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STRUCTURAL RELAXATION OF AMORPHOUS $Ge_{38}S_{62}$ STUDIED BY LENGTH DILATOMETRY AND CALORIMETRY

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Abstract

The structural relaxation of $Ge_{38}S_{62}$ glass has been studied by length dilatometry and calorimetry. The Tool–Narayanaswamy–Moynihan model was applied on obtained data of structural relaxation and parameters of this model were determined: $\Delta h^{*}= 483\pm2$ kJ mol^{-1}, $\ln(A/\mathrm{s})= -81\pm1$, $\beta= 0.7\pm0.1$ and $x=0.6\pm0.1$. Both dilatometric and calorimetric relaxation data were compared on the basis of the fictive relaxation rate. It was found that the relaxation rates are very similar and well correspond to the prediction of phenomenological model.

Keywords: enthalpy relaxation, germanium-sulphur, glasses, volume relaxation

Introduction

The amorphous semiconductors as $Ge_{38}S_{62}$ are perspective materials for infrared optics and optical recording media. Therefore these materials are studied by many authors. There are many data on basic physical and chemical properties but only a few studies were aimed deeply on such behavior of amorphous semiconductors as structural relaxation. Although this behavior is given by non-equilibrium state of amorphous body and it influences long-time using of all amorphous materials.

It is well known that non-crystalline materials exist in non-equilibrium state below the glass transition temperature T_g. This non-equilibrium state leads to structural rearrangement toward equilibrium. This process is called structural relaxation or physical aging. The work of Tool [1–3] and Kovacs [4, 5] established basis for development of phenomenological models [6, 7] of structural relaxation of non-crystalline materials below the glass transition temperature. The phenomenological model has to express non-linearity and non-exponentiality of structural relaxation process. Non-linearity arises from the asymmetry of relaxation response following positive or negative departures

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from equilibrium. Non-exponentiality is demonstrated by well known memory effect, in which relaxation from some initial state depends on how that state was reached.

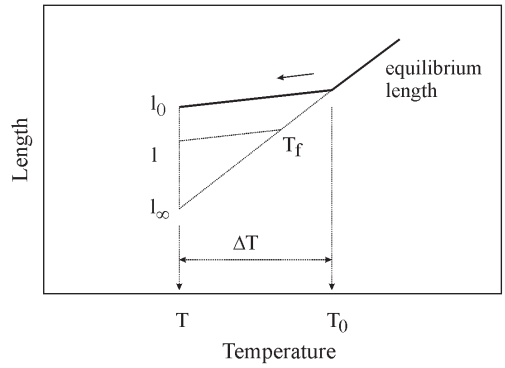

Fig. 1 Schematic illustration of the length changes in the glass-transition range. Stabilized non-crystalline material is subjected to a temperature jump from T_0 to T. During the isothermal hold at T the length changed from the initial value l_0 toward its equilibrium

The structure of glass during the relaxation process can be characterized by means of the fictive temperature T_f defined by Tool [2] as the temperature at which the specimen length would be equal to that of equilibrium length (Fig. 1). The dependence of relaxation time τ on temperature and also on instantaneous structure of glass is often expressed in the form of the Tool–Narayanaswamy–Moynihan (TNM) equation [8, 9]:

$$\tau(T, T_f) = A\exp\left[x\frac{\Delta h^*}{RT} + (1-x)\frac{\Delta h^*}{RT_f}\right] \tag{1}$$

where A is the pre-exponential constant, x is the parameter of non-linearity ($0<x\leq 1$) and Δh^* is the effective activation energy. Narayanaswamy [6] showed that linearity can be restored using the reduced time defined by:

$$\xi = \int_0^t \frac{dt}{\tau(T, T_f)} \tag{2}$$

Then the fictive temperature can be expressed as:

$$T_f = T + \Delta T\exp(-\xi^\beta) \tag{3}$$

where the non-exponentiality parameter β ($0<\beta\leq 1$) is inversely proportional to the width of corresponding distribution of relaxation times.

Equations (1)–(3) are sufficient to describe quantitatively the response (volume, enthalpy, etc.) of a glass to isothermal treatment below T_g. The parameters β, x, A and Δh^* can be evaluated from experimental data by numerical curve fitting technique [8, 10] or by the peak-shift method [11].

Experimental

The $Ge_{38}S_{62}$ glass was prepared by conventional method. Pure elements (5N) weighted into quartz ampoule were melted and homogenized at 900°C for 24 h. The melt was quenched in water. For dilatometric measurements the thermomechanical analyzer TMA CX03R (R.M.I. Czech Republic) was used. For calorimetric measurements the differential scanning calorimeter Pyris 1 (Perkin Elmer) was used.

Dilatometric measurements

First intrinsic cycles (cooling and consecutive heating with the same ratio of cooling and heating rates) were performed to determine the glass transition temperature and the thermal expansion coefficients of glass and equilibrium undercooled liquid. Temperature jump experiments were chosen to analyze volume relaxation process. The thermal history of the sample was erased by heating to 410°C before each experiment. Then the specimen was equilibrated in the dilatometer at a temperature T_0 (close to T_g) for 5 h and consequently it was cooled to temperature T, at which the sample relaxed toward equilibrium. The temperature jump $\Delta T(T_0-T)$ was made in the range to 40 K. The example of this temperature jump experiment is in Fig. 2. The isothermal structural relaxation is expressed as the relative departure of actual specimen length l from the original specimen length l_0:

$$\delta_0=\frac{l-l_0}{l_0} \tag{4}$$

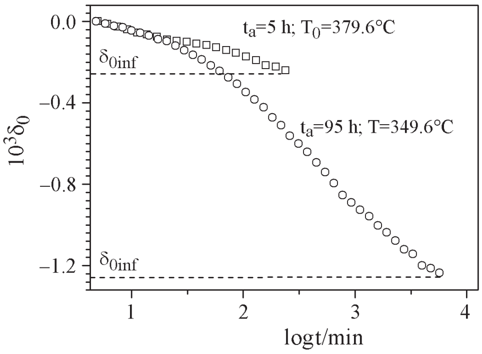

Fig. 2 Typical temperature jump experiment relaxation response. Broken lines correspond to the equilibrium length

Calorimetric measurements

The enthalpy relaxation process can not be measured directly. The relaxation process of the sample reflects (typical overshoots above T_g) in reheating scan made after annealing the sample at temperature T for annealing time t_a. Temperature jump method was used for enthalpic relaxation of $Ge_{38}S_{62}$ glass. The sample was equilibrated at the temperature T_0 for 5 h, then cooled to temperature T and annealed for different times t_a. After annealing the sample was cooled well below T_g to stop relaxation process. The reheating scan was made with heating rate 10 K min^{-1}.

Results and discussion

Figure 3 shows typical intrinsic cycles of $Ge_{38}S_{62}$ measured by length dilatometry. The glass transition temperature T_g is defined as the temperature of intersection of the slope corresponding to the glassy state and undercooled liquid. It has been found that T_g ranges from 363 to 395°C depending on heating (cooling) rate (0.1–10 K min^{-1}). The thermal expansion coefficient is defined as $\alpha=(1/l_0)(\mathrm{d}l/\mathrm{d}T)$ and thus it corresponds to the slope of $l(T)$ curve. The α_g value of glassy material determined from non-isothermal experiments is $(11.1\pm0.2)\cdot10^{6}$ K^{-1}. The value of thermal expansion coefficient of equilibrium undercooled liquid can not be determined because of viscous flow. But the value of difference between the thermal expansion coefficient of equilibrium undercooled liquid α_l and the thermal expansion coefficient of glass α_g can be determined from isothermal experiments. The dependence of equilibrium length $\delta_{0\mathrm{inf}}$ (Fig. 2) on temperature jump ΔT can be expressed as:

$$\delta_{0\mathrm{inf}}=\Delta\alpha\Delta T \qquad (5)$$

Using Eq. (5) the value of $\Delta\alpha$ is $(40\pm1)\cdot10^{-6}$ K^{-1}.

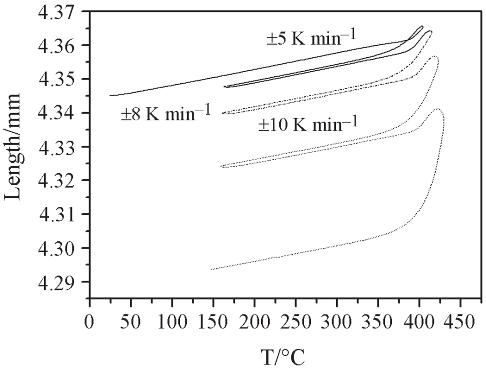

Fig. 3 Illustration of non-isothermal dilatometric experiments (F=10 mN) of $Ge_{38}S_{62}$ glass for different heating rates (shown above the curves)

Intrinsic cycles can be used to determine parameter Θ of Kovacs–Aklonis–Hutchinson–Ramos model (KAHR) [7, 11]:

$$\Theta^{-1}=\left(\frac{\partial T_p}{\partial \ln q_2}\right)_{q_1/q_2=\mathrm{const}} \qquad (6)$$

where T_p is the temperature corresponding to the maximum value of thermal expansion coefficient and q_2 is the heating rate. The dependence of T_p on heating rate is shown in Fig. 4 and determined value of parameter Θ is 0.131 K^{-1}. Parameter Θ of KAHR model is related to the parameter Δh^* of TNM model [11]:

$$\Theta = \frac{\Delta h^*}{R T_g^2} \tag{7}$$

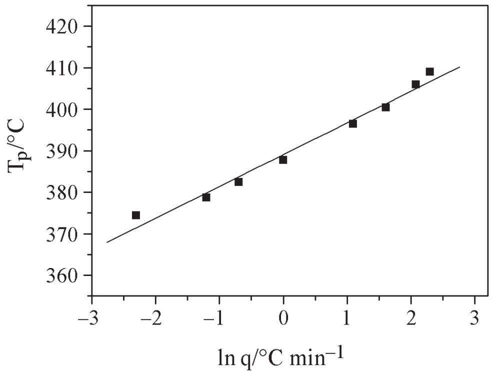

Fig. 4 The dependence of temperature corresponding to the maximum value of thermal expansion coefficient on heating rate and the best fit

The value of effective activation energy calculated for the glass transition temperature T_g=388°C (heating rate 5 K min^{-1}) and parameter Θ=0.131 K^{-1} is 475±27 kJ mol^{-1}. This value is close to the activation energy of viscous flow (E_η=478±12 kJ mol^{-1}) reported by Málek and Shánělová [12]. It is apparent that the value of activation energy of viscous flow and the value of effective activation energy correspond very well. This is in a good agreement with result of Hodge [8], that Δh^* is essentially the same as E_η for most inorganic amorphous materials.

Parameters of TNM model can be evaluated from isothermal dilatometric data by numerical curve fitting. A computer program was written to perform these calculations. The initial value of parameter $\Delta h^*/R$ was set close to the value of E_η/R determined from viscosity measurements. The values of fitted parameters of TNM model for length relaxation data for T_0=379.4±0.2°C are shown in Table 1. The comparison of experimental data and fitted curves is shown in Fig. 5.

Volume relaxation can be compared to enthalpy relaxation on the base of the fictive relaxation rate R_f [13–15]. It is defined as the change of the fictive temperature per decade of time:

$$R_f = \left[\frac{dT_f}{d\log t}\right]_i \tag{8}$$

Table 1 Fitted Tool–Narayanaswamy–Moynihan parameters for dilatometric isothermal data of $Ge_{38}S_{62}$ for different temperature jumps for T_0=379.4±0.2°C

ΔT/°C	β	$-\ln A$/s^{-1}	$\Delta h^*/R$/kK	x
24.9	0.74	81.9	58.1	0.59
30.0	0.69	81.2	58.0	0.55
34.5	0.66	81.0	58.0	0.55
40.0	0.64	81.5	58.4	0.56

According to Eq. (8) the fictive relaxation rate of enthalpy relaxation data can be calculated. The fictive temperature was determined by method described by Moynihan [16]. The fictive relaxation rate for volume relaxation data can be determined from isothermal experiments [14]:

$$R_f = -\frac{1}{\Delta\alpha}\left(\frac{d\delta_0}{d\log t}\right)_i \tag{9}$$

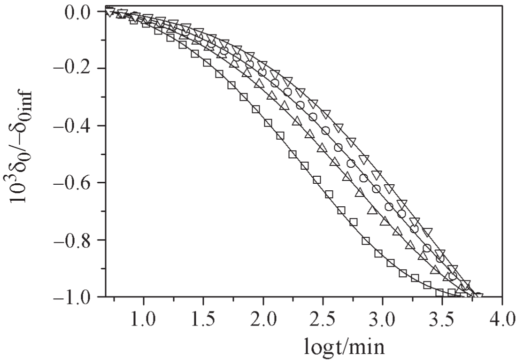

Fig. 5 Isothermal dilatometric data for temperature jumps □ – 24.9°C, △ – 30.0°C, ○ – 34.5°C, ▽ – 40.0°C and fitted curves

The fictive relaxation rate dependence on temperature jump for volume and enthalpy relaxation is shown in Fig. 6. The $R_f(\Delta T)$ values for volume relaxation are for different starting temperatures: T_0=375.3±0.2°C, T_0=379.4±0.2°C and T_0=385.3±0.1°C. Enthalpy relaxation data are for starting temperature T_0=377.7±0.1°C and temperature jump ΔT=17.5°C. The full line represents the best fit according to equation [13, 14]:

$$R_f = 2.303\left[\frac{e}{\beta\Delta T} + (1-x)\Theta\right]^{-1} \tag{10}$$

with parameters β=0.77, x=0.55 and Θ=0.130 K^{-1} for $Ge_{38}S_{62}$ glass. These parameters are very close to that obtained by fitting isothermal dilatometric data according to

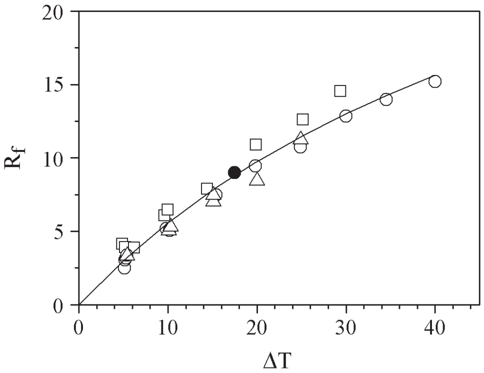

Fig. 6 The fictive relaxation rate as a function of temperature jump. (Points correspond to dilatometric data: □ – T_0=375.3°C, ○ – T_0=379.4°C, △ – T_0=385.3°C and calorimetric data: ● – T_0=377.7°C.) The solid line was calculated as a best fit using Eq. (10)

Eqs (1)–(3) (Table 1). The parameter Θ is the same as value determined by peak-shift method (Fig. 4).

Conclusions

The structural relaxation of $Ge_{38}S_{62}$ glass has been studied by length dilatometry and calorimetry. It was found that the relaxation response to the temperature jump experiment can be described well using Tool–Narayanaswamy–Moynihan phenomenological model for following parameters: Δh^*= 483±2 kJ mol^{-1}, $\ln A/\mathrm{s}^{-1}$=–81±1, β= 0.7±0.1, x= 0.6±0.1. Similar results were obtained also for calorimetric measurements. The effective activation energy Δh^* was found to be very similar to the activation energy of viscous flow determined previously (E_η= 478±12 kJ mol^{-1}). Both dilatometric and calorimetric relaxation data were compared on the basis of the fictive relaxation rate. It was found that the relaxation rates are very similar and well correspond to the prediction of phenomenological model.

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