Abstract: Differential Thermal Analysis (DTA) has been used to determine the characteristic temperatures of glass transition, crystallization and melting temperatures in amorphous Se-Te-Sn alloys. The effect of Sn on the binary SeTe system is discussed. The correlation between the glass transition temperature and coordination number of Sn atoms in multicomponent chalcogenide glasses is verified. The difference in crystallization and glass transition temperature is used to define the stability and glass forming ability in the alloys. S parameter is defined using the difference to assign stability in a quantitative way. It is found that composition containing Sn 6 at% is most stable in the present system.

Keywords: chalcogenides, differential thermal analysis, electronic structure, glass transition

1. Introduction

The electronic era in which we live is of great technological advances based primarily on the crystalline semiconductor devices. There has been considerable interest in chalcogenide glasses because of their interesting physical properties as well as their wide technological applications [1].

The goals of kinetic studies are to determine the stability of selected phases and to determine the rates at which those phases evolve as a function of temperature. Common experimental techniques used to study the phase transformation are optical microscopy [2], electrical resistivity [3] and thermal analysis [4]. The thermal stability and Glass Forming Ability (GFA) plays an important role in determining the utility of chalcogenide alloys as recording materials due to the fact that phase change optical recording and erasing techniques are based on the laser induced thermal amorphization and crystallization of chalcogenide glasses. The origin of the thermal stability and GFA is, thus a subject of great interest [5-7].

In recent years, metal containing ternary chalcogenide glasses attracted much attention due to higher melting point, metallic nature and advanced scientific interest [8]. The addition of metals as third component to the binary Se-Te chalcogenide glasses leads to the increase of their stability [1, 9]. The addition of metals in binary chalcogenide alloy affects the chemical equilibrium of existing bonds, and therefore newly formed ternary glass stoichiometry would be heavily cross-linked (makes homopolar and heteropolar bonds in respect of alloying elements) [10-12]. A systematic study of metallic additives on the electro-optical properties of some important chalcogenide glassy systems has been widely studied by many workers [13-15].

2. Experimental Details

2.1. Material Preparation
The high purity Se(99.999%), Te(99.999%) and Sn(99.99%) were weighed in desired proportions and vacuum sealed in quartz ampoule. The alloy composition was chosen as $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$. The value of $x$ was taken as 0, 3, 6 and 10. It is very difficult to prepare alloys in the glassy form for larger Sn concentration, which makes the alloy to behave metallic-like [16]. For preparing alloys of SnSeTe, 3 gm material of the required material was sealed in different quartz ampoules. To start with, the temperature of the furnace was adjusted to the melting point of the constituent having minimum melting point (505K for Sn) and kept at this temperature for two hours. After two hours, the temperature was increased to the melting point of Se (523K) and after keeping the sample for one hour, the temperature was raised to Te (723K) and kept for two hours. Finally, the temperature was increased to 973K in order to maintain the mixture in the molten state for 24 hours. The molten mixture was frequently rocked to ensure the homogeneity of the alloy as these materials are known to be viscous, and so requires sufficient time for becoming homogeneous. The quenching of the melt was done in de-ionized water. The x-ray diffraction patterns of the as-prepared samples are shown in Fig. 1 which confirmed the amorphous nature of the samples [17].

2.2. Differential Thermal Analysis (DTA)

To determine the characteristic temperatures in SeTeSn, the samples were heated at different heating rates and thermogram were obtained. Well defined endothermic and exothermic peaks were obtained in Differential Thermal Analyzer thermograms showing glass transition and crystallization phenomena in the materials. The thermal analyzer used in the present work is a Perkin Elmer STA 8000 analyzer with temperature variation from room temperature to 1773K. The weight change as a function of time is recorded. 5 mg of each sample was utilized to run the DTA scan at heating rate of 5K/min for measurements on samples with various Indium concentrations. The system is calibrated by measuring specific heat of 99.999% pure Indium between 293K and 373K.

![X-ray Diffraction of the Sn$_{80}$Se$_{20-x}$Te$_x$ samples](image)

3. Results and Discussion

3.1. DTA Thermogram

DTA thermograms of $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x=0,3,6,10$) glasses at a heating rate of 5K/min are shown in Fig.2. Two characteristic phenomena (endothermic and exothermic peaks) are evident in the DTA thermograms in the temperature range of investigation. From the analysis point of view, the DTA thermograms are divided into two parts, the first one corresponds to the glass transition region represented by the endothermic reaction and the other part is related to the crystallization process as indicated by the
exothermic part of the DTA curve. The glass transition temperatures ($T_g$) and onset crystallization temperatures ($T_c$) are defined as the temperature which corresponds to the intersection of the two linear portions adjoining the transition elbow of the DTA traces in the endothermic and exothermic direction respectively [18].

Table 1 displays the various temperatures values derived from the thermograms for a constant heating rate. Here, the $T_g$ refers to glass transition temperature, $T_c$ refers to crystallization temperature, $T_o$ refers to onset crystallization temperature, $T_p$ refers to peak crystallization temperature and $T_m$ to melting temperature.

![Fig. 2. DTA Thermogram for various atomic percentages of Sn.](image)

It is clear that in glassy $\text{Se}_{80}\text{Te}_{20-x}\text{Sn}_x$ ($x = 0, 3, 6, 10$), the glass transition temperature $T_g$ increases with increasing Sn content continuously. The slight increase of $T_g$ with increasing Sn in the present system may be explained by considering the structural changes occurring in a-SeTe. The structural model of amorphous Se includes two molecular species, meandering chains, which contain helical chains of trigonal Se and Se$_8$ ring molecules of monoclinic Se [19]. Thus Te, which is isoelectronic with Se when added to Se is not only attached to Se chain ends but also in rings. Therefore, increased Te concentration leads to cross-linking of chains and rings leading to a greater disorder by increase of inter-chain forces [20] and tendency of crystallization is retarded. Increase in Sn concentration in SeTe alloy leads to thermal stability due to increased cross-linking between Se-Te chains [21]. When Sn is incorporated in Se-Te, they probably increases the numbers of polymeric chains [22]. It is known that the glass transition temperature $T_g$ should increase with increasing chain length and decrease with increasing ring concentration [23]. The increase in $T_g$ may be related to the decrease in ring concentration on increasing Sn concentration.

<table>
<thead>
<tr>
<th>Sn at.%</th>
<th>$T_g$</th>
<th>$T_c$</th>
<th>$T_p$</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>330</td>
<td>369</td>
<td>415</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>332.5</td>
<td>367.5</td>
<td>403.5</td>
<td>498</td>
</tr>
<tr>
<td>6</td>
<td>334</td>
<td>375</td>
<td>404</td>
<td>496</td>
</tr>
<tr>
<td>10</td>
<td>335</td>
<td>361.1</td>
<td>386.4</td>
<td>493</td>
</tr>
</tbody>
</table>

### 3.2. Glass Transition and Average Coordination Number

It is observed that there is a small increase in $T_g$ with increasing Sn content. On the other hand, the average coordination number $<Z>$ increases with increasing the Sn content. The variation of $T_g$ with the
average coordination number follows the relation [24]:

\[ \ln T_g = a(Z) + b \]

where \( Z \) denotes the average coordination number per atom which is calculated in terms of covalent bonding using the relation

\[ \langle Z \rangle = \frac{\alpha N_{Se} + \beta N_{Te} + \gamma N_{Sn}}{\alpha + \beta + \gamma} \]

where \( \alpha, \beta, \gamma \) are the concentrations of Se, Te and Sn and \( N \) is the valence of three elements. The plot of the above dependence is shown in Fig. 3. It is found to obey a linear dependence and similar behavior was observed in ternary chalcogenides by Rahim et.al. [25].

![Fig. 3. Plot of glass transition temperature with coordination number](image)

The glass transition temperature \( T_g \) of a multi-component glass is known to depend on several independent parameters such as band gap, coordination number, effective molecular weight and the type and fraction of various structural units formed [26]. In the present work, result obtained obeys the well known equation followed by most of the inorganic alloys including chalcogenides [27], i.e.

\[ \ln T_g = 1.6\langle Z \rangle + 2.3 \]

The crystallization temperature \( T_c \) decreases on addition of Sn concentration except for Sn 6 at.% to a-SeTe. \( T_c \) represents the stability of the glass [28]. Similar behaviour is observed for peak temperature (\( T_p \)) although the increase is very small. At higher Sn concentration due to metallic character of Sn, large grains are available so that crystallization can be induced.

### 3.3. Thermal Stability

The glass transition temperature \( T_g \) represents the strength or rigidity of the glass structure in chalcogenide glasses. Hence, \( T_g \) offers valuable information on the thermal stability of glassy state. However, it has been found that the difference of \( T_c \) and \( T_g \) is a strong indicator of both the thermal stability and GFA. The higher the values of \((T_c - T_g)\), the greater is the GFA, because the higher the value of this difference, more is the delay in the nucleation process [29].

The values of difference of glass transition temperature \( T_g \) and crystallization temperature \( T_c \) for glassy alloys of \( Se_{80}Te_{20-x}Sn_x \) (\( x = 0, 3, 6, 10 \)) are given in Table 2. Fig. 4 shows \((T_c - T_g)\) for different compositions. It is found that the values of \((T_c - T_g)\) is highest at \( x = 6 \) in \( Se_{80}Te_{20}Sn_6 \) glass. This indicates that GFA is
highest in this case among all the glassy alloys studied.

Table 2. Relation between \((T_c - T_g)\) and S parameter with different atomic weight percentages of Sn

<table>
<thead>
<tr>
<th>Sn at.%</th>
<th>(T_c - T_g ) [K]</th>
<th>S parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39</td>
<td>1.77</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>1.105</td>
</tr>
<tr>
<td>6</td>
<td>41</td>
<td>1.89</td>
</tr>
<tr>
<td>10</td>
<td>36</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Fig. 4. The relation between stability parameter, \((T_c - T_g)\) and compositions of Sn.

There is another parameter which better characterizes and defines the stability in chalcogenides. The thermal stability parameter \(S\) is defined in the literature by the following expression [30]:

\[ S = \frac{(T_c - T_o)(T_c - T_g)}{T_g} \]

here \(T_o\) represents the bend at the onset crystallization temperature, i.e., the temperature at which crystallization peak starts. Thermal stability parameter reflects the resistance to divitrification after formation of the glass. In the expression for \(S\), the term \((T_c - T_o)\) is related to the rate of divitrification transformation of the glassy phases. On the other hand, the higher values of the term \((T_c - T_g)\) delay the nucleation process. The values of \(S\) are given in Table 2 for various glassy alloys. The highest values of \(S\) occur at 6 at% of Sn, which shows that this composition is most stable among the various compositions studied in this work.

4. Conclusions

In the present work, it has been found that the glass transition temperature \(T_g\) increases continuously with increasing Sn content but the crystallization temperature \(T_c\) decreases on addition of Sn except for Sn 6 at%. The relation of glass transition temperature dependence on the coordination number if found to be linear as observed for multicomponent chalcogenide glasses. As the increased Sn concentration leads to cross-linking of chains and rings leading to a greater disorder by increase of inter-chain forces and tendency of crystallization is retarded. The higher values of the term \((T_c - T_g)\) indicate a delay of the nucleation process. It is highest at \(x = 6\) in Se\(_{80}\)Te\(_{20}\)Sn\(_x\) glass and is an indicator of glass forming capacity GFA at this concentration. This is in conformity with the value of S parameter obtained in this work.
References


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