

KINEMATICAL STUDIES OF THE GLASS TRANSITION IN GLASSY $(\text{Bi}_2\text{Se}_3)_{1-x}(\text{Te})_x$ SYSTEM

Manish Saxena

Department of Applied Sciences and Humanities, Moradabad Institute of
Technology, Moradabad-244 001 (India)

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ABSTRACT

Crystallization studies are carried out under non isothermal conditions with samples heated at several uniform rates. Variations in two important parameters namely glass transition temperature T_g and glass forming ability K_{gl} have been studied with variation in Bi content at various heating rates. Analyzing the results that with the increase in Bi content, the glass forming ability K_{gl} , also decreases has been seen. The activation energy plays a dominant role in deciding the utility of the material for the specific purpose-here storage. From the heating rate dependence of T_g , the activation energy E , for glass transition has been evaluated. This analysis helps in finding the suitability of an alloy to be used in phase transition optical memories/switches.

Keywords: Glasses-thermal properties, Thermal Analysis, Glass-optical materials Activation energy.

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INTRODUCTION

Chalcogenide glasses have drawn attention because of their use in various solid-state devices. The growing interest in these glasses is partly because of their interesting electrical, thermal and optical properties, and hence their wide technological applications including threshold and memory switching. Threshold switches are made in those glasses near the center of the glass-forming region where the glasses are stable and show little or no tendency to crystallize when heated or cooled slowly. Memory switches come from the boundaries of the glass-forming region where the glasses are more prone to crystallization. In chalcogenide glass systems, the glasses which exhibit no exothermic crystallization reaction above the glass transition temperature, T_g could possibly be used in threshold switching system whereas glasses exhibiting an endothermic crystallization reaction above T_g show a memory type of switching^{1,2}. It has been shown that the amorphous films with composition outside the glass-forming region are more suitable for memory devices because of their fast crystallization during the application of a suitable electric pulse or by the heat of a focused laser beam. The kinematical studies are always connected with the concept of the activation energy. The values of these studies in glass crystallization phenomena are associated

with the nucleation and growth processes, which dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with individual nucleation and growth steps in a transformation, although they usually have been combined in to activation energy representative of the overall crystallization process. Among amorphous chalcogenide alloys, selenium based melt are characterized by a high viscosity^{3,4}. This feature favours the glass formation in bulk form by air-quenching or water-quenching as well as in evaporated thin film forms. Since tellurium based melts with the same elements generally have low viscosity, a high cooling rate is required to prevent nucleation and growth during quenching and to obtain bulk glasses. Among chalcogenide glasses, Se-Te based alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and smaller ageing effects as compared to pure Se glass. The tellurium alloys have often been used for the active layer of those devices because they have low melting point. Te- based alloys, which contain a small amount of Ge, As, Sb or Bi, exhibit fast crystallization processes after switching. However, these alloys present several problems like segregation and low crystallization temperature. The segregation limits the reversible transition between crystalline and amorphous states, because in every crystallization process,

the compositional deviation is likely to continue in the active layer. A ternary solid alloy with relatively low melting point may be the answer to the above problems, because no compositional changes occur in a solid solution when it is cycled between amorphous and crystalline states. In this paper, we report our studies on Bi-Se-Te ternary glasses. A fundamental observation recently made for the rapidly quenched metal alloys is that they do not usually indicate a sharp glass liquid transition characteristics of amorphous material⁵⁶. The studies of crystalline kinetics of a glass upon heating can be performed in several different ways. In calorimetric measurements, two basic methods can be used, isothermal and non-isothermal. In the isothermal methods, 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 non-isothermal method, the sample is heated at a fixed rate $|\beta|$ and the heat evolved is recorded as a function of temperature or time^7 . For phase change optical switching systems, it is important to optimize various parameters like, the glass transition temperature T_g , the crystallization temperature T_c and the melting temperature T_m by varying the composition and heating rate⁸. Crystallization studies are carried out under non-isothermal conditions with samples heated at several uniform rates. The value of this energy is associated with nucleation and growth processes that dominate the devitrification of most glassy solids^{9,10}. From the heating rate dependence of T_g , the activation energy for glass transition (E_t) has been evaluated.

EXPERIMENTAL

For the preparation of Te-Bi-Se glasses, high purity elements (99.999%) in appropriate atomic percentage were weighed in to quartz ampoules. The ampoules, sealed under high vacuum conditions (10^{-5} Torr) were suspended in a vertical furnace at 900°C for 24 hours, shaken vigorously for homogeneous mixing. The temperature was raised at a rate of 3 to 4 K/min. The melt was rapidly quenched in ice-water mixture. The quenched samples were removed from the ampoule by dissolving the ampoule in a mixture of $\text{HF} + \text{H}_2\text{O}_2$ for about 20 hours. The samples were then kept at room temperature in dark for about one month for attainment of thermodynamic

equilibrium as stressed by Abkowitz in chalcogenide glasses¹¹. Amorphous nature of the samples was ensured by the absence of any sharp peaks in the X-ray diffractograms.

The prepared solid solution in powder form has been used thermal analysis using the Differential Thermal Analysis (DTA). This material was first sealed in a standard aluminium pan and the calorimetric thermograms of various compositions of the samples were obtained with a RIGAKU DTA 8150 calorimeter in the temperature range $50\text{--}700^\circ\text{C}$ at various heating rates ($10\text{--}20^\circ\text{C min}^{-1}$). Calorimetric measurements were made under non-isothermal conditions and a multi-scan technique has been used for crystallization studies. The activation energy for glass transition (E_t) has been determined by using Kissinger's equation in different forms.

RESULT AND DISCUSSION

The transformation to a glass does not take place at one, strictly defined temperature, but within a temperature range, representing the transformation region¹². The width of the later depends on the properties of the material studied (low-temperature edge) and on the thermal history of the sample (high-temperature edge). It has been shown that for a given uniform heating rate, the glasses show a single glass transition endothermic peak and a single exothermic crystallization peak. The single endothermic glass transition peak indicates the homogeneity of the glass. T_g represents the "Strength" or the "rigidity" of the glass structure. Therefore, drastic changes in T_g cannot be expected by increase in Bi content, which results in isostructural units of nearly same bond strength. The slight increase in T_g observed is probably due to the increase in mean molecular weight of the glasses with increasing Bi content. The observed increase is attributed either to the increase in the effective molecular weight with increasing Bi content or to the increase in concentration of long polymer chains.

In the present Te-Bi-Se glass system, the glass transition temperature was found to increase with increasing the amount of Bi. The values of glass transition temperature were also found to increase with the increase in heating rates from 10 K/min to 20 K/min. This may be attributed to the fact that when heating rate is high, the system doesn't get sufficient time for nucleation and crystallization. By the time crystallization start-

taking place, the temperature goes up owing to the higher heating rates. DTA curves for Bi at 28% for different heating rates, ranging from 10K/min to 20 K/min have been shown in fig (1). The single endothermic glass transition peak indicates the homogeneity of the glass.

These observations can be explained to some extent with the help of CONM wherein the formation of heteropolar bonds is favoured over the formation of homopolar bonds. In the Te-Bi-Se system the various bonds involved are Bi-Te, Bi-Se, Te-Se, Se-Se, Te-Te etc. When the atomic percentage of Bi is increased in Te-Bi-Se glass system, Bi is expected to combine preferably with Se because the bond energy of Bi-Se (170.4 KJ/mol) is greater than that of Bi-Te (125.6 KJ/mol). This results in decreasing Se-Se bonds. This explains the increase in T_g with the increase in Bi content due to the formation of large number of heteropolar bonds Bi-Se and decrease in homopolar bonds Se-Se, Te-Te, and Te-Se bonds. The results are similar to those obtained by earlier workers¹³.

Two approaches are used to discuss the dependence of T_g on the heating rate β :

One is the empirical relationship of the form¹⁴-

$$T_g = A + B \log \beta \quad \dots(1)$$

Where A and B are constant for a given glass composition and p is the heated rate, holds good for all the samples of Te-Bi-Se glass system. The values of B are found to be different glass compositions, indicating that Te-Bi-Se alloy undergoes structural changes for different Bi concentration, because the values of B is an indication of the response of the configurational changes within the glass transition region. Transformation to a glass doesn't take place at one, strictly defined temperature, but within a temperature range, representing the transformation region. The width of the later depends on the properties of material studied (low temperature edge) and on the thermal history of the sample (high temperature edge).

The other approach, which is commonly, used in analysing crystallization data in DTA/DSC analysis for the evaluation of the activation energy for glass transition, E_t , developed by Kissinger^{5,16}, is expressed as

The plots of T_g versus p as shown in fig (2), and the plots of $\ln (T_g^2 \beta)$ versus $10^3/T_g$ as shown in fig (3) are seen to be linear for these glasses up to a heating rate of 20K/min. The activation energy, E_t , for the glass transition, using the plots of fig (3), are found to decrease from 1.896 eV to 1.565 eV with the increase in Bi content for these samples. The variation of activation energy for glass transition E_t , with Bi content is given in fig (5).

The Kissinger equation can approximated be written by the form¹⁷

$$\ln \beta = -E/kT_g + \text{constant}$$

Fig (4) shows the plots of $\ln p$ versus $10^3/T_g$ for different compositions of Te-Bi-Se system, which are seen to be linear for these glasses. The activation energy for glass transition, E_t , deduced using this relation is found to decrease from 1.982 eV to 1.652 eV with the increase in Bi content. The variation of activation energies, deduced by using relation (3) with Bi content is shown in fig (5).

From the comparison of these two results, it is evident that the two deduced values, so obtained by using relations (2) and (3), are in good agreement with each other. This means that one can use either of the two relations to calculate glass transition activation energy E_t .

Thermal stability and ease of glass formation

For a memory/switching material, the thermal stability and ease of glass formation are of crucial important. The value of $T_e - T_g$ is found to decrease with increase in Bi concentration. This indicates a decrease in thermal stability of glass¹⁴ with an increase in bismuth concentration in the Te-Bi-Se glass system. The glass forming ability can be calculated using the following relations¹⁸.

$$K_{g1} = \frac{T_c - T_g}{T_m - T_c}$$

The values of K_{g1} are found to decrease from .749 to .480 to with an increase in Bi content as represented in fig. 6. It is noticed that the glasses with lower Bi content are easy to form compared to those with higher Bi content.

Conclusions

A systematic investigation of crystallizations kinetics of Te-Bi-Se glass systems reveals a heating

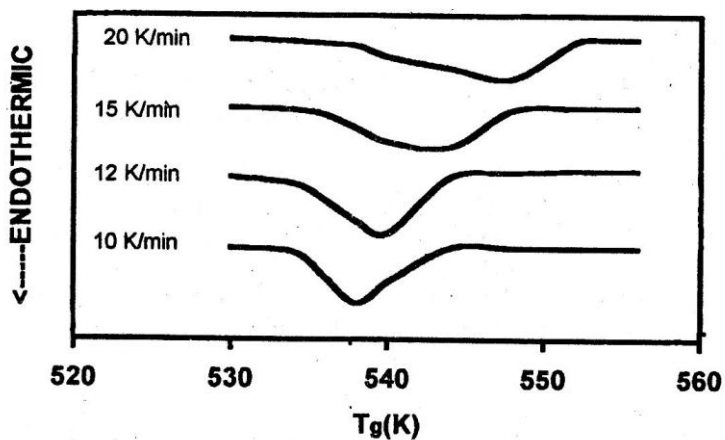
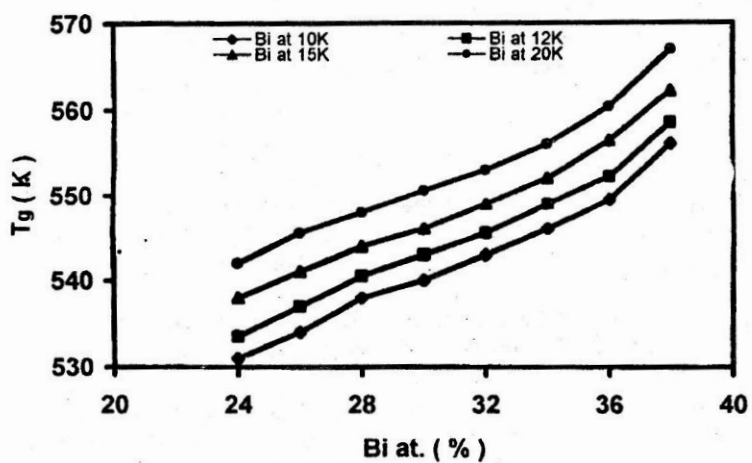
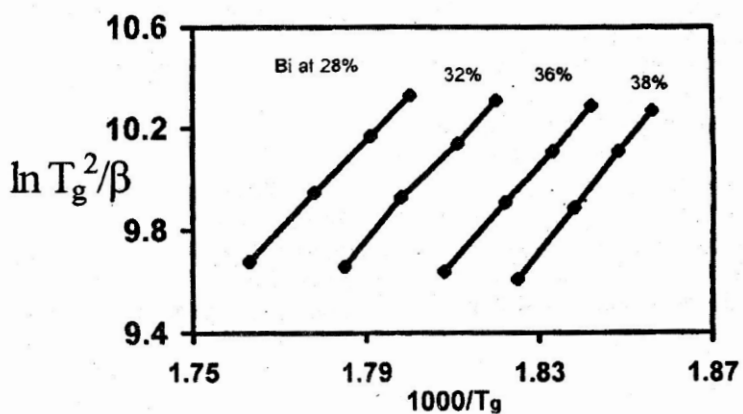


Fig. 1. DTA curves for Bi at 28% for different heating rates

Fig. 2. Variaton of T_g as a function of Bi content at different heating ratesFig. 3. Plots of $\ln T_g^2/\beta$ versus $1000/T_g$ for different Bi content

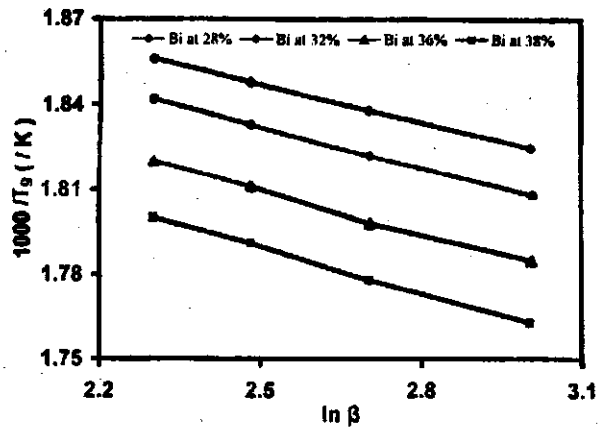


Fig. 4. Plots of $10^3/T_g$ versus $\ln \beta$ for different Bi content

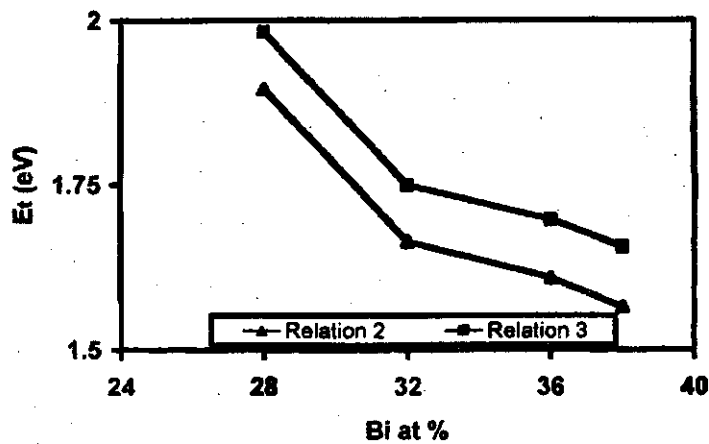


Fig.5. Variation of activation energy, E_a , with Bi content

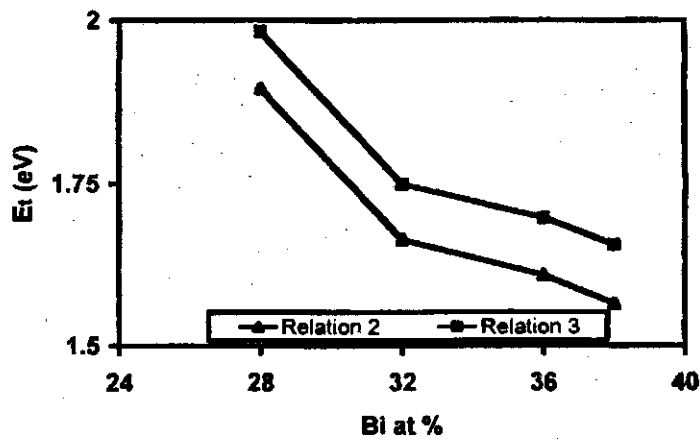


Fig. 6. Variation of K_g with Bi content

rate dependence of T_g . Drastic changes in T_g cannot be expected by increase in Bi content, which results in iso-structural units of nearly same bond strength. However, with the increase in heating rates, the glass transition temperature T_g is found to increase. The slight increase in T_g observed is probably due to the increase in mean molecular weight of the glasses with increasing Bi content. The observed increase is attributed either to the increase in the effective molecular weight with increasing Bi content or to the increase in the effective molecular weight with increasing Bi content or to the increase in concentration of long polymer chains. The glass transition temperature T_g increases slightly with the variation of Bi content from 28% to 38%. From the heating rate dependence of T_g , the activation

energy for the glass transition has been evaluated. The values of activation energies for glass transition E_a , were found to decrease with increase in Bi content. The results are discussed on the basis of Kissinger's approach and Marseglia's theory for non-isothermal crystallization. The values of activation energies, using two different methods, are in good agreement with each other. So it can be concluded that any of these two methods can be used to calculate glass transition activation energy. Thermal stability of these glasses is also found in good command to form the glasses with ease. Analyzing the results that with the increase in Bi content, the glass forming ability K_{gl} decreases has seen it. It is concluded that the glasses with lower Bi content are easy to form compared to those with higher Bi content.

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