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KINETIC PHENOMENA IN NON-CRYSTALLINE MATERIALS STUDIED BY THERMAL ANALYSIS

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Abstract

The structural relaxation and viscosity behavior of $Ge_{38}S_{62}$ glass has been studied by thermomechanical analysis. The relaxation response to any thermal history is well described by the Tool–Naraynaswamy–Moynihan model. The apparent activation energy of structural relaxation is very close to the activation energy of viscous flow (E_η=478±12 kJ mol^{-1}). However, the activation energy of crystal growth obtained by optical microscopy is about one half of this value. Similar result has been obtained from isothermal DSC measurement (E_a=220±20 kJ mol^{-1}). The kinetic analysis of these data reveals interface controlled crystal growth with zero nucleation rate.

Keywords: chalcogenide glasses, crystallization, glass transition, kinetic models, structural relaxation, viscosity

Introduction

When an equilibrium liquid is cooled down the molecular rearrangements decelerate and a metastable undercooled liquid persists because the transition to the crystalline phase is kinetically hindered. The glass transition at the temperature T_g occurs when these rearrangements slow down to a such extent that they require time considerably longer than corresponds to an experimental time scale and the structure of undercooled liquid becomes ‘frozen-in’.

It is a well known fact that if non-crystalline material is annealed at a temperature below T_g the structure approaches towards metastable equilibrium and corresponding macroscopic properties such as enthalpy or volume, etc., will change with time. This process is usually called structural relaxation. The phase transition of non-crystalline material occurs when an undercooled liquid is annealed well above T_g, which is called crystallization on reheating. These important kinetic phenomena are schematically depicted in H, V–T diagram shown in Fig. 1.

There are numerous papers published on the glass transition, structural relaxation and crystallization phenomena in non-crystalline materials and their number

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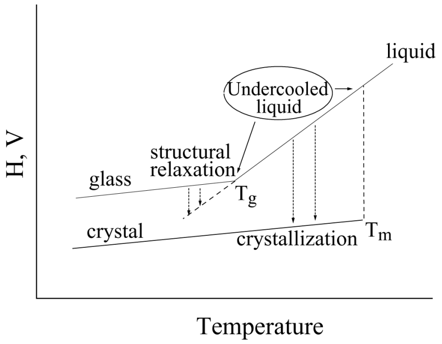

Fig. 1 Schematic diagram of the changes in the enthalpy and specific volume during structural relaxation and crystallization process

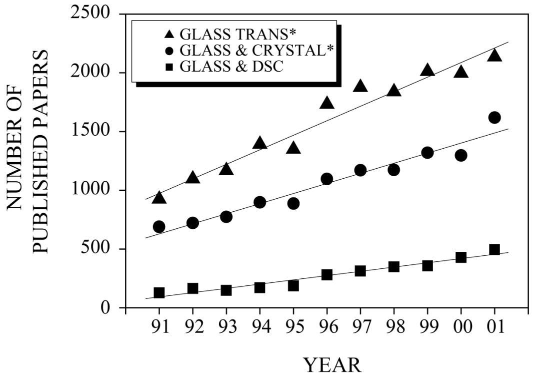

Fig. 2 The number of published papers on the glass transition and crystallization phenomena during the last decade [Source: WEB OF SCIENCE]

has increased steadily during the last decade as illustrated in Fig. 2. Although advanced thermal analysis techniques are frequently used it is still not so easy to explore the mechanism of these rather complicated processes and related properties of non-crystalline materials. The aim of this paper is to demonstrate the possibilities of kinetic studies in non-crystalline materials by using TMA, DSC and some complementary experimental techniques. This will be illustrated by using a binary glass of $Ge_{38}S_{62}$ composition.

Structural relaxation

One of the simplest experimental methods that have been used in the study of glass transition behavior is the length dilatometry. The pioneering dilatometric experiments were made by Tool [1–3] on silicate glasses. However, the DSC experiments became more typical during the last two decades. Probably the main reason for such popularity is the easy availability of DSC equipment. Enthalpy lost during annealing is usually recovered near T_g, producing the well-known overshoot. Volkenstein and Sharonov [4], Foltz and McKinney [5] and Petrie [6] made early studies of this phenomenon. The difference in areas under the DSC curves for an annealed sample and the same sample for zero annealing time is the enthalpy lost on annealing [7]. The same recovery can be observed in thermal expansion coefficient obtained from dilatometric experiments. However, in this case the relative length change of the sample on annealing can be measured directly. The non-crystalline material is annealed to equilibrium at the temperature T_0 (usually slightly below T_g) and then suddenly cooled to temperature T at which the relative length change, $\delta_0=(l-l_0)/l_0$ is recorded as a function of time t.

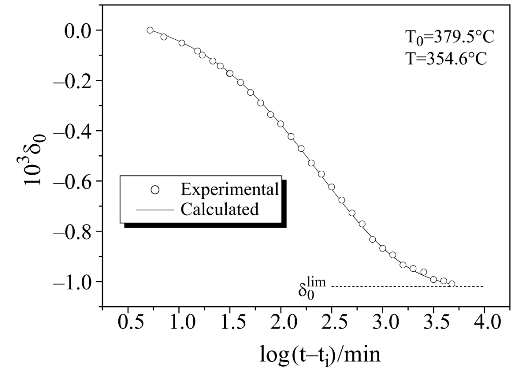

Fig. 3 Isothermal structural relaxation response of $Ge_{38}S_{62}$ glass to the temperature jump ($T_0 \rightarrow T$) experiment (points). Full line correspond to the TNM model (Δh^*=483 kJ mol^{-1}, lnA_n(s) = –81.9, x=0.59 and β=0.74). Sample length is normalized as the relative departure, δ_0 = (l-l$_0$), where l$_0$ denotes the sample length at initial time. The initial time t_i (= 5 min) is the time estimated for thermal equilibration of the dilatometer following the temperature jump.

A typical structural relaxation response of $Ge_{38}S_{62}$ glass to this temperature jump experiment is shown in Fig. 3 (points). It is seen that the plot approaches the limiting value that corresponds to the extrapolated metastable equilibrium $\delta_0^{\mathrm{lim}}=\Delta\alpha(T_0-T)$. The $\delta_0(\lg t)$ plot is non-exponential and also non-linear, i.e. it does not scale linearly with the magnitude of the temperature jump $\Delta T=T_0-T$. This non-linear behavior was first explained by Tool [3] by assuming that a characteristic time τ depends on temperature T, as well as on the instantaneous structure of the amorphous material characterized by the fictive temperature T_f. Later it was shown by Narayanaswamy [8] that the linearity can be restored by introducing the reduced time integral. The relaxation function is then defined as:

$$\delta_0(t)=\delta_0^{\mathrm{lim}}\left(1-\exp\left[-\left(\int_0^t \frac{\mathrm{d}t}{\tau(T,T_f)}\right)\right]^{\beta}\right)=\frac{T_f-T}{T_0-T} \tag{1}$$

where β is a non-exponantiality parameter related to the width of distribution of relaxation times ($0<\beta\leq 1$). The most frequently used expression for $\tau(T, T_f)$ in Eq. (1) is the

Tool–Narayanaswamy formulation [9] as modified later by Moynihan *et al.* [9] (referred to as TNM):

$$\tau(T,T_{\mathrm{f}})=A_{\mathrm{n}}\exp\left[x\frac{\Delta h^{*}}{RT}+(1-x)\frac{\Delta h^{*}}{RT_{\mathrm{f}}}\right] \tag{2}$$

where A_n is the pre-exponential constant, x is the non-linearity parameter ($0\leq x\leq 1$) and Δh^* is the effective activation energy. The curve in Fig. 3 represents the TNM model calculated by curve fitting method using Eqs (1) and (2) for the following set of the parameters: Δh^*=483 kJ mol^{-1}, lnA_n(s) = – 81.9, x=0.59 and β=0.74.

Equations (1) and (2) can be used to calculate non-isothermal structural relaxation response. The thermal history $T(t)$ is then assumed as a series of temperature steps that are small enough to ensure a linear relaxation response (usually 0.2 K). A dimensionless thermal expansion coefficient is defined as α^N=dT_f/dT and it is calculated by differentiating Eq. (1). The curves in Fig. 4a were calculated (using the same set of TNM parameters) for cooling and subsequent reheating at identical scanning rate (so called intrinsic cycles). A characteristic feature of these curves is a maximum at the temperature T_p that

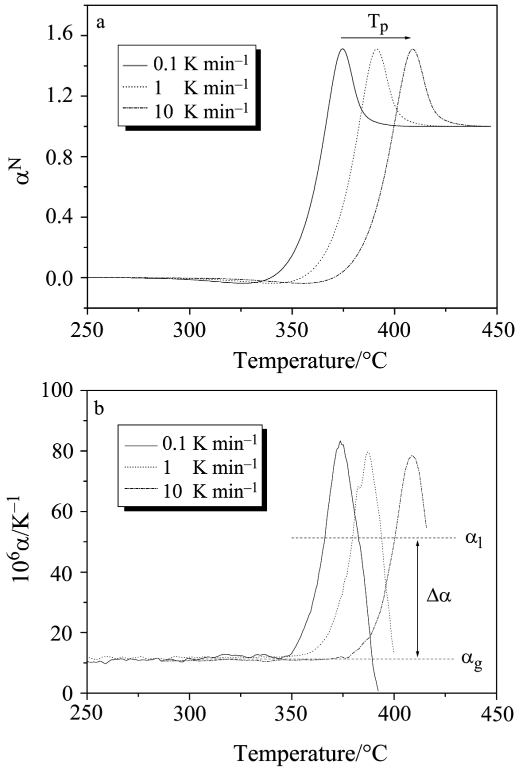

Fig. 4 The temperature dependence of thermal expansion coefficient of $Ge_{38}S_{62}$ glass for thermal history corresponding to intrinsic cycles (cooling and subsequent reheating with the same rate); a – calculated curves for the TNM model; b – experimental data

is shifted with heating rate. Figure 4b shows very similar experimental curves in the glass transition region for $Ge_{38}S_{62}$ glass. The thermal expansion coefficient of the glass can easily be determined (α_g=11.1·10^{-6} K^{-1}). However, it is practically impossible to determine the thermal expansion coefficient of the undercooled liquid because of non-negligible viscous flow above T_g. This value (α_l=51·10^{-6} K^{-1}) can be obtained from the temperature jump experiments at small ΔT, assuming that $\alpha_l \cong (\delta_0^{\lim}/\Delta T)+\alpha_g$.

Hutchinson and Ruddy [10] have shown that the following equation is valid for intrinsic cycles:

$$\left(\frac{\partial T_p}{\partial \ln q_h}\right)_{q_h=q_c}=\frac{RT_g^2}{\Delta h^*} \tag{3}$$

where q_h is the heating rate. Therefore, the effective activation energy can be determined from the slope of T_p *vs*. lnq_h plot as shown in Fig. 5 for $Ge_{38}S_{62}$ glass. The parameter Δh^*=475±27 kJ mol^{-1} obtained for T_g=388°C agrees within the limits of experimental errors with the effective activation energy calculated by curve fitting of isothermal data.

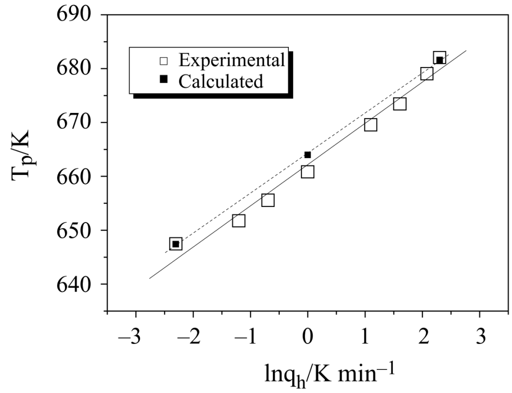

Fig. 5 The dependence of T_p as a function of logarithm of heating rate for $Ge_{38}S_{62}$ glass. Full and broken lines correspond to the linear fit of experimental and calculated data, respectively

Viscosity of undercooled liquid

The temperature dependence of viscosity in the glass transition region is important for understanding the glass structure, structural relaxation as well as crystallization kinetics. Viscosities of undercooled liquids (10^7–10^{12} Pas) in the glass transition range ($T>T_g$) can be measured by penetration viscometry using Thermomechanical Analysis (TMA). This method is based on the penetration of a hemisphere of radius R loaded by a force F into a flat specimen of the glass. It is assumed infinite rigidity of the indenter and incompressible undercooled liquid. The penetration depth l is measured as a function of time t and the viscosity is then determined using following equation [11, 12] which holds for $R>>l$:

$$\eta = \frac{9}{32\sqrt{2R}} \frac{Ft}{l^{3/2}} \tag{4}$$

Therefore, the viscosity may conveniently be determined from the time dependence of penetration of a hemispherical indenter into the sample, provided that the penetration depth is small comparing with dimension of the indenter. This method is absolute and no calibration is needed.

Figure 7 shows the temperature dependence of viscosity for $Ge_{38}S_{62}$ undercooled liquid on a semi-log scale. It is seen that in the temperature range studied the temperature dependence of viscous flow can be expressed by a simple equation of Arrhenius type. The activation energy was found to be E_η=478±12 kJ mol^{-1} [13]. Within the combined limits of experimental errors this value is close to the parameter Δh^* obtained from structural relaxation kinetics.

Crystallization on reheating

Thermal analysis methods have been used extensively as a tool for studying the crystallization of oxide and chalcogenide undercooled melts [14]. The kinetic analysis based on these crystallization data is usually described by a simple kinetic equation [15] that can be written in a differential form:

$$\left(\frac{d\alpha}{dt}\right) = Kf(\alpha) \tag{4a}$$

or integral form:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = Kt \tag{5}$$

where K is a constant with respect to time and $f(\alpha)$ represents the kinetic model of the crystallization process as a function of fractional conversion α. The nucleation-growth model formulated by Johnson and Mehl [16] and Avrami [17] gives the following expression (referred to as JMA):

$$f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m} \tag{6}$$

where the kinetic exponent m depends on the crystal growth morphology [18]. The validity of the JMA equation is based on the following assumptions [14, 19]: (i) isothermal crystallization conditions, (ii) homogeneous nucleation or heterogeneous nucleation at randomly dispersed second-phase particles, (iii) growth rate of new phase independent of time, (iv) low anisotropy of growing crystals.

It follows from Eq. (4a) that the $f(\alpha)$ function should be proportional to the measured crystallization rate ($d\alpha/dt$) under isothermal conditions. Similarly, by combining Eqs (4a) and (5) it follows that $g(\alpha)f(\alpha)=(d\alpha/dt)t$. For the JMA model this function is $g(\alpha)f(\alpha)\propto(1-\alpha)[-\ln(1-\alpha)]$, and its maximum should be close to $\alpha=0.632$. These simple transformations can be used as a convenient test of validity of the JMA

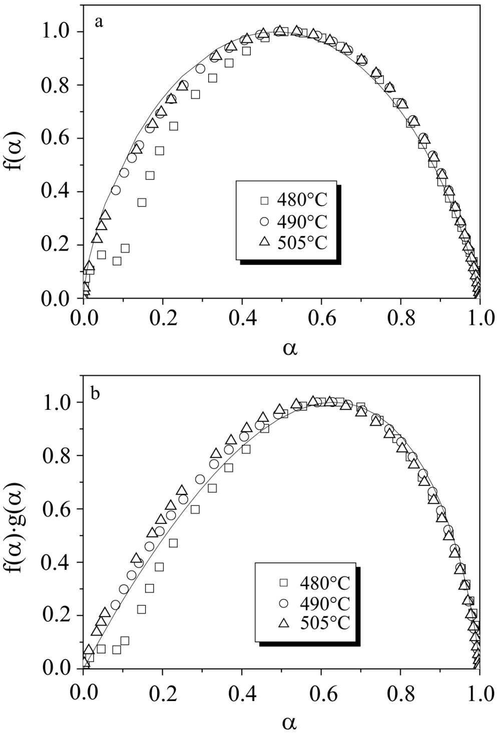

Fig. 6 Transformed isothermal DSC data (points) as a function of fractional conversion for the crystallization of $Ge_{38}S_{62}$ undercooled liquid. Solid lines in this figure were calculated for the kinetic exponent m=3

nucleation-growth model. Figure 6 shows transformed isothermal DSC data (points) corresponding to the crystallization of $Ge_{38}S_{62}$ glass. Solid lines in this figure were calculated for the kinetic exponent m=3. It is evident that the JMA nucleation-growth model well describes experimental data for T≥490°C and the value of the kinetic exponent $m≅3$ suggests interface controlled crystal growth with zero nucleation rate. However, some deviations are observed for T=480°C. This behavior may indicate the need for a slight change in the kinetic model or limited validity of the above mentioned conditions.

The rate constant in Eqs (4a) and (5) is usually assumed to take a simple Arrhenius form:

$$K(T)=A_{\mathrm{a}}\exp(-E_{\mathrm{a}}/RT) \tag{7}$$

where the pre-exponential factor A_a and apparent activation energy E_a are kinetic parameters that should not depend on the temperature T and the fractional conversion α. The value of E_a determined by the isoconversional method [21] was found to be $E_a=220\pm20$ kJ mol^{-1}. This is about one half of the activation energy of viscous flow.

The crystallization in $Ge_{38}S_{62}$ glass is a complex process involving several mutually overlapped phases. The first composition that crystallizes is germanium

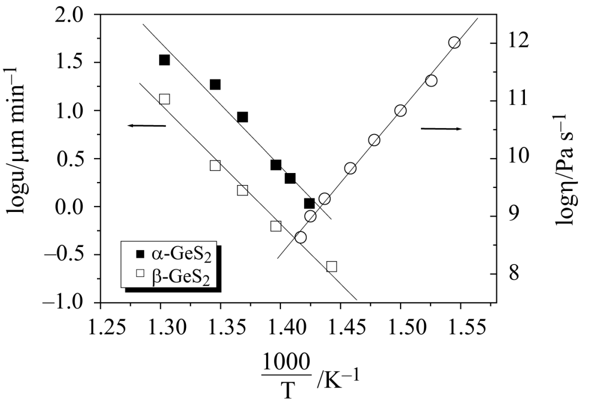

Fig. 7 The temperature dependence of crystal growth rate of α-GeS_2 and β-GeS_2 and logarithm of viscosity in $Ge_{38}S_{62}$ undercooled liquid (points). Full lines correspond to the linear fit

disulphide as corresponds to the phase diagram [21] and X-ray diffraction analysis. There are two polymorphs of this compound; i.e. low-temperature β-GeS_2 and high-temperature α-GeS_2. Although the β-GeS_2 is thermodynamically stable phase below 520°C the crystallization of α-GeS_2 is kinetically favored and its crystallization rate is considerably higher than β-GeS_2. Figure 7 shows the plot of crystal growth rate *vs.* reciprocal temperature on a semi-log scale [22]. These data were obtained by direct measurement of crystal growth kinetics by using optical microscopy. The slope of the plot shown in Fig. 7 corresponds to the activation energy of crystal growth and it was found to be E_u=247±23 kJ mol^{-1} for α-GeS_2 and E_u=239±18 kJ mol^{-1} for β-GeS_2 crystallization process. Within the combined error limits these values are close to the apparent activation energy obtained from isothermal DSC experiments. On the other hand they correspond to about one half of the activation energy of viscous flow. Similar results have been reported by Henderson and Ast [23] for crystallization of As_2Se_3 glass.

Conclusions

It has been shown that the structural relaxation below T_g and viscosity behavior of $Ge_{38}S_{62}$ glass above T_g can be studied by TMA. It seems that the structural relaxation and viscous flow exhibit similar activation behavior with practically identical activation energy (E_η=478±12 kJ mol^{-1}). The isothemal relaxation response to the temperature jump experiment as well as non-isothermal data is well described by the Tool–Narayanaswamy–Moynihan model that accounts for the non-linear (x=0.59) and the non-exponential (β=0.74) behavior.

The crystallization kinetics above T_g in $Ge_{38}S_{62}$ underccoled melt can easily be studied by DSC. The apparent activation energy corresponding to the Arrhenius rate constant was found to be E_a=220±20 kJ mol^{-1}. This value is close to the activation energy of macroscopic crystal growth obtained from optical microscopy. The kinetic data obtained by calorimetric measurement under isothermal conditions can be described by the Johnson–Mehl–Avrami nucleation-growth model and the value of kinetic exponent is $m \cong 3$, which probably correspond to interface controlled crystal growth with zero nucleation rate.

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