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Influence of sample form and thermal history on relaxation response

Pavla Honcová*, Roman Svoboda, Jiří Málek

Faculty of Chemical Technology, University of Pardubice, Studentská 573, 53009 Pardubice, Czech Republic

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ABSTRACT

In this work evaluation of the effective activation energy Δh^* from the cyclic relaxation experiments is discussed. Particular interest was paid to certain effects and processes that can influence the determined value of Δh^* parameter. The obtained values of parameter Δh^* for As_2Se_3 glass indicate that both form of the sample and type of applied thermal history influence the determined results. Moreover, the enthalpy relaxation response can be influenced by instabilities of the DSC baseline or by starting crystallization process. However, due to these two effects being not easily separable it was not possible to determine the degrees of their respective influences.

1. Introduction

Structural relaxation behaviour (usually denoted as enthalpy relaxation when studied by calorimetric techniques) is reflected in the heating scan performed through glass transition area. The heating scan can, generally, follow any previous thermal history. The relaxation response can be then described by means of Tool–Narayanaswamy–Moynihan model [1–3], which is nowadays one of the most popular models applied in order to describe structural relaxation behaviour. The Tool–Narayanaswamy–Moynihan (TNM) model is a 4-parameter phenomenological model. The parameters of this model are usually determined at once by numerical fitting; nevertheless, prior knowledge or at least an estimate of any of the initial parameter values is very helpful for finding of the true RSC minimum during the fitting procedure. That is also one of the reasons why several non-fitting methods for estimation of the TNM parameters were developed. Cyclic experiments provide a simple way for the estimation of the TNM parameter called effective activation energy Δh^*. In fact, the cycles consist of alternating cooling and heating steps through the glass transition region. Cyclic experiments for Δh^* evaluation can be performed in two ways – either the heating rate is constant for all applied cooling rates, or it is the ratio between the heating and cooling rates that remains constant for all performed cycles.

This work is focused on the enthalpy relaxation cyclic experiments and on possible influences of various experimental conditions on the Δh^* evaluation procedure. Stable and frequently studied chalcogenide glass As_2Se_3 was chosen as a suitable model material for this study. The TNM parameters as well as the activation energy of viscous flow in the glass transition region ($E_\eta = 316\ \mathrm{kJ\ mol^{-1}}$) are for the As_2Se_3 material published in [4].

2. Experimental

The amorphous As_2Se_3 was prepared by the common melt-quenching technique. First the pure elements were weighted into a quartz ampoule, which was then degassed and sealed. The ampoule was placed into a rocking furnace; homogenization of the melt proceeded at 650 °C for 20 h. Sufficiently fast cooling of the ampoule and of the melt inside was achieved by pulling the ampoule out of the furnace to ambient temperature. The amorphous nature of the prepared material was checked by X-ray diffraction.

Enthalpy relaxation of the As_2Se_3 glass was studied using differential scanning calorimeter (DSC) Pyris 1 (Perkin-Elmer). The DSC was calibrated by means of melting temperatures and enthalpies of fusion of pure metals. Measured samples were enclosed in aluminium pans; an empty pan was used as the reference.

Three different forms of samples were prepared – thin plates with both sides polished to optical quality (bulk) and two powders with particle sizes 180–250 and 20–50 μm, respectively. All performed experiments were reproduced for each of these three sample forms. Applying the Δh^* evaluation procedure to all these three forms of the As_2Se_3 glass was done in order to investigate how the sample form can influence the estimated value of Δh^*.

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* Corresponding author at: Department of Inorganic Technology, University of Pardubice, Nam. Cs. legii 565, 53009 Pardubice, Czech Republic.
Tel.: +420 466 037 179.
E-mail address: pavla.honcova@upce.cz (P. Honcová).

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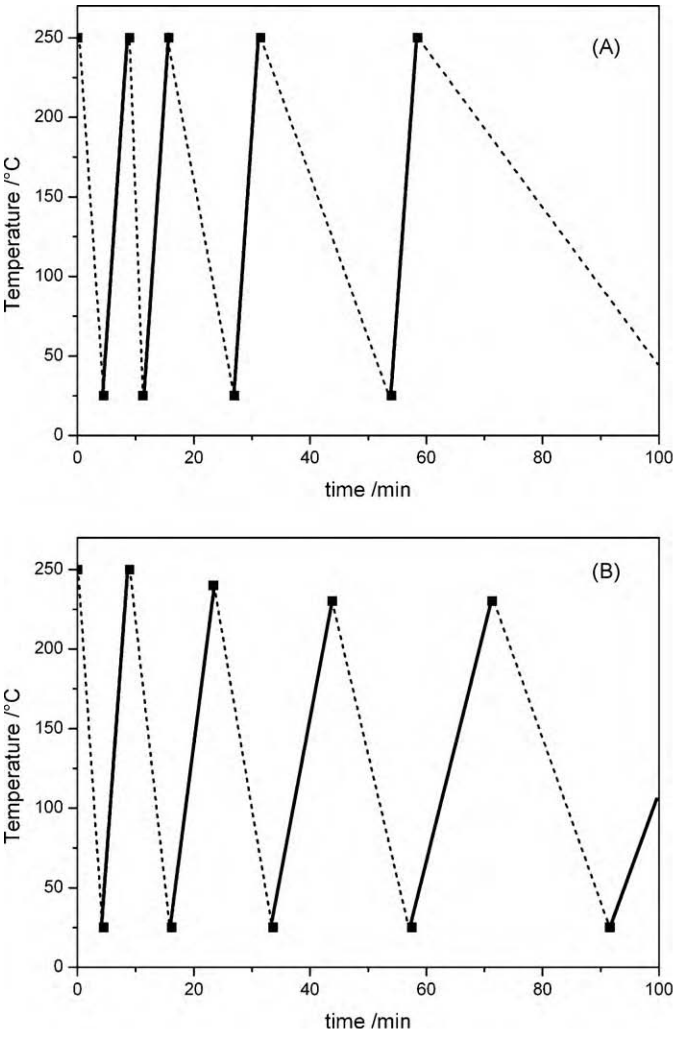

Fig. 1. Part of temperature program for cyclic experiments consisting of cooling (dashed line) and consequent heating (solid line) steps: (A) cycles performed at constant heating rate 50 K min^{-1} and varying cooling rates and (B) cycles with constant ratio of rates where the ratio between the cooling rate and consequent heating rate was equal to 1.

Enthalpy relaxation with the intention of parameter Δh^* determination was studied on the basis of the above described cyclic experiments, where the relaxation process is reflected in the observed endothermic peak (the so-called overshoot). The height, shape and position of the peak depend on the overall thermal history of the material – in the case of cyclic experiments the essential parameters are the cooling and heating rates. In our work the two above described types of cycles were applied in order to study the influence of various thermal histories on the Δh^* evaluation. Particular thermal histories of these experiments are shown in Fig. 1. Part A of Fig. 1 corresponds to the cycles performed at constant heating rate (while the cooling rates varied). Part B of Fig. 1 then corresponds to the cycles where both cooling and heating rates varied while their ratio was kept constant. Three sets of the first-type-cycles were performed for constant heating rates 10, 20 and 50 K min^{-1} whereas the cooling steps were performed at rates varying from 0.5 to 100 K min^{-1} within each set. The cycles with constant ratio of rates (where both cooling and heating rates varied but their ratio was kept constant and equal to unity) were performed for rates varying from 0.5 to 50 K min^{-1} (additional rates 0.2 and 0.3 K min^{-1} were applied only in the case of the bulk sample). In all cases a single sample was used to carry out each whole set of cyclic experiments; all cycle sets were performed starting with highest rates. The illustration of obtained relaxation endothermic peaks for both cycles with constant heating rate and cycles with constant ratio of rates, is shown in Figs. 2 and 3.

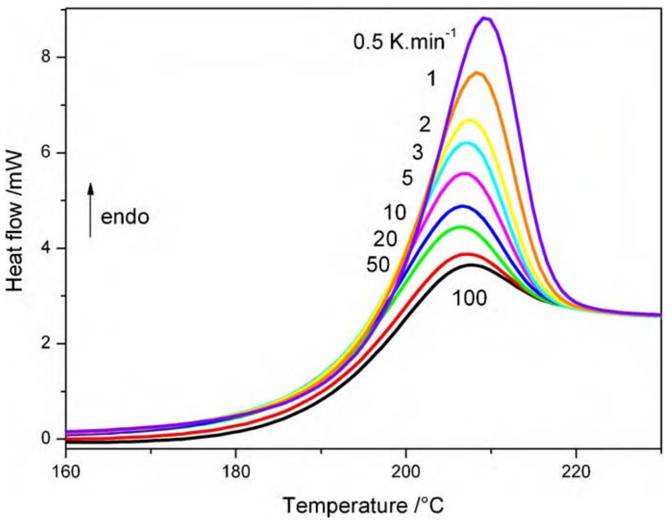

Fig. 2. DSC heating scans for a set of cycles performed at constant heating rate 50 K min^{-1} and given cooling rates (numbers) for bulk sample.

The issue, whether the enthalpy relaxation can be affected by the processes of nucleation and crystal growth proceeding in originally amorphous samples during the cooling/heating scans, was tested after each performed set of the relaxation experiments. The isothermal crystallization at 330 °C was measured for samples without any previous treatment as well as for samples where the cycles with constant ratio of rates or the cycles with constant heating rate were performed formerly. These measurements were again reproduced for all three forms of studied samples.

3. Results and discussion

Structural relaxation can be effectively studied using calorimetric techniques, one of the most common of these techniques being differential scanning calorimetry (DSC). Quite a number of works dealing with enthalpy relaxation of chalcogenide glasses can be found in the literature – e.g. [5–7]. Nowadays, it is often the TNM model which is applied in order to describe the kinetics of structural relaxation. The cyclic relaxation experiments provide an easy and relatively fast way of direct evaluation of the TNM parameter Δh^*. The value of this parameter is often correlated with the value of activation energy of viscous flow E_η [4,5,7]. In the literature both cases can be found, Δh^* values evaluated from cyclic experiments that correlate well with "expected" values (values close to the value of E_η and simultaneously comparable to values obtained from pure curve-fitting) but also very high values of Δh^* compared to E_η or the curve-fitting results [6,8–11]. This work is focused on the enthalpy relaxation cyclic experiments and on the possible influences of various experimental conditions on the Δh^* evaluation procedure. One of the conditions assumed to be influencing evaluation of Δh^* is the form of the measured sample. Three forms of samples (bulk and two powders) were measured for both types of cyclic experiments in order to study this influence. Furthermore, an influence of DSC baseline stability and a possibility of the proceeding crystallization process also have to be considered. The published TNM parameters for As_2Se_3 glass are as follows [4]: parameter of non-linearity $x = 0.57$, parameter of non-exponentiality $\beta = 0.71$, pre-exponential factor $\ln(A/s) = -79.21$ and effective activation energy $\Delta h^* = 316$ kJ mol^{-1}.

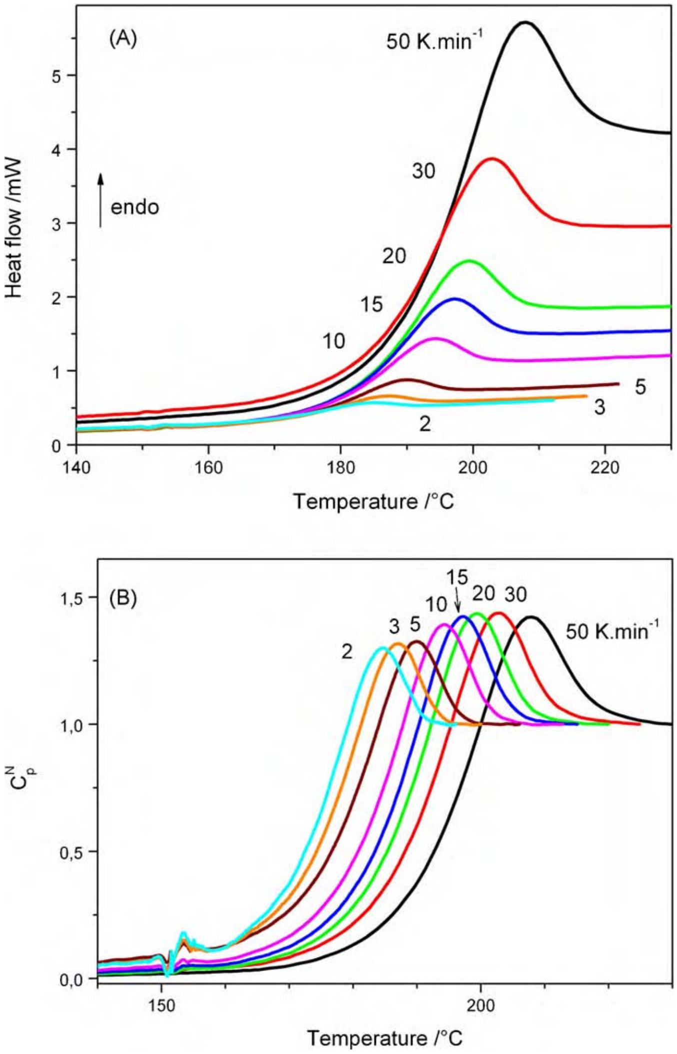

Fig. 3. DSC heating scans for a set of cycles with constant ratio of rates performed at given cooling/heating rates (numbers given in figure) for bulk sample: (A) heat flow dependence on temperature and (B) data recalculated to heat capacity dependence on temperature.

The activation energy of viscous flow in the glass transition region is for the As_2Se_3 material equal to $E_\eta = 316 \pm 8\,kJ\,mol^{-1}$ [4].

Cycles with constant ratio of rates consist of alternating cooling and heating steps performed at different rates where the ratio between the two rates remains constant (in our case equal to unity, see Fig. 1(B)). An example of obtained relaxation curves for these cycles is shown in Fig. 3(A). As can be seen from the figure, the position of the temperature maximum of the relaxation peak changes as the consequence of different cooling and heating rates (i.e. of the whole respective applied thermal histories) the particular heating scans were performed for. Based on this fact, the following evaluation of parameter Δh^* from cycles with constant ratio of rates can be made [12,13]:

$$-\frac{\Delta h^*}{R} = \left[\frac{d\ln|q_+|}{d(1/T_p)}\right]_{q_-/q_+=const} \qquad (1)$$

where T_p is the temperature of the maximum of endothermic relaxation peak, q_+ is the heating rate and R is the universal gas constant.

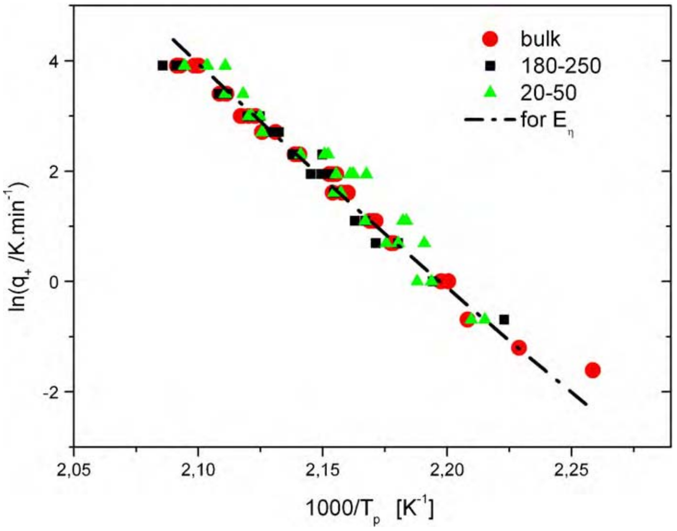

Fig. 4. Dependence of the temperature of the relaxation peak maximum T_p on the heating rate for samples in the form of bulk and for two powders with particle sizes 180–250 and 20–50 μm, respectively. Activation energy of viscous flow $E_\eta = 316\,kJ\,mol^{-1}$ was used to calculate the line.

Fig. 3(A) also shows that in the case of these cycles the particular relaxation peaks differ in shape and height when the raw temperature dependence of heat flow is plotted. Although the data for relaxation peaks were after recalculating to the heat capacity (Fig. 3(B)) of practically the same height (in compliance with what theory postulates), the agreement was not perfect due to the peaks slightly broadening for higher heating rates. The relaxation peaks broaden with increasing heating rates as a result of thermal gradients in the sample [14]. Hutchinson et al. in their paper [14] described a procedure for the correction of DSC scans for thermal lag (it is in fact a correction of T_p values based on the theoretical invariance of the peak width for the cycles with constant ratio of rates). Our data for cyclic experiments with constant ratio of rates were analysed and corrected according to this procedure (the corrections were based on the reference width of the peak measured at $10\,K\,min^{-1}$). The dependence of reciprocal temperature of the peak maximum T_p on the heating rate is shown in Fig. 4 for all three forms of the sample. As can be seen, these dependencies can be fit linearly, so that the slope of the fit and its error is used to calculate parameter Δh^* and its error limits. The cycles with constant ratio of rates provide values of parameter Δh^* which correlate very well with activation energy of viscous flow E_η (see Table 1). Slightly higher value of Δh^* was obtained for powder sample with particle size 20–50 μm for which the data exhibit higher dispersion. This also correlates with the need for thermal lag corrections – the bulk sample has a good heat transfer during the DSC experiment and the data exhibit only a small scatter of T_p values whereas the powder sample has worse thermal contact during the measurements and the changes of T_p values were even after the correction higher, especially for the powder sample with particle size 20–50 μm. The influence of sample form (i.e. the heat transfer influence) on relaxation experiment can be directly seen in the case of the DSC data measured at very slow rates – the noise in the data is higher for the powder samples, especially for the one with particle size 20–50 μm. Therefore, the T_p values were not evaluated for the powder samples measured at rates lower than $0.5\,K\,min^{-1}$. On the other hand, for the bulk sample the evaluation was possible to perform even for these low rates (although the error of T_p value determination for rates as low as 0.3 and $0.2\,K\,min^{-1}$ was high).

Cycles for constant heating rate q_+ (measurement sets performed for heating rates 50, 20 and $10\,K\,min^{-1}$) and cooling rates q_- varying from 0.5 to $100\,K\,min^{-1}$ were performed for all three sample forms. Generally, the advantage of this type of cyclic experiments is a broad range of cooling rates which can be used. The

Table 1
The values of effective activation energy Δh^* (in kJ mol^{-1}) evaluated from cycles with constant ratio of rates and from cycles with constant heating rate (10, 20 or 50 K min^{-1}).

Sample form	Cycles with constant ratio of rates	Cycles with constant heating rate		
		10 K min^{-1}	20 K min^{-1}	50 K min^{-1}
Bulk	307 ± 6	365 ± 6	337 ± 4	310 ± 5
180–250 μm	309 ± 8	404 ± 15	359 ± 7	341 ± 5
20–50 μm	326 ± 14	438 ± 17	347 ± 2	349 ± 3

wide range of rates then implies a more accurate determination of the Δh^* parameter. During the cyclic experiments with constant heating rate the shape and height of particular peaks vary (due to the different applied thermal histories – different cooling rates); however, the temperature of the maximum of the relaxation peaks remains during these experiments almost the same, which is the consequence of applying always the same heating rate (rigorously said, the value of T_p slightly changes in a known and specific way even during the cycles with constant heating rate – see Fig. 2). Constant heating rate also minimizes the influence of thermal gradients in measured sample. The illustration of experimental results for different heating rates and sample in the form of powder with particle size 20–50 μm is given in Fig. 5. As can be seen, the advantage of higher heating rate consists in larger change of heat flow in the glass transition area. If the DSC instrument shows instability of the baselines, then its influence is much more likely to be negligible in the case when the higher heating rate is used. So, from this point of view the heating rate 50 K min^{-1} seems to be optimal. However, the high heating rate has also a consequence of the shift of the glass transition towards higher temperatures. Thus the sample has to be heated to higher temperature to obtain a complete relaxation response (whole peak). This heating to higher temperatures can accelerate the nucleation or crystal growth processes in the sample. The tendency for the crystal phase formation depends of course mainly on the particular composition of studied glasses. When the glass transition temperature is very closely followed by the crystallization, then the enthalpy relaxation is quite difficult to measure on its own and it becomes even more difficult if high heating rates would be applied. In the case of As_2Se_3 glass the crystallization is relatively slow and the non-isothermal crystallization DSC peak can be observed only for low heating rates (2 K min^{-1} and lower) [15]. That was also one of the reasons why this particular composition was chosen for this study. Nevertheless, the influence of crystal phase growth had to be considered also for this composition (more will be discussed in the part describing the crystallization behaviour).

From the cycles with constant heating rate the parameter Δh^* can be evaluated according to the following equation [1]:

$$-\frac{\Delta h^*}{R} = \frac{d\ln|q_-|}{d(1/T_f)} \tag{2}$$

where T_f is fictive temperature. Fictive temperature represents the structure of the glass during the cooling step. T_f can be evaluated using the “equal area method” [1]. This method is based on the following equation:

$$\int_{T^*}^{T_f} (C_{pl} - C_{pg}) dT_f = \int_{T^*}^{T'} (C_p - C_{pg}) dT \tag{3}$$

where T^* is any temperature above the glass transition temperature T_g at which the heat capacity is equal to the equilibrium undercooled liquid value C_{pl} and T' is a temperature well below T_g where a constant glassy value of C_{pg} was achieved. In other words, the integral area under the measured curve needs to be calculated in order to determine T_f. How the T_f value can be affected by sample form or selected heating rate is discussed in the following text.

When comparing relaxation peaks for different forms of the sample measured under the same temperature program, not a big difference can be observed. However, when the fictive temperature is calculated for each, its values are slightly different as can be seen in Fig. 6. The obtained values of parameter Δh^* (and its error limits determined from the linear regression of the data) for all sample forms and all tested heating rates are summarized in Table 1. Regarding the sample form it can be said that with the decreasing particle size the value of parameter Δh^* increases. The difference in the DSC signal for various sample forms can be explained in terms of a varying contacts and resulting thermal gradients within the sample itself and between the sample and the DSC pan. In other words, the best heat transfer has the bulk sample, whereas smaller

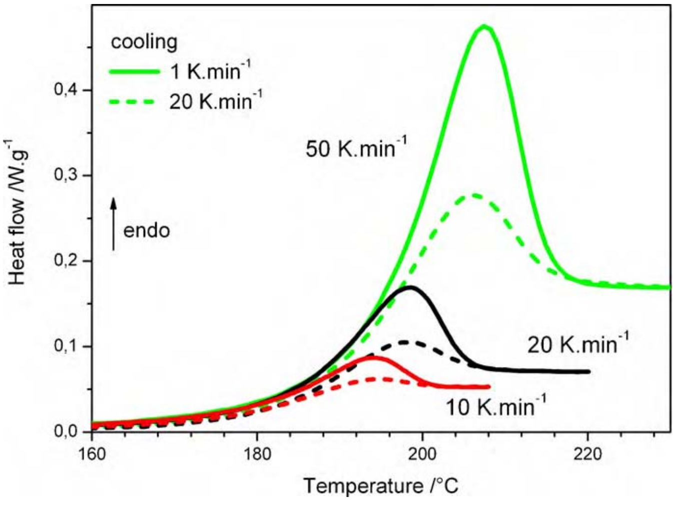

Fig. 5. Heating scans performed at rates 50, 20 and 10 K min^{-1} after the previous cooling steps performed at rates 1 and 20 K min^{-1} for sample in the form of powder with particle size 20–50 μm.

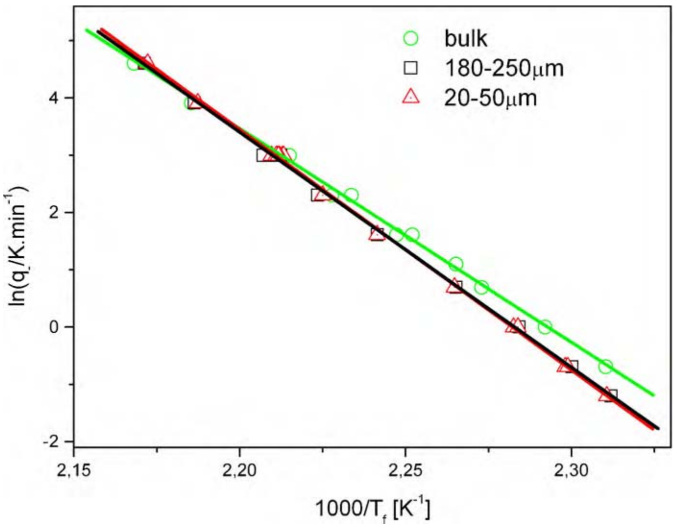

Fig. 6. The dependence of fictive temperature on cooling rate for different forms of the sample. Heating scans measured at rate 50 K min^{-1}.

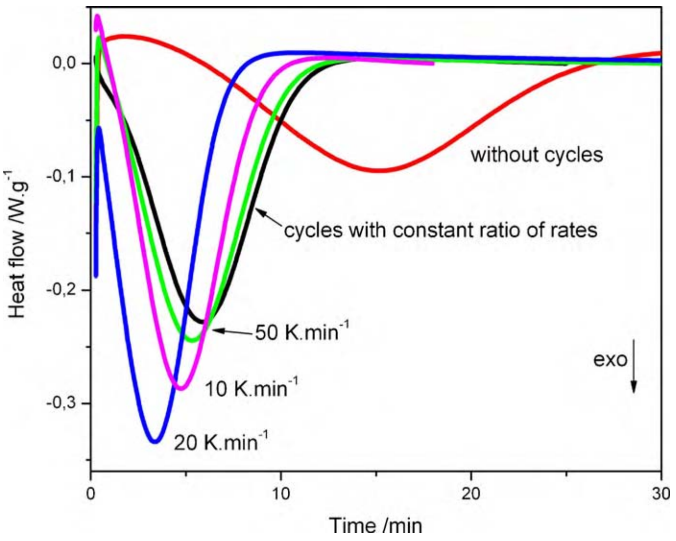

Fig. 7. The isothermal crystallization response at 330 °C for powder sample with particle size 20–50 μm measured after cycles with constant ratio of rates, after cycles with constant heating rate and for sample without any treatment.

particle sizes result in worse heat transfer. As a result the bulk sample has lower values of T_f than the powder samples for the same experimental conditions.

Assuming that the true Δh^* value should be close to E_η, then the best results were obtained for the combination of the bulk sample and cycles with constant heating rate 50 K min^{-1}. However, not a big difference from the E_η value was also obtained for the bulk sample and constant heating rate 20 K min^{-1}. Exceedingly high values of Δh^* were obtained for the heating rate 10 K min^{-1}. This could be mainly a consequence of the DSC baseline instability which influenced the calculated area below the curve during the T_f determination. Nevertheless, the influence of thermal lag on calculated Δh^* T_f values should be kept in mind. As is clearly seen in Fig. 5 the relaxation peak broadens with higher heating rate so that the area below the relaxation peak (necessary to calculate T_f) is larger – compared to the rate 10 K min^{-1} the area is about 38% larger for rate 20 K min^{-1} and about 55% larger for rate 50 K min^{-1}. When the theoretical data of cycles with constant heating rate (the cycles similar to experimental conditions and data calculated for parameters published in [4]) were tested the calculated value of parameter Δh^* was the same for all heating rates. But considering the thermal lag (the area below the curves was modified similarly to results from Fig. 5) the calculated value of parameter Δh^* decreases with increasing heating rate. The same downward trend with increasing heating rate has parameter Δh^* summarized in Table 1 so that the influence of thermal lag is also significant in the case of cycles with constant heating rate.

4. Crystallization following relaxation cycles

One of the expected influences on enthalpy relaxation results is the nucleation or crystallization proceeding during relaxation measurements. In the case of a fully crystallized sample no glass transition can be observed; however, in the case of a partially crystallized or nucleated sample the remaining amorphous fraction still exhibits T_g. When the devitrificated fraction is small then the relaxation curve might seem not to be affected at first sight; however, the area under the curve can slightly change. In case of all sets of relaxation cycles a specific cooling/heating cycle was several times inserted in-between regular cycles in order to check for possible changes of the baseline course, ΔC_p or the shape of the relaxation peak. In this way the larger degradation influences can be detected/eliminated. Smaller changes in the amorphous nature of the samples can then be reflected by performing a crystallization measurement after the relaxation cycle experiments. The crystallization behaviour was measured under isothermal conditions at 330 °C for each performed set of cyclic experiments. The nucleation or crystallization during relaxation measurements accelerates the consequent crystallization, when compared to the sample without any treatment (with no previous relaxation measurements performed).

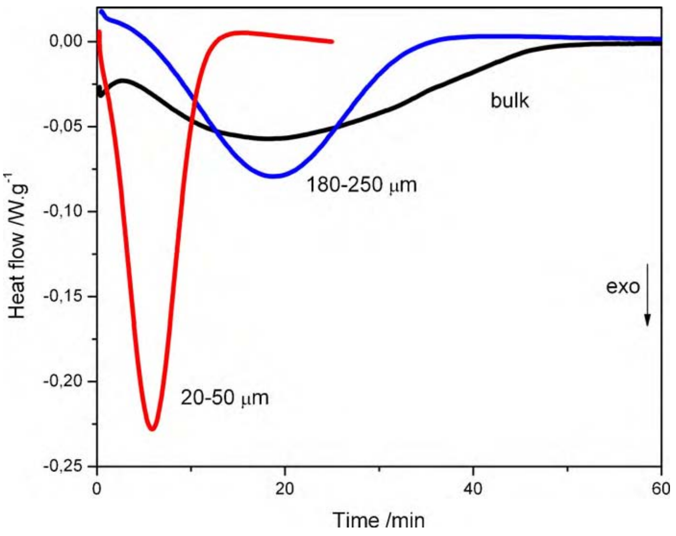

Fig. 8. Isothermal crystallization peaks measured after relaxation cycles with constant ratio of rates for different forms of samples.

The results in Fig. 7 support the assumption that during the measurements of relaxation cycles (where repeated heavy thermal stresses are applied to the studied material) starting nucleation or crystallization processes can occur despite of the fact that the respective controlling scans indicated no significant difference in the relaxation curves. The crystallization is faster for samples with previously performed relaxation measurements in comparison to the sample without any treatment. Almost no difference was obtained for the enthalpy change of crystallization ΔH (ΔH changed for less than 10% independently on the type of relaxation measurement). For all sample forms it was observed that crystallization after cycles with constant ratio of rates is slower than that after cycles with constant heating rate. No dependence of the crystallization rate was observed for varying constant heating rates (10, 20 and 50 K min^{-1}).

Generally, the form of the glassy sample influences the rate of crystallization. When the crystallization process is surface activated then the increasing sample surface increases the rate of crystallization. The curves in Fig. 8 illustrate that the crystallization of bulk sample takes more time than that for the powder samples with particle sizes 180–250 and 20–50 μm. From the comparison of all measured isothermal crystallization curves it is apparent that the general rules for the dependence of crystallization rate on the sample form hold for all measurements performed after the same respective type of relaxation cycles.

5. Conclusion

This work is focused on the enthalpy relaxation cyclic experiments and on the possible influences of various experimental conditions on the Δh^* evaluation procedure. The As_2Se_3 glass was chosen as a model system and the assumptions of the DSC baseline instability as well as that of the nucleation and crystallization proceeding in the amorphous sample during the relaxation measurements were examined. The evaluated values of parameter Δh^* indicate that both the sample form and the exact type of the cyclic experiments influence the relaxation measurements. The cycles with constant ratio of rates provide values of parameter Δh^* which for all studied forms of the sample correlate very well with activation energy of viscous flow E_η. In the case of cycles with constant heating rate and assuming that the true Δh^* value should be close to E_η, the best results were obtained for the combination of the bulk sample and heating rate $50\,\mathrm{K\,min^{-1}}$. Regarding the sample form it can be said that with the decreasing particle size the value of parameter Δh^* increases. The enthalpy relaxation response can also be negatively influenced by the DSC baseline instability or by the proceeding crystallization process. However, due to these two effects being not easily separable it was not possible to determine the degrees of their respective influences.

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