Kinetic analysis of the crystallization processes in the glasses of the Bi–As–S system

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Abstract Kinetic analysis of the crystallization process in $Bi_4(As_2S_3)_{96}$ and $Bi_6(As_2S_3)_{94}$ glasses was performed based on DSC curves recorded under non-isothermal measurement conditions. Samples were thermally treated at different heating rates in the temperature range 300–770 K. The activation energy of crystallization E and the pre-exponential factor K_0 are determined by the Kissinger method and the characteristic crystallization parameters m and n of investigated glasses by the Matusita method. For both crystallization processes the glass with 4 at.% of Bi is characterized by the mechanism of volume nucleation, which is manifested in the form of two-dimensional growth at the first crystallization process, and as three-dimensional at the second one. On the other hand, in the sample with 6 at.% Bi, the average value of the parameter m is close to one, which indicates one-dimensional crystal growth. Compatibility of the values of the parameters m and n suggests that this sample has a large number of crystallization centers, which do not increase significantly during the thermal treatment.

Keywords Chalcogenide glasses · Thermal properties · Crystallization · Crystal growth

Introduction

Doping of chalcogenide glasses with metal atoms with the aim of improving their physical characteristics influences significantly their electronic structure in the sense of inducing new defect states, which may also be reflected on the dominant type of conductivity exhibited by the given glass [1, 2].

The investigation of electric properties of the system $Bi_x(As_2S_3)_{100-x}$ showed a significant increase of its conductivity with the increase in the content of dopant atom [3]. The reason for this lies in the fact that the introduction of Bi into the amorphous matrix results in an increased number of defect states in the optical gap and thus in an increased number of possible hoppings of electric charge carriers [4, 5]. However, X-ray measurements have shown that in the glasses with $x = 8$ and 10 at.% Bi exist crystalline centers incorporated into the matrix [6] and that such a structure could also be responsible for the registered increase in the conductivity of the samples with higher Bi contents.

Hence, the knowledge of crystallization kinetics is of essential importance for the realization of the process of controlled microcrystallization in chalcogenide glasses aimed at the preparation of uniformly distributed microcrystals in the amorphous matrix. The crystallization study in amorphous materials by differential scanning calorimetry has been widely discussed in literature [7, 8].

This study presents the results of the kinetic analysis of a crystallization processes in the glasses with 4 and 6 at.% Bi aimed at the determination of parameters indicating the mechanism and dimensionality of the crystallization process as well as the tendency to crystallization of the investigated glasses.

Experimental

Samples encompassed by the kinetic analysis of crystallization processes belong to the system $Bi_x(As_2S_3)_{100-x}$. The

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procedure of cascade heating to a temperature of 800 °C and annealing in air was applied to prepare glasses with different contents of Bi ($x = 0.5, 2, 4, 6, 8,$ and 10 at.%), and, because of the specific features characterizing the amorphous phase, the compositions with $x = 4$ and 6 at.% Bi were selected for the analysis. Measurements were carried out at DSC Mettler Toledo 822 instrument in the temperature range 300–770 K. With the aim of performing the kinetic analysis of the process, the investigated glasses were treated at four different heating rates.

Results and discussion

A detailed analysis of glasses of the investigated system indicated the absence of the crystallization peak with the samples without and with small contents of Bi [6]. On the other hand, our earlier investigations have showed that in the case of samples that are richer in Bi ($x = 8$ and 10 at.%) the absence of the crystallization peak on DSC curves is a consequence of the presence of crystallization centers already at room temperature (Fig. 1) [6]. In the case of samples with smaller Bi content, crystallization centers occur only after annealing. Thus, doping of the As–S glass system with bismuth atoms in a relatively small range of mass contents influences remarkably its tendency to crystallization.
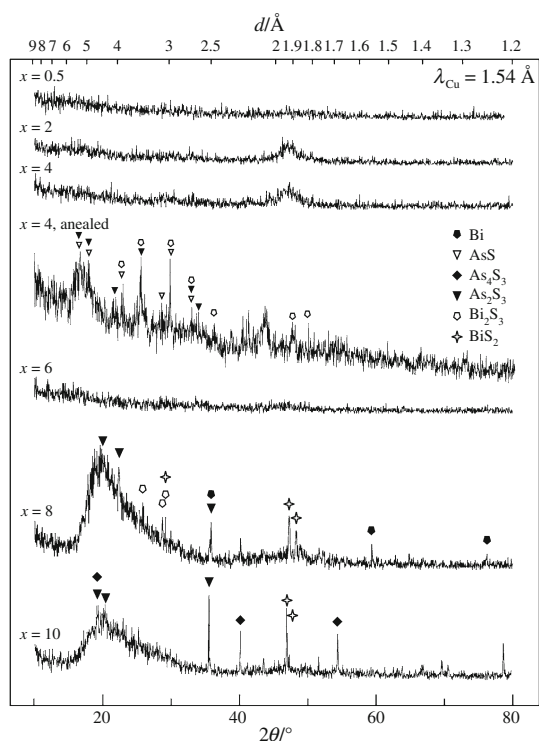
Figures 2 and 3 show the DSC curves for the glasses $Bi_4(As_2S_3)_{96}$ and $Bi_6(As_2S_3)_{94}$ recorded at the different heating rates β.

Their complete interpretation, indicating the existence of different complex effects, was given in relation to the determination of the corresponding thermal parameters [6]. Because of the observed temperature overlapping of the processes of crystallization and melting, thermal treatment of the glasses with lower Bi contents was carried out at lower heating rates. A careful analysis of the DSC curves registered for the sample with 4 at.% Bi indicates the existence of a crystallization processes in the temperature interval of 510–560 K (Fig. 2), which are at lower heating rates observed as two peaks (1 and 2), which enabled analysis of the crystallization process of the glass $Bi_4(As_2S_3)_{96}$ in two stages. The inset of Fig. 2 shows the enlarged segment A of the DSC curve registered at the heating rate $\beta = 5$ K/min in the temperature interval of the occurrence of the two-stage crystallization process. On the other hand, samples with 6 at.% Bi were heated at higher rates with the aim of increasing the enthalpic relaxation
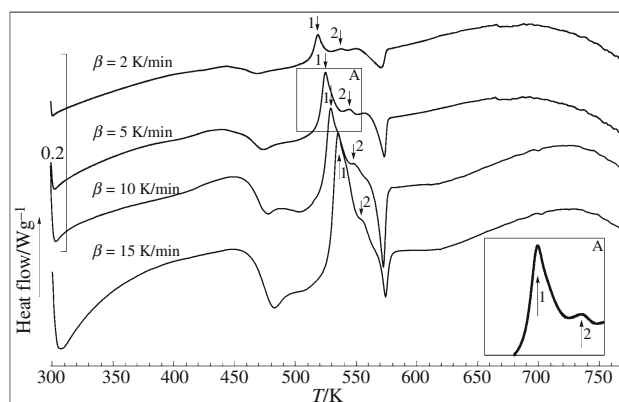

Fig. 1 XRD spectra of the glasses $Bi_x(As_2S_3)_{100-x}$

Fig. 2 DSC curves for the glass $Bi_4(As_2S_3)_{96}$ recorded at different heating rates

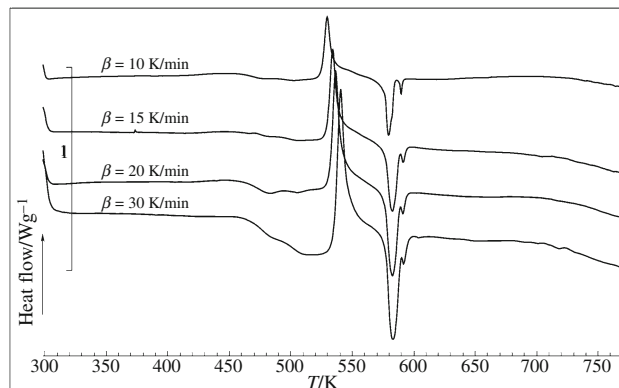**Fig. 3** DSC for the glass $Bi_6(As_2S_3)_{94}$ recorded at different heating rates

peak because of the impossibility of reading the parameter T_g at lower rates of thermal treatment.

A trend of shifting of the range of crystallization and melting to higher temperature with increase in the heating rate was registered with both glasses, which is a common phenomenon observed in the thermal treatment of chalcogenide glasses. At the same time, with the increase in the heating rate, the endothermic peaks of melting of crystalline phases in the glass $Bi_6(As_2S_3)_{94}$ tend to merge into one peak. This can be explained by the small difference in the melting temperatures of the crystalline centers AsS and As_2S_3 identified on the diffractograms of the annealed sample (Fig. 1). Identification of some crystalline centers was made by comparison with diffraction data files [9].

The crystallization process plays a significant role in the determination of the stability of a material and assessment of its practical application. The activation energy of crystallization E can be reduced to the contribution of the activation energy of crystal growth E_G [10, 11]:

$$E \cong \frac{m}{n} E_G \tag{1}$$

where n and m are the parameters whose ratio is determined by the behavior of the nucleation process during the sample heating. The determination of these parameters is of a great importance for the understanding of the process of crystallization as it indicates the mechanism and dimensionality of the crystal growth.

The Kissinger method [12] is based on the calculation of the activation energy E and of the pre-exponential factor K_0. This method describes kinetic parameters in a satisfactory way in a wide range of heating rates β (≤ 100 K/min) in the cases of both homogeneous and heterogeneous reactions of crystallization by the relation:

$$\ln\left(\frac{T_p^2}{\beta}\right) = \ln\left(\frac{E}{RK_0}\right) + \frac{E}{RT_p} \tag{2}$$

where T_p is the temperature corresponding to the maximum of the enthalpy change and R is the universal gas constant. Kisinger equation is frequently used in literature [13, 14] for determining the activation energy of glasses.

Graphical presentation of the dependence described by Eq. 2 for the investigated glasses is given in Fig. 4, and the corresponding quantities in Table 1. For the glass $Bi_4(As_2S_3)_{96}$, the Kissinger method was applied on the crystallization peaks 1 and 2 (Fig. 2). A lower value of the activation energy for the glasses with higher Bi content is in agreement with the conclusion on the enhanced tendency to crystallization of Bi-doped glasses, derived on the basis of the DSC recordings for the investigated system [6].

The characteristic parameters of crystallization m and n were also determined by the method of Matusita et al. [15–17], based on the analysis of the overall temperature
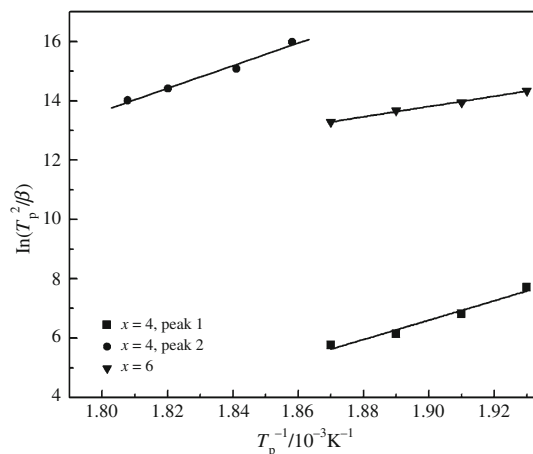

Fig. 4 Dependence of the function $\ln(T_p^2/\ln\beta)$ on $1/T_p$ for the glasses $Bi_x(As_2S_3)_{100-x}$

Table 1 Parameters of the Kissinger analysis of glasses of the system $Bi_x(As_2S_3)_{100-x}$

x/at.%	E/kJ mol^{-1}	K_0/s^{-1}
4	271 ± 3 (peak 1)	9.822×10^{27}
	317 ± 5 (peak 2)	2.998×10^{28}
6	228 ± 2	4.882×10^{15}

interval in which the process of material crystallization takes place.

The Matusita–Sakka relation is of the form [15]:

$$\ln[-\ln(1 - \chi)] = -n \ln \beta - 1.052 \frac{mE}{RT} + \text{const.} \tag{3}$$

where χ is the degree of crystallization at the corresponding temperature and E is the activation energy of crystallization.

The order of reaction n was calculated from the slope of the linear dependence of $\ln(-\ln(1 - \chi)) = f(\ln\beta)$ for the selected temperature by the Ozawa method [18, 19].

Figure 5 illustrates the mentioned functional dependence for the investigated glasses. When concerning the glasses with lower Bi contents, it is necessary to emphasize that this method could be applied only for the temperature region of crystallization of peak 1 (Fig. 2) since the narrow temperature intervals of the appearance of the crystallization peak 2 for this glass do not overlap at the different heating rates.

Values of the parameter n (Table 2) indicate the different mechanisms by which the crystallization process takes place. In a glass with a lower Bi content the first crystallization process is realized as volume nucleation, whereas with the glasses richer in Bi crystallization proceeds from the surface to the bulk. Also, a decreasing trend of the parameter n with increase in temperature of the first
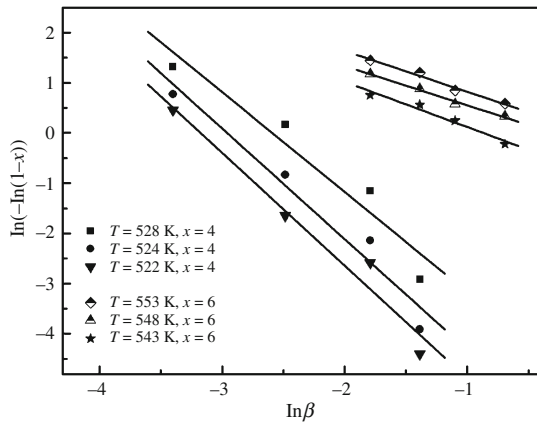
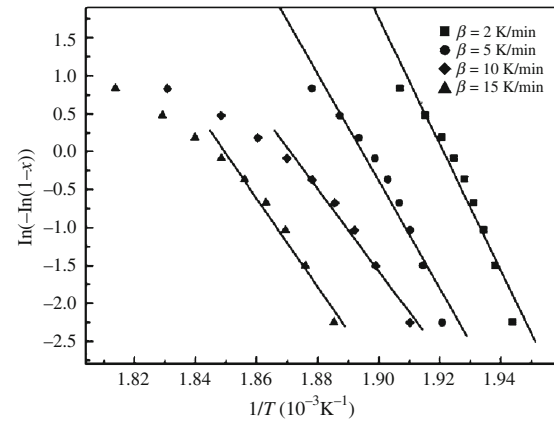**Fig. 5** Dependence of the function $\ln(-\ln(1-\chi))$ on $\ln\beta$ for the glasses $Bi_x(As_2S_3)_{100-x}$

Fig. 6 Dependence of the function $\ln(-\ln(1-\chi))$ on $1/T$ for the glass $Bi_4(As_2S_3)_{96}$

Table 2 Parameters of the Matusita–Sakka relation

$Bi_4(As_2S_3)_{96}$	n	mE/kJ mol^{-1}	m^{cal}	$\frac{mE}{n}$/kJ mol^{-1}	n^{cal}
Peak 1	2.24 (30)	657 (8)	2.42	263 (5)	2.27
		587 (7)	2.16	233 (5)	
	2.21 (31)	428 (6)	1.58	209 (6)	
	1.99 (38)	461 (6)	1.70		
Peak 2		750 (4)	2.37	293 (7)	3.41
		898 (5)	2.83	223 (5)	
		884 (8)	2.79	218 (5)	
		804 (7)	2.54		
$Bi_6(As_2S_3)_{94}$	0.90 (13)	270 (7)	1.18	244 (3)	0.85
	0.78 (5)	202 (4)	0.89		
	0.81 (8)	175 (10)	0.77	245 (2)	
		184 (3)	0.81	246 (3)	

Fig. 7 Dependence of the function $\ln(-\ln(1-\chi))$ on $1/T$ for the glass $Bi_6(As_2S_3)_{94}$

crystallization process in the glass $Bi_4(As_2S_3)_{96}$ indicates a lower rate of nucleation and, most probably, is a consequence of the fact that the process of creating new crystallization centers in the material attains saturation, as mentioned in the literature [20].

The parameter mE, in concordance with the Šatava's model [17, 21], is obtained by fitting the functional dependence $\ln(-\ln(1-\chi)) = f(1/T)$. The obtained results are illustrated in Figs. 6 and 7. Figure 6 presents the functional dependence $\ln(-\ln(1-\chi)) = f(1/T)$ based on data for the first crystallization peak of glass $Bi_4(As_2S_3)_{96}$. The same procedure is applied for the second crystallization peak and appropriate values are presented in Table 2.

In the case of the glass $Bi_4(As_2S_3)_{96}$ certain deviation of experimental points from the linear dependence is observed only at high temperatures at which terminal phase of the first crystallization process takes place, and can be explained in terms of the mentioned saturation of
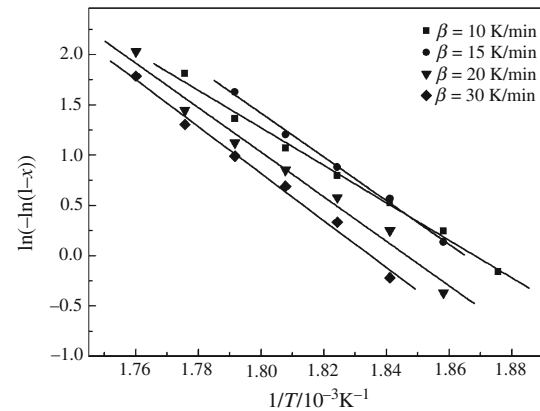
crystallization centers. This explanation is also supported by the fact that the deviation is observed only at higher heating rates.

The calculated values of parameter m are obtained by dividing the quantity mE for particular heating rates with the value of activation energy according to the Kissinger method (Table 1) and they are presented in Table 2.

The value of mE/n was calculated from the slope of the functional dependence $\ln\beta = f(1/T)$ for the corresponding crystalline fractions χ, according to the modified Ozawa–Chen method [14], which is for the investigated glasses illustrated in Figs. 8 and 9. Figure 8 again presents the results related to the first crystallization peak of glass $Bi_4(As_2S_3)_{96}$. The same calculation is done for the second crystallization peak and corresponding values are presented in Table 2.

The value of the reaction order n was also estimated by calculation from the ratio of the quantities mE and mE/n (n^{cal}: Table 2). A very good agreement of the calculated and experimental values was obtained for both samples.
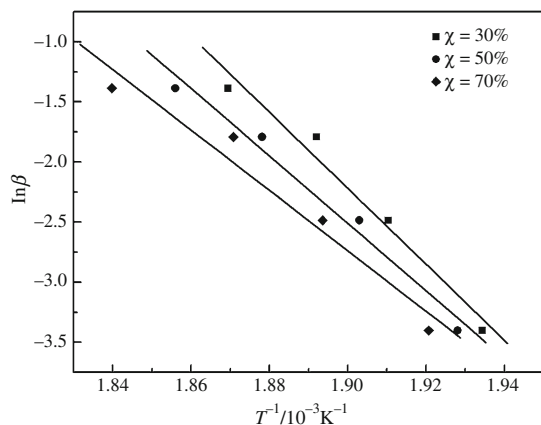
Fig. 8 Dependence of the function $\ln\beta$ on $1/T$ for the glass $Bi_4(As_2S_3)_{96}$

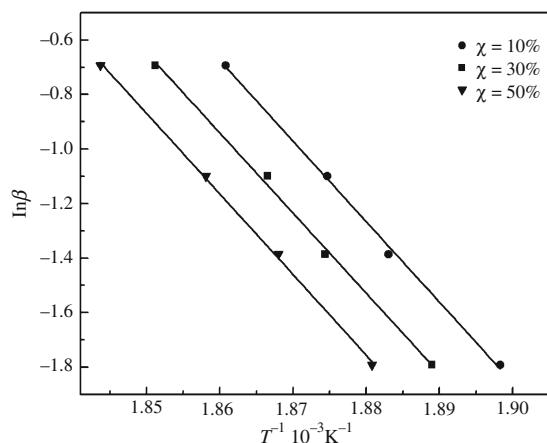**Fig. 9** Dependence of the function $\ln\beta$ on $1/T$ for the glass $Bi_6(As_2S_3)_{94}$

The mean value of the parameter m close to unity for the samples with 6 at.% Bi indicates the one-dimensional growth of crystals. Also, the congruence of the values for parameters m and n suggests that one deals with the case denoted as "site saturation", i.e., that the given sample contained also a sufficiently large number of crystalline centers before the thermal treatment, which does not increase significantly during the heating. The deviations of the parameters m and n from integer values as well as a marked change of the value with the change in heating rate is explained by the dependence of the rate of crystal growth on time.

During the first crystallization process, this dependence is of decreasing nature since it holds that $m < n < m + 1$ (considering mean values of both parameters). Both crystallization processes are characterized by the volume nucleation mechanism, where the first crystallization process is characterized by the dominant two-dimensional and the second one by three-dimensional crystal growth.

Conclusions

Kinetic analysis of the crystallization processes occurring in the glasses $Bi_4(As_2S_3)_{96}$ and $Bi_6(As_2S_3)_{94}$ was carried out based on the DSC curves recorded under non-isothermal conditions. With increase in heating rate the areas of crystallization and melting shift to higher temperatures and there are two crystallization processes in the glasses with lower Bi content. The lower value of activation energy for the crystallization process of glasses with higher Bi contents is in agreement with the assumption on enhanced tendency to crystallization of more Bi-doped glasses. The deviations of the crystallization parameters m and n from integer values for samples with lower Bi content as well as the marked change of the values with the change in heating rate is explained by the time dependence of the rate of crystal growth in this composition. Both crystallization processes in the glass with 4 at.% Bi are characterized by a volume mechanism of nucleation, with a dominant two-dimensional crystal growth in the first and three-dimensional in the second crystallization process. On the other hand, the mean value of parameter m, which is close to unity for the sample with 6 at.% Bi, indicates one-dimensional crystal growth, whereas the correspondence between values of parameters m and n suggests that the given sample possessed a sufficiently large number of crystallization centers before the thermal treatment which does not increase significantly during the heating.

References

1. El-Mandouh ZS, EL-Meleegi HA. Physical properties of Pb–Ge–Se glasses. J Appl Sci Res. 2008;4:296–302.
2. Thoge N, Minami M, Tanaka T. Preparation and conduction mechanism of n-type semiconducting chalcogenide glasses chemically modified by bismuth. J Non Cryst Solids. 1979;38–39:283–8.
3. Šiljegović M, Lukić SR, Skuban F, Petrović DM, Slankamenac M. Analysis of conductivity of glasses from the $(As_2S_3)_{100-x}Bi_x$ system in direct and alternating regimes. J Optoelectron Adv Mater. 2009;11:2049–52.
4. Thoge N, Yamamato Y, Minami T, Tanaka M. Preparation of n-type semiconducting $Ge_{20}Bi_{10}Se_{70}$ glass. J Appl Phys Lett. 1979;34:640–2.
5. Bhatia KL, Parthasarathy G, Sharma A, Gopla ESR. Carrier-sign reversal in Bi-doped bulk amorphous semiconductors $Ge_{20}Te_{80-x}Bi_x$. Phys Rev B. 1988;38:6342–4.
6. Šiljegović M, Štrbac GR, Skuban F, Lukić Petrović SR. Determination of thermal parameters of glasses from the system $Bi_x(As_2S_3)_{100-x}$ based on DSC curves. J Therm Anal Calorim. 2011;105:947–51.

7. Shaaban ER, Kansal I, Shapaan M, Ferreira JMF. Thermal stability and crystallization kinetics of ternary Se–Te–Sb semiconducting glassy alloys. J Therm Anal Calorim. 2009;98:347–54.

8. Tripathi SK, Patial BS, Thakur N. Glass transition and crystallization study of chalcogenide $Se_{70}Te_{15}In_{15}$ glass. J Therm Anal Calorim. 2011;107:31–8.

9. Powder Diffraction File, Inorganic Phases, International centre for diffraction data, Swarthmore, PA, 1986.

10. Ranganathan S, Von Heimendahl M. The three activation energies with isothermal transformations: applications to metallic glasses. J Mater Sci. 1981;16:2401–4.

11. Von Heimendahl M, Kuglstatter G. The activation energies of crystallization in the amorphous alloy METGLAS® 2826A. J Mater Sci. 1981;16:2405–10.

12. Kissinger HE. Variation of peak temperature with heating rate in differential thermal analysis. J Res Nat Bur Stand. 1956;57:217–21.

13. Shaaban ER, Tomsah IBI. The effect of Sb content on glass-forming ability, the thermal stability, and crystallization of Ge–Se chalcogenide glass. J Therm Anal Calorim. 2011;105:191–8.

14. Patial BS, Thakur N, Tripathi SK. Crystallization study of Sn additive Se–Te chalcogenide alloys. J Therm Anal Calorim. 2011;106:845–52.

15. Matusita K, Sakka S. Kinetic study of non-isothermal crystallisation of glass by thermal analysis. Bull Inst Chem Res Kyoto Univ. 1981;59:159–71.

16. Matusita K, Tashiro M. Effect of added oxides on the crystallisation $Li_2O_2SiO_2$ glasses. Phys Chem Glasses. 1973;14:77–80.

17. Matusita K, Komatsu T, Yokota R. Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials. J Mater Sci. 1984;19:291–6.

18. Ozawa T. Kinetics of non-isothermal crystallization. Polymer. 1971;12:150–8.

19. Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jap. 1965;38:1881–6.

20. Colemenero J, Barandiaran JM. Crystallization of $Al_{23}Te_{77}$ glasses. J Non Cryst Solids. 1978;30:263–71.

21. Šatava V. Mechanism and kinetics from non-isothermal TG traces. Thermochim Acta. 1971;2:423–8.