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THE THERMAL STABILITY OF CHALCOGENIDE GLASSES*

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Crystallization processes of Ge_xS_{1-x} ($0.322 \leq x \leq 0.44$) glasses have been studied by thermal analysis and a new simple method of kinetic analysis is proposed. This method allows the definition of an appropriate model characterizing the crystallization process of glass, as well as calculation of reliable kinetic parameters. Results of kinetic analysis allow definition of a thermal stability criterion which has a general applicability for any glass-forming system.

Keywords: chalcogenide glasses, glass-formation system, kinetics

Introduction

During the last two decades much attention has been devoted to the properties of chalcogenide glasses. The main motivation for research in this field is their relatively high infrared transparency and , therefore, the possibility of using these materials for construction of passive optical elements for the IR region [1–3].

It is evident that such optical materials should be stable at working temperatures and free from microcrystallites which may lower their optical transparency due to scatter losses.

The aim of the present investigation is to study the crystallization of germanium-sulphur glasses by methods of thermal analysis (TA). Results of kinetic analysis of these crystallization processes can be used to formulate thermal stability criteria for glasses which are generally applicable to any glass-forming system.

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Theory

It is well known that the crystallization of a glass starts in the undercooled liquid above the glass transition temperature (T_g). The exothermal heat flow ($\dot{H}$) corresponding to the crystallization process as measured by TA techniques can be expressed by following equation [4]:

$$\dot{H} = \Delta H_c K(T) f(\alpha) \tag{1}$$

where ΔH_c is the heat of crystallization and α the degree of crystallization. The temperature term $K(T)$ represents the crystallization rate constant and usually takes the Arrhenius exponential form:

$$K(T) = A\,e^{-x} \tag{2}$$

where $x = E/RT$. The symbols A, E, T have the usual meaning of pre-exponential factor, activation energy and temperature, respectively. The form of the kinetic term $f(\alpha)$ depends on the kinetic mechanism. The $f(\alpha)$ functions most frequently used for description of crystallization processes are summarized in Table 1.

Table 1 Kinetic models for crystallization processes [4]

Model	Symbol	$f(\alpha)$
Johnson-Mehl-Avrami eq.	JMA (n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Šesták-Berggren eq.	SB(m, n)	$\alpha^m(1-\alpha)^n$

Many papers have been published on how to determine kinetic parameters from TA data. Numerous methods aim to evaluate all kinetic parameters from one only TA curve. The main problem inherent in these methods is a strong mutual correlation of all kinetic parameters. Thus it is practically impossible to perform successfully the kinetic analysis of a single TA curve by conventional regression algorithms unless at least one kinetic parameter is a priori known. Bearing this in mind, the best approach for kinetic analysis is first to calculate the activation energy by one of a number of multiple-scan methods [5–7] and then determine the kinetic model by the method described below.

It can be shown that for this purpose it is useful to define two special functions, $y(\alpha)$ and $z(\alpha)$ which can easily be obtained by a simple transformation of TA data. These functions can be formulated as follows [8, 9]:

$$y(\alpha) = \dot{H}\,e^{x} \tag{3}$$

$$z(\alpha) = \pi(x)\,\dot{H}\,\frac{T}{\beta} \tag{4}$$

where β is the heating rate and $\pi(x)$ is the temperature integral approximation which has to be introduced because Eq. (1) cannot be integrated exactly. This approximation is usually expressed as a rational function and is described in more detail in [10]. Acceptable results can be obtained even for the simple Gorbachev approximation [11] in the form: $\pi(x) = 1/(x + 2)$.

Both the $y(\alpha)$ and $z(\alpha)$ functions can be used to guide the choice of a kinetic model. It can be shown relatively simply that the $z(\alpha)$ function has a maximum exactly at $\alpha_p^\infty = 0.632$ for the JMA(n) model. Because this characteristic value does not depend on the value of the kinetic exponent and is only slightly affected (within 1%) by activation energy used to calculate the $z(\alpha)$ function, it can be used as a very sensitive test of applicability of the JMA(n) model. The α_p^∞ function should not be confused with the degree of conversion at the maximum of the DSC peak, α_p, which of course depends on E. On the other hand, the maximum, α_M of the $y(\alpha)$ function varies in the interval $0 \le \alpha_M < \alpha_p$ depending on the value of both the kinetic exponents and the activation energy for the JMA(n) and SB(m,n) models.

Therefore, by checking the maximum value of the $z(\alpha)$ function it can be determined whether the TA data can be interpreted using the JMA(n) or SB(m,n) models. Once the kinetic model has been chosen, the kinetic exponent n (or m) can be calculated using the methods described below.

JMA(n) model

If the function $y(\alpha)$ has a maximum at $\alpha_M > 0$ the kinetic exponent n can be calculated using the Eq. [9]

$$n = \frac{1}{1 + \ln(1 - \alpha_M)} \tag{5}$$

If there is a maximum of the $y(\alpha)$ function at $\alpha_M = 0$ then the parameter n can be calculated by means of the Šatava method [12], i.e. from the slope of the plot of $\ln[-\ln(1 - \alpha)]$ *vs.* $1/T$ which is nE/R. An alternative method of calculation is based on the relationship derived from the condition for the maximum of the DSC peak [13]

$$n = \frac{1 - x_p\,\pi(x_p)}{\ln(1 - \alpha_p) + 1} \tag{6}$$

It is known that the Šatava method gives slightly higher values of the parameter n. On the other hand Eq. (6) gives a lower value. In the author's experience an average of these two values is a good approximation of the kinetic exponent.

SB(m, n) model

The kinetic parameter ratio $q = m/n$ can be calculated using the Eq. [9]

$$q = \frac{\alpha_M}{1 - \alpha_M} \tag{7}$$

Then Eq. (1) may be expressed in the form:

$$\ln(\dot{H}e^x) = \ln(\Delta H_c A) + n \ln[\alpha^q(1-\alpha)] \tag{8}$$

The kinetic parameter n corresponds to the slope of linear dependence of $\ln(H\,e^x)$ *vs.* $\ln[\alpha^q(1-\alpha)]$ for $\alpha \in (0.2, 0.8)$. Then the second kinetic exponent is $m = q\,n$.

Knowing the values of activation energy and kinetic exponent, the pre-exponential factor can be calculated using Eq. (9)

$$A = -\frac{\beta x_p}{T_p f'(\alpha_p)} \exp(x_p) \tag{9}$$

The heat of crystallization ΔH_c is then expressed by

$$\Delta H_c = \frac{1}{A} \sum_{i=1}^{n} \frac{\dot{H}_i \exp(x_i)}{f(\alpha_i)} \tag{10}$$

The reliability of kinetic parameters and consistency of the kinetic model applied should be assessed by testing the invariance of theoretically calculated kinetic parameters for several scans at different heating rates [14].

Experimental

The studied glasses of composition Ge_xS_{1-x} (x = 0.322, 0.33, 0.333, 0.34, 0.36, 0.38, 0.40, 0.42, 0.44) were prepared using germanium and sulphur with nominal purity of 5*N*. A mixture of these elements (7 g total weight) was placed in quartz ampoules (inner diameter 13 mm, length 80 mm). The ampoules were then evacuated to a pressure of 10^{-4} Pa for 6h, sealed, then placed in a rotary furnace. After heating for 4h at 710 K and subsequent homogenization at 1173 K for 24h, the ampoules were rapidly cooled in water to room temperature.

The amorphous nature of the glasses prepared was confirmed by X-ray diffraction analysis (XRD). Identification of crystalline phases in crystallized samples was carried out by XRD and electron microanalysis. Crystallization kinetics of prepared glasses were studied using a Perkin-Elmer microcomputer-based DTA-1700 system operating in heat-flux DSC mode [15]. Due to the high reactivity of sulphide glasses with oxygen at elevated temperatures, all measurements were carried out with the sample in small evacuated quartz ampoules within platinum cups. Freshly prepared powder samples (average particle size 100 μm) of Ge_xS_{1-x} glasses were used for measurements.

Results and discussion

The phase diagram of the germanium-sulphur system [16] is shown in Fig. 1; the dashed line corresponds to the compositional dependence of the glass transition temperature $T_g(x)$ [17]. This temperature can be considered as an upper limit for the existence of glass because at higher temperatures irreversible processes involving nucleation and subsequent crystal growth for certain chemical compositions x of the starting material begin. With respect to the type of crystallization processes, Ge_xS_{1-x} glasses can be divided into two compositional regions: (i) $x > 1/3$ and (ii) $x \leq 1/3$.

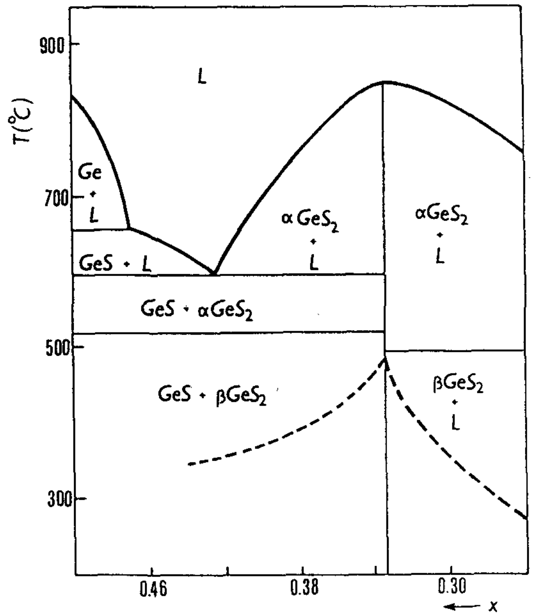

Fig. 1 Phase equilibria in the Ge_xS_{1-x} system [16]: x corresponds to atomic percent of germanium. The dashed line shows the compositional dependence of T_g [17]

Crystallization of both GeS and GeS_2 phases were observed in the first compositional range (i) by electron microanalysis. XRD phase analysis of completely crystallized samples shows that amounts of both crystalline compounds correspond to the equilibrium phase diagram shown in Fig. 1. It would appear therefore that no amorphous phase remains uncrystallized in the sample. These two crystallization processes overlap for $0.4 \leq x < 1/3$ and are manifested by one DSC crystallization peak [17, 18]. The peak splits only at very low heating rates (Fig. 2).

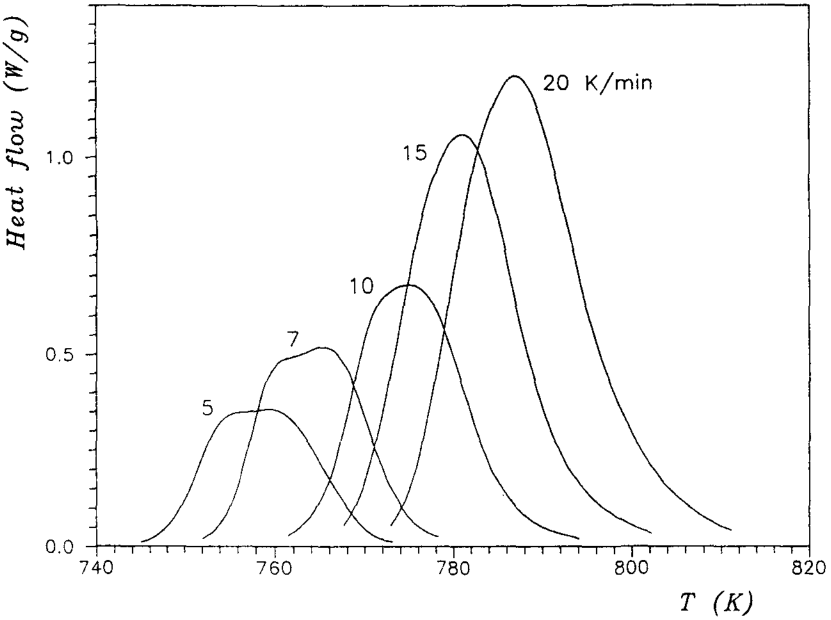

Fig. 2 Crystallization DSC data for $Ge_{0.38}S_{0.62}$ glass at different heating rates

On the other hand, two well separated crystallization peaks were observed for glasses of composition $x \geq 0.42$ for all heating rates in the interval 2–20 deg·min^{-1}. In agreement with [19] it was found that the first peak is associated with crystallization of GeS and the second with GeS_2 compounds. Crystallization of germanium disulphide was confirmed in the second compositional range (ii). In contrast to previous results [20], only one well-defined crystallization peak was observed for both bulk and powder samples in this compositional region.

It was confirmed by scanning electron microscopy that the crystallization processes for all studied glass compositions started at the surface of the samples. This is in agreement with the observation that the crystallization peaks for pulverized samples shifted to lower temperatures in comparison with bulk samples due to increasing concentration of surface nuclei.

It is known that germanium disulphide has two polymorphs at normal pressure, i.e. low-temperature β-GeS_2 [21] (space group $P2_1/c$) and high-temperature α-GeS_2 [22] (space group Pc). In order to decide which polymorph crystallizes during the reheating of Ge_xS_{1-x} glasses, XRD analyses were carried out on samples annealed for a long period of time just above T_g, as well as at temperatures corresponding to the end of the crystallization peak. In Fig. 3, XRD patterns of both polymorphs calculated from crystallographic data [21, 22] are compared with XRD patterns of the crystallized GeS_2 glass. It is apparent that the diffraction pattern of the sample annealed just above T_g (803 K for 24 hours) corresponds to β-GeS_2 (curve a). This is interesting because at this temperature the β–GeS_2 phase is no longer stable according to the equilibrium phase diagram (Fig. 1). Curve b shows the XRD pattern of a sample heated to the end of the DSC crystallization peak. Distinguishable reflections of the α–GeS_2 crystalline phase are present. It would appear that the α-GeS_2 phase forms during the first stages of the crystallization process and the $\beta \rightarrow \alpha$ transformation takes place at a higher temperature. Similar results were obtained for other germanium-sulphur glass compositions.

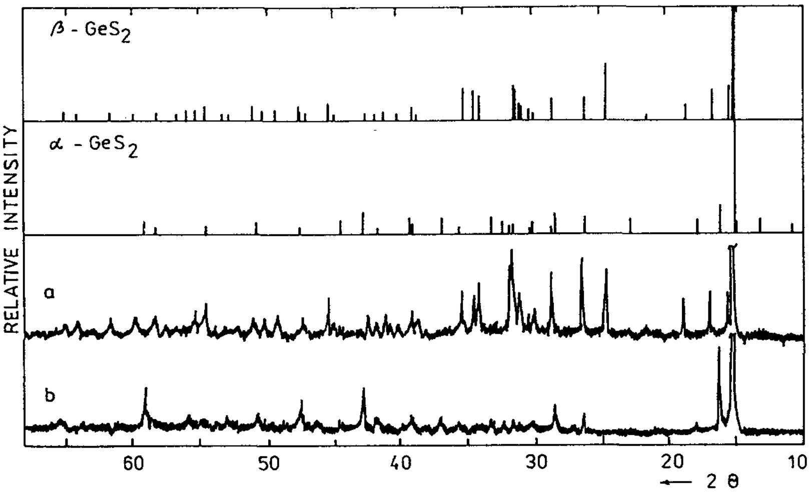

Fig. 3 Theoretical X-ray patterns (CuK_α radiation) of β–GeS_2, α–GeS_2 and experimental patterns of crystallization of GeS_2 glass, (a) after annealing at 693 K for 24 hours, (b) after DSC run (β = 10 K/min, T_{final} = 950 K)

Typical displacements of crystallization peak maxima (T_p) with heating rate are shown in Fig. 2. From this $T_p(\beta)$ dependence the activation energy can easily be calculated using the Kissinger method [5]. The results are summarized in Table 2 for all studied compositions of glasses.

These values were used to calculate the $z(\alpha)$ functions by means of Eq. (4). The maximum values, α_p^∞ of these functions are significantly lower than 0.632 for all compositions, and therefore the JMA(n) model cannot be used for the description of the crystallization processes. From this point of view the SB(m, n) model seem to be more suitable in this instance.

Table 2 The activation energy of crystallization of Ge_xS_{1-x} glasses

x	E / kJ·mol^{-1}
0.322	168 ± 10
0.33	226 ± 12
0.333	211 ± 7
0.34	201 ± 7
0.36	175 ± 5
0.38	228 ± 17
0.40	315 ± 9
0.42	349 ± 15*
	263 ± 9**
0.44	309 ± 17*
	256 ± 11**

* First crystallization peak, ** Second crystallization peak

The kinetic parameters for crystallization of Ge_xS_{1-x} glasses are summarized in Table 3. These parameters were calculated by the method described above using four data sets corresponding to heating rates ranging from 2–20 deg·min^{-1}. Therefore the parameters given in Table 3 represent the arithmetical mean and standard deviations of these results. Figure 4 compares the experimental TA data (points) measured at 10 deg·min^{-1} and the theoretical data (curves) calculated using Eq. (1) for kinetic parameters summarized in Table 3. Taking into account

Table 3 Kinetic parameters for the crystallization of Ge_xS_{1-x} glasses

x	m	n	ln A / s^{-1}	ΔH_c / J·g^{-1}
0.322	0.7 ± 0.1	1.30± 0.99	19.6 ± 0.4	–70 ± 4
0.33	0.61 ± 0.06	1.2 ± 0.2	26.3 ± 0.2	–72 ± 4
0.333	0.56 ± 0.05	1.1 ± 0.1	23.8 ± 0.2	–121 ±10
0.34	1.0 ± 0.1	0.9 ± 0.2	26.8 ± 0.4	–58 ± 7
0.36	0.8 ±0-.3	0.9 ± 0.1	23.7 ± 0.4	–68 ± 3
0.38	0.5 ± 0.1	1.2 ± 0.2	31.9 ± 0.2	–72 ± 2
0.40	0.6 ± 0.1	1.50 ± 0.09	45.8 ± 0.3	–71 ± 5
0.42	0.55 ± 0.07	1.49 ± 0.06	54.2 ± 0.1	–36 ± 2
	0.73 ± 0.01	1.1 ± 0.1	37.3 ± 0.1	–43 ± 4
0.44	0.46 ± 0.06	1.7 ± 0.2	58.9 ± 0.3	–48 ± 5
	0.80 ± 0.03	1.2 ± 0.2	37.1 ± 0.1	–23 ± 2

experimental errors, both experimental and calculated TA curves are in acceptable agreement. The invariance of the kinetic parameters calculated was verified for heating rates in the range 2–20 deg·min^{-1}.

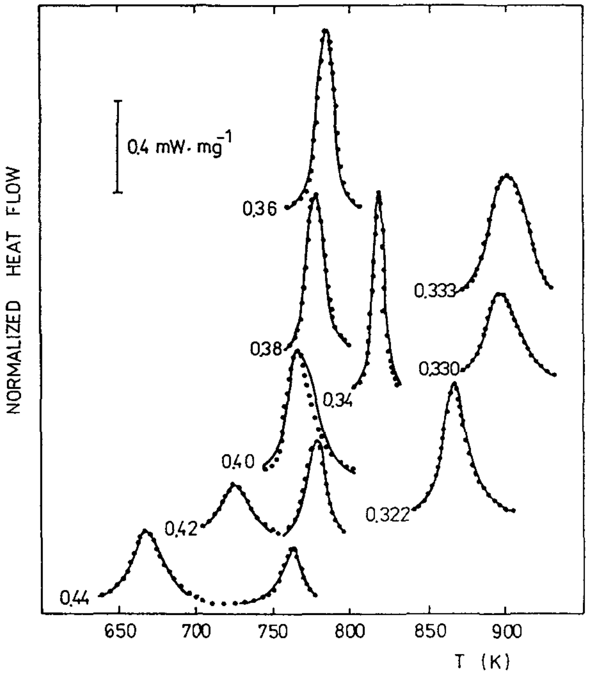

Fig. 4 Experimental (points) and calculated (full lines) crystallization DSC data for Ge_xS_{1-x} glasses at a heating rate of 10 K/min. Chemical composition are marked by numbers

This good agreement of the model with experimental data is very important for any prediction of the behaviour of the glass under study at selected thermal conditions. It has been shown [23] that the glass thermal stability (GTS) can be estimated reasonably well on the basis of the crystallization rate constant at the glass transition temperature, i.e. $K(T_g)$. After converting Eq. (2) to logarithms the GTS can be expressed as follows:

$$-\log K(T_g) = 0.434\,[E/RT_g - \ln A] \tag{11}$$

The compositional dependence of $pK(T_g) = -\log K(T_g)$ is plotted in Fig. 5 for the Ge_xS_{1-x} system. It is evident that the $0.34 \leq x \leq 0.36$ compositional range is associated with minimum thermal stability. This corresponds also to previous results [24] where the gap between two glass-forming regions of the Ge_xS_{1-x} system was found to be $0.40 > x > 1/3$. On the other hand, the thermal stability maximum (Fig. 5) is observed near to the eutectic composition $0.40 \le x \le 0.42$ (see also Fig. 1), where the highest undercooling of the melt can be observed. A relatively high thermal stability can also be expected for compositions with higher sulphur contents ($x > 1/3$).

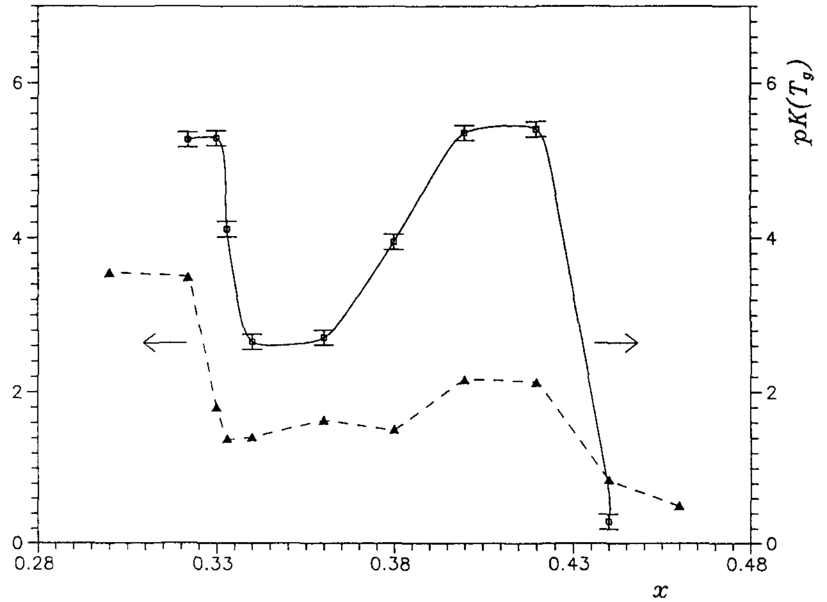

Fig. 5 Compositional dependence of the thermal stability criteria $pK(T_g)$ (solid line) and G (dashed line) for Ge_xS_{1-x} glasses

This approach for GTS based on crystallization kinetics seems to be more quantitative than other concepts [25–27] because the values of $pK(T_g)$ are independent of experimental technique and can thus be directly compared even for different glass-forming systems. Nevertheless, it should be borne in mind that obtaining reliable $pK(T_g)$ data is a rather tedious procedure as a complete kinetic analysis has to be performed. Moreover, there are some problems if the crystallization process is more complicated and associated with multiple or overlapping DSC peaks.

It has been found, however, that the thermal stability of a glass can be estimated even from one DSC curve using the following dimensionless criterion

$$G = \frac{(T_g - T_c)\, c_p^*}{\Delta H_\Sigma} \qquad (12)$$

where T_c is the extrapolated onset of crystallization peak, c_p^* is the heat capacity of undercooled melt (it can be estimated using the formula c_p^* (J/mol·K) $\cong 28 + \Delta C_p$, where ΔC_p is the heat capacity change at T_g) and ΔH_Σ is the total heat of crystallization. The $G(x)$ dependence is shown in Fig. 5 by a dashed line. It is evident that the G criterion corresponds well with the compositional dependence of $pK(T_g)$ in the Ge_xS_{1-x} system. Similar behaviour was observed [28] in another glass-forming systems. It seems therefore that this criterion can be considered as a good parameter for estimating the thermal stability of glasses.

Conclusion

In the crystallization kinetics of Ge_xS_{1-x} glasses it appears that there are two crystallization processes corresponding to the formation of both GeS and GeS_2 phases for compositions $x > 1/3$. Conversely, only the GeS_2 phase crystallizes in $x \leq 1/3$ glasses. The β–GeS_2 phase forms during the first stages of the crystallization process and then transforms to α–GeS_2.

A simple and consistent method of kinetic analysis for crystallization processes has been developed. This method allows determination of the most probable kinetic model and calculation of meaningful kinetic parameters.

The thermal stability criterion $pK(T_g)$ has been calculated for all compositions of the glasses studied. It was found that the glasses of $0.36 > x > 0.34$ exhibit the lowest thermal stability in the Ge_xS_{1-x} system. The highest thermal stability was confirmed for the $0.42 > x > 0.40$ compositional range or for glasses with sulphur over-stoichiometry. A new empirical criterion, G, to describe the thermal stability of glasses is also proposed. The compositional trend of this criterion is comparable with that of the parameter $pK(T_g)$.

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Zusammenfassung — Mittels Thermoanalyse wurden die Kristallisationsprozesse von Ge_xS_{1-x} ($0.322 \leq x \leq 0.44$) untersucht eine neue einfache Methode für die kinetische Analyse vorgeschlagen. Diese Methode gestattet die Definition eines entsprechenden Modelles zur Beschreibung des Kristallisationsprozesses als auch die Berechnung zuverlässiger kinetischer Parameter. Die Ergebnisse der kinetischen Analyse ermöglichen die Festlegung eines thermischen Stabilitätskriteriums, was bei allen glasbildenden Systemen Anwendung finden kann.