

EFFECT OF COMPOSITIONAL VARIATION ON PHYSICAL PARAMETERS OF QUATERNARY CHALCOGENIDE GLASSES $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($6 \leq x \leq 14$)

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The glassy alloys $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ (where $x = 6, 8, 10, 12, 14$) are prepared by melt quench technique. The physical parameters have been studied such as average coordination number, number of constraints, floppy mode, Lone pair electron, mean bond energy and glass transition temperature etc. The chemical bond approach has been used to calculate cohesive energy of the samples. The mean bond energy and glass transition temperature has been calculated using Tichy-Ticha Approach. It has been observed from the study that with addition of Sb, the parameters such as average coordination number, mean bond energy and glass transition temperature decreases.

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Keywords: Quaternary chalcogenide glasses, Cohesive energy, Glass transition temperature, X- Ray diffraction (XRD) and scanning electron microscopy (SEM)

1. Introduction

The unique features of chalcogenide glasses such as quasi-stability, photoconductivity, infrared transparency, non-linear optical properties and ionic conduction, have led to their applications in field of infrared optics, fiber optics, optical and electronic memory devices, inorganic photoresists and antireflection coating [1]. The addition of impurity in amorphous semiconductors may alter the mobility of the charge carriers or may introduce structural changes which are quite different from the crystalline semiconductors. Pure Selenium System has short life time and low photosensitivity which can be overcome with addition of impurity atoms like Ge, Te, Bi, Ga, In, Sb, Ag etc. [2]. The Selenium based alloy may have high photosensitivity and crystallization temperature but also have low ageing effect [3]. The addition of Sb creates compositional and configuration disorder which can yields p-type conduction in particular composition in some specific concentration region. The Sb-Se glassy matrix has poor stability which can be overcome by doping with Ge [1]. The structural studies of Se-Ge alloy doped by Sb have compositional variation that can be advantageous for knowing the structure-property relationships. The element Ge atoms act as bond modifier and form covalent bonds in the glassy system. Se-Ge-Sb glassy system have low transmission loss and high infrared transparency region varying from 2-16 μm [4]. The addition of Sn acts as chemical modifier. The bond constraint theory helps in explanation of structure and physical properties of amorphous glassy system [5]. The motive behind the present work is to study the effect of Sb on the theoretically calculated physical parameters of $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ (where $x = 6, 8, 10, 12, 14$). The X-ray diffraction (XRD) characterization has been used to know the amorphous nature of the prepared samples.

2. Experimental details

Bulk sample of chalcogenide $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($x = 6, 8, 10, 12, 14$) glasses have been prepared by melt quenching technique. Se, Sn, Sb in powder form with 99.999% purity (Alpha Aesar) and Ge with 99.999% purity (Acros organics) are weighted according to their atomic

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weight percentage. These materials are put in quartz tube cleaned with chromic acid, distilled water and then with acetone. These quartz ampoules have length about 10 cm and diameter of 0.8 cm. The ampoules are sealed at very high vacuum pressure of 10^{-5} Torr in order to avoid the oxygen contamination and counter balance the high vapour pressure in the ampoule created at higher temperature. The sealed ampoules are heated in a furnace at a heating rate of 3- 4°C/minute and temperature is raised to 1000°C. The ampoules are kept at highest temperature for 13 hours and continuously rocked at an interval of 1 hour to ensure the homogenous mixture. The quenching is done in ice-cold water immediately after taking out the ampoules from the furnace. The glass samples prepared are extracted by breaking the quartz ampoules.

The synthesized samples are grinded to get fine powder for X-ray diffraction (XRD) characterization. The vitreous nature of samples is confirmed by using X' Pert Pro XRD. Data were collected using Ni filtered Cu-K α (1.54 Å) radiation in the $10^\circ < 2\theta < 70^\circ$ range at a scanning speed of 1°/min for glasses. X' Pert Pro XRD is equipped with x' Celerator solid-state detector.

SEM provides information about the surface of the material and composition of the region near the surface of the material. The topographical investigation of sample depends upon material-electrons interactions. The EDX Analysis has been done by using HITACHI SU8010 model.

3.Results and discussion

3.1. Structural characterization

3.1.1 XRD analysis

The XRD spectra do not contain any sharp prominent peak which confirms that samples have amorphous nature. Fig.1 shows the X-ray diffraction pattern of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (where x= 6, 8, 10, 12, 14).

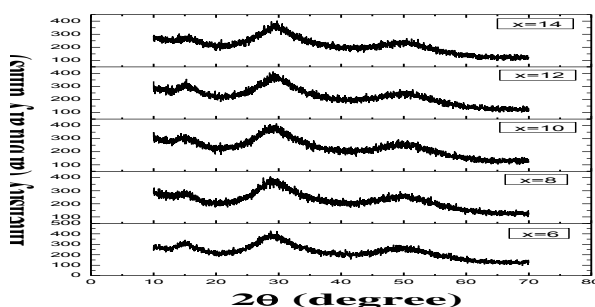


Fig.1. X-ray diffraction pattern of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$).

3.1.2 Surface morphology

Fig.2 shows the surface morphological analysis of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (where x= 6, 8, 10, 12, 14). The SEM images don not contain any crystalline from, pin holes and cracks but only has uniform conchoidal shape which confirms amorphous nature of the prepared glassy samples.

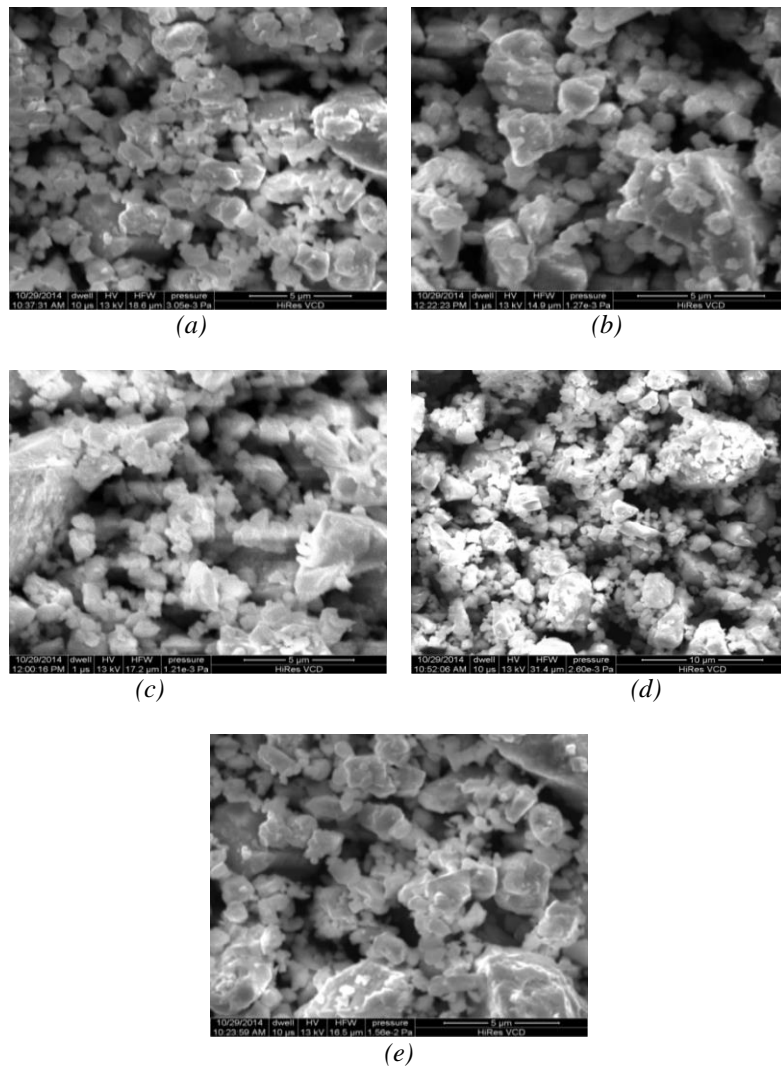


Fig.2. SEM micrographs of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x=6, 8, 10, 12, 14$) glassy system.

The elemental analysis of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x=6, 8, 10, 12, 14$) glassy system is analyzed by energy dispersive X-ray analysis (EDX). Fig.3 shows the dispersive X-ray (EDX) spectroscopy of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x=6, 8, 10, 12, 14$) glassy system. The compositional analysis according to atomic and weight percentage of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x=6, 8, 10, 12, 14$) glassy system listed in Table 1.

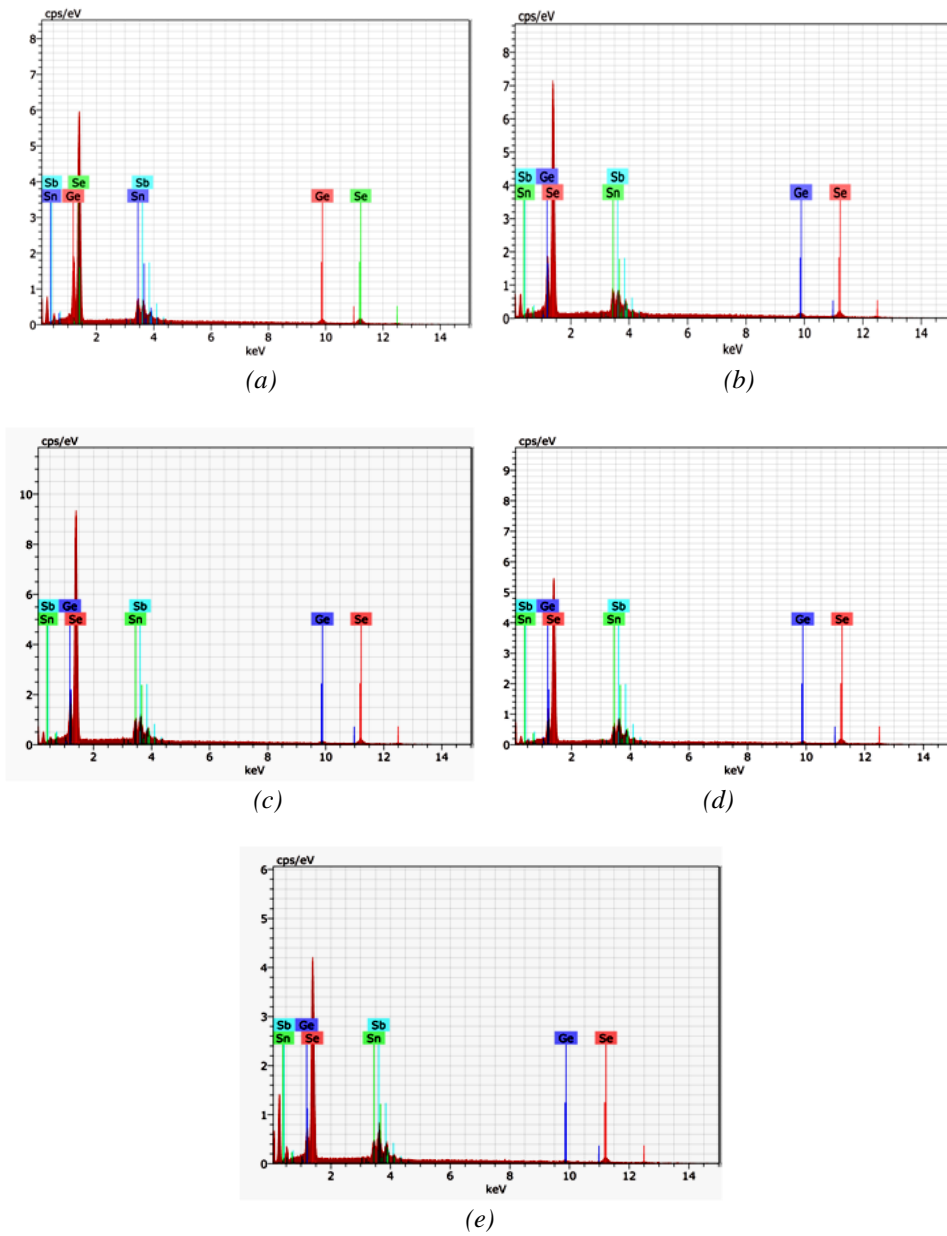


Fig.3. Energy dispersive X-ray (EDX) analysis of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x = 6, 8, 10, 12, 14$) glassy system.

Table 1. The compositional analysis of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x = 6, 8, 10, 12, 14$).

$Se_{69}Sn_{10}Ge_{21-x}Sb_x$	Weight %					Atomic %				
	Se	Sn	Ge	Sb	Total	Se	Sn	Ge	Sb	Total
X = 6	61.99	15.30	13.34	9.37	100	66.84	10.97	15.64	6.55	100
X = 8	61.25	15.20	10.58	12.97	100	67.10	11.08	12.60	9.22	100
X = 10	61.70	14.19	8.98	15.13	100	68.01	10.41	10.77	10.82	100
X = 12	59.89	14.20	6.62	19.30	100	67.26	10.61	8.08	14.06	100
X = 14	59.45	13.05	5.31	22.19	100	67.33	9.83	6.54	16.30	100

3.2. Physical properties

3.2.1. Calculation of Average Coordination Number and Number of Constraints in glassy network

Glasses with varying composition have a varying coordination number. For quaternary chalcogenide system of Se, Sn, Ge, Sb under investigation, the average coordination number $\langle r \rangle$ for covalently bonded materials is given by [6],

$$\langle r \rangle = \frac{\alpha Z(\text{Se}) + \beta Z(\text{Sn}) + \gamma Z(\text{Ge}) + \delta Z(\text{Sb})}{\alpha + \beta + \gamma + \delta} \quad (1)$$

where coordination numbers $Z_{(\text{Se})} = 2$, $Z_{(\text{Sn})} = 4$, $Z_{(\text{Ge})} = 4$, $Z_{(\text{Sb})} = 3$ are calculated by 8N rule and α , β , γ , δ are the atomic weight percentages of Se, Sn, Ge and Sb respectively. The average coordination numbers $\langle r \rangle$ is calculated from equation (1) lies in the range 2.48 to 2.56 and listed in the Table 2. It is clear from Fig.4 that by replacing Ge element having higher coordination number by Sb having lower coordination number, the average coordination number of the quaternary chalcogenide glass system decreases from 2.56 to 2.48.

The covalent bonded glassy networks are influenced by mechanical constraints (N_c) i.e. bond stretching (N_α) and bond bending constraints (N_β). Mechanical constraints (N_c) are associated with atomic bonding and effective coordination number ($\langle r_{\text{eff}} \rangle$). The number of constraints per atom arising from bond stretching is given by,

$$N_\alpha = \frac{\langle r \rangle}{2} \quad (2)$$

The number of constraints per atom arising from bond bending is given by,

$$N_\beta = 2\langle r \rangle - 3 \quad (3)$$

The total number of constraints is given by,

$$N_c = N_\alpha + N_\beta \quad (4)$$

The effective average coordination number is given by,

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

The values of N_α , N_β , N_c and $\langle r_{\text{eff}} \rangle$ for the quaternary chalcogenide glass system $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ (where $x = 6, 8, 10, 12, 14$) are listed in Table 2. Fig.4 shows that with increase in concentration of Sb, the average coordination number decreases, hence average number of the constraints also decreases.

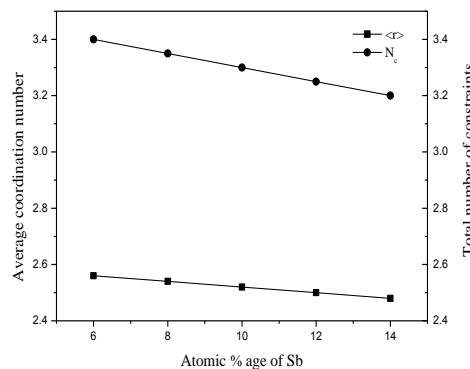


Fig. 4. Variation of coordination number and total number of constraints with atomic % age of Sb.

The cross linking density (X) is equal to the average coordination number of cross linked chain less the coordination number of initial chain [8],

$$X = N_c - 2 \quad (6)$$

The values of floppy modes for quaternary chalcogenide glass system $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($x=6, 8, 10, 12, 14$) are listed in Table 2. It has been observed from the Table 2 that the value of f becomes more and more negative with increase in Sb content. According to constrain theory [7], the investigated composition are over-constrained, stressed-rigid and with lower connectivity, as the value of $\langle r \rangle$ are larger than 2.41. The lower connectivity of composition is due to decrease in average coordination number which in turns decreases the degree of cross linking in the network. Hence, the floppy mode increases in the network due to fall in degree of cross linking which makes the material spongy [9].

Table 2. Average coordination number ($\langle r \rangle$), number of constraints per atom arising from bond stretching (N_α), number of constraints per atom arising from bond bending (N_β), total number of constraints (N_c), effective average coordination number ($\langle r_{\text{eff}} \rangle$), fraction of floppy modes (f) for composition $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($x=6, 8, 10, 12, 14$).

Composition	$\langle r \rangle$	N_α	N_β	N_c	r_{eff}	f
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{15}\text{Sb}_6$	2.56	1.28	2.12	3.40	2.56	0.133
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{13}\text{Sb}_8$	2.54	1.27	2.08	3.35	2.54	0.116
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{11}\text{Sb}_{10}$	2.52	1.26	2.04	3.30	2.52	0.100
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_9\text{Sb}_{12}$	2.50	1.25	2.00	3.25	2.50	0.083
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_7\text{Sb}_{14}$	2.48	1.24	1.96	3.20	2.48	0.066

3.2.3. Deviation from the Stoichiometry of Composition

Parameter R indicates the deviation of the glassy system from stoichiometry and is expressed as the ratio of covalent bonding possibilities of chalcogen atoms to the non-chalcogen atoms [10].

$$R = \frac{\alpha Z(\text{Se})}{\beta Z(\text{Sn}) + \gamma Z(\text{Ge}) + \delta Z(\text{Sb})} \quad (7)$$

where $\alpha, \beta, \gamma, \delta$ are the atomic weight percentages of Se, Sn, Ge and Sb respectively. As shown in Table 3 values of R for the prepared system are found to be greater than unity indicates Se-rich materials which imply heteropolar bonds and chalcogen-chalcogen bonds are present.

3.2.4. Role of Lone-Pair Electrons in Glass Forming Ability

The numbers of lone pair of electrons are calculated by using relation [11],

$$L = V - \langle r \rangle \quad (8)$$

where L is the lone pair electrons, V is the valence electrons and $\langle r \rangle$ is the average coordination number. For the composition $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($x=6, 8, 10, 12, 14$) the number of lone pair of electrons are obtained by using equation (8) and are listed in Table 3. It has been seen that for all the Se compositions, lone pair electrons increases with increase of Sb contents.

In the present composition lone pair electrons are present which confirms its vitreous nature. According to Ovshinsky [12], interaction between lone pair electrons on different atoms and their interaction with the local environment results localised states in chalcogenide glasses. Thus valence alternation pairs (VAPs) have to be created in the alloys due to non bonding orbital interactions. In the present composition, the number of lone-pair electrons increase because the sharing of lone-pair electrons of bridging Se atoms by Sb ion is comparatively low as compared to Ge ion.

Table 3. Deviation of stoichiometry (R), Average coordination number ($\langle r \rangle$), average valence electrons (V) and number of lone-pair electrons (L) for the composition $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x = 6, 8, 10, 12, 14$).

Composition	R	$\langle r \rangle$	V	$L = V - \langle r \rangle$
$Se_{69}Sn_{10}Ge_{15}Sb_6$	1.1695	2.56	5.44	2.88
$Se_{69}Sn_{10}Ge_{13}Sb_8$	1.1897	2.54	5.46	2.92
$Se_{69}Sn_{10}Ge_{11}Sb_{10}$	1.2105	2.52	5.48	2.96
$Se_{69}Sn_{10}Ge_9Sb_{12}$	1.2321	2.50	5.50	3.00
$Se_{69}Sn_{10}Ge_7Sb_{14}$	1.2545	2.48	5.52	3.04

3.2.5. Heat of atomization

Heat atomization H_S (A-B) at standard temperature and pressure of binary semiconductor formed from atoms A and B was proposed by Pauling [13], as the sum of the heat of formation ΔH and the average of the heats of atomization H_S^A and H_S^B corresponding to the average non polar bond energies of the two atoms.

$$H_S(A-B) = \Delta H + \frac{1}{2}(H_S^A + H_S^B) \quad (9)$$

The first term (ΔH) in the above equation is proportional to the square of the electronegativity difference of the two atoms i.e.

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (10)$$

where χ_A and χ_B are electronegativity of atom A and B. In most of cases the heat of formation of chalcogenide glasses is unknown. Even for those few glasses, for which the heat of formation is known, its value is not greater than 10%, so it can be neglected [14]. In case of ternary and higher semiconductor compounds, heat of atomization for quaternary compound $A_\alpha B_\beta C_\gamma D_\delta$ can be written as [15],

$$H_S = \frac{\alpha H_S^A + \beta H_S^B + \gamma H_S^C + \delta H_S^D}{\alpha + \beta + \gamma + \delta} \quad (11)$$

where $\alpha, \beta, \gamma, \delta$ are the atomic percentages of Se, Sn, Ge, Sb. Heat of atomization (H_S) values for Se, Sn, Ge and Sb are 227 KJ/mol, 302 KJ/mol, 377 KJ/mol and 262 KJ/mol [16, 17]. For the composition $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ (where $x = 6, 8, 10, 12, 14$) heat of atomization are obtained by using equation (12) and are listed in Table 4.

Table 4. Heat of atomization (H_s) for the composition $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$).

Composition	H_s (KJ/mol)	H_s (Kcal/mol)
$Se_{69}Sn_{10}Ge_{15}Sb_6$	259.10	61.88
$Se_{69}Sn_{10}Ge_{13}Sb_8$	256.80	61.33
$Se_{69}Sn_{10}Ge_{11}Sb_{10}$	254.50	60.78
$Se_{69}Sn_{10}Ge_9Sb_{12}$	252.20	60.23
$Se_{69}Sn_{10}Ge_7Sb_{14}$	249.90	59.68

It is clear from Fig.5 that with the increase in atomic % age of Sb, the heat of atomization of compound goes on decreasing. This decrease is due to increase in Se-Sb bonds having low heat of atomization.

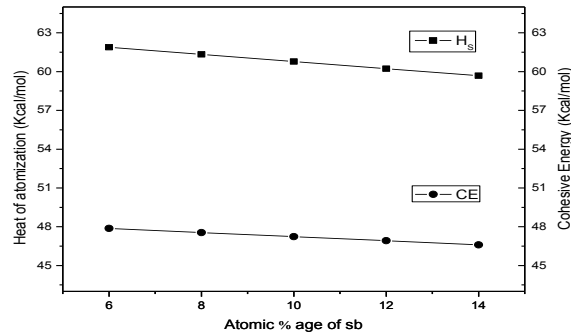


Fig. 5. Variation of heat of atomization with atomic % age of Sb.

3.2.6. Bond Energy and Cohesive Energy

The heteropolar bonds have greater tendency of formation as compare to homopolar bonds [18]. The bond formation in the similar kind of atoms takes place only if there is excess of similar atoms. Chemical bond approach (CBA) explained possible bond distribution [14]. The approach assumes that different type of atoms combine more easily as compare to same atoms and bonds formed in the sequence of decreasing bond energies.

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 [19]

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{1/2} + 30 (\chi_A - \chi_B)^2 \quad (12)$$

where E_{A-A} and E_{B-B} are bond energies of homonuclear bonds. χ_A and χ_B are the electronegativity values of A and B element respectively. The bond energy of homopolar bonds E_{Se-Se} , E_{Sn-Sn} , E_{Ge-Ge} and E_{Sb-Sb} are 44 Kcal/mol, 34.20 Kcal/mol, 37.6 Kcal/mol and 30.2 Kcal/mol [16, 17]. The electronegativity values for Se, Sn, Ge and Sb are 2.55, 1.96, 2.01 and 2.05 [16, 17]. By using equation (12), calculated values of heteropolar bonds E_{Se-Ge} , E_{Se-Sn} and E_{Se-Sb} are 49.42Kcal/mol, 49.23 Kcal/mol and 43.95Kcal/mol. The bonds are formed in order of decreasing bond energy. Se-Ge bonds formed first because having high heteropolar bond energy followed by Se-Sn and Se-Sb bonds are formed.

Based on the chemical bond approach, where the bond energies are assumed to be additive, we can find the cohesive energy (CE) by adding the bond energies over all the possible chemical bonds expected in the glasses. Cohesive energy is given by using,

$$CE = \sum C_i E_i \quad (13)$$

where C_i is the probability of formation of expected bonds and E_i is energy of formation of the corresponding bond present in the system. For the composition $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$) cohesive energy are calculated by using equation (13) and are listed in Table 5. The variation of cohesive energy with atomic % age of Sb is shown in Fig. 5. It is clear from Fig. 5 that with the increase in atomic % age of Sb, cohesive energy of compound goes on decreasing. Cohesive energy decreases because with increase in Sb content, consequently weaker Se-Sb bonds increases and Se-Ge bonds decreases.

Table 5. Electronegativity, Distribution of chemical bonds and cohesive energy for the composition $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$).

Composition	Electronegativity	Distribution of Chemical Bonds				Cohesive Energy (Kcal/mol)
		Se-Ge	Se-Sn	Se-Sb	Se-Se	
$Se_{69}Sn_{10}Ge_{15}Sb_6$	2.3800	0.4348	0.2899	0.1304	0.1449	47.8663
$Se_{69}Sn_{10}Ge_{13}Sb_8$	2.3808	0.3768	0.2899	0.1739	0.1594	47.5497
$Se_{69}Sn_{10}Ge_{11}Sb_{10}$	2.3816	0.3188	0.2899	0.2174	0.1739	47.2332
$Se_{69}Sn_{10}Ge_9Sb_{12}$	2.3824	0.2609	0.2899	0.2609	0.1883	46.9172
$Se_{69}Sn_{10}Ge_7Sb_{14}$	2.3832	0.2029	0.2899	0.3043	0.2029	46.6007

3.2.7. Degree of covalence

According to Philips – Thorpe bond constraint theory for coordination number $\langle r \rangle = 2.4$ all bonds are absolutely covalent. But for any other value of $\langle r \rangle$ the covalent bonds have some ionic character that is molecule becomes polar. The ionicity introduces a tendency towards ordering because of the non-directional character. Ionicity of a bond is calculated using the Pauling formula [20].

$$\text{Amount of ionic character} = 1 - e^{-0.25(\chi_A - \chi_B)^2} \quad (14)$$

where $(\chi_A - \chi_B)$ is the difference in the electronegativities of atoms A and B. Since chalcogenide glasses are made from materials such as sulphur, selenium, arsenic, germanium, antimony and tellurium, which predominantly have covalent bonds, the degree of covalency in the bond of amorphous glass under investigation can be calculated by using the Pauling relationship as

$$\text{Amount of covalent character} = e^{-0.25(\chi_A - \chi_B)^2} \quad (15)$$

Elements having more than 90% covalent character are more favourable for glass formation. Calculated bond energies, ionic character, covalent character of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$) as shown in Table 6.

Table 6. Bond energies, ionic character and covalent character of $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$).

Type of Chemical Bond	Bond Energy (Kcal/mol)	Ionic Character (%)	Covalent Character (%)
Se-Ge	49.42	7.03	92.97
Se-Sn	49.23	8.33	91.67
Se-Sb	43.95	6.06	93.94
Sn-Ge	35.93	0.06	99.94
Ge-Sb	33.75	0.04	99.96
Sn-Sb	32.38	0.02	99.98

3.2.8 Mean Bond Energy and Glass Transition Temperature

The glass transition temperature is the most important parameter for the characterization of glassy state. According to Thorpe and Tichy in a chemically ordered system, there should be an empirical correlation between the glass transition temperature (T_g) and overall mean bond energy. The glass transition temperature is proportional to the mean bond energy E , which depends on factors like average coordination number, degree of cross linking, bond energy and the nature of the bonds formed. The glass transition temperature calculated theoretically for the composition $Se_{69}Sn_{10}Ge_{21-x}Sb_x$ ($x= 6, 8, 10, 12, 14$) by using Tichy-Ticha Approach [21]. Tichy and Ticha gives relation between the glass transition temperature (T_g) and overall mean bond energy ($\langle E \rangle$) is given as,

$$T_g = 311[\langle E \rangle - 0.9] \quad (16)$$

where $\langle E \rangle$ is the mean bond energy of the system and the overall mean bond energy for the system $Se_aSn_\beta Ge_\gamma Sb_\delta$ is given by,

$$\langle E \rangle = E_{cl} + E_{rm} \quad (17)$$

where E_{cl} is the overall contribution towards bond energy arising from the average cross-linking per atom and E_{rm} is the average bond energy per atom of the remaining matrix i.e. contribution from weaker bonds that remains after the strong bonds have been maximized. E_{cl} is given by,

$$E_{cl} = P_r D_{hb} \quad (18)$$

where P_r is the degree of cross linking and is given as,

$$P_r = \frac{\beta Z(Sn) + \gamma Z(Ge) + \delta Z(Sb)}{\beta + \gamma + \delta} \quad (19)$$

where D_{hb} is the average heteropolar bond energy and is given as,

$$D_{hb} = \frac{\beta Z(Sn) E(Se-Sn) + \gamma Z(Ge) E(Se-Ge) + \delta Z(Sb) E(Se-Sb)}{\beta Z(Sn) + \gamma Z(Ge) + \delta Z(Sb)} \quad (20)$$

and E_{rm} is given as,

$$E_{rm} = \frac{[\alpha Z(Se) - \beta Z(Sn) - \gamma Z(Ge) - \delta Z(Sb)]}{r} E_{Se-Se} \quad (21)$$

For the composition $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($x= 6, 8, 10, 12, 14$) value of mean bond energy calculated by using equation (17) and the value of glass transition temperature calculated by using equation (16) are listed in Table 7.

The mean bond energy and glass transition temperature decreases with increase in atomic % age of Sb as shown in Fig. 6. The decrease in results is due to increase in density of weaker bonds containing Sb. The variation of glass transition temperature with mean bond energy is shown in Fig. 7.

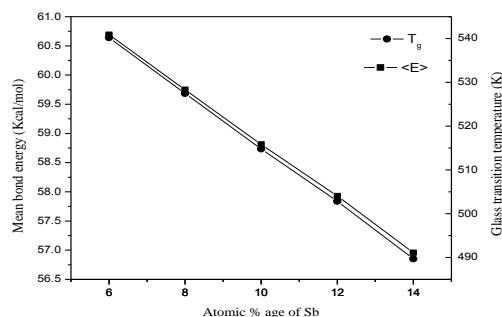


Fig. 6. Variation of mean bond energy and glass transition temperature with atomic % age of Sb.

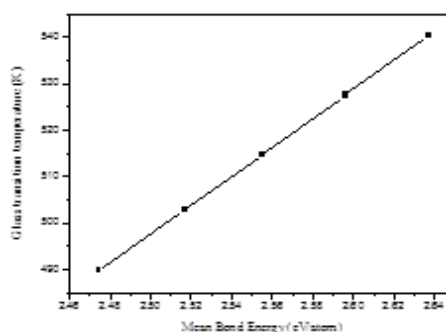


Fig. 7. Variation of glass transition temperature with mean bond energy.

Table 7. Mean bond energy (<E>) and glass transition temperature (T_g) for the composition $\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{21-x}\text{Sb}_x$ ($x= 6, 8, 10, 12, 14$).

Composition	<E> (Kcal/mol)	T_g (K)
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{15}\text{Sb}_6$	60.6925	540.207
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{13}\text{Sb}_8$	59.7494	527.456
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_{11}\text{Sb}_{10}$	58.8123	514.798
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_9\text{Sb}_{12}$	57.9280	502.856
$\text{Se}_{69}\text{Sn}_{10}\text{Ge}_7\text{Sb}_{14}$	56.9563	489.701

4. Conclusions

The amorphous nature of the material has been verified by using XRD and SEM technique. The energy dispersive X-ray (EDX) analysis gives atomic % and weight % of the prepared glassy alloys. The glass forming tendency of the material increases due to increase in floppy modes. With addition of Sb in Se-Sn-Ge system the value of stoichiometric deviation

increases ($R > 1$) which implies chalcogen rich system. The heat of atomization and the mean bond energy are found to decrease with increasing Sb content due to the lesser value of heat of atomization of Sb as compare to Ge or due to rise in weaker bond density of Sb containing bonds. All these variations account for the fall of glass transition temperature with increasing bond density of Sb in bond matrices.

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