

APPLICABILITY OF KISSINGER'S RELATION IN THE DETERMINATION OF ACTIVATION ENERGY OF GLASS TRANSITION PROCESS

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The present paper reports the non-isothermal DSC measurements on 30 binary and ternary chalcogenide glasses. The activation energy of glass transition (E_t) is calculated using Kissinger's relation which is basically derived for amorphous to crystalline transformation. The results show that E_t values obtained from Kissinger's relation are in good agreement with the E_t values which are obtained using Moynihan's relation derived, based on the concept of thermal relaxation. It has also been found that the composition dependence of E_t , obtained from the two different relations, is similar in most of the glassy systems. This shows that Kissinger's relation can be applied in determining the activation energy of glass transition process also. This shows that the phase transformation near glass transition temperature is analogous to phase transformation near crystallization temperature.

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1. Introduction

There has been considerable interest in chalcogenide glasses because of their interesting physical properties as well as their wide technological applications. However, since glassy materials are not in equilibrium, their properties strongly depend on the thermal history of samples. In the glass transition region, the properties are dependent on time because, in this region, the experimental time scale becomes comparable to the time scale for structural rearrangements; the material will relax towards equilibrium, this phenomenon being called structural relaxation.

One of the most important problems in the area of glasses is the understanding of glass transition kinetics [1-3] which can be studied in terms of glass transition temperature (T_g) and activation energy of thermal relaxation (E_t). The evaluation of E_t using the theory of glass transition kinetics and structural relaxation as developed by Moynihan and other workers [4 - 6] from the heating rate dependence of glass transition temperature is widely discussed in literature. In our laboratory also, different glassy systems were prepared by quenching technique and the activation energy of glass transition of these samples were evaluated using Moynihan's relation in a series of papers [7 - 10]. However, the E_t 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_t values determined from this relation must be viewed as apparent activation energy.

Some attempts have also been made to evaluate E_t using Kissinger's relation [11 - 29]. Since E_t evaluated from this relation has less dependence on thermal history [13], this method seems to have some extra advantage. Since this method is basically given for amorphous to crystalline transformation, the validity of its use for glass transition kinetics has always been questionable. The application of this relation for glass transition means that some kind of transformation is assumed in this case also. Some authors have given the name of this transformation as glass to amorphous transformation [19, 24]. It is, therefore, interesting to see whether the Kissinger's relation can be

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applied in general for chalcogenide glasses for evaluating the activation energy of structural relaxation, which is normally obtained by Moynihan's relation. This motivates us to compare the values of activation energy of glass transition process by both the relations in a large number of glassy alloys prepared in our laboratory. For each glassy alloy, same set of Differential Scanning Calorimetry (DSC) data has been used for this purpose. The results shows that E_t values obtained for these glasses using Kissinger's relation are in good agreement with that obtained using Moynihan's relation in our past work [7 – 10].

2. Theoretical basis

2.1 Moynihan's relation

The heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted by Moynihan et. al. [6] in terms of thermal relaxation phenomenon. In this kinetic interpretation, the enthalpy at a particular temperature and time $H(T, t)$ of the glassy system, after an instantaneous isobaric change in temperature, relaxes isothermally towards a new equilibrium value $H_e(T)$. The relaxation equation can be written in the following form [4]:

$$(\delta H / \delta t)_T = - (H - H_e) / \tau \quad (1)$$

where τ is a temperature dependent structural relaxation time and is given by the following relation:

$$\tau = \tau_0 \exp(-E_t / RT) \exp[-c(H - H_e)] \quad (2)$$

Where τ_0 and c are constants and ΔE_t is the activation energy of relaxation time. Using the above equations, it can be shown [5, 6] that:

$$d(\ln \beta) / d(1 / T_g) = - E_t / R \quad (3)$$

Equation (3) states that $\ln \beta$ vs $1 / T_g$ plot should be 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.

2.2 Kissinger's relation

This method is most commonly used in analyzing crystallization data in DSC. During the isothermal transformation, the extent of crystallization (α) of a certain material is represented by the Avrami's equation [30, 31]:

$$\alpha(t) = 1 - \exp(-K t^n) \quad (4)$$

where 'K' is 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:

$$K = K_0 \exp[-E_c / k T] \quad (5)$$

According to Kissinger, the Eq. (4) can be approximated as:

$$d\alpha / dt = (1 - \alpha) n K^n t^{n-1} \quad (6)$$

Expressing t in terms of α from Eq. (4), the crystallization rate $d\alpha / dt$ becomes:

$$d\alpha / dt = A n K (1 - \alpha) \quad (7)$$

where $A = [-\ln(1 - \alpha)]^{(n-1)/n}$.

In non-isothermal crystallization, it is assumed that there is a constant heating rate in the experiment. The relation between the sample temperature T and the heating rate β can be written in the form:

$$T = T_i + \beta t \quad (8)$$

where T_i is the initial temperature.

The derivative of K with respect to time can be obtained from Eqs. (5) and (8) as follows:

$$dK / dt = (dK / dT) \cdot (dT / dt) = (\beta E_c / R T^2) K \quad (9)$$

Using the equations (7) and (9), Kissinger showed that:

$$\ln (\beta / T_c^2) = - E_t / R T_c + \text{constant} \quad (10)$$

where T_c is peak crystallization temperature.

Although originally derived for the crystallization process, it is suggested that this relation is valid for glass transition process [12,13] and hence the above equation takes the following form for its use in glass transition kinetics:

$$\ln (\beta / T_g^2) = - E_t / R T_g + \text{constant} \quad (11)$$

3. Results

Using Moynihan's relation [Eqn. (3)], the plots of $\ln \beta$ against $10^3 / T_g$ were plotted for various glassy alloys. The slopes of these plots were used to calculate the activation energy of glass transition process. Table 1 shows the E_t values obtained from Eqn. (3).

Table 1. E_t values of different chalcogenide glasses using theory of Moynihan et al and Kissinger's relation.

S. No.	Sample	Values of E_t using theory of Moynihan et al (kJ/mol)	Values of E_t using Kissinger's relation (kJ/mol)
1	Se ₉₅ Te ₅	67.9	59.2
2	Se ₉₀ Te ₁₀	106.0	105.4
3	Se ₈₅ Te ₁₅	112.2	109.4
4	Se ₈₀ Te ₂₀	116.4	110.8
5	Se ₇₅ Te ₂₅	124.7	114.2
6	Se ₇₀ Te ₃₀	153.1	146.4
7	Se ₉₅ In ₅	72.7	67.7
8	Se ₉₀ In ₁₀	86.6	85.2
9	Se ₈₅ In ₁₅	92.4	79.4
10	Se ₈₀ In ₂₀	103.9	85.2
11	Se ₇₀ In ₃₀	116.9	98.3
12	Se ₇₅ Te ₂₀ In ₅	108.0	101.7
13	Se ₇₀ Te ₂₀ In ₁₀	103.0	102.3
14	Se ₆₅ Te ₂₀ In ₁₅	71.0	64.5
15	Se ₆₀ Te ₂₀ In ₂₀	120.0	118.3
16	Se ₇₅ Te ₂₀ Sb ₅	133.0	160.6
17	Se ₇₀ Te ₂₀ Sb ₁₀	172.6	184.9
18	Se ₆₅ Te ₂₀ Sb ₁₅	155.7	149.7
19	Se ₇₅ Te ₂₀ Cd ₅	143.0	168.1
20	Se ₇₀ Te ₂₀ Cd ₁₀	141.2	136.3
21	Se ₆₅ Te ₂₀ Cd ₁₅	147.7	142.0
22	Se ₇₅ Te ₂₀ Ag ₅	166.2	196.4
23	Se ₇₀ Te ₂₀ Ag ₁₀	161.5	152.9
24	Se ₆₅ Te ₂₀ Ag ₁₅	141.5	135.9
25	Se ₇₀ Te ₂₈ Ag ₂	191.4	185.6
26	Se ₇₀ Te ₂₆ Ag ₄	203.2	197.3
27	Se ₇₀ Te ₂₄ Ag ₆	198.2	192.7
28	Se ₉₀ Ge ₈ In ₂	165.7	159.7
29	Se ₉₀ Ge ₆ In ₄	148.3	142.3
30	Se ₉₀ Ge ₄ In ₆	172.4	166.4

The values of E_t are also evaluated using Kissinger's relation [Eqn. (11)] from the slopes of plots of $\ln(\beta/T_g^2)$ against $10^3/T_g$ for various glassy systems. These values are also given in Table 1.

It is clear from Table 1 that E_t values obtained from Kissinger's relation are in good agreement with the E_t values obtained using Moynihan's relation. The E_t values obtained from these two relations for various glassy alloys are plotted against the composition of chalcogenide glassy systems [see Fig. 1 (a) and Fig. 1 (b)]. It is clear from Fig. 1 that the composition dependence of E_t values obtained using the two relations are similar in most of the glassy systems.

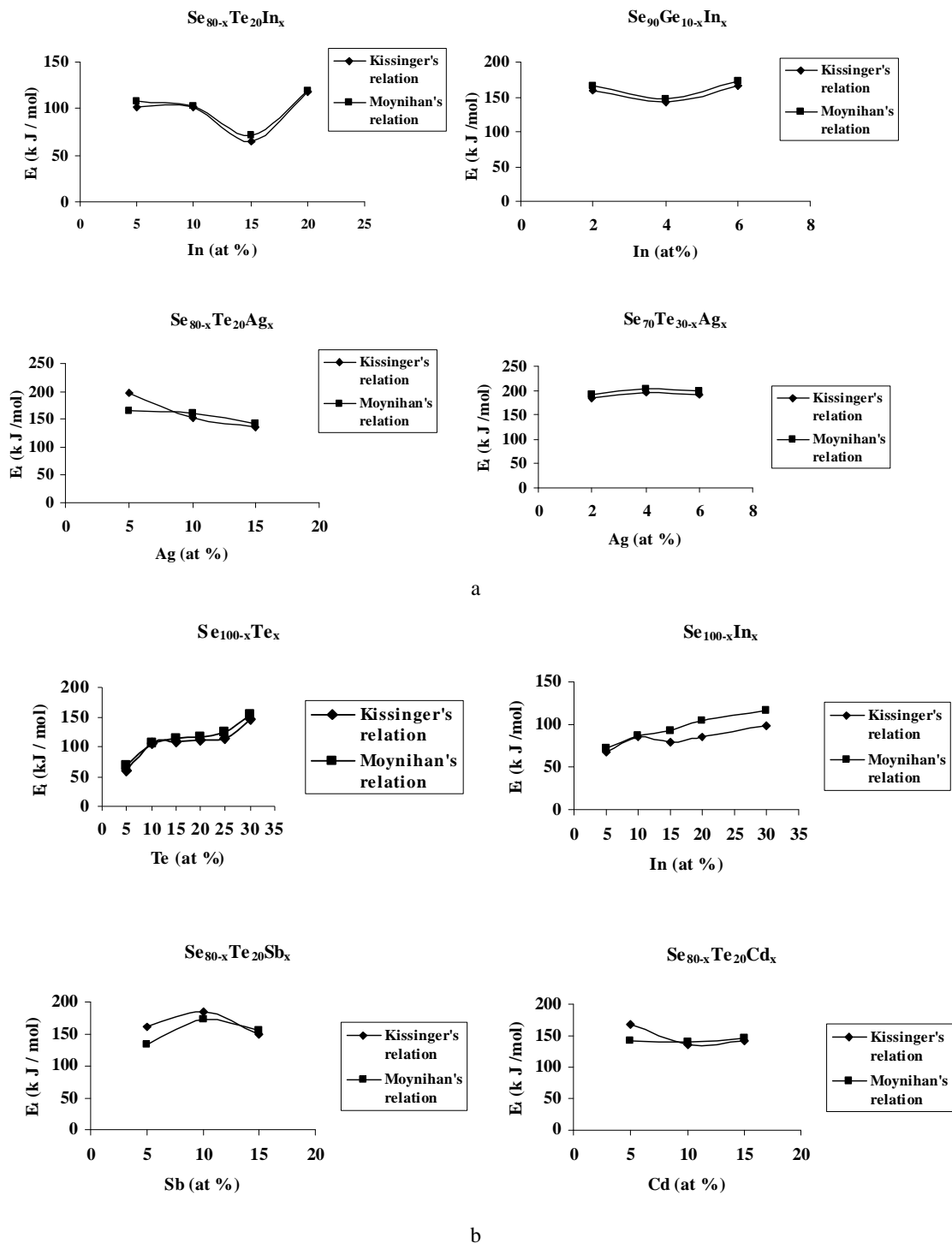


Fig. 1. Plots of composition dependence of E_t values obtained from Moynihan's relation and Kissinger's relation in different glassy systems.

It is interesting to note that the Eqn. (3) can also be obtained using the Mahadevan et al approximation [29] in Eqn. (11). According to this approximation, when the variation of $\ln(1/T_g^2)$ with $\ln \beta$ is much slower than that of $1/T_g$ then Eqn. (11) converts in to the form:

$$\ln \beta = - E_t / R T_g + \text{constant} \quad (12)$$

which is exactly similar to the the Eqn. (3). This indicates that the structural relaxation phenomenon during glass transition can also be explained by Kissinger's relation.

According to Moharram et al [19, 24], 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 Kissinger's relation.

4. Discussion

Glassy solid state has a large viscosity, the relaxation kinetics are very slow leaving a few opportunities for local arrangements of bonds and atomic displacements. This type of thermal relaxation depends upon the annealing temperature and may be quite fast near the glass transition temperature. Thus, it is reasonable to associate the glass transition temperature with the structural rearrangements. On the basis of this, the glass transition phenomenon can be divided into following three regimes:

$T > T_g \Rightarrow$ it describes liquid equilibrium region where the return to equilibrium is almost instantaneous.

$T \sim T_g \Rightarrow$ it describes glass transition region.

$T < T_g \Rightarrow$ it describes glass region, where the structure is frozen.

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.

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, it is clear that the glass transition phenomenon can be treated as glass to amorphous phase transformation. For $T < T_g$, the sample is in glassy phase, while it transforms into amorphous phase for $T > T_g$. Since Kissinger's relation is derived for crystallization process, which is also a phase transformation from amorphous phase to crystalline phase, it may be valid for glass to amorphous transformation process also. The present results support this argument as the E_t 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 Kissinger's relation for various glassy alloys in order to compare the E_t values obtained from this relation with the E_t values evaluated by us in our previous work using Moynihan's relation.

The results show that E_t values obtained from Kissinger's relation are in good agreement with the E_t values which were obtained using Moynihan's relation. It has also been found that the composition dependence of E_t values obtained using the two relations are similar in most of the glassy systems. Thus, one can use any of the two relations (Kissinger's relation and Moynihan's relation) for the evaluation of E_t values.

The major conclusion of the present work is that, analogous to crystallization process, the glass transition phenomenon is also a phase transformation process in chalcogenide glasses. Hence, the Kissinger's relation can be used for evaluation of activation energy of glass transition as well as crystallization processes in chalcogenide glasses.

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