

# THERMAL PROPERTIES OF OXIDE GLASSES

## Part II. Activation energy as a criterion of thermal stability of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot n\text{TiO}_2$ glass systems against crystallization

E. Jóna<sup>1\*</sup>, P. Šimon<sup>2</sup>, K. Nemčeková<sup>1,3</sup>, V. Pavlík<sup>1</sup>, G. Rudinská<sup>1</sup> and E. Rudinská<sup>1</sup>

<sup>1</sup>Department of Chemistry and Technology of Inorganic Materials, Faculty of Industrial Technologies, Trenčín University of Alexander Dubček, 020 32 Púchov, Slovakia

<sup>2</sup>Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, 812 37 Bratislava, Slovakia

<sup>3</sup>Institute of Materials and Technologies Research, Faculty of Industrial Technologies, Trenčín University of Alexander Dubček, 020 32 Púchov, Slovakia

Three glasses with the composition of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  (a),  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.03\text{TiO}_2$  (b) and  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.1\text{TiO}_2$  (c) were prepared and the relationship between structural and kinetic parameters of thermal stability vs. crystallization has been studied by X-ray diffraction, IR spectra and thermal analysis. The XRD patterns proved the presence of lithium metasilicate as a primary crystalline phase which subsequently transformed to lithium disilicate where the transformation is supported by the presence of  $\text{TiO}_2$ . The order of thermal stability vs. crystallization of studied glass systems based on the results of XRD is  $(a)<(b)<(c)$ . The same order was obtained from the values of activation energy. It has been shown that the values of activation energies obtained from the Ozawa and Kissinger methods are equivalent and that the Kissinger method should be used to obtain the activation energy from the dependence of the maximum peak temperature on the heating rate. It has been discussed that the activation energy represents only an incomplete description of the kinetics of the crystallization process.

**Keywords:** diffraction and spectral properties,  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot n\text{TiO}_2$  glass systems, thermal stability

### Introduction

Thermal analysis is an indispensable tool for studying the thermal stability of glasses vs. crystallization [1, 2]. In order to characterize the tendency of glass to crystallize it can be encountered that, as a criterion, characteristic temperatures from DTA curves [3–5], values of activation energy, ( $E_a$ ) [6, 7] or combined criteria such as  $E_a/RT$  [8] or the crystallization rate constant  $k(T)$  [9] are used.

In our previous paper the criteria have been reviewed and tested [3]. The results have shown that, for a set of glasses, individual criteria provide different order of thermal stability [3, 8]. Therefore, a new criterion for evaluating the thermal stability of glasses based on the induction period of crystallization has been suggested and verified [10]. In this paper the relation between structural parameters (diffraction and IR spectral data) and kinetic parameters (the values of activation energy) for  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot n\text{TiO}_2$  systems ( $n=0; 0.03$  and  $0.1$ ) has been studied from the point of view of thermal stability vs. crystallization.

### Experimental

#### Preparation of glasses

Analytical grade reagents  $\text{Li}_2\text{CO}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  were mixed by ball-milling and then melted in a platinum crucible at  $1400^\circ\text{C}$  for 2 h. The melts were quenched by pouring them into a cold steel mold.

#### Methods

The thermal stability of glass was studied using a TA Instrument 2960 SDT (USA). The DTA curves were measured in air using a platinum crucible. About 20–24 mg of powdered samples with a particle size of 0.16–0.10 mm and heating rates of 5, 10, 15, 20 and  $25^\circ\text{C min}^{-1}$  were used. Calibration of the temperature and enthalpy scales was made using pure  $\text{SiO}_2$  ( $T_{\alpha\rightarrow\beta} = 575^\circ\text{C}$ ;  $\Delta H = 20.19 \text{ J mol}^{-1}$ ).

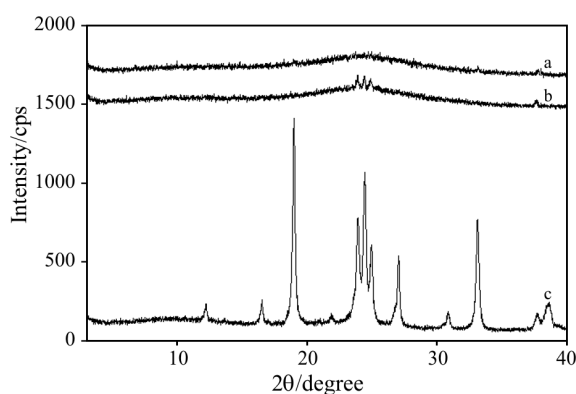
Powder diffraction patterns were taken using a Philips 1730/50 (USA) reflection diffractometer with  $\text{CuK}_\alpha$  radiation.

The infrared spectra were recorded at room temperature with a Nicolet Magna 750 FTIR (USA) spectrometer in the range of  $4500\text{--}400 \text{ cm}^{-1}$ .

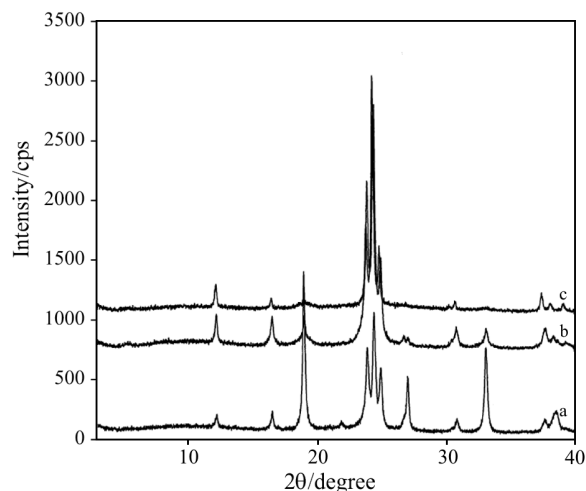
\* Author for correspondence: jona@fpt.tnuni.sk

## Results and discussion

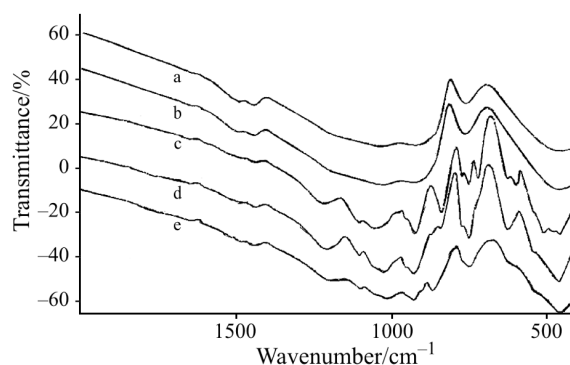
The glass samples will be further denoted as follows: (a)  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ ; (b)  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.03\text{TiO}_2$ ; (c)  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.1\text{TiO}_2$ . Figure 1 shows the XRD patterns of the powdered sample (a) heated for 2 h at various temperatures and subsequently quenched to the room temperature. In Fig. 2 there are shown the XRD patterns of all three glass samples after being heated for 2 h at 595°C. The diffraction data are summarized in Table 1. Infrared spectra of the heat-treated samples are compared in Fig. 3 and the assignment of the infrared bands of studied glass systems is given in Table 2. Table 3 contains the characteristic temperatures recorded at the heating rates of 5, 10, 15, 20 and 25°C min<sup>-1</sup>. The activation energies of crystallization of the glass samples are listed also in Table 3.



**Fig. 1** XRD patterns of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass heated for 2 h and quenched to the room temperature. Curves: a – heated at 535°C; b – heated at 555°C; c – heated at 595°C



**Fig. 2** XRD patterns of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot n\text{TiO}_2$  systems heated at 595°C for 2 h and quenched to the room temperature. Curves: a –  $n=0$ , b –  $n=0.03$ , c –  $n=0.1$



**Fig. 3** Infrared spectra of powdered glass samples heated for 2 h and quenched to the room temperature. Curves: a –  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  heated at 535°C; b –  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  heated at 555°C; c –  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  heated at 595°C; d –  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.03\text{TiO}_2$  heated at 595°C; e –  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot 0.1\text{TiO}_2$  heated at 595°C

The XRD patterns shown in Fig. 1a and b are typical for the amorphous state of the as-quenched  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  system. When the temperature of heat treatment changed from 550 to 595°C, the crystalline phases are formed (Fig. 1c). Although lithium disilicate has been also formed, the lithium metasilicate  $\text{Li}_2\text{SiO}_3$  was the primary crystalline phase (Table 1) [11]. Diffraction peaks at  $2\Theta=18.94^\circ$  ( $d=4.68$  Å) and  $2\Theta=27.50^\circ$  ( $d=3.3$  Å) are especially characteristic for  $\text{Li}_2\text{SiO}_3$ . On the other hand, the addition of  $\text{TiO}_2$  to  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  system heated at 595°C results in a successive transformation of  $\text{Li}_2\text{SiO}_3$  to  $\text{Li}_2\text{Si}_2\text{O}_5$ . In this case, the diffraction peaks of  $\text{Li}_2\text{SiO}_3$  disappear and the intensities of the peaks characteristic for  $\text{Li}_2\text{Si}_2\text{O}_5$  increase ( $2\Theta=23.78^\circ$  and  $24.29^\circ$ , curves b and c in Fig. 2). The peak at  $2\Theta=18.94^\circ$  is diagnostic for the formation of crystalline form of  $\text{Li}_2\text{SiO}_3$ . Its intensity increases in the order (a)>(b)>(c). Hence, it can be concluded that the order of the stability of the studied glass systems against crystallization is (a)<(b)<(c).

The structural changes occurring in the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  system during heating at different temperature and/or increasing of  $\text{TiO}_2$  content are manifested also in infrared spectra (Fig. 3). It is evident that the increase of the heat treatment temperature of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  system brings about the appearance of new absorptions, especially for the treatment at 595°C in the region 450–1000 cm<sup>-1</sup>. The broad band at 780 cm<sup>-1</sup> corresponding to the  $\nu_{\text{sym}}(\text{Si}-\text{O}-\text{Si})$  vibration, splits into three components and the sharp band at ~850 cm<sup>-1</sup> can be connected with  $\text{Li}_2\text{CO}_3$  impurities [12–14]. As Table 2 shows, the addition of  $\text{TiO}_2$  to  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  system causes two main effects. There are observed the down shifts of the fundamental modes  $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$  ( $\nu_1, \nu'_1$ ),  $\nu(\text{Si}-\text{OH})$  and  $\nu(\text{Si}-\text{O}-\text{M})$  and further the disappearance of some ab-

**Table 1** Diffraction data of the studied glass systems heated at 595°C for 2 h: a – Li<sub>2</sub>O·2SiO<sub>2</sub>, b – Li<sub>2</sub>O·2SiO<sub>2</sub>·0.03TiO<sub>2</sub>, c – Li<sub>2</sub>O·2SiO<sub>2</sub>·0.1TiO<sub>2</sub>

a			b			c			Li <sub>2</sub> SiO <sub>3</sub>		Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	
2θ/°	J/J <sub>0</sub>	d/Å	2θ/°	J/J <sub>0</sub>	d/Å	2θ/°	J/J <sub>0</sub>	d/Å	J/J <sub>0</sub>	d/Å	J/J <sub>0</sub>	d/Å
12.16	9	7.273	12.16	12	7.273	12.12	10	7.296	–	–	6	7.29
16.47	2	5.378	16.48	12	5.375	16.42	4	5.394	–	–	17	5.395
18.94	100	4.682	18.97	13	4.674	–	–	–	81	4.679	–	–
21.83	3	4.068	–	–	–	–	–	–	–	–	–	–
23.86	49	3.726	23.87	64	3.725	23.78	35	3.739	–	–	71	3.727
24.39	73	3.646	24.38	100	3.648	24.29	100	3.661	–	–	45	3.646
24.92	37	3.570	24.94	34	2.567	24.81	26	3.586	–	–	100	3.575
27.00	33	3.300	27.04	2	3.295	–	–	–	100	3.302	–	–
30.84	7	2.897	30.80	8	2.901	30.71	3	2.909	–	–	9	2.904
33.09	54	2.705	33.13	7	2.702	–	–	–	42	2.699	–	–
37.5	5	2.396	37.57	6	2.392	37.45	8	2.399	–	–	26	2.387
37.67	7	2.386	37.77	8	2.380	–	–	–	–	–	–	–
38.38	11	2.343	38.36	5	2.345	38.23	3	2.352	–	–	15	2.348
38.53	13	2.335	–	–	–	–	–	–	23	2.335	–	–
38.69	12	2.325	–	–	–	–	–	–	42	2.33	–	–
–	–	–	39.32	3	2.229	39.14	3	2.3	–	–	–	–

**Table 2** Selected absorption maxima of the glass systems heated at 595°C for 2 h: a – Li<sub>2</sub>O·2SiO<sub>2</sub>, b – Li<sub>2</sub>O·2SiO<sub>2</sub>·0.03TiO<sub>2</sub>, c – Li<sub>2</sub>O·2SiO<sub>2</sub>·0.1TiO<sub>2</sub>

Assignment [13]		Band position/cm <sup>-1</sup>		
		a	b	c
ν <sub>as</sub> Si–O–Si	ν <sub>1</sub> '	1221(s)	1213(s)	1188(s)
	ν <sub>1</sub>	1063(br)	1027(br)	1018(br)
νSi–OH		962(sh)	960(sh)	935(sh)
νSi–O–M		932(s)	936(s)	–
		783(sh)	781(sh)	–
δ/ν <sub>sym</sub> Si–O–Si	ν <sub>2</sub>	761(s)	760(s)	760(s)
		731(s)	–	–
νM–O		636(sh)	636(s)	–
		609(sh)	–	–
ν <sub>as</sub> Si–O–Si		468(br)	469(br)	467(br)

sorptions with increasing the titanium content. These effects in infrared spectra are in a close relation with the structural transformations observed in the diffraction patterns.

The exothermic DTA peaks having the maximum at about 587–647°C (Table 3) arise due to the crystallization process which is related to the formation of crystalline phase of lithium metasilicate and/or lithium disilicate as dominant components, as detected in the X-ray diffraction measurements. To determine the activation energy associated with the crystallization process, the Kissinger and Ozawa

**Table 3** Kinetic parameters of the glass systems under study: a – Li<sub>2</sub>O·2SiO<sub>2</sub>; b – Li<sub>2</sub>O·2SiO<sub>2</sub>·0.03TiO<sub>2</sub>; c – Li<sub>2</sub>O·2SiO<sub>2</sub>·0.1TiO<sub>2</sub>

Criterion/sample	a	b	c
T <sub>p</sub> /°C*	588, 602, 610, 619, 628	597, 611, 620, 625, 632	614, 625, 632, 631, 647
E(T <sub>p</sub> )/kJ mol <sup>-1</sup>	251	289	298
E(β)/kJ mol <sup>-1</sup>	266	304	332

\*heating rates 5, 10, 15 and 25°C min<sup>-1</sup>

methods, expressed by Eqs (1) and (2), were applied [3]:

$$\ln(\beta/T_p^2) = -E(T_p)/(RT_p) - \ln E/R + \ln A \quad (1)$$

$$\ln \beta = -E(\beta)/(RT_p) + C \quad (2)$$

where T<sub>p</sub> is the maximum peak temperature on the DTA record, E(T<sub>p</sub>) and E(β) are the activation energies obtained from the Kissinger and Ozawa methods, respectively.

The activation energies E(T<sub>p</sub>) and E(β) are given in Table 3. On the basis of their values the resulting order of the stability against crystallization is (a)<(b)<(c) [3], i.e. the glasses with TiO<sub>2</sub> are more stable against crystallization than the glass without TiO<sub>2</sub>. This order is in agreement with the one based on the induction period of crystallization [10]. The increase of activation energy with TiO<sub>2</sub> content in the glass composition can be explained

by the formation of lithium disilicate. The activation energy for crystallization of lithium metasilicate is much lower than that for the crystallization of lithium disilicate [11, 15]. When the temperature and  $\text{TiO}_2$  content increase, the lithium metasilicate transforms into lithium disilicate which should bring about a higher value of the activation energy of the global crystallization process (Table 3). Consequently, it can be assumed that the formation of  $\text{Li}_2\text{Si}_2\text{O}_5$  from  $\text{Li}_2\text{SiO}_3$  belongs to rate-limiting steps of the crystallization mechanism, at least in the case of glasses containing  $\text{TiO}_2$ .

As seen from Table 3, the activation energies  $E(T_p)$  and  $E(\beta)$  give the same order of the glass stability. This agreement is self-explanatory since it can be shown that  $E(T_p)$  and  $E(\beta)$  are not independent. After expressing  $\ln\beta$  both from Eqs (1) and (2) and differentiating the resulting equations with respect to  $T_p$ , one can get:

$$E(T_p) = E(\beta) - 2RT_p \quad (3)$$

Hence,  $E(T_p)$  is lower than  $E(\beta)$  by  $2RT_p$ ; this fact is seen also from the data presented in Table 3. Equation (3) shows that  $E(T_p)$  and  $E(\beta)$  are equivalent so that only one of them should be used as a criterion for the thermal stability of glass against crystallization. The Ozawa method is isoconversional so that the activation energy is obtained from a dependence of the isoconversional temperature on the heating rate using Eq. (2). Our experience is that the conversion corresponding to the peak maximum is not constant, it slightly moves with the heating rate. In the Kissinger method, the activation energy is obtained from a dependence of the temperature of peak maximum on the heating rate using Eq. (1); the constant value of conversion is not a prerequisite [16]. Thus, the Kissinger method should be used for obtaining the activation energy from the peak maxima temperatures and the activation energy  $E(T_p)$  should be preferred to  $E(\beta)$  as a criterion of the glass stability against crystallization.

The order of the stability against crystallization  $(a)<(b)<(c)$ , resulting from the values of activation energy, correlates with the order of maximum peak temperatures and the inflexion point temperatures. These characteristic temperatures increase with the increasing content of  $\text{TiO}_2$ ; the greater these temperatures, the more stable the glass should be. The characteristic temperatures increase with the increasing heating rate. The advantage of the use of activation energy as a criterion is that it is constant and independent of the heating rate. However, one should be extraordinarily careful when drawing conclusions since the activation energy is only one of the three components of the kinetic triplet. Knowing just the value of the activa-

tion energy, description of the kinetics of the crystallization process is incomplete.

## Conclusions

The relation between structural and kinetic parameters of thermal stability vs. crystallization of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2\cdot n\text{TiO}_2$  systems ( $n=0; 0.03$  and  $0.1$ ) has been studied by X-ray diffraction, IR spectra and thermal analysis. The XRD patterns proved the presence of lithium metasilicate as a primary crystalline phase which subsequently transformed to lithium disilicate. The transformation is supported by the presence of  $\text{TiO}_2$ . This structural change causes down shifts and disappearance of some fundamental modes in IR spectra.

The order of thermal stability vs. crystallization of studied glass systems based on the values of activation energy is  $(a)<(b)<(c)$ . The increasing value of activation energy is connected with the formation of lithium disilicate which is accompanied with higher value of activation energy than the formation of lithium metasilicate. It has been shown that the values of activation energies obtained from the Ozawa and Kissinger methods are equivalent and that the Kissinger method should be used to obtain the activation energy from the dependence of the maximum peak temperature on the heating rate. It has been discussed that the activation energy represents only an incomplete description of the kinetics of the crystallization process and one should keep this in mind when drawing conclusions.

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