CHAPTER V

Compositional Dependence of Physical Parameters in Ge-Se-Te System


In this chapter we have determined some physical parameters viz. coordination number, density, molar volume, compactness, lone pair electrons, theoretical band gap, average heat of atomization, cohesive energy and electronegativity of Ge-Se-Te system.

5.1 Introduction

Recently, variation of physicochemical, mechanical and optical properties of multicomponent chalcogenide glasses and thin films caused by changes in the average coordination number \( m \), has been the subject of intensive research [1-3]. The model of bond arrangement [4,5] and topological models such as the constraints model [6,7] and the structural transition model [8], have been used in the interpretation of the compositional dependence of these properties. Distinct features such as an extremum or a kink caused by chemical ordering are observed in the compositional dependence at the stoichiometric or tie-line compositions (also known as chemical thresholds of the system [9]). The topological model based on the constraints theory is also employed to explain the peculiarities in property-compositional dependence of covalently bonded chalcogenide glasses. In this model the properties are discussed in terms of the average coordination number, \( m \), which is not influenced by the nature of the atoms [8]. At \( m = 2.4 \) the glass network has a mechanical or floppy-to-rigid percolation threshold. At this \( m \) the network structure changes from an elastically floppy type to a rigid type [7]. Taking into account not only the short range constraints, but also the constraints of the medium range order (MRO), Tanaka [8] has predicted another structural phase transition. It is the transition from two dimensional (2D) layer-like structures to 3D cross-linked network. This transition is observed at \( m \approx 2.67 \) and may be regarded as a topological one. The above mentioned thresholds have been observed in several chalcogenide systems such as glasses [8] and thin films [3].

5.2 Coordination number

Nearest neighbour coordination number \( m \) in the ternary system \( Ge_{10}Se_{90-x}Te_x \) \( (x = 0, 10, 20, 30, 40, 50) \) is suitable for testing the validity of topological concepts
because of its large glass forming domain. The average coordination number in $Ge_{10}Se_{50-x}Te_x$ system has been calculated using the relation

$$m = \frac{\alpha N_{Ge} + \beta N_{Se} + \gamma N_{Te}}{\alpha + \beta + \gamma}$$  \hspace{1cm} (5.1)

where $\alpha$, $\beta$ and $\gamma$ are the at.% of Ge, Se and Te respectively and $N_{Ge} = 4$, $N_{Se} = 2$ and $N_{Te} = 3$ are their respective coordination numbers. The calculated coordination number ($m$) values lie in range $2.2 \leq m \leq 2.7$ and are given in Table 5.1.

The calculated values of $m$, listed in Table 5.1, indicate that $m$ increases with increase of Te content. In compositions with Te content i.e. $x = 0$ and 10; the value of $m$ is less than 2.4. According to Phillips [6] these compositions have a floppy or spongy glass network and are assumed to be undercoordinated, while in compositions with Te content $x = 20$, 30, 40 and 50; $m \geq 2.4$. These have a rigid glass network and hence more closely packed structure and are assumed to be overcoordinated. This conclusion is confirmed if correlated with the increases of density with Te content.

5.3 Density and molar volume

Density of bulk samples was measured by Archimedes (buoyancy) method. The apparatus consists of a beaker filled with double distilled water as a reference liquid. A thermometer was placed in the liquid to measure the temperature. The method is first to calculate the weight of the sample in air. Then the sample is placed on the sinker part and is plunged into the beaker in such a way that the sample is covered with at least 10 mm of liquid. After making sure that no bubbles are trapped in between the sample and the sinker the weight of the sample is measured in the liquid. The density of double distilled water ($\rho_{\text{water}}$) is obtained from a calibrated table knowing its temperature. Thus the density of the sample is calculated using the formula

$$\rho = \left[ \frac{w_1}{w_1 - w_2} \right] \rho_{\text{water}}$$  \hspace{1cm} (5.2)

where $w_1$ and $w_2$ are the weight of the sample in air and the weight of the sample in the reference liquid (double distilled water) respectively. Each sample was weighed five times and average density was recorded. The average recorded densities for
Table 5.1 Values of average coordination number \( (m) \), density \( (\rho) \), molar volume \( (V_m) \) and compactness \( (\delta) \) for Ge\(_{10}\)Se\(_{90-x}\)Te\(_x\) \((x = 0, 10, 20, 30, 40, 50)\) glassy alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( m )</th>
<th>( \rho )</th>
<th>( V_m )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(<em>{10})Se(</em>{90})</td>
<td>2.2</td>
<td>4.473</td>
<td>17.96</td>
<td>-0.10278</td>
</tr>
<tr>
<td>Ge(<em>{10})Se(</em>{80})Te(_{10})</td>
<td>2.5</td>
<td>4.395</td>
<td>18.32</td>
<td>-0.09998</td>
</tr>
<tr>
<td>Ge(<em>{10})Se(</em>{70})Te(_{20})</td>
<td>2.4</td>
<td>4.678</td>
<td>18.79</td>
<td>-0.09918</td>
</tr>
<tr>
<td>Ge(<em>{10})Se(</em>{60})Te(_{30})</td>
<td>2.5</td>
<td>4.863</td>
<td>19.11</td>
<td>-0.09301</td>
</tr>
<tr>
<td>Ge(<em>{10})Se(</em>{50})Te(_{40})</td>
<td>2.6</td>
<td>5.028</td>
<td>19.45</td>
<td>-0.08799</td>
</tr>
<tr>
<td>Ge(<em>{10})Se(</em>{40})Te(_{50})</td>
<td>2.7</td>
<td>5.179</td>
<td>19.82</td>
<td>-0.08461</td>
</tr>
</tbody>
</table>
different compositions are given in Table 5.1. This is found that the density of the system increases monotonically with the increase of Te content.

Another parameter related to the density, namely the molar volume \( V_m \) was determined from the density data by the equation

\[
V_m = \frac{1}{\rho} \sum x_i M_i
\]

(5.3)

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 values of \( V_m \) for the prepared compositions are listed in Table 5.1. The molar volume was found to increase with Te content, which is a result of substituting Se atoms with the heavier and larger Te atoms in the glass network.

### 5.4 Compactness

The compactness \( \delta \) of the structure of the glasses is determined from the measured densities of the glasses. The compactness \( \delta \) was calculated using the relation [10-12]

\[
\delta = \frac{\sum c_i A_i}{\rho} - \frac{\sum c_i A_i}{\rho}
\]

(5.4)

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 glass and \( \rho \) is the measured density of the glass. 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 a given solid [13].

Consequently, it is more sensitive to changes in the structure of the glass network as compared to the mean atomic volume. The compositional variation of compactness, characterized by \( m \) of the investigated glassy alloys is shown in Figure 5.4.1. From the figure, it is evident that the compactness increases with the increase of coordination number while a little kink is observed at \( m = 2.4 \), which may be considered in light of constraint theory and rigidity percolation concept [6,14,15].
Figure 5.4.1 Plot of compactness vs. average coordination number for Ge_{10}Se_{50-x}Te_{x} (x = 0, 10, 20, 30, 40, 50) system.
Thus with the increase of Te content in Ge-Se system the system becomes more compact i.e. the prepared compositions are becoming more rigid in structure.

5.5 Lone pair of electrons and glass forming ability

Most of the substances which can solidify in the vitreous state are found to possess structural ‘bridges’, that give rise to tri-dimensional, bi-dimensional or linear heteropolymeric formation. In most glasses, the bridges are formed of elements of group VI and VII. The chalcogen (S, Se, Te) atoms in glass structures have two pairs of lone-pair electrons. The existence of bridging atoms with lone-pair electrons can eliminate the strain force caused by the formation of amorphous materials. In terms of the viewpoint proposed by Pauling [16], the chemical bonds with lone-pair electrons have a character of flexibility. Increasing the number of lone-pair electrons decreases the strain energy in a system, and structures with large numbers of lone-pair electrons favor glass formation. The lone pair of electrons is calculated using the relation

\[ L = V - m \]  

(5.5)

where \( L \) is the number of lone pair electrons, \( V \) is the valance electron which is equal to unshared lone-pair electrons and \( m \) is the average coordination number. The values of \( L \) for different \( m \) are listed in table 5.2.

Figure 5.5.1 shows the variation of lone pair electrons with Te content. It is seen from the figure that the number of lone-pair electrons decreases continuously with the increase of Te in the system. This is caused by the interaction between the Te ion and the lone pair electrons of a bridging Se atom. The interaction decreases the role of lone-pair electrons in the glass formation. Liang [17] introduced a simple criterion for computing the ability of a chalcogenide system to retain its vitreous state; the criterion contains the number of lone-pair electrons which is necessary for obtaining the system in its vitreous state. For a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1. This is clear from the table that the minimum value of lone pair of electrons in present study is 3.1 leading to conclude that the system under study is a good glass former.
Table 5.2 Values of lone pair of electrons (L) for Ge$_{10}$Se$_{30-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) glassy alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$m$</th>
<th>$V$</th>
<th>$L = V - m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{10}$Se$</em>{30}$</td>
<td>2.2</td>
<td>5.8</td>
<td>3.6</td>
</tr>
<tr>
<td>Ge$<em>{10}$Se$</em>{20}$Te$_{10}$</td>
<td>2.3</td>
<td>5.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Ge$<em>{10}$Se$</em>{20}$Te$_{20}$</td>
<td>2.4</td>
<td>5.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Ge$<em>{10}$Se$</em>{20}$Te$_{30}$</td>
<td>2.5</td>
<td>5.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Ge$<em>{10}$Se$</em>{30}$Te$_{40}$</td>
<td>2.6</td>
<td>5.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Ge$<em>{10}$Se$</em>{30}$Te$_{50}$</td>
<td>2.7</td>
<td>5.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Figure 5.5.1 Variation of lone pair of electrons (L) with the Te content.
5.6 Optical band gap

The variation of energy gap with composition in amorphous alloys can be calculated using relation [18]

\[ E_g(AB)(Y) = YE_g(A) + (1-Y)E_g(B) \]  (5.6)

where \( Y \) is the volume fraction of element A, \( E_g(A) \) and \( E_g(B) \) are the optical gaps for A and B elements, respectively. The conversion from atomic composition (at%) or molecular composition (mol %) to volume fraction \( Y \) is made using atomic or molecular mass and density. Figure 5.6.1 shows the variation of theoretically calculated and experimentally observed band gap for \( a\text{-Ge}_{1-x}\text{Se}_{x}\text{Te}_{x} \) thin films. In conclusion both the optical gap \( E_{opt}^{g,th} \) for \( a\text{-Ge}_{10}\text{Se}_{90-x}\text{Te}_{x} \) determined by volume fraction and the optical gap \( E_{opt}^{g,exp} \) calculated using the experimental data decrease with the increase of Te content leading to the conjecture that a modified virtual crystal approach for mixed crystals is acceptable for an amorphous system. The decrease of optical band gap with the increase of Te content is discussed in detail in chapter 4 section 4.3.

5.7 Average heat of atomization

In chalcogenide glasses containing a high concentration of group VI element, the lone-pair form the top of the valence band and the antibonding band forms the bottom conduction band [19]. The optical gap corresponds closely to the energy difference between the top of the valence band and the bottom of the conduction band. Metal atoms can form a dative bond with group VI atoms (lone pair with empty orbital) without any cost of energy, due to the presence of high-energy lone pair on the latter. Dative bonds have corresponding (empty) antibonding levels which could give localized acceptors states in the gap [20].

It is interesting to relate the optical band gap with the chemical bond energy. For this purpose we calculate the heat of atomization. According to Pauling [16], the heat of atomization \( H_s(A-B) \) at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of heat of formation \( \Delta H \) and
Figure 5.6.1 Plot of optical band gap (theoretical and experimental) vs. Te content for $Ge_{10}Se_{90-x}Te_{x}$ ($x = 0, 10, 20, 30, 40, 50$) system.
the average heats of atomization $H_s^A$ and $H_s^B$ that corresponds to the average non-polar bond energy of the two atoms

$$H_s(A - B) = \Delta H + \frac{1}{2}(H_s^A + H_s^B) \quad (5.7)$$

The first term in above equation is proportional to the square of the difference between the electronegativities $\chi_A$ and $\chi_B$ of the two atoms

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (5.8)$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization $\overline{H}_s$ (in kcal per gram-atom) is defined for a compound $A_xB_yC_z$ as a direct measure of the cohesive energy and thus of average bond strength, as

$$\overline{H}_s = \frac{\alpha H_s^A + \beta H_s^B + \gamma H_s^C}{\alpha + \beta + \gamma} \quad (5.9)$$

Obviously the $\overline{H}_s$ values do not contain the heat of formation ($\Delta H$) as part of cohesive energy; however $\overline{H}_s$ is useful parameter for correlating the physical properties of semiconducting compounds. In case of chalcogenide glasses the heat of formation contributes very little towards the average heat of atomization because the electronegativities of the constituent elements i.e. Ge, Se, Te are very similar and in most of the cases of chalcogenide glasses the heat of formation is unknown. In few materials for which heat of formation is known it accounts only 10% of the heat of atomization and is therefore neglected. Hence for binary chalcogenide glasses $H_s(A - B)$ is given by

$$H_s(A - B) = \frac{1}{2}(H_s^A + H_s^B) \quad (5.10)$$

whereas for ternary and higher order compounds, $\overline{H}_s$ is given by the equation (5.9). The heat of atomization for Ge, Se, Te elements [21] and average heat of atomization $\overline{H}_s$ (kcal/g-atom) and average single bond energy $\overline{H}_s/m$ are given in Table 5.3, where $m$ is the average coordination number calculated in section 5.1. From the Table 5.3 it is found that the heat of atomization decreases with the increase of Te content i.e. the average single bond energy decreases. This decrease in the average single bond
Table 5.3 Values of average coordination number \((m)\), average heat of atomization \((\overline{H}_s)\), average single bond energy \((\overline{H}_s/m)\) and heat of atomization for Ge, Se, Te elements in \(\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x\) \((x=0, 10, 20, 30, 40, 50)\) system.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(m)</th>
<th>(\overline{H}_s) (kcal/g-atom)</th>
<th>((\overline{H}_s/m)) (kcal/g-atom)</th>
<th>Element</th>
<th>Heat of atomization (kcal/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.2</td>
<td>53.46</td>
<td>24.30</td>
<td>Ge</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>2.3</td>
<td>53.17</td>
<td>23.00</td>
<td>Se</td>
<td>40.4</td>
</tr>
<tr>
<td>20</td>
<td>2.4</td>
<td>52.78</td>
<td>21.99</td>
<td>Te</td>
<td>46</td>
</tr>
<tr>
<td>30</td>
<td>2.5</td>
<td>52.44</td>
<td>20.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.6</td>
<td>52.10</td>
<td>20.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.7</td>
<td>51.76</td>
<td>19.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
energy with the increase of Te content may be the cause of the decrease in optical band gap.

5.8 Cohesive energy and electronegativity

Using the chemical bond approach (CBA) method [22], the cohesive energy (CE) (the stabilization energy of an infinitely large cluster of material per atom) for investigated samples has been calculated. According to CBA, the bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied and the bond energies are assumed to be additive. Thus the cohesive energies were calculated by summing the bond energies over all bonds expected in the material. Consequently, bonds between like atoms will only occur if there is an excess of certain type of atoms. In the present compositions, the Ge-Se bonds with the highest possible energy (49.1 kcal/mol) are expected to occur first, followed by Se-Te bonds (40.6 kcal/mol). In all the compositions Ge is saturated by Se as compare to Te since Ge-Se bonds (49.1 kcal/mol) are stronger than Ge-Te bonds (37.4 kcal/mol). Up to x = 20 at % composition there is still unsatisfied Se which must be satisfied by Se-Se defect homopolar bonds. For x > 20 at % Te becomes excessive and remain unsatisfied which must be satisfied by Te-Te defect homopolar bonds. Calculated values of CE along with the distribution of chemical bond for all the compositions are tabulated in table 5.4. The results show the decrease in CE of these glassy alloys. Therefore, it can be concluded that the decrease of optical band gap [23,24] with increasing Te content (Fig. 5.7.1) is most probably due to the reduction of the average stabilization energy by Te content. The decrease of CE of the Ge–Se–Te system tends to decrease the energy of the conduction band edge causing a reduction in the gap between bonding ($\sigma$) and antibonding ($\sigma^*$) orbitals and thus resulting a decrease in optical band gap. It should be mentioned that the approach of the chemical bond neglects dangling bond and other valence defects as a first approximation. Also Vander Walls interactions are neglected, which can provide a means for further stabilization by the formation of much weaker links than regular covalent bonds. According to Yamaguchi [21] average single bond energy ($\overline{H}_f/m$), where $\overline{H}_f$ is average heat of atomization and m is average coordination number, is a direct measure of cohesive energy. This is reported in
Figure 5.8.1 Variation of cohesive energy (kcal/mol) and optical band gap (eV) with Te content (at. %) for Ge_{10}Se_{90-x}Te_{x} (x = 0, 10, 20, 30, 40, 50) glassy alloys.
Table 5.4 Values of electronegativity ($\chi$), optical band gap ($E_g^{opt}$), distribution of chemical bonds and cohesive energy (C.E.) for Ge$_{10}$Se$_{90-x}$Te$_x$ ($x = 0, 10, 20, 30, 40, 50$) glassy alloys.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\chi$</th>
<th>$E_g^{opt}$ (eV)</th>
<th>Distribution of Chemical bonds</th>
<th>C.E. (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ge-Se</td>
<td>Se-Te</td>
</tr>
<tr>
<td>0</td>
<td>2.489</td>
<td>1.87</td>
<td>0.2222</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2.442</td>
<td>1.62</td>
<td>0.2500</td>
<td>0.1875</td>
</tr>
<tr>
<td>20</td>
<td>2.394</td>
<td>1.46</td>
<td>0.2857</td>
<td>0.4286</td>
</tr>
<tr>
<td>30</td>
<td>2.348</td>
<td>1.27</td>
<td>0.3333</td>
<td>0.5556</td>
</tr>
<tr>
<td>40</td>
<td>2.303</td>
<td>1.12</td>
<td>0.2424</td>
<td>0.4546</td>
</tr>
<tr>
<td>50</td>
<td>2.259</td>
<td>1.03</td>
<td>0.3061</td>
<td>0.2449</td>
</tr>
</tbody>
</table>
section 5.6 that there is a decrease in average single bond energy with the increase of Te content. So it is interesting to correlate the optical band gap with cohesive energy for Ge-Se-Te glassy alloys.

Thus, both cohesive energy and average single bond energy supports for the decrease in optical band gap with the increase of Te content in Ge_{10}Se_{90-x}Te_x system. Moreover the decrease in optical band gap is also confirmed by the decrease of electronegativity which is calculated using Sanderson’s principle [25]. According to this principle electronegativity of the alloy is the geometric mean of electronegativity of its constituent elements. It is evident from the table 5.4 that optical band gap decreases as electronegativity decreases with the increasing content of Te.

5.9 Conclusion

The average coordination number, density, molar volume, compactness, lone pair of electrons, theoretical optical band gap and average heat of atomization is studied for Ge_{10}Se_{90-x}Te_x (x = 0, 10, 20, 30, 40, 50) glassy alloys. The coordination number increases with the addition of Te on replacing Se. The density and molar volume increases monotonically with the increasing content of Te. Compactness has been found to increase with the increase of Te content showing that structure is becoming rigid. The number of lone pair of electrons decreases with the addition of Te but still, in the present study, has a minimum value 3.1 which is much more than 1 as suggested by Liang for good glass former indicating that the compositions under investigation are good glass forming. The theoretical optical band gap has also been found to decrease with the increase of Te content and is in concordance with the experimental optical band gap. Average heat of atomization (\overline{H_a}) which is a measure of the average binding energy decreases with increase of Te content. The decrease of optical band gap may be correlated with the decrease of average binding energy of the system.
References
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