

# Assessment of Physical Parameters for Quaternary Antimony Substituted Ge–Se–Te Alloys<sup>1</sup>

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**Abstract**—New quaternary glassy compositions  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  ( $x = 0, 2, 4, 6, 8$ ) have been synthesized using melt quench technique. We have determined various physical parameters i.e. average coordination number, floppy modes, lone pair electrons, average heat of atomization, density, molar volume, compactness and cohesive energy. It is observed that on increasing Sb content density, cohesive energy, average heat of atomization and compactness increases while molar volume decreases. The chemical bond approach has been used to calculate the cohesive energy of the samples under investigation.

**Keywords:** quaternary chalcogenide glasses, cohesive energy, average heat of atomization, compactness

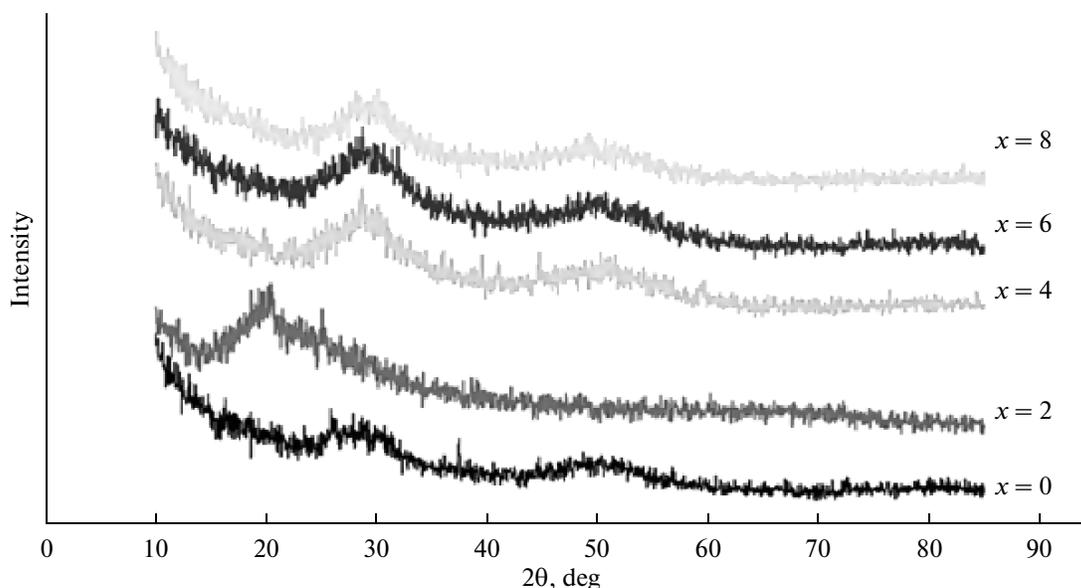
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## INTRODUCTION

In chalcogenide glasses almost all the properties are compositional dependent. The properties such as infrared transmission, switching, photoconductivity, optical wave guide and semiconduction makes chalcogenide glasses different from other glasses. Chalcogenide glasses are made up from chalcogen (S, Se, Te; group VI elements in periodic table) on adding elements of group III to VI group. Between chalcogens, Se has more flexibility to form glassy network in comparison to others. The main drawback of pure Se is its short life time and low photosensitivity, which can be rectified by making its compounds with other elements [1]. Addition of Ge to Se improves its sensitivity and makes the crystallization temperature high leading to increase in thermal stability. Se has chain-like structure and the addition of Ge modifies and strengthens the network by cross-linking the chains. Sharma et al. have observed an increase in the glass transition temperature [2]. The addition of Te gives high reflective index, high transmittance, high photosensitivity and reduces the losses in IR region [3–5]. The alloys of Se–Te system are widely used for various application such as in memory devices, fiber optics, laser printing and photo copying [6, 7]. Thus Se based chalcogenide glasses have wide range of applications, e. g. in optical fibres, memory devices, xerography, photolithography, reversible phase change materials and in IR transmittance [8–11]. On the other hand, Te based glasses such as GST ( $\text{GeSb}_2\text{Te}_4$ ,  $\text{GeSb}_4\text{Te}_7$ ,

$\text{Ge}_3\text{Sb}_2\text{Te}_6$ ,  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ) have found applications as recording material such as rewriteable DVD. GST have small glass formation regions i. e. with increase in Te amount the tendency of crystallization becomes more prominent but these materials have low melting temperature and ability to reversibly transform between amorphous to crystalline state with high speed [12–17]. The Ge–Se–Sb glasses have a large glass forming region and found potential applications in IR transmission [18]. The Ge–Se–Sb family is also considered as one of the most promising families with low transmission loss and high transparency to infrared radiation from 2–16  $\mu\text{m}$  [19]. The Ge–Se–Te glasses found applications in optoelectronics due to their low phonon energy and high refractive index. The Ge–Se–Te systems have long term temperature stability and used in many commercial applications [20]. Also glass forming regions are not well defined yet in quaternary glasses like ternary glasses. These points make the motivation to work with quaternary Ge–Se–Te–Sb glassy alloys to make new phase change material where some of the properties may be coupled from above discussed alloys. Moreover, many works have been reported on the compositions where Se is greater than 75% and compositions with Se nearly 50% are scarcely reported for there physical parameters. Therefore by choosing Se to 52% and decreasing the Te with increasing Sb we may get advantages to get the properties of both GST as well as Se based glasses. In the present work, we report the determination of physical parameters i. e. average coordination number, floppy modes, lone pair elec-

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X-ray diffraction patterns of glasses of  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  system.

trons, cohesive energy ( $CE$ ), average heat of atomization, density, molar volume and compactness of quaternary  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  ( $x = 0, 2, 4, 6, 8$ ) glassy system.

#### EXPERIMENTAL DETAILS

Bulk glasses of  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  ( $x = 0, 2, 4, 6, 8$ ) system were prepared from high purity (99.999%) Ge, Se, Te and Sb elements using melt quench technique. The materials were weighted according to their atomic percentage and then sealed in cleaned evacuated ( $\sim 10^{-3}$  Pa) quartz ampoules. The ampoules were put inside a furnace where the temperature was increased up to  $1100^\circ\text{C}$  at a heating rate of  $2\text{--}3^\circ\text{C}/\text{min}$  and at the highest temperature ampoules were kept for 24 h. The ampoules were agitated at regular intervals to make the melt homogeneous. The ampoules were quenched in ice cooled water to avoid crystallization. The sample ingots were obtained by breaking the ampoules. The obtained ingots were used to measure their density using the Archimedes method. The samples were then crushed to powder using mortar and pestle. The powder samples were used to obtain their X-ray diffraction spectra using a Philips X'pert Pro diffractometer. The diffraction patterns were obtained using  $\text{CuK}\alpha$ -radiation ( $\lambda = 1.54056 \text{ \AA}$ ).

#### RESULTS AND DISCUSSION

Figure shows the XRD diffractograms for  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  ( $x = 0, 2, 4, 6, 8$ ) system. The vitreous nature of samples was confirmed by the absence of crystallization/sharp peaks in any of the diffractograms.

#### Nearest Neighbour Coordination and Floppy Modes

The bonding character in the nearest neighbour region i. e. average coordination number characterizes the electronic properties of the semiconducting materials and considered to be suitable for testing the validity of topological concepts [21]. In our quaternary chalcogenide system, the average coordination number  $\langle r \rangle$  is given by

$$\langle r \rangle = \frac{aZ_{\text{Ge}} + bZ_{\text{Se}} + cZ_{\text{Te}} + dZ_{\text{Sb}}}{a + b + c + d}, \quad (1)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are the atomic weight percentages of the Ge, Se, Te and S.

Chalcogenide glasses contain either floppy or rigid regions which depends on their average coordination number [22, 23]. The average coordination number  $\langle r \rangle = 2.4$  represents a percolation threshold at which floppy to rigid transition occurs in glasses. Systems in which  $\langle r \rangle$  is less than 2.4, are known as under coordinated networks having a finite fraction of zero frequency normal vibrational modes called floppy modes [22]. The fraction of floppy modes available in a network is given by the equation:

$$f = 2 - \frac{5}{6}\langle r \rangle, \quad (2)$$

where  $\langle r \rangle$  is the average coordination number. The values of  $\langle r \rangle$  and  $f$  obtained for  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  are listed in Table 1. It has been observed that with increase in Sb content in the system the value of fraction of floppy modes decreases, this shows that the system is shifting from floppy to rigid and at  $x = 8$  the floppy modes are completely absent.

**Table 1.** Values of average coordination number ( $\langle r \rangle$ ), lone pair electrons ( $L$ ), average heat of atomization ( $H_s$ ), number of excess bonds and cohesive energy ( $CE$ ) for  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  glasses

$x$	$\langle r \rangle$	$f$	$L$	$H_s$ , kcal/g atom	Excess Te–Te bonds	Excess Sb–Sb bonds	$CE$ , eV/atom
0	2.32	0.066	1.28	54.81	12	–	2.311
2	2.34	0.050	1.24	55.13	7	–	2.322
4	2.36	0.033	1.20	55.45	2	–	2.333
6	2.38	0.016	1.16	55.77	–	3	2.344
8	2.40	0	1.12	56.09	–	8	2.354

### Lone Pair Electrons

The presence of lone pair electrons in a chalcogenide system reduces its strain energy. This reduction in strain energy is due to the formation of valence alternation pairs which have relatively small energy. Hence, the chalcogenide system with a large number of lone pair electrons favours the glass formation. Thus, the number of lone pair electrons plays an important role in forming the chalcogenide glasses. The numbers of lone pair electrons in a chalcogenide system can be calculated by using the formula [24–25]:

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

where  $L$  and  $V$  denotes the number of lone pair electrons and the number of valence electrons respectively. The numbers of lone pair electrons obtained by using this equation are listed in Table 1. It is clear from Table 1 that the number of lone pair electrons decreases with increase in Sb content which means that bond deformation decreases with increase in Sb content, leading to decrease in the flexibility of the system.

**Average heat of atomization.** Heat of atomization is the amount of heat required to change one mole of a chemical compound in its standard state at 298 K to gaseous atoms. According to Pauling [26], the heat of atomization  $H_s(\text{A–B})$  at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of the formation heat  $\Delta H$  and the average of the heats of atomization  $H_s^A$  and  $H_s^B$ , respectively, that corresponds to the average non-polar bond energy of the two atoms [27–29]:

$$H_s(\text{A–B}) = \Delta H + \frac{1}{2}(H_s^A + H_s^B), \quad (4)$$

where  $\Delta H$  is related to the electronegativities  $\chi_A$  and  $\chi_B$  of the two atoms A and B as:

$$\Delta H \propto (\chi_A - \chi_B)^2. \quad (5)$$

In the case of ternary and higher order semiconductor compounds, the average heat of atomization is defined for quaternary compound  $\text{A}_a\text{B}_b\text{C}_c\text{D}_d$  [30]:

$$H_s = \frac{aH_s^A + bH_s^B + cH_s^C + dH_s^D}{a + b + c + d}, \quad (6)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are the atomic percentage of A, B, C and D respectively. The values of  $H_s$  for  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  alloys, obtained using the values of  $H_s(\text{Ge}) = 90$  kcal/g atom,  $H_s(\text{Se}) = 49.4$  kcal/g atom,  $H_s(\text{Sb}) = 62$  kcal/g atom,  $H_s(\text{Te}) = 46$  kcal/g atom. [30, 31]. In our system the value of average heat of atomization increases with addition of Sb (Table 1). This is due to the fact that we are replacing Te with Sb and hence concentration of group VI element decreases, which decreases the concentration of lone pair electrons from top of the valence band, so heat of atomization increases.

**Bond energy, relative bond probability and cohesive energy.** In our quaternary chalcogenide system of Ge–Se–Te–Sb, there is formation of Ge–Se, Se–Te, Sb–Te, Te–Te and Sb–Sb bonds. The Chemical Order Network model [32] suggests that heteropolar bonds are favoured over homopolar bonds and they are formed in the sequence of their decreasing bond energy. The bond energy of heteropolar bonds is estimated by using the bond energy of homopolar bonds and the electronegativity of the atoms are calculated using [30]:

$$D(\text{A–B}) = [D(\text{A–A})D(\text{B–B})]^{1/2} + 30(X_A - X_B)^2, \quad (7)$$

where  $D(\text{A–B})$  is the bond energy of heteropolar bond,  $D(\text{A–A})$  and  $D(\text{B–B})$  is the bond energy of homopolar bonds.  $X_A$  and  $X_B$  are the electronegativity values of A and B, respectively. The values of calculated bond energy for homopolar and heteropolar bonds are given in Table 2. The electronegativity values for Ge, Se, Sb and Te are 2.01, 2.55, 2.05 and 2.1 respectively [30, 31].

The bond probabilities of forming different bonds are calculated using the formula  $e^{E/kT}$ , where  $E$  is the difference in energy of respective bonds,  $k$  is Boltzmann's constant and  $T$  is the temperature when probability is calculated [32]. Taking the probability of Ge–Se bond as unity, the relative probabilities of different bonds in Ge–Se–Te–Sb system are calculated and listed in Table 2.

**Table 2.** Bond energies and relative bond probabilities of formation of various bonds in glasses of  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  system, taking the probability of Ge–Se bond as unity

Bond	Bond energy, kcal/mol	Relative probability at	
		$T = 298.15 \text{ K}$	$T = 1373.15 \text{ K}$
Ge–Se	49.44	1	1
Te–Se	44.20	$1.42 \times 10^{-4}$	$1.46 \times 10^{-1}$
Sb–Se	43.98	$9.87 \times 10^{-5}$	$1.35 \times 10^{-1}$
Se–Se	44.04	$1.09 \times 10^{-4}$	$1.38 \times 10^{-1}$
Ge–Te	35.47	$5.62 \times 10^{-11}$	$5.97 \times 10^{-3}$
Sb–Te	31.65	$8.97 \times 10^{-14}$	$1.47 \times 10^{-3}$
Te–Te	33.00	$8.7 \times 10^{-13}$	$2.42 \times 10^{-3}$
Ge–Sb	33.75	$3.12 \times 10^{-12}$	$3.19 \times 10^{-3}$
Ge–Ge	37.60	$2.0 \times 10^{-9}$	$1.30 \times 10^{-2}$
Sb–Sb	30.22	$7.94 \times 10^{-15}$	$8.73 \times 10^{-4}$

**Table 3.** Values of density ( $\rho$ ), molar mass ( $M_m$ ), molar volume ( $V_m$ ) and compactness ( $\delta$ ) for  $\text{Ge}_{16}\text{Se}_{52}\text{Te}_{32-x}\text{Sb}_x$  glasses

$x$	$\rho$ , g/cm <sup>3</sup>	$M_m$ , g/mol	$V_m$ , cm <sup>3</sup> /mol	$\delta$
0	4.85	93.513	19.28	−0.10551
2	4.86	93.397	19.22	−0.10492
4	4.87	93.280	19.15	−0.10433
6	4.88	93.163	19.09	−0.10375
8	4.89	93.046	19.03	−0.10317

Knowing the bond energies, we can estimate the number of different bonds expected in the system and then cohesive energy ( $CE$ ) can be calculated using the equation

$$CE = \sum \frac{C_i D_i}{100}, \quad (8)$$

where  $C_i$  are the number of chemical bonds and  $D_i$  is the energy of each corresponding bond, respectively. From the data (Table 1) it is clear that there is continuous increase in cohesive energy with increase in the concentration of Sb. This is due to increase in number of bonds with increase in Sb content as coordination number of Sb(3) is greater than Te(2).

**Compactness and molar volume.** The density ( $\rho$ ) of glasses were measured by Archimedes method using double distilled water as a reference liquid, which has a density of 1.0 g/cm<sup>3</sup> at 20°C. The density values were obtained from

$$\rho = \left[ \frac{w_1}{w_1 - w_2} \right] \rho_{\text{water}}, \quad (9)$$

where  $w_1$  and  $w_2$  are the weights of the sample in air and in the reference liquid, respectively. It has been

found that the density of the system increases with the increase of Sb content (Table 3). This may be due to replacement of less denser Te (6.24 g/cm<sup>3</sup>) by high denser Sb (6.7 g/cm<sup>3</sup>).

The compactness ( $\delta$ ) was calculated (Table 3) using the relation [33]

$$\delta = \frac{\sum_i \frac{c_i A_i}{\rho_i} - \sum_i \frac{c_i A_i}{\rho}}{\sum_i \frac{c_i A_i}{\rho}}, \quad (10)$$

where  $c_i$  is the atomic fraction,  $A_i$  is the atomic weight,  $\rho_i$  is the atomic density of the  $i$ th element of the system and  $\rho$  is the measured density of the system. Thus  $\delta$  is a measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of the given solid. The value of compactness becomes less negative for our system i. e. shifts towards zero.

Another factor, molar volume ( $V_m$ ) was determined (Table 3) from the density data using equation [34]:

$$V_m = \frac{1}{\rho} \sum_i x_i M_i, \quad (11)$$

where  $M_i$  is the molecular weight of the  $i$ th component and  $x_i$  is the atomic percentage of the same element in the sample. The decrease in molar volume with an increase in Sb content supports our density results i.e. an increase in density with Sb.

## CONCLUSION

Addition of Sb at the expense of Te in Ge–Se–Te system leads to change in physical properties of the glasses. The results indicate that there is small increase in the heat of atomization and cohesive energy. The density and compactness increases while molar volume decreases with increase in Sb content. This may be due to replacement of less dense Te element by denser Sb element.

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