

# KINETIC PARAMETERS DETERMINATION IN NON-ISOTHERMAL CONDITIONS FOR THE CRYSTALLISATION OF A SILICA-SODA-LEAD GLASS

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Two integral isoconversional methods (Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose) and the invariant kinetic parameters method (IKP) were used in order to examine the kinetics of the non-isothermal crystallisation of a silica-soda-lead glass. The objective of the paper is to show the usefulness of the IKP method to determine both the activation parameters and the kinetic model of the investigated process. This method associated with the criterion of coincidence of kinetic parameters for all heating rates and some procedures of the evaluation of the parameter from Johnson–Mehl–Avrami–Erofeev–Kolmogorov (JMAEK) equation led us to the following kinetic triplet: activation energy,  $E=170.5\pm 2.5$  kJ mol<sup>-1</sup>, pre-exponential factor,  $A=1.178\pm 0.350\cdot 10^{10}$  min<sup>-1</sup> and JMAEK model ( $A_m$ )  $m=1.5$ .

**Keywords:** non-isothermal kinetics, silica-soda-lead glass

## Introduction

The glasses containing lead are known from the ancient time and are frequently used for the fabrication of the so-called 'crystal glass' due to their high refractive index. The interest for the glasses containing PbO was reconsidered in the last time due to the possible application in domains as: optics, electronics, nuclear techniques [1–9], as well as due to the possibility offered for toxic and nuclear wastes inertisation [10–14].

The physical-chemical properties of the glasses could be evaluated by their tendency of crystallisation and the quantitative characterisation of this tendency could be obtained by calculation of the kinetic parameters of crystallisation.

Generally, when glasses are heated (the thermal treatment depends on the chemical composition) they may undergo crystallisation and oxide compounds occur (according to the phase diagrams), phenomenon that appears in the DTA curves as an exothermic effect.

The glass crystallisation could occur either in the presence of nucleation agents (method used for the glassceramics production) [15] or in their absence. In the absence of the nucleation agents the crystallisation starts from the surface and only some systems could crystallise in the volume [16]. The crystallisation tendency is strongly influenced by the presence of different oxides due to the asymmetry centres induced into the lattice.

It is important to know the kinetic parameters of crystallisation to establish the technological conditions

of obtaining the glasses, for controlling the fabrication process (determination of the annealing temperature, softening temperature, etc.) as well as for obtaining of pre-established chemical, mechanical and thermal properties.

Several authors studied the crystallisation tendency of the oxide glasses by determining the kinetic parameters of the process [17–25].

The purpose of the present work is the kinetic analysis of the non-isothermal crystallisation of a glass in the ternary system SiO<sub>2</sub>–PbO–Na<sub>2</sub>O.

## Experimental

*The methods used to evaluate the kinetic parameters*

Experimental data for the kinetic analysis of the processes that take place with participation of solid phases, including the crystallisation, can be obtained under different conditions. We are going to analyse data obtained under non-isothermal conditions, with a linear regime of temperature increase in time  $\beta=dT/dt=const.$ , where  $\beta$  is the heating rate,  $T$  is the temperature, and  $t$  is the time). Under such conditions, for a process occurring in a single step, the rate is expressed by the known general equation [26]:

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = Af(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (1)$$

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where  $\alpha$  is the conversion degree,  $A$  is the pre-exponential factor,  $E$  is the activation energy,  $f(\alpha)$  is the differential conversion function and  $R$  is the gas constant.

The use of Eq. (1) assumes that the kinetic triplet ( $E, A, f(\alpha)$ ) describes the time evolution of a physical or chemical change.

Starting from Eq. (1) various methods of kinetic triplet evaluation were developed. Some relatively recent papers [27–39] contain critical analyses of these methods. Such analyses evidenced the importance of the isoconversional methods, which necessitate to record curves  $\alpha$  vs.  $T$  at several heating rates. These methods allow obtaining only the dependence of the activation energy on the conversion degree, without knowing the expression of the conversion function. For  $A$  and  $f(\alpha)$  evaluation other methods are used. Below the methods taken into consideration for kinetic analyses of the glass crystallisation are presented.

### *Isoconversional methods*

The isoconversional procedures can be classified as linear and non-linear ones. In the linear procedures (Friedman (FR) [40], Flynn–Wall–Ozawa (FWO) [41, 42], Kissinger–Akahira–Sunose (KAS) [43], Li–Tang (LT) [44]) the activation energy is evaluated from the slope of a straight line, while in the integral [45, 46] and differential [47] non-linear procedures, the activation energy is evaluated from a specific minimum condition. It was shown [47] that if  $E$  does not depend on  $\alpha$ , all the methods lead to the same value of the activation energy. Therefore in this paper we used only the integral linear isoconversional methods FWO and KAS.

• Flynn–Wall–Ozawa method [41, 42] (FWO method)  
This is an isoconversional linear integral method based on the equation:

$$\ln\beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (2)$$

where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$

is the integral conversion function.

For  $\alpha$ =constant, the plot  $\ln\beta$  vs.  $1/T$ , obtained from curve recorded at several heating rates, should be straight line from the slope of which the activation energy can be evaluated.

• Kissinger–Akahira–Sunose method [43] (KAS method)

This isoconversional integral method is based on the following relationship:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \quad (3)$$

Thus, for  $\alpha$ =constant, the plot  $\ln(\beta/T^2)$  vs.  $1/T$ , obtained from curve recorded at several heating rates, should be a straight line of which slope can be used to evaluate the activation energy.

• The invariant kinetic parameters method [48, 49] (IKP method)

The IKP method is based on the observation [50, 51] that the same experimental curve  $\alpha$ = $\alpha(T)$  can be described quite correctly by several functions of conversion. For a single  $\alpha$ = $\alpha(T)$  curve, the values of the activation parameters, obtained for various forms of  $f(\alpha)$ , are correlated through an apparent compensation effect:

$$\ln A = \alpha^* + \beta^* E \quad (4)$$

where  $\alpha^*$  and  $\beta^*$  are constant parameters (compensation effect parameters).

In order to apply this method for a given heterogeneous reaction,  $\alpha$ = $\alpha(T)$  curves for several heating rates ( $\beta_v, v=1, 2, 3 \dots$ ) should be recorded. A set of conversion functions,  $f_j, j=1, 2, 3 \dots$  is also considered (the expressions of the conversion functions corresponding to heterogeneous processes are given in [37, 52]).

For each heating rate,  $\beta_v$ , the pairs ( $A_{vj}, E_{vj}$ ), characteristic for each conversion function, are determined, using an integral or differential method. In this work the integral method suggested by Coats and Redfern (CR method) [53] that is based on relation (5) will be used.

$$\ln[g(\alpha)/T^2] = \ln[AR/\beta] - E/RT \quad (5)$$

A plot  $\ln[g(\alpha)/T^2]$  vs.  $1/T$  for a given analytical form of  $g(\alpha)$  should be a straight line of which parameters are  $\ln A$  and  $(-E/R)$ .

Using the relation of the apparent compensation effect, the compensation parameters ( $\alpha_v^*, \beta_v^*$ ) are determined for each heating rate. The straight lines  $\ln A_v$  vs.  $E_v$  for several heating rates should intersect in a point which corresponds to the true values of  $A$  and  $E$ . These were called by Lesnikovich and Levchik [48, 49], the invariant activation parameters ( $A_{inv}, E_{inv}$ ). Certain variations of the experimental conditions actually determine a region of intersection in the space ( $\ln A; E$ ). For this reason, the evaluation of the invariant activation parameters is performed using the relation:

$$\ln A_{inv} = \alpha_v^* + \beta_v^* E_{inv} \quad (6)$$

which leads to super correlation equation:

$$\alpha_v^* = \ln A_{inv} - \beta_v^* E_{inv} \quad (7)$$

Thus, a plot  $\alpha_v^*$  vs.  $\beta_v^*$  is actually a straight line the parameters of which allow evaluating the invariant activation parameters.

The IKP method can be used for numerical evaluation of  $g(\alpha)$ , by introducing in Eq. (3) the value of the invariant kinetic parameters. The numerical values of  $g(\alpha)$  could be used for numerical evaluation of  $f(\alpha)$ . Obviously, for each considered  $\alpha$ , the values of  $g(\alpha)$  should not depend on the heating rate. Concerning the accuracy of this procedure of evaluating the function of conversion, one has to emphasise that for each  $g(\alpha)$  from the considered initial set, there are standard deviations of  $\ln A$  and  $E$ , which introduce standard deviations of  $\alpha_v^*$  and  $\beta_v^*$ . By applying the IKP method for the kinetic analysis of simulated and experimental data [37] one has observed that: (a) The standard deviations of  $\alpha_v^*$  and  $\beta_v^*$  have practically the same values for all heating rates; (b) The standard deviations of  $\beta_v^*$  are small and practically negligible, while the standard deviations of  $\alpha_v^*$  can have relatively high values; (c) The values of  $E_{inv}$  are similar to those obtained by using isoconversional methods. The relatively high standard deviations of  $\alpha_v^*$  lead to relatively high errors in the evaluation of  $\ln A_{inv}$ .

Discrimination procedure of the conversion function from a set of pre-established expressions of  $f(\alpha)$

For discrimination among several  $f(\alpha)$  expressions we shall apply the method in accordance with analytical form of  $f(\alpha)$  that, for several heating rates, lead to the same value of the pre-exponential factor [54, 55]. By the application of this method to the kinetic analysis of same non-isothermal data obtained at several heating rates, for a given process, Perez-Maqueda *et al.* [55] have drawn the lines  $\ln[\beta(d\alpha/dT)/f(\alpha)]$  vs.  $1/T$  for a set of conversion functions and for all heating rates. For a given function of conversion one of the following curves family resulted: (a) non-linear curves; (b) linear curves, parallels, but with intercept depending on heating rate; (c) one line for all heating rates. The real conversion function corresponds to the case (c). In this paper, the Eq. (3), according to which  $\ln[\beta(g(\alpha)/T^2)]$  vs.  $1/T$  should be a straight line for all heating rates, will be used for discrimination of the conversion function.

## Experimental

### Glass preparation

The raw materials were PbO, SiO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> produced by Merck (analytical grade reagents). They were weighed according to the chosen receipts, mechanically homogenised for 30 min, melted in an electrical oven at 1200–1300°C and then quenched quickly in cold water. The X-ray diffraction preliminary measurements on thus obtained glasses showed that the glass with a molar composition 49% SiO<sub>2</sub>, 12.8% PbO,

38.2% Na<sub>2</sub>O was the most easily crystallised and therefore it was subsequently used for determining the kinetic parameters of the crystallisation process.

### XRD analysis

X-ray analysis of the glasses was performed with a DRON-3 equipment using CuK $\alpha$  radiation.

### DTA analysis

DTA curves of powder samples with size between 0.3–0.5 mm were recorded with a Q-1500D (MOM, Hungary) Paulik–Paulik–Erdey derivatograph in static air atmosphere in the temperature range 20–1000°C at average heating rate values of 2.32, 5.62, 9.87, 21.54 K min<sup>-1</sup>.

For each crystallisation degree, the local heating rate was determined. These values of the heating rates were used for evaluation of the kinetic parameters.

## Results and discussion

### XRD analysis

From the XRD results the vitreous character of the elaborated glass was established. In order to determine the crystalline phase formed by thermal treatment, XRD analysis were realised on the samples crystallised up to 500°C and in the vitreous transition domain 400°C. In both cases, similar XRD patterns were obtained indicating the crystallisation of one crystalline phase, respectively, the Na<sub>2</sub>OSiO<sub>2</sub>, according to the 15-818 ASTM (Fig. 1).

### DTA analysis

Figure 2 depicts the crystallisation exothermal effect for the investigated material recorded at 5 K min<sup>-1</sup>. Similar curves were obtained for all heating rates. It comes out that the exothermal peak corresponding to the glass crystallisation (noted by CRY) is preceded by a change of the baseline, which corresponds to the vitreous transition (noted by GT). In order to establish

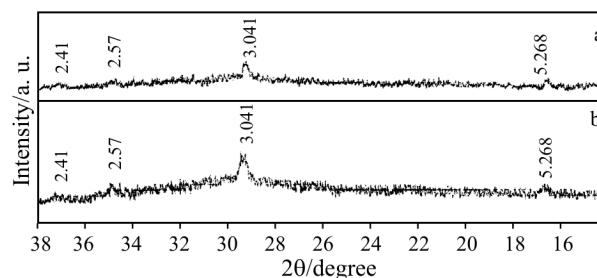
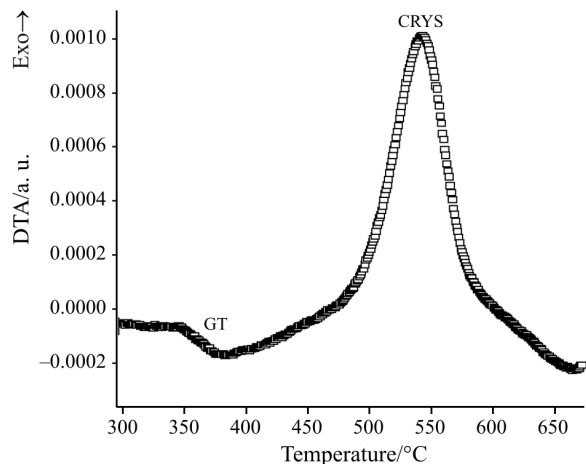
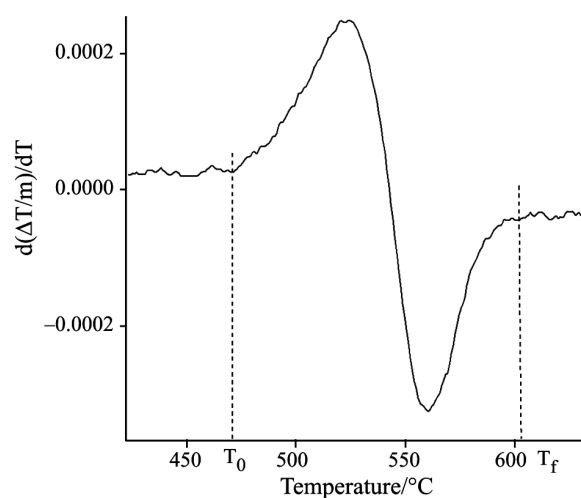


Fig. 1 XRD diffraction patterns of the glass sample heated: a – 400°C, b – up to 500°C



**Fig. 2** The DTA curve for crystallisation of the glass with 49% mol SiO<sub>2</sub>, 12.8% mol PbO, 38.2% mol Na<sub>2</sub>O composition, recorded at the heating rate of 5 K min<sup>-1</sup>



**Fig. 3** The curves  $d(\Delta T/m)/dT$  vs.  $T$  for the crystallisation of investigated glass. ( $\Delta T$  is the various of the temperature,  $m$  is the sample mass)

the temperatures of the beginning and the end of the crystallisation process ( $T_0$ , respectively  $T_f$ ), were drawn the curve  $[d(\Delta T/m)/dT]$  vs.  $T$ . Figure 3 shows a curve obtained using the data from Fig. 2.

The crystallisation degree, corresponding to a given temperature, was evaluated using the relation:

$$\alpha(E) = \frac{s_T}{S} \quad (8)$$

where  $s_T$  is DTA curve area between the initial temperature ( $T_0$ ) and the temperature  $T$ ;  $S$  is the total peak area delimited by the DTA curve.

The principal cause of evaluation of the  $\alpha(T)$  errors in this method is the drawing of the baseline, due to a substantial change of sample heat capacity during measurements. These errors are relatively high at the small and high values of the conversion degree  $\alpha$  (at the beginning and the end of the DTA curve). For this

reason, in the present work, the kinetic analyses of non-isothermal data will be realised for a conversion degree in the range 0.1–0.7.

Through application to Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose isoconversional methods were obtained:

- in the range  $0.1 \leq \alpha \leq 0.7$ , the activation energy does not depend on the crystallisation degree ( $\bar{E}_{FWO} = 173.4 \pm 6.4$  kJ mol<sup>-1</sup>;  $\bar{E}_{KAS} = 168.8 \pm 6.6$  kJ mol<sup>-1</sup>)
- in the range  $0.1 \leq \alpha \leq 0.5$  standard deviations of  $E_{FWO}$  and  $E_{KAS}$  are lower than 10%, while in the range  $0.5 \leq \alpha \leq 0.7$  those deviations increase with  $\alpha$  up to 13.9% for  $E_{FWO}$  method and up to 15.1% for  $E_{KAS}$  method.

The small difference between  $E_{FWO}$  and  $E_{KAS}$  can be assigned to different approximations of the temperature integral, which leads to slight deviations of the relations (2) and (3).

Malek [56] summarised the possible causes of relatively high standard deviations (>10%): (a) erroneous drawing of the DTA baseline due to substantial change of sample heat capacity during the measurements, (b) the measured data correspond to a complicated process (parallel or consecutive processes, branching), (c) thermal inertia effects caused by lower thermal contact between the sample and temperature sensor, (d) low thermal conductivity of amorphous material.

In order to apply IKP method we are going to focus on the  $0.1 \leq \alpha \leq 0.7$  range where  $E$  values are practically constant. The kinetic models  $F_{2/3}$ ;  $F_1$ ;  $F_2$ ;  $F_{2.5}$ ;  $F_3$ ;  $A_{0.5}$ ;  $A_{0.8}$ ;  $A_{1.3}$ ;  $A_2$ ;  $A_3$ , were considered. For these models a straight line is drawn, corresponding to Coats–Redfern method of kinetic parameters evaluation. The values on this straight line are characterised by  $|r|$  close to 1.

The activation parameters were evaluated by Coats–Redfern method. The values of these parameters are shown in Table 1. One can note that the values of the activation parameters depend on the kinetic model as well as on the heating rate. This last dependence is not monotonous (decreasing or increasing). All the  $E$  values differ from those evaluated by means of isoconversional method. That means that none of the considered kinetic models corresponds to the true kinetic model.

As expected, for each heating rate the activation parameters are correlated through the compensation effect relationship (Eq. (4)). The compensation effect parameters are listed in Table 2.

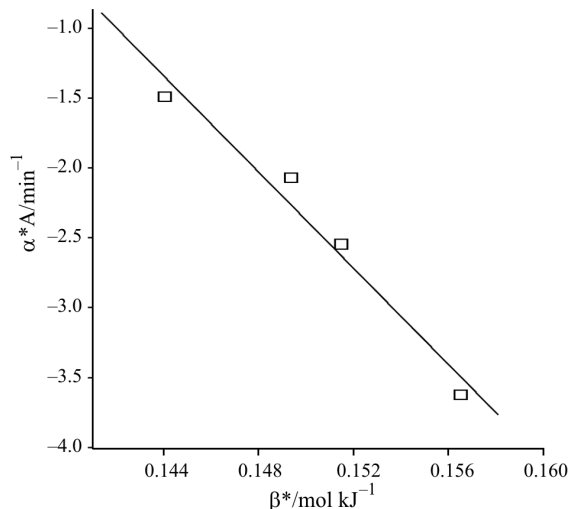
As  $\alpha_v^*$  and  $\beta_v^*$  and are correlated by super-correlation relation (Eq. (7), Fig. 4), one obtains:  $\ln A_{inv} = 23.376 \pm 3.378$  ( $A_{inv}$  expressed in min<sup>-1</sup>),  $E_{inv} = 171.6 \pm 22.5$  kJ mol<sup>-1</sup>. Thus, the value of  $E_{inv}$ , practically equals the values of the activation energy obtained by means of isoconversional methods for  $0.1 \leq \alpha \leq 0.7$ , although the values of  $E$  from Table 2 are

**Table 1.** Values of the activation parameters, obtained for various kinetic models by means of Coats–Redfern method

Model	$\bar{\beta}=2.32\pm 0.22 \text{ K mol}^{-1}$			$\bar{\beta}=5.62\pm 0.27 \text{ K mol}^{-1}$			$\bar{\beta}=9.87\pm 0.19 \text{ K mol}^{-1}$			$\bar{\beta}=21.54\pm 0.35 \text{ K mol}^{-1}$		
	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	$-r$	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	$-r$	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	$-r$	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	$-r$
F <sub>2,3</sub>	221.2±7.6	30.832±1.163	0.9902	281.2±5.0	39.874±0.751	0.9978	270.8±15.6	38.214±0.820	0.9969	231.8±3.8	31.715±0.540	0.9977
F <sub>1</sub>	239.6±6.6	33.824±1.020	0.9936	305.0±3.4	43.691±0.500	0.9992	291.8±4.1	41.470±0.606	0.9985	253.4±2.4	34.963±0.343	0.9992
F <sub>1,5</sub>	269.4±5.0	38.678±0.768	0.9971	343.6±0.7	49.636±0.106	0.9999	325.9±1.6	46.737±0.235	0.9998	284.9±0.2	39.688±0.033	0.9999
F <sub>2</sub>	302.0±3.1	43.963±0.482	0.9991	386.0±3.3	56.235±0.488	0.9995	363.0±1.5	52.459±0.228	0.9999	319.4±2.7	44.829±0.376	0.9995
F <sub>2,5</sub>	337.3±1.5	49.661±0.239	0.9998	431.9±7.2	63.363±1.078	0.9981	403.0±4.9	58.617±0.721	0.9989	356.6±5.8	50.368±0.813	0.9979
F <sub>3</sub>	377.5±2.9	56.137±0.443	0.9995	481.0±11.6	70.985±1.735	0.9959	445.8±8.6	65.182±1.273	0.9972	396.4±9.2	56.279±1.299	0.9957
A <sub>0,5</sub>	492.1±13.2	72.579±2.035	0.9939	623.3±6.7	91.039±0.997	0.9992	597.1±8.2	86.306±1.207	0.9986	520.9±4.8	72.736±0.681	0.9993
A <sub>0,8</sub>	302.7±8.3	43.567±1.273	0.9937	384.5±4.2	55.506±0.624	0.9992	368.1±5.1	52.732±0.756	0.9986	320.3±3.0	44.460±0.427	0.9993
A <sub>1,3</sub>	181.3±5.1	24.768±0.785	0.9933	231.5±2.6	32.530±0.386	0.9991	221.3±3.2	31.012±0.467	0.9985	191.7±1.9	26.133±0.265	0.9992
A <sub>2</sub>	113.3±3.3	14.058±0.512	0.9928	145.9±1.7	19.486±0.252	0.9991	139.1±2.1	18.669±0.305	0.9984	119.7±1.2	15.686±0.173	0.9992
A <sub>3</sub>	71.2±2.2	7.254±0.343	0.9918	92.7±1.1	11.245±0.169	0.9990	88.9±1.4	10.868±0.204	0.9982	75.1±0.8	9.044±0.117	0.9990

**Table 2** The values of the compensation parameters for the data from Table 1

$\beta/\text{K min}^{-1}$	$-\alpha^*, A/\text{min}^{-1}$	$\beta^*/\text{mol kJ}^{-1}$	$r$
2.32	$3.609 \pm 0.323$	$0.1565 \pm 0.0011$	0.99977
5.62	$2.538 \pm 0.327$	$0.1515 \pm 0.0009$	0.99984
9.87	$2.064 \pm 0.332$	$0.1494 \pm 0.0010$	0.99982
21.54	$1.489 \pm 0.322$	$0.1441 \pm 0.00011$	0.99976

**Fig. 4** Verifying the supercorrelation relation Eq. (7)

different. Even the standard deviation of  $E_{\text{inv}}$  ( $\pm 13.1\%$ ) is close to that corresponding to  $E_{\text{FWO}}$  and  $E_{\text{KAS}}$  for  $0.5 \leq \alpha \leq 0.7$ . It follows that IKP method leads to correct values of the activation parameters even if none of the considered kinetic models described correctly the investigated system from kinetic standpoint.

The values of the invariant parameters and the values of  $\alpha(T)$  experimentally determined were used for numerical evaluation of  $f(\alpha)$  for each heating rate. The results are shown in Fig. 5. As one can see, there are some differences among the  $f(\alpha)$  values corresponding to various heating rates. These can be due to the experimental errors, and to the errors of  $\alpha$  evaluation from DTA curves. These errors are reflected in the standard deviations of  $\ln A_{\text{inv}}$  and  $E_{\text{inv}}$ .

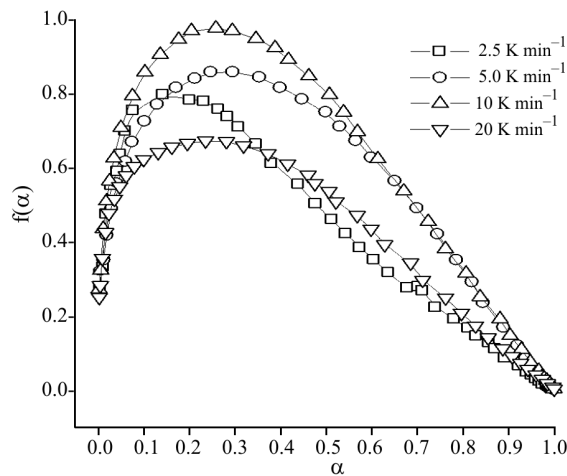
The shapes of the curves  $f(\alpha)$  vs.  $\alpha$  from Fig. 5 suggest the following form for the expression of  $f(\alpha)$ :

$$f(\alpha) = m(1-\alpha)[- \ln(1-\alpha)]^{\left(\frac{1-\alpha}{m}\right)} \quad (9)$$

which corresponds to the kinetic model  $A_m$  (JMAEK model). This kinetic model is characteristic to crystallisation by rapid growth of the nuclei inside an existing (given) matrix [57].

For evaluation of the parameter ' $m$ ' the following methods will be used:

(a) The relation between conversion degree which corresponds to the maximum value of  $f(\alpha)$  (Fig. 5) and  $m$  [56]

**Fig. 5** Dependence of  $f(\alpha)$  on  $\alpha$ 

$$\alpha_M = 1 - \exp\left(\frac{1-m}{m}\right) \quad (10)$$

(b) The method suggested by Malek [56] based on the relation:

$$\frac{d \ln[-\ln(1-\alpha)]}{d\left(\frac{1}{T}\right)} \cong -\frac{mE}{R} \quad (11)$$

It resulted that  $m$  can be calculated from the slope of line  $\ln[-\ln(1-\alpha)]$  vs.  $(1/T)$ , using the value  $E$  determined with an isoconversional method (the  $E_{\text{FWO}}$  will be used).

(c) The method that was suggested by Ozawa [58] according to which  $m$  is the slope of line  $\ln[-\ln(1-\alpha)]$  vs.  $\ln \beta$  at a constant temperature.

The obtained results are presented in Table 3. One may notice that all methods lead to the similar values of ' $m$ ' parameter with acceptable errors. In the other recent works, similar errors in the evaluation of ' $m$ ' parameter were reported [56, 59]. The mean value of  $m$  is  $1.47 \pm 0.19$ . It was pointed out [60, 61] that the values of  $f(\alpha)$  determined by IKP method are especially affected by the errors in evaluation. Consequently, the values of  $f(\alpha)$  determined by IKP method are proportional to the real  $f(\alpha)$  values. In order to discriminate the kinetic model, the shape of  $f(\alpha)$  vs.  $\alpha$  curve determined by IKP could be compared with the shapes of  $f(\alpha)$  vs.  $\alpha$  curves corresponding to known kinetic models. The true kinetic model can be obtained by successive application of IKP method and the criterion of the independence of kinetic parameters on the heating rate. For this purpose the following relation which results from the Coats–Redfern method Eq. (5) was used.

$$\ln \beta \frac{g(\alpha)}{T^2} = \ln \frac{AR}{E} - \frac{E}{RT} \quad (12)$$

**Table 3** The evaluation of the  $m$  parameter

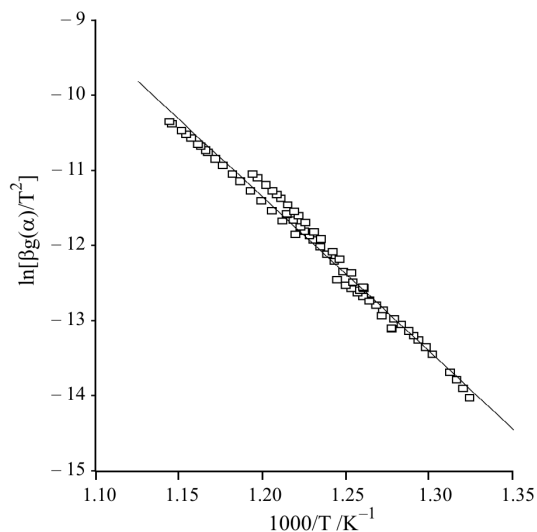
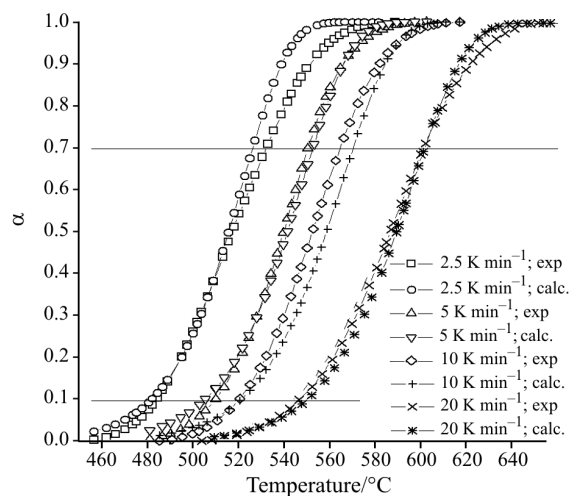
From maximum $f(\alpha)$ vs. $\alpha$		Malek method		Ozawa method	
$\bar{\beta}/\text{K min}^{-1}$	$m$	$\beta/\text{K min}^{-1}$	$m$	$T/^\circ\text{C}$	$m$
2.32	1.20	2.5	$1.41\pm 0.03$	535	$1.38\pm 0.19$
5.62	1.54	5	$1.85\pm 0.02$	540	$1.35\pm 0.19$
9.87	1.43	10	$1.74\pm 0.02$	550	$1.34\pm 0.19$
21.54	1.37	20	$1.54\pm 0.01$		

$$\bar{m}=1.47\pm 0.19$$

The curves  $\ln[\beta(g(\alpha)/T^2)]$  vs.  $1/T$  for the  $g(\alpha)$  corresponding to  $A_m$  kinetic model with  $m=1.3, 1.4, 1.5, 1.6, 1.7$ , and all used heating rates were drawn. All points are placed around/on the same line only for  $m=1.5$  (Fig. 6). From the parameters of this straight line the activation parameters were evaluated obtaining  $\ln A=23.190\pm 0.293$  ( $A$  expressed in  $\text{min}^{-1}$ ) and  $E=170.5\pm 2.5$   $\text{kJ mol}^{-1}$  ( $r=-0.9930$ ). The value  $m=1.5$  can be explained by assuming any of two following mechanism [62]: (1) instantaneous nucleation (saturation of the sites capable of nucleation prior to the process) and subsequent three-dimensional growth of the nuclei by diffusion controlled rate, or (2) constant rate of homogeneous nucleation and one-dimensional growth of the nuclei (branching) through diffusion controlled process.

It comes out that these values of the activation parameters are in good agreement with the values obtained by the other methods mentioned above.

Figure 7 shows comparatively the experimental and reconstructed  $\alpha=\alpha(T)$  curves using kinetic triplet  $\ln A=23.190$  ( $A$  expressed in  $\text{min}^{-1}$ ) and  $E=170.5$   $\text{kJ mol}^{-1}$  and  $A_{1.5}$  model. It comes out that a satisfactory agreement among the experimental and reconstructed  $\alpha=\alpha(T)$  curves exist.

**Fig. 6** The  $\ln[\beta(g(\alpha)/T^2)]$  vs.  $1/T$  line for the Malek model, with  $m=1.5$  and all heating rates**Fig. 7** The experimental and reconstructed  $\alpha=\alpha(T)$  curves for kinetic model  $A_{1.5}$ ,  $E=170.5$   $\text{kJ mol}^{-1}$  and  $\ln A=23.190$  ( $A$  expressed in  $\text{min}^{-1}$ )

## Conclusions

The isoconversional methods Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose as well as IKP method were used for the kinetic analysis of the non-isothermal crystallisation of a soda-lead-silica glass.

The use of the IKP method led to the evaluation of the invariant activation parameters, which were used for numerical evaluation of the function of conversion. In order to determine the kinetic model, IKP method was associated with the criterion of coincidence of the kinetic parameters for all heating rates and some procedures for evaluation of the parameter from the JMAEK equation. The application of isoconversional method and IKP method led to the values of the activation energy, which are all in a very good agreement. It was pointed out that the investigated process is well described by JMAEK model with  $m=1.5$ . The obtained kinetic triplet  $E=170.5\pm 2.5$   $\text{kJ mol}^{-1}$ ,  $A=1.178\pm 0.350\cdot 10^{10}$   $\text{min}^{-1}$  and  $f(\alpha)$  given by JMAEK equation with  $m=1.5$  was used for calculation of  $\alpha$  vs.  $T$  curves.

A satisfying agreement of these calculated curves with those experimentally obtained was put in evidence.

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