Effect of an addition of TiO_2 on the thermal stability of $Li_2O.SiO_2$ glasses – application of various criteria

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Abstract

To compare the thermal stability of $Li_2O.2SiO_2$ and $Li_2O.2SiO_2.0.1TiO_2$ glasses, various criteria have been used. Not only characteristic temperatures, values of activation energy (E) and enthalpy changes (ΔH), but also the combined criteria E/RT and $k_f(T) = A \exp [(-E/RT) (T_p-T_f)/T_f]$ (T_p is the maximum peak temperature, T_f is the inflection point temperature on the differential thermal analysis curves) have been taken into account. The results indicate that order of the thermal stability against of different glass systems crystallization depends not only on their composition but also on the mechanism of crystallization which is connected with the used parameter.

Introduction

Glasses in the $Li_2O.2SiO_2$ system crystallize easily at temperatures at which their viscosity is still high enough to retain the shape of a formed article and consequently this system has been used as a basis of a number of glass-ceramics or crystallized glasses [1,2]. There have been published many papers concerning the effect of addition of different oxides on thermal stability of $Li_2O.2SiO_2$ glasses. Studies of the influence of P_2O_5 [3], TiO_2 [4], NiO and V_2O_5 [5] on the crystallization process showed that these components acted as nucleating agents.

For evaluation of the thermal stability of glasses against crystallization, various criteria have been used. Dietzel [6] introduced the first simple criterion,

$\Delta T = T_x - T_g$ (T_x is the crystallization onset temperature, T_g is the glass transition temperature). Hrubý [7] proposed the H_r criterion, where $H_r = (T_x - T_g)(T_x - T_g) / T_g$. Some authors [8-10] suggested that the crystallization activation energy (E) and crystallization rate constants, $k(T)$, could also be used to evaluate the glass stability [11].

In this paper, some of these criteria have been applied for the $Li_2O.2SiO_2$. $nTiO_2$ system ($n \underline{=} 0$ and 0,1). Comparison is also made between these criteria and enthalpic changes (ΔH) corresponding to the crystallization process.

Experimental

Preparation of glasses

Analytical grade reagents of Li_2CO_3, SiO_2 and TiO_2 were well mixed by ball-milling and then melted in a platinum crucible at 1400 °C for 2 hours. The liquid glasses 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 studied samples was studied using a TA INSTRUMENT 2960 SDT. The measurements of DTA curves were carried out in air using a platinum crucible. Sample masses of about 20-24 mg and rates of temperature increase of 5, 10, 15, 20 and 25 °C.min^{-1}. Calibration of the temperature change of the enthalpy axes was made with pure SiO_2 ($T_{\alpha \rightarrow \beta}$ = 848,15 K; ΔH = 20,19 J.mol^{-1}).

Results and discusion

All characteristic temperatures from the DTA curves are summarized in Table 1 The glass transformation temperature (T_g), the crystallization starting temperature (T_x) and the maximum peak temperature (T_p) were directly determined from DTA curves. The inflection point temperature (T_f) was determined from the maximum peak on the DDTA curve. The characteristic temperatures increase with the increasing heating rates. Since the greater these temperatures, the more stable the glass showed to be, the system with TiO_2 (b) is more stable against crystallization then the one without TiO_2 (a).

For determining the activation energy, many authors used the Kissinger plot:

$$\ln (T_n^2/\beta) = E/RT_n + \ln E/R - \ln A \tag{1}$$

(n = p or f, β is heating rate), or the Ozawa plot, based on the equation (2)

$$\ln \beta = -E(\beta) / RT_n + C \tag{2}$$

The plots of $\ln (T_n^2/\beta)$ versus $1/T_n$ and $\ln \beta$ versus $1/T_n$ are given in Figs.1 and 2 and the kinetic parameters and enthalpic changes are listed in Table 1. From these results a similar conclusion follows that the glass with TiO_2 (b) is more stable against crystallization than the glass without TiO_2 (a).

Besides the single parameters (T_g, T_x, T_p, E, ΔH), combined criteria also exist. Branda et al. [10] suggested that the ratio E/RT could be used to evaluate the thermal stability of glasses.

Table 1: Characteristic parameters of thermal stability of oxide glasses $Li_2O.2SiO_2$ (a) and $Li_2O.2SiO_2. 0,1TiO_2$ (b).

Parameter	Glasses									
	(a)					(b)				
	5	10	15	20	25	5	10	15	20	25
T_x /K	805	814	821	828	836	832	846	850	859	859
T_p /K	861	875	883	892	901	887	898	905	913	920
T_f /K	849	861	868	879	886	874	885	889	900	907
$E(T_p)$ / kJ mol^{-1}	251					316,8				
$E(T_f)$ / kJ mol^{-1}	257					298,6				
$E(\beta)$ / kJ mol^{-1}	266					331,9				
$-\Delta H$ / kJ mol^{-1}	43,13					35,25				
E/RT_p	37,17	36,57	36,19	35,99	35,71	40,41	39,91	39,63	39,28	38,95
$k_f(T_p)$ / s^{-1}	8,9E+14	8,0E+14	8,2E+14	8,7E+14	8,2E+14	3,2E+17	3,1E+17	3,5+17	2,9E+17	3,02E+17
E/RT_f	36,33	35,87	35,56	35,13	34,83	41,01	40,49	40,32	39,81	39,51
$k_f(T_f)$ / s^{-1}	8,9E+14	7,9E+14	8,1E+14	8,6E+14	8,2+14	3,2E+17	3,1E+17	3,5+17	2,9E+17	3,05E+17

Higher values of E/RT imply greater devitrification tendency. Cheng [11] proposed a new criterion:

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

According to Cheng, not only the kinetic parameters of the crystallization of glasses, namely activation energy and frequency factor, but also the 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 poor thermal stability of glasses. These combined criteria are also summarized in Table 1.

Fig. 1: Plots of ln (T_f^2/β) versus $1/T_f$ for $Li_2O.2SiO_2$ (a) and $Li_2O.2SiO_2. 0,1TiO_2$ (b)
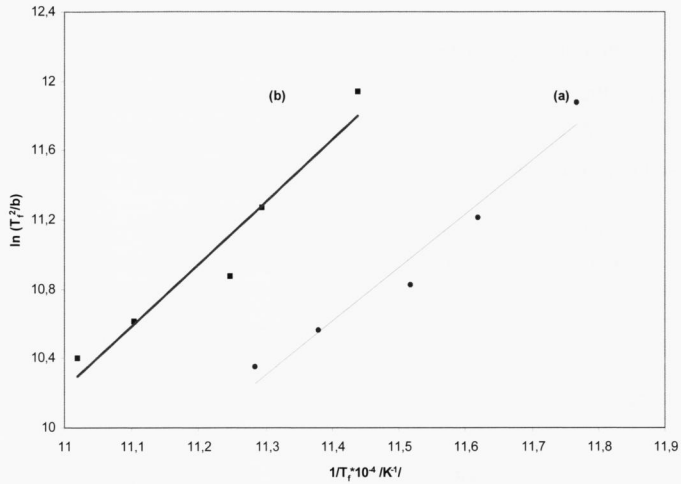
Fig. 2 : Plots of ln (T_p^2/β) versus $1/T_{fp}$ for $Li_2O.2SiO_2$ (a) and $Li_2O.2SiO_2. 0,1TiO_2$ (b)
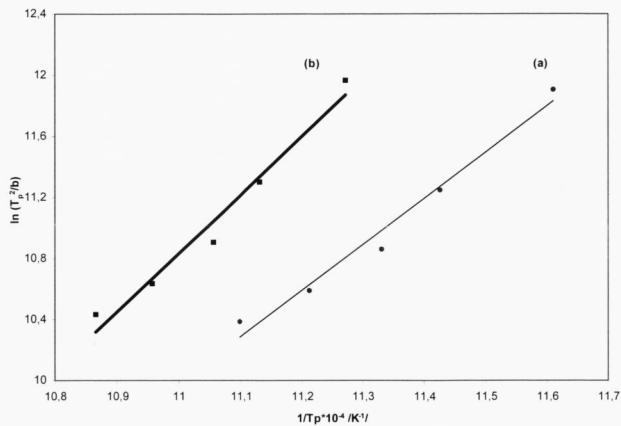
On the contrary to the simple parameters, these combined criteria indicate that the glass $Li_2O. 2SiO_2$ is more stable than the glass with TiO_2. In accordance with Branda et al. [8], devitrification occurs in the range of temperatures in which the number of nuclei formed and the crystal growth frequency factor are high enough that the crystal growth kinetic barrier can be overcome. Therefore, greater activation energies obtained from DTA should not necessarily be indicative of greater thermal stability. On the other hand, the values of E/RT_n for the studied glasses are rather close. Extreme accuracy in determining the values of E and T_n is required for correct evaluations. Otherwise, contrary evaluation could have been given by E/RT_n criterion.

Conclusion

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, $E(T_p)$, $E(T_f)$, and $E(\beta)$, but also the combined criteria, such as E/RT and $k_f(T)$ are taken into account. The validity of these parameters is tested by applying them to evaluate the thermal stability of $Li_2O.2SiO_2$ (a) and $Li_2O.2SiO_2. 0,1TiO_2$ (b) glasses. On the basis of single parameters, (b) is more stable than (a) glass. On the basis of combined parameters, opposite order has been obtained. Then, order of the thermal stability of studied glasses depends not only on their composition and mechanism of crystallization, but also on the used parameters. On the other hand, the combined criteria have been derived only for two-component systems [8,11]. As known from literature, the bulk nucleation is dominant in $Li_2O.2SiO_2$ glass. In the glass containing TiO_2, the surface crystallization is dominant [13]. Thus, the nucleation mechanism is needed to be known.

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