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# Thermal properties of oxide glasses

## Part IV. Induction period of crystallization as a criterion of thermal stability of $M_2OSiO_2$ (M = Li, Na) glass systems against crystallization

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**Abstract** A criterion based on the length of induction period of crystallization was used to evaluate the thermal stability of $M_2O{\cdot}SiO_2$ (M = Li, Na) glasses against crystallization. It was founded out that the stability of studied glasses against crystallization is $Li_2O{\cdot}SiO_2 < Na_2O{\cdot}SiO_2$. The results coincide with the order determined by stability criteria based on temperatures and the values of activation energy. A criterion based on the length of induction period enables to discriminate among the thermal stabilities of the silicate glass systems.

**Keywords** $M_2O{\cdot}SiO_2$ (M = Li, Na) glasses · Thermal stability · The length of induction period of crystallization

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## Introduction

Glass and glass–ceramics have attracted much attention because of their unique properties, such as excellent chemical durability, amazing optical transparency, and excellent electrical properties. Besides the traditional silicate glass, numerous new glass systems have been developed under the demand of modern industrial applications [1–3].

Therefore, it is very important to evaluate the thermal stability of glasses against crystallization [4–6]. Dietzel introduced the first simple criterion, $\Delta T = T_x - T_g$, where $T_x$ is the crystallization starting temperature and $T_g$ is the glass transition temperature. Hrubý [7] proposed the $H_f$ criterion, $H_f = (T_x - T_g){\cdot}(T_m - T_p)$. Several authors [8, 9] suggested that the crystallization activation energy could also be used to evaluate the glass stability, but criteria based on the activation energy, or crystallization rate constants do not always fit with the actual experimental observations. Cheng [6] evaluated a criterion $k_f(T) = \upsilon\exp\left[-E/RT(T_p - T_f)/T_f\right]$, where $T_f$ is the inflection point temperature and $T_p$ is the maximum peak temperature on the DTA curves. Unfortunately, these stability criteria are not fixed physical parameters, since they mostly depend on the heating rate and temperature. Thermal and spectral analyses are very useful methods for materials characterization. Therefore, many authors have used these techniques for various materials characterization [10–30].

In this paper, criterion for evaluating the thermal stability of glasses based on the induction period on the crystallization is used [31] and its validity is verified by applying it to $Li_2O{\cdot}SiO_2$ and $Na_2O{\cdot}SiO_2$ systems. Comparisons are also made between this criterion and some existing criteria.

## Experimental

### Preparation of glasses

Analytical grade reagents $Li_2CO_3$, $Na_2CO_3$, and $SiO_2$ were mixed by ball-milling and then melted in a platinum crucible at ~1,400 °C for 2 h. The melts were quenched by pouring into a cold steel mold. The amorphous nature of the quenched glasses was confirmed by X-ray diffraction.

### Measurements

Thermal stability of glasses was studied on a computerized Derivatograph OD 102 (MOM Budapest). DTA measurements were carried out in a platinum crucible, the purge gas war air. About 200 mg of powdered samples with a particle size 0.10–0.16 mm and heating rates of 10, 15, 20, and 25 °C/min were used.

## Results and discussion

Typical DTA curves of $Li_2O{\cdot}SiO_2$ (a) and $Na_2O{\cdot}SiO_2$ (b) systems at the heating rate 10 °C/min are shown in Fig. 1.

The onset temperature, $T_x$, and the maximum peak temperature, were directly determined from DTA curves. The inflection point temperature, $T_f$, was determined from the maximum peak temperature on DTA curves. All these characteristics are summarized in Table 1. As shown in Fig. 1, as the crystallization proceeds, an exothermic peak is observed since the crystallization is accompanied by a rapid heat evolution. The point of the steep increase of DTA record due to crystallization is taken as the onset temperature $T_x$.

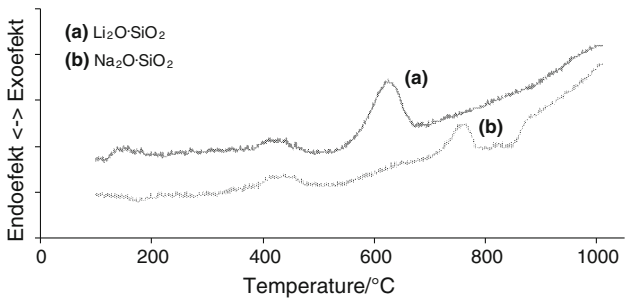


**Fig. 1** DTA curves of $Li_2O{\cdot}SiO_2$ (*a*) and $Na_2O{\cdot}SiO_2$ (*b*) systems at the heating rate 10 °C/min

The theoretical values of onset temperature $T_x$ are given by Eq. (1) ($\beta$—heating rate) [31]:

$$\beta = \int_0^{T_x} \frac{dT}{A\exp[B/T]} \tag{1}$$

The parameters $A$ and $B$ in Eq. (1) have been obtained by minimizing the sum of squares between experimental and theoretical values of onset temperature $T_x$ for various heating rates by the simplex method [32]. The agreement between experimental and calculated values of onset temperatures for various heating rates is shown in Fig. 2.

The values $A$ and $B$ are given as

$$A = \frac{A_K}{F(\alpha_i) - F(0)}, \quad B = E_a/R \tag{2}$$

($A_k$ is the pre-exponential factor; $E_a$ is the activation energy) and the adjustable parameter $B$ for studied systems is approximately constant (Table 2). The difference in the stabilities can be accounted for by the difference in the values of the parameter $A$.

To evaluate the thermal stability of studied systems the length of induction period of crystallization, $t_i$, has been used [31]:

$$t_i = A\exp[B/T] \tag{3}$$

The range of temperatures for the calculation of the length of induction period of crystallization was chosen from the interval where the onset temperatures of crystallization have been observed. The temperature dependence of the lengths of isothermal induction period for individual glasses is shown in Fig. 3.

It can be seen that the stability of the studied glasses against crystallization in the temperature region 540–740 °C is a < b, i. e. the system $Na_2O{\cdot}SiO_2$ is more stable against crystallization than the $Li_2O{\cdot}SiO_2$ system.

The order of stabilities evaluated by this criterion is in agreement with the order based on the characteristic temperatures (Table 1) and on the values of activation energy (Table 3). However, on the basis of combined criteria, such as $E(T_p)/RT$, an opposite order of the thermal stabilities has been found. Branda at al. [8] also observed a difference

**Table 1** Characteristic temperatures of oxide glasses $Li_2O{\cdot}SiO_2$ and $Na_2O{\cdot}SiO_2$ ($T \pm 1.5$ °C)

| Glass | $T_x$/°C | | | | $T_f$/°C | | | | $T_p$/°C | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 10 | 15 | 20 | 25 | 10 | 15 | 20 | 25 | 10 | 15 | 20 | 25 |
| $Li_2O{\cdot}SiO_2$ (a) | 541 | 576 | 599 | 602 | 605 | 628 | 646 | 653 | 625 | 645 | 660 | 675 |
| $Na_2O{\cdot}SiO_2$ (b) | 712 | 728 | 735 | 742 | 746 | 774 | 780 | 784 | 759 | 799 | 804 | 813 |

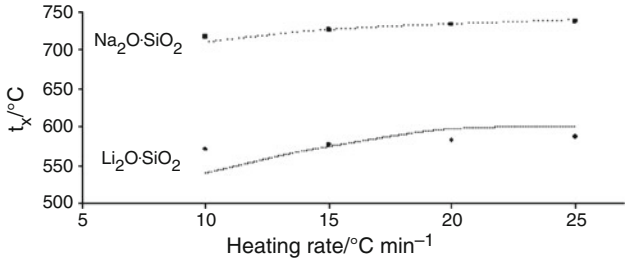


**Fig. 2** Experimental and calculated values of onset temperatures of glass crystallization for various heating rates

**Table 2** Parameters $A$ and $B$ and length of induction period (at 850 K)

| Glass | $A$/min | $B$/K | $T_i$/min |
|---|---|---|---|
| $Li_2O{\cdot}SiO_2$ (a) | $3.89 \times 10^{-21}$ | $40.11 \times 10^3$ | 1.21 |
| $Na_2O{\cdot}SiO_2$ (b) | $1.53 \times 10^{-19}$ | $43.72 \times 10^3$ | $3.32 \times 10^3$ |

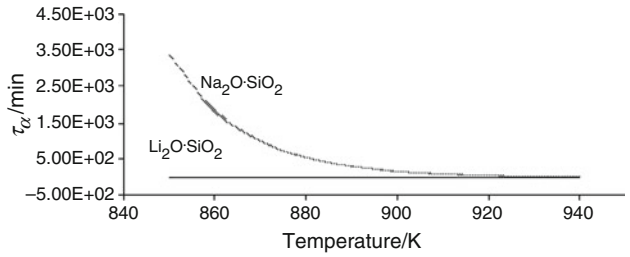


**Fig. 3** Induction periods of crystallization for individual glass samples calculated by Eq. (3)

**Table 3** Values of activation energies (±8%) for studied systems ($\beta = 10$ °C/min)

| Glass | $E$ ($T_f$)/ kJ mol$^{-1}$ | $E$ ($T_p$)/ kJ mol$^{-1}$ | $E$ ($\beta$)/ kJ mol$^{-1}$ | $E$ ($T_p$)/ $RT_p$ |
|---|---|---|---|---|
| $Li_2O{\cdot}SiO_2$ (a) | 109 | 116 | 131 | 15.5 |
| $Na_2O{\cdot}SiO_2$ (b) | 176 | 127 | 145 | 14.8 |

between the sequence of thermal stabilities of studied glass systems determined by using $E(T_p)/RT_p$ values. Therefore, greater activation energies obtained from DTA should not necessarily be indicative of greater thermal stability. A criterion based on the length of induction period of crystallization can be employed generally for the assessment of the stability of any glass against crystallization (ADOS version of the program KINPAR for the calculation of parameters $A$ and $B$ in Eq. (1) is available on request).

## Conclusions

The length of induction period of crystallization is suggested as a criterion to evaluate the thermal stability of glasses, where the parameters $A$ and $B$ are obtained from the dependence of onset temperature of the crystallization peak on the heating rate in the non-isothermal DTA measurements. For a set of two glasses, the order of stabilities obtained of this method coincides with the order determined by stability criteria based on the characteristic temperatures and the values of activation energy.

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