Crystallization Studies on Se-Te-Cd Chalcogenide Glasses

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The thermal crystallization behavior of bulk Se_{90-x}Te_{10}Cd_x (x = 0, 3, 9, and 15 at%) glasses was studied by differential thermal analysis (DTA), under non-isothermal conditions. The glass transition temperature, \( T_g \), the onset crystallization temperature, \( T_p \), and the peak temperature of crystallization, \( T_c \), were found to be dependent on both the composition and the heating rates. From the dependence on the heating rates (\( \alpha \)) of \( T_g \) and \( T_p \), the activation energy for the glass transition, \( (E_g) \), and the activation energy for crystallization, \( (E_c) \), were calculated and their composition dependence is discussed. The crystalline phases resulting from DTA and scanning electron microscopy (SEM) have been identified using X-ray diffraction. The results indicate one dimensional growth from the surface to the inside for all the studied compositions. The kinetic parameters determined have made it possible to discuss the glass forming ability.

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1. Introduction

Chalcogenide glasses exhibit many useful properties and have recently drawn great attention because of their use in various solid state devices. The electrical properties are influenced by the structural effects associated with the thermal effects and can be related to thermal induced transitions. Common experimental techniques used to study the structure of chalcogenide glasses are electron microscopy, X-ray diffraction, electrical resistivity and thermal Analysis. The study of the crystallization kinetics of a glass upon heating can be undertaken in several different ways. In calorimetric measurements two techniques have been employed for the study of the crystallization behavior upon heating, namely isothermal and non-isothermal crystallization analyses. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature, \( T_g \), and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time. In the other method, the sample is heated from room temperature, at a fixed heating rate (\( \alpha \)), and the heat evolved is again recorded as a function of temperature.

The present work is concerned with the study of the crystallization kinetics and the evaluation of the crystallization parameters for Se_{90-x}Te_{10}Cd_x (x = 0, 3, 9 and 15 at%) chalcogenide glasses by using the non-isothermal method. The effect of composition on the crystallization mechanism has been reported.

2. Experimental

The bulk materials of Se_{90-x}Te_{10}Cd_x (x = 0, 3, 9 and 15 at%) were prepared by the usual melt quench technique; the highly pure materials (99.999%) were weighted according to their percentages and sealed in evacuated silica tubes which were heated at 900°C for 20 h. During the melt process the tube was frequently rocked to intermix the constituents and to increase homogenization of the liquid. This treatment was followed by quenching in an ice/water mixture. The amorphous nature of the sample was proved by X-ray diffraction. Differential Thermal Analyses (DTA) was carried out by using a DTA Perkin-Elmer DTG-60 under non-isothermal conditions.

The glass transition temperatures \( (T_g) \), the onset crystallization temperatures \( (T_p) \), and the peak crystallization temperatures \( (T_c) \), were determined with an accuracy of ±1 K using the microprocessor of a thermal analyzer. The crystallized fraction \( (\chi) \) was calculated using the partial area analysis. For scanning electron microscopy (SEM) examination, sample surfaces were etched using a mixed solution of sodium hydroxide and hydrogen peroxide. The X-ray diffractometer, Philips type 1710, was used to identify the crystalline phases in the annealed glassy samples.

3. Results and Discussions

Differential thermal analysis (DTA) experiments were performed at different heating rates ranging from 5 to 25 K/min to investigate the crystallization kinetics of Se_{90-x}Te_{10}Cd_x chalcogenide glasses. Figure 1 shows the thermograms of as-prepared Se_{90-x}Te_{10}Cd_x glasses (x = 0, 3, 9 and 15 at%) at a heating rate of 10 K/min. Three characteristic phenomena are clear in the studied temperature region. The first one, \( T_g \), corresponds to the glass transition temperature. The second one, \( T_p \), corresponds to the onset crystallization temperature. The last characteristic temperature, \( T_c \), identified the crystallization temperature. Numerical values of these temperatures are given in Table 1.

The morphology of the studied samples after annealing to crystallization temperature using the same heating and cooling rate as used in DTA measurements were examined by SEM. The sample was fractured and gold coated before SEM examination to study both the internal and surface morphology. The scanning micrographs of specimens of different compositions, annealed at 398 K for 1 h, are shown in Fig. 2(a)–(d). The microstructure of the annealed sample for the composition Se_{90}Te_{10} is shown in Fig. 2(a). The
The photomicrograph shows the existence of a polycrystalline structure consisting of crystallites embedded in amorphous phases. The crystalline morphology is not distinct due to the fact that the crystallization is only in its initial stages. On the other hand, the area covered by the crystalline particles increased by increasing the Cd content in the Se$_{90}$Te$_{10}$Cd$_{x}$ chalcogenide glasses. The crystalline morphology of the annealed sample for the composition Se$_{87}$Te$_{10}$Cd$_{3}$ is shown in Fig. 2(b). The surface morphology showed the appearance of a homogeneously distributed dendrite crystalline phase embedded in the glass matrix. Further increase of the Cd content in Se-Te-Cd system reveals that the amount of the crystalline phase increases.

![Image](image1.png)

**Fig. 1** The DTA Thermograms for the as-prepared compositions (Se$_{90}$Te$_{10}$), (Se$_{87}$Te$_{10}$Cd$_{3}$), (Se$_{81}$Te$_{10}$Cd$_{9}$) and (Se$_{75}$Te$_{10}$Cd$_{15}$).

![Image](image2.png)

**Fig. 2** The SEM photograph for the compositions annealed at 398 K for 1 h: (a) Se$_{90}$Te$_{10}$, (b) Se$_{87}$Te$_{10}$Cd$_{3}$, (c) Se$_{81}$Te$_{10}$Cd$_{9}$ and (d) Se$_{75}$Te$_{10}$Cd$_{15}$.

![Image](image3.png)

**Fig. 3** X-ray diffraction for compositions annealed at 398 K for 1 h: (a) Se$_{90}$Te$_{10}$, (b) Se$_{87}$Te$_{10}$Cd$_{3}$, (c) Se$_{81}$Te$_{10}$Cd$_{9}$ and (d) Se$_{75}$Te$_{10}$Cd$_{15}$.

![Image](image4.png)

**Table 1** $T_g$, $T_c$, $T_p$, $T_c-T_g$, (at 10 K/min) B, $E_t$ and $H_r$ of the Se-Te-Cd glasses.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Se$<em>{90}$Te$</em>{10}$</th>
<th>Se$<em>{87}$Te$</em>{10}$Cd$_{3}$</th>
<th>Se$<em>{81}$Te$</em>{10}$Cd$_{9}$</th>
<th>Se$<em>{75}$Te$</em>{10}$Cd$_{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$ (K)</td>
<td>2</td>
<td>2.12</td>
<td>2.36</td>
<td>2.6</td>
</tr>
<tr>
<td>$T_g$ (K)</td>
<td>335</td>
<td>336.1</td>
<td>337</td>
<td>338.2</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>374.9</td>
<td>370.6</td>
<td>368.2</td>
<td>365.6</td>
</tr>
<tr>
<td>$T_p$ (K)</td>
<td>414.7</td>
<td>407.4</td>
<td>402.9</td>
<td>382.4</td>
</tr>
<tr>
<td>$T_c-T_g$ (K)</td>
<td>39.8</td>
<td>34.5</td>
<td>31.2</td>
<td>27.5</td>
</tr>
<tr>
<td>$E_t$ (kCal/mol)</td>
<td>37.70</td>
<td>38.52</td>
<td>39.56</td>
<td>40.70</td>
</tr>
<tr>
<td>$H_r$</td>
<td>0.30</td>
<td>0.25</td>
<td>0.22</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The crystalline morphology is not distinct due to the fact that the crystallization is only in its initial stages. On the other hand, the area covered by the crystalline particles increased by increasing the Cd content in the Se$_{90-}$Te$_{10}$Cd$_{x}$ chalcogenide glasses. The crystalline morphology of the annealed sample for the composition Se$_{97}$Te$_{10}$Cd$_{3}$ is shown in Fig. 2(b). The surface morphology showed the appearance of a homogeneously distributed dendrite crystalline phase embedded in the glass matrix. Further increase of the Cd content in Se-Te-Cd system reveals that the amount of the...
transformed crystalline phase increased and the crystallized particles decrease in size. The photomicrograph in Fig. 2(c) shows the surface microstructure of the annealed Se\(_{81}\)Te\(_{10}\)Cd\(_{9}\) composition. A polycrystalline structure consisting of different crystalline phases embedded in an amorphous matrix is observed. Some of these crystallized particles are interconnected and others are isolated. The scanning electron micrograph for the annealed Se\(_{81}\)Te\(_{10}\)Cd\(_{9}\) composition is shown in Fig. 2(d). The photomicrograph shows very fine structure with different crystalline phases and sizes. The crystallites are dispersed homogeneously and occupy most of the structure.

In order to identify the crystalline phases that appeared in the DTA and SEM examinations, the X-ray diffraction for specimens annealed at a temperature close to the crystallization temperature is shown in Fig. 3. Analysis of the X-ray diffraction pattern reveals that the composition, Se\(_{80}\)Te\(_{10}\)Cd\(_{10}\), which was annealed at 398 K for 1 h, has two phases of Se and Te embedded in an amorphous matrix as shown in Fig. 3(a). Addition of Cd to the composition leads to the formation of new phases like CdTe, SeTeCd and CdSe as shown in Figs. 3(b), (c) and (d).

The variation of \(T_g\) with composition for Se\(_{80-x}\)Te\(_{10}\)Cd\(_{x}\) (\(x = 0, 3, 9\) and 15 at\%) is shown in Fig. 4. It is observed that there is a small increase in \(T_g\) with increasing Cd content. On the other hand, the average coordination number \(Z\) increases with increasing the Cd content. The variation of \(T_g\) with the average coordination number follows the relation:

\[
\ln T_g = aZ + b
\]

where \(Z\) denotes the average coordination number per atom which is calculated in terms of covalent bonding. The \(T_g\) 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.\(^8\)\(^-\)\(^11\) The slight increase of \(T_g\) with increasing Cd content in the present system may be explained by considering the structural changes occurring due to the further addition of Cd content. The generally accepted structural model for amorphous Se includes\(^3\) two molecular species meandering chains which contain helical chains of trigonal Se and Se\(_x\) ring molecules of monoclinic Se. In the present case, the addition of Cd makes bonds with Se and is probably dissolved in the Se chains. Hence, the number of Se\(_x\) rings decreases while the number of long Se-Te polymeric chains and Se-Te mixed rings increases. It is known that the glass transition temperature, \(T_g\), should increase with increasing chain length and decreases with increasing ring concentration\(^12\) hence \(T_g\) increases with increasing Cd content. Furthermore, we attribute the increase of \(T_g\) with increasing Cd content to the marginal increases which occur in the coordination number (shown in Fig. 4) and the mean atomic masses of these glasses.

On the other hand, the glass transition activation energy (\(E_t\)) deduced by Kissinger, formula:\(^13\)

\[
\ln(\frac{\alpha}{T_g^2}) = (-\frac{E_t}{RT_g}) + \text{const.}
\]

Where \(\alpha\) is the heating rate, \(E_t\) is the activation energy for the glass transition and \(R\) is the gas constant. Figure 5 shows \(\ln(\alpha/T_g^2)\) versus 1000/\(T_g\) plots for Se\(_{80-x}\)Te\(_{10}\)Cd\(_x\) glasses, from which the activation energy for the glass transition, \(E_t\), was evaluated and listed in Table 1. The \(E_t\) values lie in the range generally observed for chalcogenide glasses.\(^14\)\(^\)\(^15\) It is clear from Table 1, the activation energy for glass transition, \(E_t\), increases with increasing Cd content. The increase of \(E_t\) with increasing Cd content resulted in an apparent increase of \(T_g\) with increasing Cd content at all the heating rates. These results are in good agreement with those obtained by others.\(^5\)\(^\)\(^15\)

The values of the onset crystallization temperature, \(T_c\), and \(T_c-T_g\) at heating rates 10 K/min are listed in Table 1. It is clear from the table that both \(T_c\) and \(T_c-T_g\) decrease with increasing Cd content. Both \(T_c\) and \(T_c-T_g\) represented the thermal stability of the glass.\(^14\)\(^\)\(^16\) The kinetic resistance to crystallization is given by the difference between \(T_c\) and \(T_g\). The larger difference gives higher resistance to crystallization. The glass samples with lower \(T_c-T_g\) values are expected to have higher electrical conductivity.\(^17\) These results are in good agreement with other workers.\(^5\)\(^\)\(^18\)\(^\)\(^19\) Another parameter usually employed to estimate the glass forming tendency (GFT) is the one introduced by Hruby,\(^20\) and is defined as follows:

\[
H_t = (T_c - T_g)/(T_m - T_c)
\]

\((T_c\) and \(T_m\) are the crystallization and melting temperatures of the glass).
the Henderson equation, the authors obtained the following relation:

\[ \ln(\alpha/T_p^2) = -E_c/RT_p + \text{const.} \]  

(4)

Figure 6 shows the plot of \( \ln(\alpha/T_p^2) \) versus 1000/T_\( \text{p} \) for the studied compositions. From the slopes of the straight lines, the activation energies, \( E_c \), for the crystallization process are deduced and listed in Table 2. The activation energy, \( E_c \), and the frequency factor, \( k_p \), were calculated using the method proposed by Augis and Bennett. 

\[ \ln(\alpha/T_p) = (-E_c/RT_p) + \ln k_p \]  

(5)

The plots of \( \ln(\alpha/T_p) \) versus 1000/T_\( \text{p} \) of different heating rates for the studied compositions are shown in Fig. 7. From the slopes of the fitted to the data we calculated the activation energy, \( E_c \), for the crystallization process. In addition, the origin ordinate of these curves gives the frequency factor, \( k_p \), values which are given in Table 2 together with the \( E_c \) values.

Table 2  Calculated values of \( E_c \), \( \ln(k_p) \) and \( n \) for Se-Te-Cd composition glasses.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( E_c ) (kCal/mol)</th>
<th>( \ln(k_p) )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se\textsubscript{90}Te\textsubscript{10}Cd\textsubscript{10}</td>
<td>16.71</td>
<td>17.54</td>
<td>15.28</td>
</tr>
<tr>
<td>Se\textsubscript{90}Te\textsubscript{10}Cd\textsubscript{15}</td>
<td>13.63</td>
<td>13.95</td>
<td>12.78</td>
</tr>
<tr>
<td>Se\textsubscript{90}Te\textsubscript{10}Cd\textsubscript{3}</td>
<td>11.55</td>
<td>12.36</td>
<td>10.27</td>
</tr>
<tr>
<td>Se\textsubscript{87}Te\textsubscript{10}Cd\textsubscript{15}</td>
<td>10.33</td>
<td>11.11</td>
<td>8.13</td>
</tr>
</tbody>
</table>

where \( T_m \) is the peak melting temperature. The parameter \( H_t \) gives the probability of obtaining a glass which increases as \( T_m-T_c \) decreases and \( T_c-T_g \) increases. It is usually difficult to prepare glasses with \( H_t \leq 0.1 \) while good glasses can be formed if \( H_t \geq 0.4 \). The deduced values of \( H_t \) for the studied compositions are listed in Table 1. The table reveals that the GFA decreases with increasing Cd content.

The activation energy, \( E_c \), of amorphous crystalline transformation were calculated using the equation derived by Kissinger:

\[ \ln(\alpha/T_p^2) = (-E_c/RT_p) + \text{const.} \]  

(4)

Figure 6 shows the plot of \( \ln(\alpha/T_p^2) \) versus 1000/T_\( \text{p} \) for the studied compositions. From the slopes of the straight lines, the activation energies, \( E_c \), for the crystallization process are deduced and listed in Table 2. The activation energy, \( E_c \), and the frequency factor, \( k_p \), were calculated using the method proposed by Augis and Bennett. 

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(5)

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The kinetic parameters of our four compositions have also been evaluated through the technique used by Gao and Wang. Based on the Johnson-Mehl-Avrami equation and the Henderson equation, the authors obtained the following relation:

\[ \ln(\alpha/T_p^2) = (-E_c/RT_p) + \ln k_p \]  

(5)

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The kinetic parameters of our four compositions have also been evaluated through the technique used by Gao and Wang. Based on the Johnson-Mehl-Avrami equation and the Henderson equation, the authors obtained the following relation:
This fact is also confirmed by the difference in the value of $E_c$ calculated by different procedures has also been observed in binary and ternary chalcogenide glass. Conventional equation for evaluation of the activation energy for crystallization because of the convenience and accuracy of the measurements of heating rate. A similar considerable decrease in the values of $T_c$ and $E_c$ for crystallization because of the convenience and accuracy of the measurements of heating rate. A similar considerable difference in the value of $E_c$ calculated by different procedures has also been observed in binary and ternary chalcogenide glass.

In general, there is a decrease in this parameter as the Cd concentration increases. These results indicate that the crystallization ability increases with increasing Cd content, which agrees with the conclusions reached by others. This fact is also confirmed by the $E_c$, $H_c$ and $k_p$ values given in Tables 1, 2. The observed decreases in $E_c$ with increasing Cd content indicated a decrease of the potential barrier height connected with the amorphous to crystalline phase transition or, in other words, a decrease of the preserving ability of the amorphous state in these alloys. Furthermore, the frequency factor, $k_p$, (which measures the probability of effective molecular collisions for the formation of the activated complexes in each case) decreases with increasing Cd concentration. This effect shows that the rate of crystallization is faster as the Cd content increases.

4. Conclusions

Kinetic studies made on various glassy alloys in the Se-Te-Cd system indicate that all compositions have single glass transitions and single stage crystallization. The values of $T_g$ and $E_c$ were found to increase with increasing Cd content. This is explained in terms of a change in chemical bonding at higher concentrations of Cd. The crystallization parameters namely $T_c$, $T_p$, $k_p$, $H_c$ and $E_c$ were found to be composition dependent. The calculated activation energies of crystallization and the frequency factor indicate that the glass forming ability (GFA) decreases with increasing Cd content.

In general, the results show that the crystallization mechanism in Se$_{90-x}$Te$_x$Cd$_x$ occurs in one dimensional growth from the surface to the inside according to the Avrami exponent $n$.

REFERENCES