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Influence of experimental conditions on enthalpy relaxation observed by cyclic measurement with constant heating rate

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ABSTRACT

The cyclic experiments with constant heating rate following cooling by various cooling rates were done using DSC to be able to apply different methods of estimation of TNM model parameters. The advantage and limitation of employed experimental procedure is discussed and the composition of $(GeS_2)_y(Sb_2S_3)_{1-y}$ glasses for $y = 0.2$ and 0.3 was used as model systems.

1. Introduction

The amorphous materials such as chalcogenide glasses are very often studied because of their practical importance in infrared optics [1], X-ray image sensors [2] as well as in phase change materials for data recording media [3]. The attention is often paid to the glass transition but not too much right to the structural relaxation. Structural relaxation is a consequence of non-equilibrium state in which amorphous material occurs below the glass transition temperature T_g. During relaxation process the structural arrangement is changing towards equilibrium state. It is reflected in the changes of properties of amorphous materials such as volume (V), enthalpy (H), and refractive index (n_D) (Fig. 1). In practical point of view the change in properties with time is very important for application of any non-crystalline material.

The bases of relaxation studies were put by Tool [4,5] and Kovacs [6,7] (using dilatometry). The fast development and easy accessibility of calorimetric methods caused that the structural relaxation is mainly studied from the view of enthalpy relaxation changes using differential scanning calorimetry (DSC) [8–12] although the dilatometry method is able to directly observed the volume changes during relaxation process [6,13–15]. In the case of enthalpy the relaxation process can be studied only indirectly because of very small thermal changes in large time scale. Thus, the enthalpy relaxation is reflected in the reheating scan done after cooling the sample or after annealing the sample at temperature below T_g (Fig. 2). The structure of material during the relaxation can be described by the fictive temperature T_f introduced by Tool [5]. The fictive temperature is defined as temperature at which the sample property (enthalpy, volume, etc.) would be equal to the equilibrium value at temperature T_f (see Fig. 1). When the sample is cooled from equilibrium state (high above T_g) to temperature T_g and then consequently cooled to temperature T, the fictive temperature during annealing at temperature T is moving from T_g to T as is illustrated in Fig. 1. Generally, the phenomenological model of structural relaxation has to express nonlinearity and non-exponentiality of the structural relaxation process. The nonlinearity of structural relaxation arises from the asymmetry of relaxation response following positive or negative departures from equilibrium. Non-exponentiality is demonstrated by the well-known memory effect, where relaxation from some initial state depends on how that state was reached [16].

The most frequently used expression for relaxation time τ is the Tool–Narayanaswamy [17] formulation as modified later by Moynihan et al. [18] (referred to as TNM):

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

where A is the pre-exponential factor, x is the parameter of nonlinearity ($0 < x \le 1$) and Δh^* is the effective activation energy. Narayanaswamy showed that linearity can be restored by introducing the reduced-time

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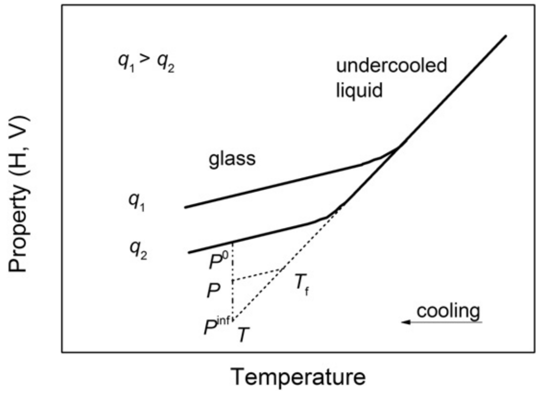

Fig. 1. Schematic illustration of specific property (enthalpy, volume) dependence on temperature for cooling by different cooling rates (q). Scheme of T_f determination during annealing of the sample at temperature T is given.

integral defined by [17]:

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

Then the fictive temperature can be expressed as [7]:

$$T_f = T_g - \Delta T\left[1 - \exp(-\xi)^{\beta}\right] \tag{3}$$

where β ($0 < \beta \le 1$) is the non-exponentiality parameter and ΔT is a temperature jump before annealing.

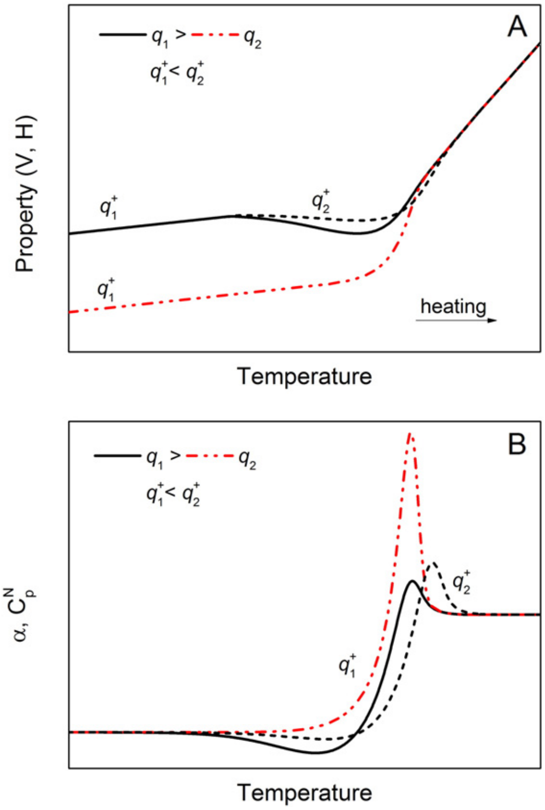

Fig. 2. Schematic illustration of temperature dependence of (A) specific property (enthalpy, volume) and (B) thermal expansion coefficient and normalized heat capacity for heating by different heating rates (q^+) done after cooling by various rates (q).

Tool–Narayanaswamy–Moynihan (TNM) model based on Eqs. (1)–(3) is appropriate to quantitatively describe the enthalpy relaxation. This four-parameter model is purely empirical and the parameters A, x, β and Δh^* have no clear physical meaning. Nevertheless, it is assumed that parameter β is inversely proportional to the width of corresponding continuous distribution of relaxation times [12] and parameter Δh^* is very close to the activation energy of viscous flow E_η for many materials [19–26]. The parameters of TNM model can be obtained by curve fitting method or directly from the experimental calorimetric data.

The curve fitting method is based on Eqs. (1)–(3). The thermal history $T(t)$ is assumed as a series of temperature steps that are small enough to ensure a linear relaxation response (usually 0.2 K). In the case of isothermal conditions the temperature step is replaced by time step (for more details see Ref. [27]). The data are normalized within ⟨0,1⟩ interval for the numerical fitting. In the case of enthalpy relaxation data the level of heat flow before glass transition is recalculated as 0 and the level after the glass transition is recalculated as 1, the data in this format are indicated as normalized heat capacity, C_p^N. The four parameter optimization is better made up for the three parameter one. The value of $x \cdot \Delta h^*$ does not change very much with thermal history, therefore the optimization of three parameters is better (Δh^* is usually fixed). The set of parameters used as the first estimation for the fitting method is very important. Therefore, it is always better to use some other method of parameter determination at first.

The best for relaxation studies is the realization of a complex set of experiments covering cycles for significantly different rates and annealing for significantly different times — this allows applying several methods for TNM parameters' estimation directly from data and finally the optimization of parameters by numerical fitting [27]. Unfortunately, complex attitude to relaxation study is very time consuming. Thus, the fastest is performing of non-isothermal measurements which can be used for estimation of Δh^* as well as for fitting procedure.

The temperature corresponding to the maximum of relaxation peak and its shift with heating rate can be used to calculate parameter Δh^* when the measurement is done for constant value of cooling/heating ratio [28,29]. This method provides good results (good correlation between determined value of Δh^* and fitted value) but the thermal gradient influence on experiment must be taking in mind. Thus, it is not the optimal dataset for numerical fitting. On the contrary, cycles with different cooling rates and constant heating rate eliminate the thermal gradient problem in the experimental dataset and numerical fitting provides valuable information when the range of cooling rates is broad enough. The parameter Δh^* can be calculated from the fictive temperature dependence on cooling rate q (for the same heating rate) [8]:

$$\frac{\Delta h^*}{R} = -\frac{d\ln q}{d(1/T_f)}. \tag{4}$$

The fictive temperature from the DSC signal can be calculated according to Moynihan et al. [9] (the symbols are described in Fig. 3):

$$\int_{T^*}^{T'_f} (C_{pe} - C_{pg})\, dT_f = \int_{T^*}^{T'} (C_{pl} - C_{pII})\, dT. \tag{5}$$

However, the values of Δh^* estimated in this way are for certain amorphous materials higher than values obtained by using other fitting or non-fitting methods [10,13,14,20,27,30–34], it can be also lower [35] or correlate well with other results [20,33–38].

The exact values of theoretical model parameters describing the structural relaxation are published only for few compositions of chalcogenide glasses. The relaxation process is mainly studied by calorimetric methods [10,27,30,31] but dilatometry is being used as well [6,14,32,39,40]. In the case of GeS_2–Sb_2S_3 composition the enthalpy