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THE CRYSTALLIZATION OF $Ge_{40}S_{60}$ GLASS

JIŘÍ MÁLEK

Joint Laboratory of Solid State Chemistry of the Czechoslovak Academy of Sciences and the Institute of Chemical Technology, 532 10 Pardubice (Czechoslovakia)

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ABSTRACT

The crystallization kinetics of $Ge_{40}S_{60}$ glass were studied by heat flux differential scanning calorimetry (DSC). It is shown that there is one well-defined crystallization peak corresponding to the crystallization of both GeS and GeS_2 compounds. The scanning rate variations have no splitting effect on the crystallization peak.

The kinetic analysis of the crystallization of the studied glass was performed using Arrhenian rate constant and the Šesták-Berggren kinetic model in the form: $f(\alpha) = \alpha^m(1-\alpha)^n$. The kinetic parameters were calculated by multiparameter non-linear regression of experimental DSC curves. The consistency of the kinetic model proposed was confirmed by the invariance of the kinetic parameters at different heating rates.

INTRODUCTION

The condensed system germanium–sulphur was carefully studied by Viaene and Moh [1]. It was found that there are two compounds, i.e. congruently melting GeS_2 (1123 K) and incongruently melting GeS (931 K) which decomposes into Ge and a peritectic melt containing about 53% S. Germanium disulphide has two polymorphic forms, low temperature β-GeS_2 and high temperature α-GeS_2. The latter polymorph is thermodynamically stable above 793 K. On the other hand the germanium monosulphide has probably one crystalline form only. The eutectic point between GeS and GeS_2 composition occurs at 870 K and 57.5% sulphur.

Recently [1] it was found that the glasses can be formed for compositions between the eutectic point and approximately 95% sulphur. The crystallization of glasses in the Ge–S system was studied by means of DTA [2], and it has been concluded that the crystallization of these glasses proceeds in two stages. It was believed [2] that the two crystallization events correspond to the formation of GeS and GeS_2, respectively. Contrary to these results, it was recognized later [3] that, e.g. for $Ge_{40}S_{60}$ glass, these two thermal events merge to one crystallization thermal effect.

In the present paper an attempt is made to describe the crystallization kinetics of $Ge_{40}S_{60}$ glass by means of a suitable kinetic model. The usual

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method of kinetic parameters evaluation is based on the invariance of the rate equation

$$(\mathrm{d}\alpha/\mathrm{d}t) = \mathrm{f}(\alpha)k(T) \tag{1}$$

under any thermal conditions. In this equation α is the fraction of material crystallized at time t and the temperature dependence is given by the Arrhenius equation $k(T) = A\ \exp(-E/RT)$. There are many kinetic models for the description of solid-state processes. However, the proper kinetic model $\mathrm{f}(\alpha)$ for the description of crystallization kinetics of glasses remains a matter of discussion [4–6]. The most frequently used is the Johnson-Mehl-Avrami (JMA) kinetic model [7,8]. Nevertheless, the JMA model has its limitations and shortcomings [9]. Recently [10] it was found that the JMA model cannot be used for the quantitative description of the crystallization process in GeS_2 glass, and the formal Šesták-Berggren (SB) kinetic model $\mathrm{f}(\alpha) = \alpha^m(1-\alpha)^n$ has been proposed.

The aim of this paper is to test the applicability of the SB kinetic model for a quantitative description of crystallization of $Ge_{40}S_{60}$ glass using our kinetic software written for the Perkin-Elmer thermal analysis data system.

KINETIC ANALYSIS

The kinetic analysis of the crystallization of $Ge_{40}S_{60}$ glass was performed using the rate equation (1) and the SB kinetic model. It is assumed that the effects of thermal inertia are negligible and that the following equation is valid [11,12]

$$(\mathrm{d}Q/\mathrm{d}t) = k_N(\mathrm{d}\alpha/\mathrm{d}t) \tag{2}$$

where $\mathrm{d}Q/\mathrm{d}t$ is heat flow measured and k_N is a constant for given heating rate β. Thus, combining eqns. (1), (2) and the SB kinetic model for measured heat flow yields

$$\mathrm{d}Q/\mathrm{d}t = A'\ \exp(-E/RT)\alpha^m(1-\alpha)^n \tag{3}$$

where $A' = k_N A$. Kinetic equation (3) is used for non-linear regression of experimental curves using the Gauss-Newton method [10], and parameters A', E, m and n are determined in this way.

The parameter A is then calculated independently, using the condition for the maximum of crystallization peak, i.e.

$$(\mathrm{d}^2\alpha/\mathrm{d}t^2)_{T=T_p} = 0 \tag{4}$$

which can be rewritten in the following form

$$A = \frac{\beta E}{RT_p^2 Q_p}\ \exp(E/RT_p) \tag{5a}$$

$$Q_p = n\alpha_p^m(1-\alpha_p)^{n-1} - m\alpha_p^{m-1}(1-\alpha_p)^n \tag{5b}$$

where T_p is the peak temperature and α_p is the fraction of the glass crystallized at T_p. It is evident that eqn. (5a) is valid only if the relation $n/m > (1 - \alpha_p)/\alpha_p$ is fulfilled.

Rearranging eqn. (5a) and taking the natural logarithm the following equation can be written

$$\ln(\beta/T_p^2) = \ln(ARQ_p/E) - E/RT_p \qquad (6)$$

It can be shown that the term Q_p (eqn. 5b) is practically constant and independent on heating rate. Thus the activation energy E can be estimated from the slope of $\ln(\beta/T_p^2)$ vs. $1/T_p$ dependence. This dependence is known as a Kissinger plot [13,14].

The kinetic analysis described above was performed using the kinetic software which was written [9,10] for the Perkin-Elmer on-line system DTA-1700/TADS.

EXPERIMENTAL

The studied glass, of composition $Ge_{40}S_{60}$, was prepared using germanium and sulphur with nominal purity 5N. A mixture of these elements (7 g total weight) was placed in a quartz ampoule (inner diameter 13 mm, length 80 mm). The ampoule was then evacuated to a pressure of 10^{-4} Pa for 6 h, sealed, and placed in a rotary furnace. After heat treatment for 4 h at 710 K and subsequent homogenization at 1173 K for 24 h, the ampoule was cooled in water to room temperature.

The sample prepared in this way was analysed for chemical composition and trace impurities using the energy dispersive LINK 860 microanalysis system. These results confirmed the stoichiometry and high purity of the prepared glass.

The crystallization kinetics of $Ge_{40}S_{60}$ glass were studied using a Perkin-Elmer microcomputer based DTA-1700 system operating in heat flux DSC mode. For the acquisition and processing of experimental data a PE 3600 computer was used. Due to the high reactivity of sulphide glasses with oxygen at elevated temperatures, all measurements were carried out with the sample placed in a small evacuated quartz ampoule fitting into a measuring platinum cup. Freshly prepared bulk fragments (~ 10mg) were used for measurements.

Identification of the crystalline phases in the crystallized samples was carried out by means of X-ray diffraction analysis (XRD). Powder XRD patterns were obtained with Ni-filtered Cu K_α radiation.

RESULTS AND DISCUSSION

As we pointed out in the Introduction, there is a controversy in the literature concerning the thermal events corresponding to the crystallization

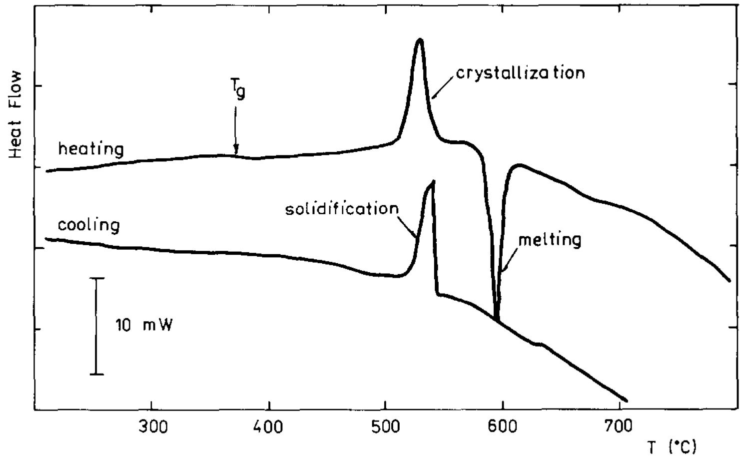

Fig. 1. Heating and cooling DSC curves for $Ge_{40}S_{60}$ glass ($\beta = 10$ K min^{-1}, sample weight: 12.1 mg).

of $Ge_{40}S_{60}$ glass. We observed, however, only one well-defined thermal event corresponding to the crystallization of the glass for both the bulk and the powder sample. This single peak occurs for various heating rates and no tendency for its splitting has been observed. However, the maximum heating rate is limited by eutectic melting at 870 K due to the shifting of the crystallization peak with heating rate.

Both the heating and cooling curves for the bulk sample of the glass studied are shown in Fig. 1. The relatively high undercooling can be explained by proximity to the eutectic composition. The enthalpy changes associated with crystallization and melting were estimated as -110 and 108 J g^{-1}, respectively. The XRD pattern of the completely crystallized sample is presented in Fig. 2 together with published data for crystalline α-GeS_2 and GeS [1]. There are two most intense lines (5.72 and 2.61 Å) in the crystallized sample of $Ge_{40}S_{60}$ glass. The intensity ratio of these lines corresponds to the molar ratio of GeS and GeS_2 compounds in the studied glass. Thus it is evident that both α-GeS_2 and GeS compounds crystallized in this glass. However, it is very interesting that these two crystallization processes are associated with a single crystallization peak only.

The comparison between the experimental and calculated DSC curves is presented in Fig. 3 and the corresponding kinetic parameters are summarized in Table 1. It is clear that the set of kinetic parameters (A, m, n, E) is independent of the heating rate. Thus the proposed kinetic model is shown to be consistent.

The fraction of the glass crystallized at T_p and the values of function Q_p (eq. 5b) are summarized in Table 2. As mentioned above the Q_p values are almost independent of the heating rate and thus the activation energy can be

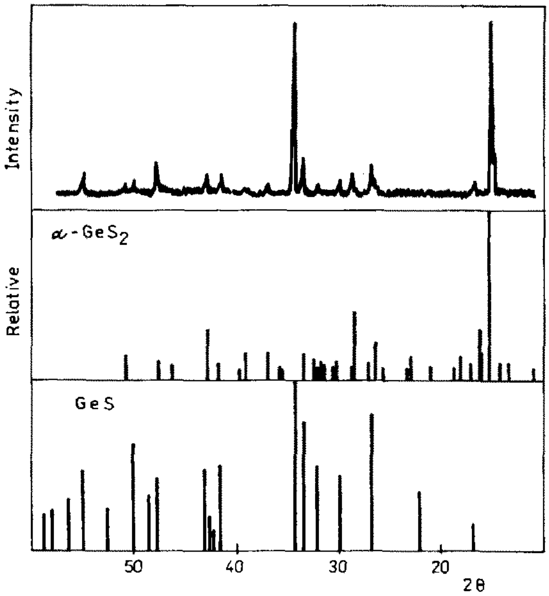

Fig. 2. XRD pattern of completely crystallized $Ge_{40}S_{60}$ glass (upper part) and diffractograms (plotted by using results of ref. 1) for both GeS and α-GeS_2 (lower part).

estimated independently using a Kissinger plot. The value of the activation energy $E = 255 \pm 11$ kJ mol^{-1} estimated in this way agrees well with its value determined by non-linear regression of the experimental data. Thus the Kissinger plot can be used for a quick estimation of sufficiently accurate values of E.

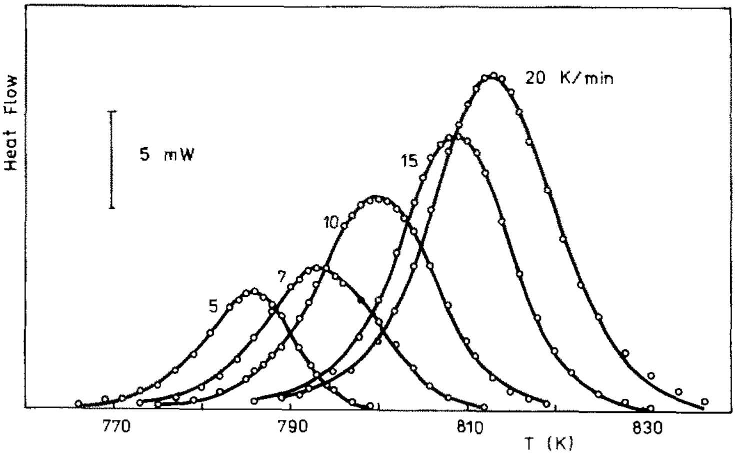

Fig. 3. Comparison of the experimental (open circles) and calculated DSC curves (full lines) for various heating rates. Corresponding kinetic parameters are reported in Table 1.

TABLE 1

Calculated kinetic parameters for crystallization of $Ge_{40}S_{60}$ glass

β (K min^{-1})	m	n	E (kJ mol^{-1})	A (s^{-1})	k_N (mcal)
5	0.825	0.928	250.8	3.46×10^{15}	67.4
7	0.738	1.082	257.7	4.82×10^{15}	119.7
10	0.767	1.095	253.1	2.13×10^{15}	154.3
15	0.837	1.137	251.1	2.53×10^{15}	88.8
20	0.835	1.301	254.7	2.21×10^{15}	189.8

TABLE 2

The values of α_p ad Q_p for crystallization of $Ge_{40}S_{60}$ glass at different heating rates

β (K min^{-1})	α_p	Q_p
5	0.523	0.108
7	0.465	0.127
10	0.471	0.130
15	0.492	0.138
20	0.467	0.154

The morphology of crystal growth was observed using optical microscopy. It was confirmed that the crystallization process starts at the surface of the bulk sample. The crystallization peaks are shifted to lower temperatures because of the pulverizing of the sample due to increasing concentration of the surface nuclei. The activation energy of the crystallization process, however, remains unchanged compared with that of bulk samples (see Fig. 4).

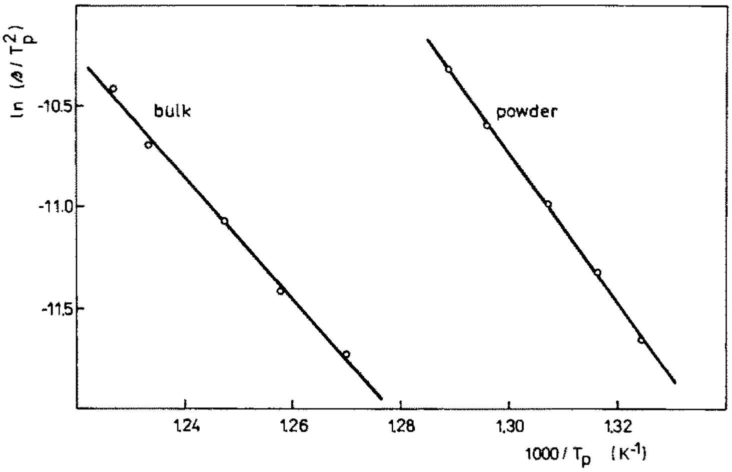

Fig. 4. Kissinger plots for both bulk and powder samples of glassy $Ge_{40}S_{60}$.

CONCLUSION

We analysed the crystallization behaviour of $Ge_{40}S_{60}$ glass obtained by water quenching. The crystallization kinetics were studied by means of heat flux DSC.

It was found that the crystallization starts at the surface of the bulk sample and that the single crystallization peak observed corresponds to the crystallization of both germanium monosulphide and germanium disulphide. No tendency toward peak splitting at different heating rates was observed.

The kinetic analysis of experimental data by means of non-linear regression was based on the Šesták-Berggren kinetic model and the Arrhenius form of temperature dependence of the rate constant. The applicability of this kinetic model was confirmed at different heating rates.

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