Available online at www.sciencedirect.com
ScienceDirect
Journal of Physics and Chemistry of Solids 68 (2007) 850–854
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

Relaxation behavior of glassy selenium

Roman Svoboda[a,*], Pavla Pustková[b], Jiří Málek[a]

[a]Department of Physical Chemistry, University of Pardubice, Cs. Legii 565, 532 10 Pardubice, Czech Republic
[b]Department of Inorganic Technology, University of Pardubice, Cs. Legii 565, 532 10 Pardubice, Czech Republic

Abstract

The dynamics of the glass transition of amorphous selenium was investigated by using differential scanning calorimeter. The heat capacity data were analyzed applying the phenomenological Tool–Narayanaswamy–Moynihan (TNM) model in order to describe the relaxation behavior of a-Se. The TNM parameters were evaluated by fitting the enthalpic cycles and also one isothermal experiment. Furthermore, peak-shift method and several other methods of evaluating the TNM parameters were applied to confirm the results of curve fitting. The results are compared with the other published enthalpy and viscosity data, volume and enthalpy relaxation are compared on account of our previous mercury dilatometry measurements. We found out that the pre-exponential factor A and the apparent activation energy Δh^* of structural relaxation are similar for volume and enthalpy relaxation and Δh^* is very close to the activation energy of viscous flow.

Keywords: A. Chalcogenides; A. Glasses; C. Differential scanning calorimetry; D. Phase transitions

1. Introduction

Wide application options of non-crystalline materials are closely related to the question of their long-term stability at various temperatures. At temperatures below the glass transition [1], the occurring phenomenon is the structural relaxation, process whereas the material changes its thermodynamic properties (e.g., enthalpy, volume, etc.) towards the local equilibrium represented by the undercooled liquid state. The instantaneous state of the relaxing material can be described by the fictive temperature T_f [2] (Fig. 1).

Enthalpy relaxation belongs among important and therefore usually studied aspects of glassy dynamics. It is characterized by an endothermic effect at glass transition region during heating of an annealed glass. The peak area under this effect can be used to determine the fictive temperature of the measured material [3] and thus is used to define the enthalpy relaxation process. The quantitative description of structural relaxation nowadays frequently follows the phenomenological Tool–Narayanaswamy–Moynihan (TNM) model [3,4] involving expression for relaxation time τ and expression for stretched exponential relaxation function M_H called Kohlrausch–Williams–Watts [5] function:

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

$$\delta(t) = \delta_0 \exp\left[-\left(\int_0^t \frac{\mathrm{d}t}{\tau}\right)^{\beta}\right], \quad (2)$$

where δ is function of the relaxing property (enthalpy) defined as $\delta = (H–H_\infty)/H_\infty$ and δ_0 is then equal to $\delta(H_0)$–both in agreement with Fig. 1, t is time, T is temperature, T_f is the fictive temperature, R is the universal gas constant, β is the parameter on non-exponentiality, A is the pre-exponential factor, x is the parameter of non-linearity and Δh^* is the apparent activation energy of structural relaxation.

TNM parameters (x, β, Δh^*, A) for the specific material can be evaluated either from direct numerical fit of the measured data or by using some of the non-fitting methods based on the simple data conversion. Among these methods belongs the peak-shift method [6,7] defined

---

[*]Corresponding author. Tel.: +420 466 037 045.
E-mail address: roman.svoboda@upce.cz (R. Svoboda).

0022-3697/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.jpcs.2006.12.032

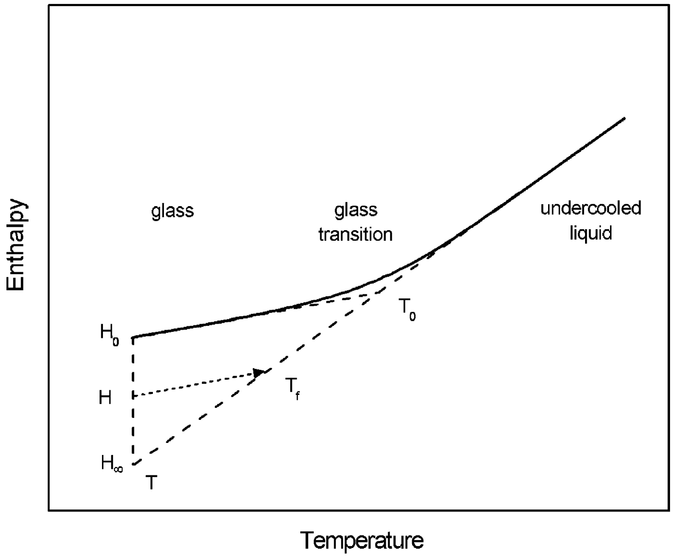

Fig. 1. Temperature dependence of a material's enthalpy at constant pressure during structural relaxation. Index "0" represents initial state of the formed glass while index "∞" represents the equilibrium state of the material. Evaluation of the fictive temperature T_f is demonstrated.

according to the following equations:

$$F(x) = \Delta C_p \frac{\mathrm{d}T_p}{\mathrm{d}\Delta H}, \tag{3}$$

$$F(x) = x^{-1} - 1, \tag{4}$$

where $F(x)$ is the peak-shift function, ΔC_p is the difference in heat capacity between the undercooled liquid and glassy state, T_p is the temperature of the maximum of endothermic effect, ΔH is the enthalpy change related to this effect and x is the non-linearity parameter. This method of parameter x determination can be used in the case of isothermal relaxation experiments–the relaxation peak is changing with the time of annealing at temperature below T_g.

Evaluation of parameter Δh^* can be performed according to another non-fitting method. The determination is based on the dependence of the fictive temperature vs. cooling rate during enthalpic cycles i.e., the same heating rate of reheating scan after the cooling at different rates. The apparent activation energy Δh^* can be estimated [8] according to the equation:

$$\frac{\Delta h^*}{R} = \frac{\mathrm{d}\ \ln|q^-|}{\mathrm{d}(1/T_f)} \tag{5}$$

where q^- is the cooling rate. However, this way estimated values of Δh^* are for certain chalcogenide glasses higher than values obtained by using other fitting or non-fitting methods [9–11].

Amorphous selenium as the model system of chalcogenide glass is often chosen to study the structural relaxation. Enthalpy relaxation of a-Se using differential scanning calorimeter (DSC) was studied in a number of publications [10–12]. First aim of this paper was to study enthalpy relaxation of a-Se and describe the relaxation behavior using TNM model. The intention was to find one set of TNM parameters that would describe all the performed experiments. The second aim of this work was to compare the results with literature and our previous volume relaxation data.

2. Experimental

Selenium pellets (5 N purity) were inserted into the fused silica ampoule that was after that evacuated and sealed. The ampoule was placed into the rocking furnace and annealed at 350 °C for 24 h. Glassy selenium was prepared from its melt by cooling the ampoule on air. Amorphous character of the prepared glass was verified using X-ray diffraction.

Enthalpy relaxation of a-Se was studied using conventional DSC 822^e (Mettler Toledo). Melting temperatures of In and Zn were used to calibrate the calorimeter. The sample in the form of powder was inserted into standard aluminum pans and sealed, the mass of each batch was approximately 11 mg. Two procedures were used to measure the relaxation process. Non-isothermal enthalpic cycles were performed as a set of consecutive heating ($q^+ = 10\,^\circ\mathrm{C\,min^{-1}}$) and cooling ($q^- = 0.2$–$20\,^\circ\mathrm{C\,min^{-1}}$) steps between −30 and 65 °C.

During isothermal down-jump experiment the first step was annealing at initial temperature ($T_0 = 39\,^\circ\mathrm{C}$, for 60 min) to achieve equilibrium. During next step, the sample was cooled ($q^- = 40\,^\circ\mathrm{C\,min^{-1}}$) to $T = 27\,^\circ\mathrm{C}$ and annealed at this temperature for certain period of time then immediately heated ($q^+ = 10\,^\circ\mathrm{C\,min^{-1}}$) to 65 °C. Immediate heating following the annealing at temperature T was essential due to the fast part of the relaxation process. Stopping the relaxation process by fast cooling of the pan was not possible due to the insufficient cooling rate attained at such a low temperatures.

The volume relaxation measurements were performed using mercury dilatometry [13]. The set of isothermal down-jump experiments, where temperature T_0 was 39 °C and temperature T varied, was performed. This set also includes the experiment analogous to the enthalpic down-jump experiment described in previous paragraph. Further details of these and other our volumetric relaxation measurements of a-Se are described elsewhere [14].

3. Results and discussion

Four complete sets of enthalpic cycles (cooling rates 0.2, 0.5, 1, 3, 5, 10, 20 $^\circ\mathrm{C\,min^{-1}}$) were performed on the studied material. The obtained curves were fitted using TNM model and one set of TNM parameters was determined (Table 1). Volume relaxation parameters were taken for the first approximation in the fitting process of the enthalpic data. Several example curves are shown in Fig. 2. For the purposes of consequential fitting, it is convenient to normalize heat capacity to zero for glassy state and to