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An assessment of topology and compositional dependent physical parameters of Ge-Se-Te-Bi lone pair semiconductors

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Using average coordination number ($\langle r \rangle$), lone pair electrons (L) are calculated and found to decrease with an increase in Bi content. L value greater than 3 indicates that $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) alloys can retain their vitreous nature. Packing density shows subsequent decrease with an increase in density values. Compactness of the structure and molar volume are calculated from the measured density values. Polaron radius is found to decrease with an increase in Bi content. Mean bond energy is found to be proportional to the glass transition temperature and shows maxima at the chemical threshold. Cohesive energy of the system is calculated using the Chemical Bond Approach (CBA) model and a linear relationship is found between cohesive energy and the theoretical band gap. Results are explained on the basis of decrease in average stabilization energy and electronegativity of the system. Degree of the covalency character of different heteropolar bonds is also calculated. An effort is made to discuss the results in terms of average coordination number or equivalently structure of the glassy matrix.

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1. Introduction

Chalcogenide glasses and its dimensionality have attracted much attention in recent years as they exhibit unique thermal, physical and optical properties. They are also relatively easier to prepare from the melt when compared to the traditional glasses. Unlike conventional glasses, and more akin to semiconductors and crystals, chalcogenides can actively interact with photons and electrons. This combination of passive and active properties of chalcogenide glasses makes it unique among optical and electronic materials and can be considered as the optical equivalent of silicon. Glasses of Se-Te have extensive commercial technological applications including xerography, optical recording and laser printing [1]. But limited reversibility and aging effect due to their low glass transition/crystallization temperatures also leads to some drawbacks to these binary glassy systems [2]. Properties of chalcogenide glasses can be enhanced by doping with metal impurities to synthesize multi-component glasses (ternary or quaternary alloys). This helps in making them multipurpose materials with potential applications in nano-based and solid state devices along with numerous other applications [3-4].

On addition of Ge to Se, the Ge atoms act as bond modifiers and help strengthen the average bond by cross-linking the Se chain structure. This further increases the glass transition temperature and resistivity [5]. The addition of Ge atoms also helps to overcome some other drawbacks of pure Se including low sensitivity and shorter life time [6]. Properties of chalcogenide glasses can be tailored by doping with different elements. The effect of the addition of Indium and Bismuth on Ge-Se glassy alloys have been studied by the author earlier. Various physical properties including optical and electrical were analyzed and the results proved that there is an enhancement of these properties when doped with In and Bi [7-9]. Therefore, in the present manuscript, authors have decided to keep Ge-Se-Te as a parent matrix.

The addition of Bi in the Ge-Se-Te glassy system helps to improve its various properties including enhancement in chemical durability. Also, the replacement of Se with Bi in the Ge-Se host matrix causes a reduction in the activation energy and exhibition of electronic switching [10]. Addition of Bi in Se systems also leads to a decrease in the optical band gap for the n-type conducting samples which further results in the enhancement of the photoconduction for n-type samples [11, 12]. The addition of Bi extends the multiphonon absorption edge 17.6 µm, which is 1.2 µm longer as compared with the Ge-Se-Te glass. This offers Ge-Se-Te-Bi glass system a broader IR transparency region [13].

The choice of this particular composition - $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) in the present work was done to avoid nanophase separation [14]. As the refractive index (linear and non-linear) drops down when the Ge content is too high, it is kept at 18%. The incorporation of Bi on the other hand causes an increase in the crystallization ability of the glasses as the glasses partially crystalize when Bi goes beyond 13 at. % [15]. Studies have stated that when the Ge content is 20 at. %, the upper limit of the Bi content which can be contained into the Ge–Se matrix is only 13 at. % [16]. Furthermore, a significant change in the optical band gap and electrical activation energy is noted when Bi content increases from 0 to 10 at. %, approximately 8-9 at. % of Bi [17, 18]. It was observed that the composition at lower Bi content showed luminescence while the composition which had n-type conduction failed to exhibit any luminescence [19].

The theoretical study of the physical parameters of a system is vital for the development of better materials for those involved in experimental research. Therefore, in the present paper, the topological and composition dependent physical parameters of $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloys have been studied. The effect of Bi addition replacing Se was investigated. Using topological concepts average coordination number and total number of constraints were investigated. Correlation between the glass transition temperature and mean bond energy was evaluated. Other physical parameters, *viz.* lone pairs, glass forming ability, density, compactness, molar volume, free volume percentage, electronegativity, average heat of atomization, cohesive energy, theoretical band gap, polaron radius and field strength were also calculated. Efforts were also made to correlate the variation in different physical properties in terms of atomic arrangements, *i.e.*, atomic radius, bond energy, bond length, defects or equivalently with average coordination number.

2. Theoretical considerations

The present paper deals with the theoretical investigation of physical parameters with the addition of Bi to the Ge-Se-Te system. The structure of the glass was explained based on the continuous random network models. To check the glass forming ability, number of lone pairs are calculated using valence electrons. Tichy-Ticha approach was used to understand the deviation from stoichiometry and calculate the mean bond energy and glass transition temperature. The theoretical band gap was calculated using Shimakawa's relation. Distribution of bonds and stabilization energy is calculated using Chemical Bond Approach (CBA) model to evaluate the overall energy of the system. Density values were calculated using Fayek's relationship and efforts are made to explain glass transition temperature with density values. Other parameters *viz.* molar volume, excess volume, compactness, and packing density for the Ge-Se-Te-Bi glassy system are also calculated using the density values. Results are explained on the basis of decrease in electronegativity in the system which is calculated from Sanderson's principle. Se atomic density was calculated using Naster-Kingery formula which was further used for the calculation of the Polaron radius. The values of the Polaron radius were then used to calculate the Field strength.

3. Results and discussion

3.1. Average coordination number ($\langle \mathbf{r} \rangle$)

The average coordination number or nearest neighbor coordination ($\langle r \rangle$) is one of the most critical parameters that gives the number of the nearest neighboring atoms. It characterizes the electronic behavior of the semiconducting materials [20]. The calculation of the average coordination number for amorphous molecules differs from that of the crystals. Specifically for covalently bonded materials, the coordination number follows the $'8-N'$ rule where $'N'$ is the valence of the atom [21]. For quaternary glasses, the average coordination number $\langle r \rangle$ can be calculated using $\langle r \rangle = \frac{aX+bY+cZ+d\delta}{a+b+c+d}$, where, a, b, c and d are the % at. wt. of Ge, Se, Te and Bi, respectively and X= 4, Y= 2, Z=2, and δ=3 are their respective coordination numbers. The formulated values of $\langle r \rangle$ for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) are given in table 1. The result shows an increase in the values of $\langle r \rangle$ after the incorporation of Bi into the glassy alloy. According to the constraint model and development theories, the covalent network or the value of $\langle r \rangle$ in a chalcogenide glassy system is considered to be influenced by mechanical constraints (N_{con}). Therefore, the analysis of constraints for a network helps us to uncover various substructures and mechanical softening of covalently bonded networks [22]. N_{con} is given by the sum of N_α (bond stretching constraint) and N_β (bond bending constraint). Therefore, the total number of mechanical constraints per atom (N_{con}) is given by $N_{con} = \frac{5}{2}\langle r \rangle - 3$ or $N_{con} = N_\alpha + N_\beta$, where, $N_\alpha = \frac{\langle r \rangle}{2}$ and $N_\beta = 2\langle r \rangle - 3$. The calculated values of N_α and N_β are also listed in table 1 and are found to increase from 2.90 to 3.15 with an increase in Bi content. When $N_{con} = N_d = 3$, *i.e.*, when N_{con} becomes equal to the degree of freedom number (N_d), it is the optimal condition for the most stable glass formation to occur as suggested by Phillips and Thorpe [23]. For this condition to occur, it is assumed that $\langle r \rangle = 2.4$ and is also called as the rigidity percolation, critical connectivity threshold or the mechanical threshold. It indicates the threshold of mode change, *i.e.*, floppy ↔ intermediate region. For $Ge_{18}Se_{68}Te_{10}Bi_4$ composition, $\langle r \rangle = 2.4$ which is theoretically the most stable composition among all the compositions under investigation. At this value of $\langle r \rangle$, the 2-D structural network transforms into 3-D structural network.

Table 1. Values of average coordination number ($\langle r\rangle$), bond bending (N_α), bond stretching forces (N_β), total number of constraints (N_{con}), cross-linking density (D_{CL}), number of floppy modes (M_f), valence electrons (V), and lone pair electrons (L) with Bi at. % for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system.

x	$\langle r\rangle$	N_α	N_β	N_{con}	D_{CL}	M_f	V	L
0	2.36	1.18	1.72	2.90	0.90	0.33	5.64	3.28
2	2.38	1.19	1.76	2.95	0.95	0.0166	5.62	3.24
4	2.40	1.20	1.80	3.00	1.00	0	5.60	3.20
6	2.42	1.21	1.84	3.05	1.05	-0.0166	5.58	3.16
8	2.44	1.22	1.88	3.10	1.10	-0.033	5.56	3.12
10	2.46	1.23	1.92	3.15	1.15	-0.05	5.54	3.08

When $\langle r\rangle < 2.4$, the glassy network is considered to be floppy or under-coordinated in which the rigid regions are isolated. With $\langle r\rangle > 2.4$, networks form over-coordinated glasses and become rigid and continuous which eventually leads to crystallization. From the tabulated data, it can be inferred that with the addition of Bi, the system under investigation moves from floppy to rigid mode. Using N_{con} and $\langle r\rangle$, the values of cross-linking density (D_{CL}) [24] and floppy modes (M_f) [25] are calculated as $D_{CL} = N_{con} - 2$ and $M_f = 2 - \frac{5\langle r\rangle}{6}$. The corresponding values of D_{CL} and M_f are also listed in table 1 and it is found that D_{CL} increases while M_f values are found to decrease.

3.2. Relation between lone pair electrons of the structure and glass forming ability

Lone pair electrons have a great impact on chalcogenide glass formation. This can be understood in accordance with valence shell electron pair repulsion theory. Liang correlated the number of lone pair electrons [26] with the ability of a chalcogenide system to retain its vitreous state. Chemical bonds with lone-pair electrons possess a character of flexibility. So, it is easier to form bonds and extend the network [27] with higher number of lone pair electrons. Most of the substances which can solidify in the vitreous state are found to possess structural bridges, *e.g.* in chalcogenide glasses, the bridges are formed by group VI elements. Se atoms in glass structures have two pairs of lone-pair electrons. This existence of bridging atoms, with lone-pair electrons, causes decrease in the strain forces in amorphous materials. Hence, it is easier to deform a bond with lone pair electrons, thereby, stabilizing the glass formation. Number of lone pair electrons is calculated using the formula, $L = V - \langle r\rangle$, where L is the number of lone pair electrons, V is the number of valence electrons which is equal to the unshared lone- pair electrons and $\langle r\rangle$ is the coordination number. The calculated values of 'L' are listed in table 1. It is seen that with an increase in Bi content, the number of lone pair electrons decreases continuously. This behavior is presumed to occur due to interaction between Bi ion and the lone pair electrons bridging the Se atoms. The impact of lone pair electrons in glass formation is therefore reduced due to this interaction. This decrease in the value of 'L' shows that bond deformation in the system is not easy which can further be attributed to the decrease in the flexibility of the system. Same trend can be seen in figure 1, where lone pair electrons decreases with an increase in $\langle r\rangle$ value for Ge-Se-Te-Bi alloys.

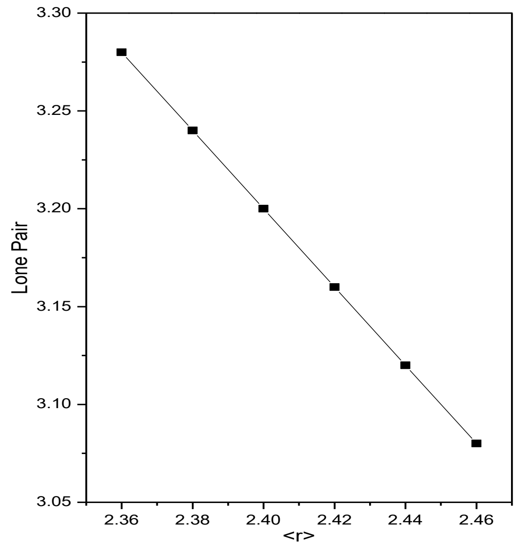

Fig. 1. Variation of lone pair electrons with average coordination number for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloys.

Decrease in number of lone pair electrons increases the strain energy in the system, making it tough to deform bonds as the system also moves towards the intermediate region. Since the calculated values of 'L' are found to be greater than 3, it is clear that the investigated system can form glass and retain its vitreous nature easily [28].

3.3. Calculation of density (ρ) and compactness (δ)

Density(ρ), compactness (δ) and molar volume (V_m) are considered to be the main parameters that greatly affect the various physical properties of a material. The atomic mass and structure of the different components constituting the glassy system, attribute to density and molar volume values. Density of chalcogenide glass is calculated using the formula deduced by [29],

$\rho = (\sum \frac{x_i}{d_i})^{-1}$, where x_i is the weight fraction and d_i is the density of the i^{th} structural unit. Density values calculated for the different compositions are given in table 2. It can be concluded from the results that Bi substitution for Se results in an increase in density values. The empirical equation of the density variation with Bi content is given as; $\rho = 4.96 + 0.027x \quad g/cc^3$, where x is Bi at. %.

Table 2. Values of density (ρ), packing density, compactness (δ), molar volume (V_m) and excess volume (V_e) for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system

x	ρ (g/cm^3)	Packing Density (*10^{22})	δ	V_m (cm^3/mol)	V_e (cm^3/mol)
0	5.03	3.66	-0.005	16.43	0.107
2	5.09	3.59	-0.018	16.75	0.327
4	5.14	3.52	-0.032	17.09	0.566
6	5.20	3.46	-0.042	17.38	0.756
8	5.26	3.40	-0.053	17.68	0.955
10	5.32	3.33	-0.063	17.98	1.155

This increase is presumably because of the greater density and radius of Bi as compared to Se. This variation in density is also attributed to the change in the structural unit arrangement of the different constituting components in the system [30]. On the basis of increase in density values, refractive index of the system is also expected to increase. This can be understood following Lorentz-Lorentz relation [31], $\frac{n^2-1}{n^2+1} = \frac{1}{3\varepsilon_o}\sum_i N_i\alpha_{pi}$, where ε_o is the vacuum permittivity, N_i is the number of polarizable units of type i per unit volume with polarizability, α_{pi}. Atoms with larger atomic radius are presumed to have larger polarizability which indicates a larger refractive index. Incorporation of Bi (1.46 Å) at the expense of Se (1.16 Å) attributes to a larger refractive index value making this material suitable for use as IR mirrors and filters. Ratio of the used space to the allocated space is expressed as the packing density. The values of packing density are determined using the formula, $Packing\ density = \frac{N_A * \rho}{M}$, where N_A is Avogadro's number and M is the molecular weight [32]. The formulated values of packing density are given in table 2. Decrease in the values of packing density with an increase in Bi content (inset of figure 2) results due to the subsequent increase in glass density.

Compactness is given as the measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of a given solid [33]. It is associated with the free volume and flexibility of the network and is, therefore, more sensitive to the changes in structure of the glass network when compared to mean atomic volume [7].

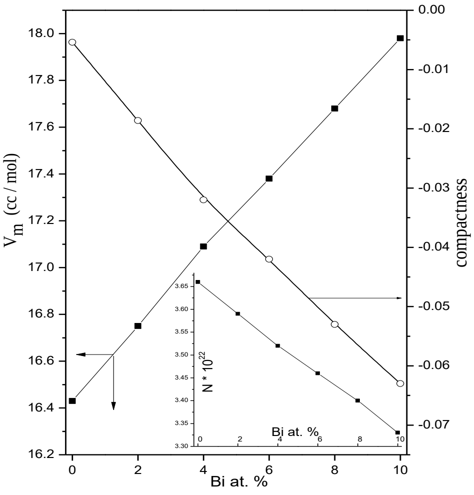

Fig. 2. Variation of molar volume and compactness with Bi at. %; inset shows the variation of packing density with Bi at. % for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloy.

Compactness is calculated using the formula, $\frac{\sum_i \frac{c_iA_i}{\rho_i} - \sum_i \frac{c_iA_i}{\rho}}{\sum_i \frac{c_iA_i}{\rho}}$, where, ρ is the measured density of the glass, c_i, ρ_i and A_i are the atomic fraction, the atomic density and the atomic weight of the i^{th} element of the glass, respectively [34]. The calculated values of compactness are listed in the table 2 and are found to be decreasing with an increase in Bi content. When Bi enters the Ge-Te-Se system, it makes a bond with Se. New bonds are formed with a longer bond length, since the bond length of Se-Bi is 2.7 Å and that of Se-Se is 2.1 Å. Due to this, the atomic arrangements become less tightly bound which causes increase in the molar volume (figure 2) and decrease in compactness [7]. Also, values of compactness show negative values which correspond to a larger free volume and flexibility [21].

3.4. Determination of molar volume (V_m) and excess volume (V_e)

Molar volume (V_m) is the volume occupied by 1g-molecule of the glass. It is calculated using the formula, $V_m = \frac{1}{\rho}\sum x_iM_i$, where x_i represents the atomic fraction of component i and ρ represents the density [35]. The calculated values of V_m are tabulated in table 2 and it is found to increase with an increase in Bi content. This may be attributed to the fact that Se is substituted by larger Bi atoms leading to an increase in V_m with increasing Bi content [36]. Figure 2 shows the variation of molar volume and compactness with increase in Bi content. It is clear from the figure that the decrease in compactness and packing density can be directly attributed to the increase in the molar volume. The following empirical equations $V_m = -26.54\delta_m + 16.2$ and $V_m = -4.74N * 10^{22} + 33.8$ show the molar volume variation with compactness and packing density, respectively. Change in composition structure due to variation created in the interatomic spacing might be a reason for this change. Further, change in the number of bonds per unit volume in the glassy network due to Bi addition may also influence this variation in V_m [35]. Generally, it is expected for the molar volume and density to show opposite trend. But in the system under investigation, both V_m and ρ show an increase in values with increase in Bi content. This kind of behavior supports the open structure concept [37]. This anomalous behaviour has been previously reported in other semiconductors as well [7, 38].

The excess volume (V_e) is calculated using the following relation, $V_e = V_m - \sum_i x_i V_m(i)$, where, x_i is the molar fraction of the sample and $V_m(i)$ is the molar volume of each component [39]. The tabulated values of V_e are also given in table 2. The positive values of the result imply that the samples at all compositions are loosely packed structures. This is in fair agreement with the results published by other workers on semiconducting glassy alloys [40].

3.5. Calculation of polaron radius $(\mathrm{R_P})$ and field strength (F)

A polaron is a quasi-particle which is used to understand the interactions between electrons and atoms in solid materials. The polaron comprises of the electron and its surrounding lattice deformation. It is studied for both ordered and disordered solids. By extending the general concept of polaron, interactions between electrons and ions have also been studied. The polaron radius (R_P) must be greater than the radius of the atom on which the electron is localized but also lesser than the distance, r, separating these sites. Size of the polaron decreases as the number of atoms increases [30, 41]. The polaron radius [39] is calculated using the following relation, $R_P = \frac{1}{2}(\frac{\pi}{6N})^{\frac{1}{3}}$, where, N is the number of Se atoms per unit volume of the Se atomic density existing in the Ge-Se-Te-Bi glass composition. $'N'$ is calculated using the Naster-Kingery [42] equation, $N = \frac{\rho_S W_P N_A}{AW*100}$, where, ρ_S is the sample density, N_A is Avogadro's number, AW is the atomic weight of Se in grams and W_P is the weight percent of the Se content in the Ge-Se-Te-Bi matrix. The average spacing between Se-Se atoms or the interatomic distance (r) of the $\mathrm{Ge_{18}Se_{72-x}Te_{10}Bi_x}$ sample is calculated using the formula [30], $r = (\frac{1}{N})^{\frac{1}{3}}$. Field strength is calculated using the relation, $F = \frac{V_{NO.}}{R_P^2}$, where, $V_{NO.}$ is the valence number of the Se element and R_P is the calculated polaron radius [30, 43]. The formulated values of N, the average spacing, polaron radius and the field strength are given in table 3.

Table 3. Values of N, average spacing (r), polaron radius (R_P) and the field strength (F) for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system.

x	$N*10^{22}$ (cm^{-3})	r (Å)	R_P (Å)	$F*10^{16}$ (cm^{-2})
2	4.63	2.78	1.121	4.47
4	4.68	2.77	1.117	4.48
6	4.73	2.76	1.113	4.49
8	4.78	2.75	1.110	4.51
10	4.81	2.74	1.107	4.52

Fig. 3 shows the decrease in the polaron radius and simultaneous increase in field strength with increase in the Se atomic density (N). The decrease in R_P with increase in Bi content is presumably due to the increase in the number density (N) [44]. This decrease also suggests an increase in free space within the glass structure, and subsequent decrease in compactness values, indicating a loosely packed glassy matrix. From the tabulated values, it is clearly seen that average spacing is also decreasing with the increase in Bi content which might be the reason for the increase in the field strength. The linear increment in $'F'$ values with an increase in Bi concentration is found to obey the following equation, $F = (4.45 + 0.0065x) * 10^{16}\ cm^{-2}$ [44].

In chalcogenide glasses, the energy of the conduction band edge is decided by the number of atoms per unit volume (N) [29]. An increase in N leads to a presumable decrease in the energy of conduction band edge, corresponding to lower band gap values (calculated later).

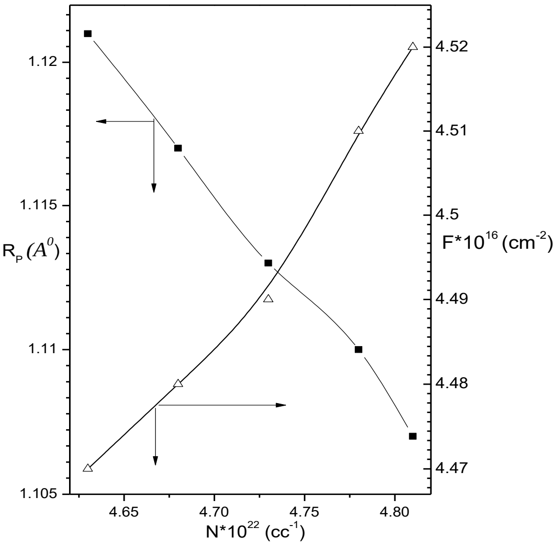

Fig. 3. Variation of Polaron radius (R_P in Å) and Field Strength ($F*10^{16}\ cm^{-2}$) with Se atomic density ($N*10^{22}$) for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system glassy alloys.

3.6. Assessment of glass transition temperature (T_g) and mean bond energy ($\langle E \rangle$)

3.6.1. Determination of deviation from stoichiometry R

The ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom is expressed as R which also determines the deviation of stoichiometry. $R > 1$, indicates a chalcogen-rich material which consists of both heteropolar bonds and chalcogen-chalcogen bonds. $R < 1$, indicates a chalcogen-poor material consisting of heteropolar and metal-metal bonds. $R = 1$ is indicative of stoichiometric composition containing only heteropolar bonds and basically shows the minimum chalcogen content at which a chemically ordered network is formed. For $Ge_xSe_yTe_zBi_\delta$ system, the value of 'R' is determined using the following formula, $R = \frac{y\langle r \rangle(Se)}{x\langle r \rangle(Ge) + z\langle r \rangle(Te) + \delta\langle r \rangle(Bi)}$, where, x, y, z and δ are the atomic fractions of Ge, Se, Te and Bi, respectively and $\langle r \rangle$ is the coordination number of each element [33, 45]. The calculated values of R are given in table 4. In $Ge_{18}Se_{72-x}Te_{10}Bi_x$ system, R values for each composition come greater than unity indicating a chalcogen rich material having heteropolar and chalcogenide- chalcogenide bonds.

3.6.2. Calculation of glass transition temperature (T_g)

Glass transition temperature (T_g) represents the temperature above which an amorphous matrix can attain various structural configurations and below which the matrix is frozen into a structure which cannot easily change into another structure. T_g is an important parameter that denotes the strength and rigidity of glass structure [46]. The value of T_g is directly related to the energy required to break or re-from the covalent bonds of the amorphous composition or the random network. It is also indirectly related to other factors like the average coordination number, degree of cross-linking, nature of the chemical bonds and average bond energy per atom [41]. A chemically ordered network is expected to be formed in Ge-Se-Te-Bi system as there is a significant difference between the bonding energies of the heteropolar bonds, *i.e.*, Ge-Se, Se-Bi, Se-Te and those of the homopolar bonds of Se-Se. The number of heteropolar bonds formed is maximized as they're more favorably formed as compared to homopolar bonds [47]. If the element added has a coordination number greater than 2, T_g and $\langle r \rangle$ are related as, $T_g = f(\langle r \rangle)$. Therefore, an increase in T_g, with increasing Bi content, attributes to the increase in the quality of connectivity of glassy network as shown by Saiter *et. al.* [48]. It is assumed that T_g is related to the magnitude of the cohesive forces within the network since these forces must be overcome to allow atom movement. According to Tichy and Ticha [49], in a chemical ordered system, besides a fair relationship between T_g and the connectedness of the network $\langle r \rangle$, T_g also holds an excellent correlation with the overall mean bong energy ($\langle E \rangle$). Using a set of approximately 200 glasses, an impressive theoretical relationship between T_g and $\langle E \rangle$ has been derived by Tichy and Ticha [33, 45] which is given as, $T_g = 311\,[\langle E \rangle - 0.9]$. A major limitation of this model is that it does not account for the molecular interaction which plays a major role in the relaxation process in the glass- transition region [47].

3.6.3. Calculation of mean bond energy ($\langle E \rangle$)

The overall mean bond energy can be related to the type and energy of the chemical bonds between the glass forming atoms and the mean coordination number. It is one of the most significant parameters which affect the different properties of the glassy system [20]. It depends strongly on the cohesive forces or the rigidity of the network, assuming a chemical bond ordering model. Mean bond energy can be determined using Tichy's equation [33], $\langle E \rangle = \overline{E_c} + \overline{E_{rm}}$.

Here, $\overline{E_c}$ is the overall contribution towards the bond arising from strong heteropolar bonds or the average energy of cross-linking/ atom. $\overline{E_{rm}}$ refers to the contribution arising from weaker bonds that remain after the strong bonds have been maximized, *i.e.*, the average bond energy per atom of the 'remaining matrix'. Values of $\overline{E_c}$ and $\overline{E_{rm}}$ further depend on the values of 'R' [7]. For $R < 1$, $\overline{E_c} = P_P E_{hb}$ and for $R > 1$, $\overline{E_c} = P_r E_{hb}$. Here, E_{hb} is the average heteropolar bond energy of the $Ge_xSe_yTe_zBi_\delta$ glassy system and is given by

$$E_{hb} = \frac{x\langle r \rangle(Ge)\,E_{Ge-Se} + z\langle r \rangle(Te)\,E_{Se-Te} + \delta\langle r \rangle(Bi)\,E_{Se-Bi}}{x\langle r \rangle(Ge) + z\langle r \rangle(Te) + \delta\langle r \rangle(Bi)}$$

where, E_{Ge-Se}, E_{Se-Te} and E_{Se-Bi} are the heteropolar bond energies of Ge-Se, Se-Te and Se-Bi bonds, respectively.

The degrees of cross-linking per atom (P_P) for $R < 1$ and (P_r) for $R > 1$ are given by – $P_P = \frac{y\langle r \rangle(Se)}{x+y+z+\delta}$ and $P_r = \frac{x\langle r \rangle(Ge) + z\langle r \rangle(Te) + \delta\langle r \rangle(Bi)}{x+y+z+\delta}$

$\overline{E_{rm}}$ is given by $\overline{E_{rm}} = \frac{2(0.5\langle r \rangle - P_P)}{\langle r \rangle} E_{<>}$, when $R < 1$, where, $E_{<>} = \frac{E_{Ge-Ge} + E_{Te-Te} + E_{Bi-Bi}}{3}$

and $E_{rm} = \frac{2(0.5\langle r \rangle - P_r)}{\langle r \rangle} E_{Se-Se,}$ when $R > 1$,

The values of $\langle E \rangle$, T_g and R are given in table 4 along with the bond energies of various bonds.

Table 4. Values of R, mean bond energy $\langle E\rangle$, glass transition temperature (T_g), heat of atomization $(\overline{H_s})$, average heat of atomization $(\overline{H_s}/\langle r\rangle)$ and bond energies of the respective bonds in the $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2,4,, 6, 8, 10) system.

x	R	$\langle E\rangle$ (eV)	T_g (K)	$\overline{H_s}$ (kcal/g-atom)	$\overline{H_s}/\langle r\rangle$ (kcal/g-atom)	Bonds	Bond energies (kcal/mol)
0	1.56	2.33	444.73	56.368	23.88	Ge-Se	49.1
2	1.428	2.36	454.73	56.362	23.68	Se-Te	44.36
4	1.307	2.38	460.28	56.356	23.48	Se-Bi	40.7
6	1.200	2.40	466.50	56.350	23.28	Se-Se	44.0
8	1.103	2.43	475.83	56.344	23.09	Bi-Bi	25.0
10	1.016	2.46	485.16	56.338	22.90	Te-Te	33.0

It is observed that as the Bi content increases in the system, both $\langle E\rangle$ and T_g values increase and reach maxima at $R = 1.01$ (approaching chemical threshold) as can be seen in Fig. 4.

Equations $< E > = 51.09 + 0.273x$ (kcal/g-atom) and $T_g = 41.03 + 3.71x$ (K) show the empirical relations of both $\langle E\rangle$ and T_g respectively with an increase in Bi content.

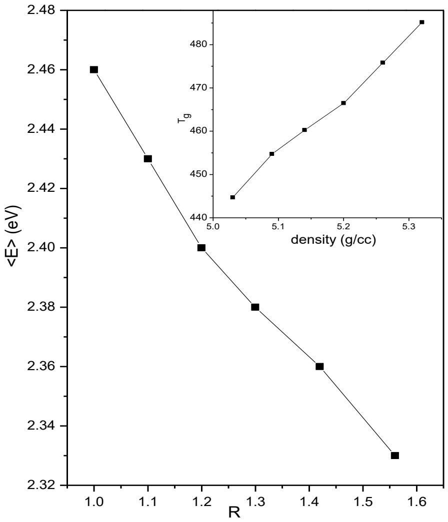

Fig. 4. Variation of mean bond energy ($\langle E\rangle$) with R and inset shows variation of glass transition temperature (T_g) with density (g/cc) for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system glassy alloys.

Also, most of the bond energies are at their maxima at this composition [33, 45]. This threshold at $R = 1$ is the point of existence of predominantly heteropolar bonds [7] which is also evident from chemical bond distribution given in table 5. This marks the minimum Se content at which a chemically ordered network is possible without metal-metal bond formation. From the tabulated values, it is found that T_g increases with increase in rigidity of the system and average bond strength. Further, the inset in figure 4 shows a linear relationship between the glass transition temperature and density, which has also been experimentally proven by other workers [50].

3.7. Heat of atomization $(\overline{H_s})$

Heat of atomization $(\overline{H_s})$ is defined as the energy required to dissociate one mole of a given substance into its atoms or the amount of energy required to convert an appropriate amount of an element in its standard state to a mole of atoms in the gaseous state. Many physical parameters of semiconductors are directly related to $\overline{H_s}$. Aigrain *et. al.* [51] state that there is a linear correlation between the energy band gap and the average heat of atomization, i.e, $\Delta E = a(H - b)$, where a and b are characteristic constants. Therefore, the average heat of atomization can also be considered as a measure of cohesive energy of the system. It also represents the relative bond strength and is related by given empirical relation; $CE = 37.16 + 0.395\ H_s/< r >\ (kCal/g - atom)$ with CE. This in turn correlates to the band gap of isostructural semiconductors. In Ge-Se-Te-Bi matrix (containing a high concentration of Se), lone pair electron states create valence band (σ state) whereas the conduction band arises from anti-bonding (σ*) states. It is, therefore, interesting to relate the optical gap with the average single bond energy. Decrease in bond strength causes less splitting between σ and σ * which results in decrease in band gap [7]. According to Pauling [24], for a binary semiconductor system at a standard temperature and pressure comprising of atoms A, B, C and D, the heat of atomization $(\overline{H_s})$ is given by the following equation, $\overline{H_s}(A - B) = \Delta H + \frac{1}{2}\overline{H}_s^A + \overline{H}_s^B)$ where, $\Delta H \propto (\chi_A - \chi_B)^2$ and χ_A and χ_B are their respective electronegativities. The average bond strength is given by the formula [52], $\overline{H_s} = \frac{\alpha H_S^A + \beta H_S^B + \gamma H_S^C + \delta H_S^D}{\alpha+\beta+\gamma+\delta}$, where, α, β, γ and δ are the ratios of A, B, C and D, respectively. The calculated values of average heat of atomization are given in table 4 along with the average single bond energy $(\frac{\overline{H_s}}{\langle r\rangle})$. The values of heat of atomization for Ge, Se, Te and Bi atoms are 90, 49.4, 49.1 and 46 (kcal/g-atom), respectively. Generally $\overline{H_s}$ is a composition dependent parameter, but it is clear from the tabulated values that in the present system under investigation, there is a negligible change in $\overline{H_s}$ with the addition of Bi. It is seen that for low connectivity glasses, (*i.e.* $2 \leq <r> \leq 3$), $\frac{\overline{H_s}}{\langle r\rangle}$ shows almost a constant value. Same trend has been observed earlier [47].

3.8. Correlation between cohesive energy (CE) and theoretical band gap (E_g^{th})

The optical behavior of glass can be explained in terms of cohesive energy which is the stabilization energy of an infinitely large cluster of material per atom. It also reflects the bond strength. The Chemical Bond Approach [53] is used to calculate CE which also allows to determine the number of possible bonds and their types, *i.e.*, heteropolar or homopolar. According to CBA, atoms combine more easily with atoms of different type rather than the same type, and the heteropolar bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied. Each constituent atom is coordinated by $'8 - N'$ rule. Bonds between like atoms only occur if there is an excess of certain type of atoms. In this approach, the van der Waals interactions are neglected as they form much weaker links than regular covalent bonds. Also, the dangling bonds and other valence defects are neglected according to this approach. The possible bonds in $Ge_{18}Se_{72-x}Te_{10}Bi_x$ system are Ge-Se, Se-Te, Se-Bi and Se-Se. Bond energies are supposed to be additive. Therefore, cohesive energies for this system are calculated by summing up the bond energies over all expected bonds in the system and follows '*CE* = 46.60-0.0388*x*' as an empirical relationship with an increase in Bi content. The heteropolar bond energies are calculated from the bond energies of the homopolar bonds and the electronegativity of the atoms [6, 24]. Electronegativity values of the various elements have been taken from Pauling's scale, *i.e.*, χ_{Ge}= 2.01, χ_{Se}= 2.55, χ_{Te}= 2.1, χ_{Bi}= 2.02. Calculated values of the chemical bond distribution for all compositions, *CE* and electronegativity are listed in table 5. The results indicate that the *CE* of the glassy system decreases with an increase in Bi content. In the Ge-Se-Te-Bi system, fixed amount of Ge attributes to fixed number of Ge-Se heteropolar bonds with highest bond energy. The decrease in the average bond energy, with the increase in Bi content, can be ascribed to the increase in the number of heteropolar Bi-Se (40.7 kcal/mol) and decrease in homopolar Se-Se bonds (44 kcal/mol). This decrease in *CE* implies lower bonding strength, *i.e.*, high defect bonds.

Table 5. Values of the distribution of chemical bonds, cohesive energy, theoretical band gap (E_g^{th}) and electronegativity (χ) in glassy $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system

x	Distribution of chemical bonds				Cohesive energy (kcal/mol)	χ	E_g^{th} (eV)
	Ge-Se	Te-Se	Se-Se	Bi-Se			
0	0.50	0.142	0.357	-	46.60	2.396	1.63
2	0.514	0.142	0.3	0.428	46.53	2.384	1.59
4	0.529	0.147	0.235	0.882	46.46	2.373	1.55
6	0.545	0.151	0.166	0.136	46.38	2.362	1.50
8	0.562	0.156	0.937	0.187	46.30	2.351	1.46
10	0.58	0.161	0.016	0.241	46.21	2.340	1.42

The variations in theoretical values of the energy gap (E_g^{th}) with composition for a quaternary alloy is described by Shimakawa's relation [38].

The conversion from volume fraction to atomic percentage is made by using atomic weights and densities. The values of E_g^{th} for all the compositions are also listed in table 5. Due to the decrease in the average single bond energy in the system, a decrease in the E_g^{th} values with increase in Bi content is seen. This decrease may also be due to the decrease in the average stabilization energy and the electronegativity of the system calculated from Sanderson's principle [54] (Figure 5). This principle states that the electronegativity of an alloy is the geometric mean of the electronegativity of its constituents. Structural modifications are clearly seen with the reduction of band gap.

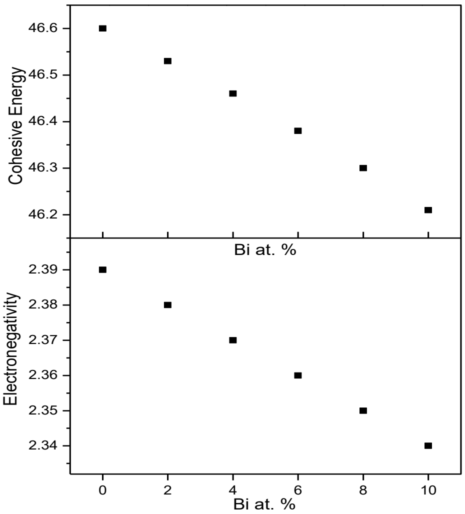

Fig. 5. Variation in the cohesive energy and electronegativity with Bi at. % for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) system glassy alloys.

There are compositional changes in the host material, *i.e.*, alloying effect. This lowering of band gap with Bi addition can also be explained in accordance with Mott and Davis model [55]. Width of localized states near mobility edges depends on the degree of disorder and defects present in the system. Bi addition increases the degree of disorder in the alloy. Moreover, reduction in the average bond energy also accounts for reduced band gap.

The degree of the covalency character (C_c) [20] of the different heteropolar bonds formed in the quaternary system is calculated using the following formula, $C_c = 100\exp[-(\chi_A - \chi_B)^2/4]$ where, χ_A and χ_B are the electronegativities of atoms A and B. The calculated values of C_c are given in the table 6 and indicate that the covalent character of bonding is dominant in the parent sample as compared to the quaternary sample. When Bi is incorporated into the parent glass replacing Se, the covalent bonds change to iono-covalent bond with change in structure of the glass matrix.

Table 6. Values of covalence character for glassy $Ge_{18}Se_{72-x}Te_{10}Bi_x$ *(x = 0, 2, 4, 6, 8, 10) system.*

Type of bond	Covalence character (%)
Ge-Se	92.96
Se-Te	95.06
Se-Bi	93.21

4. Conclusion

The physical properties of Ge-Se-Te-Bi alloys were studied and discussed. The average coordination number, total number of constraints, cross linking density, density, molar volume, excess volume, number density, average spacing, field strength, mean bond energy and glass transition temperature were found to increase with an increase in Bi content. Both $\langle E \rangle$ and T_g values reach maxima at $R = 1.01$ and approach chemical threshold. On the other hand a decrease in lone pair, compactness, polaron radius, cohesive energy, theoretical band gap and bond strength was observed. With an addition of Bi, atomic arrangements were found to become less tightly bound. The system under investigation is found to be chalcogen-rich. For low connectivity glasses, average single bond energy shows almost constant trend. The decrease in cohesive energy of the system reflects decrease in bond strength and subsequent increase in defect states. An attempt has been made to interpret the results on the basis of Mott and Davis Model. Physical properties *viz.* bond strength, average coordination number, density are sensitive to changes in network of glassy matrix. Physical parameters could be tuned as required for optical, electrical, thermal, etc. properties. Thus, an understanding of the physical parameters for $Ge_{18}Se_{72-x}Te_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) lone pair semiconductor was achieved. A considerable amount of further research on the effect of Bi addition in this semiconductor glassy system would include various experimental characterizations to validate theoretical data.

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