

## **The Influence of Ge content on Physical Parameters of $Ge_xSb_{35-x}Te_{65}$ Glass System**

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### **ABSTRACT**

*The investigation of composition dependence of various properties of chalcogenide glasses has been increased in recent years. In the present work, the effect on the physical properties viz. average coordination number, mean bond energy, glass transition temperature, Average heat of atomization etc., with the variation in Ge content has been studied theoretically for  $Ge_xSb_{35-x}Te_{65}$  ( $x = 4, 8, 12, 16, 20$  at. %) glassy semiconductors. It has been found that almost all the parameters, studied here, except the parameter R, were increased with the increase in Ge content, thus making this suitable for phase change optical recording.*

**Keywords:** Chalcogenide Glasses; Average Coordination Number; Glass Transition; mean bond energy; Average heat of atomization.

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### **INTRODUCTION**

Recently, chalcogenide glasses have attracted vast interest due to their extensive uses in photo resist, microelectronics, optoelectronics applications [1-3]. The major advantage of these materials is that these can transmit across a wide range of infrared electromagnetic spectrum [4]. Some chalcogenide experience thermal driven amorphous – crystalline phase changes, forming the basis of rewritable optical discs and non-volatile memory devices. More recently, amorphous chalcogenide switching has been applied quite successfully to DVD technology where the quest for discovery of better-suited materials continues. The switching grants researches with an active area of technology as well as fundamental study now a days [5]. The bond constraint theory and rigidity theory provide a powerful framework for understanding the structure and physical properties of amorphous materials. Applications of these theories to switching in amorphous chalcogenide materials leads to developing the best composition suited for switching applications [6]. The long researches into amorphous semiconductors have now borne technologies fruit in the development of phase change memory devices that exploit rapidly crystallizing chalcogenide alloy materials in programmable memory devices [7].

The compositional dependence studies on glassy alloys were reported for Bi-Se, Ge-Se, Bi-Se-Te, Ge-Se-Te, Ge-Se-Ga, Ge-Se-Ag etc. [8 – 12]. Through a number of amorphous chalcogenide alloys are reported in the literature, amorphous Ge-Sb-Te glass has received particular attention [13, 14]. Ge atoms act as bond modifiers thus they strengthen the average bond by cross-linking the Te chain structure, thereby enhancing the properties like glass transition temperature and resistivity. Chalcogenide glasses can also be used as reference materials in order to develop a better understanding of the glassy state and its specific properties. Moreover, as these materials show a continuous change of their various properties with change in their chemical composition, it is possible to investigate the correlation of the features observed in the property-composition dependence with the structural arrangement in

the glass. Such studies on the thermal, mechanical, electrical, optical and physicochemical have recently been reported [15 – 17].

In Ge-Sb-Te system, bond energies for Sb-Sb (39.6 kcal/mol) and Sb-Te (40.6 kcal/mol) suggest that the Sb-Te bonds account for most of the backscattering signal from Sb atoms [18]. The shorter Sb-Te distance can be attributed to an electrostatic bond between Sb and a positively charged three fold coordinated Te atom. The homopolar Ge bond data suggest that virtually all Ge atoms are bonded to one Ge atom and three Sb atoms are then interspersed evenly throughout the structure with three Te neighbours in  $Sb_2Te_3$  arrangements.

In the present work, we have incorporated Ge in the Sb-Te alloy for the compositions belonging to  $Ge_xSb_{35-x}Te_{65}$  ( $x = 4, 8, 12, 16, 20$  at. %). The addition of third element used to create compositional and configurational disorder in the material with respect to the binary alloys [10]. It has been established that physical properties in this system are highly composition dependent [19, 20]. The present paper is concerned with the theoretical prediction of some physical parameters related to composition, viz. coordination number, mean bond energy and the glass transition temperature etc. for  $Ge_xSb_{35-x}Te_{65}$  alloys.

## THEORETICAL STUDIES AND DISCUSSION

### Bonding Constraints & Average Coordination Number

Phillips [3] gave the mechanical-constraint counting algorithms to explain glass forming tendencies. Constraints associated with the weaker forces of more distant neighbours must be intrinsically broken leading to the absence of long-range order. The well known Phillips-Thorpe approach [4, 5] is based on comparing the number of atomic degrees of freedom with the number of inter-atomic force field constraints. The bond constraint theory maintains the balance between stressed and floppy materials in terms of arrange number of constraints per atom in the inter-atomic force field space and the number of degree of freedom in real space.

The average coordination number ( $Z$ ) was calculated using standard method [17, 21] for the composition  $Ge_xSb_{35-x}Te_{65}$ ,  $Z$  is given by

$$Z = \frac{xN_{Ge} + yN_{Sb} + zN_{Te}}{x + y + z}$$

where  $x$ ,  $y$  and  $z$  are the at. % of Ge, Sb and Te respectively and  $N_{Ge}(4)$ ,  $N_{Sb}(3)$ ,  $N_{Te}(2)$  are their respective coordination number [22]. fig. 1 shows values of  $Z$  increase from 2.39 to 2.55 with increase in concentration of Ge from 4 to 20 at. % using the calculated values of average coordination number for  $Ge_xSb_{35-x}Te_{65}$  ( $x = 4, 8, 12, 16, 20$  at. %) system.

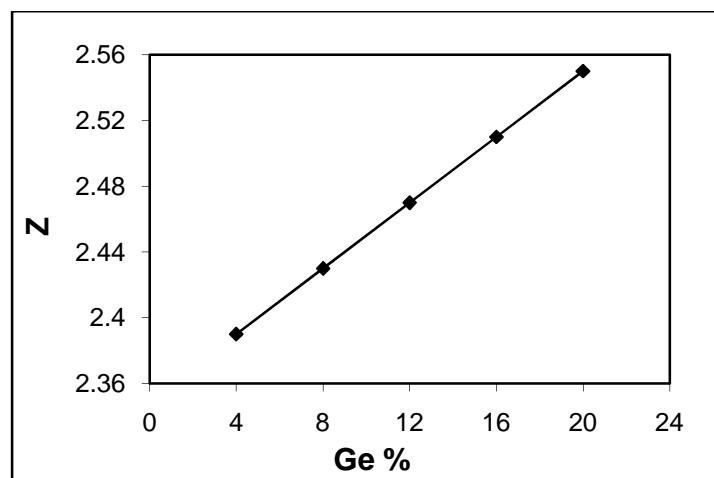


Fig. 1: Variation of Average Coordination Number with Ge at. %

### Deviation from the stoichiometry of composition

The parameter R that determines the deviation from stoichiometry is expressed by the ratio of content bond possibilities of chalcogen atoms to that of non-chalcogen atoms. For  $Ge_xSb_{35-x}Te_{65}$  system, the parameter R is given by [23]

$$R = \frac{zCN(Te)}{xCN(Ge) + yCN(Sb)}$$

where x, y, z are atomic fractions of Ge, Sb, and Te respectively. The values of R are mentioned in Table 1 which shows that R decreases from 1.19 to 1.04 with increase in concentration of Ge from 4 to 20 at. %. The threshold at  $R=1$  (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For  $R>1$ , the system is chalcogen rich and for  $R<1$ , the system is chalcogen poor. From fig. 2, it is clear that our system is chalcogen rich and may turn towards chalcogen poor with the increase in content of Ge in the system.

### Mean Bond Energy And Glass Transition Temperature

There are many properties of chalcogenide glasses which are related to overall mean bond energy  $\langle E \rangle$ . According to Tichy and Ticha [24, 25], the value of glass transition temperature should not only be related to connectedness of the network which is related to Z, but should also be related to the quality of connections, i.e., the mean bond energy between the atoms of the network. The overall mean bond energy for the  $Ge_xSb_{35-x}Te_{65}$  system is given by

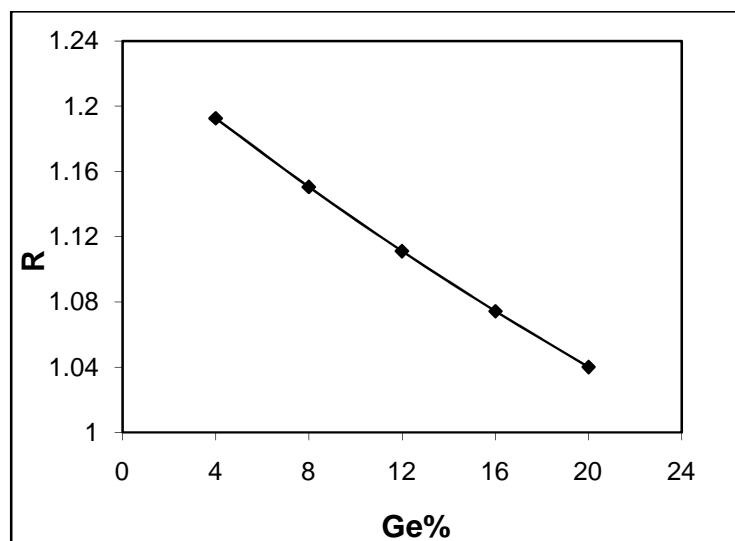


Fig. 2: Variation of parameter R with Ge content

$$\langle E \rangle = E_c + E_{rm}$$

where  $E_c$  is overall contribution towards bond energy arising from strong heteropolar bonds and  $E_{rm}$  is contribution arising from weaker bonds that remains after the strong bonds have been maximized. For  $Ge_xSb_yTe_z$  system, where  $(x + y + z) = 1$ , in selenium rich systems ( $R>1$ ) where there are heteropolar bonds and chalcogen-chalcogen bonds

$$E_c = 4xE_{Ge-Te} + 3zE_{Te-Sb}$$

$$E_{rm} = \left[ \frac{2z - 4x - 3y}{Z} \right] E_{Te-Te}$$

It is clear from fig. 3 that  $\langle E \rangle$  increases from 1.71 to 1.89 with increase in concentration of Ge from 4 to 20 at. % i.e. in selenium rich region.

An impressive correlation of mean bond energy with glass transition temperature  $T_g$  was illustrated by Tichy and Ticha by the relation [24, 25]

$$T_g = 311[\langle E \rangle - 0.9]$$

The variation of  $T_g$  with Ge content is shown in fig. 4, which is clearly depicting the rise in glass transition temperature from 253.37 to 308.46 with increasing the content of Ge due to rise in mean bond energy of the glassy system.

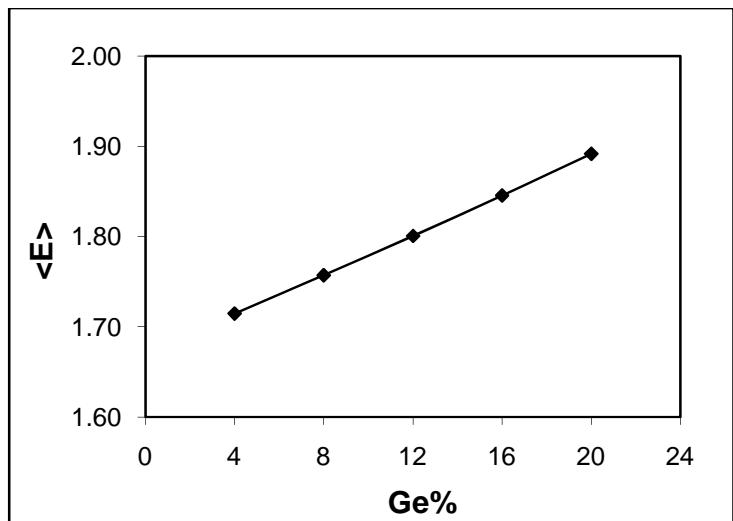


Fig. 3: Variation of overall mean bond energy with Ge content

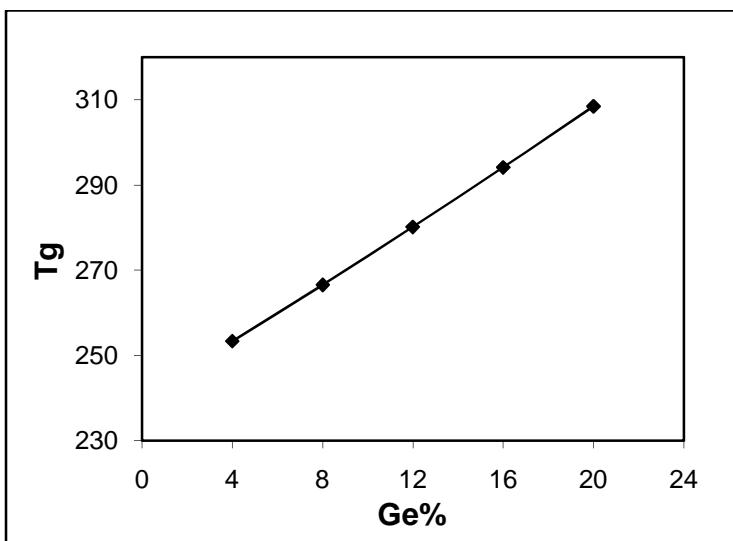


Fig. 4: Variation of glass transition temperature  $T_g$  with Ge content

### Average Heat of Atomization

As proposed by Pauling [26], the heat of atomization  $H_s(A-B)$  at standard temperature and presence of a binary semiconductor formed from atom A and B is a sum of heats of formation  $\Delta H$  and average of heats of atomization  $H_s^A$  and  $H_s^B$  that correspond to the average non-polar energies of the two atoms, is given by the relation

$$H_s = \Delta H + \frac{1}{2}(H_s^A + H_s^B)$$

The term  $\Delta H$  in the above relation is proportional to the square of the difference between the electro negativities  $\chi_A$  and  $\chi_B$  of two atoms involved i.e.

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

In case of ternary and higher order semiconductor materials, the average heat of atomization  $H_s$  is defined for a compound  $A_x B_y C_z$  is considered as a direct measure of the cohesive energy and thus average bond strength, as

$$H_s = \frac{xH_s^A + yH_s^B + zH_s^C}{x + y + z}$$

where x, y, z are the ratios of A(Ge), B(Sb), and C(Te) respectively. From the Table 1, it is clear that average heat of atomization  $H_s$ , increases from 52.42 to 54.84 with increase in Ge content from 4 to 20 at. %, resulting in increase of optical band gap. A graphical representation of average heat of atomization  $H_s$  with the variation in Ge content is shown in fig. 5.

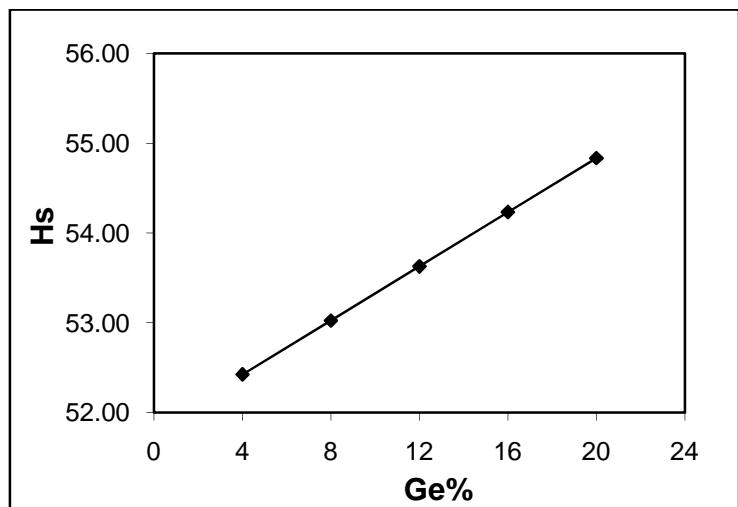


Fig. 5: Variation of average of heats of atomization  $H_s$  with Ge content

Table 1.

Ge	Sb	Te	Z	R	$\langle E \rangle$	Tg	Hs
x	y	z					
4	31	65	2.39	1.19	1.71	253.37	52.42
8	27	65	2.43	1.15	1.76	266.56	53.03
12	23	65	2.47	1.11	1.80	280.15	53.63
16	19	65	2.51	1.07	1.85	294.13	54.23
20	15	65	2.55	1.04	1.89	308.46	54.84

## CONCLUSION

It is concluded here that the variation in Ge content in Ge-Sb-Te glassy alloys leads to change in the physical properties. As it is clear from various figures and table given that almost all the parameters, except the parameter R, increase with the increase in content of Ge in  $Ge_xSb_{35-x}Te_{65}$  system. It has been found that mean bond energy  $\langle E \rangle$  is proportional to glass transition temperature and both increases with the increase in content of Ge. It is also found that average heat of atomization  $H_s$ , increases with increase in Ge content from 4 to 20 at %, resulting in increase of optical band gap.

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