# CRYSTALLIZATION KINETICS OF GLASSY GeS$_2$

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The crystallization kinetics of glassy GeS$_2$ was investigated by non-isothermal heat flux differential scanning calorimetry (DSC) on both bulk and powder samples. It was shown that high-temperature modification of germanium disulphide crystallizes from an undercooled melt of composition GeS$_2$. The crystallization kinetics can be described by the Šesták–Berggren (SB) kinetic model, using the Arrhenius dependence of the rate constant. It was found that the Johnson-Mehl-Avrami (JMA) kinetic model is less suitable for the description of the studied crystallization process.

A BASIC program has been written for both SB and JMA models to evaluate kinetic data from experimental DSC curves recorded with the Perkin–Elmer Thermal Analysis Data Station system.

Germanium disulphide is a congruently melting (1123 K) semiconducting compound [1] which can be obtained in the glassy state by cooling of the melt at a rate of 17 deg s$^{-1}$ or higher [2]. While the structure and optical properties of glassy GeS$_2$ have received great attention [3–5], the crystallization of this material has been studied only in some papers. It has been shown that the nominal purity of the sulphur used for the synthesis of GeS$_2$ has a significant influence on the crystallization behaviour of glassy GeS$_2$ [6]. Voigt and Wolf [7] have reported that small traces of sulphur and/or arsenic cause a lowering of the crystallization tendency of the GeS$_2$ melt, and increase its glass-forming ability. From isothermal measurements, the linear growth rate at 800 K was determined as 0.1 μm·s$^{-1}$ [8]. Voigt and Ludwig [1] reported the analysis of data obtained under non-isothermal conditions, using the Kissinger rate equation [9]. It was shown that the growth of spherulitic crystals starts at the surface of the sample.

However, no kinetic model has been proposed to describe the crystallization of GeS$_2$ glass. The aim of this paper was the study of the crystallization kinetics of bulk and powder samples of glassy GeS$_2$, in order to propose a reasonable kinetic model for a quantitative description.

## Material preparation

Both the germanium and the sulphur used for the preparation of the germanium disulphide glass had a nominal purity of 99.999% (sulphur was purified as described in [10]). A mixture of these elements (8 g total weight) was placed in a quartz ampoule (inner diameter 13 mm, wall thickness 0.8 mm and ampoule length 80 mm). The ampoule was then evacuated to a pressure of $10^{-3}$ Pa for 6 hours, sealed and placed in a rotary furnace. After heat treatment for 4 hours at 710 K and subsequent homogenization at 1173 K for 24 hours, the ampoule was cooled in water to room temperature.

The synthesized material had a light-yellow colour with a typical conchoidal fracture. The absence of crystalline phases was confirmed by x-ray diffraction analysis (XRD). For DSC measurements, freshly prepared bulk fragments (10 mg) and a powdered glassy sample with an average particle size of 0.01 mm were used.

## Measurement methods

The crystallization kinetics of glassy $GeS_2$ was studied in a series of non-isothermal experiments performed with a Perkin–Elmer microcomputer-based DTA–1700 system in heat-flux DSC mode. A built-in scanning autozero function was used for automatic baseline control. For the acquisition and storage of raw experimental data, a Thermal Analysis Data Station (TADS) computer system was used.

To minimize the high reactivity of $GeS_2$ with oxygen traces at elevated temperatures, all measurements were carried out with the sample placed in small evacuated ($p \sim 10^{-3}$ Pa) quartz ampouled fitting into measuring platinum cups. Aluminium oxide powder in an evacuated quartz ampoule was used as the reference sample.

Identificaton of crystalline phases in the crystallized sample after the DSC scan was carried out by XRD. Powder XRD patterns were obtained with Ni-filtered $Cu_{K_\alpha}$ radiation.

## Kinetic analysis

For the calculation of the crystallization kinetics of glassy $GeS_2$, a BASIC program has been written. Figure 1 is a simple schematic representation of the overall program. The file of raw experimental data created by the TADS system inputs into the main program and is converted by subroutine GRAF to the new file.
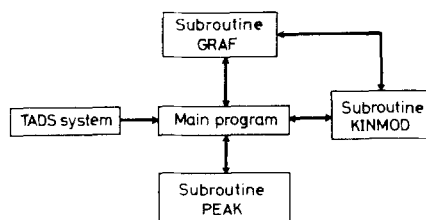
Fig. 1 Scheme of the program for kinetic analysis

This conversion proceeds as follows: The baseline is first extrapolated between chosen lower $(T_1)$ and upper $(T_2)$ temperature limits (see Fig. 2). In the next step, the experimental data $\alpha_i$ and $(dQ/dt)_i$ are determined at selected temperatures $T_i$. These values are stored in a new file DATA.
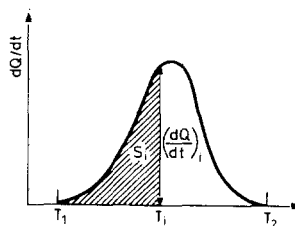


Fig. 2 Typical non-isothermal heat-flux DSC trace for crystallization of the glass

It is assumed that the effects of thermal inertia are negligibly small and that the following conditions (known as the Borchard assumptions) are fulfilled [11, 12]:

$$(dQ/dt)_i = K_N (d\alpha/dt)_i \tag{1a}$$

$$S_i = \alpha_i \int_{T_1}^{T_2} (dQ/dt)\, dT \tag{1b}$$

where $K_N$ is a normalization constant, $\alpha_i$ is the fraction of material crystallized between $T_1$ and $T_i$, and $(d\alpha/dt)_i$ is the crystallization rate at temperature $T_i$.

File . DATA is used in subroutine KINMOD (sse Fig. 1), which permits calculation of the kinetic parameters for the given kinetic model. The calculation is based on several assumptions. It is presumed that the rate of crystallization can be described by the kinetic equation:

$$(d\alpha/dt) = K(T) \cdot f(\alpha) \tag{2}$$

where $K(T)$ is a temperature-dependent rate constant in the Arrhenius form:

$$K(T) = A \exp(-E/RT) \tag{3}$$

For the purpose of this paper, the preexponential term $A$ in Eq. (3) was taken as temperature-independent.

Parameter $E$ in Eq. (3) can be interpreted as the effective activation energy of crystallization, and $R$ is the gas constant. The function $f(\alpha)$ in Eq. (2) is given by the kinetic model of the crystallization process. Two kinetic models have been used:
  (i) the Šesták–Berggren (SB) model [13]:

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{4}$$

  (ii) the Johnson–Mehl–Avrami (JMA) model* [14, 15]:

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{5}$$

where exponents $m$ and $n$ are kinetic parameters of the overall crystallization process. Thus, by combining Eqs (1a), (2), (3) and (4), for the SB model we obtain:

$$(dQ/dt)_i = A' \exp(-E/RT_i)\alpha_i^m(1-\alpha_i)^n \tag{6}$$

and analogously, for the JMA model we obtain*:

$$(dQ/dt)_i = A' \exp(-E/RT_i)n(1-\alpha_i)[-\ln(1-\alpha_i)]^{1-1/n} \tag{7}$$

where $A' = K_N \cdot A$. Kinetic equations (6) and (7) were used in subroutine KINMOD for non-linear regression of experimental data stored in file DATA. Parameters $A'$, $E$, $m$ and $n$ are determined in this way. The parameter $A$ is calculated from Eq. (A6) when the standard deviation of the calculated and experimental data reaches its minimum value.

Subroutine PEAK (see Fig. 1) is used for the calculation of parameter $E$, using the peak method described in the Appendix.


## Results and discussion

Figure 3 shows both heating and cooling DSC curves for bulk $GeS_2$ at a scanning rate of 20 deg/min. It is evident that there is a well-defined single crystallization peak with a maximum at 971 K. This result is in contradiction with the DTA measurements reported by Voigt and Ludwig [1], who observed non-reproducible multiple peaks for bulk $GeS_2$ glassy samples. Similar multiple peaks were observed by Hrubý [6], who concluded that this complicated process is probably due to the presence of crystalline centres of foreign origin as a result of sulphur contamination.

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* The function $f(\alpha)$ for the JMA model has been derived from the Avrami equation [14] in the form $\alpha = 1 - \exp[-(Kt)^n]$, where $t$ is time. It has also been verified to be valid under non-isothermal conditions [16].
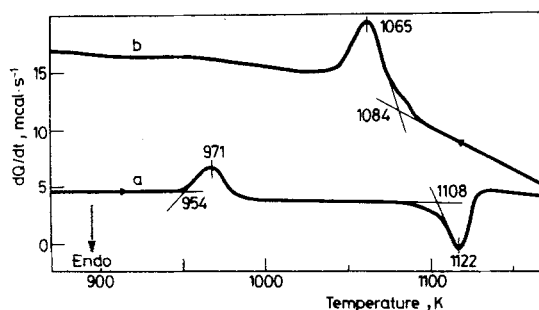
**Fig. 3** Heating (a) and cooling (b) DSC curves for the bulk of glassy $GeS_2$ ($\beta = 20$ deg/min, sample weight: 12.9 mg)

**Table 1** Temperatures ($T_p$) and crystallized fraction ($\alpha_p$) at the peak of the DSC trace for the crystallization of bulk and powder samples of glassy $GeS_2$

| $\beta$, K/min | Powder | | Bulk | |
|---|---|---|---|---|
| | $T_p$, K | $\alpha_p$ | $T_p$, K | $\alpha_p$ |
| 10 | 898 | 0.4443 | 950 | 0.6071 |
| 15 | 913 | 0.4323 | 965 | 0.5569 |
| 20 | 920 | 0.4458 | 971 | 0.5790 |
| 40 | 941 | 0.4173 | 1004 | 0.4584 |
| 50 | 949 | 0.4020 | 1011 | 0.4549 |

Table 1 lists the temperature ($T_p$) and the crystallized fraction ($\alpha_p$) evaluated at the tip of peak of the DSC trace for the crystallization of glassy $GeS_2$. It is evident that $T_p$ depends on the heating rate ($\beta$), and thus the crystallization has a kinetic nature. While the value of $\alpha_p$ depends on the heating rate for the bulk sample, it remains nearly constant for the powder sample.

From the Kissinger plot of $\ln (\beta/T_p^2)$ versus $1/T_p$, effective activation energies for both bulk ($E_{bulk} = 188 \pm 10$ kJ/mol) and powder ($E_{powder} = 210 \pm 7$ kJ/mol) samples of glassy $GeS_2$ have been determined (see Fig. 4). There is approximately a 10% difference between these values. However, the value of $E_{powder}$ is close to that determined by Voigt and Ludwig [1] ($E = 219 \pm 15$ kJ/mol).

Figures 5 and 6 compare measured DSC curves (open circles) and calculated ones using the SB (full lines) and JMA (dotted lines) kinetic models for bulk and powder samples. The kinetic parameters and standard deviations ($\sigma$) corresponding to the calculated curves are given in Tables 2 and 3 for both kinetic models used. The best agreement between the experimental and calculated DSC curves is obtained for the SB model. Thus, the SB model gives better results than the JMA model.

The enthalpy change associated with the crystallization of glassy $GeS_2$ is
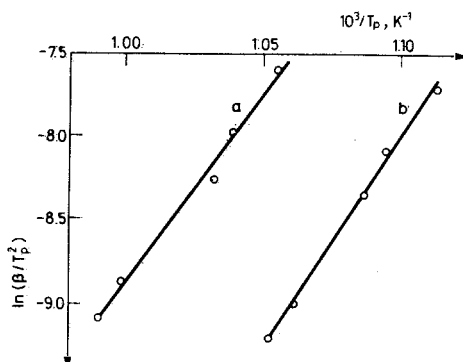
**Fig. 4** Kissinger plots for bulk (a) and powder (b) samples of glassy $GeS_2$
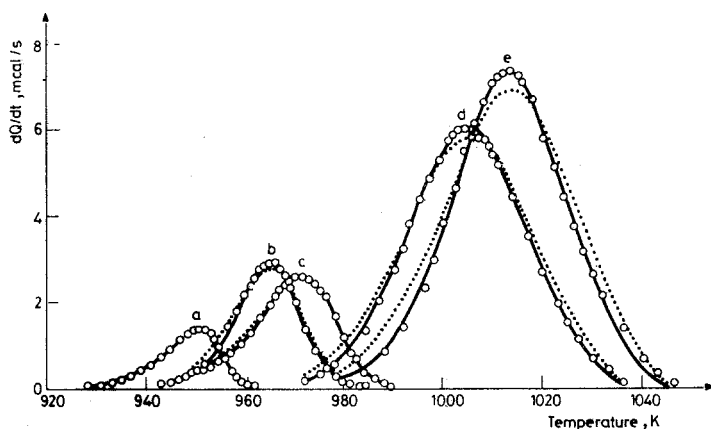


**Fig. 5** Comparison of experimental (open circles) and calculated DSC curves of crystallization of the bulk of glassy $GeS_2$, using the SB model (full lines) and the JMA model (dotted lines). Heating rates: (a) 10, (b) 15, (c) 20, (d) 40, (e) 50 deg/min

independent of the heating rate, being $\Delta H_{cryst} = -121 \pm 10$ J/g. Similarly, the enthalpy change corresponding to melting of the crystallized sample is $\Delta H_f = 129 \pm 10$ J/g.

It has been shown previously [17, 18] that $GeS_2$ has two polymorphs, low-temperature $\beta\text{-}GeS_2$ and high-temperature $\alpha\text{-}GeS_2$. In Fig. 7, XRD patterns of a crystallized glassy $GeS_2$ sample are compared with theoretical diffractograms of both polymorphs calculated from crystallographic data [19, 20]. It is clear that glassy $GeS_2$ crystallizes to $\alpha\text{-}GeS_2$. This conclusions is in agreement with the proposed structure of glassy $GeS_2$ [4] and with the thermodynamic stability of $\alpha\text{-}GeS_2$ above 793 K [18].
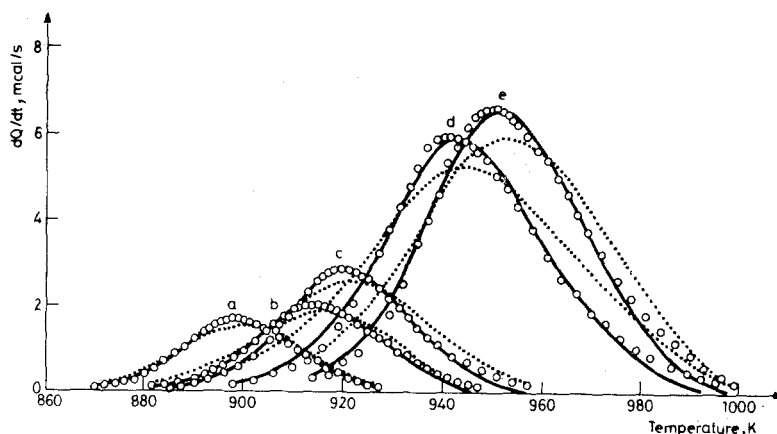
**Fig. 6** Comparison of experimental (open circles) and calculated DSC curves of crystallization of the powder of glassy $GeS_2$, using the SB model (full lines) and the JMA model (dotted lines). Heating rates: (a) 10, (b) 15, (c) 20, (d) 40, (e) 50 deg/min

**Table 2** Kinetic parameters for the crystallization of glassy $GeS_2$, calculated by means of subroutine KINMOD for the SB model

| Sample | $\beta$, deg/min | $m$ | $n$ | $E$, kJ/mol | $A$, $s^{-1}$ | $K_N$, mcal | $\sigma$ |
|--------|--------|------|------|-------|----------------|------|-------|
| Powder | 10 | 0.57 | 1.05 | 207.6 | $3.08 \cdot 10^{10}$ | 190 | 0.038 |
|        | 15 | 0.59 | 1.09 | 215.3 | $1.07 \cdot 10^{10}$ | 116 | 0.069 |
|        | 20 | 0.69 | 1.24 | 197.1 | $7.84 \cdot 10^{9}$ | 208 | 0.082 |
|        | 40 | 0.63 | 1.35 | 203.4 | $3.76 \cdot 10^{10}$ | 109 | 0.150 |
|        | 50 | 0.55 | 1.25 | 211.2 | $3.67 \cdot 10^{10}$ | 231 | 0.229 |
| Bulk   | 10 | 0.90 | 0.67 | 184.9 | $7.65 \cdot 10^{8}$ | 77 | 0.052 |
|        | 15 | 0.89 | 0.93 | 182.6 | $3.23 \cdot 10^{8}$ | 248 | 0.080 |
|        | 20 | 0.93 | 0.88 | 185.9 | $5.81 \cdot 10^{8}$ | 160 | 0.037 |
|        | 40 | 0.66 | 0.97 | 182.8 | $4.15 \cdot 10^{8}$ | 114 | 0.083 |
|        | 50 | 0.72 | 1.06 | 185.2 | $6.26 \cdot 10^{8}$ | 142 | 0.158 |

## Conclusion

The crystallizations of bulk and powder samples of glassy $GeS_2$ have been studied. It was shown that the high-temperature modification of germanium disulphide crystallizes in this glass. The enthalpy change corresponding to the crystallization is $\Delta H_{cryst} = -121 \pm 10$ J/g, and the enthalpy change of the melting is $\Delta H_f = 129 \pm 10$ J/g.

**Table 3** Kinetic parameters for the crystallization of glassy $GeS_2$, calculated by means of subroutine KINMOD for the JMA model

| Sample | $\beta$, deg/min | $n$ | $E$, kJ/mol | $A$, s$^{-1}$ | $K_N$, mcal | $\sigma$ |
|---|---|---|---|---|---|---|
| Powder | 10 | 1.71 | 202.6 | $2.75 \cdot 10^9$ | 461 | 0.098 |
|  | 15 | 1.70 | 199.6 | $1.80 \cdot 10^9$ | 357 | 0.139 |
|  | 20 | 1.57 | 206.8 | $5.73 \cdot 10^9$ | 346 | 0.270 |
|  | 40 | 1.48 | 179.2 | $0.21 \cdot 10^9$ | 302 | 0.622 |
|  | 50 | 1.45 | 198.8 | $8.19 \cdot 10^9$ | 87 | 0.590 |
| Bulk | 10 | 8.16 | 199.7 | $1.15 \cdot 10^7$ | 1589 | 0.042 |
|  | 15 | 3.12 | 179.9 | $1.69 \cdot 10^7$ | 759 | 0.144 |
|  | 20 | 3.79 | 182.5 | $3.27 \cdot 10^7$ | 356 | 0.092 |
|  | 40 | 2.04 | 183.5 | $2.61 \cdot 10^7$ | 903 | 0.266 |
|  | 50 | 2.04 | 173.8 | $1.31 \cdot 10^7$ | 573 | 0.457 |
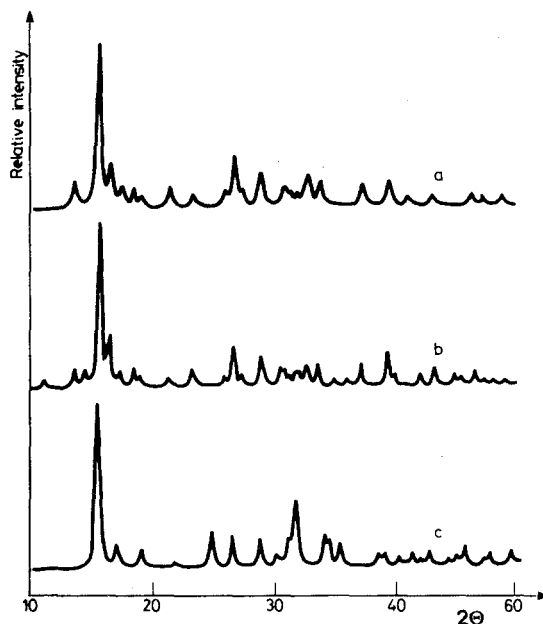


**Fig. 7** XRD patterns of crystallized glassy $GeS_2$ (a) and calculated diffractograms of $\alpha$-$GeS_2$ (b) and $\beta$-$GeS_2$ (c) for the $Cu_{K_\alpha}$ line

It was found that the crystallization kinetics can be described using the Šesták–Berggren kinetic model. On the other hand, the Johnson–Mehl–Avrami kinetic model is less suitable for the description of the studied process.

# Appendix

The analysis below is developed in terms of basic kinetic equation (2) for simple Arrhenius behaviour of the rate constant with respect to temperature during the crystallization process, i.e. Eq. (3). Both the Šesták–Berggren function (SB) and the Johnson–Mehl–Avrami function (JMA) are used as kinetic models for the crystallization.

## Determination of preexponential term

The condition for the maximum in the crystallization rate can be written in the form:

$$(\mathrm{d}^2\alpha/\mathrm{d}t^2)_{T=T_p} = 0 \tag{A1}$$

If the basic kinetic equation (2) is differentiated with respect to time, Eq. (A1) can be rewritten in a somewhat different form:

$$\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha} \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}t} K(T_p) + \frac{\mathrm{d}K(T_p)}{\mathrm{d}t} f(\alpha) = 0 \tag{A2}$$

Substituting Eq. (3) into Eq. (A2) and taking $T = \beta \cdot t$ (it is assumed that the scan rate $\beta$ is constant), we obtain:

$$\frac{\beta}{T_p^2} = \frac{ARQ_p}{E} \exp\left(-E/RT_p\right) \tag{A3}$$

where the function $Q_p$ is defined as

$$Q_p = -(\mathrm{d}f(\alpha)/\mathrm{d}\alpha)_{\alpha=\alpha_p} \tag{A4}$$

Taking natural logarithms of Eq. (A3), we can write the Kissinger equation [12] as:

$$\ln(\beta/T_p^2) = \ln(ARQ_p/E) - E/R(1/T_p) \tag{A5}$$

Thus, the activation energy $E$ can be determined from the slope of the $\ln(\beta/T_p^2)$ versus $1/T_p$ dependence (Kissinger plot) and its value is independent of the kinetic model.

## Determination of preexponential term

Rearrangement of Eq. (A3) for the preexponential term $A$ yields:

$$A = \frac{\beta E}{RT_p^2 Q_p} \exp(E/RT_p) \tag{A6}$$

For the SB model, the function $Q_p$ can be written in the following form:

$$Q_p = n\alpha_p^m (1 - \alpha_p)^{n-1} - m\alpha_p^{m-1}(1 - \alpha_p)^n \qquad (A7)$$

and for the JMA model in the form:

$$Q_p = n[-\ln(1 - \alpha_p)]^{1 - 1/n} - (n - 1)[-\ln(1 - \alpha_p)]^{-1/n} \qquad (A8)$$

The preexponential term $A$ can be calculated from Eq. (A6) using the corresponding form of function $Q_p$ for the suggested kinetic model. However, it is clear that this procedure can be applied only if the condition $Q_p > 0$ is fulfilled [21].

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**Zusammenfassung** — Es wurden die kinetischen Kristallisationseigenschaften von glasartigem GeS$_2$ mittels einem nichtisothermen Wärmefluß-DSC sowohl an Stück- als auch an Pulverproben untersucht. Es wurde gezeigt, daß aus einer unterkühlten Schmelze von GeS$_2$ eine Hochtemperaturmodifikation des Germaniumdisulfides auskristallisiert. Die Kinetik der Kristallisierung kann unter Ausnutzung der Abhängigkeit der Reaktionsgeschwindigkeit vom Arrheniusfaktor mittels des kinetischen Šesták–Berggren (SB) Modells beschrieben werden. Das kinetische Modell von Johnson–Mehl–Avrami (JMA) wurde zur Beschreibung des untersuchten Kristallisierungsprozesses als für weniger geeignet

befunden. Zur Auswertung der kinetischen Daten aus den mit einem Perkin–Elmer Thermal Analysis Data Station System aufgenommenen DSC-Kurven wurde sowohl für das SB- als auch für das JMA-Modell ein BASIC Programm gefertigt.

**Резюме** — Методом неизотермической ДСК теплового потока изучена кинетика кристаллизации массивных и порошковых образцов стеклообразного дисульфида германия. Показано, что из переохлажденного расплава дисульфида германия выкристаллизовывается его высокотемпературная модификация. Кинетика кристаллизации может быть описана кинетической моделью Шестака–Берггрена (ШВ), используя аррениусовскую зависимость константы скорости. Установлено, что кинетическая модель Джонсона–Мехл–Аврами (ДМА) менее приемлема для описания изученного процесса кристаллизации. Для обоих ШБ и ДМА моделей написана на языке Бейсик программа, для определения кинетических данных, исходя из экспериментальных кривых ДСК, измеренных с помощью Перкин–Эльмер базовой системы данных термического анализа.