In recent years the growing interest in the investigation of the properties of chalcogenide glasses stems from the actual and potential technological applications of these materials in microelectronics, optoelectronics, memory devices etc. Moreover, it has been established that these glasses are easily formed by melt-quenching over a large range of compositions making them suitable model systems for the investigation of the composition dependence of their properties. In the present article, the effect on the various physical properties viz. average coordination number, mean bond energy, glass transition temperature, average heat of atomization etc., has been studied theoretically for Ge$_{x}$Sb$_{28-x}$Te$_{72}$ (x = 3, 6, 9, 12, 15, 18, 21 at. %) glassy semiconductors with the variation in Ge content. The major advantage of chalcogenide materials is that these can transmit across a wide range of infrared electromagnetic spectrum [1]. Some chalcogenide experience thermal driven amorphous – crystalline phase changes, forming the basis of rewritable optical discs and non-volatile memory devices. For crystalline materials, understanding the relationships between microscopic structures and macroscopic properties has been a subject in solid-state physics. As it is well known that amorphous solids possess no long-range order, and not many established techniques capable of identifying non-periodic configurations have been available, physics on amorphous materials is far behind that of the crystalline materials. The switching grants researches with an active area of technology as well as fundamental study [2]. Chalcogenide glasses can also be used as reference materials in order to develop a better understanding of the glassy state and its specific properties. However, compositional studies seem to be vitally important for amorphous materials. On the basis of the amorphous structure of covalent glasses, building elements may be classified into two components; one is normal bonding structure consisting of covalent bonds of densities on orders of 10$^{22}$-10$^{23}$ cm$^{-3}$, which can be specified by chemical and topological natures, and the other one is defects, e.g., impurities, valence-alternation pairs, dangling and wrong bonds, i.e., the homopolar bonds in stoichiometric alloys [3, 4]. The density of defective bonds is, in general, less than 10$^{-7}$ of that for the covalent bonds, and therefore structural behaviours are determined mostly by the normal configurations. Further, these are primarily responsible for such electronic properties as the band-gap energy. Thus, consideration of glassy characters using topological concepts may give fruitful ideas similar to those obtained through the unified understanding of crystalline properties based on periodic lattices. 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. The long researches into amorphous semiconductors have exploit rapidly crystallizing chalcogenide alloy materials in programmable memory devices [5]. The compositional dependence studies on glassy alloys were reported for Ge-Se, Bi-Se, Bi-Se-Te, Ge-Se-Te, Ge-Se-Ga, Ge-Se-Ag, Ge-Se-Sb etc. [6 – 11]. Though a number of amorphous chalcogenide alloys are reported in the literature, amorphous Ge-Sb-Te glass has received particular attention [12, 13]. 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. Compositional dependence studies on the thermal,
mechanical, electrical, optical and physicochemical have recently been reported [14 – 18]. The bond energies for Sb – Sb and Sb – Te in Ge-Sb-Te system suggest that the Sb–Te bonds account for most of the backscattering signal from Sb atoms. 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 Sb2Te3 arrangements. The molecular structure of Ge-Sb-Te glasses then include three local bonding arrangements, viz: (a) Sb2Te3 (b) GeTe2 and (c) 3-fold coordinated Te atoms, the nearest neighbours of which are Sb and Ge [19].

In the present work, we have taken alloy for the compositions belonging to Ge,Sb28-xTe72 (x = 3, 6, 9, 12, 15, 18, 21 at. %). It has been established that physical properties in this system are highly composition dependent [8, 20]. The present paper is concerned with the theoretical prediction of some physical parameters viz. average coordination number, mean bond energy, glass transition temperature, average heat of atomization for Ge8Sb28-xTe72 alloys for various composition.

2. Materials and Methods

2.1 Bonding Constraints & Average Coordination Number
The mechanical-constraint counting algorithms to explain glass forming tendencies were first proposed by Phillips [21]. According to this theory, the strongest covalent forces between nearest neighbours serve as Lagrangian (mechanical) constraints defining the elements of local structure (building blocks). The Constraints associated with the weaker forces of more distant neighbours must be intrinsically broken leading to the absence of long-range order. The Phillips-Thorpe approach [22, 23] was 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 range number of constraints per atom in the inter-atomic force field space and the number of degree of freedom in real space. Local configurations play a major role in the application of bond constraint theory. The average coordination number (Z) was calculated using standard method [24] for the composition Ge8Sb28-xTe72. Z is given by

\[ Z = \frac{aN_{Ge} + bN_{Sb} + cN_{Te}}{a + b + c} \]

where a, b and c are the atomic % of Ge, Sb and Te respectively and \( N_{Ge} (4), N_{Sb} (3), N_{Te} (2) \) are their respective coordination number [25, 26].

2.2 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 Ge8Sb28-xTe72 system, the parameter R is given by [27 – 29]

\[ R = \frac{cCN(Se)}{aCN(Ge) + bCN(Sb)} \]

where a, b, c are atomic frictions of Ge, Sb, and Te respectively.

The parameter R, also play an important role in the analysis of the results. Depending on R values, the chalcogenide systems can be organized into three different categories [30]:

a) For R = 1, the system reaches the stoichiometric composition since only hetero polar bonds are present.

b) For R > 1, the system is chalcogen-rich. There are hetero-polar bonds and chalcogen–chalcogen bonds present.

c) For R < 1, the system is chalcogen-poor. There are only hetero-polar bonds and metal–metal bonds present.

2.3 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 [27, 28], 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 \( Ge_xSb_{28-x}Te_{72} \) system is given by

\[ \langle E \rangle = E_c + E_{rm} \]

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 \( Ge_x Sb_{28-x}Te_{72} \) system, where \( a + b + c = 1 \), in selenium rich systems (R>1) where there are heteropolar bonds and chalcogen-chalcogen bonds

\[ E_c = 4aE_{Ge–Te} + 3cE_{Te–Sb} \]

\[ E_{rm} = \left[ \frac{2c - 4a - 3b}{Z} \right] E_{Te–Te} \]

An impressive correlation of mean bond energy with glass transition temperature \( T_g \) was illustrated by Tichy and Ticha by the relation [27, 28]

\[ T_g = 31 \ln(\langle E \rangle - 0.9) \]

2.4 Average Heat of Atomization
As proposed by Pauling [31], 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 few materials, the amount of heat of formation $\Delta H$ is about 10% of the heat of atomization and may therefore be neglected. Hence

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

In case of ternary and higher order semiconductor materials, the average heat of atomization $H_s$ [31, 32] is defined for a compound $A_B \cdot B^c$ as

$$H_s = \frac{a H_s^A + b H_s^B + c H_s^C}{a + b + c}$$

where $a, b, c$ are the ratios of $A(Ge), B(Sb),$ and $C(Te)$ respectively.

3. Results and Discussion

The calculated values of average coordination number for $Ge_x Sb_{28-x} Te_{72}$ are listed in Table 1. The variation of $Z$ with $Ge$ content are shown in fig. 1, which shows that the values of $Z$ increase from 2.31 to 2.49 with increase in concentration of $Ge$ from 3 to 21 at. % using the calculated values of average coordination number for $Ge_x Sb_{28-x} Te_{72}$ ($x = 3, 6, 9, 12, 15, 18, 21$ at. %) system. The values of $R$ are mentioned in table 1. 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 as $R$ decreases from 1.66 to 1.37 with increase in concentration of $Ge$ from 3 to 21 at. %, and may turn towards chalcogen poor with the increase in content of $Ge$ in the system.

It is clear from fig. 3 that overall mean bond energy $\langle E \rangle$ increases from 1.758 to 1.927 with increase in concentration of $Ge$ from 3 to 21 at. %, i.e., in selenium rich region. The variation of $T_g$ with $Ge$ content is shown in fig. 4, which is clearly depicting the rise in glass transition temperature from 266.72 to 319.54 with increasing the content of $Ge$ due to rise in mean bond energy of the glassy system. From the table 1, it is clear that average heat of atomization $H_v$ increases from 51.77 to 54.49 with increase
in Ge content from 3 to 21 at. %, thus resulting in increase of optical band gap. A graphical representation of average heat of atomization $H_\text{a}$ with the variation in Ge content is shown in fig. 5.

![Graph showing variation of average heats of atomization $H_\text{a}$ with Ge content](image)

**Fig. 5:** Variation of average of heats of atomization $H_\text{a}$ with Ge content

<table>
<thead>
<tr>
<th>Ge</th>
<th>Z</th>
<th>R</th>
<th>$&lt;E&gt;$</th>
<th>$T_\text{g}$</th>
<th>$H_\text{s}$</th>
</tr>
</thead>
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<td>51.77</td>
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<td>1.37</td>
<td>1.927</td>
<td>319.54</td>
<td>54.49</td>
</tr>
</tbody>
</table>

### Table 1

### 4. 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 above that almost all the parameters, except the parameter R, increase with the increase in content of Ge in Ge$_{28}$Sb$_{x}$Te$_{2}$ system. It has been found that mean bond energy $<E>$ is proportional to glass transition temperature and both increases with the increase in content of Ge. Average heat of atomization $H_\text{a}$ is also found to increase with increase in Ge content from 3 to 21 at. %. This results an increase of optical band gap and hence the present composition may be useful for optical memory devices.

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