Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 428 (2005) 11–14
thermochimica acta
www.elsevier.com/locate/tca

Thermal stability of glass evaluated by the induction period of crystallization

P. Šimon[a,*], K. Nemčeková[b], E. Jóna[b], A. Plško[b], D. Ondrušová[b]

[a] Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, 81237 Bratislava, Slovakia
[b] Department of Chemistry and Technology of Inorganic Materials, Faculty of Industrial Technologies, Trenčín University of A. Dubček, 020 32 Púchov, Slovakia

Received 28 May 2004; received in revised form 13 September 2004; accepted 13 September 2004
Available online 5 November 2004

Abstract

To evaluate the thermal stability of oxide glasses against crystallization, a new criterion based on the length of induction period of crystallization is suggested. It is discussed that the end of the induction period of crystallization corresponds to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts. Three glasses with the composition of $Li_2O{\cdot}2SiO_2$ (a), $Li_2O{\cdot}2SiO_2{\cdot}0.03TiO_2$ (b) and $Li_2O{\cdot}2SiO_2{\cdot}0.1TiO_2$ (c) were prepared and the validity of the criterion was tested by applying it to these glasses. The results indicate that the new criterion enables to discriminate among the thermal stabilities of the silicate glass samples. It can be expected that it can be employed generally for the assessment of the thermal stability of any glass against crystallization, including metal and organic glasses.

Keywords: Glass; Thermal stability; Induction period; Crystallization

1. Introduction

Features of the nucleation and crystallization processes are of basic importance in the control of glass formability in technological applications where the formation of nuclei and the subsequent crystal growth must be avoided [1–3]. On the other hand, the formation of nuclei and crystal growth by controlled crystallization can give rise to polycrystalline solids containing residual glass phase called the glass ceramics [4]. Therefore, it is very important to evaluate the thermal stability of glasses against crystallization [5,6]. Many authors based the evaluation of glass stability employing the characteristic temperatures of DTA or DSC curves [7–10], crystallization activation energy [11–13] or crystallization rate constants [14,15]. Unfortunately, these stability criteria are not fixed physical parameters, since they mostly depend on the heating rate and temperature [16].

In our previous paper, several criteria of glass stability have been reviewed and tested [17]. The results indicate that, in some cases, the criteria do not correspond fully to the order of thermal stability of glass systems under study. In this paper, a new criterion for evaluating the thermal stability of glasses based on the induction period of crystallization is suggested and its validity is verified by applying it to $Li_2O{\cdot}2SiO_2$ and $Li_2O{\cdot}2SiO_2{\cdot}nTiO_2$ systems. Comparisons are also made between the new criterion and some existing criteria.

2. Theoretical analysis

For any mechanism, the rate of a process can be described by the general rate equation [18]

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

where α is the conversion of the process and $f(\alpha)$ is the conversion function. The temperature dependence of the rate

---

[*] Corresponding author.
E-mail address: peter.simon@stuba.sk (P. Šimon).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.09.016

constant k is usually expressed by the Arrhenius equation

$$k = A_k \exp\left[-\frac{E_a}{RT}\right] \tag{2}$$

where A_k is the pre-exponential factor; E_a, the activation energy; T, absolute temperature and R stands for the gas constant.

Since Eq. (1) is general, we assume that it describes also the kinetics of the processes occurring during the induction period. Existence of these processes is not detected by the experimental technique used; however, they have to take place as a preparatory stage preceding the main crystallization process. Combination of Eqs. (1) and (2), after the separation of variables, gives the result:

$$\int_0^{\alpha_i} \frac{d\alpha}{f(\alpha)} = \int_0^{t_i} A_k \exp\left[-\frac{E_a}{RT}\right] dt \tag{3}$$

The conversion α_i in Eq. (3) is the conversion of the processes occurring during the induction period and corresponding to the end of the induction period, i.e., to the start of the main process detected by the apparatus, and t_i is the length of the induction period. Further, it is assumed that the conversion α_i is the same for any temperature. Then, after integration of the left side of Eq. (3), one can get:

$$F(\alpha_i) - F(0) = \int_0^{t_i} A_k \exp\left[-\frac{E_a}{RT}\right] dt \tag{4}$$

Since the conversion α_i corresponding to the end of the induction period is assumed to be independent of temperature, also the value of the integrated function $F(\alpha)$ at the point α_i, $F(\alpha_i)$, is constant. Therefore, Eq. (4) can be rewritten as:

$$1 = \int_0^{t_i} \frac{dt}{A \exp[B/T]} \tag{5}$$

where the constants A and B are given as:

$$A = \frac{A}{F(\alpha_i) - F(0)}, \qquad B = \frac{E}{R} \tag{6}$$

The physical meaning of the denominator in Eq. (5) can be simply demonstrated for a special case of isothermal processes where the denominator is a constant equal to the induction period at the given temperature. Thus, the temperature dependence of the induction period can be expressed as

$$t_i = A \exp\left[\frac{B}{T}\right] \tag{7}$$

For the linear increase of temperature in DSC measurements, the furnace temperature can be expressed as

$$T_F = T_0 + \beta t \tag{8}$$

where T_F is the furnace temperature, T_0 is the starting temperature of the measurement and β stands for the heating rate. If one assumes that the temperature of the sample equals that of the furnace, combination of Eqs. (5) and (8) gives the result [19]

$$\beta = \int_0^{T_X} \frac{dT}{A \exp[B/T]} \tag{9}$$

where T_X is the temperature of the end of induction period, i.e., the onset temperature of the crystallization peak. The starting temperature in Eq. (9) is set as $T = 0$ K since the rate of the process at the starting temperature is negligible. When deriving Eqs. (3) and (4), the assumption is implied that the conversion function $f(\alpha)$ holds during the induction period which means that no change of the mechanism occurs. As Eq. (9) indicates, when increasing the rate of heating, the onset temperature also increases.

3. Experimental

3.1. Preparation of glasses

Analytical grade reagents Li_2CO_3, SiO_2 and TiO_2 were mixed by ball-milling and then melted in a platinum crucible at 1400 °C for 2 h. The liquid glasses were quenched by pouring them onto a cold steel mold. The amorphous nature of the as-quenched glasses was confirmed by X-ray diffraction.

3.2. Instruments

The thermal stabilities were studied by a TA INSTRUMENT 2960 SDT. The measurements of DTA curves were carried out in air using platinum crucible. Sample masses of about 20–22 mg and rates of temperature increase of 5, 10, 15, 20 and 25 K min^{-1} were used. Calibration of the temperature change of the enthalpy axes was made with pure SiO_2 ($T_{\alpha\rightarrow\beta} = 848.15$ K, $\Delta H = 20.19$ J mol^{-1} [18]).

4. Results and discussion

Typical curves of $Li_2O{\cdot}2SiO_2$ (a), $Li_2O{\cdot}2SiO_2{\cdot}0.03TiO_2$ (b) and $Li_2O{\cdot}2SiO_2{\cdot}0.1TiO_2$ (c) at the heating rate 10 K min^{-1} are shown in Fig. 1. The onset 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 temperature on DDTA curves [16,17]. 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 crystallization occurs in several stages. The point of the steep increase of the DTA record due to crystallization is taken as the onset temperature.

The parameters A and B in Eq. (9) have been obtained by minimizing the sum of squares between experimental and theoretical values of the onset temperature T_X for various

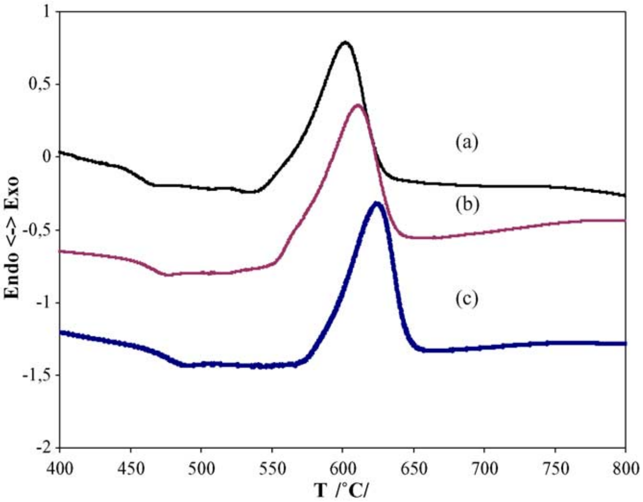

Fig. 1. DTA curves of $Li_2O{\cdot}2SiO_2$ (a), $Li_2O{\cdot}2SiO_2{\cdot}0.03TiO_2$ (b) and $Li_2O{\cdot}2SiO_2{\cdot}0.1TiO_2$ (c) glass samples at the heating rate 10 K min^{-1}.

heating rates by the simplex method [20]. The theoretical values of onset temperature are given by Eq. (9). The integration indicated in Eq. (9) has been carried out by the Simpson method. The standard deviations of A and B were calculated assuming a quadratic surface near the minimum [20]. The agreement between experimental and calculated values of onset temperatures for various heating rates is shown in Fig. 2. The resulting values of A and B are listed in Table 2. It can be seen from Table 2 that the adjustable parameter B is approximately constant for the glass samples under study. The difference in the stabilities can be accounted for by the difference in the values of the parameter A.

Since the onset temperature is determined as a point of the steep increase of the DTA record due to crystallization, the end of the induction period of crystallization corresponds to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts. Using the new criterion, the stability of glasses is evaluated as the length of isothermal induction period for a given temperature. The length of induction period is calculated by Eq. (7). The range of temperatures for the calculation of the lengths of induction period of crystallization was chosen from the interval where the onset temperatures of crystallization have been observed. Hence, it can be expected that the values of calculated induction periods are quite realistic since no extrapolation outside the temperature region of the measurement has been carried out. 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 glass samples against crystallization in the temperature region 750–850 K is in the order $a < b \ll c$, i.e., the glasses containing TiO_2 are more stable against crystallization than the one without TiO_2. Eq. (5) enables to calculate the length of induction period for any temperature regime and, thus, to evaluate the order of thermal stabilities for that regime.

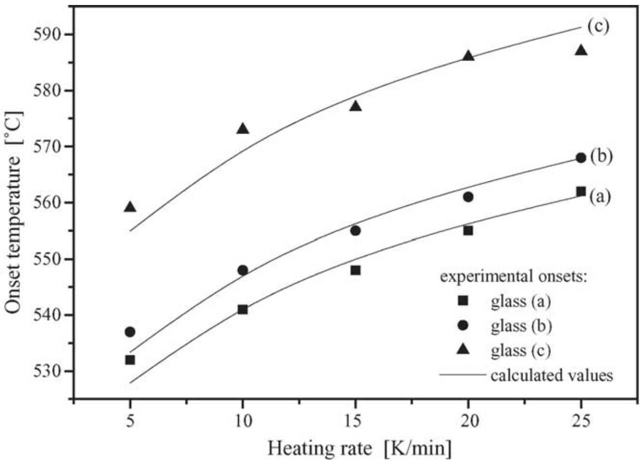

Fig. 2. Experimental and calculated values of onset temperatures of glass crystallization for various heating rates.

The order of stabilities evaluated by the new criterion is in agreement with the order based on the characteristic temperatures and on the values of activation energy (Table 1). However, on the basis of combined criteria, such as E/RT and $k(T)$ [17], an opposite order of thermal stabilities has been found. Branda et al. [13] also observed a difference between the sequence of thermal stabilities of studied glass systems determined by using E_a or E_a/RT_p values. According to [13], when glass is heated in a DTA apparatus, devitrification occurs in the range of temperatures where 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

Table 1
Characteristic parameters for the evaluation of thermal stability of oxide glasses $Li_2O{\cdot}2SiO_2$ (a), $Li_2O{\cdot}2SiO_2{\cdot}0.03TiO_2$ (b) and $Li_2O{\cdot}2SiO_2{\cdot}0.1TiO_2$ (c)

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

$E(T_p)$, $E(T_f)$: activation energy determined from the Kissinger plot [17]; $E(\beta)$: activation energy determined from the Ozawa plot [17].

Table 2
Parameters A and B describing the length of induction period using Eq. (7) for the glass samples under study

Sample	$A \times 10^{16}$ (min)	$B \times 10^{-3}$ (K)
a	0.90 ± 0.13	30.7 ± 0.3
b	2.88 ± 0.21	30.0 ± 0.2
c	7.78 ± 2.04	30.0 ± 0.3

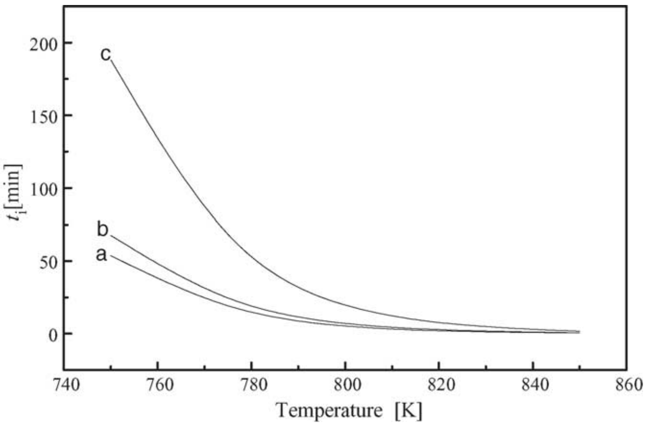

Fig. 3. Induction periods of crystallization for individual glass samples calculated by Eq. (7).

DTA should not necessarily be indicative of greater thermal stability.

We believe that the new criterion presented here can be employed generally for the assessment of the stability of any glass against crystallization, including metal and organic glasses. A DOS version of the program KINPAR for the calculation of the parameters A and B in Eq. (9) is available on request.

5. Conclusions

The length of isothermal induction period of crystallization is suggested as a new criterion to evaluate the thermal stability of glass. The lengths of induction periods are calculated using Eq. (7), where the parameters A and B are obtained from the treatment of the dependence of onset temperature of the crystallization peak on the heating rate in the non-isothermal DTA measurements. It is discussed that the end of the induction period of crystallization corresponds to the moment where the crystallization nuclei have already been formed and the intense growth of crystals starts. For a set of three glasses, the order of stabilities obtained by the new method coincides with the order determined by stability criteria based on the characteristic temperatures and on the values of activation energy.

References

[1] E.D. Zanotto, Nucleation and Crystallization in Glasses and Liquids, American Ceramic Society, Westerville, 1993, p. 65.
[2] A.K. Varshneya, Fundamentals of Inorganic Glasses, Academic Press, New York, 1994, p. 13.
[3] A.P. Novaes de Oliveira, O.E. Alarcon, T. Manfredini, G.C. Pellacani, C. Siligardi, Phys. Chem. Glasses 41 (2000) 100.
[4] R. Iordanova, E. Lefterova, I. Uzunov, Y. Dimitriev, D. Klissurski, J. Therm. Anal. Cal. 70 (2002) 393–404.
[5] C. Păcurariu, D. Tita, R.I. Lazău, G. Kovacs, I. Lazău, J. Therm. Anal. Cal. 72 (2003) 23.
[6] M.H. Lewis, Glasses and Glass Ceramics, Chapman and Hall, London, 1989, p. 226.
[7] A. Dietzel, Glass Technol. Berl. 22 (1968) 41.
[8] D.R. Uhlman, J. Non-Cryst. Solids 25 (1977) 42.
[9] A. Hrubý, Czech. J. Phys. 22 (1972) 1987.
[10] M. Saad, M. Poulain, Mater. Sci. Forum 19–20 (1987) 11.
[11] A. Marotta, A. Buri, F.J. Branda, J. Non-Cryst. Solids 95–96 (1987) 593.
[12] X. Zhao, S.J. Sakka, J. Non-Cryst. Solids 95–96 (1987) 487.
[13] F. Branda, A. Marotta, A.J. Buri, J. Non-Cryst. Solids 134 (1991) 123.
[14] L.L. Hu, Z.H. Jiang, J. Chin. Ceram. Soc. 18 (1990) 315.
[15] S. Surinach, M.D. Baro, M.T. Clavaguera-Mora, N. Clavaguera-Mora, J. Mater. Sci. 19 (1984) 3005.
[16] K. Cheng, J. Phys. Chem. B 103 (1999) 8272.
[17] E. Jóna, K. Nemčeková, A. Plško, D. Ondrušová, P. Šimon, J. Therm. Anal. Cal. 76 (2004) 85.
[18] G. Höhne, W. Hemminger, H.J. Flammersheim, Differential Scanning Calorimetry, Springer–Verlag, Berlin, Heidelberg, 1996, ISBN 3-540-59012-9.
[19] P. Šimon, Ľ. Kolman, J. Therm. Anal. Cal. 64 (2001) 813.
[20] J.A. Nelder, R.A. Mead, Comput. J. 7 (1965) 308.