

## **THERMAL PROPERTIES OF OXIDE GLASSES**

### **Part I. Verification of various criteria of thermal stability vs. crystallization**

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### **Abstract**

To evaluate the thermal stability of oxide glasses, various criteria have been used. Not only the simple parameters, as characteristic temperatures and values of activation energy and enthalpy changes, but also the combined criteria  $E/RT_p$  and  $k_f(T)$  have been taken into account. 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 validity of the criteria was tested by applying them to these glasses. The results indicate that the sequence thermal stability of the studied glass system vs. crystallization depends not only on their composition but also on the used criteria.

**Keywords:** crystallization, oxide glasses, thermal stability

### **Introduction**

The critical issue for the existing or potential applications of glasses is their thermal stability vs. crystallization. They should be stable vs. thermal aging during their application. On the other hand, those glasses that serve as intermediate products for fabricating glass-ceramics are expected to possess an appropriate thermal stability [1–4]. Therefore, it is very important to evaluate the thermal stability of glasses vs. crystallization. In practice, many authors usually base their glass stability evaluation on the characteristic temperatures from DTA or DSC curves [5–10].

It is a matter of current observation that unstable glasses show a crystallization exotherm (maximum peak temperature,  $T_p$ ) close to the glass transition temperature ( $T_g$ ), while this exotherm is closer to the melting temperature ( $T_m$ ) for stable glasses. Thus, glass forming ability, as related to the ease of devitrification, may be evaluated from the difference between  $T_p$ ,  $T_x$  (onset of crystallization) and  $T_g$ . But all these stability factors are not fixed physical parameters, since they depend on the experimen-

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tal conditions and some practical problems may arise as well since several peaks are usually observed for the crystallization and melting [5].

Some authors [11, 12] suggested that crystallization activation energy ( $E_c$ ) could also be used to evaluate the glass stability. The crystallization rate constant  $k(T)$  takes into account both activation energy  $E$  and frequency factor  $A$ , so it was believed to be a good criterion for the evaluation of the glass stability [13]. Unfortunately, it was found that  $k(T)$  criterion is susceptible to the heating rate and temperature and, therefore, further criteria were suggested [3, 14–16]. Cheng [3] has proposed a new criterion, in which kinetic and also thermodynamic parameters are taken into account.

In this paper, some of these criteria have been applied to the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  (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) systems. It is well known that  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{TiO}_2$  system exhibits strong bulk crystallization. Comparisons are also made between these criteria and enthalpy of crystallization ( $\Delta H$ ).

## Experimental

### *Preparation of glasses*

Analytical grade reagents of  $\text{Li}_2\text{CO}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  were well 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. The amorphous nature of the as-quenched glasses was confirmed by X-ray diffraction.

### *Instruments*

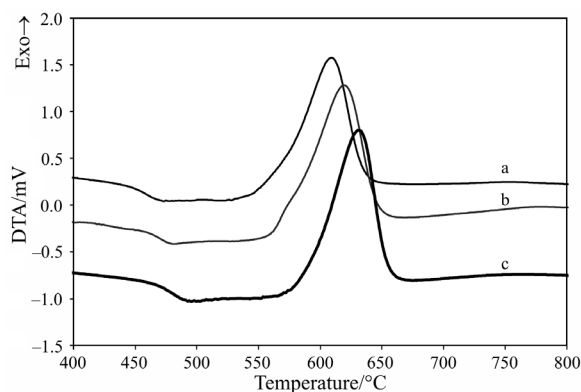
The thermal stability of glasses was studied using a TA Instrument 2960 SDT. The measurements of DTA curves were carried out in air using a platinum crucible. About 20–24 mg of powdered samples with a particle size of 0.16–0.10 mm and heating rates of 5, 10, 15, 20 and  $25^\circ\text{C min}^{-1}$  were used. Calibration of the temperature and enthalpy scales was made using pure  $\text{SiO}_2$  ( $T_m = 848.15 \text{ K}$ ;  $\Delta H = 20.19 \text{ J mol}^{-1}$ ).

## Results and discussion

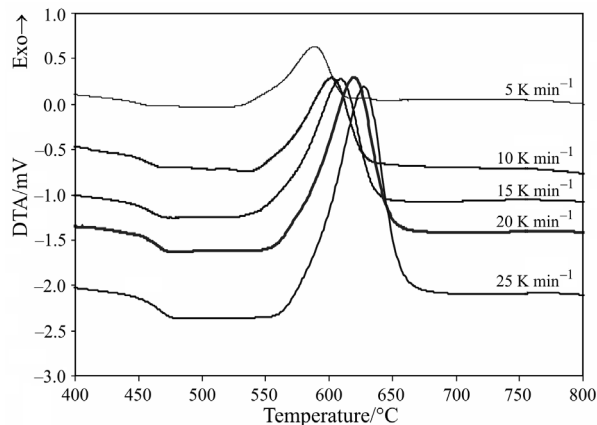
The typical DTA curves of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  (a),  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2 \cdot 0.03\text{TiO}_2$  (b) and  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2 \cdot 0.1\text{TiO}_2$  (c) glasses at heating rate  $15 \text{ K min}^{-1}$  are shown in Fig. 1. The maximum peak temperatures,  $T_p$ , were determined directly from DTA curves. The inflection point temperature,  $T_i$ , were determined from the maximum peak temperatures on the DTA curves. Some of these characteristic temperatures are summarized in Table 1. All these characteristic temperatures increase with the increasing heating rates (Fig. 2) and with increasing content of  $\text{TiO}_2$ . Since the greater these temperatures, the more stable the glass should be, the systems containing  $\text{TiO}_2$  (especially (c) system) are more stable vs. crystallization than the system without  $\text{TiO}_2$  (system (a)).

**Table 1** Characteristic single parameters of thermal stability of oxide glasses  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  (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)

Parameter heating rate	Glasses														
	a					b					c				
	5	10	15	20	25	5	10	15	20	25	5	10	15	20	25
$T_x/\text{K}$ 1 K	805	814	821	828	835	810	821	828	834	841	832	846	850	859	860
$T_p/\text{K}$ 1 K	861	875	882	892	901	870	884	893	898	905	887	898	905	904	920
$T_f/\text{K}$ 1 K	850	860	868	879	886	855	869	879	886	890	874	885	889	901	907
$\Delta H/\text{kJ mol}^{-1}$			43					42					35		
$E(T_p)/\text{kJ mol}^{-1}$			251					289					317		
$E(T_f)/\text{kJ mol}^{-1}$			257					268					298		
$E(\dots)/\text{kJ mol}^{-1}$			266					304					332		



**Fig. 1** DTA curves of 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> and c – Li<sub>2</sub>O 2SiO<sub>2</sub> 0.1TiO<sub>2</sub> glasses at heating rate 15 K min<sup>-1</sup>



**Fig. 2** DTA curves of a – Li<sub>2</sub>O 2SiO<sub>2</sub> glass at heating rate 5, 10, 15, 20 and 25 K min<sup>-1</sup>

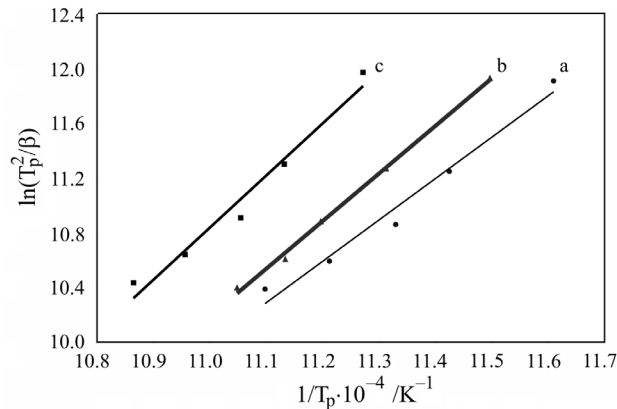
For determining the activation energy, many authors use the Kissinger plot (Fig. 3):

$$\ln \frac{T_0^2}{\beta} = \frac{E}{RT_0} + \ln \frac{E}{R} - \ln A \quad (1)$$

where  $0 < p < f$ , and  $\beta$  stands for the heating rate. The Ozawa plot, based on the Eq. (2), is also used:

$$\ln \beta = -\frac{E(\beta)}{RT_p} + C \quad (2)$$

All these kinetic parameters, together with enthalpic changes ( $\Delta H$ ) are also listed in Table 1. From the values shown it follows that glasses with TiO<sub>2</sub> are more stable vs. crystallization than the glass without TiO<sub>2</sub>; thus, the thermal kinetic stability correlate with thermodynamic stability.



**Fig. 3** Plots of  $\ln(T_p^2/\beta)$  vs.  $1/T_p$

Besides these ‘single’ parameters of thermal stability based on  $T_p$ ,  $T_f$ ,  $E(T_0)$ ,  $E(\ )$ , combined criteria have also been proposed. Branda *et al.* [11] suggested that value of  $E/RT$  could be used to evaluate the stability of glasses. The glasses with greater devitrification tendency should possess higher values of  $E/RT$ . Cheng [3] proposed a new criterion:

$$k_f(T) = A \exp\left[\frac{-E}{RT}(T_p - T_f)/T_f\right] \tag{3}$$

According to Cheng, not only the kinetic parameters of the crystallization of glasses, namely activation energy,  $E$ , and frequency factor,  $A$ , but also thermodynamic factor  $(T_p - T_f)/T_f$  have been taken into account in the  $k_f(T)$  criterion. A higher value of  $k_f(T)$  means a poorer stability of glasses. These combined criteria are summarized in Table 2.

On the contrary to single parameters, these criteria indicate that the  $\text{Li}_2\text{O SiO}_2$  glass is more stable than the glasses containing  $\text{TiO}_2$ . As shown in Table 2, the values of  $E/RT$  for the glasses studied are rather close; thus, extreme accuracy in determining the values of  $E$  and  $T_p$  is required. In extreme cases, the changed relative order of thermal stability can be obtained due to improper determination of  $E$  and  $T_p$ .

**Table 2** Combined criteria of thermal stability of glasses

Glass	$E/RT_p$	$k_f(T_p)$	$E/RT_f$	$k_f(T_f)$
a	35	$8.4 \cdot 10^{14}$	36	$8.3 \cdot 10^{14}$
b	36	$3.3 \cdot 10^{15}$	37	$3.3 \cdot 10^{15}$
c	40	$3.0 \cdot 10^{17}$	40	$3.2 \cdot 10^{15}$

### Conclusions

Various criteria have been used for evaluating the thermal stability of glasses from DTA curves. Not only the single criteria, such as  $T_p$ ,  $T_f$ ,  $E(T_p)$ ,  $E(T_f)$ ,  $E(\ )$  and  $\Delta H$  but also the

combined criteria, such as  $E/RT_0$  and  $k_f(T_0)$  are employed. Applying them to evaluate the stability 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) glasses, the validity of these parameters was tested. On the basis of single parameters, the following order of kinetic and thermodynamic stability was obtained: (a) < (b) < (c). On the basis of combined parameters, an opposite order has been found. Thus, in some cases the criteria used do not fully corresponds with the order of thermal stability. Branda *et al.* [4] also observed difference between the thermal stability of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  and  $1.1 \text{Li}_2\text{O} \cdot 1.9\text{SiO}_2$  glasses determined by using  $E_c$  and  $E_c/RT_p$  values. According to [4], the devitrification occurs in the temperature range where the number of nuclei formed and the crystal growth frequency factor are high enough so that the crystal growth kinetic barrier is overcome. Therefore, greater activation energies obtained from DTA should not necessarily be indicative of greater thermal stability. On the other hand, the combined criteria have been used only for two-component systems ( $\text{Li}_2\text{O} \cdot x\text{SiO}_2$ ) [3, 11]. From the literature it is namely known that the bulk nucleation is usually dominant in  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass. In the glass containing  $\text{TiO}_2$ , the surface crystallization is dominant [16]. Thus, the results obtained can also be affected by different nucleation mechanisms, which depends on the  $\text{TiO}_2$  content.

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