Physical Topology and Bonds Arrangement of As-Se-Tl Chalcogenide Glasses

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Abstract: Topological consideration of As\textsubscript{10} Se\textsubscript{80-x} Tl\textsubscript{x} (5\% \leq x \leq 35\% at.) chalcogenide glasses prepared by melt quenching technique, is reported and discussed in light of the ordered bond network model (ORBNM). The DSC results show that the glass transition temperature, T\textsubscript{g} is not linearly decrease with increasing Tl content. The crystallization temperature, the thermal stability of the glass and the glass formation ability increases with increasing Tl content until 20 at.% Tl and then decreases. According to CONM the possibility bond distribution is given. An attempt has been made to correlate the optical energy gap, E\textsubscript{g} and estimated bond energy, E\textsubscript{b} through the Manca relationship:

\[ E_b = 1.61(E_g - 3.11) \]

Key word: Chalcogenide • Glasses • Topological • Floppy • Rigid

INTRODUCTION

The growing interest in the investigation of the properties of chalcogenide glasses stems from the actual and potential technological applications of these materials in solid state devices[1]. The As-Se-Tl chalcogenide glasses are semiconducting and infrared transmitting and have gained much industrial and research interest. A wide compositional range of glass formation of the As-Se-Tl system was observed and reported by many authors [2-5]. The measurements of DC conductivity of glassy As\textsubscript{8}Se\textsubscript{8} containing Tl have been performed by many investigators [6-8]. Also the effect of the addition of Tl to As\textsubscript{9}Se\textsubscript{8} on differential thermal analysis [9], the conductivity and absorption coefficient [4] and the structural studies [10] have already been demonstrated. The composition dependence of physical property of thin films As-Se-Tl thin films have already been studied [11-13]. They show a continuous change in the physical properties of these alloys with change in chemical composition.

The ordered bond network model [14,15], also known as the chemically ordered network model, is usually used to explain the peculiarities observed in the compositional dependence of physical properties of chalcogenide glasses[16-18]. According to this model, the structure of the glass is assumed to be composed of three-dimensional (3-D) cross-linked structural units of the stable chemical compounds of the system with excess, if any, of the elements dispersed among these units[19].

The model of bond arrangement[14,20] and topological models such as the constraints model[21,22] and the structural transition model [23], have been used in the interpretation of the compositional dependence of these properties.

The composition dependence of the mean atomic volume, V\textsubscript{g}, a fundamental physicochemical property, is an important aspect in the investigation of chalcogenide glasses. In this paper the compositional dependence of V\textsubscript{g} for glasses belonging to the As-Se-Tl system, is reported and discussed in light of the ordered bond network model (OBNM). The composition dependence of the glass formation ability, K\textsubscript{g} and the thermal stability of glass, T\textsubscript{g}-T\textsubscript{p} have been studied. An attempt is made to estimate the possible bond arrangement of ternary chalcogenide As\textsubscript{10} Se\textsubscript{80-x} Tl\textsubscript{x} (5\% \leq x \leq 35\% at.) glass is given. Estimated band gap, E\textsubscript{g}, has been calculated and compared to the experimental optical band gap, E\textsubscript{opt} through the Manca relationship.

Experimental Procedure: Bulk glasses of As\textsubscript{10} Se\textsubscript{80-x} Tl\textsubscript{x} (5\% \leq x \leq 35\% at.) system were prepared by a standard melt quenching techniques. The appropriate quantities of pure As, Se and Tl (5N) required to prepared 5 g of each composition were introduced in a dry clean silica tubes, which were sealed under vacuum of 10\textsuperscript{-5} Torr.
The synthesis was carried out in an oscillatory furnace in the following sequence, the temperature was raised to 350 °C for 4 h and then to 650 °C for a further 2 h and, finally, a furnace temperature was gradually raised to 875°C and kept at this temperature for approximately 16 h. The molten materials were then quenched in an ice water mixture to obtain the glasses.

The Archimedian’s method was used for the measurement of the, \( \rho_g \), of as-prepared glasses The weight of a piece of the As-Se-Tl alloys was measured in air and in water using electronic balance. The accuracy of the density measurement, is estimated to be better than ±2%.

Thermal studies have been carried out on the bulk glasses using a Shimadzu DSC-50 differential scanning calorimetry (DSC). The DSC thermograms of 15 mg of samples were recorded as the temperature of the sample was increased from room temperature to about 800 k at a uniform rate (α) 10 k/min. The values of the glass transition temperature, \( T_g \), the crystallization temperature, \( T_c \) and the melting point, \( T_m \) were determined with accuracy ±0.1 k.

The experimental optical band gap, \( E_g \), has been found using the Tauc Plot \((\alpha hv)^{2\alpha} = f(hv)\). The absorption coefficient \( \alpha \) has been calculated from the optical transmission spectra of the samples. Technological and experimental details are given in [13,24].

RESULT AND DISCUSSION

Topological Consideration: The densities of the glasses, \( \rho_g \), were calculated using the formula:

\[
\rho_g = \left[ \frac{w_a}{(w_a - w_l)} \right] \rho_i
\]

where \( w_a \) and \( w_l \) are, respectively, the weight of the sample in air and in liquid (water) and \( \rho_i \) is the density of the immersion liquid (water) which is equal to 1g cm\(^{-3}\) at room temperature. The values of \( \rho_g \) for glasses \( \text{As}_{20} \text{Se}_{60-x} \text{Tl}_x (5 \leq x \leq 35 \text{ at.\%}) \) system, measured by using Archimedian technique and the calculated density by using mixing rule are shown in Fig. 1. The densities of pure As, Se and Tl used in the mixing rule calculation were 5.73 g/cm\(^3\), 4.82 g/cm\(^3\) and 11.89 g/cm\(^3\), respectively [2]. It can be noticed that the experimental densities are less than that of the calculated ones. Its expected since the densities of the As, Se and Tl crystalline solids at room temperature were used in the mixing rule calculation. In the most cases, amorphous materials have a smaller density than their respective crystalline materials [2]. Such linear variation in Fig. 1, indicates the additive nature of the density as a character of glassy structure [8].

The mean atomic volumes of the glasses, \( V_g \), were calculated from the formula:

\[
V_g = \sum_i \left( c_i A_i / \rho_i \right)
\]

where \( c_i \) and \( A_i \) are the atomic concentration and the atomic weight of the \( i \)-th component, respectively. The mean atomic volume, \( V_g \), as a function of the amount of Tl at.% in the glass is depicted in Fig. 2. It is worth noting that this figure can be looked at as consists of two regions; the first one extending up to Tl-content <20 at.%, while the second one starts at Tl-content > 20 at.% and it exhibits a clear maximum at Tl-content = 20 at.%.

The general formula representing this system can be written as \( \text{As}_{20} \text{Se}_{60-x} \text{Tl}_x \text{Se}_y + \Delta c \), where \( \Delta c \) an excess of Se or Tl elements. On the basic of the OBNM, the glass structure

Fig. 1: Shows the variation of \( \rho_g \) with Tl content for \( \text{As}_{20} \text{Se}_{60-x} \text{Tl}_x (5 \leq x \leq 35 \text{ at.\%}) \) chalcogenide glasses

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of this tie-line composition, defined as the line joining the crystalline compounds As\_5\_Se\_5 and Tl\_5\_Se\_5, is visualized to be composed of 3-D completely cross-linked As\_5\_Se\_5-type and Tl\_5\_Se\_5-type structural units consisting of heteropolar bonds only, with no excess of elements for 20 at.\% Tl. At Tl content < 20 at.\% the glass structure defined as a composed of 3-D completely cross-linked As\_5\_Se\_5-type and Tl\_5\_Se\_5-type structural units with an excess of Se-element. At Tl content > 20 at.\%, it can be defined as a composed of 3-D completely cross-linked of As\_5\_Se\_5 and Tl\_5\_Se\_5 structural units with an excess of Tl-elements. Therefore, the observed maximum in \( V_a \) for the tie-Line composition which contains 20 at.\% Tl is ascribed to chemical order effects tacking place at this composition. These chemical ordering effects occurring at the tie line composition, were recently reported for Ge-In-Se and Ge-S-Ag glasses.[17,19]

Lately, the mean coordination number has been widely used for the description of the structure of network glasses. It is defined as the average number of bonded neighbours per atom in the structure. For As\_x\_Se\_y\_Tl\_z system the the mean coordination number <z> is given by:

\[
<z>= (xN_{As} + yN_{Se} + zN_{Tl})
\]

Where \( x, y \) and \( z \) are the respective atomic concentration of As, Se and Tl and \( N_{As}, N_{Se} \) and \( N_{Tl} \) are the coordination numbers of As, Se and Tl respectivity. The evaluation of <z>, requires the knowledge of the coordination numbers of the individual atoms in the amorphous alloy. It is well known that the coordination number of Se atoms in S-containing alloys conform with the Mott (8-N) rule [25] where \( N \) is the number of valence electrons. Therefore, coordinations of 3, 2 and 3 for As, Se and Tl atoms, respectively, are used for the evaluation of <z> and Eq. (3) for As\_3\_Se\_2\_Tl, alloys reduces to the formula

\[
<z>=2.2+0.01x
\]

The dependence of Tl-content on the mean value of <z> are listed in Table 1.

The variation of \( V_a \) with <z> are depicted in Figure 3. It is worth noting that this figure can be looked at as consists of two regions; the first one extending up to <z> < 2.4, while the second one starts at <z> > 2.4 and is characterized by a maximum at <z>=2.4. This maximum is

<table>
<thead>
<tr>
<th>Tl (at.%)</th>
<th>&lt;z&gt;</th>
<th>( T_m ) (K)</th>
<th>( T_c ) (K)</th>
<th>( T_{cr} ) (K)</th>
<th>( T_{m-c} ) (K)</th>
<th>( K_{as} )</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>2.25</td>
<td>356</td>
<td>443</td>
<td>713</td>
<td>87</td>
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<tr>
<td>10</td>
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<td>448</td>
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</tr>
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<td>353.5</td>
<td>583</td>
<td>701</td>
<td>230.5</td>
<td>2.004</td>
</tr>
<tr>
<td>20</td>
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<td>593</td>
<td>697</td>
<td>241</td>
<td>2.410</td>
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<tr>
<td>25</td>
<td>2.45</td>
<td>351.5</td>
<td>538</td>
<td>693</td>
<td>186.5</td>
<td>1.218</td>
</tr>
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<td>2.5</td>
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<td>513</td>
<td>687</td>
<td>164</td>
<td>0.943</td>
</tr>
<tr>
<td>35</td>
<td>2.55</td>
<td>348</td>
<td>463</td>
<td>683</td>
<td>115</td>
<td>0.523</td>
</tr>
</tbody>
</table>
Fig. 3: Shows the variation of the mean atomic volume, \( V_0 \), with coordination number \( \langle z \rangle \) for \( \text{As}_{200} \text{Se}_{80-x} \text{TI}_x (5 \leq x \leq 35 \text{ at.\%}) \) chalcogenide glasses.

Fig. 4: Shows the variation the number of floppy with TI content for \( \text{As}_{200} \text{Se}_{80-x} \text{TI}_x (5 \leq x \leq 35 \text{ at.\%}) \) chalcogenide glasses.

understood using the notion of rigidity percolation in covalent glasses which was initially presented by Phillips and subsequently modified by Thorpe [22,26-28]. They developed a mean field theory for the number of zero-frequency modes in a covalent network glass. Taking into account the constraints by bond-stretching and bond-bending force and equating the number of topological constraints per atoms, \( N_c = \langle z \rangle / 2 + (2 \langle z \rangle - 3) \) where \( \langle z \rangle \) is the constant on bond length and \( (2 \langle z \rangle - 3) \) is the number of constraints on the bond angle to the number of degrees of freedom per atom \( (N_z=3) \), rigidity percolation exists at \( \langle z \rangle = 2.4 \). Networks with \( N_c < N_s \) are referred to as under-cross-linked and contain large floppy regions with a few rigid inclusions while those with \( N_c > N_s \), referred to as over-cross-linked, the rigid regions have percolated to form a solid with a few floppy inclusions. The network with \( N_c = N_s \), for which \( \langle z \rangle = 2.4 \), is a percolation threshold at which the transition from a floppy to a rigid takes place and at which the mechanical stability of the network is optimized[29]. The stability of the network with \( \langle z \rangle = 2.4 \) is associated with atomic arrangements that become more tightly bound and having shorter bond lengths thus resulting in a maximum in \( V_0 \), as shown in figure 2. The obseved thresholded in this work at \( \langle z \rangle = 2.4 \) making the floppy-to-rigid transition in glasses with 20 at.\% TI.

The fraction, \( F \), of zero-frequency (floppy) modes \( F \) is given by[30]:

\[
F = 2 - 5/6 \langle z \rangle
\]  

(5)

Figure 4 shows the fraction of floppy modes, \( F \), against TI content, we can notice that the values of \( F \) decreases with increasing TI content reaches to zero at 20 at.\% TI. For TI content < 20 at.\%, the number of floppy
modes, equal to 0.125. Finally, for Tl content > 20 at.%, the number of floppy has a negative values, this means that, the network becomes rigid as it goes through a phase transition from floppy to rigid at 20 at.% Tl.

**Glass Forming Ability:** From the DSC thermograms obtained at a heating rate of 10 K / min for our system. The values of glass transition temperature, $T_g$, crystallization temperature, $T_c$, and melting point, $T_m$, were measured to an accuracy ±1K. Numerical values of these quantities as well as the values of interval ($T_c - T_g$) and the ration $K_g = (T_c - T_g) / (T_m - T_g)$, are listed in Table 1. It can be seen, that both $T_g$ and $T_m$ decreases with increasing Tl content, while the values of $T_c$ increases with increasing Tl content until 20 at.% Tl. For greater amount of Tl content >20 at.%Tl, the values of $T_c$ is decreases.

Figure 5 shows the variations of $T_g$ with the amount of Tl present in the glass. It is worth noting that this figure can be looked at as consisting of two regions; the first one extending up to the glassy composition with 15 at.% Tl, while the second one starts at the composition with 20 at.% Tl where a sudden drop in $T_g$ is observed. This is taken as an indication that the underlying glass structure for composition with =20 at.%Tl is different from that corresponding to the compositions with less than 20 at.%Tl and suggesting that a phase change might be taking place at composition of 20 at.% Tl. In general, the decreases of $T_g$ for a glassy alloy, observed in this work, leads to an increase in its configurational entropy and thus to a decrease in its stability. A slight contribution to the decreases of $T_g$ with increasing Tl content in the glass is attributed to the replacement of the strong As-Se bonds (bond energy = 41.68 kcal/mol) by the weak Tl-Se bonds (bond energy = 38.71 kcal/mol).

The values ($T_c - T_g$) may be used to assess the thermal stability of the glasses or equivalently the relative ease with which a glass can be formed, where a short interval signifies that the glass contains structural units with a hight crystallization tendency [31]. As seen from Table 1, the values of ($T_c - T_g$) increases with increasing Tl content and reaches a maximum value at 20 at.% Tl. For greater amount of Tl content > 20 at.%Tl, the thermal stability of the glasses is increases. The thermal stability for As-Se-Tl, glasses has a maximum for As$_{30}$Se$_{60}$Tl$_{10}$ composition, (corresponding to As$_{2}$Se$_{3}$+$Tl$_5$Se$_{7}$, structural units).

It has been suggested by Hruby [32] that an appropriate measure for the glass forming ability is given by the ratio:

$$K_g = (T_c - T_g) / (T_m - T_g)$$  \(6\)

Figure 6 shows the variation of $K_g$ with Tl content for As$_{30}$Se$_{60}$Tl$_x$ (5≤x≤35 at.% ) glasses. It could be noticed that the glass formation ability of this glasses increases with increasing Tl content reaches to a maximum values at 20 at.% Tl corresponding to As$_{30}$Se$_{60}$Tl$_{10}$ composition.

**Bond Arrangement:** In order to estimate the possible bond arrangement in chalcogenide glass systems two models have often been applied: (1) The random bond
network model (RBNM). In this model the distribution of the various kinds of bonds is statistical and is determined by the fractional concentration $c_i$ of an atom $i$ and the number of bonds of the same atom. (2) The ordered bond network model (OBNM) suggests the prevalence of heteropolar bonds and minimum number of weak homopolar bonds. In this work we applied the second model, because the first model is suitable only for the characterization of freshly evaporated films where the chemical ordering is very small [33].

According to ordered bond network model (OBNM) in chalcogen rich alloys as in our case, the relative fraction of As-Se, Ti-Se and Se-Se, expected to exist in the As$_{20}$ Se$_{60-x}$ Ti$_x$ alloys at $x<$20 at.% Ti, while the relative fraction As-Se,Ti-Se and Ti-Ti at Ti content $>20$ at. % where the Se-Se bond replaced by Ti-Ti bonds. The relative fraction of the bonds is summarized in Table 1 and Figure 7. It is seen from this table that the fraction of As-Se and Se-Se bonds decreases with increasing Ti content, while the fraction of of Ti-Se bonds increases with increasing Ti content until 20 at.% Ti and then decreases with increasing Ti content.

The heteropolar bond energy $E_{A,B}$ for a covalent bond between atoms A and B is estimated from the Pauling formula [34-36].

$$E_{A,B} = [E_{A,A} E_{B,B}]^{1/2} + 30 (\phi_A - \phi_B)^3$$  \hspace{1cm} (7)

where $E_{A,A}$ and $E_{B,B}$ are the single bond energies for atoms A and B in kcal/mol, respectively, and $\phi_A$ and $\phi_B$ are their corresponding electronegativities. The single bond energies in kcal/mol, are 32.1 for As, 44 for Se and 15.4 for Ti. Using electronegativity values of 2.18, 2.55 and 1.9 for As, Se and Ti, respectively [37]. The bond energies $E_{AsSe}$ and $E_{TiSe}$ are calculated. The types of bond expected to occur in As$_{20}$ Se$_{60-x}$ Ti$_x$ system are As-Se ($E_{AsSe} = 41.68$ kcal/mol), Ti-Se ($E_{TiSe} = 38.71$ kcal/mol).
Fig. 8: Shown the dependence of estimated binding energy, $E_b$, on the optical energy gap $E_g$ for As$_{20}$Se$_{10-x}$Tl $(5 \leq x \leq 35$ at.%) chalcogenide glasses.

<table>
<thead>
<tr>
<th>Tl (at.%)</th>
<th>As-Se</th>
<th>Tl-Se</th>
<th>Se-Se</th>
<th>Tl-Tl</th>
<th>$E_g$(eV)</th>
<th>$E_g$(eV)[12]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.533</td>
<td>0.133</td>
<td>0.343</td>
<td>------</td>
<td>1.83</td>
<td>1.80</td>
</tr>
<tr>
<td>10</td>
<td>0.521</td>
<td>0.261</td>
<td>0.217</td>
<td>------</td>
<td>1.80</td>
<td>1.73</td>
</tr>
<tr>
<td>15</td>
<td>0.511</td>
<td>0.383</td>
<td>0.106</td>
<td>------</td>
<td>1.77</td>
<td>1.63</td>
</tr>
<tr>
<td>20</td>
<td>0.500</td>
<td>0.500</td>
<td>------</td>
<td>------</td>
<td>1.74</td>
<td>1.55</td>
</tr>
<tr>
<td>25</td>
<td>0.492</td>
<td>0.406</td>
<td>------</td>
<td>0.102</td>
<td>1.64</td>
<td>1.38</td>
</tr>
<tr>
<td>30</td>
<td>0.480</td>
<td>0.320</td>
<td>------</td>
<td>0.200</td>
<td>1.54</td>
<td>1.28</td>
</tr>
<tr>
<td>35</td>
<td>0.471</td>
<td>0.235</td>
<td>------</td>
<td>0.294</td>
<td>1.49</td>
<td>1.23</td>
</tr>
</tbody>
</table>

For Tl content = 5, 10, 15 at.%, the excess of bonds are Se-Se $(E_{Se-Se} = 44\text{ kcal/mol})$ but for Tl content = 25, 30 and 35 at.%, the number of excess bonds are Tl-Tl bond with $(E_{Tl-Tl} = 15.4\text{ kcal/mol})$. This results in a good agreement with the results obtained from (As$_2$Se$_3$)$_x$Tl$_y$ system [35].

If we now further assume that the bond energies are additive, we can estimate the bond energy (the cohesive energy), $E_b$, i.e., the stabilization energy of an infinitely large cluster of the material per atom, by summing the bond energies expected in the materials. This is equivalent to assuming a simplified model consisting of non-interacting electron pair bonds highly localized between adjacent pairs of atoms. The average bond energies of the different compositions, $E_b$, are listed in Table 2, where the $E_b$ of the prepared bulk samples is evaluated from the following equation:

$$E_b = \sum f_i E_b/100 \quad (8)$$

where $f_i$ and $E_b$ are the number of the expected chemical bonds and the energy of each corresponding bond, respectively. It can be seen from Table 2 that the average bond energy decreases with increasing Tl content. This decrease of the average bond energy of the system tends to decrease the energy of the conduction band edge, causing a narrow splitting between bonding, $\sigma$ and antibonding band, $\sigma'$, and thus resulting in the observed decreases in the band gap.

The experimental optical energy gap, $E_{g}$, of As$_{20}$Se$_{10-x}$Tl $(5 \leq x \leq 35$ at.%) thin film are determined by El.Nahass et al. [13]. They shows that the values of $E_{g}$ decreases linearly with increasing Tl content as shown in Table 2. The difference between $E_b$ and $E_{g}$ of our system deviate by 1.64-17.45%. This difference increases with increasing Tl content until 20% Tl and then it has a constant value As is well know, the bond energy, $E_b$, is closely connected to the optical energy gap $E_{g}$ of the chalcogenide semiconductors and usually $E_b > E_g$ [38]. Fig.7 shows the relation between $E_b$ and $E_{g}$ for our system. The linear relation has a slope(=1.61) and intercept (=1.93). An attempt has been made to correlate the optical energy gap, $E_{g}$ and estimated bond energy, $E_b$ through the Manca relationship[39]:

$$E_{g} = 1.61(E_b - 3.11) \quad (9)$$
CONCLUSION

The variation of mean atomic volume ($V_g$), with Tl content for chalcogenide $\text{As}_{1-x}\text{Se}_{x}\text{Tl}_x$ ($5 \leq x \leq 35$ at.%) glasses were investigated. The $V_g$ dependence were discussed in the light of the ordered bond network model (ORBNM). The thermal stability of the glass as well as the glass forming ability has non linear decreases with Tl content. According to CONM the possible bond distribution as well as the binding energy in ternary $\text{As}_{1-x}\text{Se}_{x}\text{Tl}_x$ ($5 \leq x \leq 35$ at.%) glasses are s given. An attempt has been made to correlate the optical energy gap, $E_g$ and estimated bond energy, $E_b$ through the Mancu relationship

REFERENCES