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Crystallization in glasses monitored by thermomechanical analysis

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Abstract Thermomechanical analysis (TMA) can be used as a sensitive tool to follow crystallization behavior in non-crystalline materials. Newly developed method is based on slowing down of sample deformation caused by viscous flow above the glass transition due to macroscopic crystal growth. It is shown that a typical TMA sigmoidal curve reasonably well corresponds to direct measurement of crystal growth kinetics by means of optical microscopy. The method has been used to study crystallization kinetics in $Ge_{38}S_{62}$ glass. The TMA measurement is able to detect earlier stages of crystallization than obtained by differential scanning calorimetry measurement. The activation energy obtained from the shift of extrapolated end of TMA curve with heating rate ($E = 263 \pm 7$ kJ mol^{-1}) is similar to the activation energy of α-GeS_2 crystal growth in $Ge_{38}S_{62}$ glass ($E_G = 247 \pm 23$ kJ mol^{-1}) obtained from direct optical microscopy measurements.

Keywords Crystallization · Glasses · Kinetics · TMA

Introduction

More than 1,200 articles are published every year in scientific journals that are related to crystallization of glasses. This number was four times larger than 20 years ago. However, most of those articles published within two decades time span 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 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 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 effect is hidden in baseline noise.

There is another experimental approach to glass crystallization kinetics that is based on detailed study of crystal growth morphology and 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 [6–10]. Nevertheless, these methods 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 certain glasses seems to be excluded from crystallization kinetic studies by DTA and DSC methods or direct microscopic crystal growth study. Recently, a novel method to study crystallization behavior in non-crystalline materials has been developed [11]. The method is based on sample deformation changes due to the viscous flow and crystal growth process. As the crystal growth takes place in highly viscous glass-forming liquid it can be expected that continuously growing crystals gradually slow down and finally

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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). The aim of this article is to describe the application of such a method of measurement in the study of crystallization kinetics of $Ge_{38}S_{62}$ glass that has been previously studied by optical microscopy and DSC [12–14].

Experimental

The $Ge_{38}S_{62}$ glass was prepared by synthesis from pure Ge, Sb element (5N purity) and sulfur (purified by Wartenberg method, as described in Ref. [15]). A mixture of these elements (7 g total weight) was placed in a clean silica 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 homogenization at 950 °C 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 calorimetric experiments were performed in non-isothermal conditions by using a DTA-1700 (Perkin-Elmer) operating in DSC heat flux mode. The instrument was calibrated with In, Pb, Zn, and Al standards. Freshly prepared bulk fragments of $Ge_{38}S_{62}$ glass (about 10 mg) were placed in a small evacuated silica ampoule. These containers were used for the measurement. Pure Al_2O_3 placed in the same silica container was used as a standard material. The measurement at selected heating rates (5, 7, 10, 15, and 20 °C min^{-1}) was carried out under atmosphere of dry nitrogen (flow rate about 20 mL min^{-1}).

The TMA measurement of crystal growth was performed by using Thermomechanical analyzer CX03RA-T (R.M.I. Company). A detailed specification of this instrument is described elsewhere [16]. The TMA instrument was calibrated with high purity Ga, In, Pb, Zn, and Al standards with exactly measured sample height using a slow scanning rate of 0.5 K min^{-1}. The melting point was detected by rapid change of the sample height due to melting of the standard material. The following procedure was used for measurement of crystallization kinetics. Flat rectangular specimen of as-prepared glass about 3 × 3 mm (sample height $h_0 = 1$ or 2 mm), polished to optical quality, was placed in the TMA cell, on top of a silica plate. The TMA cell was then heated at selected heating rate ($\beta = 1$, 2, 3, 4, or 5 °C min^{-1}) using a loading force $F = 10$ mN and the sample height h was then accurately recorded as a function of temperature.

The XRD analysis of amorphous and crystallized sample was performed using an AXS diffractometer D8 Advance (Bruker) equipped with horizontal goniometer and scintillation counter, utilizing Cu K_α radiation (40 kV, 30 mA). The scans were taken over scattering angles 2θ from 5° to 65° at the low scanning speed of 0.12° 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 α-GeS_2 and GeS. The samples were analyzed by an ESM 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.

Results and discussion

Figure 1 shows typical measurement of thermal expansion of $Ge_{38}S_{62}$ glass measured by TMA in the glass transition range. The inset shows the temperature dependence of thermal expansion coefficient corresponding to derivative of $h(T)$ curve. The shape of the sample is well defined slightly above the glass transition $T_g = 388$ °C [17], that is higher than the value corresponding to viscosity of 10^{12} Pa s ($T_{12} = 373$ °C) [16]. The thermal expansion in glassy state $\alpha_g = 11.2 \times 10^6$ K^{-1} is well defined and it is maintained nearly constant in a wide temperature range. For a moderate heating rate ($\beta = 5$ °C min^{-1}) it is possible to determine the thermal expansion of supercooled liquid $\alpha_l = 50.0 \times 10^6$ K^{-1}. However, it is rather problematic to measure the expansion of supercooled liquid at higher heating rates as the viscosity of supercooled melt significantly decreases, causing gradual sample deformation.

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., $h \approx h_0$) as shown in Fig. 2. In this

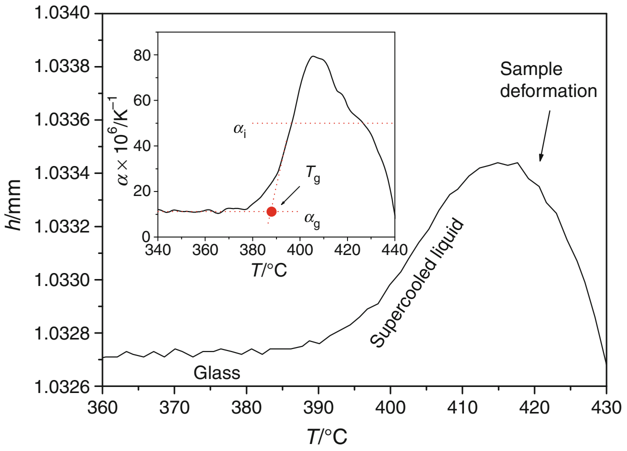

Fig. 1 TMA of $Ge_{38}S_{62}$ glass in the glass transition range measured at 5 °C min^{-1}. The *inset* shows the temperature dependence of thermal expansion coefficient corresponding to derivative of TMA curve

temperature range sample height starts to decrease due to the viscous flow. The crystal growth may take place at lower viscosities of 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, corresponding to fully crystallized sample.

According to equilibrium phase diagram [18] there are three polymorphs that can crystallize at $T > T_g$ under normal pressure, i.e., GeS, low temperature β-GeS$_2$ and high temperature α-GeS$_2$. The transformation of low temperature form to high temperature form of GeS$_2$ ($\beta \rightarrow \alpha$) takes place at 520 °C [18]. This seems to be confirmed by the XRD measurement of the sample after TMA experiment indicating the presence of α-GeS$_2$ and GeS. However, the crystal growth of GeS phase has not been observed by optical microscopy. From microscopic analysis of the sample after crystallization it seems that the crystallization starts close to the surface of the sample. It cannot be excluded that inside the sample there is still some uncrystallized core surrounded by the shell of GeS$_2$ and GeS crystals. This core might flow at temperatures well above T_g. However, the crystalline shell impedes further deformation of the sample and the sample height at higher temperatures $T > T_f$ reaches nearly a constant value. As a consequence, the TMA curve exhibits a typical sigmoidal shape that resembles inverse dependence of fraction crystallized versus temperature, well known from DSC studies. Two characteristic extrapolated temperature points T_0 and T_f can be defined (see Fig. 2).

As expected the force applied on the sample significantly affects the measurement. Figure 3 shows the relative sample height defined as $h_{rel} = h/h_0$, where h is actual sample height and h_0 is initial sample height, as a function of temperature for the forces ranging from 2 to 60 mN at heating rate of 5 °C min^{-1}. The inset shows the variation of characteristic temperatures of TMA curve as a function of applied force. However, the overall change of the temperature T_f is considerably smaller (4.9 °C) than change of T_0 (14.1 °C). Very similar TMA response is obtained when curves shown in Fig. 3 are normalized to the final sample height change. The force of 10 mN has been used for all experiments described in this article.

Figure 4 shows normalized sample height dependence of Ge$_{38}$S$_{62}$ glass on temperature for different heating rates. The normalized sample height is defined as $h_n = (h - h_f)/(h_0 - h_f)$. In this particular case the sample thickness was 1 mm. Very similar result can be obtained also for 2 mm

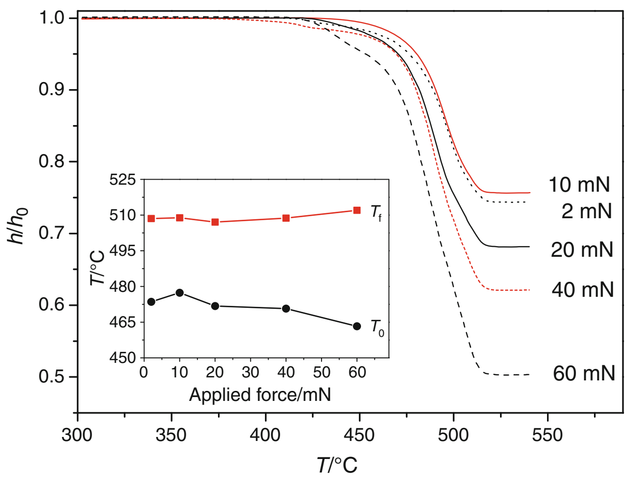

Fig. 3 The effect of applied force on the relative sample height of Ge$_{38}$S$_{62}$ sample measured at 5 °C min^{-1}. The *inset* shows the variation of characteristic temperatures of TMA curve as a function of applied force

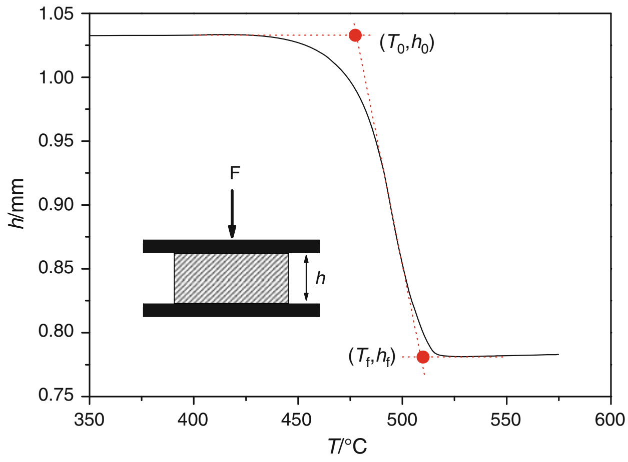

Fig. 2 A schematic experimental setup and typical TMA crystallization curve for Ge$_{38}$S$_{62}$ glass ($\beta = 5$ °C min^{-1}) with characteristic extrapolated points (T_0, h_0) and (T_f, h_f)

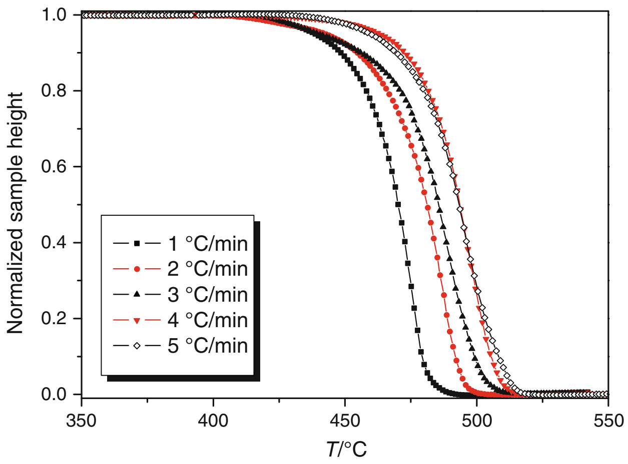

Fig. 4 The effect of heating rate on the TMA crystallization curve for Ge$_{38}$S$_{62}$ sample measured at applied force 10 mN

sample. Table 1 summarizes the characteristic temperatures T_0 and T_f.

It is evident that both these temperatures shift with heating rates in a similar way as the DSC crystallization peaks. 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 TMA curves shown in Fig. 4 resemble typical integral non-isothermal crystallization curves obtained from DSC data. This suggests the possibility to evaluate activation energy of crystallization from the shift of characteristic temperatures with heating rate, β. Recently it has been shown [11] that the activation energy of crystallization process can be estimated by using the Kissinger's method [19]:

$$\ln \frac{\beta}{T_f^2} = K - \frac{E}{RT_f}. \tag{1}$$

The activation energy E is then calculated from the slope of $\ln(\beta/T_f^2)$ versus $1/T_f$ plot. In fact, the first term on the right hand side of Eq. 1 is constant only for first order process. Nevertheless, it was shown [20] 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.

Figure 5 shows the Kissinger's plot for TMA crystallization curves corresponding to 1 and 2 mm sample. The activation energy obtained from the slope of this linear plot was found to be $E = 263 \pm 7$ and 267 ± 9 kJ mol^{-1}, respectively. These values are comparable within the combined error limits to the activation energy of α-GeS$_2$ crystal growth ($E_G = 247 \pm 23$ kJ mol^{-1}) obtained from optical microscopy measurements [12]. Very similar result was obtained also for the crystallization of $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ glass [11].

Table 1 Characteristic temperatures for the $Ge_{38}S_{62}$ glass

β/K min^{-1}	$h_0 = 1$ mm		$h_0 = 2$ mm	
	T_0/°C	T_f/°C	T_0/°C	T_f/°C
1	458.8	484.7	450.8	477.0
2	463.5	494.1	460.5	488.9
3	470.3	501.0	464.6	495.5
4	480.4	507.2	468.6	501.9
5	477.4	509.9	469.3	504.3

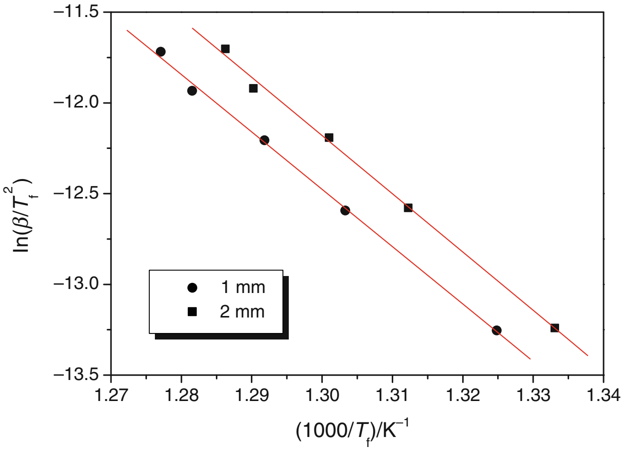

Fig. 5 Estimation of activation energy for crystallization of $Ge_{38}S_{62}$ glass ($h_0 = 1$ mm, $h_0 = 2$ mm) according to Kissinger's method from T_f data taken at different heating rate β

It is interesting to compare TMA measurement with direct measurement of crystal growth by optical microscopy. Two different types of crystal morphology of GeS$_2$ are observed in $Ge_{38}S_{62}$ glass [12]. The habitus of growing crystals suggests that α-GeS$_2$ crystallites follow two-dimensional (plate-like) growth in the whole temperature range examined (i.e., up to 494 °C). A higher dimensionality is observed for β-GeS$_2$. The length of these crystallites increases linearly with time in the whole temperature range. Shánělová et al. [12] reported that the crystal growth of GeS$_2$ in $Ge_{38}S_{62}$ glass probably corresponds to interface controlled 2D nucleated growth. In this case, the crystal growth rate can be expressed as [6]

$$u = \frac{C}{\eta} \exp\left(-\frac{B}{T\Delta T}\right), \tag{2}$$

where η is temperature-dependent viscosity, T is temperature, ΔT is supercooling with respect to the melting point of GeS$_2$ crystals, and B and C are constants. Figure 6 combines experimental growth rate data [12], calculated curve

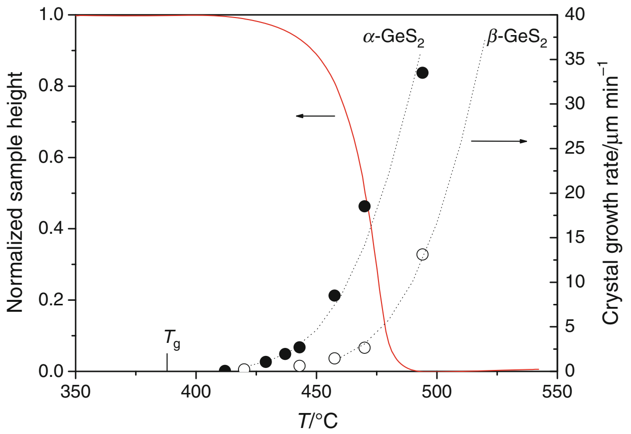

Fig. 6 The comparison of TMA curve measured at 1 °C min^{-1} and crystal growth rate of α-GeS$_2$ and β-GeS$_2$ in $Ge_{38}S_{62}$ glass (*points*) and prediction for interface controlled 2D nucleated growth (*broken lines*), calculated by Eq. 2

(combining reported viscosity data [16]) and TMA curve measured at low heating rate (1 °C min^{-1}). The growth rate curve calculated by Eq. 2, for parameters B, C summarized in Table 2, is plotted by broken line. The TMA curve and crystal growth data matches very well. The lowest crystal growth rate observable by optical microscopy is close to temperature T_0 and crystal growth rate of α-GeS_2 about 30 μm min^{-1} is observed at T_f. The initial sample height is maintained up to the temperature slightly above calorimetric T_g. Then the sample height starts to decrease due to gradual increase of viscous flow. The crystalline phase is formed and as it grows the sample deformation caused by viscous flow slows down and finally is ceased. As a consequence of competition between viscous flow and crystal growth the resulting TMA curve exhibits sigmoidal shape reaching final sample height before the maximum growth rate is observed (not shown in Fig. 6).

In contrast the TMA curve for identical heating rate and similar sample size does not match with DSC curve taken at comparable experimental conditions as shown in Fig. 7. Initial sample height is maintained up to the temperatures well above calorimetric T_g where the dilatometric glass transition is observed (see Fig. 1). Then the sample height starts to decrease as the viscous flow gradually deforms the sample shape. The deformation slows down and finally is stopped at T_f. This occurs around the onset of DSC crystallization curve. It is interesting to compare TMA curve with integral crystallization curve obtained from DSC data.

Table 2 Crystal growth parameters for GeS_2

Crystal	$B \times 10^{-7}/\mathrm{K}^2$	ln (C/N m^{-1})
α-GeS_2	1.12 ± 0.06	41.7
β-GeS_2	0.79 ± 0.01	28.0

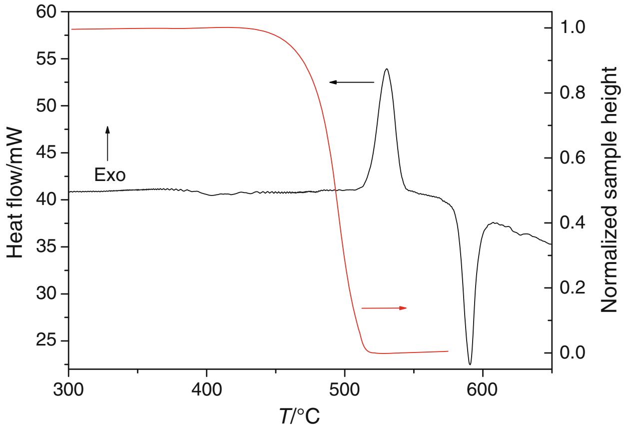

Fig. 7 The normalized TMA curve corresponding to the crystallization of $\mathrm{Ge}_{38}\mathrm{S}_{62}$ glass compared with DSC measurement at the same heating rate $\beta = 5$ K min^{-1}

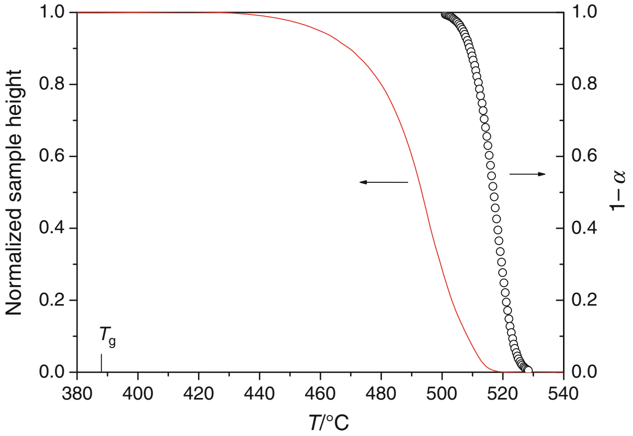

Fig. 8 The comparison of TMA curve for samples of $\mathrm{Ge}_{38}\mathrm{S}_{62}$ glass measured at 5 K min^{-1} (*full line*) and the $1-\alpha$ dependence calculated by Eq. 2 from DSC data measured at the same heating rate (*points*)

The kinetic interpretation of DSC data is based on the assumption that measured heat flow ϕ is proportional to the crystallization rate [1, 21]. The integral curve then can be obtained by partial integration of measured heat flow in the area of crystallization peak. The fraction crystallized α_i is defined as

$$\alpha = \frac{1}{\Delta H_\mathrm{c}} \int_0^t \phi \cdot \mathrm{d}t, \tag{3}$$

where $\Delta H_\mathrm{c} = -81 \pm 5$ kJ mol^{-1} is the crystallization enthalpy corresponding to the total area under DSC crystallization peak. Figure 8 shows experimental TMA curve ($h_0 = 1$ mm, $\beta = 5$ °C min^{-1}) for $\mathrm{Ge}_{38}\mathrm{S}_{62}$ glass and $1-\alpha$ dependence calculated by Eq. 3 from DSC data taken at the same experimental conditions (see Fig. 7). Both TMA and integral DSC curves are shifted by about 70 °C around their onset point. However, this difference becomes much smaller (around 10 °C) at T_f. It seems that TMA measurement reflects early stages of crystallization than measured by DSC under comparable conditions. Further study is needed to explain these differences in a more detail.

Conclusions

The TMA has been used as a sensitive tool to follow crystallization behavior in $\mathrm{Ge}_{38}\mathrm{S}_{62}$ glass. Newly developed method is based on slowing down of sample deformation by viscous flow above the glass transition due to macroscopic crystal growth. It is shown that a typical TMA sigmoidal curve reasonably well corresponds to direct measurement of crystal growth kinetics by means of optical microscopy. The TMA measurement is able to detect earlier stages of crystallization than obtained by DSC measurement. The activation energy obtained from the shift of extrapolated end of TMA curve with heating rate ($E = 263 \pm 7$ kJ mol^{-1}) is similar to the activation energy of α-GeS_2 crystal growth in $Ge_{38}S_{62}$ glass ($E_G = 247 \pm 23$ kJ mol^{-1}) obtained from direct optical microscopy measurements. Very similar results were obtained recently for different glass-forming system [11].

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References

1. Henderson DW. Thermal analysis of non-isothermal crystallization kinetics in glass forming liquids. J Non-Cryst Solids. 1979;30:301–15.
2. Yinnon H, Uhlmann DR. Thermal analysis of non-isothermal crystallization kinetics in glass forming liquids. J Non-Cryst Solids. 1983;54:253–75.
3. Málek J. The kinetic-analysis of nonisothermal data. Thermochim Acta. 1992;200:257–69.
4. Málek J. Kinetic analysis of crystallization processes in amorphous materials. Thermochim Acta. 2000;355:239–53.
5. Koga N, Šesták J. Crystal nucleation and growth in lithium diborate glass by thermal analysis. J Am Ceram Soc. 2000;83:1753–60.
6. Uhlmann DR. Crystal growth in glass forming system. In: Hench LL, Freiman SW, editors. Advances in nucleation and crystallization in glasses. Ohio: American Ceramic Society; 1971. p. 91–115.
7. Henderson DW, Ast DG. Viscosity and crystallization kinetics of As_2Se_3. J Non-Cryst Solids. 1984;64:43–70.
8. Burgner LL, Weinberg MC. Crystal growth mechanisms in inorganic glasses. Phys Chem Glasses. 2001;42:184–90.
9. Burgner LL, Weinberg MC. An assessment of crystal growth behavior in lithium disilicate glass. J Non-Cryst Solids. 2001;279:28–43.
10. Málek J, Švadlák D, Mitsuhashi T, Haneda H. Kinetics of crystal growth of Sb_2S_3 in $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ glass. J Non-Cryst Solids. 2006;352:2243–53.
11. Málek J, Zmrhalová Z, Barták J, Honcová P. A novel method to study crystallization of glasses. Thermochim Acta. 2010;511:67–73.
12. Shánělová J, Málek J, Alcalá MD, Criado JM. Kinetics of crystal growth of germanium disulfide in $Ge_{0.38}S_{0.62}$ chalcogenide glass. J Non-Cryst Solids. 2005;351:557–67.
13. Málek J, Tichý L, Klikorka J. Crystallization kinetics of Ge_xs_{1-x} glasses. J Thermal Anal Calorim. 1988;33:667–72.
14. Málek J. The glass-transition and crystallization of germanium sulfur glasses. J Non-Cryst Solids. 1989;107:323–7.
15. Tichý L, Tichá H, Frumar M, Klikorka J, Tříska A, Barta Č, Němečková A. Index of refraction and dc electrical-conductivity in Ge_{40-x} Sb_x S_{60} glasses. Czech J Phys. 1982;B32:1363–73.
16. Málek J, Shánělová J. Viscosity of germanium sulfide melts. J Non-Cryst Solids. 1999;243:116–22.
17. Málek J, Švejka R. Dilatometric measurement of structural relaxation in Ge38S62 glass. J Non-Cryst Solids. 1994;172:635–9.
18. Viaene W, Moh GH. Das binare system germanium-schwefel und p-T relation im Druckbereich bis 5 kb. J Miner Abh. 1973;119:113–44.
19. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702–6.
20. Criado JM, Ortega A. Non-isothermal transformation kinetics: remarks on the Kissinger method. J Non-Cryst Solids. 1986;87:302–11.
21. Málek J, Klikorka J. Crystallization kinetics of glassy GeS_2. J Therm Anal Calorim. 1987;32:1883–93.