STUDY OF STRUCTURAL RELAXATION
OF Ge-Se AND Ge-S CHALCOGENIDE GLASSES

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The structural relaxation of chalcogenide glasses related to the viscosity behaviour of their undercooled liquids was studied. The volume and enthalpy relaxation of Ge_ySe_{100-y} (y = 0, 8 and 10) and Ge_yS_{100-y} (y = 38 and 40) glasses was studied by using length dilatometry, mercury dilatometry and calorimetry. Both volume and enthalpy relaxation were studied under isothermal and non-isothermal conditions. It was found that the equilibrium time scale of relaxation experiments are practically the same for both volume and enthalpy relaxation. Relaxation behaviour of studied chalcogenide glasses was described by Tool-Narayanaswamy-Moynihan model and the parameters of this model (effective activation energy Δh^*, parameter of non-exponentiality β, parameter of nonlinearity x, and pre-exponencial factor A) were determined. The volume and enthalpy relaxation can be sufficiently well predicted by using the same set of TNM parameters. The effective activation energy of TNM model is close to the activation energy of viscous flow of undercooled liquid.

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Introduction

Chalcogenide glasses are very often studied because of their practical importance. Attention is paid mainly to the glass transition but not so much directly to the structural relaxation. The 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 the calorimetric method but the dilatometry is used as well.

From practical point of view, the change in properties with time is very important for application of any non-crystalline 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 towards metastable equilibrium and corresponding macroscopic properties (enthalpy H, volume V, etc.) will change with time. This process is usually called structural relaxation or physical ageing. An example of relaxation behaviour is in Fig. 1. Amorphous material in equilibrium at temperature T_0 is cooled down to the temperature T and the observed property P (H, V, etc.) change from equilibrium to P_0. But the relaxation process proceeds during annealing at temperature T, where the property P_0 changes towards its metastable equilibrium P^* at temperature T.

A change of property P (H, V, etc.) during annealing can be expressed by the fictive temperature T_f introduced by Tool [1]. Structural relaxation of property P during annealing after temperature jump can be described in the form of relative departure δ_0 of actual property P from the initial value P_0

$$\delta_0 = \frac{P - P_0}{P_0} \tag{1}$$

An empirical function was successfully used to describe the structural relaxation process of a variety of amorphous materials [2]

$$\delta_0(t) = \delta_0^* \left[1 - \exp\left(-\frac{t}{\tau} \right)^\beta \right] \tag{2}$$

where τ is a relaxation time and the non-exponentiality parameter β ($0 < \beta \leq 1$) is inversely proportional to the width of corresponding distribution of relaxation times. Equation (2) well describes the $\delta_0(t)$ data for small temperature jumps but it fails for temperature jumps higher than 1 K. This nonlinear behaviour was

explained by Tool [1]. Tool established that relaxation time depends on temperature and also on instantaneous structure of a glass characterized by T_f. Narayanaswamy [3] showed that linearity can be restored using the reduced time defined as

$$\xi = \int_0^t \frac{dt}{\tau(T, T_f)}$$ (3)

Then the relaxation function $\delta_0(t)$ can be expressed [3] as

$$\delta_0(t) = \delta_0^* \left\{ 1 - \exp\left[-\left(\int_0^t \frac{dt}{\tau(T, T_f)} \right) \right]^{\beta} \right\}$$ (4)
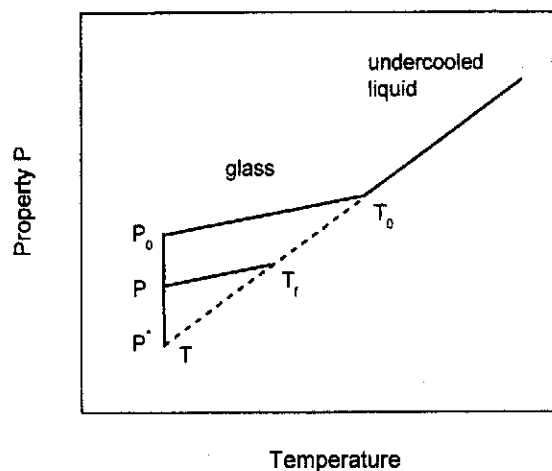

Fig. 1 Schematic illustration of changes in property P of amorphous material during the temperature jump from T_0 to T and consecutive annealing

The most frequently used expression for $\tau(T, T_f)$ in Eq. (4) is the Tool–Narayanaswamy–Moynihan formulation [3,4]

$$\tau(T, T_f) = A \exp\left[x \frac{\Delta h^*}{RT} + (1 - x) \frac{\Delta h^*}{RT_f} \right]$$ (5)

where A is the pre-exponential constant, x is the parameter of nonlinearity ($0 < x \leq 1$) and Δh^* is the effective activation energy.

The phenomenological model has to express nonlinearity and non-exponenciality of 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. Tool–Narayanaswamy–Moynihan model (TNM) based on Eqs (3) – (5) is appropriate to describe quantitatively the volume and enthalpy relaxation not far from T_g. This four-parameter model is empirical and the parameters A, x, β and Δh^* have no clear physical meaning yet. However, it has been found that the effective activation energy is very close to the activation energy of viscous flow for many materials [5,6].

Relaxation time τ can be described by Kovacs–Aklonis–Hutchinson–Ramos equation (KAHR) too [7] but the TNM equation is more frequently used. The parameter Θ of KAHR equation can be related to the parameter Δh^* of TNM equation [8] as $\Theta = [\Delta h^*/(RT_g^2)]$. Parameter Θ is characteristic of amorphous materials [2]. The value of Θ is close to 1 K^{-1} for polymer and for inorganic glasses it is in the range of $0.1 - 0.3$ K^{-1}.

Theory

All dilatometric and calorimetric experiments of selected chalcogenide glasses done within this work were described by using the TNM model. The parameters of TNM model can be obtained by the curve fitting method or directly from the experimental calorimetric and dilatometric data.

The curve fitting method is based on Eqs (3) – (5). The thermal history $T(t)$ is defined 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.

Appropriate conditions of dilatometric or calorimetric experiments can be used to determine the parameters of TNM model directly. The parameter Δh^* can be determined from non-isothermal measurements. The temperature of maximum T_p of the temperature dependence of thermal expansion coefficient α is changed depending on heating rate q_h during the so-called intrinsic cycles (cooling and consecutive heating with the same ratio of cooling/heating rate). This dependence on heating rate $(RT_g^2)/\Delta h^* = (d\,T_p/d \ln q_h)$ for T_g corresponding to heating rate 3 or 5 °C min^{-1} is often used to calculate the effective activation energy [7]. The fictive temperature dependence on cooling rate q_c (for the same heating rate) is used to determine Δh^* from calorimetric experiments as $\Delta h^*/R = -[d \ln q_c/d(1/T_f)]$ [2]. The fictive temperature from DSC signal is determined according to Moynihan

154

et al. [4].

Structural relaxation of amorphous material can be studied directly under isothermal condition by using dilatometry. Enthalpy relaxation exhibits a peak in reheating scan after annealing. Only the parameter of nonlinearity can be directly obtained from the calorimetric isothermal experiments [8]. The temperature of maximum of DSC effect T_p and the enthalpy lost during annealing shift with annealing time. The parameter of nonlinearity can be calculated as $x^{-1} - 1 = \Delta C_p (dT_p/d\Delta H)$, where ΔC_p is the difference between heat capacity of undercooled liquid and glass [8].

Parameters of TNM model can be determined from time dependence of dilatometric experiments in the form of relative volume/length change δ_0 according to Eq. (1). In Fig. 2 there is a schematic illustration of relative volume/length change dependence on annealing time after temperature jump ΔT and the determination of characteristic times is described. The characteristic times t_0, t_m, the so-called stabilization period $\log(t_m/t_0)$ and their dependence on temperature or temperature jump can be expressed using TNM parameters [9]. The temperature jump dependence of characteristic time t_m can be described as

$$\frac{d\log(t_m)}{d\Delta T} \cong \frac{\Delta h^*}{2.303\,RT_g^2} \tag{6}$$
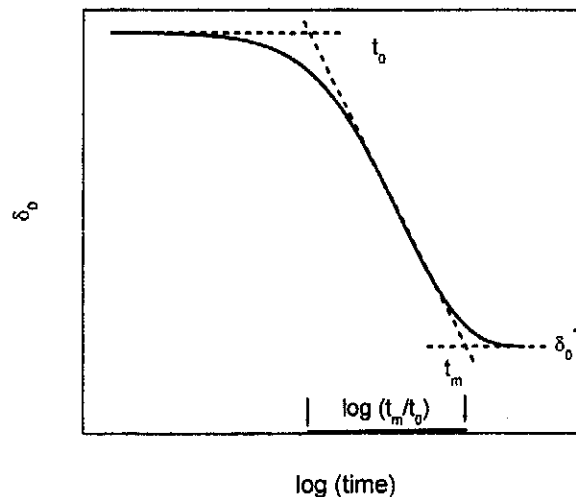

Fig. 2 Relative departure of volume/length of the amorphous material depending on time of annealing at temperature T after temperature jump $T_0 \rightarrow T$. Illustration of determining of characteristic times t_0, t_m and stabilization period $\log(t_m/t_0)$. The metastable equilibrium value of relative volume/length change δ_0^* is identified

The uncertainty of T_g value can be eliminated by using the temperature dependence of characteristic time t_m: $[d\log t_m/d(1/T)] \cong (\Delta h^*/2.303R)$. Temperature jump dependence of stabilization period is expressed as [9]

$$\log \frac{t_m}{t_0} = \frac{1.18}{\beta} + \frac{(1-x)\Delta h^*}{2.303 RT_g^2} \Delta T \tag{7}$$

The parameter of non-exponentiality can be calculated directly using this equation. Equations (6) and (7) can be used to determine the parameter of nonlinearity.

The pre-exponential constant can be calculated by using the fictive temperature in the glass transition area. When the relaxation time in this area is 100 s (one of the T_g definition), the pre-exponential constant is in the form $\ln A = -(\Delta h^*/RT_g) + 4.6$ assuming that $T_f \cong T_g$ [2].

The structural relaxation of chalcogenide glasses was studied for one-component (Se) and two-component glasses (Ge-Se, Ge-S). Calorimetric and dilatometric experiments of $Ge_y Se_{100-y}$ (y is 0, 8 and 10) and $Ge_y S_{100-y}$ (y is 38 and 40) glasses were carried out and the methods of determination of TNM model parameters mention above were applied.

Experimental

The studied chalcogenide glasses $Ge_y Se_{100-y}$ ($y = 0$, 8 and 10) and $Ge_y S_{100-y}$ ($y = 38$ and 40) were prepared by conventional method. Pure elements (5N) weighed into a quartz ampoule were melted and homogenized at a temperature well above the melting temperature for 20 hours. The melt was quenched in ice-water (Se, $Ge_8 Se_{92}$), water ($Ge_{38} S_{62}$, $Ge_{40} S_{60}$) or in the air ($Ge_{10} Se_{90}$). The amorphous nature of prepared glasses was checked by x-ray diffraction.

Dilatometry is a technique in which the volume or the length of the sample is measured depending on temperature or time. The relaxation process studied using dilatometry is called volume relaxation. The thermomechanical analyzers TMA CX02 and CX04 [10] (measurement of sample's length) were used to study the relaxation process of all the prepared chalcogenide glasses except Se. The volume of Se was measured using mercury dilatometry [11]. The mercury dilatometer is made of borosilicate glass — the tube filled with the sample and mercury is connected with a capillary. The actual sample volume can be calculated from the level of mercury in the capillary, when the mercury dilatometer is calibrated. TMA is a common experimental technique. Mercury dilatometry has been newly introduced at the Faculty of chemical technology, University of

Pardubice. This kind of dilatometer is mainly used for studying organic polymers. The present work is partly concentrated on application of mercury dilatometry to structural relaxation study of chalcogenide glasses. The insufficient temperature stability of TMA at lower temperatures and estimated influence of viscous flow were the main reasons to test the mercury dilatometry for relaxation experiments of Se. Differential scanning calorimetry DSC was used to study the enthalpy relaxation of chalcogenide glasses.

Non-isothermal experiments can be used to characterize the glass transition area — the glass transition temperature T_g, the difference between the thermal expansion coefficient of undercooled liquid and glass $\Delta\alpha$ and the difference between heat capacity of undercooled liquid and glass ΔC_p can be determined. The non-isothermal experiments described in theoretical part were used to study the structural relaxation.
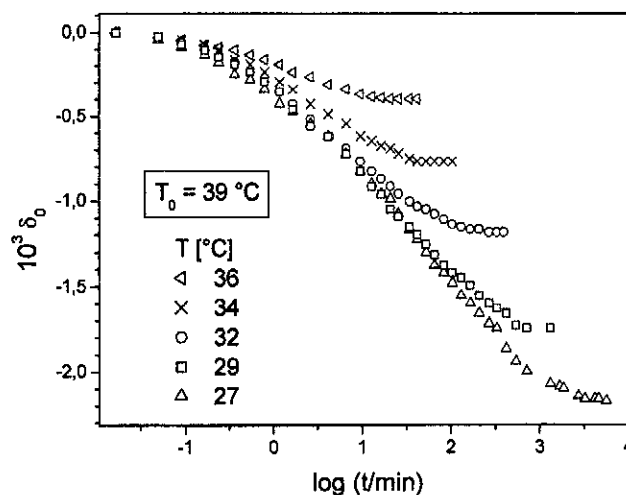

Fig. 3 Logarithmic time dependence of relative volume change of Se after temperature jump from $T_0 = 39$ °C to temperature T

As described in introduction the structural relaxation occurs during annealing at a temperature below T_g. The volume relaxation is studied directly during annealing but the enthalpy relaxation is shown in reheating scan after annealing known as overshoot. The temperature jump experiments were chosen to analyze the relaxation process: the sample was annealed for 300 min at temperature T_0 near T_g, then the temperature was rapidly changed and the sample was annealed at temperature T for a time necessary to reach equilibrium. Mercury dilatometer cannot be cooled or heated at appropriate rates to be able to apply exactly the same thermal history as for consecutive temperature jumps in TMA and DSC. The temperature jump method was used too, but the mercury dilatometer was annealed at temperature T_0 in water bath for a time necessary to reach

Pustková P. et al./Sci. Pap. Univ. Pardubice Ser. A 11 (2005) 151–167

157

equilibrium, then it was quickly transferred to the other bath and annealed at temperature T. The examples of relaxation response of Se equilibrated at temperature 39 °C and then annealed at different temperatures up to temperature jump ($\Delta T = T_0 - T$) 12 K are shown in Fig. 3.

The viscosity of chalcogenide undercooled liquids was measured by using TMA. The viscosity in the range from 10^8 to 10^{13} Pa s was determined by penetration method [12,13].

The experimental techniques used to study the structural relaxation require different arrangement and amount of the sample. The powder of amorphous materials (about 10 mg) was used for calorimetric measurements. The samples for length dilatometry (TMA) were both sides polished to optical quality, the sample length in the direction measured was about 8 mm. In the case of viscosity measurements the thin plate of the sample (about 2 mm high) was both sides polished to optical quality. The amount of the sample for mercury dilatometry depends on the dilatometer construction details and the thermal expansion coefficient of studied material. In the case of Se filled in mercury dilatometer, the sample was about 6×100 mm in size (14.1 g) and the accuracy of the Se volume change was 5×10^{-5} cm^3.

Results and Discussion

The present work deals with relaxation behaviour of selected one-component (Se) and two-component (Ge-Se, Ge-S) chalcogenide glasses with respect to the viscosity behaviour of their undercooled liquids. The experimental results and their discussion are divided into three parts. First, the viscosity behaviour of studied amorphous materials is described. The study of structural relaxation is discussed according to the way of determination of TNM model parameters. Both non-isothermal and isothermal experiments as well as the method of direct determination of TNM parameters are discussed. Then the results of curve fitting method are summarized.

Temperature Dependence of Viscosity

The relaxation process can be considered as a continuation of viscous flow below the glass transition temperature. Therefore, the knowledge of viscosity behaviour can help to understand the nature of structural relaxation behaviour. The viscosity of studied chalcogenide glassformers can be found in the literature [14–16]. In the case of Se and Ge-S system the viscosity measurements [14,17] were carried out with the same TMA as was used for the relaxation experiments.

Temperature dependence of viscosity η is nonlinear but, in the narrow

temperature range, can be described by a simple equation of Arrhenius type

$$\eta = A' \exp \frac{E_\eta}{RT} \tag{8}$$

where E_η is the activation energy of viscous flow, R is the gas constant and A' is a constant. In Table I there are the values of E_η for all studied undercooled liquids and the temperature ranges corresponding to the viscosity $10^{13} - 10^8$ Pa s. The glass transition temperature T_{12} determined from viscosity experiments is the temperature for $\eta = 10^{12}$ Pa s. The experimental results of viscosity behaviour of Ge_8Se_{92} and $Ge_{10}Se_{90}$ correspond with published data [15,16]. The viscosity data for Se, $Ge_{38}S_{62}$ and $Ge_{40}S_{60}$ were reported elsewhere [14,17].

Table I Results of viscosity measurements of Ge-Se and Ge-S undercooled liquids: temperature range corresponds to the viscosity $10^{13} - 10^8$ Pa s, the activation energy of viscous flow E_η, the glass transition temperature T_{12} and fragility m

Composition		T, °C	E_η, kJ mol^{-1}	T_{12}, °C	m
Ge-Se	Se[*]	22 – 50	346 ± 17	25	52 ± 2
	Ge_8Se_{92}	63 – 104	318 ± 14	76	54 ± 1
	$Ge_{10}Se_{90}$	76 – 126	255 ± 11	83	35 ± 2
Ge-S[**]	$Ge_{38}Se_{62}$	374 – 432	478 ± 12	374	39 ± 1
	$Ge_{40}Se_{60}$	350 – 417	512 ± 11	358	42 ± 1

Viscosity measurements from the literature [17][*], [14][**]

Angell [18,19] used the temperature T_{12} to normalize the temperature dependence of viscosity. Viscosity behaviour can be classified on the basis of viscosity dependence on dimensionless temperature T_{12}/T. Fragility m indicates the proportion of divertivity towards temperature dependence of Arrhenius type

$$m = \frac{d\log\eta}{d(T_{12}/T)} \tag{9}$$

The viscosity measurements of studied chalcogenide glasses in the form of normalized temperature dependence are shown in Fig. 4. There is also an example of low fragility (SiO_2) and high fragility (o-terphenyl) system.

The values of fragility (Table I) are related to the relaxation behaviour of amorphous material. Hutchinson [20] conects the high value of fragility with high

Pustková P. et al./Sci. Pap. Univ. Pardubice Ser. A 11 (2005) 151–167

159

nonlinearity, broad distribution of relaxation times and high value of effective activation energy. On the contrary, the low value of fragility can be connected with relatively linear relaxation behaviour, narrow distribution of relaxation times and low value of Δh^*.
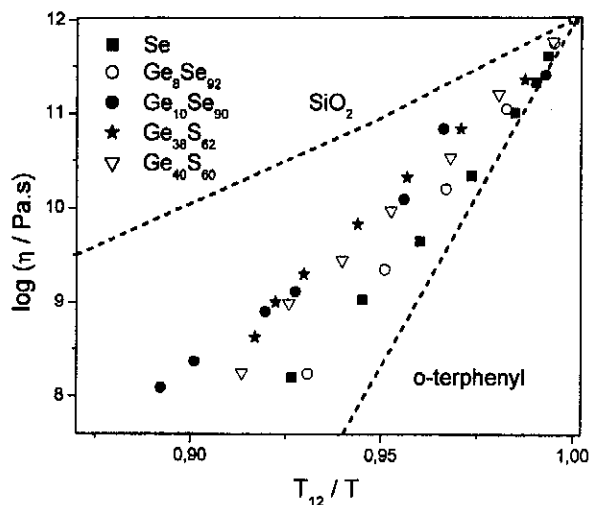

Fig. 4 Normalized temperature dependence of viscosity of studied chalcogenide glasses. Examples of low fragility (SiO_2) and high fragility (o-terphenyl) materials are illustrated

Determination of Parameters of TNM Model Directly from Experimental Data

Both dilatometric and calorimetric non-isothermal experiments can be used to determine the effective activation energy Δh^*. The experimental conditions and way of calculation of Δh^* are described in theoretical part. The temperature dependence of the thermal expansion coefficient α can be obtained from the volume/length temperature dependence measured by dilatometry. Temperature of maximum of α and its shift with heating rate are important for the calculation of Δh^*. But this kind of calculation could be used only for $Ge_{38}S_{62}$ glass ($\Delta h^* = 475 \pm 27$ kJ mol^{-1}) [21]. The viscous flow of other studied chalcogenide glasses influences dilatometric (length) experiment so much that T_p cannot be observed. The influence of viscous flow can be seen in the absence of clear value of thermal expansion coefficient of studied undercooled liquid α_l too, except for Ge_8Se_{92} glass [22]. But the value of α_l can be determined from isothermal experiments using temperature jump dependence of δ_0^* (way of δ_0^* determination is illustrated in Fig. 2) [23].

Different cooling rates $0.1 - 100$ K min^{-1} and subsequent heating for 10 K min^{-1} was used to determine Δh^* from calorimetric non-isothermal experi-
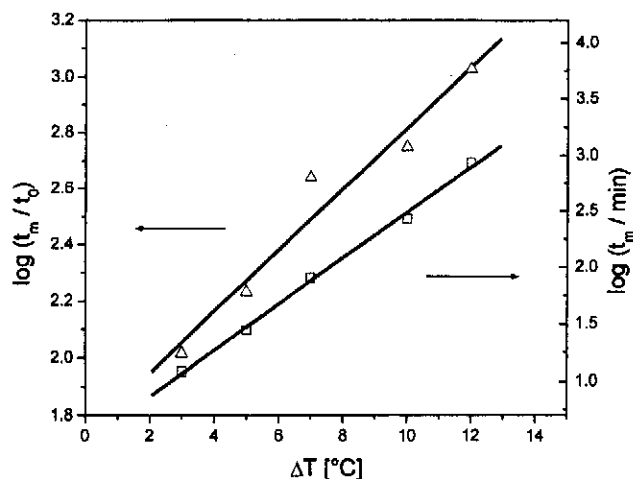
160

Fig. 5 Temperature jump dependence of characteristic time t_m and stabilization period for $T_0 =$ 39 °C of Se glass

ments. Fictive temperature of DSC heating scan T_f' [4] changes with cooling rate. The value of $\Delta h^* = 299 \pm 27$ kJ mol^{-1} obtained for $Ge_{10}Se_{90}$ glass is slightly higher than the activation energy of viscous flow ($E_\eta = 255 \pm 11$ kJ mol^{-1}) of this composition. The results of the same experiment of Se and Ge_8Se_{92} glasses were published [24,25], but the values of the parameter Δh^* obtained are higher compared to E_η. High difference between Δh^* and E_η was found for $Ge_{45}S_{55}$ (published results [26]) and $Ge_{40}S_{60}$ glass, where Δh^* was also calculated from T_f' shift with cooling rate. On the basis of these results it can be concluded that this way of Δh^* determination from calorimetric experiments is only a rough estimation and must be completed with other relaxation experiments.

Isothermal experiments afford more possibilities to determine the parameters of TNM model. Dilatometric relaxation responses in the form of relative departure of sample volume/length were used to determine the characteristic times t_0 and t_m. The parameters of TNM model Δh^*, β and x were calculated from the characteristic times dependence on temperature and temperature jump. The temperature stability of TMA was not very good in the case of relaxation experiments of $Ge_{10}Se_{90}$ glass, so that only the effective activation energy can be calculated. Parameters of TNM model determined on the basis of characteristic times are summarized in Table II. In Fig. 5 there is an illustration of temperature jump dependence of characteristic time t_m and stabilization period for dilatometric experiments of Se shown in Fig. 3.

Similar temperature jump method was used for calorimetric measurements too. The parameter of nonlinearity can be calculated from changes of maximum of overshoot T_p and enthalpy lost during annealing depending on annealing time. The temperature jump from 358 °C to 348 °C for $Ge_{40}S_{60}$ glass was studied up to

Table II Parameters of TNM model determined by using the characteristic time t_0 and t_m of dilatometric experiments of studied chalcogenide glasses

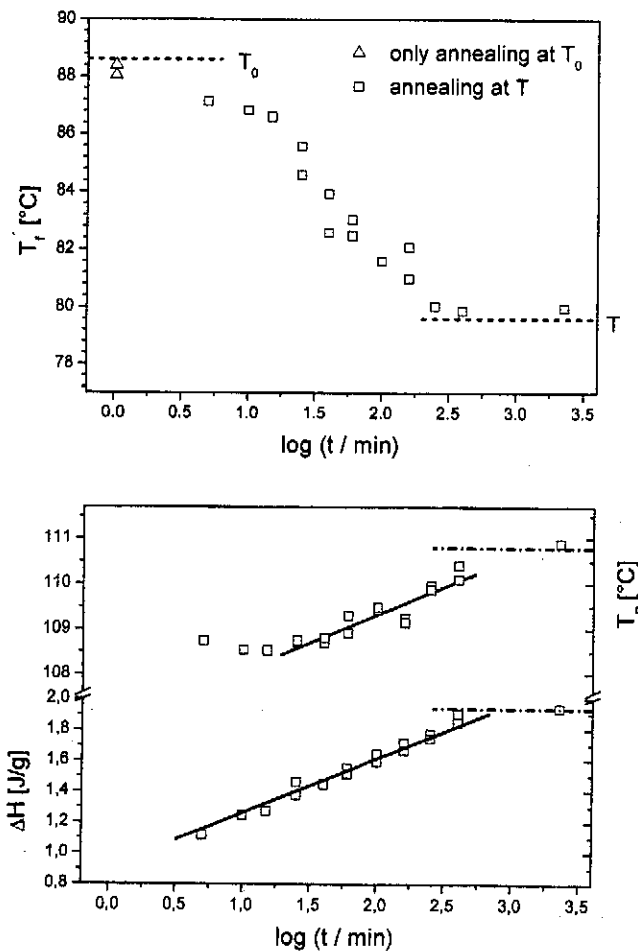| Composition		Δh^*, kJ mol^{-1}	β	x
Ge-Se	Se	357 ± 13	0.68 ± 0.04	0.47 ± 0.08
	Ge_8Se_{92}	298 ± 52	0.66 ± 0.04	0.49 ± 0.09
	$Ge_{10}Se_{90}$	234 ± 60	–	–
Ge-S	$Ge3_8Se_{62}$	496 ± 21	0.69 ± 0.08	0.64 ± 0.09
	$Ge_{40}Se_{60}$	519 ± 22	0.60 ± 0.03	0.62 ± 0.10

Fig. 6 Enthalpy relaxation of $Ge_{10}Se_{90}$ glass, annealing at 88.6 °C for 300 min and consecutive annealing at 79.6 °C. Annealing time dependence of fictive temperature T_f, enthalpy loss during annealing ΔH and temperature T_p corresponding to the maximum of DSC peak is illustrated
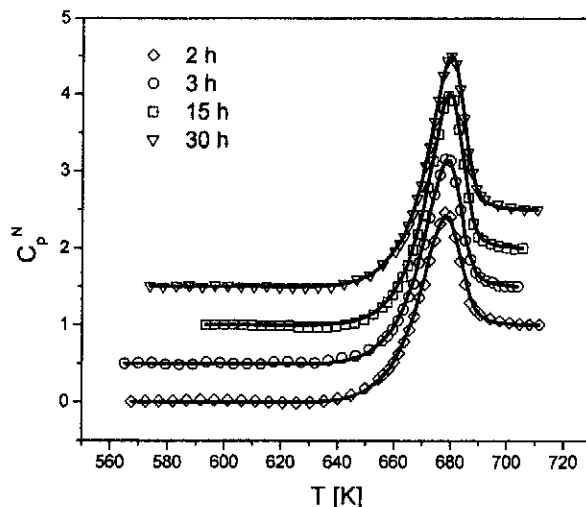
Fig. 7 Normalized relative volume changes of Se after temperature jump from $T_0 = 39\ ^\circ$C to temperature T. Lines represent the best fit of experimental data using the TNM parameters summarized in Table III
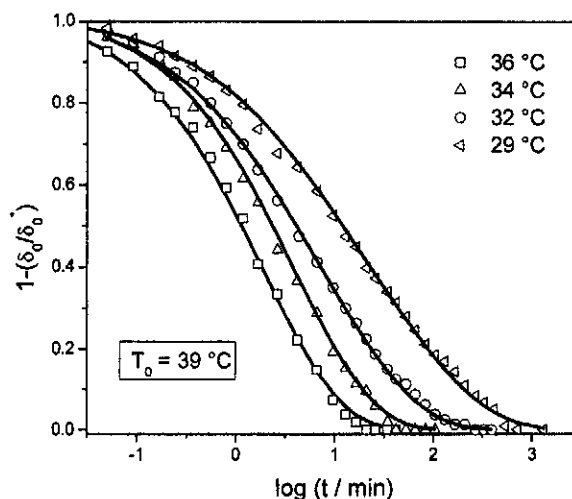

Fig 8 Normalized reheating DSC scan ($C_p^N = dT_f/dT$) of $Ge_{38}S_{62}$ glass after annealing at 378 °C for 300 min and at 360 °C for the time indicated in the figure. Lines represent the best fit of experimental data using the TNM parameters summarized in Table III

55 hours of annealing. The value of parameter of nonlinearity 0.62 ± 0.08 is close to the value determined from isothermal dilatometric experiments but the error of estimation is higher.

The composition $Ge_{10}Se_{90}$ was annealed at 79.6 °C after temperature jump $\Delta T = 9$ K and the parameter of nonlinearity 0.60 ± 0.03 was calculated. Experi-

Table III Parameters of TNM model determined by curve fitting method describing length (l), volume (V) and calorimetric (H) experiments of studied chalcogenide glasses. The TNM parameters for calorimetric experiments of Se are from literature [25,29]

Composition	Method	Parameters of TNM model			
		Δh^*, kJ mol^{-1}	β	x	$-\ln (A/s)$
Se	V	355 ± 1	0.58 ± 0.05	0.42 ± 0.05	133.0 ± 0.5
	H	354 ± 5	0.67 ± 0.03	0.48 ± 0.05	132 ± 2
		338 ± 25	0.67 ± 0.03	$-$	$-$
Ge$_8$Se$_{92}$	l	318 ± 1	0.61 ± 0.04	0.46 ± 0.04	102.8 ± 0.6
Ge$_{10}$Se$_{90}$	l	255 ± 1	0.55 ± 0.05	0.43 ± 0.02	78.8 ± 0.5
	H	259 ± 3	0.51 ± 0.03	0.48 ± 0.02	79.3 ± 0.9
Ge$_{38}$Se$_{62}$	l	483 ± 2	0.68 ± 0.04	0.56 ± 0.02	81.4 ± 0.3
	H	487 ± 3	0.85 ± 0.03	0.79 ± 0.01	83.6 ± 0.6
Ge$_{40}$Se$_{60}$	l	519 ± 1	0.58 ± 0.02	0.69 ± 0.01	91.5 ± 0.4
	H	519 ± 1	0.58 ± 0.03	0.68 ± 0.03	92.3 ± 0.1

mental results of these measurements are described in Fig. 6. Isothermal calorimetric experiments of Se and Ge$_8$Se$_{92}$ can be found in literature [24,25], but the samples were annealed only at one temperature. The parameter of nonlinearity for Se annealed at 19.8 °C $x = 0.67 \pm 0.02$ was obtained [25] and for annealing at temperature 26 °C was $x = 0.57 \pm 0.03$ [24]. Annealing of Ge$_8$Se$_{92}$ was done at 64 °C and the nonlinearity parameter 0.60 ± 0.03 was determined [24]. As is seen the values of x for studied Ge-Se glasses are higher compared to results from isothermal dilatometric experiments (Table II). This method of nonlinearity parameter determination from calorimetric experiments is rather a rough estimation than calculation of correct value.

Determination of Parameters of TNM Model by Curve Fitting Method

The way of numerical calculation of relaxation response based on TNM model is described in literature [27,28]. The computer program for curve fitting calculations was written and was successfully applied to the length (l), volume (V) and calorimetric (H) experiments. The first set of parameters at the beginning of the calculation is very important for curve fitting method. The value of effective activation energy was chosen close to the activation energy of viscous flow at the beginning of optimization.

The calculated TNM parameters describing all kinds of dilatometric and calorimetric experiments of studied chalcogenide glasses are summarized in Table III. The examples of experimental and calculated relaxation response of volume and enthalpy relaxation are shown in Figs 7 and 8. As is seen the calculated relaxation responses correspond very well with the experimental data. The TNM parameters obtained by fitting of different experiments are very similar. So volume and enthalpy relaxation of studied glasses can be described with the same set of TNM parameters. Only the parameter β and x of $Ge_{38}S_{62}$ glass are significantly different in the dilatometric and calorimetric experiments.

Conclusion

Volume and enthalpy relaxation of Ge_ySe_{100-y} ($y = 0$, 8 and 10) and Ge_yS_{100-y} ($y = 38$ and 40) chalcogenide glasses was studied and related to the viscosity behaviour of their undercooled liquids. Both non-isothermal and isothermal conditions were applied to the sample measured by using the length dilatometry, mercury dilatometry and calorimetry. The Tool–Narayaswamy–Moynihan model

Table IV The TNM parameters used to describe both volume and enthalpy relaxation data for Ge-Se and Ge-S chalcogenide glasses

Composition	Parameters of TNM model				Θ, K^{-1}
	Δh^*, kJ mol^{-1}	β	x	$-\ln (A/s)$	
Se	352 ± 6	0.66 ± 0.04	0.47 ± 0.05	130 ± 2	0.435 ± 0.007
Ge_8Se_{92}	318 ± 1	0.64 ± 0.04	0.48 ± 0.07	103 ± 1	0.295 ± 0.001
$Ge_{10}Se_{90}$	257 ± 2	0.53 ± 0.04	0.46 ± 0.03	79 ± 1	0.223 ± 0.002
$Ge_{38}Se_{62}$	485 ± 8	0.74 ± 0.08	0.66 ± 0.09	83 ± 1	0.133 ± 0.004
$Ge_{40}Se_{60}$	519 ± 1	0.58 ± 0.03	0.66 ± 0.06	92 ± 1	0.150 ± 0.002

was used to describe the relaxation behaviour of studied glasses. The parameters of TNM model were determined by several methods. The ways of direct determination of TNM parameters from calorimetric experiment are not very successful in comparison with the results obtained using the other methods (direct determination from dilatometric experiments, curve fitting method).

Calorimetric and dilatometric experiments can be described with the same set of TNM parameters. The obtained values of TNM parameters of studied chalcogenide glasses are summarized in Table IV. As is seen the effective activation energy is very closed to the activation energy of viscous flow.

The effective activation energy in the form of parameter Θ is characteristic

Pustková P. et al./Sci. Pap. Univ. Pardubice Ser. A 11 (2005) 151–167

165

for amorphous materials. The relaxation behaviour of amorphous selenium, in relation to the value of parameter Θ, varies from behaviour of the other studied chalcogenide glasses toward polymers.

Acknowledgements

References

[1] Tool A.Q.: J. Am. Ceram. Soc. **29**, 240 (1946).

[2] Hodge J.M.: J. Non-Cryst. Solids **169**, 211 (1994).

[3] Narayanaswamy O.S.: J. Am. Ceram. Soc. **54**, 491 (1971).

[4] Moynihan C.T., Easteal A.J., DeBolt M.A., Tucker J.: J. Am. Ceram. Soc. **59**, 12 (1976).

[5] De Bolt M.A., Easteal A.J., Macedo P.B., Moynihan C.T.: J. Am. Ceram. Soc. **59**, 16 (1976).

[6] Kovacs A.J., Hutchinson J.M., Aklonis J.J.: *Isobaric Volume and Enthalpy Recovery of Glasses. (I) A Critical Survey of Recent Phenomenological Approaches, The Structure of Non-Crystalline Materials*, (P.H. Gaskell, Ed.) Taylor&Francis (1977), 153–163.

[7] Kovacs A.J., Aklonis J.J., Hutchinson J.M., Ramos A.R.: J. Polym. Sci **17**, 1097 (1979).

[8] Hutchinson J.M., Ruddy M.: J. Polym. Sci. B **26**, 2341 (1988).

[9] Málek J.: Thermochim. Acta **313**, 181 (1998).

[10] Málek J., Švejka R.: Sci. Pap. Univ. Pardubice Ser. A **2**, 211 (1996).

[11] ASTM D864–52

[12] Cox S.M.: J. Sci. Instrum. **20**, 113 (1943).

[13] Douglas R.W., Amstrong W.L., Edward J.P., Hall D.: Glass Technol. **6**, 52 (1965).

[14] Málek J., Shánělová J.: J. Non-Cryst. Solids **243**, 116 (1999).

[15] Borisova Z.U.: *Glassy Semiconductors*, Plenum Press, New York, 1981.

[16] Stolen S., Grande T., Johnsen H.B.: Phys. Chem. Chem. Phys. **4**, 3396 (2002).

[17] Shánělová J.: PhD Thesis, The University of Pardubice, Prdubice, 2001.

[18] Angell C.A.: J. Chem. Phys. Solids **49**, 863 (1988).

[19] Angell C.A.: J. Non-Cryst. Solids **131–133**, 13 (1991).

[20] Hutchinson J.: M., Polym. Intern. **47**, 56 (1998).

[21] Pustková P., Shánělová J., Čičmanec P., Málek J.: J. Therm. Anal. Cal. **72**,

355 (2003).

[22] Pustková P., Shánělová J., Málek J Čičmanec P.: J. Therm. Anal. Cal. **80**, 643 (2005).

[23] Málek J.: Macromolecules **31**, 8312 (1998).

[24] Cortés P., Montserrat S., Ledru J., Saiter J.M.: J. Non-Cryst. Solids **235–237**, 522 (1998).

[25] Echeverría I., Kolek P. L., Plazek D. J., Simon S. L.: J. Non-Cryst. Solids **324**, 242 (2003).

[26] Zumailan A.: Mat. Lett. **57**, 94 (2002).

[27] Hodge I. M., Berens A. R.: Macromolecules **15**, 762 (1982).

[28] Asami T., Matsuishi K., Onari S., Arai T.,: J. Non-Cryst. Solids **226**, 92 (1998).

[29] Matsuishi K., Nogi K., Ogura H., Onari S., Arai T.,: J. Non-Cryst. Solids **227-230**, 799 (1998).