

## RELAXATION BEHAVIOR OF SELENIUM BASED GLASSES

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Relaxation behavior of Ge<sub>y</sub>Se<sub>100-y</sub> (y=8 and 10) glasses related to the viscosity behavior was studied by dilatometry. The method of two consecutive temperature jumps was applied to study the volume relaxation. The relaxation response can be described by Tool–Narayanaswamy–Moynihan model and the parameters of this model  $\Delta h^*$ ,  $\beta$ ,  $x$ ,  $A$  were determined using curve fitting method and characteristic times method. Viscosities of studied materials in the range of  $10^8$ – $10^{13}$  Pa s were measured by penetration method. The calculated values of activation energies of viscous flow  $E_\eta$  are close to the values of effective activation energies of relaxation  $\Delta h^*$  for studied chalcogenide materials.

**Keywords:** dilatometry, Ge–Se glasses, structural relaxation, TNM model, viscosity

## Introduction

The relaxation behavior of amorphous materials has been studied for the last 60 years. These studies were predominantly focused on polymer materials that are significantly influenced by physical aging. There are several studies of relaxation in selenium based glasses [1, 2] because these glasses have a wide utilization in many branches especially in optical recording media.

The basis of relaxation studies were put by Tool [3, 4] and Kovacs [5, 6] (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 DSC methods [2, 7]. In spite of the enthalpy the relaxation process can be studied only indirectly because of very small thermal changes in large time scale. On the contrary the original dilatometry method is able to observe directly the volume changes during relaxation process. Similarly it is possible to record a course of relaxation by thermomechanical analysis. In this case the change of sample length is observed. Provided that the material is isomorphous then studied process is called volume relaxation.

Structural relaxation is a consequence of non-equilibrium state in which amorphous material occurs below the glass transition temperature  $T_g$ . During this process the structural arrangement is changing towards equilibrium state. It is reflected in changes of properties of amorphous materials such as volume ( $V$ ), enthalpy ( $H$ ), refractive index ( $n_D$ ), etc.

Relaxation process occurs during annealing at temperature below  $T_g$  where the structure of amorphous ma-

terial is changing in time and it is not possible to describe such material by standard thermodynamic quantity. Tool [4] introduced the fictive temperature  $T_f$  to characterize the structure during the relaxation. The fictive temperature is defined as temperature at which the sample volume (enthalpy, etc.) would be equal to the equilibrium value at temperature  $T_f$ . 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  $T$ . The relaxation time  $\tau$  dependence on temperature and structure (in the form of fictive temperature) is usually expressed by Tool–Narayanaswamy–Moynihan equation (TNM) [8]:

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

where  $A$  is the pre-exponential constant,  $x$  is the parameter of non-linearity ( $0 < x \leq 1$ ) and  $\Delta h^*$  is the effective activation energy of relaxation process. Narayanaswamy [6] showed that linearity can be restored using the reduced time integral and then the fictive temperature can be expressed as:

$$T_f = T_g - \Delta T \left[ 1 - \exp \left( - \int_0^t \frac{dt}{\tau(T, T_f)} \right)^\beta \right] \quad (2)$$

where  $\beta$  ( $0 < \beta \leq 1$ ) is the non-exponentiality parameter and  $\Delta T = T_g - T$  is a temperature jump before annealing.

TNM model based on Eqs (1) and (2) is sufficient to describe the relaxation behavior of amorphous materials [7]. The parameters of TNM model ( $\Delta h^*$ ,  $\beta$ ,  $x$

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and  $A$ ) can be calculated by numerical curve fitting technique [9, 10] or evaluated from experimental data on the base of characteristic times  $t_0$  and  $t_m$  [11, 12].

Using length dilatometry, the relative length change during annealing can be expressed as  $\delta_0=(l-l_0)/l_0$ , where  $l_0$  is the initial sample length. During the annealing the  $\delta_0$  changes from 0 to its equilibrium value  $\delta_0^*$ . The inflection tangent of relative length change dependence on annealing time is used to determine the characteristic times. Time  $t_0$  corresponds to the extrapolation of inflection tangent to  $\delta_0=0$ . Characteristic time  $t_m$  corresponds to the extrapolation of inflection tangent to equilibrium value of relative length change  $\delta_0^*$ . Temperature jump dependence of characteristic times can be expressed using TNM parameters [11]. The dependence of characteristic time  $t_m$  on temperature jump can be described as:

$$\frac{d\log(t_m)}{dT} \cong \frac{\Delta h^*}{2.303RT_g^2} \quad (3)$$

of course the value of glass transition temperature depends on thermal history of the sample and experimental technique. The uncertainty of  $T_g$  value included in Eq. (3) can be eliminated by using the temperature dependence of characteristic time  $t_m$  [12]:

$$\frac{d\log(t_m)}{d(1/T)} \cong \frac{\Delta h^*}{2.303R} \quad (4)$$

the parameter  $\Delta h^*$  of TNM model can be determined according to Eq. (4). The temperature jump dependence of difference between characteristic times  $\log(t_m/t_0)$ , so called stabilization period, can be expressed as [11]:

$$\log \frac{t_m}{t_0} = \frac{1.18}{\beta} + \frac{(1-x)\Delta h^*}{2.303RT_g^2} \Delta T \quad (5)$$

the parameter of non-exponentiality can be calculated directly using this equation. Equations (3) and (5) can be used to determine the parameter of non-linearity.

## Experimental

The amorphous materials  $\text{Ge}_y\text{Se}_{100-y}$  ( $y=8$  and  $10$ ) were prepared by conventional method. Pure elements (5N) were weighed into quartz ampoule. The ampoule was closed after evacuation and put into the heater. Melting and homogenization was done at temperature well above the melting temperature. The melt was quenched in ice-water ( $\text{Ge}_8\text{Se}_{92}$ ) or on the air ( $\text{Ge}_{10}\text{Se}_{90}$ ). The amorphous character of prepared glasses was checked by X-ray diffraction.

The volume relaxation of prepared chalcogenide glasses was studied by dilatometry. The length change

of  $\text{Ge}_8\text{Se}_{92}$  and  $\text{Ge}_{10}\text{Se}_{90}$  glass was recorded by thermomechanical analyzer. The parallel areas of the sample in the check dimension were polished to optical quality. The accuracy of the measured length was  $0.01 \mu\text{m}$ . The non-isothermal experiments were used to characterize the glass transition area. So called intrinsic cycles, cooling and consecutive heating with the same rate, were done in the temperature range from  $40$  to  $120^\circ\text{C}$ , respectively,  $135^\circ\text{C}$  for  $\text{Ge}_{10}\text{Se}_{90}$  glass and the cooling/heating rate  $0.5\text{--}10 \text{ K min}^{-1}$  was applied.

Structural relaxation of Ge–Se chalcogenide glasses was studied under isothermal conditions. The two consecutive temperature jump method was chosen to analyze the relaxation behavior of  $\text{Ge}_8\text{Se}_{92}$  and  $\text{Ge}_{10}\text{Se}_{90}$  glasses. First the previous thermal history was erased by heating to the temperature well above  $T_g$ . Then the sample was cooled to the temperature  $T_0$  and annealed for 300 min. The temperature  $T_0$  was chosen as the temperature at which the annealed glass takes equilibrium length into 300 min. After the first annealing the sample was cooled (down-jump) or heated (up-jump) to temperature  $T$  and annealed for time necessary to take equilibrium. The isothermal experiment was done for the temperature jumps  $\Delta T=T_0-T$  in the range from  $6$  to  $28^\circ\text{C}$  for  $\text{Ge}_8\text{Se}_{92}$  glass ( $T_0=79^\circ\text{C}$ ) and from  $-10$  to  $25^\circ\text{C}$  for  $\text{Ge}_{10}\text{Se}_{90}$  glass ( $T_0=85\text{--}90^\circ\text{C}$ ).

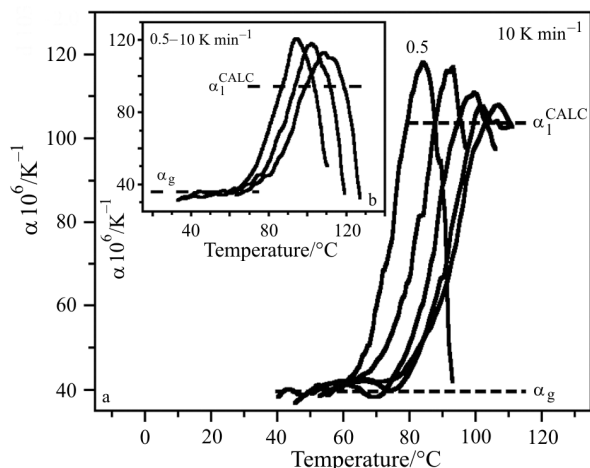
The viscosity behavior of Ge–Se chalcogenide materials was studied too. The viscosity in the range  $10^8\text{--}10^{13} \text{ Pa s}$  was measured by penetration method [13] using the thermomechanical analyzer. In the temperature range of viscosity measurement the amorphous material should be called undercooled liquid rather than glass. In the case of spherical indenter the viscosity can be calculated as [14]:

$$\eta = \frac{9}{32\sqrt{2r}} \frac{Ft}{h^{3/2}} \quad (6)$$

where  $r$  is a radius of spherical indenter,  $F$  is a force loads into indenter,  $t$  is time of penetration and  $h$  is a penetration depth. For the viscosity measurements the thin plates of the sample were both sides polished to the optical quality.

## Results and discussion

Intrinsic cycles described in experimental part were used to determine the glass transition temperature  $T_g$  as a temperature corresponding to the intersection of temperature dependence of length of glass and undercooled liquid. The values of  $T_g$  for heating rate  $5 \text{ K min}^{-1}$  were found to be  $87^\circ\text{C}$  for  $\text{Ge}_8\text{Se}_{92}$  and  $98^\circ\text{C}$  for  $\text{Ge}_{10}\text{Se}_{90}$ . The slope of temperature dependence of length denote a thermal expansion coefficient as  $\alpha=(1/l_0)(dl/dT)$ . The thermal dependence of  $\alpha$  for studied glasses is illus-



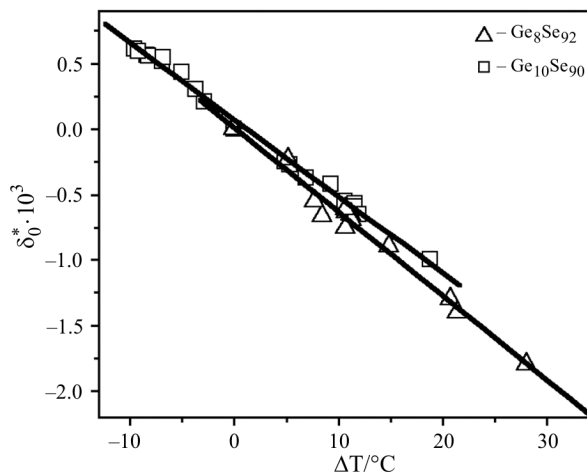
**Fig. 1** Temperature dependence of thermal expansion coefficient of a –  $\text{Ge}_8\text{Se}_{92}$  and b –  $\text{Ge}_{10}\text{Se}_{90}$  glass for different heating rate. The value of thermal expansion coefficient of glass  $\alpha_g$  is illustrated, the way of calculation of thermal expansion coefficient of undercooled liquid  $\alpha_1$  is described in text

trated in Fig. 1. Herefrom the thermal expansion coefficients below  $T_g$  as  $\alpha_g = (39.5 \pm 0.7) \cdot 10^{-6} \text{ K}^{-1}$  and  $\alpha_g = (35.5 \pm 0.5) \cdot 10^{-6} \text{ K}^{-1}$  were determined for  $\text{Ge}_8\text{Se}_{92}$ , respectively,  $\text{Ge}_{10}\text{Se}_{90}$  glasses. The thermal expansion coefficient above  $T_g$  is not constant at the value corresponding to the thermal expansion coefficient of undercooled liquid  $\alpha_1$  because of viscous flow. Although it is possible to estimate the value of  $\alpha_1$  such as for  $\text{Ge}_8\text{Se}_{92}$  material it is better to evaluate this quantity from isothermal relaxation experiments where the equilibrium value of relative length change should be proportional to the temperature jump [11]:

$$\delta_0^* = -(\alpha_1 - \alpha_g) \Delta T \quad (7)$$

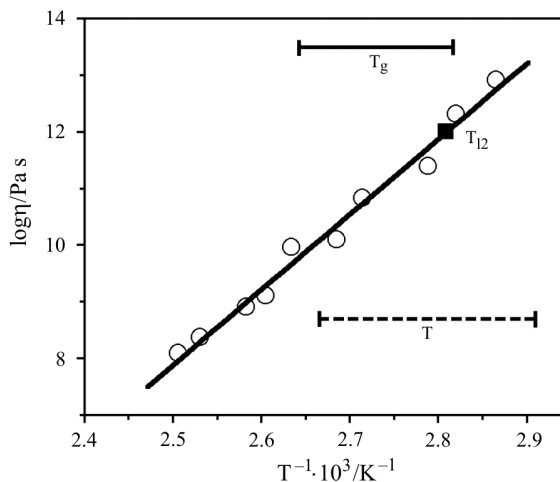
this equation is valid for down-jump as well as for the up-jump experiments as is shown in Fig. 2. The determined value of difference between thermal expansion coefficient of undercooled liquid and glass ( $\alpha_1 - \alpha_g$ ) is  $\Delta\alpha = (64 \pm 1) \cdot 10^{-6} \text{ K}^{-1}$  for  $\text{Ge}_8\text{Se}_{92}$  and  $\Delta\alpha = (59 \pm 1) \cdot 10^{-6} \text{ K}^{-1}$  for  $\text{Ge}_{10}\text{Se}_{90}$ . The corresponding thermal expansion coefficients of undercooled liquids  $\alpha_1$  are  $103.5 \cdot 10^{-6}$  and  $94.5 \cdot 10^{-6} \text{ K}^{-1}$ , respectively (Fig. 1). Especially for  $\text{Ge}_8\text{Se}_{92}$  the calculated  $\alpha_1$  value corresponds very well with former estimation from intrinsic cycles experiments.

The study of structural relaxation of chalcogenide glasses was combined with the viscosity measurements of their undercooled liquids to prove the relationship between the activation energy of viscous flow  $E_\eta$  and the parameter  $\Delta h^*$  of TNM model which was formerly assumed by several authors [7, 12, 15]. Therefore the temperature dependences of viscosity were measured for both of materials. It was found out that this dependence



**Fig. 2** Temperature jump dependence of equilibrium value of relative length change during annealing of  $\text{Ge}_8\text{Se}_{92}$  and  $\text{Ge}_{10}\text{Se}_{90}$  glass

can be described in measured temperature range by simple equation of Arrhenius type  $\eta = A' \exp(E_\eta / RT)$ , where  $E_\eta$  is the activation energy of viscous flow,  $R$  is a gas constant and  $A'$  is a constant. According to this formulation the value of activation energy of viscous flow was  $E_\eta = 318 \pm 14 \text{ kJ mol}^{-1}$  calculated for  $\text{Ge}_8\text{Se}_{92}$  and  $E_\eta = 255 \pm 11 \text{ kJ mol}^{-1}$  for  $\text{Ge}_{10}\text{Se}_{90}$  composition. Further the temperature range of viscosity measurements was compared with the range of dilatometric experiments. And it was verified that the viscosity measurements were performed in the glass transition range as is illustrated in Fig. 3. It is apparent that viscosity in dilatometric  $T_g$  region (heating rate  $0.5\text{--}10 \text{ K min}^{-1}$ ) moves from  $10^{10}$  to  $10^{12} \text{ Pa s}$ . Here temperature corresponding



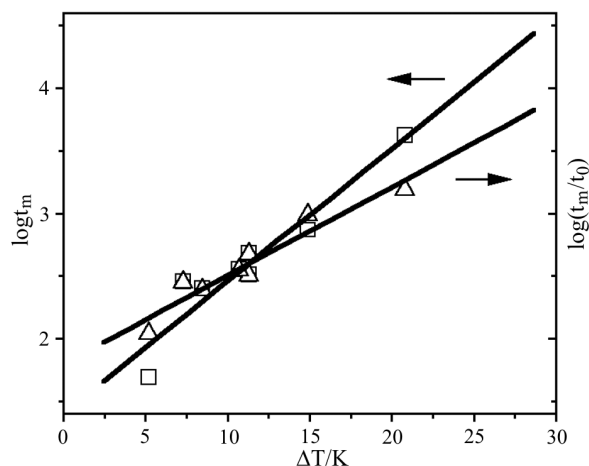
**Fig. 3** Viscosity dependence on temperature of  $\text{Ge}_{10}\text{Se}_{90}$  material. Glass transition temperature  $T_{12}$  from viscosity measurements is indicated. The correlation among temperature range of viscosity measurement,  $T_g$  values from intrinsic cycles for heating rate  $0.5\text{--}10 \text{ K min}^{-1}$  and annealing temperatures  $T$  used for relaxation experiments is illustrated

value of viscosity  $10^{12}$  Pa s is called the viscosity glass transition temperature  $T_{12}$  [16]. For both studied chalcogenide materials the value of  $T_{12}$  is close to dilatometric  $T_g$  for heating rate  $0.5 \text{ K min}^{-1}$ .

Volume relaxation of  $\text{Ge}_y\text{Se}_{100-y}$  ( $y=8$  and  $10$ ) glasses was studied using the two temperature jumps method by thermomechanical analysis as it is described in experimental part. The comparison of temperature jump range and the temperature range of viscosity measurement is in Fig. 3. Value of the first annealing temperature  $T_0$  at which the sample was annealed for 300 min is close to the value of  $T_g$  for heating rate  $2 \text{ K min}^{-1}$  for studied materials.

Parameters of TNM model which describe the volume relaxation process were determined using the characteristic times  $t_0$  and  $t_m$  based on Eqs (3)–(5) that are valid only for down-jumps experiments ( $T_0 > T$ ).

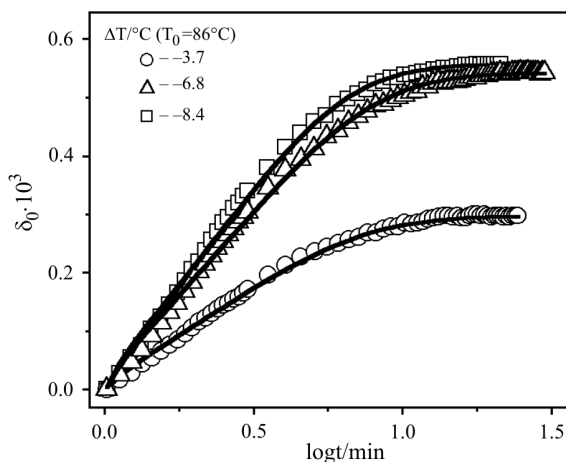
The calculated effective activation energies are  $\Delta h^* = 298 \pm 52 \text{ kJ mol}^{-1}$  for  $\text{Ge}_8\text{Se}_{92}$  and  $\Delta h^* = 234 \pm 60 \text{ kJ mol}^{-1}$  for  $\text{Ge}_{10}\text{Se}_{90}$  glass. These values are close to the value of  $E_\eta$  although their errors are higher. These errors can be produced by longer stabilization period which is needed to achieve a required annealing temperature with a deviation smaller than  $0.2 \text{ K}$ . So the part of relaxation data is lost and it influences the accuracy of calculated TNM parameters. Longer stabilization period in the case of  $\text{Ge}_{10}\text{Se}_{90}$  relaxation experiments reflects especially on high uncertainty of determination of characteristic time  $t_0$ . That is why the parameter  $\beta$  and  $x$  were not evaluated for  $\text{Ge}_{10}\text{Se}_{90}$  glass using method of characteristic times. Characteristic time  $t_0$  and  $t_m$  were determined only for  $\text{Ge}_8\text{Se}_{92}$  glass and their dependence on the temperature jump is plotted in Fig. 4. The parameters  $\beta = 0.66 \pm 0.04$  and  $x = 0.49 \pm 0.09$  were calculated on the base of Eqs (4) and (5).



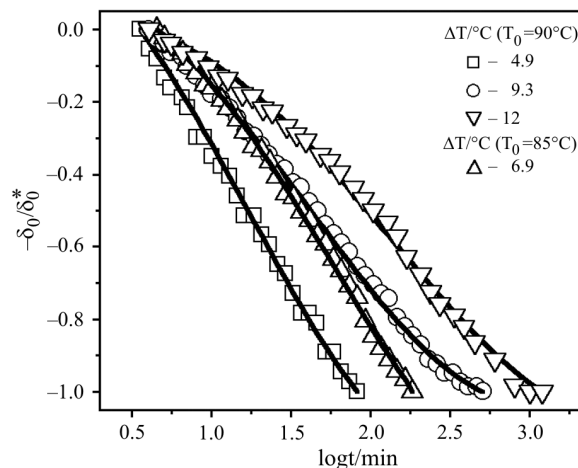
**Fig. 4** Temperature jump dependence of characteristic time  $t_m$  and stabilization period  $\log(t_m/t_0)$  determined from relaxation experiments of  $\text{Ge}_8\text{Se}_{92}$  glass

The previous parameters of TNM model can be compared with results obtained from curve fitting method. The best fits of volume relaxation data were performed to obtain TNM parameters which are summarized in Table 1. The agreement between experimental relaxation data and a curve calculated by best fit method are shown in Figs 5, 6 for up-jump and down-jump experiments, respectively. The relaxation data in Fig. 6 are expressed in the form of normalized relative length change  $-\delta_0 / \delta_0^*$  to show that time to reach equilibrium does not depend on temperature  $T_0$  but only on temperature jump in the temperature range not far from  $T_g$ .

The values of  $\Delta h^*$  determined by curve fitting method (Table 1) for both studied Ge–Se glasses are equal to the activation energy of viscous flow. Parameters  $\beta$  and  $x$  are consistent with the result of method of characteristic times. Although these results do not



**Fig. 5** Experimental relaxation data of  $\text{Ge}_{10}\text{Se}_{90}$  glass for temperature up-jump ( $T_0 < T$ ) and curves calculated for TNM parameters summarized in Table 1



**Fig. 6** Experimental relaxation data of  $\text{Ge}_{10}\text{Se}_{90}$  glass for temperature down-jump ( $T_0 > T$ ) and curves calculated for TNM parameters summarized in Table 1

**Table 1** Fitted Tool–Narayanaswamy–Moynihan parameters for dilatometric isothermal data of studied  $\text{Ge}_y\text{Se}_{100-y}$  glasses

Composition	$\Delta h^*/\text{kJ mol}^{-1}$	$\beta$	$x$	$-\ln A/s$
$\text{Ge}_8\text{Se}_{92}$	$318 \pm 1$	$0.61 \pm 0.04$	$0.46 \pm 0.04$	$102.8 \pm 0.6$
$\text{Ge}_{10}\text{Se}_{90}$	$255 \pm 1$	$0.55 \pm 0.05$	$0.43 \pm 0.02$	$78.8 \pm 0.5$

agree with results reported by Cortés *et al.* [2], the obtained values of TNM parameters can be used to calculate theoretical relaxation curves corresponding very well with dilatometric experiments.

## Conclusions

Volume relaxation of  $\text{Ge}_8\text{Se}_{92}$  and  $\text{Ge}_{10}\text{Se}_{90}$  glasses was studied and related to the viscosity behavior. The glass transition area was characterized using non-isothermal, isothermal (relaxation) and viscosity experiments. The method of two consecutive temperature jumps was used to study the structural relaxation. Relaxation experiments were successfully described by TNM model and the parameters of this model were calculated using the curve fitting method and the characteristic times method. The values of parameters obtained using both the method are very similar. It was validated that the effective activation energy is close to the value of activation energy of viscous flow. The viscous flow is probably a rate control process of structural rearrangement during physical aging.

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