Thermal stability of Ge–As–Te–In glasses

K.A. Aly\textsuperscript{a,}\textsuperscript{*}, A. Dahshan\textsuperscript{b}, F.M. Abdel-Rahim\textsuperscript{a}

\textsuperscript{a} Physics Department, Faculty of Science, Al-Azhar University, Assiut Branch, Assiut, Egypt
\textsuperscript{b} Department of Physics, Faculty of Science, Suez Canal University, Port Said, Egypt

\textbf{A R T I C L E  I N F O}

\textbf{Article history:}
Received 24 December 2007
Received in revised form 29 February 2008
Accepted 6 March 2008
Available online 14 April 2008

Keywords:
Thermal stability
Differential scanning calorimetry
Glasses

\textbf{A B S T R A C T}

The present paper reports the effect of replacement of Te by In on the crystallization kinetics and the thermal stability for Ge\textsubscript{15}As\textsubscript{20}Te\textsubscript{65−}\textsubscript{x}In\textsubscript{x}\ (x = 0, 3, and 6 at.%) glasses. Differential scanning calorimetry (DSC) results under non-isothermal conditions for Ge\textsubscript{15}As\textsubscript{20}Te\textsubscript{65−}\textsubscript{x}In\textsubscript{x}\ glasses were reported and discussed. The thermal stability of the studied glasses has been evaluated using various thermal stability criteria (\(\Delta T\), \(H_g\), \(H_p\) and \(S\)), based on the characteristic temperatures such as the glass transition temperature (\(T_g\)), the temperature at which crystallization begins (\(T_c\)), the temperature corresponding to the maximum crystallization rate (\(T_p\)), or the melting temperature (\(T_m\)). Moreover, in the present work, the \(K(T)\) criterion has been considered for the evaluation of glass stability from DSC data. A comparison of various simple quantitative methods to assess the level of stability for Ge\textsubscript{15}As\textsubscript{20}Te\textsubscript{65−}\textsubscript{x}In\textsubscript{x}\ (x = 0, 3, and 6 at.%) glasses is presented.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Chalcogenide glasses exhibit many useful properties including threshold and memory switching [1–3]. These properties are influenced by the structural changes and could be related to thermally induced transitions [4,5]. Memory switches come from the boundaries of the glass-forming regions, where glasses have a tendency to crystallize when heated or cooled slowly [6–8]. Glasses of chalcogen elements were the initial object of study because of their interesting semi-conducting properties [9,10] and more recent importance in optical recording [11]. Recording materials must be influenced by the structural changes and could be related to thermal stability [1–3]. These properties are obtained two other criteria, weighted thermal stability \(K(T)\) (\(c\)), the temperature corresponding to the maximum crystallization rate (\(T_p\)), or the melting temperature (\(T_m\)). Moreover, in the present work, the \(K(T)\) criterion has been considered for the evaluation of glass stability from DSC data. A comparison of various simple quantitative methods to assess the level of stability for Ge\textsubscript{15}As\textsubscript{20}Te\textsubscript{65−}\textsubscript{x}In\textsubscript{x}\ (x = 0, 3, and 6 at.%) glasses is presented.

\(T_p\), \(T_c\), \(T_p\) and \(T_m\) are easily and accurately obtained by the differential scanning calorimetry [18] during the heating processes of the glass sample. Dietzel introduced the first glass criterion, \(\Delta T = T_p - T_g\) (\(T_g\) is the temperature at which crystallization begins), which is often an important parameter to evaluate the glass-forming ability of the glasses. By the use of the characteristic temperatures, Hruby developed the \(H_r\) criterion, \(H_r = \Delta T/T_m - T_g\) and the compositional dependence of the Hruby coefficient were surveyed by Sestak [19]. On the basis of the \(H_r\) criterion, Saad and Poulain [20] obtained two other criteria, weighted thermal stability \(H_p = \Delta T/T_p\) and \(S = (T_p - T_g)/\Delta T/T_p\) criterion where \(T_p\) is the initial temperature.

In the present work, the above-mentioned criteria have been applied to the Ge\textsubscript{15}As\textsubscript{20}Te\textsubscript{65−}\textsubscript{x}In\textsubscript{x}\ (x = 0, 3, and 6 at.%) glasses. It is found that the parameters \(\Delta T, H_g, H_p, T_m\) and \(S\) decrease with increasing In content. Bearing in mind that, the values of these parameters increase with increasing stability, it is possible to suggest that, the free In content glass, the greater is its glass thermal stability. In addition, a kinetic parameter, \(K(T)\), with an Arrhenian temperature dependence, is introduced to the stability criteria. \(K(T)\) increases with increasing In content which confirms that, the free In content glass is the most stable.

2. Experimental details

Different compositions of bulk Ge\textsubscript{15}As\textsubscript{20}Te\textsubscript{65−}\textsubscript{x}In\textsubscript{x}\ (x = 0, 3, and 6 at.%) chalcogenide glasses were prepared starting by Ge, As, Te and In elements with high purity (99.999) by the usual melt quench technique. The elements were heated together in an evacuated (10\textsuperscript{−3} Pa) silica ampoule up to 1250 K, then the ampoule temperature kept constant for about 24 h. During the heating process the ampoules were shaken several times to maintain their homogeneity, then the ampoule was quenched in ice-cooled water to avoid the crystallization process. The amorphous state of the materials was checked using X-ray (Philips type 1710 with Cu as a target and Ni as
3. Theoretical background

The theoretical basis for interpreting kinetic data is provided by the formal theory of transformation kinetics. This theory describes the evolution with time \( t \) of the volume fraction crystallized \( \chi \) by Johnson, Mehl and Avrami equation [21]:

\[
\chi = 1 - \exp(- (Kt)^n)
\]  

(1)

where \( n \) is an integer or half integer depends on the mechanism of growth and the dimensionality of the crystal, \( K \) is the effective (overall) reaction rate constant, which obeys an Arrhenius expression for the absolute temperature:

\[
K(T) = K_0 \exp \left( \frac{E}{RT} \right)
\]  

(2)

where \( K_0 \) is the frequency factor, \( T \) is the absolute temperature and \( E \) is the effective activation energy describing the overall crystallization process that can be expressed as

\[
E = E_n + E_g \frac{n}{n_m}
\]  

(3)

where \( E_n \) and \( E_g \) are the effective activation energies for nucleation and growth, respectively. \( E_n \) can be neglected over the temperature range of concern in the thermo-analytical study [21] then:

\[
E \approx \left( \frac{m}{n} \right) E_g
\]  

(4)

where \( n = m \) for the nucleation frequency \( I_v = 0 \) and \( n = m + 1 \) for \( I_v \neq 0 \) [22]. The rate constant \( K \) in a non-isothermal DSC experiment was found to changes continually with time due to the change in the temperature, therefore Eq. (1) can be generalized to

\[
\chi(t) = 1 - \exp \left[ - \left( \int_0^t K[I(T')] \, dt' \right)^n \right] = 1 - \exp(-I^n)
\]  

(5)

where \( K[I(T')] \) is still given by Eq. (2), and \( T(t') \) is the temperature at time \( t' \) [22]. The crystallized volume fraction depends on time \( t \) through the temperature \( T(t) \) and the same is true for the integral \( I \). The time integral in Eq. (5) is transformed to temperature integral, yielding:

\[
I(T) = K_0 \frac{1}{\alpha} \int_0^T \exp \left( \frac{-E}{RT} \right) \, dT
\]  

(6)

which is represented by several approximate analytical expressions [23]. By using the substitution \( y = E/RT \), the above integral has been represented by the sum of the alternating series:

\[
S(y) = -\frac{1}{y^\alpha} \sum_{k=0}^{k=\infty} (-1)^k (K + 1)! \frac{y^k}{y^k}
\]  

(7)

Considering that, in this type of series the error produced is less than the first term neglected and bearing in mind that in most crystallization reactions \( y = E/RT \gg 1 \). Therefore, it is possible to use only the two first terms of this series and the error introduced is not greater than 1%. By assuming that, \( T^2(1 - 2RT/E) \exp(-E/RT) \gg T^2_0(1 - 2RT_0/E) \exp(-E/RT_0) \), where \( T_0 \) is initial temperature, then Eq. (6) can be rewritten in the form of

\[
I = K_0 \exp(\alpha R^\gamma T) \exp(-E/RT_0)
\]  

(8)

The maximum crystallization rate in a non-isothermal process which occurs at the peak of the exotherm at time \( t_p \) and temperature \( T_p \) [21] is found by putting \( \frac{d^2 \chi}{dt^2} = 0 \), thus obtaining the relationship:

\[
\frac{d^2 \chi}{dt^2} = nK_p[I^n]_p - (n-1)K_p - \frac{\alpha E[I]}{RT_p^2} = 0
\]  

(9)

Substituting for \( y = E/RT \) and \( (K = K_0 \exp(-E/RT)) \) into Eq. (8), one obtains:

\[
I = \frac{RT^2}{K_0} \exp(\alpha E)^{-1} \left( \frac{1 - 2RT_p}{E} \right)
\]  

(10)

Substituting the last expression for \( I \) into Eq. (9), one obtains the relationship:

\[
I_p = \left( \frac{1 - 2RT_p}{nE} \right)^{1/\alpha}
\]  

(11)

When this relationship is equated to Eq. (10) this gives:

\[
RT_0^2(\alpha E)^{-1} \exp \left( \frac{-E}{RT_p} \right) = \left( \frac{1 - 2RT_p}{nE} \right)^{1/\alpha} \left( \frac{1 - 2RT_p}{E} \right)^{-1}
\]  

or in a logarithmic form:

\[
\ln \left( \frac{T_p^2}{\alpha} \right) + \ln \left( \frac{K_0R}{E} \right) - \frac{E}{RT_p} = \frac{2RT_p}{nE} \left( 1 - \frac{1}{n^\alpha} \right)
\]  

(12)

where the function \( \ln(1 - z) \) with \( z = 2RT_p/nE \) or \( 2RT_p/E \) is expanded as a series and only the first term has been taken.

Note that Eq. (12) reduces to the Kissinger expression for the \( n = 1 \) case as one might have anticipated since this corresponds to the homogeneous reaction case. Thus, it can be seen that, the Kissinger method is appropriate for the analysis not only of homogeneous reactions, but also for the analysis of heterogeneous reactions which are described by the JMA equation in isothermal experiments [21]. The right-hand side (RHS) of Eq. (12) is generally negligible in comparison to the individual terms on the left-hand side for \( \alpha \leq 100 \, \text{K} \, \text{min}^{-1} \). This approximation in Eq. (12) (RHS) implies:

\[
\frac{\ln \left( T_p^2 \alpha \right)}{\alpha} = \frac{E_c}{RT_p} - \ln \left( \frac{K_0R}{E} \right)
\]  

(13)

where \( E_c = E \) (the activation energy for crystallization) and the quoted approximation might introduce a 3% error in the value of \( E_c/R \) in the worst cases. For crystallization processes with spherical nuclei, it has been suggested [21,22] that the dependence of the glass transition temperature on \( \alpha \) may be written as

\[
\frac{\ln \left( T_g^2 \alpha \right)}{\alpha} = \frac{E_g}{RT_g} + \text{const.}
\]  

(14)

a straight line between \( \ln(T_g^2/\alpha) \) and \( 1/T_g \), whose slope yields the value of \( E_g/R \) where \( E_g \) is the activation energy for glass transition and \( R \) is the gas constant.

In order to evaluate the thermal stability of glassy materials, Surinach et al. [24] and Hu and Jiang [25] introduced two criterion \( K(T_g) = K_0 \exp(-E/RT_0) \) and \( K(T_p) = K_0 \exp(-E/RT_p) \), respectively. Thus, the values of these two parameters indicate the tendency of glass to devitrify on heating. The larger their values, the greater is the tendency to devitrify. The formation of glass is a kinetic process. It is reasonable to assess the glass stability by a
kinetic parameter, $K(T)$. Also, the $H_r$ parameter itself is a stability factor based on characteristic temperatures. Here a stability criterion is defined as

$$K_r(T) = K_0 \exp \left( \frac{-H_r E}{RT} \right)$$  \hspace{1cm} (15)$$

where $T$ is any temperature between $T_g$ and $T_p$. The theoretical background for the definition of the parameter $K_r(T)$ would be based on the analysis of the relation between the parameters $K(T)$ and $K_r(T)$. Differentiating Eqs. (2) and (15) with respect to temperature and rewrite each parameter per Kelvin we get:

$$\frac{\Delta K_r}{K_r RT^2} = \frac{H_r E}{RT^2} \quad \text{and} \quad \frac{\Delta K}{K R T^2} = \frac{E}{RT^2}$$

The above-mentioned variation of the parameter $K_r(T)$ is $H_r$ times the variation in parameter $K(T)$, which could justify the accuracy of the parameter $K_r(T)$. Just like the $K(T)$ criteria, the smaller the values of $K_r(T)$, the greater is thermal stability of the glass. The obvious advantage of this method is that it can evaluate the glass stability over a broad temperature range other than at only one temperature such as $T_g$ or $T_p$.

4. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the amorphous Ge$_{15}$As$_{20}$Te$_{65}$–In$_x$ ($x$ = 0, 3, and 6 at.%) glasses. The absence of the diffraction lines in the X-ray patterns indicates that the glasses have amorphous structures.

Fig. 2 shows the DSC thermogram for the amorphous Ge$_{15}$As$_{20}$Te$_{65}$ glass recorded at heating rate 10 K/min. As shown in this figure, there is a very small single endothermic peak. This peak is attributed to the glass transition temperature range which represents the strength or rigidity of the glass structure. Also there is an exothermic peak originating from the amorphous-crystalline transformation. The exo-peak has two characteristic points: the first is

Fig. 3. The plots of $T_g$ vs. $\ln(\alpha)$ for Ge$_{15}$As$_{20}$Te$_{65}$–In$_x$ ($x$ = 0, 3 and 6 at.%) glasses.

Fig. 4. The plots of $\ln(T_g^2/\alpha)$ vs. $(1/T_g)$ for Ge$_{15}$As$_{20}$Te$_{65}$–In$_x$ ($x$ = 0, 3 and 6 at.%) glasses.
the characteristics temperatures \((T_c, T_p, T_m)\) and the \(\Delta T, H_\alpha, H_m, S\) criteria for Ge_{15}As_{20}Te_{65-6}\%In \((x = 0, 3\) and 6 at.\%) glasses.

**Table 1**

![Table 1](image)

The characteristics temperatures \((T_c, T_p, T_m)\) and the \(\Delta T, H_\alpha, H_m, S\) criteria for Ge_{15}As_{20}Te_{65-6}\%In \((x = 0, 3\) and 6 at.\%) glasses.

**Table 2**

<table>
<thead>
<tr>
<th>Composition</th>
<th>(N_c)</th>
<th>(E_g) (kJ/mol)</th>
<th>(E_c) (kJ/mol)</th>
<th>(K_0) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge_{15}As_{20}Te_{65}</td>
<td>2.5</td>
<td>117.17</td>
<td>125.57</td>
<td>5.53 \times 10^{10}</td>
</tr>
<tr>
<td>Ge_{15}As_{20}Te_{63}In_{3}</td>
<td>2.53</td>
<td>148.72</td>
<td>151.57</td>
<td>1.59 \times 10^{14}</td>
</tr>
<tr>
<td>Ge_{15}As_{20}Te_{65}In_{6}</td>
<td>2.56</td>
<td>190.32</td>
<td>183.63</td>
<td>2.69 \times 10^{17}</td>
</tr>
</tbody>
</table>

The onset temperature of crystallization \((T_c)\) and the second is the temperature corresponding to the maximum crystallization rate \((T_p)\). The characteristic temperatures \((T_g, T_c, T_p, T_m)\) given by the DSC scans are listed in Table 1.

It is found that the variation of the glass transition temperature as a function of the heating rates follows the empirical relation:

\[ T_g = A \times \ln \alpha \]  
(16)

where \(A\) and \(B\) are constants for any given glass composition \([26]\).

Plots of \(T_g \) versus \(\ln(\alpha)\) for Ge_{15}As_{20}Te_{65-6}\%In \(_x\) glasses as shown in Fig. 3 indicates the validity of Eq. (16) for the studied glasses.

From this figure we can notice that the glass transition temperature increases with increasing the In content. The glass transition temperature is known to depend on several independent parameters such as the average coordination number \([27,28]\).

**Table 3**

<table>
<thead>
<tr>
<th>Composition</th>
<th>(\alpha) (K/min)</th>
<th>(K(T_c))</th>
<th>(K(T_p))</th>
<th>(K(T_m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge_{15}As_{20}Te_{65}</td>
<td>2.5</td>
<td>3.96 \times 10^{-6}</td>
<td>3.19 \times 10^{-3}</td>
<td>65.54</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>7.23 \times 10^{-5}</td>
<td>5.53 \times 10^{-3}</td>
<td>70.06</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.30 \times 10^{-6}</td>
<td>9.47 \times 10^{-3}</td>
<td>75.45</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.25 \times 10^{-5}</td>
<td>0.016</td>
<td>86.19</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.31 \times 10^{-5}</td>
<td>0.022</td>
<td>102.07</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.75 \times 10^{-5}</td>
<td>0.032</td>
<td>112.22</td>
</tr>
<tr>
<td>Ge_{15}As_{20}Te_{63}In_{3}</td>
<td>2.5</td>
<td>7.54 \times 10^{-6}</td>
<td>3.62 \times 10^{-3}</td>
<td>8.98 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>1.36 \times 10^{-5}</td>
<td>6.31 \times 10^{-3}</td>
<td>9.02 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.42 \times 10^{-5}</td>
<td>0.011</td>
<td>9.15 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.98 \times 10^{-5}</td>
<td>0.018</td>
<td>9.86 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.70 \times 10^{-5}</td>
<td>0.025</td>
<td>1.08 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.03 \times 10^{-5}</td>
<td>0.037</td>
<td>1.14 \times 10^{-4}</td>
</tr>
<tr>
<td>Ge_{15}As_{20}Te_{65}In_{6}</td>
<td>2.5</td>
<td>1.37 \times 10^{-5}</td>
<td>4.19 \times 10^{-3}</td>
<td>5.48 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>2.44 \times 10^{-5}</td>
<td>7.33 \times 10^{-3}</td>
<td>5.58 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>4.39 \times 10^{-5}</td>
<td>0.014</td>
<td>5.73 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>6.89 \times 10^{-5}</td>
<td>0.022</td>
<td>6.11 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>9.62 \times 10^{-5}</td>
<td>0.030</td>
<td>6.17 \times 10^{-1}</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.34 \times 10^{-4}</td>
<td>0.043</td>
<td>6.45 \times 10^{-1}</td>
</tr>
</tbody>
</table>
greater the glass thermal stability should be. Table 1 show that $\Delta T$, $H_t$, $H_g$, and $S$ decrease with the increase of In content, so we can say that the Ge$_{15}$As$_{20}$Te$_{65}$ glass is the most stable one.

Fig. 4 shows the plots of $\ln(T_f^2/\alpha)$ versus $1/T_f$ according to Eq. (14) for the Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ ($x = 0, 3$, and 6 at.%) glasses. From this figure we can obtain the values of the activation energy for glass transition ($E_g$) of Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ glasses. Values of $E_g$ for Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ ($x = 0, 3$, and 6 at.%) glasses were listed in Table 2. Values of $E_g$ for the Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ glasses lie within the observed values for chalcogenide glasses [32–34]. As shown in this table $E_g$ increases with the increase of In content. The increase in $E_g$ is due to the increase in $T_g$ (increasing the rigidity) with increasing In content. This result is in good agreement with Coftmenero and Barandiaran [35].

The linear relation of $\ln(T_f^2/\alpha)$ versus $1/T_f$ for Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ ($x = 0, 3$, and 6 at.%) glasses are plotted in Fig. 5 to obtain the activation energy of crystallization ($E_c$) and the frequency factor $K_0$. The obtained values of the activation energy of crystallization and the frequency factor are listed in Table 2. It is found that $E_c$ increases with increasing In content, this increase is a result of the increase of $T_p$ with increasing In content.

After known the values of $E_c$ and $K_0$, the kinetic parameters $K(T)$ and $K(T)$ for the studied glasses were calculated by using Eqs. (2) and (15). These calculations were carried out to compare the stability sequence of the studied materials. Values of $K(T)$ and $K(T)$ for the temperatures $T_g$ and $T_p$ are listed in Table 3. The smaller the values of the two criteria $K(T)$ and $K(T)$, the better the thermal stability of glass should be. The obtained data of these criteria (Table 3) indicates that the Ge$_{15}$As$_{20}$Te$_{65}$ glass is the most stable one, and the stability orders at different heating rates are Ge$_{15}$As$_{20}$Te$_{65}$ > Ge$_{15}$As$_{20}$Te$_{62}$In$_3$ > Ge$_{15}$As$_{20}$Te$_{59}$In$_6$.

Figs. 6 and 7 represent the plots of $K(T)$ versus $T$ for Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ ($x = 0, 3$, and 6 at.%) glasses at heating rates 10 and 20 K/min, respectively. From these figures, one can notice that, $K(T)$ for the first composition, Ge$_{15}$As$_{20}$Te$_{65}$, varies slowly with increasing the temperature indicating a relatively high stability, while it varies more rapidly with increasing $T$ for the other two compositions, which signifies a less stability.

5. Conclusions

The addition of In at the expense of Te in Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ glasses results in an apparent increase in the characteristic temperatures ($T_g$, $T_c$, and $T_p$), the activation energy for glass transition and the activation energy for crystallization. The thermal stability for the Ge$_{15}$As$_{20}$Te$_{65-x}$In$_x$ glasses has been evaluated by using various criteria. The $K(T)$ criterion has been considered in the present work for the evaluation of glass stability by using DSC data. The obtained results of the $K(T)$ and $K(T)$ agree satisfactorily with the $\Delta T$, $H_t$, $H_g$ and $S$ criteria for the studied glasses. The obtained data of the thermal stability criteria indicates that, the Ge$_{15}$As$_{20}$Te$_{65}$ glass is the most stable, and the stability orders at different heating rates are Ge$_{15}$As$_{20}$Te$_{65}$ > Ge$_{15}$As$_{20}$Te$_{62}$In$_3$ > Ge$_{15}$As$_{20}$Te$_{59}$In$_6$.

Acknowledgement

The authors thank Al-Azhar University for financial support.

References