

Theoretical prediction of physical parameters of $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) bulk glassy alloys

ISHU SHARMA*, MONISHA MAHESHWARI

Department of Physics, AIAS, Amity University, Noida, India

Physical properties of $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) bulk glassy alloys are examined theoretically. Lone pair electrons are calculated using an average coordination number ($\langle r \rangle$) and the number of valence electrons, and are found to decrease with an addition of Ge. Mean bond energy ($\langle E \rangle$) is proportional to glass transition temperature (T_g) and shows maxima near the chemical threshold. Cohesive energy of the system is calculated using chemical bond approach. A linear relation is found between cohesive energy, band gap (calculated theoretically and confirmed experimentally) and average heat of atomization. All these parameters are increasing with an increase in Ge content. A relation between average single bond energy and photon energy is discussed. Compactness of the structure is measured from the calculated density of the glass. An attempt is made to discuss the results in terms of structure of the glass or equivalently with average coordination number.

Keywords: *amorphous semiconductors; mean bond energy; glass transition temperature; cohesive energy; theoretical band gap*

© Wrocław University of Technology.

1. Introduction

The semiconductor technology has always been challenged to develop the next generation materials for many demanding applications. In this context, chalcogenide glass and its dimensionality is a subject of intensive current research. Chalcogens have an important role in the field of optoelectronics [1], precision glass molding (PGM) [2], etc. Higher value of linear and non linear refractive index and substantial absorption in visible to NIR part of spectrum make them irreplaceable materials for mid-infrared sensing, integrated optics and ultrahigh-bandwidth signal processing. Recently, a new term – “chalcogenide photonics” – has been coined [3] and has also been used in plasmonics applications [4]. Thin films of chalcogenide glass are promising materials for use as high-resolution, gray scale photo- and electron-beam resists for nanoscale and ultrathin applications in MEMS/NEMS technology [5].

The glasses made from heavy chalcogens, such as Se or Te, offer a huge potential for developing materials transparent in the infrared. Since Te

is heavier, its use instead of Se increases the IR transparency range up to 20 μm . However, the semi metallic nature of Te limits its glass formation ability and this glass family is known to be unstable and consequently it has found application as phase change material in the DVD technology. Infrared glasses synthesis is based on the creation of a covalent polymeric framework involving elements having similar electro-negativity. Therefore, Te has to be combined with close neighbor atoms in the periodic table, such as As, Sb, Ge, Ga, etc. [6]. The simplest binary phase change material is Ge–Te, but the quality improves with the addition of Sb. Ge–Te and Ge–Sb–Te alloys have been widely studied and utilized for electrical and optical memory applications due to their fast and reversible crystalline-amorphous phase transitions, resulting in significant changes in resistivity and reflectivity [7, 8].

The investigation of physical parameters of any system is useful to those engaged in experimental research and development on these materials. In the present manuscript physical properties of $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) glassy alloys are discussed. Average coordination number

*E-mail: ishuphy@gmail.com, isharna@amity.edu

and total number of constraints are investigated using topological concepts. Correlation between the glass transition temperature and mean bond energy was calculated using Tichy-Ticha approach [9, 10]. Cohesive energy and theoretical band gap are calculated using Chemical Bond Approach (CBA) and Shimakawa's relation, and both have been further compared with optical band gap calculated experimentally [11]. Other physical parameters, viz. average heat of atomization, density, compactness, molar volume, are also calculated. An effort is done to correlate these parameters in terms of composition, bond strength, bond energies or equivalently with average coordination number $\langle r \rangle$.

2. Theoretical analysis

2.1. Nearest neighbor coordination

Nearest-neighbor coordination is particularly suitable for testing the validity of topological concepts in a ternary system because of its large glass forming region [12]. The average coordination number $\langle r \rangle$ in our system is defined by:

$$\langle r \rangle = \frac{aX + bY + cZ}{a + b + c} \quad (1)$$

where a , b and c are the at.% of Ge, Sb and Te, respectively, and $X = 4$, $Y = 3$ and $Z = 2$ are their respective coordination numbers. The obtained values of $\langle r \rangle$ for $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) are listed in Table 1. On the basis of equating the total number of interatomic force field constraints per atom (N_{con}) to the total number of degree of freedom per atom (N_d), it has been stated that a percolation threshold exists at $\langle r \rangle = 2.4$ [13]. In glassy networks consisting of $N = \sum n_i$ atoms, the mechanical constraints (N_{con}) is given by addition of bond bending (N_α) and bond stretching (N_β) forces, i.e.:

$$N_{con} = N_\alpha + N_\beta \quad (2)$$

where:

$$N_\alpha = \sum n_i r_i / 2 \quad (3)$$

and:

$$N_\beta = \sum n_i (2r_i - 3) \quad (4)$$

According to the constraint theory, chalcogenides glasses can be classified in three types as: (a) floppy or under-coordinated bonds with $\langle r \rangle < 2.4$ and $N_{con} < 3$; (b) optically coordinated with $\langle r \rangle = 2.4$ and $N_{con} = 3$; (c) rigid and over-coordinated with $\langle r \rangle > 2.4$ and $N_{con} > 3$ [14].

In the system under investigation $\langle r \rangle$ increases from 2.31 to 2.39. This increase in $\langle r \rangle$ can be attributed to the replacement of Sb (coordination number 3) with Ge (coordination number 4). The value of N_{con} is increasing from 2.77 to 2.97 (Table 1), but is still less than 3. Thus, the system behaves as it is in a floppy mode. Since, for $\text{Ge}_{19}\text{Sb}_1\text{Te}_{80}$ composition, $\langle r \rangle$ and N_{con} are approaching 2.4 and 3, respectively, therefore, this glass network lies nearly at the threshold of the mode change and is moving towards optically-coordinated mode from under-coordinate mode. It is also the most stable composition among all compositions under investigation.

2.2. Lone pair electrons of structure and glass forming ability

Most of substances, which can solidify in the vitreous state, are found to have structural bridges with lone pairs. The existence of these bridging atoms can eliminate the strain force caused by the formation of amorphous material. In most chalcogenide glasses the bridges are formed and, hence, they are also called lone pair semiconductors. Te atoms in glass structures have two pairs of lone-pair electrons. According to the viewpoint proposed by Pauling [15], the chemical bonds with lone-pair electrons are characterized by flexibility. Increase in the number of lone-pair electrons decreases the strain energy in a system, i.e. it is easier to deform a bond with a lone pair electrons.

Therefore, a structure with a large number of lone-pair electrons favors glass formation. On the basis of the presence of lone pairs, Liang introduced an easy criterion for computing the ability of a chalcogenide system to maintain its vitreous state [16]. For a ternary system the number

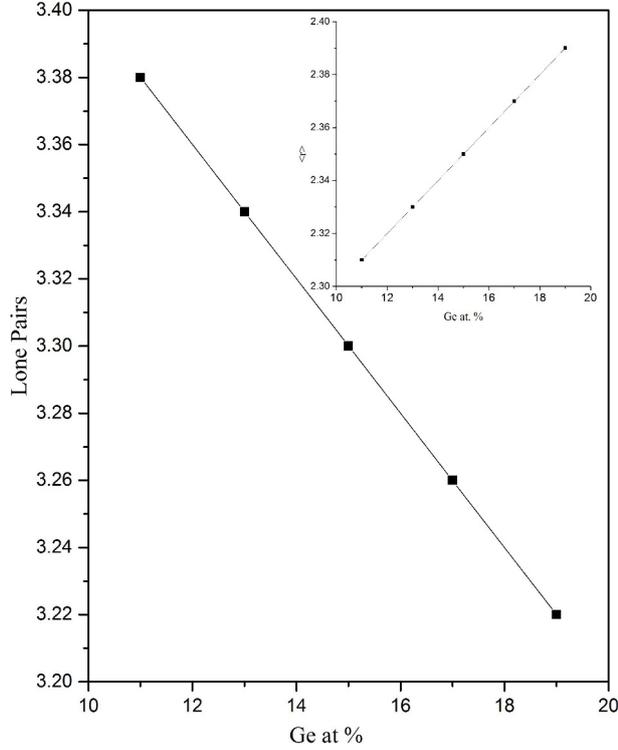


Fig. 1. Variation of lone pairs with Ge at.%; the inset shows the variation of $\langle r \rangle$ with Ge at.%.

of lone-pair electrons must be larger than 1 and for binary system it must be larger than 2.6. The lone pairs of electrons are calculated by: $L = V - \langle r \rangle$, where V is the valance electron, which is equal to unshared lone-pair electrons, $\langle r \rangle$ is the coordination number. The results are listed in Table 1. It is seen from Fig. 1 that the number of lone-pair electrons decreases with the increase of Ge in the system. Thus, the bond deformation in the system

Table 1. Average coordination number ($\langle r \rangle$), bond bending (N_α), bond stretching forces (N_β), total no. of constraints (N_{con}), valence electrons (V) and lone pair electrons with Ge at.%.

| x | $\langle r \rangle$ | N_α | N_β | N_{con} | V | $L = V - \langle r \rangle$ |
|----|---------------------|------------|-----------|-----------|------|-----------------------------|
| 11 | 2.31 | 1.15 | 1.62 | 2.77 | 5.69 | 3.38 |
| 13 | 2.33 | 1.16 | 1.66 | 2.82 | 5.67 | 3.34 |
| 15 | 2.35 | 1.17 | 1.70 | 2.87 | 5.65 | 3.30 |
| 17 | 2.37 | 1.18 | 1.74 | 2.92 | 5.63 | 3.26 |
| 19 | 2.39 | 1.19 | 1.78 | 2.97 | 5.61 | 3.22 |

is not easy. This may be attributed to the decrease in the flexibility of the system. It is also clear from the values of average coordination number that the system is heading towards rigid region from floppy mode. However, the number of lone pairs computed in the investigated system is greater than 3, so the system can form glass or retain its vitreous nature easily.

2.3. Glass transition temperature, mean bond energy and correlation between the parameters

In Ge–Sb–Te system there is a noteworthy difference between the bonding energies of homopolar and heteropolar bonds. Thus, a chemical ordered network is probable. According to Tichy and Ticha [9, 10], in the chemical ordered system there should be an excellent correlation between glass transition temperature (T_g) and mean bond energy ($\langle E \rangle$) in addition to the relationship between T_g and connectedness of the network $\langle r \rangle$.

Glass transition temperature is a temperature, below which amorphous matrix is frozen into a structure that continuously changes to another structure, and above which a matrix can achieve a variety of structural compositions. Prediction of T_g is usually based on simple models, where it is assumed that T_g is related to the magnitude of the cohesive forces within the network and mean bond energy that further strongly depend on rigidity of the network. Here, a chemical bond ordering model is assumed. Tichy et al. [17], using a set of about 200 glasses, gave a remarkable relation between T_g and mean bond energy $\langle E \rangle$ i.e.:

$$T_g = 311(\langle E \rangle - 0.9) \quad (5)$$

where $\langle E \rangle$ is a mean bond energy. Based on this assumption the mean bond energy is given by:

$$\langle E \rangle = E_c + E_{rm} \quad (6)$$

where E_c is the overall contribution towards bond energy arising from strong heteropolar bonds, and E_{rm} is 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 E_c and E_{rm} depend

also on a parameter, which determines the deviation of stoichiometry (R).

Table 2. Values of R, $\langle E \rangle$, T_g for $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) system and bond energies of their respective bonds.

| x | R | $\langle E \rangle$ (kcal/mol) | T_g (K) | Bonds | Bond energies (kcal/mol) |
|----|------|-----------------------------------|--------------|-------|-----------------------------|
| 11 | 2.25 | 36.86 | 219.56 | Ge-Ge | 37.6 |
| 13 | 2.19 | 37.40 | 227.03 | Sb-Sb | 30.22 |
| 15 | 2.13 | 37.95 | 234.49 | Te-Te | 33 |
| 17 | 2.07 | 38.52 | 241.95 | Ge-Te | 35.46 |
| 19 | 2.02 | 39.08 | 248.80 | Sb-Te | 31.65 |

2.3.1. Determination of R

R is expressed by the ratio of covalent bonding possibilities of a chalcogen atom to that of a non-chalcogen atom. $R > 1$, indicates chalcogen rich materials, and $R < 1$ shows chalcogen poor materials. For $\text{Ge}_x\text{Sb}_y\text{Te}_z$ system, the quantity R is defined by: $R = \frac{zCN(\text{Te})}{xCN(\text{Ge}) + yCN(\text{Sb})}$, where x, y and z are respective atomic fractions of Ge, Sb and Te. However, the calculation of R also requires the knowledge of coordination number (CN) of all the constituents of glassy alloys, which have been discussed earlier. Values of R are tabulated in Table 2. There are no signs of chalcogen poor region, since minimum value of R is 1.

2.3.2. Determination of mean bond energy for $\text{Ge}_x\text{Sb}_y\text{Te}_z$ system

In the tellurium rich region ($R > 1$), there are heteropolar bonds and chalcogenide-chalcogenide bonds, where: $E_c = 4xE_{\text{Ge-Te}} + 3yE_{\text{Sb-Te}}$ and: $E_{rm} = \frac{[2z - 4x - 3y]}{\langle r \rangle} E_{\text{Te-Te}}$. Here, $E_{\text{Te-Te}}$ is the homopolar bond energy of Te-Te bonds. In the tellurium poor region ($R < 1$) there are heteropolar and metal-metal bonds. Here, $E_c = \frac{2z(4xE_{\text{Ge-Te}} + 3yE_{\text{Sb-Te}})}{4x + 3y}$ and $E_{rm} = \frac{(4x + 3y - 2z)}{\langle r \rangle} E_{\langle \rangle}$, where $E_{\langle \rangle} = \frac{1}{2} [E_{\text{Ge-Ge}} + E_{\text{Sb-Sb}}]$ denotes the average bond energy of metal-metal bond for $R < 1$.

The values of $\langle E \rangle$ along with T_g and R are tabulated in Table 2. With the increase in Ge content in the Ge-Sb-Te system both $\langle E \rangle$ and T_g are increasing and reach a maximum value at the lowest value of R. In general, T_g in various glassy system shows maximum value near $R = 1$, i.e. chemical threshold, because the chemical bond energies are maximized at this composition [9, 10]. Hence, T_g increases with the increase in rigidity of the system and average bond strength.

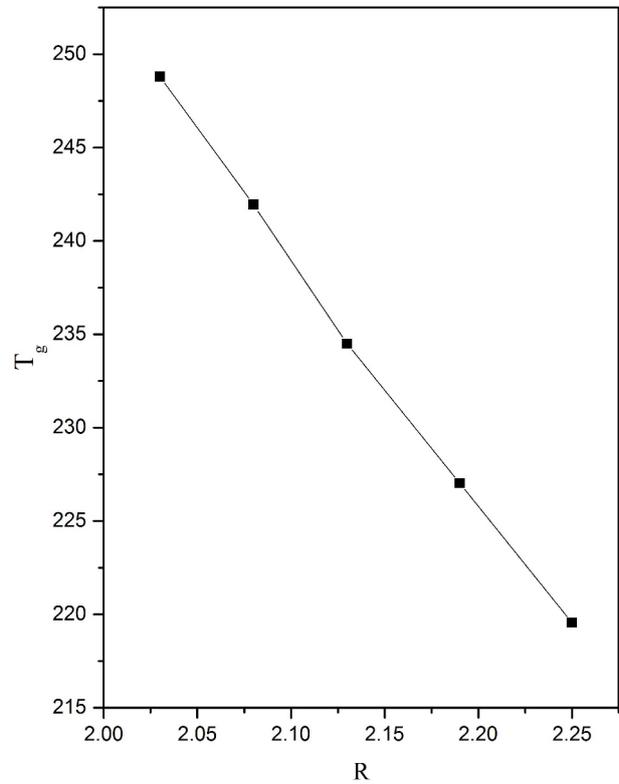


Fig. 2. Variation of T_g vs. R for $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) system.

Maximum T_g is found for $\text{Ge}_{19}\text{Sb}_{01}\text{Te}_{80}$ glassy alloy with $\langle r \rangle \approx 2.4$, which is also the most stable composition among the investigated system. An account of these features is given by the existing Phillips model and the chemically ordered network model. This model does not account for the molecular interaction, which plays a vital role in the relaxation process in glass transition region and is the constraint of this model.

2.4. Cohesive energy of the system

The cohesive energy is a stabilization energy of an infinitely large cluster of material per atom, which also reflects the average bond strength. The cohesive energy is calculated using chemical bond approach (CBA) [18] and also allows determining the number of possible bonds and their types, i.e. heteropolar or homopolar. Here, van der Waals interactions are neglected, as they form much weaker links than regular covalent bonds. CBA model also neglects the dangling bonds and other valence defects, as a first approximation and a constituent atom is coordinated by 8-N atom, where N is the outer shell electron. According to CBA, bond energies are assumed to be additive. Here, formation of heteropolar bonds is favorable and they are formed in the sequence of decreasing bond energies until the available valence of atom is satisfied. The possible bonds in $Ge_xSb_{20-x}Te_{80}$ system are Ge-Te, Sb-Te and Te-Te. The cohesive energy is calculated by summing up the bond energies over all bonds expected in the material.

The heteropolar bond energies are calculated from the bond energies of homopolar bonds and the electronegativity of the atoms using the formula proposed by Pauling [15]:

$$D(A-B) = [D(A-A) \cdot D(B-B)]^{\frac{1}{2}} + 30(\chi_A - \chi_B)^2 \quad (7)$$

where $D(A-A)$ and $D(B-B)$ are the homopolar bond energies of atoms A and B, respectively, and χ_A and χ_B are their respective electronegativities. Homopolar bond energies used to calculate heteropolar energies are tabulated in Table 2. Electronegativity values are taken from Pauling's scale, i.e. $\chi_{Ge} = 2.01$, $\chi_{Sb} = 2.05$ and $\chi_{Te} = 2.1$ [15]. Calculated values of cohesive energy (C.E) along with chemical bond distribution for all compositions are tabulated in Table 3.

In the Ge-Sb-Te system, the amount of Te is fixed. Variation in C.E is due to the variation in Ge and Sb content. With the increase in Ge it forms a bond with Te with the highest bond energy (35.4 kcal/mol). On the other hand, the amount of Sb-Te and Te-Te bonds with bond energies 31.6 kcal/mol and 33 kcal/mol, respectively, goes

on decreasing. Thus, the increase in C.E and band gap of the system [11] is attributed to the increase in average bond energy of the system because of the formation of Ge-Te bond on the expense of Sb-Te and Te-Te bonds. The optical band gap is a bond sensitive property [19]. Therefore, the overall trend in C.E and band gap seems to be influenced mainly by chemical bond arrangements. Both are increasing with increasing Ge content. These increases in C.E imply an increase in bonding strength and, consequently, a decrease in defect states. This decrease in defect states is also reflected in the decrease in homopolar Te-Te bonds. The increase in optical band gap is also consistent with the band gap calculated theoretically.

It was found that the variation in the theoretical values of the energy gap (E_g^{th}) with composition for ternary alloys can be described by the following relation [20]:

$$E_g^{th}(ABC) = aE_g(A) + bE_g(B) + cE_g(C) \quad (8)$$

where a, b and c are the volume fraction and $E_g(A)$, $E_g(B)$ and $E_g(C)$ are optical gaps of A, B and C elements, respectively. The conversion from volume fraction to atomic percentage is made using atomic weight and densities. The values of E_g^{th} for all the compositions are also tabulated in Table 3 and are plotted in Fig. 3 as a function of Ge at.%. It can be concluded that an increase of E_g^{th} and E_g^{opt} with increasing Ge content is due to an increase of average stabilization energy.

2.5. Relation between E_{04} , $\overline{H_s}$ and $\langle r \rangle$

E_{04} , defined as a photon energy, is an arbitrary measure, at which optical absorption coefficient has the value of 10^4 cm^{-1} . The photon energy is about 0.2 eV larger than the optical band gap (E_g^{opt}) at $\alpha = 10^4 \text{ cm}^{-1}$ [21]. The values of E_{04} are given in Table 3 and, for some systems, they can also be correlated with the average single bond energy ($\overline{H_s}/\langle r \rangle$). Chalcogenide glasses contain a fairly high concentration of a group VI elements (Te, in our case), where the valance band originates from lone pair electron states and the conduction band arises from antibonding states [22, 23]. Here, we can correlate

Table 3. Values of experimental band gap (E_g^{opt}), theoretical band gap (E_g^{th}), distribution of chemical bonds, cohesive energy, \overline{H}_s , $\overline{H}_s/\langle r \rangle$ and E_{04} for $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) system.

| x | E_g^{opt} (eV) [11] | E_g^{th} (eV) | Distribution of chemical bonds | | | Cohesive energy (kcal/mol) | \overline{H}_s (kcal/(g·atom)) | $\overline{H}_s/\langle r \rangle$ (kcal/(g·atom)) | E_{04} (eV) |
|----|---------------------------------|---------------------------|--------------------------------|-------|-------|-------------------------------|-------------------------------------|---|------------------|
| | | | Ge-Te | Sb-Te | Te-Te | | | | |
| | | | 11 | ... | 0.626 | | | | |
| 13 | ... | 0.643 | 0.325 | 0.131 | 0.543 | 33.62 | 52.84 | 22.67 | ... |
| 15 | 0.55 | 0.656 | 0.375 | 0.094 | 0.531 | 33.79 | 53.40 | 22.72 | 0.57 |
| 17 | 0.64 | 0.670 | 0.425 | 0.056 | 0.519 | 33.97 | 53.96 | 22.76 | 0.66 |
| 19 | 0.76 | 0.685 | 0.475 | 0.019 | 0.506 | 34.14 | 54.52 | 22.81 | 0.78 |

the optical gap with the average single bond energy. According to Aigrain et al. [24] there exists a linear correlation between the energy gap and the average heat of atomization, i.e. $\Delta E = a(H - b)$, where a and b are characteristic constants. To associate these values with average single bond energy for $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ system, average heat of atomization is to be calculated.

According to Pauling [15], for a binary semiconductor system comprised from atoms A and B, the heat of atomization \overline{H}_s (A-B) at a standard temperature and pressure is given as:

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

where $\Delta H \propto (\chi_A - \chi_B)^2$ and χ_A and χ_B are their respective electronegativities. For ternary and higher order semiconductor compounds, the average heat of atomization \overline{H}_s (kcal/(g·atom)) for $\text{A}_\alpha\text{B}_\beta\text{C}_\gamma$ compound is given by:

$$\overline{H}_s = \frac{\alpha H_s^A + \beta H_s^B + \gamma H_s^C}{\alpha + \beta + \gamma} \quad (10)$$

where α , β and γ are the ratios of A, B and C, respectively [21]. In the present $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ system, the values of average heat of atomization (kcal/(g·atom)) are calculated by above equation and are tabulated in Table 3. The values of heat of atomization for Ge, Sb and Te atoms, are 90, 62, and 46 in kcal/(g·atom), respectively.

Average heat of atomization is a measure of the cohesive energy and represents the relative bond strength, which, in turn, can be correlated with the

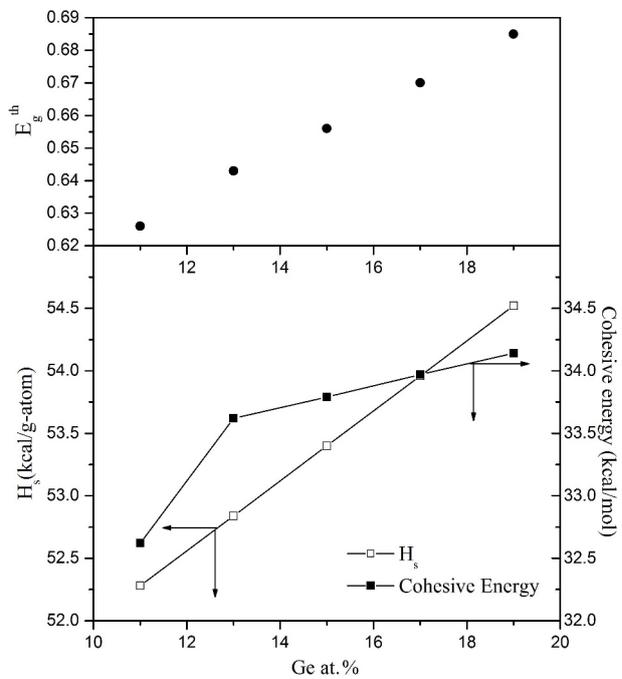


Fig. 3. Variation of average heat of atomization, cohesive energy and theoretical band gap vs. Ge at.% for $\text{Ge}_x\text{Sb}_{20-x}\text{Te}_{80}$ ($x = 11, 13, 15, 17, 19$) system.

energy gap of semiconductors. Increase in bond strength causes a high splitting between σ and σ^* , that results in an increase in the band gap. In Fig. 3 both \overline{H}_s and cohesive energy are increasing with an increase in Ge content. The values of E_{04} are also increasing with the addition of Ge. The strong dependence of photon energy on the average heat of atomization is shown for over constrained materials with the values of $\langle r \rangle$ ranging

from 3 to 4 only. For low connectivity glasses, i.e. $2 \leq \langle r \rangle \leq 3$, the parameter $\bar{H}_s/\langle r \rangle$ shows almost constant behavior and has a very insignificant effect on E_{04} [23]. In our case, the value of $\langle r \rangle$ varies from 2.2 to 2.4, which can be correlated with low connectivity glasses and no correlation is found between these two parameters. Similar behavior has been shown by different scientists conducting research on different compositions [25–27].

2.6. Density, compactness and molar volume

Density is a measure of the rigidity of a system. Theoretically density was calculated by Fayek et al. [28] as:

$$\rho = \left(\sum x_i/d_i \right)^{-1} \quad (11)$$

where x_i is the fraction of weight and d_i is the density of the i^{th} structural unit. Calculated density values are reported in Table 4. It is clear from the Table that density decreases with the addition of Ge content to the system. This decrease in density may be caused by the replacement of Sb with Ge with less density and smaller size (radius 137 pm). Packing density is defined as a ratio of used space to the allocated space and can be calculated using packing density, $\frac{N * \rho}{M}$, where N is Avogadro's number and M is molecular weight. The values of packing density are found to increase with addition of Ge content. It may be said that the decrease in glass density results in an increase in packing density (Table 4) due to smaller atomic radius and mass [14].

The compactness (δ) is a measure of a normalized change of mean atomic volume due to chemical interaction forming the network of given solids [29] and is calculated using relation:

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}} \quad (12)$$

where c_i is the atomic fraction, A_i is the atomic weight, ρ_i is the atomic density of the i^{th} element of the glass, and ρ is the measured density of the glass.

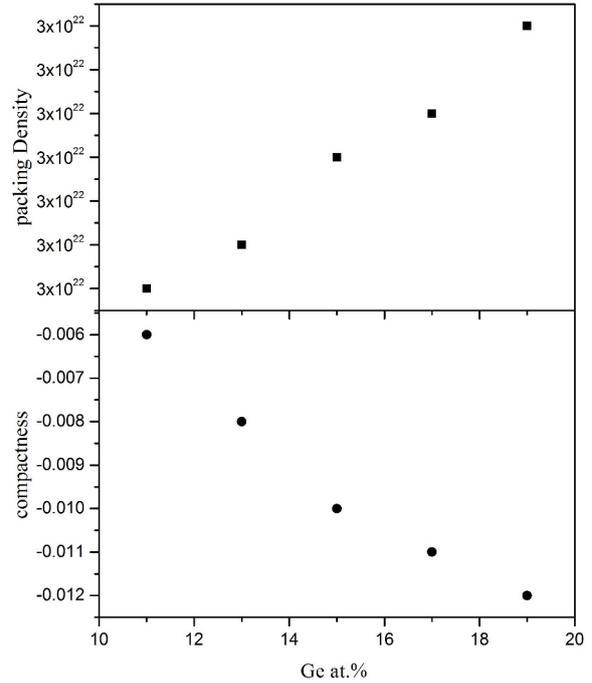


Fig. 4. Variation of compactness and packing density with Ge at.% $Ge_xSb_{20-x}Te_{80}$ system.

Compactness is more sensitive to changes in the structure of the glass network as compared to mean atomic volume. Table 4 shows the minor decrease in the compactness values. With the addition of Ge to Sb–Te alloy, compactness decreases. It can be associated with atomic arrangements that become less tightly bound with comparative longer bonds. When Ge enters an Sb–Te system, it makes a bond with Te, new bonds are forming with longer bond length, since the bond length of Ge–Te is 3.01 Å and that of Sb–Te is 2.91 Å.

Table 4. Density (ρ), packing density, compactness (δ) molar mass (M), molar volume (V_m), for $Ge_xSb_{20-x}Te_{80}$ ($x = 11, 13, 15, 17, 19$) system.

| x | ρ_{th} (g/cm ³) | Packing density × 10 ²² | δ | M (g/mol) | V_m (cm ³ /mol) |
|----|-------------------------------------|---------------------------------------|----------|--------------|---------------------------------|
| 11 | 6.16 | 3.06 | −0.006 | 121.03 | 19.64 |
| 13 | 6.13 | 3.07 | −0.008 | 120.04 | 19.58 |
| 15 | 6.10 | 3.09 | −0.010 | 119.06 | 19.51 |
| 17 | 6.07 | 3.10 | −0.011 | 118.08 | 19.45 |
| 19 | 6.04 | 3.12 | −0.012 | 117.09 | 19.36 |

3. Conclusions

With the increase in Ge content, average coordination is increasing. $\text{Ge}_{19}\text{Sb}_1\text{Te}_{80}$ alloys lie on the threshold of the mode change as $\langle r \rangle$ and N_{con} approach 2.4 and 3, respectively. Lone pair of the system is decreasing with the addition of Ge content, i.e. bond deformation is not very easy in these glassy alloys. The system under investigation is found to be chalcogens rich. Both $\langle E \rangle$ and T_g are increasing and reach a maximum near chemical threshold. The increase in cohesive energy with an increase in Ge content implies an increase in bonding strength and, consequently, a decrease in defect states. This reduction of defect states is also reflected in the increase in theoretical band gap of the system, which is also consistent with the band gap calculated optically. No correlation is found between the average single bond energy and photon energy for these low connectivity glasses. Glass density decreases with an increase in Ge content and further results in an increase in packing density. Physical properties, like bond strength, bond energy and average coordination number, are sensitive to changes in the network of the glassy system.

References

- [1] KAMIYA T., TSUCHIYA M., *Jpn. J. Appl. Phys.*, 44 (2005), 5875.
- [2] GUILLEVIC E., ZHANG X., PAIN T., CALVEZ L., ADAM J.L., LUCAS J., GUILLOUX-VIRY M., OLLIVIER S., GADRET G., *Opt. Mater.*, 31 (2009), 1688.
- [3] TODOROV R., TASSEVA J., BABEVA T., *Thin Chalcogenide Films for Photonic Applications*, in: MASARO A. (Ed.), *Photonic Crystals – Innovative Systems, Lasers and Waveguides*, Intech, Croatia, 2012, p. 143
- [4] SAMSON L., *Phys. Status Solidi RRL*, 1–3 (2010), 010.
- [5] LOVALSKIY, *J. Micro/Nanolith. MEMS MOEMS*, 84 (2009), 043012.
- [6] BUREAU B., BOUSSARD-PLEDEL C., LUCAS P., ZHANG X., LUCAS J., *Molecules*, 14 (2009), 4337.
- [7] LANKHORST M.H.R., KETELAARS B.W.S.M.M., WOLTERS R.A.M., *Nat. Mater.*, 4 (2005) 347.
- [8] LEE S.H., HWANG Y.N., LEE S.Y., RYOO K.C. AHN S.J., KOO H.C., JEONG C.W., KIM Y., KOH G.H., JEONG G.T., JEONG H.S., KIM K., *VLSI Tech. Dig.*, 20 (2004), 173.
- [9] TICHY L., TICHA H., *Mater. Lett.*, 21 (1994) 313.
- [10] TICHY L., TICHA H., *J. Non-Cryst. Solids*, 189 (1995), 141.
- [11] PANUKCHIEVA V., SZEKERS A., *Optical Mat.*, 30(7) (2008), 1088.
- [12] FOUAD S.S., *J. Phys D Appl. Phys.*, 28 (1995), 2318.
- [13] SAFFARINI G., SCHLIEPER A., *Appl. Phys. A-Matter.*, 61 (1995), 29.
- [14] PAMUKCHIEVA V., SZEKERES A., TODOROVA K., FABIAN M., SVAB E., REVAY Z., SZENTMIKLOSI L., *J. Non-Cryst. Solids*, 355 (2009), 2485
- [15] PAULING L., *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960.
- [16] ZHENHUA L., *J. Non-Cryst. Solids*, 127 (1991), 298.
- [17] THORPE M.F., TICHY L., *Properties and Applications of Amorphous Materials*, Kluwer Academic Publishers, London, 2001
- [18] BICERANO J., OVSHINSKY S.R., *J. Non-Cryst. Solids*, 74 (1985), 75.
- [19] PATTANAİK A.K., SRINIVASAN A., *JOAM*, 5 (2003), 1161.
- [20] DAHSHAN A., ALY K.A., *Philos. Mag.*, 88 (2008), 361
- [21] DENEUFVILLE J.P., ROCKSTAD H.K., STUKE J., BREINIG W., *Amorphous and liquid semiconductors*, Taylor & Frances, London, 1974.
- [22] KASTNER M., *Phys. Rev. Lett.*, 28 (1972), 355.
- [23] KASTNER M., *Phys. Rev. B*, 7 (1973), 5237.
- [24] BENOIT C., AIGRAIN P., BALKANSKI, *Selected constants relative to semiconductors*, Pergamon Press, New York, 1961.
- [25] FOUAD S.S., *Vacuum*, 52 (1999), 505.
- [26] SHARMA I, TRIPATHI S.K., BARMAN P.B., *Philos. Mag.* 88 (25), (2008) 3018.
- [27] OTHMAN A.A., ALY K.A., ABOUSEHLY A.M., *Thin Solid Films*, 515 (2007), 507.
- [28] FAYEK S.A., BALBOUL M. R., MARZOUK K.H., *Thin Solid Films*, 515 (2007) 7281.
- [29] VLCEK M., FRUMAR M., *J. Non-Cryst. Solids*, 97-98 (1987) 1223.

Received 2014-02-23

Accepted 2014-09-02