Theoretical Approach and Physical Analysis of Optimized
$(Ge_{33}Te_{67})_{1-x}Sn_x$ Chalcogenide Glassy Alloys

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Abstract: The effect of tin addition on the physical properties, i.e. coordination number, constraints, fraction of floppy modes, number of lone pair electrons, bond energy, cohesive energy, heat of atomization, ionicity, electronegativity, theoretical energy gap, density, molar volume, compactness, of $(Ge_{33}Te_{67})_{1-x}Sn_x$ (x = 0, 5, 7, 9, 11, 13, 15, 17, 19) bulk glassy alloys was investigated. The density of the glassy alloys is found to increase with increasing Sn content. The molar volume and compactness of the structure of the glass were determined from the measured density. The cohesive energy of the samples has been calculated using a chemical bond approach and is correlated with decrease in the optical energy gap with increase in the Sn content. The heat of atomization was also calculated and correlated with the optical energy gap. It is observed that band gap decreases with the increase of Sn concentration in the system. This variation in the band gap is explained on the basis of change in structure of the system due to the introduction of Sn in Ge-Te-Sn glassy system.

Keywords: Chalcogenide glass, Coordination Number, Lone pair, Cohesive Energy, molar volume, cohesive energy, Lone pair electron.

Introduction

Chalcogenide glasses (ChG’s) with their flexible structure, enormous variation in properties, and almost unlimited ability for doping and alloying are promising candidates for photonic applications due to their attractive optical properties, such as high refractive index, high photosensitivity and large optical nonlinearity. The investigation of the optical properties of ChG’s is of considerable interest and affords critical information about the electronic band structure, optical transitions and relaxation mechanisms. The optical and electrical properties of ChG’s are generally much less sensitive to non-stoichiometry and the presence of impurities is less sensitive than crystalline semiconductors. Moreover, ChG’s are conducive for use in fiber optics and integrated optics since they have many unique optical properties and exhibit a good transparency in the infrared region,[1,2]. Because of their IR transparency, photosensitivity, high optical nonlinearity, and rare-earth doping potential, these glasses have been utilized to fabricate photonic devices such as fibers,[3] planar waveguides,[4] gratings, all-optical switches, and fiber amplifiers,[5].

1. Experimental procedure

Homogeneous massive bulk ingots (2gr) of $(Ge_{33}Te_{67})_{1-x}Sn_x$ (where $x = 0, 5, 7, & 9$ at%) glassy materials were prepared by melt quenching technique[6,7]. The high purity constituent materials were taken in
elemental powders form. Mixture of these powders was then sealed in a quartz ampoule and this ampoule was heated at a maximum temperature about 850 °C for 12 hours. The ampoule was frequently shaken to achieve better homogeneity. Finally the heated ampoule was quenched in liquid nitrogen. To avoid fracture of the tube and glass ingot, and to minimize inner tension induced by a quenching step the ampoules were subsequently returned to the furnace for annealing for 5 h at 40 °C below the glass transition temperature \( T_g \). The nature of the structural phase of the as-prepared samples were confirmed using an X-ray diffraction (XRD) computerized system (model: Ital products ADP 200 diffractometer) with Cu, Ka radiation of wavelength \( \lambda = 0.15406 \text{ nm} \).

2. Results and discussion

3.1. optimization of the sample preparation

Chalcogenide glasses based on tellurium are difficult glass formers. They cannot be prepared over a wide composition range like Se based chalcogenide glasses by the normal melt quenching method where a cooling rate of \( 10^2 \text{ K/s} \) is achieved [6,7]. So that, numerous trials were carried out in order to optimize the quenching process (ampoule size, cooling media, melt temperature, batch weight). It was performed for Ge\(_{33}\)Te\(_{67}\) as can be seen in Fig.1. Trials at 900°C (melt temperature before quenching) clearly show XRD peaks on relatively broad background, of the two crystalline c-GeTe and c-Te phases. At 1100°C, the number of peaks, and its intensity increased and became more sharpness with a simple decrease in Fig.1. XRD pattern of the host sample Ge\(_{33}\)Te\(_{67}\) it’s background broad. At 850°C, Some as a function of quenching temperature. peaks still presents in the XRD pattern of the sample but it’s number and intensity decreased with a some notable increase in the background broad, so that 850°C was a typical temperature for the glassy state. In another trial, which was most useful,

![Graph showing XRD patterns at different quenching temperatures](image)

we increased the rate of quenching by quench the molten of 2gr bulk sample from 850°C in liquid nitrogen, which was the most optimum conditions for the glassy state. Fig.2. confirms the glassy nature by the absence of peaks in the XRD patterns of liquid-N\(_2\) quenched Ge\(_{33}\)Te\(_{67}\). This latter procedure was used for ternary compositions.
2.2. Theoretical Predictions of Some Physical Properties of \((Ge_{33}Te_{67})_{1-x}Sn_x\) and Discussion.

Rigidity theory introduced by J. C. Phillips [8] and later on developed by M. F. Thorpe [9] plays an important role in understanding the mechanical and structural properties of network glasses in terms of average number of mechanical constraints. Thorpe made an assumption that the most important forces between the atoms are the nearest neighbor bond stretching forces and bond bending forces. Weak forces like Vander Waals forces are neglected. The rigidity of network glasses is described as constraints counting or Maxwell counting. Hence, only bond stretching and bond bending constraints are counted. The number of bond-stretching constraints for atoms having m bonds is \(N_a = \langle r \rangle / 2\) since each bond is shared by two atoms. The number of bond-bending constraints is \(N_b = 2\langle r \rangle - 3\), since beyond \(\langle r \rangle = 2\) each new bond introduces two new angles. According to Phillips theory, glass formation will be maximized when the total number of constraints \(N_c = N_a + N_b\) is equal to total number of degrees of freedom. This is possible when average coordination number \(\langle r \rangle\) is equal to 2.4 and is known as rigidity percolation threshold. Ideal mechanical stability is achieved at \(\langle r \rangle = 2.4\) at which the number of inter-atomic force-field constraints per atom equals the number of vector degrees of freedom per atom. Specifically, for \(\langle r \rangle < 2.4\), the network is under-constrained (floppy or spongy) whereas for \(\langle r \rangle > 2.4\), the network is over-constrained (rigid). The floppy-to-rigid transition occurs at \(\langle r \rangle = 2.4\) where properties would exhibit anomalous behavior. According to constraints counting or Maxwell counting [10], the number of floppy modes can be written as:

\[
F = 2 - \frac{5}{6} \langle r \rangle
\]  

2.2.1. Average Coordination Number and Constraints

The average coordination number in ternary compounds \(A_xB_yC_z\) is defined by [11]:

\[
\langle r \rangle = \frac{\alpha N_A + \beta N_B + \gamma N_C}{\alpha + \beta + \gamma}
\]  

Where \(N_A, N_B\) and \(N_C\) are the coordination number of elements A, B and C, respectively. The average coordination number \(\langle r \rangle\) for the system \((Ge_{33}Te_{67})_{1-x}Sn_x\) was calculated, and the corresponding values are
listed in the Table (1). It is evident from the Table (1) that with the increase in the Sn concentration, the average coordination number increases hence average number of the constraints also increases. Since Te atoms have coordination number 2 while Sn atoms have coordination number 4, so $<r>$ is expected to increase with replacing Te by Sn atoms. The increase in the average coordination number increases the degree of cross linking in the net-work. The rise in the degree of cross linking in the net-work gives rise to the rigidity mode in the network which leads to over-constrained, stressed-rigid structures [12]. Also in the Table (1), It has been observed that with increase in Sn content in the system the value of fraction of floppy modes becomes more and more negative, this shows and ensure that the system becomes more and more rigid.

2.2.2. lone pair electrons and glass forming ability.

The numbers of lone-pair electrons are calculated by using the relation $L = V - Z$ where $L$ is the number of lone-pair electrons, $V$ is the valance electrons and $Z$ is the average coordination number [13]. Zhenhua proposed a simple criterion for a binary system and a ternary system, i.e., for a binary system the number of lone-pair electrons must be greater than 2.6 while for a ternary system it must be greater than 1.0 [14]. The number of lone-pair electrons for glassy composition $(Ge_{33}Te_{67})_{1-x}Sn_x$ ($x = 0, 5, 7, 9, 11, 13, 15, 17, 19$) are listed in Table (1). It is inferred from the Table (1) and Figure.3. that with the increase in content of Sn the number of lone pair of electrons decreases continuously for the $(Ge_{33}Te_{67})_{1-x}Sn_x$ glassy system. This result is caused by the interaction between the Sn ion and the lone pair electrons of a bridging Te atom. The interaction decreases the number of lone-pair electrons in the glassy system. According to Zhenhua, lone pair electrons are necessary for obtaining the system in its vitreous state [15,16].

2.2.3. 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 the present $(Ge_{33}Te_{67})_{1-x}Sn_x$ system, the parameter $R$ is given by [17,18]:

$$R = \frac{\gamma . CN(\text{Te})}{\alpha . CN(\text{Ge}) + \beta . CN(\text{Sn})}$$

(3)

where $\alpha, \beta, \gamma$ and $\delta$ are atomic frictions of Ge, Te, Sn 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 [19,20]. 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.

2.2.4. Ionic character of covalent bond.

According to Philips – Thorpe bond constraint theory for coordination number $Z = 2.4$ all bonds are absolutely covalent. But for any other value of $Z$ the covalent bonds have some ionic character, i.e., molecule becomes polar. The percent ionic character or ionicity introduces a tendency towards ordering because of the non-directional character. Using the Pauling formula, the percent ionic character of a bond may be calculated [21].

$$\text{Ionic Character} \% = \left[ 1 - e^\left(\frac{(\chi_A - \chi_B)^2}{4}\right) \right] \times 100$$

(4)

where $(\chi_A - \chi_B)$ is the difference in the electro negativities of atoms A and B. That, there should be a direct connection between bond strength and the glass formations was recognized by a number of investigators [22-25]. High value of bond strength increases the glass forming tendency. Chalcogenide glasses, made from materials such as sulphur, selenium, bismuth, germanium, and tellurium, have predominantly covalent bonds. The amount of covalent character or degree of covalency in the bond of amorphous glass under investigation can be calculated by using the Pauling formula as :
Elements with more than 90% covalent character are more promising for glass formation Table (2). The chemical bonding related atomic parameters such as electro negativity and ionicity provides a mean for classify and understand many basic properties of materials. The electro-negativity has been defined differently by different investigators. Pauling defined electro negativity as the power of an atom or molecule to attract electron to it. Electro-negativity of a composition is defined as the geometric mean of all the constituents forming a compound. The presence of Sn makes the alloy ionic in character. As the amount of covalent character between the elements of the present system (Ge\textsubscript{33}Te\textsubscript{67})\textsubscript{1-x}Sn\textsubscript{x} is exceeding the limit of 90%, so this combination is very much promising as far as glass formation is concerned.

Table .1. describes the values of the average coordination number \(< r >\), number of constraints of bond stretching (Na), constraints of bond bending (Nb), average number of constraints (Nc), number of floppy modes, deviation to stoichiometry (R) and number of lone pair electrons for (Ge\textsubscript{33}Te\textsubscript{67})\textsubscript{1-x}Sn\textsubscript{x} system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>At % Sn</th>
<th>(&lt; r &gt;)</th>
<th>Na</th>
<th>Nb</th>
<th>Nc</th>
<th>L.P</th>
<th>R</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge\textsubscript{33}Te\textsubscript{67}</td>
<td>0</td>
<td>2.66</td>
<td>1.33</td>
<td>2.32</td>
<td>3.65</td>
<td>2.68</td>
<td>1.02</td>
<td>-0.08</td>
</tr>
<tr>
<td>Ge\textsubscript{31.35}Te\textsubscript{63.65}Sn\textsubscript{5}</td>
<td>5</td>
<td>2.73</td>
<td>1.37</td>
<td>2.46</td>
<td>3.83</td>
<td>2.54</td>
<td>0.88</td>
<td>-0.10</td>
</tr>
<tr>
<td>Ge\textsubscript{30.69}Te\textsubscript{62.31}Sn\textsubscript{7}</td>
<td>7</td>
<td>2.75</td>
<td>1.38</td>
<td>2.56</td>
<td>3.88</td>
<td>2.50</td>
<td>0.83</td>
<td>-0.10</td>
</tr>
<tr>
<td>Ge\textsubscript{30.03}Te\textsubscript{60.97}Sn\textsubscript{9}</td>
<td>9</td>
<td>2.78</td>
<td>1.39</td>
<td>2.56</td>
<td>3.95</td>
<td>2.44</td>
<td>0.78</td>
<td>-0.11</td>
</tr>
<tr>
<td>Ge\textsubscript{29.37}Te\textsubscript{59.63}Sn\textsubscript{11}</td>
<td>11</td>
<td>2.81</td>
<td>1.41</td>
<td>2.62</td>
<td>4.03</td>
<td>2.38</td>
<td>0.74</td>
<td>-0.12</td>
</tr>
<tr>
<td>Ge\textsubscript{28.71}Te\textsubscript{58.29}Sn\textsubscript{13}</td>
<td>13</td>
<td>2.83</td>
<td>1.42</td>
<td>2.66</td>
<td>4.08</td>
<td>2.34</td>
<td>0.70</td>
<td>-0.13</td>
</tr>
<tr>
<td>Ge\textsubscript{28.05}Te\textsubscript{56.95}Sn\textsubscript{15}</td>
<td>15</td>
<td>2.86</td>
<td>1.43</td>
<td>2.72</td>
<td>4.15</td>
<td>2.24</td>
<td>0.65</td>
<td>-0.14</td>
</tr>
<tr>
<td>Ge\textsubscript{27.39}Te\textsubscript{55.61}Sn\textsubscript{17}</td>
<td>17</td>
<td>2.89</td>
<td>1.45</td>
<td>2.78</td>
<td>4.23</td>
<td>2.22</td>
<td>0.63</td>
<td>-0.15</td>
</tr>
<tr>
<td>Ge\textsubscript{26.73}Te\textsubscript{54.27}Sn\textsubscript{19}</td>
<td>19</td>
<td>2.91</td>
<td>1.46</td>
<td>2.82</td>
<td>4.28</td>
<td>2.18</td>
<td>0.59</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

Table .2. Electronegativity Relative probability of bond formation, Calculated iconicity and covalent character for the (Ge\textsubscript{33}Te\textsubscript{67})\textsubscript{1-x}Sn\textsubscript{x} system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>x</th>
<th>Relative probability of bond formation at Bond</th>
<th>Bond energy (K.cal)</th>
<th>27 °C</th>
<th>850 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge\textsubscript{33}Te\textsubscript{67}</td>
<td>2.070</td>
<td>Ge-Ge</td>
<td>37.60</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ge\textsubscript{31.35}Te\textsubscript{63.65}Sn\textsubscript{5}</td>
<td>2.065</td>
<td>Ge-Te</td>
<td>37.44</td>
<td>7.13×10\textsuperscript{-1}</td>
<td>9.21×10\textsuperscript{-1}</td>
</tr>
<tr>
<td>Ge\textsubscript{30.69}Te\textsubscript{62.31}Sn\textsubscript{7}</td>
<td>2.063</td>
<td>Ge-Sn</td>
<td>37.41</td>
<td>6.27×10\textsuperscript{-1}</td>
<td>9.21×10\textsuperscript{-1}</td>
</tr>
<tr>
<td>Ge\textsubscript{30.03}Te\textsubscript{60.97}Sn\textsubscript{9}</td>
<td>2.060</td>
<td>Sn-Sn</td>
<td>34.20</td>
<td>3.20×10\textsuperscript{3}</td>
<td>2.46×10\textsuperscript{4}</td>
</tr>
<tr>
<td>Ge\textsubscript{29.37}Te\textsubscript{59.63}Sn\textsubscript{11}</td>
<td>2.058</td>
<td>Te-Sn</td>
<td>34.16</td>
<td>2.99×10\textsuperscript{3}</td>
<td>2.42×10\textsuperscript{4}</td>
</tr>
<tr>
<td>Ge\textsubscript{28.71}Te\textsubscript{58.29}Sn\textsubscript{13}</td>
<td>2.056</td>
<td>Te-Te</td>
<td>33.00</td>
<td>4.21×10\textsuperscript{4}</td>
<td>1.50×10\textsuperscript{4}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Amount of covalent character</th>
<th>Ionic character %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-Te</td>
<td>99.79</td>
<td>0.20</td>
</tr>
<tr>
<td>Ge-Sn</td>
<td>99.94</td>
<td>0.06</td>
</tr>
<tr>
<td>Te-Sn</td>
<td>99.51</td>
<td>0.49</td>
</tr>
</tbody>
</table>
2.2.5. Heat of Atomization

Heat of atomization ($H_s$) is defined as the change in enthalpy when one mole of compound converts into gas atoms (i.e. free atoms). The average heat of atomization for a compound $(Ge_{3x}Te_{x})_{1-x}Sn_x$ is a direct measure of the cohesive energy [26].

$$H_s = \frac{\alpha H_{s}(Ge) + \beta H_{s}(Te) + \gamma H_{s}(Sn)}{\alpha + \beta + \gamma} \quad (6)$$

The values of heat of atomization of Ge, Te, and Sn are 90, 47, 72 kcal/g–atom respectively. The values of average heat of atomization increase with the addition of Sn content, this shows that the system move towards the more rigid side and hence rigidity of the system increases. The values of $H_s$ are listed in Table (3).

2.2.6. Bond Energy, Distribution of Bonds and Cohesive Energy

The possible bonds formed in our quaternary chalcogenide system of $(Ge_{3x}Te_{x})_{1-x}Sn_x$ are Ge-Te, Te-Sn, Ge-Ge and Sn-Sn. According to chemical bond approach (CBA) [27] combination in the atoms of different type take place more easily rather than in the atoms of same type. These bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is saturated. The bond formation in the atoms of similar kind takes place only when there is excess of similar atoms. The Ge-Te glassy system is a covalent chalcogenide system. The bond energy of heteropolar bonds can be estimated by the Pauling method in terms of the the bond energy of homopolar bonds and the electronegativity of the atoms involved. The bond energy $E (A - B)$ of heteronuclear bond can be calculated by using the following equation [28].

$$D(A - B) = [D(A - A)D(B - B)]^{1/2} + 30(\chi_A - \chi_B)^2 \quad (7)$$

$D(A - A)$ and $D(B - B)$ are the bond energies of homonuclear bonds. $\chi_A$ and $\chi_B$ are the electronegativity values of A and B elements respectively. The bond energy of the homopolar bonds $E_{Ge-Ge}$, $E_{Te-Te}$ and $E_{Sn-Sn}$ used here are 37.6 Kcal/mol, 33 Kcal/mol and 34.2 Kcal/mol and the electronegativity value for Ge, Te and Sn are 2.01, 2.55 and 1.96 respectively. By using the Equation (7) values of $E_{Ge-Te}$, $E_{Te-Sn}$ and $E_{Ge-Sn}$ have been calculated and are given as 37.44 Kcal/mol, 34.16 Kcal/mol and 37.41 Kcal/mol respectively.

The bonds are formed in order of decreasing bond energy. Ge-Te bonds having maximum energy are formed first followed by Te-Sn and Sn-Sn bonds. As these bond energies are assumed to be additive, so the cohesive energies can be calculated by summing the bond energies over all possible bonds in a compound.
Cohesive energy measures the average bond strength of the system and is defined as stabilization energy of the large cluster of material per atom. Cohesive energy is calculated as:

\[ CF = \sum C_i E_i \] (8)

where \( C_i \) is the probability of formation of expected bonds and \( E_i \) is energy of the corresponding bond present in the system[29]. Chemical distribution of bonds and cohesive energy for the composition \( c_{SnTeGe} \) are listed in Table (3). It is clear that cohesive energy of the composition decreases as Sn content in the system increases. Cohesive energy decreases because weaker Te-Sn bonds increase at the cost of stronger Ge-Te bonds.

Electronegativity of the composition is defined as geometric mean of all the constituents forming a compound. Since the bond formulation with Sn are partially ionic in nature and produces ionic character in the material. This weakens the network and deviate the structure towards fragility. The decrease in cohesive energy decreases the energy of conduction band edge that causes a decrease in the gap between bonding and antibonding orbitals and hence optical energy gap decreases [11].

2.2.7. Electronegativity, theoretical energy gap

The electronegativity has been calculated using Sanderson’s principle [30]. According to this principle, electronegativity of the alloy is the geometric mean of electronegativity of its constituents; The electronegativity of the system is decreasing with increasing content of Sn, Table (2).

The theoretical energy gap \( (E_{\text{th}}) \) is the energy difference between the top of valence band and bottom of the conduction band. Theoretical energy gap has been calculated using Shimakawa’s relation [31],

\[ E_{\text{th}} (Ge - Te - Sn) = \alpha E_g (Ge) + \beta E_g (Te) + \gamma E_g (Sn) \] (9)

where \( \alpha \), \( \beta \), \( \gamma \) are the volume fractions and \( E_g (Ge) \), \( E_g (Te) \), \( E_g (Sn) \) are the energy gaps of Ge, Te and Sn respectively. There is a correlation between the electronegativity and energy gap given by Kastner [32,33]. In chalcogenide glasses valence band is formed by the unshared or lone–pair electron of p–orbital. Te is an electronegative element with \( \chi = 2.55 \) and have a lone–pair electron in its p–orbital and the energy of this lone–pair electron is high. Sn whose electronegativity \( (\chi = 1.96) \) is less than Te and Ge element acts like an electropositive element. On the addition of such electropositive element, the energy of lone–pair state further increases. This leads to the broadening of valance band inside the forbidden gap. Hence, the energy gap and electronegativity decreases with the addition of Sn content.
Table 3. Distribution of chemical bonds, (CF) \( KJ / mol \), \( E_{gh} \) and \( H_s \) for \((Ge_{0.67}Te_{0.33})_{x-16733}Sn_x\) system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>At % Sn</th>
<th>( H_s ) KJou/mol</th>
<th>( E_{gh} ) (ev)</th>
<th>Distribution of Chemical Bonds</th>
<th>CF Kcal/atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(<em>{33})Te(</em>{67})</td>
<td>0</td>
<td>256.4</td>
<td>0.465</td>
<td>Ge-Te 0.985 Te-Sn 0.00 Sn-Sn 0.00 Te-Te 0.00</td>
<td>37.3</td>
</tr>
<tr>
<td>Ge(<em>{31.35})Te(</em>{66.65})Sn(_3)</td>
<td>5</td>
<td>258.7</td>
<td>0.446</td>
<td>Ge-Te 0.862 Te-Sn 0.013 Sn-Sn 0.124 Te-Te 0.015</td>
<td>37.0</td>
</tr>
<tr>
<td>Ge(<em>{30.69})Te(</em>{62.31})Sn(_7)</td>
<td>7</td>
<td>259.6</td>
<td>0.438</td>
<td>Ge-Te 0.814 Te-Sn 0.012 Sn-Sn 0.173 Te-Te 0.00</td>
<td>36.8</td>
</tr>
<tr>
<td>Ge(<em>{29.03})Te(</em>{60.97})Sn(_9)</td>
<td>9</td>
<td>260.5</td>
<td>0.430</td>
<td>Ge-Te 0.769 Te-Sn 0.012 Sn-Sn 0.219 Te-Te 0.00</td>
<td>36.7</td>
</tr>
<tr>
<td>Ge(<em>{28.37})Te(</em>{59.63})Sn(_{11})</td>
<td>11</td>
<td>261.4</td>
<td>0.423</td>
<td>Ge-Te 0.728 Te-Sn 0.011 Sn-Sn 0.261 Te-Te 0.00</td>
<td>36.5</td>
</tr>
<tr>
<td>Ge(<em>{27.81})Te(</em>{58.20})Sn(_{13})</td>
<td>13</td>
<td>262.3</td>
<td>0.415</td>
<td>Ge-Te 0.688 Te-Sn 0.010 Sn-Sn 0.301 Te-Te 0.00</td>
<td>36.4</td>
</tr>
<tr>
<td>Ge(<em>{27.05})Te(</em>{56.95})Sn(_{15})</td>
<td>15</td>
<td>263.2</td>
<td>0.408</td>
<td>Ge-Te 0.652 Te-Sn 0.010 Sn-Sn 0.339 Te-Te 0.00</td>
<td>36.3</td>
</tr>
<tr>
<td>Ge(<em>{27.89})Te(</em>{55.61})Sn(_{17})</td>
<td>17</td>
<td>264.2</td>
<td>0.399</td>
<td>Ge-Te 0.617 Te-Sn 0.009 Sn-Sn 0.374 Te-Te 0.00</td>
<td>36.2</td>
</tr>
<tr>
<td>Ge(<em>{25.73})Te(</em>{54.27})Sn(_{19})</td>
<td>19</td>
<td>265.1</td>
<td>0.392</td>
<td>Ge-Te 0.585 Te-Sn 0.009 Sn-Sn 0.407 Te-Te 0.00</td>
<td>36.1</td>
</tr>
</tbody>
</table>

2.2.8. Density, Molar Volume and Compactness

Density (d) is an important physical parameter and it measures the rigidity of the system. The density of the investigated glassy samples has been determined by the hydrostatic method within ± (0.05-0.1) % [34]. A small piece of Ge crystal was used as a reference material to determine the Toluene density. The density of each sample has been calculated by the following equation:

\[
d_{sample} = \frac{W_1}{W_1 - W_2} d_{Toluene}
\]  

(10)

Where: \( W_1 \) is the weight of the sample in air, \( W_2 \) is the weight of the sample in toluene, and \( d_{Toluene} \) is the density of the toluene , which calculated according to the formula :

\[
d_{Toluene} = \frac{W'_1 - W'_2}{W'_1} d_{Ge}
\]

(11)

Where: \( W'_1 \) is the weight of the Ge crystal in air, \( W'_2 \) is the weight of the Ge crystal in toluene , and \( d_{Ge} \) is the density of crystalline Ge. The obtained results listed in Table (4) are the average of three measurements, at room temperature, taken from three different parts of the same glassy samples. The results show that the addition of Sn to \( GeTe_{67} \) leads to monotonic increase in the density from 5.92 g/cm\(^3\) (\( GeTe_{67} \)) to 6.10 g/cm\(^3\) (\( Ge_{26.73}Te_{54.27}Sn_{19} \)) g/cm\(^3\).

The corresponding density values \( d_{th} \) were calculated theoretically using Myuller’s formula [35]:

\[
d_{th} = \left[ \sum P_i / d_i \right]^{-1}
\]

(12)

Where \( P_i \) is the fraction weight of the \( i^{th} \) structural unit and \( d_i \) is the density of the \( i^{th} \) structural unit, and the calculated values \( d_{th} \) are shown together with \( d_{ex} \) in the same Table (4). It is clear from these tabulated values that the density of investigated system increases by addition of Sn content. Fig (4) shows the relation between density and Sn content for the investigated compositions.

The change in density is attributed to the change in both atomic weight and atomic volume of the constituent elements. As the structural modifications take place, higher density \( Sn \) (7.3gr/cm\(^3\)) atoms replace
low density Ge (5.33 gr/cm$^3$) and Te (6.23 gr/cm$^3$) atoms. Thus, the density of the system increases for each composition with increase in Sn at. %. The linearity increasing of $d_{ex}$, $d_{th}$, shown in Fig (4), is in agreement with the result of Hilton et al [36] and Hilton and Hayes [37], who found that the densities of the chalcogenide glasses increased linearly with their molecular weights.

Molar volume ($V_m$) has been calculated using value of density expression [38];

$$V_m = \frac{1}{\rho} \sum x_i m_i$$  \hspace{1cm} (13)

where $x_i$ is the atomic fraction of ith component and $m_i$ is its atomic mass. The values of $d$ and $V_m$ are listed in Table (4) and have been found to increase with increasing content of Sn. Further, the addition of Sn content increases the crosslinking in the network and hence rigidity increases due to which density increases.

Compactness ($\delta$) measures the normalized change of the mean atomic volume on chemical interaction with the elements forming the network of a given solid [38]. $\delta$ has been calculated using the relation:

$$\delta = \frac{\sum C_i A_i - \sum C_i A_i}{\rho} \hspace{1cm} (14)$$

where $C_i$ is the atomic fraction, $w_i$ is the atomic weight and $\rho_i$ is the atomic density of the $i$th element of the glass[38]. The compactness for the system increases with the Sn addition Table (4). The density of the system increases with increasing Sn content. This leads to an increase in the compactness of the system.

**Table 4. Values of theoretical and experimental density($d_{ex}$, $d_{th}$), molar volume ($V_m$) and Compactness ($\delta$) for (Ge$_{33}$Te$_{67}$)$_x$, Sn$_{1-x}$ system.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>At % Sn</th>
<th>$d_{ex}$ g/cm$^3$</th>
<th>$d_{th}$ g/cm$^3$</th>
<th>$V_m$ (Cm$^3$/mol)</th>
<th>$\delta$</th>
<th>$&lt;r&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{33}$Te$</em>{67}$</td>
<td>0</td>
<td>5.92</td>
<td>5.97</td>
<td>18.49</td>
<td>-0.0097</td>
<td>2.67</td>
</tr>
<tr>
<td>Ge$<em>{31.35}$Te$</em>{68.65}$Sn$_5$</td>
<td>5</td>
<td>5.98</td>
<td>6.00</td>
<td>18.38</td>
<td>-0.0094</td>
<td>2.73</td>
</tr>
<tr>
<td>Ge$<em>{30.69}$Te$</em>{62.31}$Sn$_7$</td>
<td>7</td>
<td>5.99</td>
<td>6.03</td>
<td>18.38</td>
<td>-0.0117</td>
<td>2.75</td>
</tr>
<tr>
<td>Ge$<em>{30.03}$Te$</em>{60.97}$Sn$_9$</td>
<td>9</td>
<td>6.01</td>
<td>6.03</td>
<td>18.35</td>
<td>-0.0123</td>
<td>2.78</td>
</tr>
<tr>
<td>Ge$<em>{29.37}$Te$</em>{59.63}$Sn$_{11}$</td>
<td>11</td>
<td>6.02</td>
<td>6.06</td>
<td>18.36</td>
<td>-0.0145</td>
<td>2.81</td>
</tr>
<tr>
<td>Ge$<em>{28.71}$Te$</em>{58.29}$Sn$_{13}$</td>
<td>13</td>
<td>6.04</td>
<td>6.08</td>
<td>18.33</td>
<td>-0.0151</td>
<td>2.83</td>
</tr>
<tr>
<td>Ge$<em>{28.05}$Te$</em>{56.95}$Sn$_{15}$</td>
<td>15</td>
<td>6.07</td>
<td>6.11</td>
<td>18.13</td>
<td>-0.0141</td>
<td>2.86</td>
</tr>
<tr>
<td>Ge$<em>{27.39}$Te$</em>{55.61}$Sn$_{17}$</td>
<td>17</td>
<td>6.08</td>
<td>6.14</td>
<td>18.27</td>
<td>-0.0164</td>
<td>2.89</td>
</tr>
<tr>
<td>Ge$<em>{26.73}$Te$</em>{54.22}$Sn$_{19}$</td>
<td>19</td>
<td>6.10</td>
<td>6.17</td>
<td>18.24</td>
<td>-0.0170</td>
<td>2.91</td>
</tr>
</tbody>
</table>


The addition of Sn to $(Ge_{35}Te_{65})_{1-x}Sn_x$ glassy alloy leads to change in the physical properties. The coordination number and heat of atomization increases because coordination number and heat of atomization of Sn are greater than that of Ge and Te. The increase of average coordination gives an indication that the number of constraints increases hence the value of optical band gap will strongly depends upon $H_s$. Due to decrease in average stabilization energy the average heat of atomization ($H_s$) and cohesive energy decrease with increase in Sn content. The value of the theoretical band gap ($E_{th}$) has been decreased with increase in Sn content. This is due to decrease in the cohesive energy and the electronegativity of the system because optical band gap is a bond sensitive property. It can also be observed that the Ge-Te bond having more probability of formation than the Te-Sn bond. The stoichiometry R decreases due to decrease in contents of chalcogen Te and hence increases in content of Sn.
References


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