ge and Se-Sn bonds with a corresponding decrease in Se-Se bonds. Consequently cohesive energy i.e. stabilization energy per atom increases with increasing Ge concentration. Values of mean bond energy calculated for the system are shown in table 4. Since the increasing Ge content leads to increase in number of heteropolar bonds, this is reflected in the increase in term E_c i.e. contribution of heteropolar bonds to bond energy. Overall value of mean bond energy increases with increasing Ge content. Values of glass transition temperature calculated from Tichy Ticha formula, based on the mean bond energy are also shown in the table. Bond energies of Ge-Se, Se-Se and Sn-Se bonds formed in the system and their probabilities of formation are given in table 5.

Table 1. Values of Average Coordination No. (<r>), Constraints Bond bending (N_B), Bond Stretching (N_S) and Total (N), Effective Coordination Number, Floppy Modes (f) and Lone Pair Electrons (L) for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

	<r>	N_B	N_S	N	r_{eff}	f	L
$Ge_8Sn_{10}Se_{82}$	2.36	1.72	1.18	2.90	2.14	0.0333	3.28
$Ge_{10}Sn_{10}Se_{80}$	2.40	1.80	1.20	3.00	2.16	0	3.20
$Ge_{12}Sn_{10}Se_{78}$	2.44	1.88	1.22	3.10	2.18	-0.0333	3.12
$Ge_{14}Sn_{10}Se_{76}$	2.48	1.96	1.24	3.20	2.19	-0.0666	3.04
$Ge_{16}Sn_{10}Se_{74}$	2.52	2.04	1.26	3.30	2.21	-0.1	2.96
$Ge_{18}Sn_{10}Se_{72}$	2.56	2.12	1.28	3.40	2.22	-0.1333	2.88
$Ge_{20}Sn_{10}Se_{70}$	2.60	2.20	1.30	3.50	2.24	-0.1666	2.80

Table 2. Values of Heat of Atomisation (H_S), Average Single Bond Energy (H_S/<r>), Glass Transition Temperature (T_{gL} (Lankhorst)), Band Gap (E_g) for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

	H_s (kcal/g-atom)	H_S/<r>	T_{gL} (K)	E_g (eV)
$Ge_8Sn_{10}Se_{82}$	58.69	24.87	357.3	1.69
$Ge_{10}Sn_{10}Se_{80}$	59.41	24.75	367.7	1.67
$Ge_{12}Sn_{10}Se_{78}$	60.13	24.64	378.1	1.65
$Ge_{14}Sn_{10}Se_{76}$	60.85	24.54	388.4	1.63
$Ge_{16}Sn_{10}Se_{74}$	61.57	24.43	398.8	1.61
$Ge_{18}Sn_{10}Se_{72}$	62.29	24.33	409.2	1.60
$Ge_{20}Sn_{10}Se_{70}$	63.01	24.23	419.6	1.58

Table 3. Values of Electronegativity (χ), Deviation from Stoichiometry (R), Distribution of Bonds, Cohesive Energy (C_E), for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

	χ	R	Distribution of Bonds			C_E (Kcal/mol)
			Se-Ge	Se-Sn	Se-Se	
$Ge_8Sn_{10}Se_{82}$	2.45	2.28	0.1951	0.2439	0.5610	41.77
$Ge_{10}Sn_{10}Se_{80}$	2.44	2.00	0.2500	0.2500	0.5000	42.60
$Ge_{12}Sn_{10}Se_{78}$	2.43	1.77	0.3077	0.2564	0.4359	43.46
$Ge_{14}Sn_{10}Se_{76}$	2.42	1.58	0.3684	0.2632	0.3684	44.38
$Ge_{16}Sn_{10}Se_{74}$	2.40	1.42	0.4324	0.2702	0.2973	45.33
$Ge_{18}Sn_{10}Se_{72}$	2.39	1.29	0.5000	0.2778	0.2222	46.36
$Ge_{20}Sn_{10}Se_{70}$	2.38	1.17	0.5714	0.2857	0.1429	47.43

Table 4. Values of Mean Bond Energy (E), Glass Transition Temperature (T_{gT} (Tichy-Ticha), for $Ge_xSn_{10}Se_{90-x}$ (x = 8, 10, 12, 14, 16, 18, 20).

	E_c	**E_{rm}**	**E (Kcal/mol)**	**E (eV/atom)**	**T_{gT} (K)**
$Ge_8Sn_{10}Se_{82}$	35.51	17.15	52.66	2.29	432.3
$Ge_{10}Sn_{10}Se_{80}$	39.46	14.66	54.12	2.35	451.0
$Ge_{12}Sn_{10}Se_{78}$	43.41	12.26	55.67	2.42	472.7
$Ge_{14}Sn_{10}Se_{76}$	47.37	09.93	57.30	2.49	494.5
$Ge_{16}Sn_{10}Se_{74}$	51.32	07.68	59.00	2.56	516.3
$Ge_{18}Sn_{10}Se_{72}$	55.27	05.50	60.77	2.64	541.1
$Ge_{20}Sn_{10}Se_{70}$	59.23	03.38	62.61	2.72	566.0

Table 5. Values of Bond Energy, Probabilityfor Ge-Sn-Se System.

Bonds	**Bond Energy (Kcal/mol)**	**Probability**
Ge-Se	49.42	3.0×10^8
Sn-Se	49.23	2.8×10^8
Se-Se	44.00	0.35×10^8

4. Conclusion

Increasing concentration of Ge increases the number of heteropolar bonds in the system and system becomes more and more rigid. Mean bond energy and heat of atomization increases with increase in Ge concentration leading to increase in glass transition temperature. Analysis of data also reveals that variation of Ge concentration in Ge-Sn-Se system has much more pronounced effect on properties of the system as compared to the variation of Sn concentration.

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