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Crystallization kinetics of $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ glass¹

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Abstract

The influence of the sample specific surface on the crystallization kinetics of the Sb_2S_3 in $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ glass has been studied. It was found that the DSC crystallization data for the bulk sample can be described by the Johnson–Mehl–Avrami (JMA) model corresponding to three-dimensional crystal growth. The same description for powder samples is not possible and the empirical Šesták–Berggren equation had to be used. The condition of the validity for the JMA model is discussed.

Keywords: Crystallization; DSC; Glass; Kinetics; Specific surface

1. Introduction

Experimental investigations of the crystallization kinetics of glass and comparison of the data with theoretical models are of interest for a better understanding of the laws of nucleation and growth of crystals. Thermal analysis techniques have been extensively used to study the crystallization of glasses. In these cases, the measured heat flow corresponds mainly to the macroscopic crystal growth but this process is strongly influenced by the preceding nucleation. This is probably the main reason why in many cases the experimental data cannot be described within the framework of the existing theoretical models and empirical equations have to be applied. Therefore, it seems that more attention should be paid to the study of the influence of the nucleation process on the macroscopic crystal growth.

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¹ Dedicated to Professor Hiroshi Suga.

The aim of this paper is to study the influence of sample surface nucleation on the crystallization kinetics of the Sb_2S_3 in $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ glass. The applicability of the Johnson–Mehl–Avrami model and the Šesták–Berggren empirical equation is discussed.

2. Experimental

A chalcogenide glass of $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ composition was prepared in a conventional way from the elements of 5N purity. Samples of about 5 mg were encapsulated in Perkin-Elmer aluminium volatile-sample pans and the calorimetric curve was measured using a Mettler DSC12E instrument coupled with a PC working under MS Windows TA89E environment. The instrument was previously calibrated with indium, tin and lead standards ($E_{\text{in}} = 1118.75$ units per mW, $\tau_{\text{lag}} = 15$ s). Non-isothermal DSC curves were obtained with selected heating rates ($1\text{--}20$ K min^{-1}) in the range from 100 to 400°C. The original data were transformed to ASCII data files and all data treatments were performed with the TA-system software package. The method of kinetic analysis as well as all the symbols used here are described in our previous paper [1].

3. Kinetic equation

The non-isothermal crystallization of glass is the result of a nucleation process and subsequent crystal growth. When the crystallization kinetics is studied by thermal analysis techniques, the crystallization heat evolved during the crystal growth is measured. Usually it is assumed that the measured heat flow ϕ can be described by the following kinetic equation [2]

$$\phi = \Delta H A e^{-E/RT} f(\alpha) \quad (1)$$

where ΔH is the crystallization heat, A is the preexponential factor and E is the effective activation energy for the crystallization process. The activation energy can be estimated using one of many methods published in the literature. In this work, we used the Kissinger [3] and extended Friedman methods [4,5].

The function $f(\alpha)$ in Eq. (1) is an analytical expression describing the kinetic model of the studied process. For the description of the crystallization processes in glasses, the Johnson–Mehl–Avrami (JMA) model [6,7] is used

$$f(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n} \quad (2)$$

where the kinetic exponent n corresponds to the dimensionality of the crystal growth. However, the applicability of this model is restricted by the condition of site saturation, which is equivalent to the presumption that the nucleation is completed before the growth process is started [8,9]. This condition is fulfilled if there is negligible overlap between the nucleation and growth curves.

As a general test of the applicability of the JMA model, the $z(\alpha)$ function has been proposed [1]

$$z(\alpha) = T \phi \pi(\alpha) / \beta \quad (3)$$

where the $\pi(x)$ is an approximation of the temperature integral [10] (in most cases this can be neglected when calculating the $z(x)$ function from DSC data) and β is the heating rate. The maximum of the $z(x)$ function α_p^∞ should be close to 0.632. If α_p^∞ is considerably lower, the JMA model cannot be applied.

In these cases, the Šesták–Berggren (SB) equation [11] can be used for the description of crystallization processes

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (4)$$

The SB equation is an empirical equation and in fact it includes the JMA model as a special case. The kinetic exponents m and n in Eq. (4) should be linked with the mechanism of the crystallization process. Unfortunately, the link is still not clear at present. It was shown [12], however, that physically meaningful values of the parameter m should be confined to the interval $0 < m < 1$.

4. Results

To study the influence of the sample specific surface on the crystallization kinetics of the Sb_2S_3 in $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ glass, the following three types of samples were studied: (1) fine powder, (2) coarse powder (crushed bulk sample) and (3) bulk sample of glass. Fig. 1

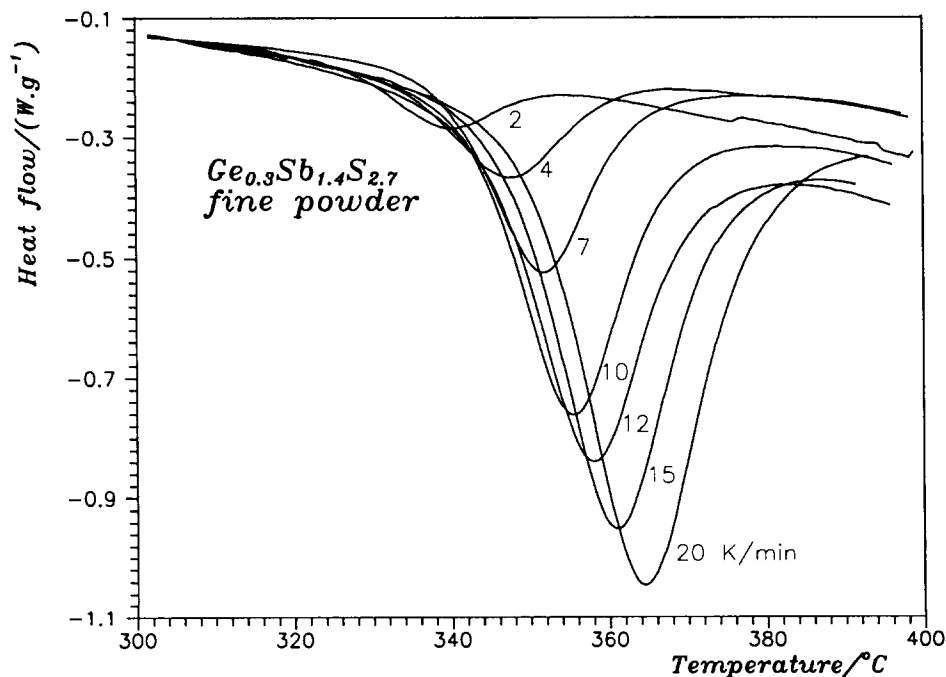


Fig. 1. DSC curves for crystallization of fine powder of $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ glass measured at different heating rates.

shows typical DSC experimental data for the fine powder sample measured at seven different heating rates. The values of the activation energy calculated by the Friedman method are shown in Fig. 2 (points) as a function of the degree of conversion. The dashed line corresponds to the value determined by the Kissinger method. As evident from the error bars, both methods give similar results within about 10% error. The value of E determined by the Kissinger method was used for the kinetic calculations presented here. It is interesting that the activation energy increases with specific surface of the sample. The activation energy found in a previous paper [13] is close to the value for coarse powder.

The crystallization heat was determined as $\Delta H = -47 \pm 5 \text{ J g}^{-1}$ for all three types of sample. The reproducibility, within about 10%, is worse when compared to metal standards. This higher scatter of data is probably caused by different thermal contact between sample and sample pan. Experimental DSC data can easily be transformed to the $z(\alpha)$ function using Eq. (3) which is very important for the determination of the most suitable kinetic model. As evident from the maxima α_p^z of the $z(\alpha)$ functions (Tables 1–3), the JMA model can be used for the description of the crystallization process in the case of the bulk sample but it cannot be applied for the fine and coarse powder samples. However, the SB empirical equation can be used for all samples. The DSC curves calculated using this equation (full lines) are compared with experimental data (points)

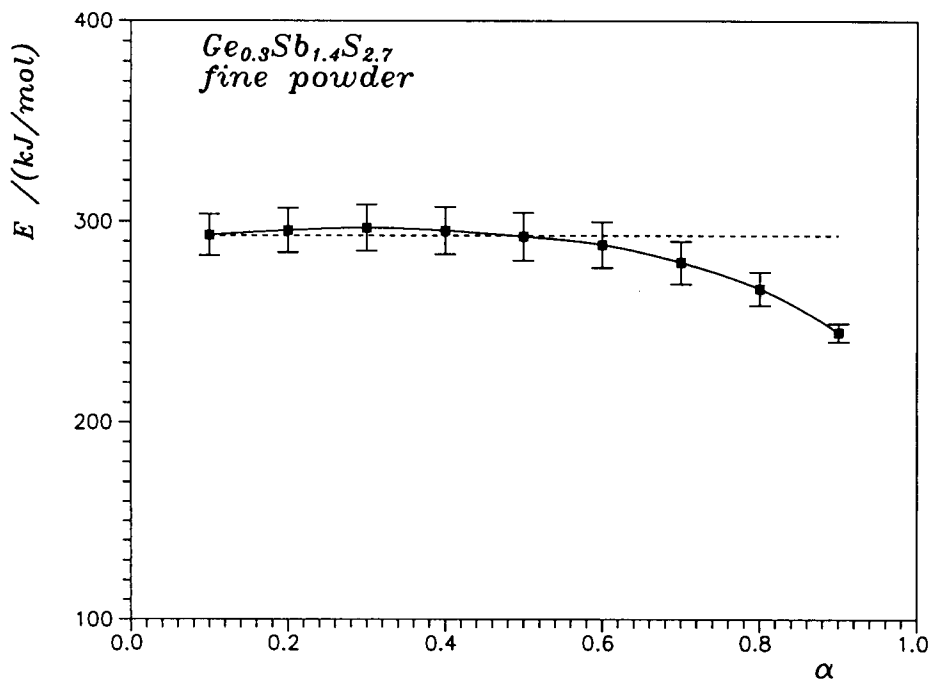


Fig. 2. The activation energy as a function of the crystallization degree. The points were calculated by the Friedman method and the dashed line corresponds to the result of the Kissinger method.

Table 1
Parameters for fine powder ($E = 293 \pm 7 \text{ kJ mol}^{-1}$)

$\beta/(\text{K min}^{-1})$	$\Delta H/(\text{J g}^{-1})$	m	n	$\ln A/(\text{s}^{-1})$	α_p^∞
1	-42.3	0.50	1.15	52.68	0.518
2	-38.5	0.45	1.10	52.41	0.537
4	-51.7	0.60	1.29	52.51	0.555
5	-51.8	0.62	1.44	52.67	0.529
7	-48.8	0.69	1.50	52.83	0.515
10	-54.9	0.68	1.52	52.87	0.507
12	-49.6	0.68	1.49	52.80	0.512
15	-49.2	0.62	1.43	52.68	0.513
18	-46.2	0.61	1.45	52.77	0.499
20	-45.8	0.62	1.45	52.66	0.507
Average:	-48	0.6	1.4	52.7	0.52
Std. dev.:	5	0.1	0.1	0.1	0.02

Table 2
Parameters for coarse powder ($E = 245 \pm 6 \text{ kJ mol}^{-1}$)

$\beta/(\text{K min}^{-1})$	$\Delta H/(\text{J g}^{-1})$	m	n	$\ln A/(\text{s}^{-1})$	α_p^∞
2	-43.0	0.57	0.99	43.05	0.563
5	-44.2	0.63	1.13	43.12	0.539
7	-50.5	0.67	1.21	43.26	0.537
10	-46.3	0.61	1.09	43.33	0.531
15	-50.4	0.62	1.15	43.16	0.544
18	-47.05	0.63	1.42	43.70	0.479
20	-42.6	0.53	1.13	42.95	0.527
Average:	-46	0.61	1.2	43.2	0.53
Std. dev.:	3	0.04	0.1	0.2	0.02

Table 3
Parameters for bulk sample ($E = 124 \pm 10 \text{ kJ mol}^{-1}$)

$\beta/(\text{K min}^{-1})$	$\Delta H/(\text{J g}^{-1})$	m	n	$\ln A/(\text{s}^{-1})$	α_p^∞
1	-41.9	0.50	0.69	17.52	0.586
2	-51.8	0.66	0.74	18.23	0.607
3	-51.6	0.52	0.76	18.23	0.557
5	-48.3	0.67	0.67	18.09	0.645
7	-40.2	0.52	0.52	18.06	0.702
Average:	-47	0.57	0.7	18.0	0.62
Std. dev.:	5	0.07	0.1	0.2	0.05

Table 4
Kinetic parameters for the JMA model

Sample	$E/(\text{kJ mol}^{-1})$	n	$\ln A/(\text{s}^{-1})$
Fine powder	293	1.62	52.17
Coarse powder	245	2.13	42.66
Bulk	124	4.02	16.83
	160	3.05	23.70

in Fig. 3. The kinetic parameters calculated by the method described previously [1] are summarized in Tables 1–3.

Fig. 4 shows the comparison of experimental DSC data (points) for all three types of samples measured at a 5 K min^{-1} heating rate, and curves calculated for the SB equation (full lines) and the JMA model (broken lines). The kinetic parameters for the JMA model are summarized in Table 4. It is evident that the prediction obtained from the $z(x)$ function is correct and that only in the case of the bulk sample does the JMA model give an acceptable approximation of the experimental DSC trace.

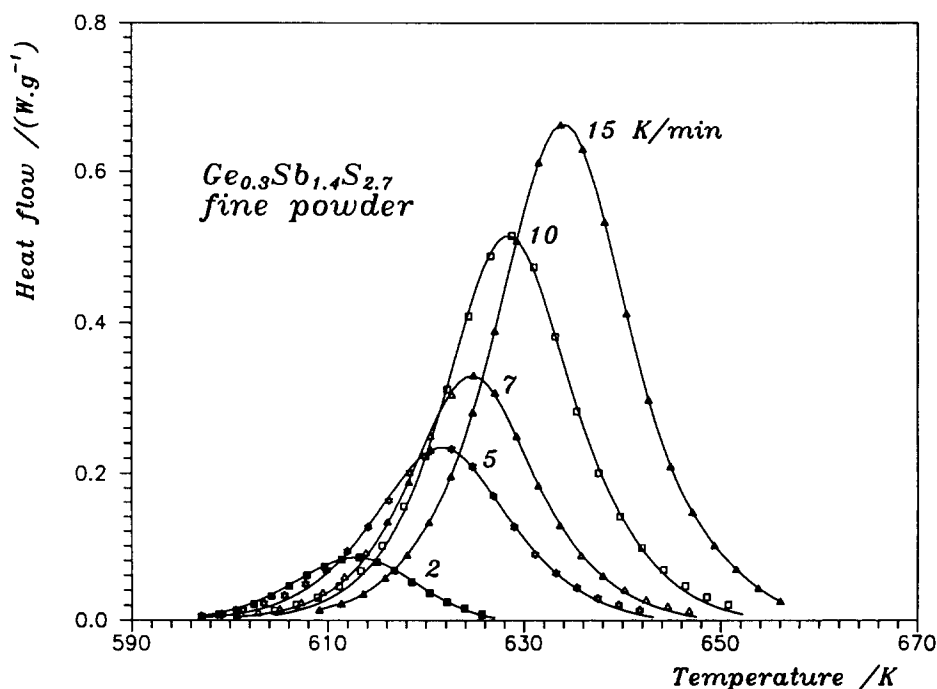


Fig. 3. Experimental DSC data (points) and curves calculated for the SB model using the kinetic parameters summarized in Tables 1–3: (a) fine powder, (b) coarse powder, (c) bulk.

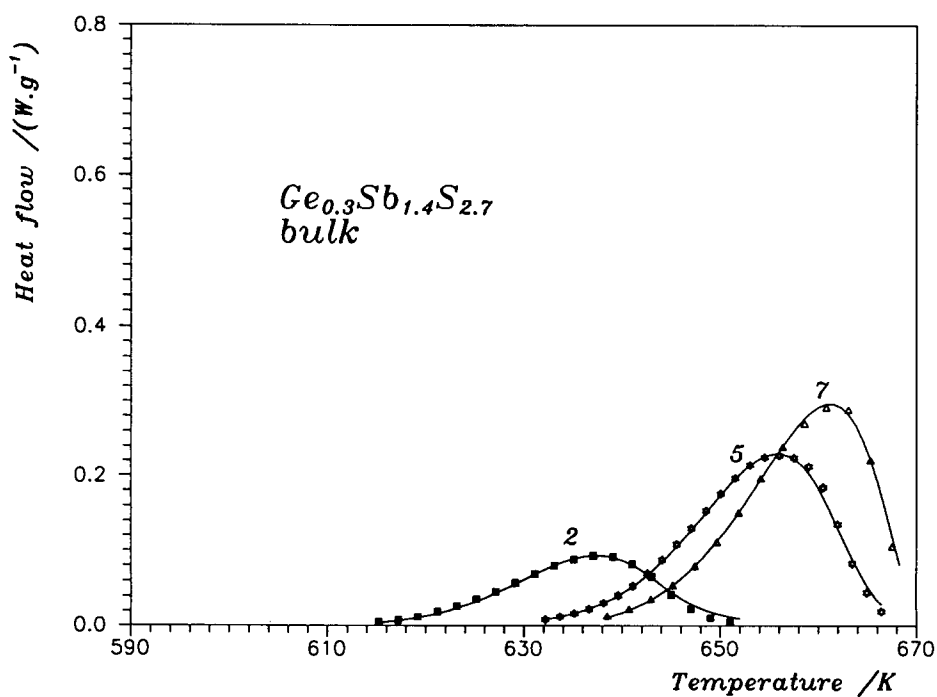
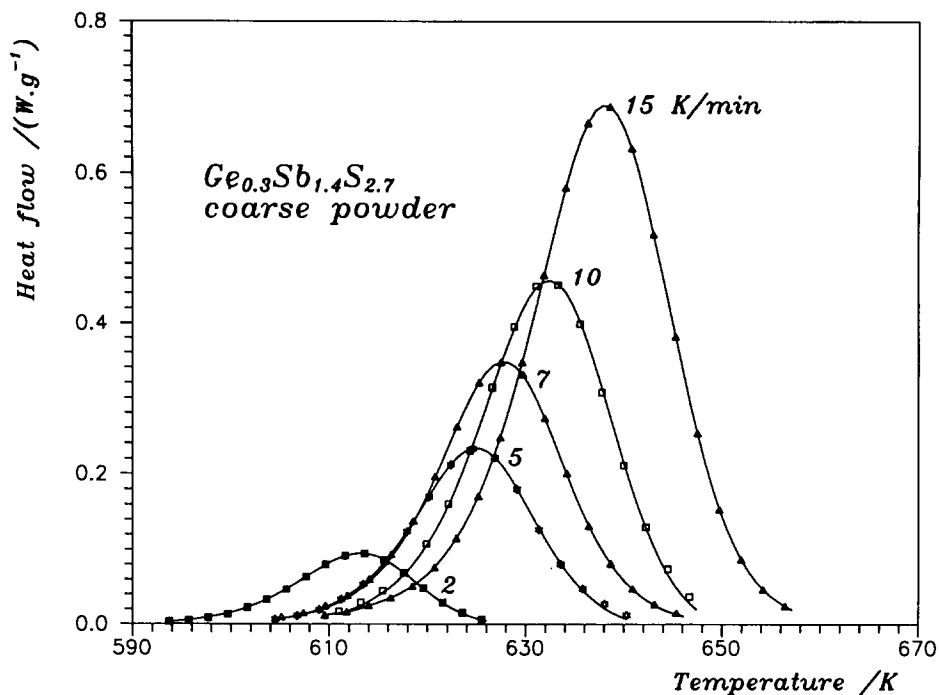


Fig. 3. (Continued)

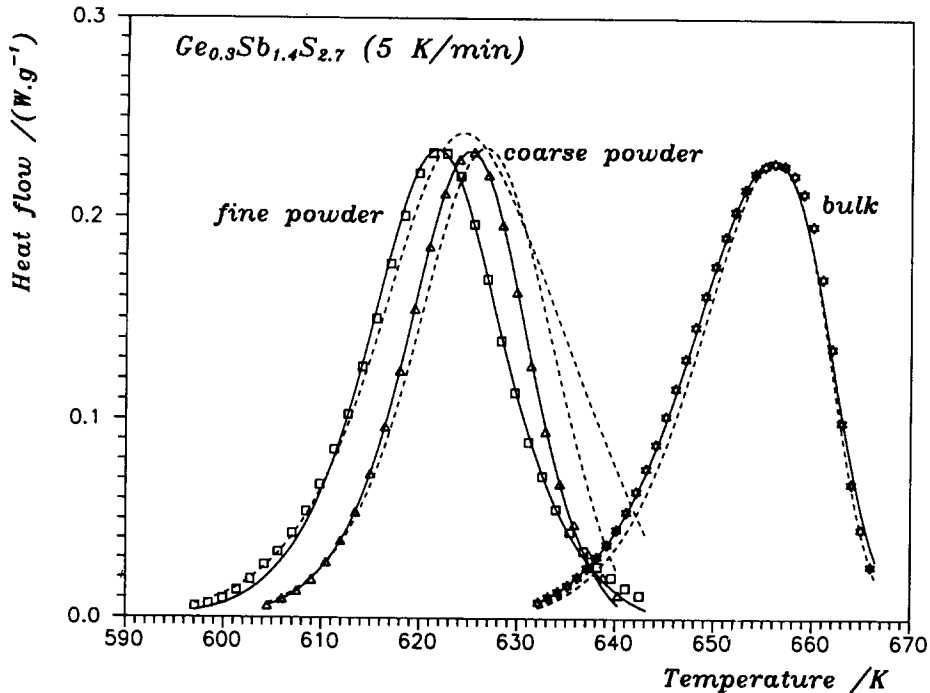


Fig. 4. Comparison of experimental DSC data measured at 5 K min^{-1} and curves calculated for the JMA model (broken lines) and for the SB equation (full line).

We have already mentioned that a DSC measurement mainly reflects the process of crystal growth. Nevertheless, this macroscopic process strongly depends on the concentration and distribution of nuclei in the sample. In the case of homogeneous nucleation, the number of nuclei per unit volume is the sum of the surface nuclei and bulk nuclei formed during the DSC run. In the powdered samples, surface nucleation is dominant due to a higher concentration of surface nuclei related to the specific surface of the sample and the number of bulk nuclei created during a DSC run is small [14]. The DSC peaks are therefore shifted to lower temperatures (Fig. 4). It seems, however, that as well as these primary surface nuclei preexisting in the sample before the DSC run, there is also probably a secondary nucleation process [15] taking place during the macroscopic crystal growth, so that the site saturation condition is no longer fulfilled. As a result, the JMA model cannot be applied in the case of powdered samples.

In the case of the bulk sample, the number of surface nuclei is small and the number of bulk nuclei created during the DSC run cannot be neglected, as in the case of powder samples [14]. The number of bulk nuclei decreases with increasing heating rate and the crystals grow at each heating rate from a different number of nuclei. It seems that the shift in the DSC peak is caused not only by the change in the heating rate but also by the nuclei concentration. So the decrease in the activation energy in the case of the bulk sample (124 kJ mol^{-1}) is probably not real. The kinetic exponent $n = 4.02$ (see Table 4)

is also too high for bulk crystallization. Rysava et al. [16] reported the value of the effective activation energy $E = 160 \text{ kJ mol}^{-1}$ for isothermal crystallization of the bulk sample. If this value is assumed, then the calculated kinetic exponent n for our data is close to 3 which corresponds to growth of three-dimensional spherulitic crystals.

5. Conclusions

It was shown that the sample specific surface has an important influence on the crystallization kinetics of $\text{Ge}_{0.3}\text{Sb}_{1.4}\text{S}_{2.7}$ glass. The DSC crystallization data for the bulk sample can be described by the Johnson–Mehl–Avrami model corresponding to three-dimensional crystal growth. However, the description of DSC data for powder samples is not possible within the JMA model and the empirical Šesták–Berggren equation had to be used. It seems that the condition of site saturation is not fulfilled in this case and that there is probably a secondary nucleation process taking place during macroscopic crystal growth.

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References

- [1] J. Málek, *Thermochim. Acta*, 200 (1992) 257.
- [2] J. Šesták, *Thermophysical Properties of Solids, Their Measurements and Theoretical Analysis*, Elsevier, Amsterdam, 1984.
- [3] H.E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- [4] H.L. Friedman, *J. Polym. Sci.*, C6 (1964) 183.
- [5] T. Ozawa, *Thermochim. Acta*, 31 (1986) 547.
- [6] W.A. Johnson and K.F. Mehl, *Trans. Am. Inst. Mining Met. Eng.*, 135 (1939) 416.
- [7] M. Avrami, *J. Chem. Phys.*, 7 (1939) 1103; *J. Phys. Chem.*, 8 (1940) 212; *J. Phys. Chem.*, 9 (1941) 177.
- [8] D.W. Henderson, *J. Non-Cryst. Solids*, 30 (1979) 301.
- [9] M.C. Weinberg, *J. Non-Cryst. Solids*, 127 (1991) 151.
- [10] G.I. Senum and R.T. Yang, *J. Therm. Anal.*, 11 (1977) 445.
- [11] J. Šesták and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- [12] J. Málek, J.M. Criado, J. Šesták and J. Militky, *Thermochim. Acta*, 153 (1989) 429.
- [13] J. Málek and V. Smrčka, *Thermochim. Acta*, 186 (1991) 153.
- [14] A. Marotta, A. Buri, F. Branda and S. Saielo, in J.H. Simmons (Ed.), *Advances in Ceramics*, Vol. 4, Nucleation and Crystallization in Glasses, The American Ceramic Society Inc., Columbus, USA, 1982, p 146.
- [15] D.W. Henderson and D.G. Ast, *J. Non-Cryst. Solids*, 64 (1984) 43.
- [16] N. Rysava, C. Barta and L. Tichý, *J. Mater. Sci. Lett.*, 8 (1989) 91.