Original Article

Applicability of Augis–Bennett relation for determination of activation energy of glass transition in some Se rich chalcogenide glasses

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ABSTRACT

The present work reports the results of non-isothermal DSC measurements on some Se-based ternary glasses for evaluation of activation of glass transition. The activation energy of glass transition (E_g) is determined using Augis–Bennett’s relation, which is basically derived for amorphous to crystalline phase transition. Moynihan’s relation which is derived on the concept of thermal relaxation and is basically used for glass transition is also used for determination of E_g values. We have observed that E_g values obtained from Augis–Bennett’s relation are in admirable agreement with the E_g values which are obtained using Moynihan’s relation.

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1. Introduction

The liquid–glass transition is one of the significant topics of condensed matter physics [1–4]. Its most well-known dynamic feature is the drastic slowing down of structural relaxation upon cooling. Significant work has been carried out by various investigators on thermal decomposition and thermal kinetics [5–7]. Keeping in mind the emerging applications of chalcogenide glasses in optics [8,9], such studies are in demand. Fundamental studies of the mechanisms and kinetics of crystal nucleation and growth in glass-forming liquids not only provide valuable scientific insight, but also have practical relevance. Indeed, a plethora of novel oxide, chalcogenide and metallic glasses, as well as micro and nano-structured glass-ceramics, are being continuously developed on basis of such knowledge [5,6]. Recently, it has been suggested that like crystallization phenomenon, the glass transition may be a novel type of critical phenomenon, where a structural order parameter is directly related to slowness. This motivated us to find the similarities between glass transition and crystallization phenomena.

The other significant problem in the area of glasses is the understanding of glass transition kinetics [1–4], which can be studied in terms of glass transition temperature (T_g) and activation energy of thermal relaxation (E_g). Moynihan et al.
developed the theory of glass transition kinetics based on structural relaxation in glasses for the evaluation of $E_g$ [10–12]. The relation derived by this group shows the heating rate dependence of glass transition temperature. This relation is widely used for evaluation of glass transition activation energy [13–18]. However, the $E_g$ values determined from this relation can depend substantially on the thermal history because of the dependence of relaxation time on temperature as well as structure. Hence, $E_g$ values determined from this relation must be viewed as apparent activation energy.

In order to search some new observations related to similarities and correlation between glass transition and crystallization phenomena, we have selected Augis–Bennett’s relation [19] as a tool. This relation was originally derived for determination of activation energy of crystallization [19] but we have used it for determination of activation energy of glass transition i.e., $E_g$ in the present study. Since $E_g$ evaluated from this relation has less dependence on thermal history, this method seems to have some extra advantage. However, the validity of its use for glass transition kinetics has always been questionable due to the fact that this method is basically derived for amorphous to crystalline transition. The application of this relation for glass transition means that similar kind of transition should be assumed in this case also. Some authors have given the name of this transition as glass to amorphous transition [20,21]. It is, therefore, interesting to see whether the Augis–Bennett’s relation can be applied in general for chalcogenide glasses for evaluating the activation energy of structural relaxation, which is normally obtained by Moynihan’s relation.

Various papers have been published by diverse groups on the crystallization kinetics. They used frequently Augis–Bennett relation for determination of activation energy of crystallization. They also compared their results with Kissinger method and other methods, which are also derived for determination of activation energy of crystallization. For example, Deepika et al. [22] reported the results of kinetic studies of glass transition and crystallization in $\text{Se}_{90-\delta}\text{Ge}_{\delta}\text{Te}_{20}$ glasses in a recent paper. In this paper, they also compared values of activation energy of crystallization determined by Augis–Bennett relation and some other relations.

From above discussion, it is clear that like other non-isothermal methods, Augis–Bennett relation is a well-known method for evaluation of activation energy of crystallization. All of these methods are originally derived from classical Johnson–Mehl–Avrami (JMA) model [23–25] in which the crystallized fraction ($\alpha$) is described as function of time. On the other hand, the kinetics of glass transition can be studied using the theory of glass transition kinetics and structural relaxation as developed by Moynihan and other investigators from the heating rate dependence of glass transition temperature.

This motivates us to compare the values of activation energy of glass transition process by both the relations in some glassy alloys prepared in our laboratory to check the validity of Augis–Bennett’s relation for glass transition phenomenon. We have found excellent agreement between the $E_g$ values obtained from both relations. These findings may shed new light not only on the fundamental nature of glass transition but also on the mechanism of crystal nucleation. To our knowledge, the invariance of Augis–Bennett’s relation from crystallization phenomenon to glass transition phenomenon has been proved for the first time.

2. Theoretical basis

The heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted by Moynihan et al. [10–12] in terms of thermal relaxation phenomenon. In this kinetic interpretation, they provided the following relation for heating rate $\beta$ dependence of glass transition temperature $T_g$:

$$\frac{d(\ln \beta)}{d(1/T_g)} = \left( \frac{E_g}{R} \right)$$

(1)

Eq. (1) states that $\ln \beta$ vs $1/T_g$ plot should be a straight line and the activation energy involved in the molecular motions and rearrangements around $T_g$ can be calculated from the slope of this plot.

During the isothermal transition, the extent of crystallization ($\alpha$) of a certain material is represented by the Avrami’s equation [23–25]:

$$\alpha(t) = 1 - \exp(-Kt^n)$$

(2)

where ‘$K$’ is the rate constant and ‘$n$’ is the order parameter, which depends upon the mechanism of crystal growth.

The rate constant $K$ is given by Arrhenius equation:

$$K = K_0 \exp \left( \frac{-E_c}{RT} \right)$$

(3)

Here $K_0$ is pre-exponential factor.

Augis and Bennett [19] developed a method for evaluation of activation energy of crystallization and the pre-exponential factor of rate constant $K$. They taking proper account of the temperature dependence of the reaction rate, and their approach resulted in a linear relation between $\ln(1/T_c/\beta)$ versus $1/T_c$ in the following form:

$$\ln \left( \frac{\beta}{T_c} \right) = \left( \frac{-E_c}{RT} \right) + \ln K_0$$

(4)

This equation is used to calculate the activation energy of crystallization by plotting $\ln(\beta/T_c)$ vs $1/T_c$ curve. This method has an extra advantage that the intercept of $\ln(\beta/T_c)$ vs. $1/T_c$ gives the value of pre-exponential factor $K_0$ of Arrhenius equation.

Although originally derived for the crystallization process, we have checked the validity of this relation for glass transition process. Hence, the above equation takes the following form for its use in glass transition kinetics:

$$\ln \left( \frac{\beta}{T_g} \right) = \left( \frac{-E_g}{RT_g} \right) + \text{constant}$$

(5)

3. Experimental

Glassy $\text{Se}_{90-\delta}\text{Te}_{\delta}\text{M}_x$ ($M = \text{Ag, Cd, Sb}; 0 \leq x \leq 15$) alloys were prepared by quenching technique. The exact proportions of high
purity (99.999%) elements, in accordance with their atomic percentages, were weighed out using an electronic balance with a sensitivity of \(10^{-4}\) g. The materials were then sealed in evacuated (~10^{-5} Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm) using a high vacuum pumping system. Each ampoule was kept inside the furnace at a temperature of 1000 °C (where the temperature was raised at a rate of 3–4 °C/min). During heating, all the ampoules were constantly rocked by rotating a ceramic rod to which the ampoules were attached in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping rapidly into ice-cooled water. The ingots were then taken out by breaking the quartz ampoules. The glassy nature of the alloys was ascertained by XRD technique.

The glasses, thus prepared, were ground to fine powder for DSC studies. 10–20 mg of the powder was heated at constant heating rate, and the changes in heat flow with respect to an empty reference pan were measured. Fig. 1 shows the typical DSC scans for glassy Se_{65}Te_{20}Ag_{15} alloy at different heating rates. It is clear from this figure that well defined peak is observed at glass transition temperatures (\(T_g\)). Similar DSC scans were obtained for the other glasses at all heating rates.

4. Results and discussion

Using Moynihan’s relation (Eq. (1)), the plots of \(\ln \beta\) against \(10^3/T_g\) are plotted for binary Se_{80}Te_{20} alloy and ternary Se_{70}Te_{20}M_{10} (M = Ag, Cd, Sb) alloys. Such plots for the present glasses are shown in Fig. 2. Similar plots were obtained for other glassy alloys. The slopes of these plots were used to calculate the activation energy of glass transition process. Tables 1–3 show the \(E_g\) values obtained from Eq. (3) for glassy Se_{80–x}Te_{20}M_x (M = Ag, Cd, Sb; 0 ≤ x ≤ 15) system.

The values of \(E_g\) are also evaluated using Augis–Bennett’s relation (Eq. (5)) from the slopes of plots of \(\ln(\beta/T_g^2)\) against \(10^3/T_g\) for binary Se_{80}Te_{20} alloy and ternary Se_{70}Te_{20}M_{10} (M = Ag, Cd, Sb) alloys. Such plots for present glasses are shown in Fig. 3. Similar plots were obtained for other glassy alloys.

Fig. 1 – DSC scans for glassy Se_{65}Te_{20}Ag_{15} alloy at heating rates \(\beta = 5, 10, 15\) and 20 K min\(^{-1}\). The measurements have been done using DSC in non-isothermal mode.

Fig. 2 – Plots of \(\ln(\beta)\) vs. \(10^3/T_g\) for binary Se_{80}Te_{20} alloy and ternary Se_{70}Te_{20}M_{10} (M = Ag, Cd, Sb) alloys. Straight line confirms the validity of Moynihan relation.

Fig. 3 – Plots of \(\ln(\beta/T_g^2)\) vs. \(10^3/T_g\) for binary Se_{80}Te_{20} alloy and ternary Se_{70}Te_{20}M_{10} (M = Ag, Cd, Sb) alloys.
Table 1 – Activation energy of glass transition for glassy $\text{Se}_{\text{80}}\text{Te}_{\text{20}}\text{Ag}_x$ ($x = 0, 5, 10, 15$) alloys determined by Augis–Bennett relation and Moynihan relation.

<table>
<thead>
<tr>
<th>Glassy sample</th>
<th>Augis–Bennett relation</th>
<th>Moynihan relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}<em>{\text{80}}\text{Te}</em>{\text{20}}$</td>
<td>185.3</td>
<td>182.0</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{75}}\text{Te}</em>{\text{20}}\text{Ag}_5$</td>
<td>203.6</td>
<td>201.1</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{70}}\text{Te}</em>{\text{20}}\text{Ag}_{10}$</td>
<td>158.7</td>
<td>156.2</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{85}}\text{Te}</em>{\text{20}}\text{Ag}_{15}$</td>
<td>141.3</td>
<td>138.8</td>
</tr>
</tbody>
</table>

Table 2 – Activation energy of glass transition for glassy $\text{Se}_{\text{80}}\text{Te}_{\text{20}}\text{Cd}_x$ ($x = 0, 5, 10, 15$) alloys determined by Augis–Bennett relation and Moynihan relation.

<table>
<thead>
<tr>
<th>Glassy sample</th>
<th>Augis–Bennett relation</th>
<th>Moynihan relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}<em>{\text{80}}\text{Te}</em>{\text{20}}$</td>
<td>185.3</td>
<td>182.0</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{75}}\text{Te}</em>{\text{20}}\text{Cd}_5$</td>
<td>174.5</td>
<td>171.2</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{70}}\text{Te}</em>{\text{20}}\text{Cd}_{10}$</td>
<td>142.1</td>
<td>139.6</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{85}}\text{Te}</em>{\text{20}}\text{Cd}_{15}$</td>
<td>147.9</td>
<td>145.4</td>
</tr>
</tbody>
</table>

Table 3 – Activation energy of glass transition for glassy $\text{Se}_{\text{80}}\text{Te}_{\text{20}}\text{Sb}_x$ ($x = 0, 5, 10, 15$) alloys determined by Augis–Bennett relation and Moynihan relation.

<table>
<thead>
<tr>
<th>Glassy sample</th>
<th>Augis–Bennett relation</th>
<th>Moynihan relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Se}<em>{\text{80}}\text{Te}</em>{\text{20}}$</td>
<td>185.3</td>
<td>182.0</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{75}}\text{Te}</em>{\text{20}}\text{Sb}_5$</td>
<td>166.2</td>
<td>163.7</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{70}}\text{Te}</em>{\text{20}}\text{Sb}_{10}$</td>
<td>179.5</td>
<td>176.2</td>
</tr>
<tr>
<td>$\text{Se}<em>{\text{85}}\text{Te}</em>{\text{20}}\text{Sb}_{15}$</td>
<td>155.4</td>
<td>152.1</td>
</tr>
</tbody>
</table>

These values are also given in Tables 1-3 for glassy $\text{Se}_{\text{80}}\text{Te}_{\text{20}}\text{M}_x$ ($\text{M} = \text{Ag, Cd, Sb}; 0 \leq x \leq 15$) system. The comparison of activation energy of glass transition obtained from both methods is shown in Fig. 4 for the present glasses. It is clear from this figure that the values of $E_g$ obtained from Augis–Bennett’s relation are in good agreement with the $E_g$ values obtained using Moynihan’s relation.

Chalcogenide glasses may be considered as amorphous semiconductors, since they have no long range order. However, many glass technologists object to this definition as they prepare a glass by cooling a melt in such a way that it does not crystallize and feel that this process is an essential characteristic of a glass. Solids lacking long range positional order are called non-crystalline solids. Non-crystalline solids produced by melt-cooling are generally referred to as glass. Non-crystalline solids made by non-conventional methods, such as vapor deposition, sol–gel and solid-state amorphization processes are sometimes referred to as glass and other times as amorphous solids. A non-crystalline solid is defined as a glass if it satisfies the condition [26]:

$$E_R(\text{glass}) = E_R(\text{melt})$$ (6)

This condition is clearly satisfied for glasses formed by melt-cooling because the structure of a melt is frozen-in during liquid to glass transition. Eq. (6) represents a condition on the structural state of a non-crystalline solid and is not a statement about its method of formation. Accordingly, whether a non-crystalline solid is made by melt-cooling or by methods other than melt-cooling, it is called glass as long as it satisfies condition (6).

Fig. 3 – Plots of $\ln(\beta/T_g)$ vs $10^3/T_g$ for binary $\text{Se}_{\text{80}}\text{Te}_{\text{20}}$ alloy and ternary $\text{Se}_{\text{70}}\text{Te}_{\text{20}}\text{M}_{10}$ ($\text{M} = \text{Ag, Cd, Sb}$) alloys. Straight line confirms the validity of Augis–Bennett relation.
Fig. 4 – Comparison of $E_g$ values for binary $\text{Se}_{80}\text{Te}_{20}$ alloy and ternary $\text{Se}_{70}\text{Te}_{30}\text{M}_{10}$ (M = Ag, Cd, Sb) alloys obtained from the slopes of straight lines of Figs. 2 and 3. The primary $y$-axis (L.H.S. $y$-axis) indicates the $E_g$ values obtained from Moynihan relation. The secondary $y$-axis (R.H.S. $y$-axis) indicates the $E_g$ values obtained from Augis–Bennett relation.

However, amorphous solids (a-solids) are the non-crystalline solids, which violate condition (6). In other words

$$\text{SRO (a-solids)} \neq \text{SRO (melt)}$$  \hspace{1cm} (7)

Such amorphous solids are good non-crystalline solid formers since the coordination numbers in both the amorphous and the crystalline states are equal. However, they disobey condition (6).

From the above discussion, it is clear that ‘amorphous’ and ‘glass’ are the two different phases of non-crystalline solids. According to Moharram et al. [20,21], glass transition kinetics can be treated as pre-crystallization kinetics and the analysis of endothermic (glass transition) peaks can be made in the same way as those made on exothermic (crystallization) peaks using Augis–Bennett’s relation. A chalcogenide glass can, therefore, said to be in ‘glass’ phase before the glass transition ($T<T_g$), which transforms into a new phase after the glass transition ($T>T_g$). Though, it faces structural rearrangements in glass transition process, yet it retains short range order structure in this new phase. The phase from glass transition temperature to crystallization temperature may be called ‘amorphous’ phase as on heating further, a transition takes place from amorphous phase to crystalline phase.

From the above discussion, one can see that the glass transition phenomenon can be treated as glass to amorphous phase transition. For $T<T_g$, the sample is in glassy phase, while it transforms into amorphous phase for $T>T_g$. Since Augis–Bennett’s relation is derived for crystallization process, which is also a phase transition from amorphous phase to crystalline phase, it may be valid for glass to amorphous transition process also. The present results support this argument as the $E_g$ values obtained from the two relations are in good agreement with each other.

5. Conclusions

The activation energy of glass transition process has been determined using Augis–Bennett’s relation for various glassy alloys in order to compare the $E_g$ values obtained from this relation with the $E_g$ values evaluated by us using Moynihan’s relation.

The results show that $E_g$ values obtained from Augis–Bennett’s relation are in good agreement with the $E_g$ values, which were obtained using Moynihan’s relation. Thus, one can use any of the two relations (Augis–Bennett’s relation and Moynihan’s relation) for the evaluation of $E_g$ values. This proves the invariance of Augis–Bennett’s from glass transition phenomenon to crystallization phenomenon.

Conflict of interest

The authors declare no conflicts of interest.

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