

EVALUATION OF PHYSICAL PARAMETERS FOR NEW QUATERNARY $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ CHALCOGENIDE GLASSES

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Tellurium based chalcogenide glasses are suitable for phase-change materials used in optical storage applications due to their rapid amorphous-to-crystalline transformation. Average coordination number and number of constraints for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ system (where $y = 0, 2, 4, 6, 8, 10$) have been discussed with two topological effects, floppy and rigid transition. Mean bond energy and glass transition temperature have been investigated using chemical bond approach to understand structural features of glasses. Relation between heat of atomization and energy gap has been studied.

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1. Introduction

Chalcogenide glasses exhibit photo-induced properties that allow them to be used as storage media [1]. These glasses having a relatively high atomic mass and weak bond strength result in a lower phonon energy than fluoride glasses, due to which they are highly transparent for light in the mid-infrared region [2,3]. Structure of chalcogenide elements (*S*, *Se*, and *Te*) can be described as a mixture of chains (forming infinite spiral) and rings and the common feature of these glasses is the presence of localized states in the mobility gap as a consequence of inherent defects (D^+ , D^0 , D^-) and short range order [4,5]. Study of gap states is of particular interest as it plays an important role for the analysis of electrical properties [4]. *Ge-Se-Sb* family is considered as one of the most promising families with low transmission loss and high transparency to the infrared radiation from 2-16 μm [6]. These glasses are attractive candidates for various applications such as optical fibres due to their good optical properties [7,8]. Host ternary glass alloys $Ge_{19}Se_{81-x}Sb_x$ (where $x = 0, 4, 8, 12, 16, 17.2, 20$) were investigated for their physical and optical behavior [9,10]. Physical and optical results show $Ge_{19}Se_{63.8}Sb_{17.2}$ composition as the most crosslinked and stable. The addition of metallic impurity to glass alloy increases the conductivity and is very suitable for device fabrication [1]. *Te* based glasses have high refractive index and photosensitivity that make them promising candidates for integrated optics [3]. Structural models reveal that glass forming ability is based on $GeTe_4$ tetrahedra in *GeTe* system [5]. With increasing content of heavier *Te* atoms, there is reduction of energy loss due to multiphonon absorption and its edges shift towards the longer wavelength. Hence, these glasses are favourable for CO_2 laser power transmitting glass fibres [2,11]. Therefore, *Te* has been added to the $Ge_{19}Se_{63.8}Sb_{17.2}$ composition to study its effect in terms of various physical, structural, optical and electrical parameters.

In the present work, the average coordination number (m) and lone pair of electrons (L) for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ system (where $y = 0, 2, 4, 6, 8, 10$) have been calculated. Mean bond energy $\langle E \rangle$ and glass transition temperature (T_g) have also been calculated. Cohesive energy (CE), heat of

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atomization (H_s) and energy gap (E_g) have been calculated. The electronegativity (χ) density (ρ), packing fraction and compactness (δ) of glass alloys have been calculated.

2. Experimental details

Synthesis of ternary samples $Ge_{19}Se_{81-x}Sb_x$ ($x = 0, 4, 8, 12, 16, 17.2, 20$) was already reported [9]. Thermo gravimetric (TG) measurements for ternary system were obtained from EXSTAR TG/DTA 6300 model. Melt quench technique has been used for alloy preparation of $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$) samples. The materials were weighed according to their at. wt. % and sealed in evacuated ($\sim 10^{-4}$ Pa) quartz ampoules. The sealed ampoules were kept inside a furnace, where the temperature was increased up to $1000\text{ }^{\circ}\text{C}$ at a heating rate of $3\text{-}4\text{ }^{\circ}\text{C min}^{-1}$. The ampoules were frequently rocked for 24 hours to make the melt homogeneous. The quenching was done in ice cold water. The amorphous nature of compositions was examined by the X-ray powder diffraction method [X'Pert Pro] (not shown here).

3. Results and discussion

Thermo gravimetric study of $Ge_{19}Se_{81-x}Sb_x$ ($x = 0, 4, 8, 12, 16, 17.2, 20$) system indicates $Ge_{19}Se_{63.8}Sb_{17.2}$ composition is most stable. Figure 1 shows that TG % for $Ge_{19}Se_{63.8}Sb_{17.2}$ composition (as reference) shows more resistance towards the decomposition at high temperature. Doping of Te in $Ge_{19}Se_{63.8}Sb_{17.2}$ composition has been investigated for evaluation of physical properties of alloys.

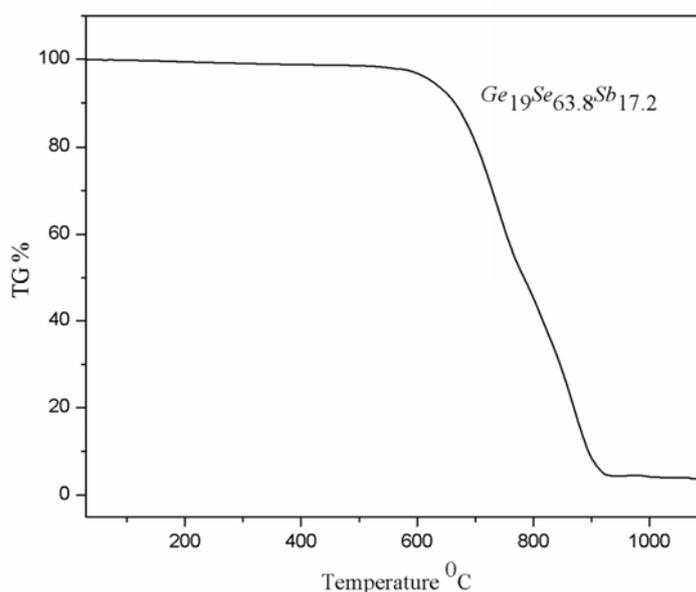


Fig. 1. Variation of TG % with temperature at the heating of $10\text{ }^{\circ}\text{C/min}$ for $Ge_{19}Se_{63.8}Sb_{17.2}$.

3.1 Average coordination number (m), number of constraints (N_T) and lone pair of electrons (L)

The bonding character in the nearest-neighbour region, *i.e.* average coordination number, characterizes the electronic properties of semiconducting materials. In the quaternary compound under investigation the average coordination number for covalently bonded materials is [12]

$$m = \frac{\alpha N_{Ge} + \lambda N_{Se} + \gamma N_{Sb} + \nu N_{Te}}{\alpha + \lambda + \gamma + \delta} \quad (1)$$

where $\alpha, \lambda, \gamma, \nu$ are the at. % and $N_{Ge} = 4, N_{Se} = 2, N_{Sb} = 3, N_{Te} = 2$ of constituent elements, respectively. The *Ge* element with higher coordination number has been replaced with *Te* having lower coordination number due to which the average coordination number of the system decreases. The total number of constraints per atom can be given as

$$N_T = N_S + N_B \quad (2)$$

where N_S and N_B are bond stretching and bond bending constraints. According to constraints theory [3], chalcogenides can be classified into three groups which are:

- (1) floppy or under-coordinated glasses with $m < 2.4$ and $N_T < 3$;
- (2) optimally-coordinated or ideal glasses with $m = 2.4$ and $N_T = 3$;
- (3) stressed-rigid and over-coordinated glasses with $m > 2.4$ and $N_T > 3$.

Values of m and N_T decrease from 2.55 to 2.35 and 3.38 to 2.88 respectively (Table 1). Pure *Se* consists of a mixture of polymeric chain and rings. On the addition of *Te* to parent ternary system, $Ge(Se_{1/2})_4$ tetrahedral, Se_6Te_2 rings and Sb_2Se_3 trigonal units are formed. For $Te \leq 6$, the system has been found to be stressed-rigid or over-coordinated and when $Te > 6$, the system behaves as floppy or under-coordinated glasses. This system has been found to be highly defective due to N_c being larger and smaller than 3 [3].

Lone pair electrons play an important role in chalcogenide glass formation. Lone pair electrons have a character of flexibility and are equal to valence electrons minus average coordination number [1]

$$L = V - m \quad (3)$$

where L is lone pair electron and V is valence electrons. Lone pair of electrons increases with the addition of *Te* (Figure 2). This is due to the increase in interaction between *Ge* atoms and lone pair electrons of *Te*. Strain energy in the glass system decreases with increasing number of lone pair electrons, so the larger number of lone pair electrons in the structure favour stable glass formation [1].

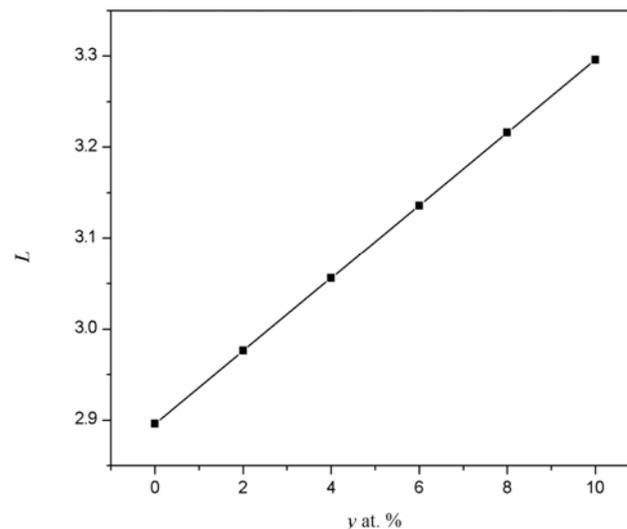


Fig. 2. Lone pair variation with *Te* content for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$).

3.2 Deviation of stoichiometry (R), mean bond energy $\langle E \rangle$ and glass transition temperature (T_g)

Parameter R determines the deviation from stoichiometry and expressed by the ratio of covalent bonding possibilities of chalcogen atom to nonchalcogen atom. For $Ge_aSe_bSb_cTe_d$ system, R is defined as [13]

$$R = \frac{bN_{Se} + dN_{Te}}{aN_{Ge} + cN_{Sb}} \quad (4)$$

where a, b, c, d is atomic fraction of Ge, Se, Sb and Te , respectively. Value of R increases with the incorporation of Te in place of Ge , showing the system is chalcogen rich.

Mean bond energy is determined by the degree of cross-linking, average coordination number, type of bond and bond energy of network. $\langle E \rangle$ is the sum of mean bond energy of the average cross-linking per atom (heteropolar bonds) $\langle E_c \rangle$ and the average bond energy per atom of the remaining matrix $\langle E_{rm} \rangle$, $\langle E \rangle$ can be given as [13]

$$\langle E \rangle = \langle E_c \rangle + \langle E_{rm} \rangle \quad (5)$$

For the present semiconductors $\langle E_c \rangle$ can be given as

$$\langle E_c \rangle = aN_{Ge}E_{Ge-Se} + cN_{Sb}E_{Sb-Se} + dN_{Te}E_{Se-Te} \quad (6)$$

Bond energy values of heteropolar bonds in the present system are calculated by using relation [12]. The calculated values of $Ge-Se$, $Te-Se$ and $Sb-Se$ bonds are 49.42 kcal/mol, 44.18 kcal/mol and 43.96 kcal/mol respectively.

$\langle E_{rm} \rangle$ is the contribution arising from weaker bonds and can be calculated as:

$$\langle E_{rm} \rangle = \frac{[bN_{Se} - aN_{Ge} - cN_{Sb} - dN_{Te}]E_{Se-Se}}{m} \quad (7)$$

and $E_{Ge-Ge} = 37$ kcal/mol, $E_{Se-Se} = 44$ kcal/mol, $E_{Sb-Sb} = 30.22$ kcal/mol and $E_{Te-Te} = 33$ kcal/mol.

Degree of covalency, C_c , of bonds can be calculated as [3]

$$C_c = 100 \exp \left[\frac{-(\chi_A - \chi_B)^2}{4} \right] \quad (8)$$

where χ_A, χ_B are the electronegativities of involved A and B atoms. Calculated values of C_c are listed in Table 1 and have been found to increase with Te addition. C_c depends on the electronegativity and it increases with the smaller χ difference between the bonds.

Table 1: Values of average coordination number (m), number of constraints (N_T), mean bond energy $\langle E \rangle$ and C_c (%) for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$).

y	m	N_S	N_B	N_T	$\langle E \rangle$ (eV)	Distribution of Bonds	C_c (%)
0	2.55	1.28	2.10	3.38	2.61	<i>Ge-Se</i>	92.97
2	2.51	1.26	2.02	3.28	2.55	<i>Te-Se</i>	95.06
4	2.47	1.24	1.94	3.18	2.49	<i>Sb-Se</i>	93.94
6	2.43	1.22	1.86	3.08	2.42	<i>Te-Ge</i>	99.80
8	2.39	1.20	1.78	2.98	2.36	<i>Sb-Ge</i>	99.96
10	2.35	1.18	1.70	2.88	2.30	<i>Te-Sb</i>	99.94

The glass transition temperature T_g is an important parameter that represents the strength and rigidity of glass structure. T_g has been calculated using Gibbs-DiMarzio model. Gibbs and DiMarzio proposed an empirical relationship between the transition temperature and the density of cross-linking agents embedded inside a system. The Modified Gibbs-DiMarzio equation can be given as [14]

$$T_g = \frac{T_0}{1 - \beta(m - 2)} \quad (9)$$

where T_0 is the glass transition temperature of the chalcogenide element and β is a system constant. Variation of R and T_g with addition of Te has been shown in Figure 3. Values of $\langle E \rangle$ are listed in Table 1. For $y = 0$, the system is completely cross linked and $Ge(Se_{1/2})_4$, pyramidal Sb_2Se_3 structural units are formed. Although, Te has strong metallic character as compared to other chalcogenide elements, so when Te is incorporated to Ge , new structural units of $Te-Se$ bonds are formed. The mean bond energy of the system decreases for $R > 1$ and makes the system chalcogen rich. Increasing the content of Te may require more edge sites for its accommodation leading to the decrease of average cluster size in the glass. Hence, T_g decreases due to weakening of average bond strength on Te addition [1].

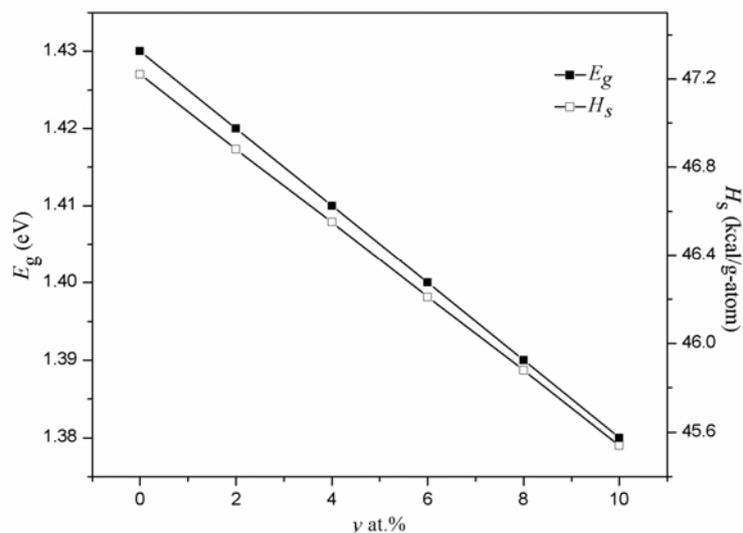


Fig. 3. Variation of E_g and H_s with Te content for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$).

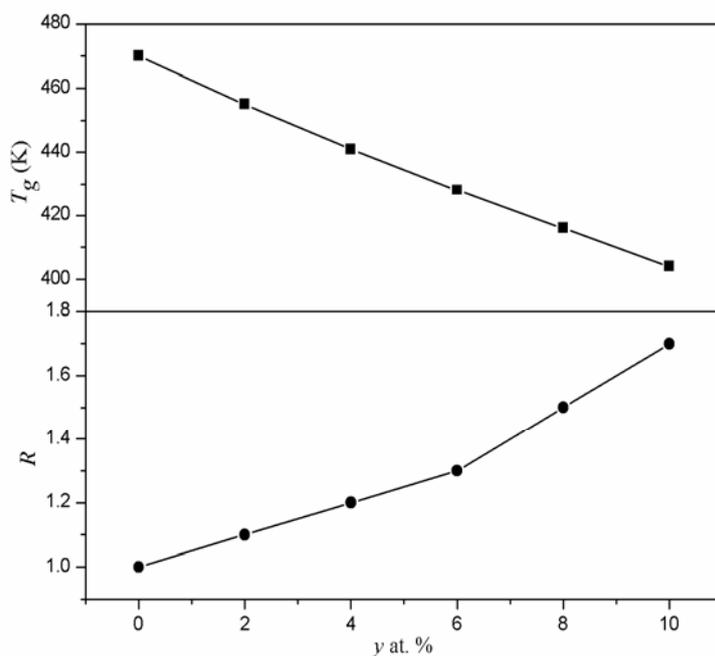


Fig. 4. R and T_g variation with Te content for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$).

3.3 Cohesive energy, heat of atomization and energy gap

According to chemical bond approach [15], atoms combine more favourably with atoms of different kind rather than the same kind and bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is saturated. The bond energy of *Ge-Se* is high and they are formed first, followed by *Te-Se* and *Sb-Se* bonds with slightly lower energy and after then unsaturated *Se-Se* bonds are formed. Distribution of chemical bonds is listed in Table 2.

Cohesive energy measures the average bond strength of the system and is calculated by summing the bond energies of the bonds present in the material [4]:

$$CE = \sum C_i D_i \quad (10)$$

where C_i is number of expected bonds and D_i is the energy of the corresponding bond present in the system.

Average heat of atomization (H_s) is a measure of cohesive energy and represents the relative bond strength among the isostructural materials. It can be calculated for the compounds as [3]

$$H_s = \frac{(\alpha H_s^{Ge} + \lambda H_s^{Se} + \gamma H_s^{Sb} + \nu H_s^{Te})}{\alpha + \lambda + \gamma + \nu} \quad (11)$$

where values of heat of atomization for *Ge*, *Se*, *Sb*, *Te* are 90, 42.4, 62, 46 kcal/g-atom, respectively.

E_g is the energy gap between the top of valence band and bottom of the conduction band. Energy gap has been calculated using relation [16]

$$E_g^{th}(Ge - Se - Sb - Te) = lE_g(Ge) + mE_g(Se) + nE_g(Sb) + pE_g(Te) \quad (12)$$

where l , m , n , p are volume fraction and the energy gap values for *Ge*, *Se*, *Sb* and *Te* are 0.95 eV, 1.95 eV, 0.101 eV and 0.65 eV respectively. Values of CE are listed in Table 2 and found to decrease with the addition of *Te*. Figure 3 shows the variation of H_s and E_g with addition of *Te*.

Table 2: Values of electronegativity (χ), distribution of bonds and cohesive energy (CE) for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$).

y	χ	<i>Ge-Se</i>	Distribution of Bonds		<i>Se-Se</i>	CE (kcal/mol)
			<i>Te-Se</i>	<i>Sb-Se</i>		
0	2.347	0.59561	-	0.40439	-	47.22
2	2.350	0.5329	0.03135	0.4044	0.03135	46.88
4	2.353	0.4702	0.0627	0.4044	0.0627	46.55
6	2.354	0.40752	0.09404	0.4044	0.09404	46.21
8	2.356	0.34483	0.1254	0.4044	0.1254	45.88
10	2.358	0.28213	0.15674	0.4044	0.15674	45.54

According to CBA, *Ge-Se* and *Sb-Se* bonds are formed for $y = 0$. When *Ge* is replaced with *Te* then the probability of *Ge-Se* bond formation decreases leading to the increase in *Te-Se* bonds along with homopolar bonds having low bond energy. The cohesive energy of the system decreases. The decrease of energy gap with increasing *Te*, may be due to reduction of average stabilization energy by *Te* incorporation [4]. It is interesting to relate average heat of atomization with energy gap using relation [3]. There exists a linear correlation between the average heat of atomization (which is a measure of cohesive energy) and energy gap. The energy gap much strongly depends upon the H_s for overconstrained material with higher connectivity than for glasses with lower connectivity [3]. The system under investigation has high connectivity up to $y =$

6, so that E_g decreases with decreasing values of H_i and CE . Electronegativity (χ) of the alloy is the geometric mean of electronegativity of its constituents. Values of χ have been listed in Table 2 and found to increase when Te is substituted for Ge . The electronegativity of Te is high, it is expected that defect states in the system increase with increase in electronegativity difference and hence, the energy gap decreases. The decrease in E_g with Te addition may be explained on the basis of alloying effect *i.e.* the compositional change of material due to variation in bond angle or bond length, disturbing the order of glass, and thus modifying the structure [17]. Te has a tendency to make defect states and create chemical disordering in the system due to the presence of lone pair which increases with Te addition [17].

3.4 Density, packing density and compactness

Density is an important physical parameter and it is related to the change in atomic weight, atomic volume of the elements constituting the system:

$$\rho = \left(\sum \frac{m_i}{d_i} \right)^{-1} \quad (13)$$

where m_i is fraction of mass and d_i is density of i^{th} structural unit density.

Packing density is defined as the ratio of used space to the allocated space and can be calculated using [3]

$$Packing\ density = \frac{N * \rho}{M} \quad (14)$$

where N is Avogadro's number and M is molecular weight.

Density of the glass increases while packing density decreases with Te addition, the values are listed in Table 3. Density and mass of the Te element is higher than Ge due to which ρ increases. As the glass density increases packing density has been found to decrease due to the larger atomic radius and mass [3].

Table 3: Values of density (ρ), packing density and compactness (δ) for $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ ($y = 0, 2, 4, 6, 8, 10$).

y	ρ (g/cm ³)	Packing density (10 ²² atom/cm ³)	δ
0	5.22	3.69	-0.0045
2	5.24	3.66	-0.0055
4	5.25	3.62	-0.0064
6	5.27	3.59	-0.0072
8	5.29	3.56	-0.0080
10	5.31	3.53	-0.0086

Compactness (δ) is a measure of normalized change of mean atomic volume due to chemical interaction of element forming the network of given solid. Compactness of structure can be calculated according to formula [3]

$$\delta = \frac{\sum (X_i A_i) / \rho_i - \sum (X_i A_i) / \rho}{\sum (X_i A_i) / \rho} \quad (15)$$

where X_i , A_i , ρ_i are atomic fraction, atomic weight and atomic density of i^{th} element of the glass. Values of δ are listed in Table 3. Decreasing value of δ may be explained on the basis of formation of homopolar bonds and decreasing packing fraction, due to which the fragility of the system increases.

For *Te* alloyed $Ge_{19}Se_{63.8}Sb_{17.2}$ system, average coordination number, number of constraints, compactness and packing fraction decreases due to decrease in connectivity, presence of defect states, large atomic radius and mass. There is an increase in the lone pair of electrons and electronegativity that enhances the defect states due to which energy gap decreases.

4. Conclusion

The addition of *Te* decreases the cross linking between the network due to which rigidity of the system and T_g decreases. Energy gap decreases on *Te* addition which has been explained on the basis of decrease in cohesive energy and increase in electronegativity. There is an increase in density of the bulk $Ge_{19-y}Se_{63.8}Sb_{17.2}Te_y$ alloys while packing density and compactness of the system decreases with the incorporation of *Te* for *Ge*.

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