

EFFECT OF SN ADDITION ON PHYSICAL PROPERTIES OF Se-Te GLASSY SEMICONDUCTORS

RAJNEESH KUMAR^a, P. SHARMA^b, PANKAJ SHARMA^{c*}, V. S. RANGRA^a

^aDepartment of Physics, H. P. University, Summer Hill, Shimla (171005) India

^bDepartment of Physics, Sri Sai University, Palampur (176061) H.P. India

^cDepartment of Physics, Jaypee University of Information Technology, Waknghat, Solan, H.P. 173215 India

The effect of tin (Sn) addition on physical properties i.e. coordination number, lone pair of electrons, no of constraints, bond energy, heat of atomization, glass transition temperature, mean bond energy, cohesive energy, density, molar volume, electro-negativity and optical band gap of $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy alloy is investigated. It is inferred that on increasing Sn content, average coordination number, average number of constraints, average heat of atomization, density, optical band gap, mean bond energy and glass transition temperature increases but lone pair of electrons, molar volume and deviation of stoichiometry (R) decreases.

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1. Introduction

Chalcogenide glasses are one of the most promising materials in the modern era because of their vivid technological applications [1] and commercial importance [2]. Chalcogenide glasses are composed of chalcogen elements of group VI elements of periodic table. Recently, there has been an increased interest in the properties of amorphous selenium (a-Se) rich semiconducting alloys due to their current uses as photoconductors in high definition TV pick-up tubes and particularly in digital X-ray imaging. Amorphous selenium binary alloys with tellurium, due to their electrophotographic applications such as photoreceptors in photocopying and laser printing, have been widely studied in both vacuum deposited amorphous film and vitreous bulk form. They are largely used in memory devices and fiber optics [3,4] as they exhibit threshold and memory switching behaviour as well as infrared transmission [5,6]. The glassy alloys of the Se-Te system based on Se are widely used for various applications in many fields as optical recording media because of their excellent laser writer sensitivity, xerography, and electrographic applications such as photoreceptors in photocopying and laser printing [7-9]. The effect of an impurity in an amorphous semiconductor may be widely different, depending upon conduction mechanism and the structure of the material [10]. While in crystalline semiconductors, the effect of a suitable impurity is always to provide a new donor or acceptor state, this is not essential in amorphous semiconductor. Instead of providing a localized impurity level in the mobility gap, an impurity may merely alter the mobility of the charge carriers or may introduce structural changes [11] in the amorphous materials with or without modification of the localized states in the forbidden gap.

Present work is based on bi-chalcogen (Se-Te) glassy system containing tin as the third substitute. Se-Te-Sn show narrow glass forming region but having advantage of higher transmittance in IR region due to reduced optical band gap and low optical losses [12]. Compositional trends in various properties have been investigated. Addition of third element tin (Sn) creates the compositional and configurational disorder in the system. Addition of Sn in Se-Te

*Corresponding author: pankaj.sharma@juit.ac.in

system may change its optical and electrical properties significantly [13]. The physical parameters viz. coordination number, lone pair electrons, bond energy of different bonds, average single bond energy, mean bond energy, glass transition temperature, cohesive energy, density, molar volume and optical band gap have been investigated.

2. Experimental details

Glassy alloys of $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) system were prepared by melt quench technique. Materials (99.999% purity, Sigma Aldrich) were weighed (4g for each batch using Mettler Toledo PL83-S) according to their atomic weight percentage and sealed in evacuated (at $\sim 10^{-3}$ Pa) quartz ampoules and heated to 900°C in rocking furnace at a heating rate of $3\text{--}4^\circ\text{C}/\text{min}$. The ampoules were frequently rocked at the highest temperature for 8 hrs. During the course of heating, the ampoules were shaken several times to maintain the uniformity of the melt. Finally, the ampoules were quenched into ice-cold water to avoid crystallization. After breaking the quartz ampoules, amorphous nature of these alloys were verified by X-ray diffraction (XRD) technique (Philips PW 1710 X-ray diffractometer, Cu-K α radiation, $\lambda = 1.540598 \text{ \AA}$, 40 kV and 35 mA, 2θ range from 5° to 100° , step size = 0.017°). The XRD spectra do not contain any prominent peak which confirms the amorphous nature of samples. Figure 1 shows the X-ray diffraction pattern for the investigated samples.

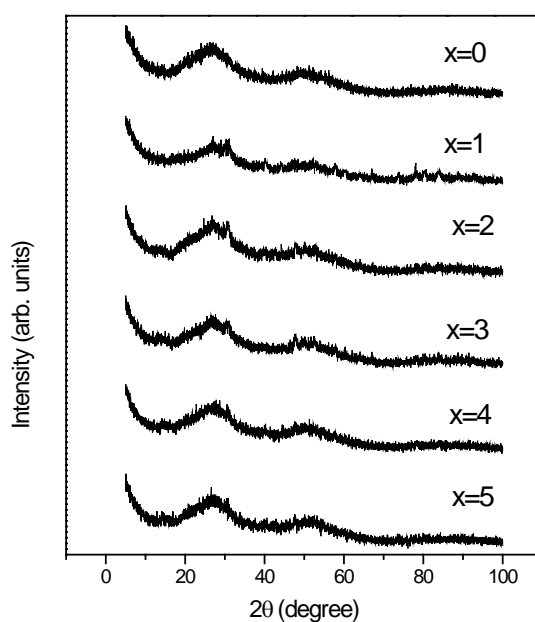


Fig. 1. X-ray diffraction pattern for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system.

3. Results and discussion

3.1. Calculation of coordination number (r) and number of constraints in glassy network

Glasses with varying composition have a varying coordination number. Hence it is useful to calculate average coordination number $\langle r \rangle$. Average coordination number $\langle r \rangle$ is calculated by using the standard method [14, 15]. For the composition $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$), average coordination number $\langle r \rangle$ is given by:

$$\langle r \rangle = \frac{\alpha N_{\text{Se}} + \beta N_{\text{Te}} + \gamma N_{\text{Sn}}}{\alpha + \beta + \gamma} \quad (1)$$

where α, β, γ are concentrations (at %) of Se, Te, Sn respectively and $N_{\text{Se}} = 2, N_{\text{Te}} = 2, N_{\text{Sn}} = 4$ are their respective coordination number. The calculated coordination numbers (r) lie in the range $2.00 \leq r \leq 2.10$ and are given in Table 1. From the calculated values of coordination numbers for the glassy system under investigation, it is inferred that $\langle r \rangle$ increases with increase of Sn content. This reveals the compactness of alloy.

Table 1. Values of average coordination number, number of constraints arising from bond stretching (N_a), number of constraints arising from bond bending (N_b), average number of constraints (N_c) for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system.

Composition	$\langle r \rangle$	N_a	N_b	N_c
$\text{Se}_{92}\text{Te}_8$	2.00	1.00	1.00	2.00
$\text{Se}_{92}\text{Te}_7\text{Sn}_1$	2.02	1.01	1.04	2.05
$\text{Se}_{92}\text{Te}_6\text{Sn}_2$	2.04	1.02	1.08	2.10
$\text{Se}_{92}\text{Te}_5\text{Sn}_3$	2.06	1.03	1.12	2.15
$\text{Sn}_{92}\text{Te}_4\text{Sn}_4$	2.08	1.04	1.16	2.20
$\text{Sn}_{92}\text{Te}_3\text{Sn}_5$	2.10	1.05	1.20	2.25

The mechanical constraints (N_c) i.e. bond stretching (N_a) and bond bending (N_b) have a great influence on covalent bonded glassy networks, which are associated with atomic bonding and effective coordination number $\langle r \rangle$. The number of constraints per atom arising from bond bending can be calculated by $N_b = 2\langle r \rangle - 3$ and from bond stretching by $N_a = \langle r \rangle / 2$ for the atomic species having coordination number (r). For different compositions of the $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system, the effective coordination number $\langle r \rangle$ can be determined by calculating the average number of constraints i.e. $N_c = N_a + N_b$,

$$\langle r \rangle = \frac{2}{5}(N_c + 3) \quad (2)$$

The calculated values of N_a, N_b, N_c and $\langle r \rangle$ for the glassy system $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) are listed in Table 1. In $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) compositions, the average coordination number varies from 2.00 to 2.10.

3.2 Role of lone pair electrons and glass forming ability

The numbers of lone pair of electrons are calculated by using the relation:

$$L = V - \langle r \rangle \quad (3)$$

where L is the lone pair electrons, V is the valence electrons and $\langle r \rangle$ is the average coordination number. For the glassy system $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) the number of lone pair of electrons are obtained by using equation-[3] and are listed in Table 2. It is observed that on increasing the Sn content number of lone pairs of electrons goes on decreasing. This may be due to the interaction between Sn ion and lone pair electrons of bridging Se atom [16]. Zhenhua [17] proposed a simple criterion for a binary and ternary system. According to him, for a binary system the number of lone pair electrons must be greater than 2.6 and for a ternary system it must be greater than 1. In our system under investigation, the values of lone pair of electrons found to be greater than 1. So this explains the fact that the system can be obtained in glassy state. Fouad et al [18] reported that increasing the number of lone pair electrons decrease the strain energy and a structure with a large lone pair of electrons favors glass formation. A system with large number of lone pair of electrons constitutes stable state. Chalcogenide glasses with lone pair electrons are characterized by flexibility [19]. This flexibility of bonds causes these atoms to readily form amorphous network either alone or with a variety of other atomic constituents. In this composition, with the addition of Sn, the number of lone pair electron shows decreasing nature due to interaction between Sn ions and lone pair of electrons of bridging Se atoms. This explains the fact that the system may be in amorphous glassy state. The variation of $\langle r \rangle$ and L for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system is shown in Fig. 2.

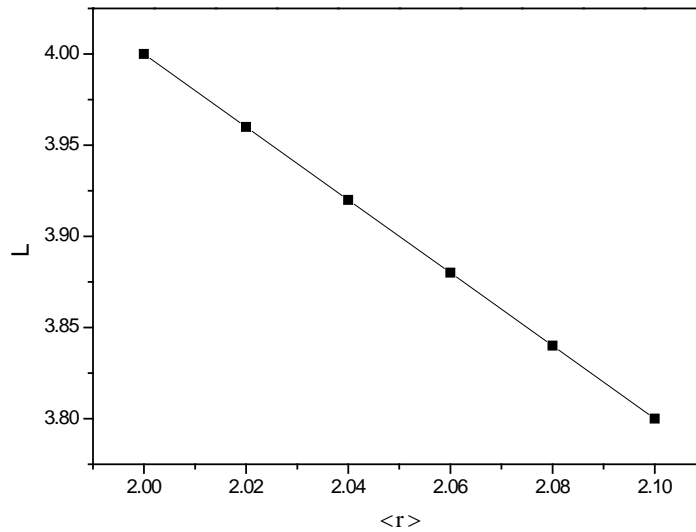


Fig. 2. Variation of lone-pair of electrons (L) with average coordination number $\langle r \rangle$ for the glassy alloys $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$).

Table 2. Values of average coordination number $\langle r \rangle$, number of lone pair electrons for $\text{Se}_{92}\text{Te}_{8-x}\text{Sn}_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system.

Composition	$\langle r \rangle$	V	$L = V - \langle r \rangle$
$\text{Se}_{92}\text{Te}_8$	2.00	6	4
$\text{Se}_{92}\text{Te}_7\text{Sn}_1$	2.02	5.98	3.96
$\text{Se}_{92}\text{Te}_6\text{Sn}_2$	2.04	5.96	3.92
$\text{Se}_{92}\text{Te}_5\text{Sn}_3$	2.06	5.94	3.88
$\text{Se}_{92}\text{Te}_4\text{Sn}_4$	2.08	5.92	3.84
$\text{Se}_{92}\text{Te}_3\text{Sn}_5$	2.10	5.90	3.80

3.3 Density and molar volume

Densities of samples were measured by Archimedean method, using distilled water as a reference liquid. It is given by the formula:

$$\rho = \left[\frac{w_1}{w_1 - w_2} \right] \rho_{\text{water}} \quad (4)$$

where w_1 and w_2 are the weights of samples in air and in the reference liquid respectively while $\rho_{\text{water}} = 1\text{g/cm}^3$ at 20°C . From Table 3 it is clear that density of glass increases with Sn content. This can be explained on the basis of bond formation probability and bond energy. Since Sn-Se has large bond formation probability (calculated but not shown here) and large bond energy in comparison to other bond present in the system which results increase in number of bonds per unit volume and increase in average cross linking density with Sn addition.

Molar volume V_m was determined from density

$$V_m = \frac{1}{\rho} \sum x_i m_i \quad (5)$$

Where m_i is molecular weight of i^{th} sample and x_i is the atomic percentage of same element. From Table 3, decrease in molar volume indicates the potential substitution of Sn for Te leads to a densification of structure system.

Table 3. Values of density ρ , molar mass M_i , molar volume V_m for $Se_{92}Te_{8-x}Sn_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system.

Composition	$\rho(\text{g/cm}^3)$	$M_i(\text{g mole}^{-1})$	$V_m(\text{cm}^3 \text{mole}^{-1})$
$Se_{92}Te_8$	4.962	82.85	16.69
$Se_{92}Te_7Sn_1$	4.972	82.76	16.64
$Se_{92}Te_6Sn_2$	4.982	82.76	16.59
$Se_{92}Te_5Sn_3$	4.987	82.58	16.55
$Se_{92}Te_4Sn_4$	4.992	82.49	16.52
$Se_{92}Te_3Sn_5$	5.00	82.40	16.48

3.4 Average heat of atomization

According to Pauling [20] the heat of atomization H_S (A-B) at standard temperature and pressure of binary semiconductor formed from atoms A and B is a sum of heats of formation ΔH and average of the heats of atomization H_S^A and H_S^B that correspond to the average non polar bond energies of the two atoms [21].

$$H_S(A-B) = \Delta H + \frac{1}{2}(H_S^A + H_S^B) \quad (6)$$

The first term in above equation is proportional to the square of difference between the electronegativity, χ_A and χ_B of two atoms, i.e.

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (7)$$

while for ternary and higher order semiconductor materials, 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 cohesive energy and thus average bond strength, as

$$\overline{H}_S = \frac{\alpha H_S^A + \beta H_S^B + \gamma H_S^C}{\alpha + \beta + \gamma} \quad (8)$$

For ternary glass system, above equation is applicable. The value of \overline{H}_S obtained by using the value of H_S for Se, Te and Sn (227 kJ/mole, 197 KJ/mole, 302 KJ/mole) are listed in Table 4.

From Table 4 it is clear that with the increase in content of Sn heat of atomization (H_S) also

increases. Average single bond energy $\overline{H_S}$ which is measure of cohesive energy decrease with increase of Sn content may cause increase of optical band gap.

3.5 Calculation of mean bond energy and glass transition temperature

The bond energies of heteronuclear bonds have been calculated by using the relation given by Pauling [22] i.e.

$$D_{A-B} = (D_{A-A} \times D_{B-B})^{0.5} + 30 (\chi_A - \chi_B)^2 \quad (9)$$

where D(A-B) is bond energy of heteronuclear bond, D(A-A) and D(B-B) are the bond energies of homonuclear bonds. The D(A-A) values for Se, Te and Sn are 44 Kcal mol⁻¹, 33 Kcal mol⁻¹ and 34.2 Kcal mol⁻¹ respectively [23]. χ_A and χ_B are the electronegativity values of atoms A and B respectively. For Se, Te and Sn the values of electronegativities are 2.55, 2.1 and 1.96 respectively. The calculated of bond energy for different bonds are given in Table 4.

Table 4. Values of average heat of atomization $\overline{H_S}$, average single bond energy $\langle E \rangle$, mean bond energy and glass transition temperature T_g (K) for $Se_{92}Te_{8-x}Sn_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system.

Composition	$\overline{H_S}$ (eV/bond)	$\frac{\overline{H_S}}{\langle E \rangle}$ (eV/bond)	Bonds	Bond Energy(eV/bond)	$\langle E \rangle$ (eV)	Tg(K)
Se ₉₂ Te ₈	2.330	1.165	Se-Se	1.908	1.906	313.71
Se ₉₂ Te ₇ Sn ₁	2.341	1.158	Te-Te	1.431	1.912	315.18
Se ₉₂ Te ₆ Sn ₂	2.351	1.152	Sn-Sn	1.483	1.917	316.81
Se ₉₂ Te ₅ Sn ₃	2.363	1.147	Se-Te	1.915	1.924	318.67
Se ₉₂ Te ₄ Sn ₄	2.374	1.141	Se-Sn	2.135	1.930	320.54
Se ₉₂ Te ₃ Sn ₅	2.385	1.135	Te-Sn	1.482	1.938	322.98

The possible bond distribution at various compositions is expressed using chemically ordered network model (CONM) by Ovshinsky et al [24]. This model assumes that:

- Atoms combine more favorably with atoms of different kind than with the same.
- Bonds are formed in the sequence of decreasing bond energy until all available valences of atoms are saturated. According to Zachariason [25] heteropolar bonds have supremacy over the formation of homopolar bonds.

The glass transition temperature is the most important parameters for characterization of glassy state. Glass transition temperature can be theoretically calculated using different method [26]. The covalent bond approach (CBO) of Tichy and Ticha [27,28] may be considered as first approximation in case of glasses. The glass transition temperature is considered to be proportional to mean bond energy $\langle E \rangle$, which depends upon the factors like coordination number, bond energy and nature of bonds. The correlation between Tg and $\langle E \rangle$ in the form of

$$T_g = 311[\langle E \rangle - 0.9] \quad (10)$$

where $\langle E \rangle$ is the mean bond energy of the system.

$$\langle E \rangle = E_c + E_{rm} \quad (11)$$

where E_c is the overall contribution towards bond energy arising from strong bonds and E_{rm} is the contribution arises from weaker bonds that remain after the number of strong bonds become maximum.

For $Se_XTe_YSn_Z$ system (where $X+Y+Z=1$)

In selenium rich region,

$$E_c = P_r D_{hb} \quad (12)$$

Here P_r is the degree of cross linking and is given by

$$P_r = \frac{YN_{Te} + ZN_{Sn}}{X + Y + Z}$$

In equation (12) D_{hb} is the average heteropolar bond energy and is given by

$$D_{hb} = \frac{XN_{Te}E_{Se-Te} + ZN_{Sn}E_{Se-Sn}}{XN_{Te} + ZN_{Sn}} \quad (13)$$

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

$$E_{rm} = 2[0.5 \langle r \rangle - P_r]E_{Se-Te} / \langle r \rangle \quad (14)$$

The calculated value of mean bond energy is given in Table 4. As Sn increases, mean bond energy increases and hence glass transition temperature also increases. The increase in T_g on substitution of Sn may be due to the stronger Se-Sn bonds (bond energy = 49.41kcal/mole). Sn makes stronger bonds with Se while it make weaker bonds with Te (Te-Sn bond energy = 34.16 kcal /mole). It is found that glass transition temperature increases with increase of Sn content indicating a cross linking of the Se-Te chains with Sn. So mean bond energy and hence glass transition temperature increases. Variation of glass transition temperature with mean bond energies of glassy samples is shown in Fig. 3.

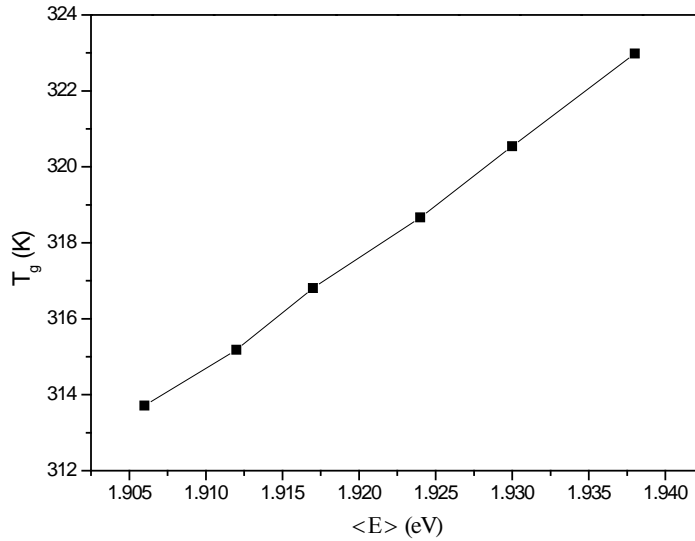


Fig. 3. Variation of glass transition temperature (T_g) with mean bond energy $\langle E \rangle$ for the glassy alloys $Se_{92}Te_{8-x}Sn_x$ ($x = 0, 1, 2, 3, 4, 5$).

3.6 Theoretical band gap, cohesive energy, deviation of stoichiometry and electronegativity

Theoretically band gap (E_g) for binary system can be calculated by the relation given by Shimakawa [29]

$$E_{g(AB)} = VE_{g(A)} + (1 - V)E_{g(B)} \quad (15)$$

where V is the volume fraction of element A and (1-V) is the volume fraction of element B. $E_{g(A)}$ and $E_{g(B)}$ are energy gaps of elements A and B respectively. Same relation can be applied to ternary system. With the addition of Sn in Se-Te alloy, band gap increases. This can be correlated with increases in average heat of atomization [30] as well as decrease in electronegativity[31]. There is linear relationship between the H_s and E_g given by Aigrain and Balkanski[32], so band gap increases with the addition of Sn. Cohesive energy of samples has been calculated by chemical bond approach [24].

$$CE = \sum \left(\frac{C_i D_i}{100} \right) \quad (16)$$

where C_i represent the number of expected chemical bonds and D_i is the energy of each bond respectively. The calculated values of cohesive energies of different glassy samples along with excess Se-Se bonds are given in the Table 5. It increases with addition of Sn content, which means average stabilization energy increases. Increase in CE, causing a gap between bonding and antibonding orbitals. Electronegativities of samples are calculated by Sanderson's principle [33]. In the present paper we observe that optical energy gap increases with decrease in electronegativity. Deviation of stoichiometry (R) is the ratio of covalent bonding possibilities of chalcogen atoms. It is calculated by the relation given by:

$$R = \frac{XN_{Se} + YN_{Te}}{ZN_{Sn}} \quad (17)$$

X, Y, Z are the atomic fractions of Se, Te and Sn respectively. For $R > 1$, system is chalcogen rich and $R < 1$, system is chalcogen poor and $R = 1$ is threshold value where heteropolar bonds exists. From Table 5 it is clear that $R > 1$ for all samples and hence system under investigation is chalcogen-rich region.

Table 5. The value of CE (in K cal/mole), optical band gap (eV), Electronegativity and R of $Se_{92}Te_{8-x}Sn_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system.

Composition	Excess Se-Se bonds	CE (Kcal/mole)	E_g (eV)	Electronegativity	R
$Se_{92}Te_8$	168	44.01	1.791	2.514	∞
$Se_{92}Te_7Sn_1$	166	44.12	1.792	2.512	49.5
$Se_{92}Te_6Sn_2$	164	44.20	1.793	2.511	24.5
$Se_{92}Te_5Sn_3$	162	44.33	1.793	2.509	16.16
$Se_{92}Te_4Sn_4$	160	44.42	1.794	2.508	12
$Se_{92}Te_3Sn_5$	158	44.55	1.795	2.507	9.5

4. Conclusion

It is seen that average coordination number, number of constraints, theoretical band gap, average heat of atomization, density, cohesive energy, mean bond energy and glass transition temperature increases with increase in Sn content or decreasing Te content in $Se_{92}Te_{8-x}Sn_x$ ($x = 0, 1, 2, 3, 4, 5$) glassy system. This behaviour is due to reduction of Te-Te bonds and increase in

average binding strength, while number of lone pair electrons, molar volume and electronegativity decreases with addition of Sn in Se-Te glass.

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