



## A novel method to study crystallization of glasses

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### ABSTRACT

A novel method to study crystallization behavior in non-crystalline materials has been developed. The method is based on slowing down of sample deformation by viscous flow above the glass transition due to macroscopic crystal growth. This process might be detected by thermomechanical analysis (TMA). The influences of sample length, applied force and heating rate have been examined. Newly developed method has been used to study crystallization in  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass. It was found that a typical TMA measurement reasonably well corresponds to previously reported crystal growth kinetics by means of optical microscopy. The activation energy obtained from the shift of extrapolated TMA onset temperature with heating rate ( $E = 286 \pm 8 \text{ kJ mol}^{-1}$ ) is very similar to the activation energy of  $\text{Sb}_2\text{S}_3$  crystal growth in  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass ( $E_G = 288 \pm 7 \text{ kJ mol}^{-1}$ ) from optical microscopy measurements. The TMA curve does not match with non-isothermal DSC curve taken at comparable experimental conditions. It seems that TMA measurement reflects early stages of crystal growth that are not associated with thermal effects measured by DSC.

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### 1. Introduction

Crystallization of glasses has become a very popular topic. More than 1000 papers that are somehow related to this topic are published every year in scientific journals. In fact, the crystallization usually takes place in supercooled glass-forming liquid rather than in glassy state but this conceptual imprecision is frequently neglected and the term crystallization of glasses is being used instead. Most of those papers are related to the application of classical thermal analysis methods such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) [1–5]. These methods are powerful and certainly provide valuable kinetic results in case that the heat evolution associated with crystallization can be measured reliably. In some cases the evolution of crystallization heat is too fast, causing that important part of kinetic information might be lost in deformed leading edge of DTA or DSC crystallization peak. On the other hand, for diluted systems or for less thermally conductive materials the evolution of crystallization heat might be below the detection limit of DTA or DSC instrument and the crystallization kinetics cannot be observed by these conventional methods.

Another experimental approach to glass crystallization is based on detailed study of crystal growth morphology and crystalliza-

tion kinetics by electron or optical microscopy. Crystal growth data are then usually combined with viscosity data. In this way the applicability of standard model of crystal growth can be assessed [6–11]. These laborious methods, however, are limited to transparent materials or materials with sizable changes in reflectivity between glassy matrix and growing crystalline phase (optical microscopy) or close-to-surface crystallization (electron microscopy).

Some of described experimental limits may cause that many glass-forming materials seem to be excluded from crystallization kinetic studies by DTA and DSC methods or direct microscopic crystal growth study. From this point of view, the development of alternative methods for crystallization of glasses is interesting as it can broaden spectrum of practical possibilities to study behavior of nucleation-growth processes in supercooled glass-forming liquids. As the crystal growth takes place in highly viscous glass-forming liquid above the glass transition it can be expected that continuously growing crystals gradually slow down and finally stop the sample deformation caused by viscous flow. Such macroscopic effects can be detected by monitoring the sample dimension by means of thermomechanical analysis (TMA). This behavior has been tested on several glass-forming systems in our laboratory and based on these experimental results a novel method to study crystallization has been developed. The aim of this paper is to describe such a method of measurement and to apply it in the study of crystallization of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass, that has been previously studied mainly by DSC as described in several papers [4,11–15].

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## 2. Experimental

The  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass was prepared by synthesis from pure Ge, Sb elements (5N purity) and sulphur (purified by Wartenberg method, as described in Ref. [16]). An appropriate mixture of these elements (10 g total weight) was placed in a clean quartz ampoule (inner diameter 13 mm, length 80 mm). The ampoule was then evacuated to a pressure of  $10^{-3}$  Pa for 30 min, sealed and then placed in a rotary furnace. After heat treatment and homogenization at 1223 K for 20 h, the ampoule was rapidly cooled in ice water. The amorphous nature of quenched glass was examined by X-ray diffraction analysis (XRD), optical and scanning electron microscopy (SEM). The glass transition temperature,  $T_g$ , was determined by DSC to be about 522 K at heating rate  $10 \text{ K min}^{-1}$ . Similar value has been previously reported by Tichá et al. (525 K) [17] and Asami et al. (525 K) [18] using the same method. The temperature corresponding to viscosity of  $\eta = 10^{12}$  Pa s is being somewhat lower, i.e. about 498 K [19].

The calorimetric experiments were performed by using a Pyris 1 differential scanning calorimeter (PerkinElmer) coupled with 2P intracooler and calibrated with Hg, Ga, In, Sn, Pb and Zn standards. The bulk samples of studied glass were prepared in the form of thin plates (about 0.8 mm high,  $m \cong 25 \text{ mg}$ ) with both sides polished to optical quality. They were measured in standard aluminum sample pans under atmosphere of dry nitrogen (flow rate about  $20 \text{ mL min}^{-1}$ ). The crystallization behavior was studied under non-isothermal conditions.

TMA measurements were performed by using Thermomechanical analyzer CX03RA-T (R.M.I. Company). This instrument is based on the principle of the measurement of sample length changes relative to a quartz sample holder with the differential capacitance displacement detector. The detector is controlled through an electronic system which ensures linearity with deviation better than 0.1% (over a full scale) and  $0.01 \mu\text{m}$  resolution. Long-term stability and reproducibility of the temperature measurement in the isothermal regime is  $\pm 0.2 \text{ K}$  and the variation of heating rate does not exceed 1%. More detailed specification of this instrument is described elsewhere [20]. The following procedure was used for all measurements described in this paper. Flat rectangular specimen of a freshly prepared glass about  $2.7 \text{ mm} \times 2.7 \text{ mm}$ , sample height  $h_0 = 1 \text{ mm}$  ( $28 \pm 1 \text{ mg}$ ) or  $h_0 = 2 \text{ mm}$  ( $54 \pm 4 \text{ mg}$ ), polished to optical quality, was placed in the TMA cell, on top of a quartz plate (Fig. 1). The TMA cell was then heated at selected heating rate ( $\beta = 1, 2, 3, 4$  or  $5 \text{ K min}^{-1}$ ) using a loading force  $F = 10 \text{ mN}$  and the sample height was accurately recorded as a function of temperature. Typical TMA measurement for the  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass is shown for a 1 mm high specimen in Fig. 2, where it is compared with DSC measurement at the same heating rate of  $5 \text{ K min}^{-1}$ . The initial sample height, i.e.  $h_0 \cong 1 \text{ mm}$  is maintained up to the temperature slightly above calorimetric  $T_g$ . Then the sample height starts to decrease as the viscous flow takes place. The crystalline phase is gradually formed at these temperatures and as it grows the sample deformation caused by viscous flow slows down and finally is ceased. This process occurs at lower temperatures before the maximum of DSC crystallization peak is reached.

XRD analysis of amorphous and crystallized sample was performed using an AXS diffractometer D8 Advance (Bruker) equipped with horizontal goniometer and scintillation counter, utilizing  $\text{Cu K}\alpha$  radiation (40 kV, 30 mA). The scans were taken over scattering angles  $2\theta$  from  $5^\circ$  to  $65^\circ$  at the low scanning speed of  $0.24^\circ \text{ min}^{-1}$ . As-prepared glass exhibits a broad halo characteristic of an amorphous specimen. All the diffraction lines of fully crystallized sample after TMA measurement can be indexed for crystalline  $\text{Sb}_2\text{S}_3$  (stibnite, JCPDS Card. No. 42-1393) as shown in Fig. 3. No characteristic peaks of crystalline impurities, such as  $\text{Sb}_2\text{O}_3$ ,  $\text{GeS}_2$  or  $\text{GeS}$  have been found in the diffraction pattern.

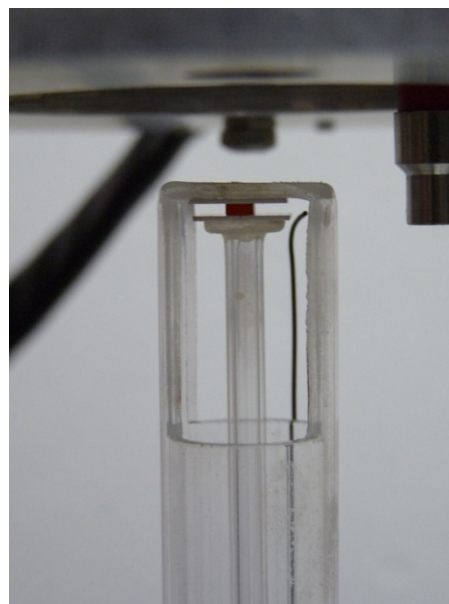


Fig. 1. Sample placement in the TMA instrument.

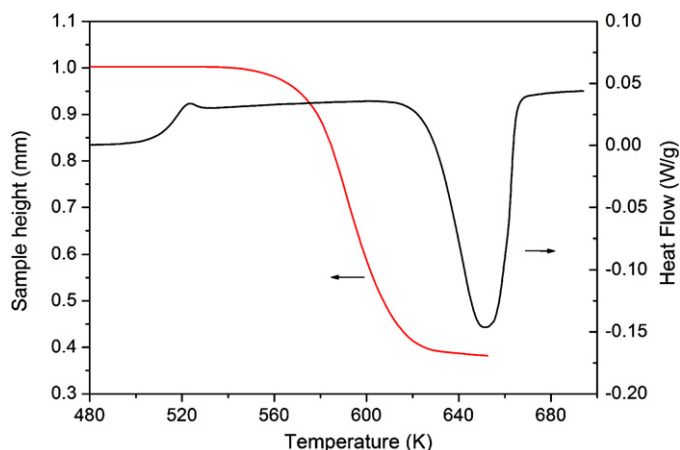


Fig. 2. Typical TMA curve corresponding to crystallization of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass ( $m = 28 \text{ mg}$ ) compared with DSC measurement ( $m = 25 \text{ mg}$ ) at the same heating rate  $\beta = 5 \text{ K min}^{-1}$ .

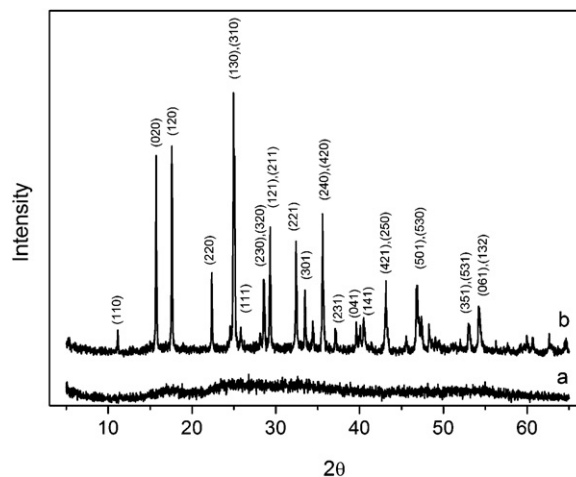


Fig. 3. XRD diffractogram of (a) freshly prepared and (b) crystallized  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample.

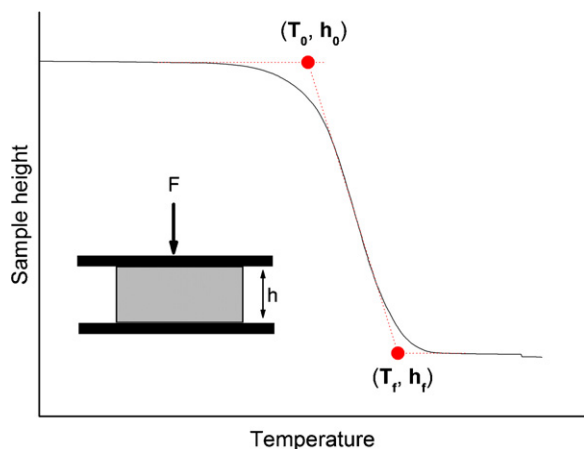


Fig. 4. A schematic experimental setup and typical TMA curve with extrapolated characteristic points.

The samples were analyzed by an electron scanning microscope JSM-5500LV (JEOL) coupled with X-ray analyzer IXRF Systems (detector GRESHAM Sirius 10). The accelerating voltage of primary electron beam was 20 kV. The quantitative analysis was performed by using standards purchased from C.M. Taylor Corp., USA.

### 3. Results

Typical TMA measurement of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass above  $T_g$  is shown in Fig. 4. The rectangular shape of the sample is maintained up to the temperature when the viscosity reaches the value of about  $10^6$  Pa s (i.e.  $h \approx h_0$ ). However, at higher temperatures the sample height starts to decrease due to deformation caused by viscous flow. Under these conditions the crystallization may take place in the highly supercooled liquid. The crystalline phase stiffens the sample and impedes its further deformation by the viscous flow. As a consequence, the sample height decreases gradually and finally reaches nearly constant value  $h_f$ . The TMA curve exhibits a typical sigmoidal shape that somewhat resembles inverse dependence of fraction crystallized vs. temperature, well known from DSC studies. Two characteristic extrapolated temperature points  $T_0$  and  $T_f$  can be defined (see Fig. 4). The crystallization of the sample is completed when the final sample height is reached (i.e.  $T > T_f$ ) which corresponds to approximately 60–40% of initial sample height, depending on experimental conditions.

Fig. 5 shows fresh fracture of the sample after such TMA measurement (303–653 K,  $F = 10$  mN,  $\beta = 5$  K min $^{-1}$ ). The surfaces of the sample are still nearly parallel but with markedly curved edges. There is distinctly different outer shell of the sample and inside core. It seems that the  $\text{Sb}_2\text{S}_3$  crystals start to grow predominantly within the outer bulk shell forming a more opened structures consisting of needle-shaped crystals. The inside core probably contains mainly crystalline phase as no residual crystallization effect was detected in subsequent DSC scan of the sample taken immediately after TMA measurement. The bunches of needle-shaped  $\text{Sb}_2\text{S}_3$  crystals somewhat resembling a spherulitic crystal growth habitat is visible near the surface of the same sample etched by KOH solution (0.05 M), as shown in Fig. 6. These observations are in agreement with previous experimental findings [11].

#### 3.1. Influence of applied force

As was expected, the force applied on the sample significantly affects the measurement. Fig. 7 shows the sample height changes as a function of temperature for the forces ranging from 2 mN to 40 mN and heating rate 5 K min $^{-1}$ . All the TMA curves have a similar trend,

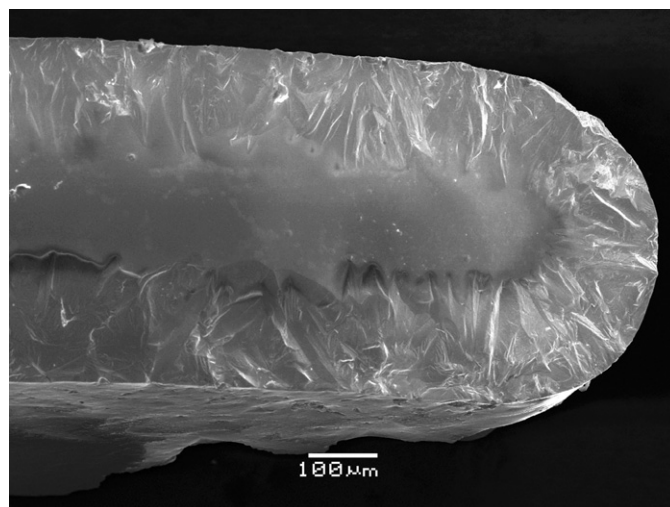


Fig. 5. SEM photograph of fresh fracture of the  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample after TMA measurement ( $T > T_f$ ,  $F = 10$  mN,  $\beta = 5$  K min $^{-1}$ ), BE, 20 kV.

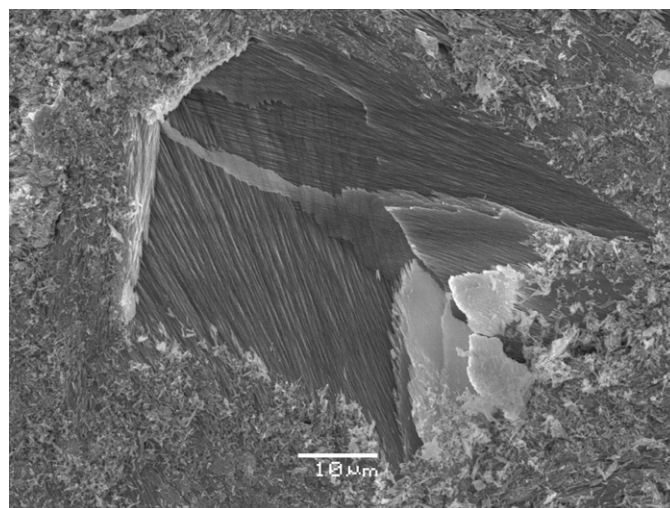


Fig. 6. SEM photograph of etched surface (0.05 M, KOH solution) of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample after TMA measurement ( $T > T_f$ ,  $F = 10$  mN,  $\beta = 5$  K min $^{-1}$ ), BE, 20 kV.

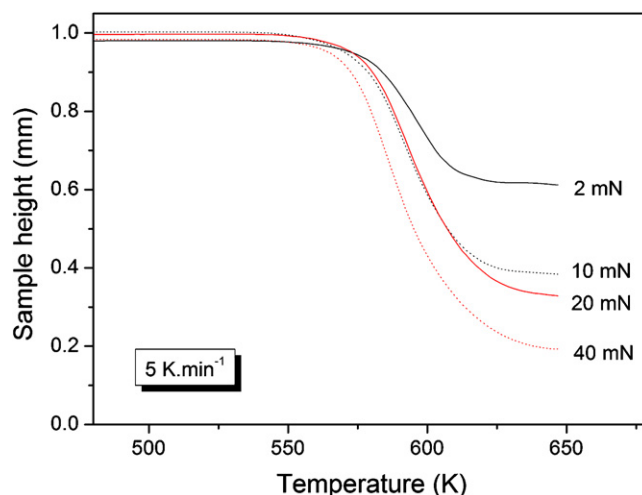


Fig. 7. The effect of applied force on sample height changes of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample measured at 5 K min $^{-1}$ .

**Table 1**  
Characteristic temperatures for the experiments with different applied force.

$F$ (mN)	$T_0$ (K)	$T_f$ (K)
2	578.0	611.7
10	575.1	611.3
20	576.4	615.8
40	571.2	609.3

however, the final value of the sample height after crystallization ( $T > T_f$ ) decreases with increasing applied force. A linear dependence with slope of about  $0.63\%(\text{mN})^{-1}$  is observed for  $F \geq 10$  mN. Both  $T_0$  and  $T_f$  slightly decrease with applied force, as summarized in Table 1. From the comparison of these temperatures it is evident that  $T_0$  is more affected by applied force (about  $0.17$  K/mN). It seems that the force of 10 mN is close to optimum for this type of measurement and it has been used for all experiments described in this paper.

### 3.2. Influence of sample length

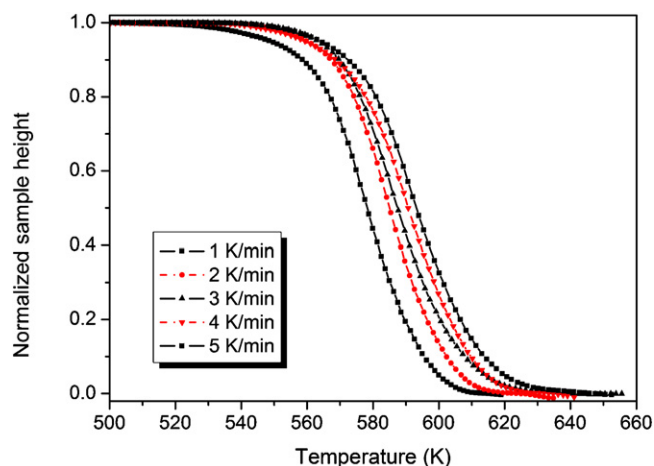
Fig. 8 shows normalized sample height dependence on temperature for two rectangular samples with similar geometry but different initial sample height of  $h_0 = 1$  mm and 2 mm (sample weights 28.2 mg and 54.1 mg, respectively). The normalized sample height  $h_n$  is defined as follows:

$$h_n = \frac{h - h_f}{h_0 - h_f} \quad (1)$$

where  $h$  is actual sample height,  $h_0$  is initial and  $h_f$  is final sample height. Both experiments were performed at identical experimental conditions for  $F = 10$  mN and  $\beta = 5$  K min $^{-1}$ . It can be seen that  $T_0$  for both samples differ by about 5.7 K while difference of  $T_f$  is about two times larger, 12.1 K. This asymmetry becomes even larger for slower heating rates. It seems that lower sample height is more suitable for measurements as the effect of thermal inertia are less important. For this reason we have used 1 mm sample for most experiments described in this paper.

### 3.3. Influence of heating rate

Fig. 9 shows typical TMA measurement of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass for different heating rates. In this particular case the initial sample height was  $h_0 = 1$  mm. However, very similar result can be obtained also for 2 mm high sample. No change of final value of sample height with heating rate was observed. Table 2 summarizes

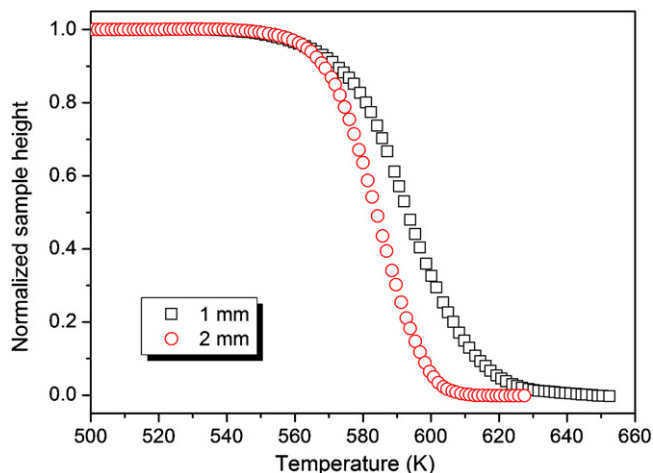


**Fig. 9.** The effect of heating rate on the TMA curve for  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample measured at applied force 10 mN.

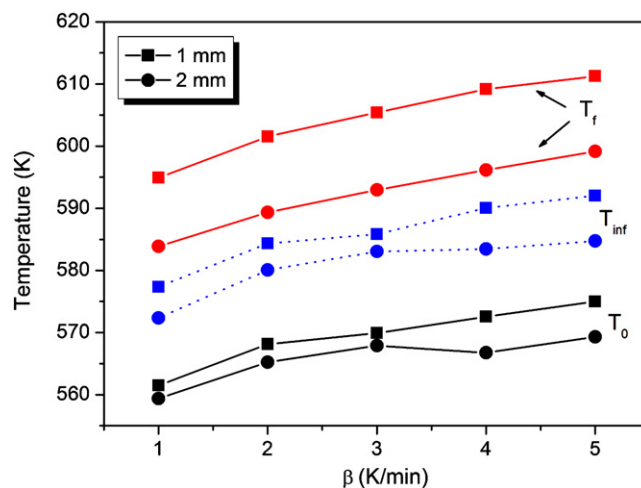
**Table 2**  
Characteristic temperatures for the experiments with different heating rates.

$\beta$ (K min $^{-1}$ )	$h_0 = 1$ mm		$h_0 = 2$ mm	
	$T_0$ (K)	$T_f$ (K)	$T_0$ (K)	$T_f$ (K)
1	561.5	594.9	559.4	583.9
2	568.1	601.6	565.2	589.4
3	569.9	605.4	567.9	593.0
4	572.6	609.2	566.8	596.2
5	575.0	611.3	569.3	599.2

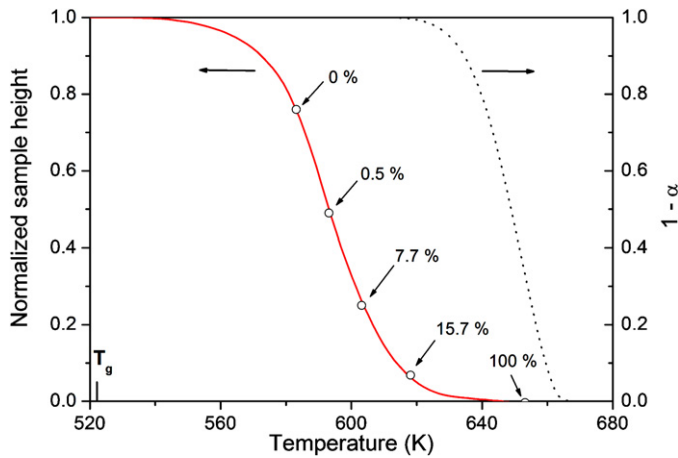
$T_0$  and  $T_f$  characteristic temperatures. It is evident that both these temperatures shift with heating rates in a similar way as the DTA or DSC crystallization peaks. However, the temperature  $T_0$  is much less sensitive to the initial sample height than  $T_f$ . Sensitivity of the temperature corresponding to the inflexion point of TMA curve  $T_{inf}$  to the initial sample height is in between these limits (see Fig. 10). It might be expected that the temperature shift of  $T_f$  with heating rate is somehow related to crystallization kinetics. The possibility to evaluate kinetic information from the TMA measurements taken at different heating rates is discussed in the next section.



**Fig. 8.** The effect of sample length on the TMA curve for  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample measured at  $5$  K min $^{-1}$  and applied force 10 mN.



**Fig. 10.** The characteristic temperatures of TMA curves for  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample measured at different heating rates and applied force 10 mN.



**Fig. 11.** The comparison of TMA curve of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass measured at  $5 \text{ K min}^{-1}$  (full line) and the  $1 - \alpha$  dependence calculated by Eq. (3) from DSC curve measured at the same heating rate (broken line). Points correspond to the samples partially crystallized at selected temperatures during TMA measurement.

#### 4. Discussion

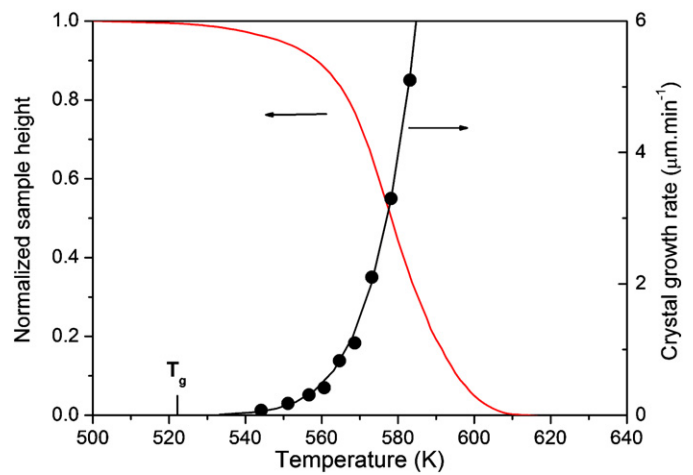
It has been mentioned already that TMA measurement reflects the crystallization starting at lower temperatures than corresponds to the DSC crystallization peak. The kinetic interpretation of DSC data is based on the assumption that measured heat flow  $\phi$  is proportional to overall crystallization rate [1,21]:

$$\phi = \Delta H_c \left( \frac{d\alpha}{dt} \right) \quad (2)$$

This assumption is acceptable for small samples and for moderate heating rates provided that temperature and calorimetric calibration have been made properly. The proportionality constant  $\Delta H_c$  equals to the enthalpy change of the overall crystallization and  $\alpha$  is the fraction transformed at temperature  $T$ . The crystallization enthalpy corresponding to the area under DSC exothermic peak was found to be  $\Delta H_c = -56.3 \text{ J g}^{-1}$  for the bulk sample of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass. Within the error limits it agrees with previously published value ( $\Delta H_c = -56 \pm 1 \text{ J g}^{-1}$ ) [11]. As the crystallization enthalpy change is constant, the fraction transformed  $\alpha_i$  can be obtained by partial integration of  $\phi(T)$  curve:

$$\alpha_i = \frac{1}{\Delta H_c} \int_0^{t_i} \phi \cdot dt \quad (3)$$

Fig. 11 shows experimental TMA curve ( $h_0 = 1 \text{ mm}$ ,  $m = 24 \text{ mg}$ ,  $\beta = 5 \text{ K min}^{-1}$ ) for the  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass sample and  $1 - \alpha$  dependence calculated by Eq. (3) from DSC peak taken at comparable experimental conditions (see Fig. 2). Both TMA and converted DSC curve are shifted by about 60 K, clearly indicating that they represent different features of crystallization in this glassy material. To examine these differences in more detail, it is interesting to inspect the fraction transformed during the TMA experiment by method of residual crystallization heat using DSC. For this purpose, several samples ( $h_0 = 1 \text{ mm}$ ) were prepared and heated in TMA instrument at heating rate of  $5 \text{ K min}^{-1}$  to 583, 593, 603, 618 and 653 K. Then the DSC curves of these partially crystallized samples were measured ( $\beta = 5 \text{ K min}^{-1}$ ) and a residual crystallization heat was determined. The fraction transformed after this treatment can be estimated from crystallization enthalpy difference of heat treated sample ( $\Delta H$ ) and the sample without any previous thermal treatment ( $\Delta H_c$ ), i.e.  $\alpha = (\Delta H_c - \Delta H) / \Delta H_c$ . These data are plotted as open circles in Fig. 11. The fraction transformed at all examined points of TMA curve is again considerably different than  $1 - \alpha$



**Fig. 12.** Comparison of TMA curve measured at  $1 \text{ K min}^{-1}$  and crystal growth rate of  $\text{Sb}_2\text{S}_3$  in  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass (points) and prediction for interface controlled 2D nucleated growth (solid line), calculated by Eq. (4).

dependence obtained from DSC crystallization peak, particularly at lower temperature range. Before the onset of DSC curve the method of residual crystallization heat indicates 15.7% crystallinity of the sample used for TMA measurement at  $T = 618 \text{ K}$ . However, the crystallization of the TMA sample appears to be completed at  $T = 653 \text{ K}$  which corresponds to about 67% conversion according to DSC integral curve (see Fig. 11). It seems, therefore, that TMA measurement reflects early stages of crystallization preceding the thermal effects measured by DSC under comparable experimental conditions.

It is interesting to compare TMA measurement with direct measurement of crystal growth obtained by optical microscopy. It was found [11] that the morphology of  $\text{Sb}_2\text{S}_3$  crystals growing in  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass is both, temperature and time independent. At lower temperatures ( $T < 560 \text{ K}$ ) the crystals develop predominantly needle-shaped twins with slightly curved side. Some of these crystals exhibit star-like branching and in some cases develop into opened structures composed with an asymmetric radiating array of crystalline fibers as shown in Fig. 6. The length of these crystallites increases linearly with time in the temperature range  $544 \leq T \leq 583 \text{ K}$ . This type of behavior is typical for crystal growth controlled by crystal–liquid interface kinetics. For molecularly complex liquids it can be assumed that the reorientation of the molecule or breaking bonds between atoms at the crystal–liquid interface must precede the incorporation of the molecule into crystal. This reorientation and bond breaking in fact controls the crystal growth rate  $u$ . Therefore, it should involve similar molecular motions and rearrangements to those involved in transport processes taking place in viscous liquid. Málek et al. [11] reported that the crystal growth of  $\text{Sb}_2\text{S}_3$  in  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass probably corresponds to interface controlled 2D nucleated growth. In this case, the crystal growth rate can be expressed as [6]

$$u = \frac{C}{\eta} \exp \left( -\frac{B}{T \Delta T} \right) \quad (4)$$

where  $\Delta T$  is supercooling with respect to melting point of  $\text{Sb}_2\text{S}_3$  crystal and the two constants were found to be  $B = (5.0 \pm 0.2) \times 10^6 \text{ K}^2$  and  $\ln(C/N \text{ m}^{-1}) = 30 \pm 2$ .

Fig. 12 combines experimental growth rate data [11], the crystal growth rate curve calculated by Eq. (4) using viscosity data taken from Ref. [19] and TMA curve measured at low heating rate ( $1 \text{ K min}^{-1}$ ). The initial sample height is maintained up to the temperature slightly above calorimetric  $T_g$ . Then the sample height starts to decrease due to sample deformation by the viscous flow. The crystalline phase is formed in this temperature range and as

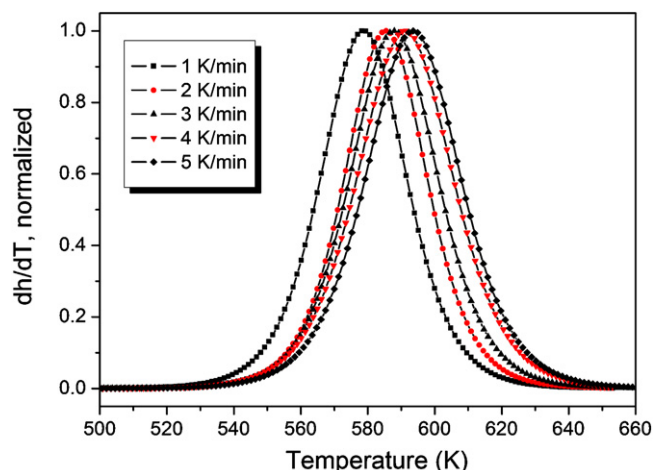


Fig. 13. The derivative of TMA curves for  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  sample measured at different heating rates and applied force of 10 mN.

it grows the sample deformation by viscous flow slows down and finally is ceased. As a consequence of competition between sample deformation and crystal growth the resulting TMA curve exhibits sigmoidal shape. The lowest crystal growth rate observable by optical microscopy is very close to temperature  $T_0$  and the maximum growth rate (predicted around 628 K [11], not shown in Fig. 12) is higher but not so far from  $T_f$ .

The derivative of sigmoidal TMA curve is peak-shaped with a maximum that shifts with increasing heating rates as shown in Fig. 13. Such behavior has not been observed when the sample deformation by viscous flow is not affected by crystallization. It seems probable, that the temperature shift with heating rate is principally controlled by crystallization kinetics. The derivatives of TMA curve shown in Fig. 13 resemble typical non-isothermal DSC crystallization curve, which suggests the possibility to evaluate activation energy of crystallization from the peak shift with heating rate  $\beta$ . The Kissinger's method [22] is based on the condition for the maximum of DSC peak

$$\ln \frac{\beta}{T_p^2} = K - \frac{E}{RT_p} \quad (5)$$

where  $T_p$  is the temperature corresponding to the peak maximum. The activation energy  $E$  is then calculated from the slope of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  plot. In fact, the first term on the right-hand side of Eq. (5) is constant only for first order process. Nevertheless, it was shown [23] that for more complex kinetic models the errors in the activation energy determined by this method do not exceed 5%. Therefore, a simple Kissinger's method can be used to estimate the value of activation energy with acceptable reliability even for more complex processes. Fig. 14 shows the Kissinger's plot for peak-shaped TMA crystallization curves obtained for 1 mm high sample. The activation energy obtained from the slope of this linear plot was found to be  $E = 292 \pm 16 \text{ kJ mol}^{-1}$ . A similar value of activation energy was found also when applying the same method of analysis to the final temperatures  $T_f$  of TMA curve, i.e.  $E = 286 \pm 8 \text{ kJ mol}^{-1}$ . These values are very close to the activation energy of  $\text{Sb}_2\text{S}_3$  crystal growth ( $E_G = 288 \pm 7 \text{ kJ mol}^{-1}$ ) obtained from direct optical microscopy measurements [11]. Very similar results were found for various compositions of chalcogenide glasses studied in our laboratory [24]. It seems, therefore, that TMA measurements described in this paper can provide a valuable tool how to estimate the value of activation energy of crystal growth from several simple measurements taken at different heating rates.

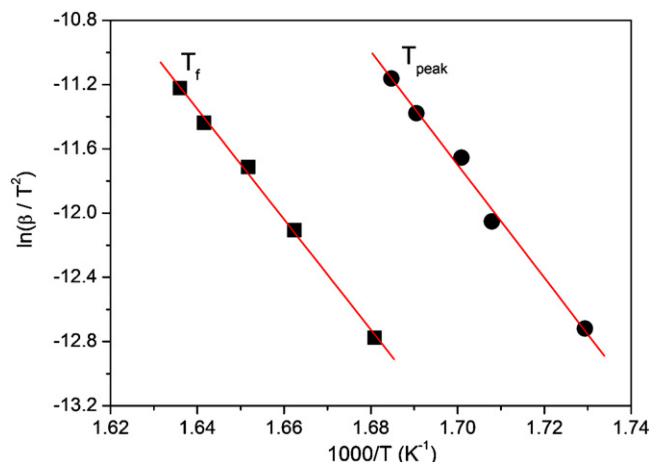


Fig. 14. Estimation of activation energy according to Kissinger's method from TMA curve measured at different heating rates  $\beta$ .

## 5. Conclusions

A novel method to study crystallization behavior of glassy materials has been developed. This method is based on slowing down of sample deformation by viscous flow above the glass transition due to macroscopic crystal growth. Such macroscopic effects can be detected by monitoring the sample dimension by means of thermomechanical analysis. The influences of sample length, applied force and heating rate have been examined. The newly developed method has been used to study crystallization of  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass.

It was found that a typical TMA sigmoidal curve reasonably well corresponds to crystal growth kinetics measured by means of optical microscopy. The activation energy obtained from the shift of extrapolated final temperature of TMA curve with heating rate ( $E = 286 \pm 8 \text{ kJ mol}^{-1}$ ) is very close to the activation energy of  $\text{Sb}_2\text{S}_3$  crystal growth in  $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$  glass ( $E_G = 288 \pm 7 \text{ kJ mol}^{-1}$ ) obtained from direct microscopic measurements. The TMA curve, however, does not match with non-isothermal DSC taken at comparable experimental conditions. It seems probable, that TMA measurement reflects early stages of crystallization that are not associated with thermal effects measured by DSC under comparable experimental conditions.

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