Original Article

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

Shipra Saraswat [a,b,*], Neeraj Mehta [a,b], Surendra Dutt Sharma [a,b]

[a] *Department of Chemistry, IFTM University, , Moradabad , India*
[b] *Department of Physics, Banaras Hindu University, Varanasi, India*

ARTICLE INFO

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.

© 2015 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda.

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 $Se_{58}Ge_{42-x}Pb_x$ 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 (α) 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 β dependence of glass transition temperature T_g:

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

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 (α) of a certain material is represented by the Avrami's equation [23–25]:

$$\alpha(t) = 1 - \exp(-Kt^n) \tag{2}$$

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:

$$K = K_0 \exp \left(\frac{-E_c}{RT} \right) \tag{3}$$

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 $\ln(T_c)/\beta$ versus $1/T_c$ in the following form:

$$\ln \left(\frac{\beta}{T_C} \right) = \left(\frac{-E_C}{RT} \right) + \ln K_0 \tag{4}$$

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:

$$\ln \left(\frac{\beta}{T_g} \right) = \left(-\frac{E_g}{RT_g} \right) + \text{constant} \tag{5}$$

3. Experimental

Glassy $Se_{80-x}Te_{20}M_x$ (M = Ag, Cd, Sb; $0 \leq x \leq 15$) alloys were prepared by quenching technique. The exact proportions of high