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CRYSTALLIZATION KINETICS OF Ge_xS_{1-x} GLASSES

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The crystallization processes of Ge_xS_{1-x} glasses were studied by means of heat flux DSC. It was shown that germanium disulphide crystallizes at $x \leqslant 1/3$. On the other hand, a higher germanium content ($x > 1/3$) led to the crystallization of both GeS_2 and GeS. Kinetic analysis of the processes of crystallization of the studied glasses was performed using the Arrhenius rate constant and the Šesták-Berggren kinetic model. The kinetic parameters were calculated through non-linear regression of the experimental DSC curves.

The Ge_xS_{1-x} glasses are still of interest for both scientific and technological reasons. In recent years, considerable attention has been devoted for example, to studies of the glass-forming processes [1–3], and the optical properties in the regions of the short [4, 5] and the long [6] wavelength edges in these glasses. Less attention has been paid to study of the crystallization processes in Ge_xS_{1-x} glasses. The crystallization of glassy GeS_2 has been studied for instance, in [7, 8]. In the former paper the effective activation energy under non-isothermal conditions was estimated. In the latter paper, the Šesták–Berggren and the Johnson–Mehl–Avrami kinetic models were tested for a quantitative desorption of the crystallization process. The linear rate of crystal growth of α-GeS_2 on the reheating of Ge_xS_{1-x} glasses was studied in [9].

In the present paper, our attention is mainly focused on a phenomenological quantitative description of the crystallization kinetics of Ge_xS_{1-x} glasses, where $0.33 \leqslant x \leqslant 0.40$. The aim of the work is to propose a kinetic model which consistently fits the experimental non-isothermal DSC curves and which is invariant with respect to the temperature program.

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Experimental

The studied glasses of composition Ge_xS_{1-x} were prepared in a conventional way described elsewhere [10]. The crystallization kinetics of these glasses was studied by using the microcomputer-based Perkin–Elmer DTA–1700 system operating in the heat flux DSC mode. For the acquisition and processing of the 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 samples placed in small evacuated quartz ampoules fitting into the platinum measuring cups. Freshly prepared bulk fragments of Ge_xS_{1-x} glasses (approx. 10 mg) were used for the measurements.

Kinetic parameter calculations

The kinetic analysis of the processes of crystallization of Ge_xS_{1-x} glasses was performed with the rate equation in the following form:

$$\alpha = A\exp(E/RT)f(\alpha) \tag{1}$$

where $f(\alpha)$ is a kinetic model of the crystallization process. In this paper, application of the Šesták–Berggren model [11] is proposed, i.e. $f(\alpha) = \alpha^m(1-\alpha)^n$. The kinetic parameters A, m, n and E were calculated by non-linear regression (Gauss–Newton method) of the experimental DSC data [8]. The kinetic analysis was performed for at least five different scanning rates, and thus at least five sets of kinetic parameters were obtained. The results presented here were calculated as averages of these parameters. The confidence limits were estimated in the customary way.

Results and discussion

The DSC curves of the Ge_xS_{1-x} glasses obtained at the scanning rate of 10 deg min^{-1} are presented in Fig. 1. As concerns the crystallization processes, the studied glasses can be devided into two regions:

(i) $x \leqslant 1/3$
(ii) $x > 1/3$

In region (i), the crystallization process can be described by using the following equation:

$$Ge_xS_{1-x(\mathrm{glass})} \rightarrow xGeS_{2(\mathrm{cr})} + (1-3x)\,S \tag{2}$$

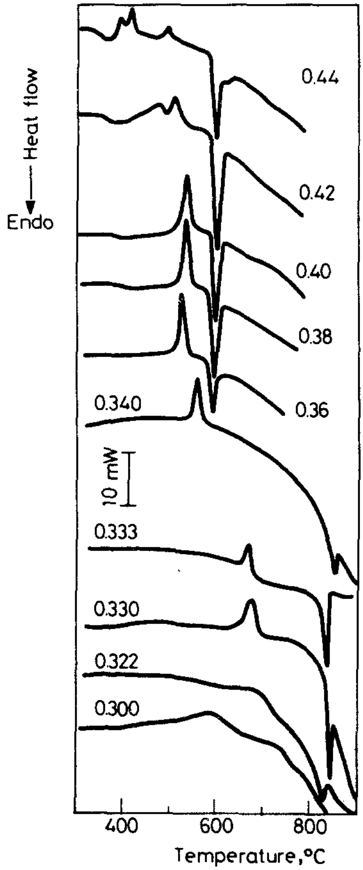

Fig. 1 Heat flux DSC curves of Ge_xS_{1-x} glasses (10 mg) (scanning rate 10 deg min^{-1})

It is not yet clear whether the sulphur remains in amorphous form after the devitrification of these glasses, or whether it crystallizes. It may be noted that crystalline sulphur has not been detected by X-ray diffraction analysis (XRDA). However, crystalline sulphur was found by means of highly sensitive DSC [12] and d.c. conductivity [13] measurements in a sulphur-rich glass ($x = 0.2$). Only one well-defined crystallization peak corresponding to Eq. (2) was observed for all composition in the region $1/3 \leqslant x \leqslant 0.3$. The crystallization processes in the glasses with higher sulphur contents ($x < 0.3$) are too slow to be detected with the equipment used.

In region (ii), the crystallization process can be described by means of the equation:

$$Ge_xS_{1-x(\mathrm{glass})} \rightarrow (1-2x)GeS_{2(\mathrm{cr})} + (3x-1)\,GeS \tag{3}$$

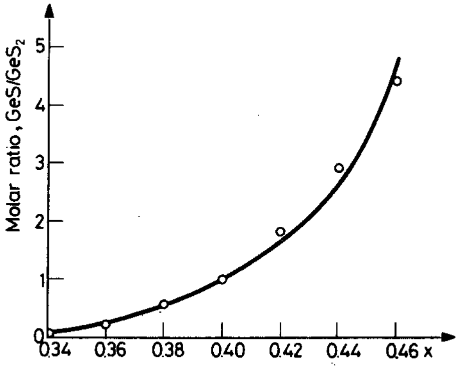

Fig. 2 Theoretical molar ratio of GeS/GeS_2 corresponding to the Eq. (3) (full line) and ratio of the integral intensities of the most intensive XRDA lines of these compounds (open circles) in completely crystallized Ge_xS_{1-x} glasses

We observed multiple crystallization peaks at $x > 0.4$ (Fig. 1). In agreement with Hrubý [2], we found that the first peak corresponds to the crystallization peak in the region $0.40 \leqslant x \leqslant 1/3$. It is evident (Fig. 2) that the theoretical molar ratio of GeS and GeS_2 calculated according to Eq. (3) agrees well with the integral intensity ratio of the most intense XRDA lines of these compounds (i.e. $d_{(040)} = 260.8$ pm, GeS, and $d_{(002)} = 517.7$ pm, GeS_2) in the completely crystallized Ge_xS_{1-x} glasses. Thus, the validity of Eq. (3) seems to be confirmed.

The kinetic parameters were calculated by using the above procedure for the $0.40 \geqslant x \geqslant 0.33$ glasses. These parameters and their confidence limits are listed in Table 1.

Table 1 Kinetic parameters for Ge_xS_{1-x} glasses

x	m	n	E, kJ/mol	ln A, s^{-1}
0.330	0.7 ±0.1	0.8±0.1	215±3	23.1±1.2
0.333	0.8 ±0.1	0.9±0.1	184±2	20.0±0.9
0.340	0.7 ±0.1	0.9±0.1	161±3	20.5±0.5
0.360	0.9 ±0.1	1.1±0.1	184±2	27.0±0.4
0.380	0.82±0.07	0.9±0.1	212±3	28.3±1.1
0.400	0.80±0.05	1.1±0.2	253±3	35.6±0.7

The resistance of the undercooled liquid crystallization can be related to the activation energy of the crystallization process. To evaluate the glass-forming tendency qualitatively, we used the relation from [2]:

$$K_{gl} = (T_k - T_g)/(T_m - T_k)$$

where T_g, T_k and T_m are the temperatures of the glass transition, crystallization and melting, respectively. It can be seen from Fig. 3, where the compositional dependences of E and K_{gl} are compared, that both parameters show a minimum near the composition $x = 0.34$. Thus, the region of low glass-forming tendency exists at around this composition.

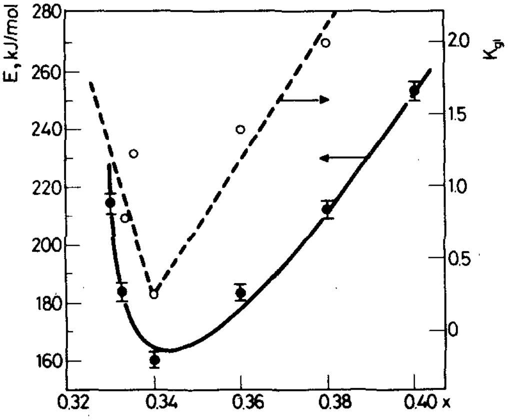

Fig. 3 Compositional dependence of the activation energy of the crystallization process and parameter K_{gl} for Ge_xS_{1-x} glasses.

Conclusions

A series of experiments were carried out to describe the crystallization processes of Ge_xS_{1-x} glasses. Germanium disulphide GeS_2 crystallized in these glasses at $x \leqslant 1/3$. Both GeS_2 and GeS crystallize in the region $0.40 \geqslant x > 1/3$ and these processes are represented by one well-defined crystallization peak. Two separate peaks, associated with the crystallization of GeS_2 and GeS, respectively, are observed at $x > 0.40$.

The kinetic analysis was performed by using the Arrhenius rate constant and the Šesták–Berggren kinetic model. The calculated kinetic parameters are listed in Table 1. The minimum in the glass-forming ability lies near the composition $x \approx 0.34$.

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Zusammenfassung — Die Kristallisationsprozesse von Gläsern Ge_xS_{1-x} wurden durch Wärmefluss—DSC untersucht. Bei $x \leqslant 0{,}33$ kristallisiert GeS_2, während bei höherem Germaniumgehalt ($x > 0{,}333$) Kristallisation von GeS_2 und GeS eintritt.

Für die kinetische Analyse des Kristallisationsprozessen wurden Arrhenius-Geschwindigkeitskonstanten und das Šesták-Berggren-Modell verwendet. Die kinetischen Parameter wurden durch nichtlineare Regression der experimentellen DSC-Kurven berechnet.

Резюме — Методом ДСК теплового потока изучены процессы кристаллизации стеклообразных Ge_xS_{1-x}. Показано, что в стеклах с $x \leqslant 1/3$ кристаллизуется дисульфид германия, а в стеклах с более высоким содержанием германия ($x > 1/3$) — кристаллизуются как сульфид, так и дисульфид германия. Кинетический анализ процесса кристаллизации в изученных стеклах был проведен на основе константы скорости аррениусовского типа и кинетической модели Шестака-Берггрена. Кинетические параметры были вычислены на основе нелинейного регрессионного анализа экспериментальных кривых ДСК.