Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 3, 849–852

THERMAL STABILITY OF Li_2O–SiO_2–CaO–P_2O_5–F GLASS

Eva Kuzielová[*], *V. Kovár and M. Palou*

Institute of Inorganic Chemistry, Technology and Materials, Slovak University of Technology, Radlinského 9, 812 37 Bratislava
Slovak Republic

Two glasses, the first one with the composition of $Li_2O\cdot 2SiO_2$ and the second one with the addition of CaO, P_2O_5 and CaF_2 in the stoichiometric ratio corresponding to fluoroapatite were prepared and their tendency to crystallize has been studied by non-isothermal DTA analysis. The values of kinetic parameters calculated using the isoconversional integral method have been used to determine the temperature dependencies of both the length of isothermal induction period and the length of overall isothermal crystallization for both glasses. The estimated dependencies indicate that the glass containing CaO, P_2O_5 and CaF_2 has a lower thermal stability.

Keywords: *activation energy, bio-glasses, isoconversional methods, thermal stability*

Introduction

The glasses and glass ceramics of the composition Li_2O–SiO_2–CaO–P_2O_5–F have found the applications in medicine, chiefly as dental biomaterials [1, 2]. The formation of polycrystalline solids takes place by a controlled nuclei formation and by a controlled crystal growth process. In comparison with glasses, the glass ceramics disposes of better mechanical properties. The process of heat treatment provides the possibility to affect their optical properties such as the colour, degree of opalescence and gloss, and thereby it is possible to mimic the natural appearance of teeth. Of course, the tampering and the improvement of final glass ceramics properties need to be familiar with the crystallization process. The information on the tendency of glasses to crystallize and the knowledge of the crystallization mechanism are very important and aid to design the suitable thermal treatment process. However, the overall crystallization process that occurs in glasses during reheating is a complex structural reorganization that is the result of various chemical and physical processes. The processes may occur in multiple steps that have different rates. Consequently, it is hard to classify the crystallization uniquely into the so-called internal (bulk) or surface mechanism and the exact description of general crystallization kinetics is very difficult [3].

An investigation of the crystallization mechanism of pure lithium disilicate glass and the glass with CaO, P_2O_5 and CaF_2 addition has been carried out in our previous paper [4] using the method developed by Ray and Day [5]. In this method the temperature corresponding to the maximum of the DTA crystallization peak, T_P, the maximum height of the DTA crystallization peak, $(\delta T)_P$ and the ratio $T_P^2/(\Delta T)_P$, where $(\Delta T)_P$ is the half-width of the DTA peak are determined as a function of the size of glass particles used for DTA measurements. The results indicated that the crystallization of both glasses proceeds by either the surface or the internal mechanism as a function of particle size. The smaller particles crystallize preferably by the surface crystallization which changes to the internal crystallization in the case of larger particle sizes. CaO, P_2O_5 and CaF_2 additions to the lithium disilicate composition support the surface mechanism.

Recently, bioactive properties have been indicated in this particular system, when the additions of CaO, P_2O_5 and CaF_2 in the relative ratio corresponding to fluoroapatite are introduced into the lithium disilicate composition [4, 6]. Bioactivity of these glasses and glass ceramics opens up the way to other applications of this material type. According to the mentioned studies [4, 6], the amount of 33 mass% of ‘apparent fluoroapatite’ considered as the most suitable to promote the bioactivity, was used to study the crystallization of glasses from Li_2O–SiO_2–CaO–P_2O_5–F system.

The present work is a continuation of studies concerning the thermal stability of glasses against crystallization. Frequently, the thermal stability of glasses is evaluated upon the estimation of characteristic temperatures from DTA or DSC curves [7], on the base of activation energy values [8, 9] or by means of combined criteria such as E_a/RT (E_a is the activation energy, R represents the gas constant and T is the absolute temperature) [10]. However, the mentioned stability criteria depend mostly on the heating rate and the temperature. Addi-

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[*] Author for correspondence: eva.kuzielova@stuba.sk

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

tionally, the tendency of glasses to crystallize determined according to individual criteria does not correspond each other in some cases [7].

In [11], a new criterion for evaluating the thermal stability of glasses has been suggested and verified. The criterion is based on the induction period of crystallization and issues from the so-called single-step approximation. According to this, the set of kinetic equations describing the kinetics of processes occurring during the overall crystallization is substituted by the sole single-step kinetics equation. This approximation is based on the assumption that the temperature and conversion functions, $k(T)$ and $f(\alpha)$, are separable [12]. Then, the rate of the complex multi-step condensed-state process can be described as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{1}$$

The isoconversional methods originate from Eq. (1). Their basic idea is that the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion [13]. Consequently, the reaction rate is a function of temperature only. Under non-isothermal conditions, when the temperature function is expressed by the Arrhenius equation, Eq. (2) expressed the integral isoconversional method can be obtained after some manipulations [14]:

$$\beta=\int_0^{T_i}\frac{\mathrm{d}T}{A\exp[E_a/RT]} \tag{2}$$

where β is the heating rate and T_i is the temperature at which the fixed conversion, α_i, is reached.

The temperature dependence of induction period can be expressed for a special case of isothermal processes, where the denominator in Eq. (2) is a constant equal to the induction period at the given temperature, as [14]:

$$t_i=A\exp\left[\frac{E_a}{RT}\right] \tag{3}$$

In this paper the effect of CaO, P_2O_5 and CaF_2 addition on the tendency of lithium disilicate glass to crystallize has been evaluated by evaluating the length of induction period and the length of overall isothermal crystallization. The values of corresponding kinetic parameters have been calculated using the isoconversional integral method.

Experimental

The samples of pure lithium disilicate glass (glass a) and of the glass with CaO, P_2O_5 and CaF_2 addition in the stoichiometric ratio corresponding to fluoroapatite (33 mass%) denoted as the glass b were prepared by mixing Tosil (colloidal solution of silica containing 30.93 mass% SiO_2, Silchem s.r.o., Czech Republic), Li_2CO_3 (≥98%, Fluka, USA), CaF_2 (99.9%, Aldrich, USA) and $Ca_3(PO_4)_2$ (96%, Fluka, USA). The composition of glasses under study is listed in Table 1. The resulted suspensions were stirred for 1 h under heating. After partial evaporation of water, the drying under IR lamp and in the oven followed. The as-prepared powdered samples were melted in Pt-crucibles in a supercanthal furnace at the temperature of 1450°C (2 h, 10°C min^{-1}). Subsequently, the glass melts were cooled down by pouring onto stainless steel plate. The amorphous character of the as-prepared glasses was confirmed by X-ray diffraction (STOE, type θ/θ diffractometer).

The thermal studies were performed by a TA Instrument 2860 SDT. For that purpose, the samples were ground and sieved and the fraction from 71 to 125 μm was used for measurements. The samples of about 20 mg were heated in a platinum crucibles from room temperature until the crystallization was completed at the heating rates of 2, 4, 6, 8 and 12°C min^{-1}. The measurements were carried out in the atmosphere of nitrogen.

Results and discussion

Typical DTA curves of glass a and b recorded at the heating rate of 12°C min^{-1} are shown in Fig. 1. The characteristic temperatures of the crystallization

Table 1 The composition of mixtures designated for the preparation of glasses (mass%)

	Glass	
	a	b
SiO_2 – Tosil	84.00	72.87
Li_2CO_3	16.00	13.51
CaF_2	0.00	1.05
$Ca_3(PO_4)_2$	0.00	12.57

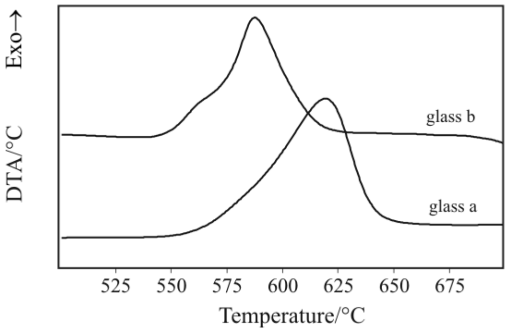

Fig. 1 DTA curves of glass a and b recorded at the heating rate of 12°C min^{-1}

Table 2 Characteristic parameters for the evaluation of thermal stability of glasses from $Li_2O–SiO_2–CaO–P_2O_5–F$ system

Glass	a					b				
Heating rate/°C min^{-1}	2	4	6	8	12	2	4	6	8	12
T_x/K	793	801	806	810	815	787	796	802	806	812
T_p/K	853	868	877	883	893	824	838	847	853	863

Table 3 Characteristic parameters of crystallization process of glasses from $Li_2O–SiO_2–CaO–P_2O_5–F$ system

Glass	a		b	
Parameters	A/min	E_a/kJ mol^{-1}	A/min	E_a/kJ mol^{-1}
Induction period	$7.74\cdot10^{-27}$	408±7	$4.59\cdot10^{-24}$	364±8
Crystal growth	$2.91\cdot10^{-16}$	270±2	$1.42\cdot10^{-15}$	249±2
Overall crystallization	$1.90\cdot10^{-16}$	273±2	$2.55\cdot10^{-16}$	262±3

peak, T_x (the onset temperature) and T_p (temperature corresponding to the maximum height of the peak), are summarized in Table 2. The parameters A and E_a in Eq. (2) were calculated by the program KINPAR developed by Šimon *et al.* [15]. The program minimizes the squared deviations between the experimental and theoretical values of isoconversional temperatures for various heating rates by the simplex method. The theoretical values of temperature are given by Eq. (2) and the integration indicated in Eq. (2) is carried out by the Simpson method.

It is discussed in [11] 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. When the induction period is assumed, T_i represents the temperature of the end of induction period, i.e. T_x. The kinetic parameters obtained from the treatment of T_x values thus correspond to prevailing nucleation process. If the overall crystallization process, i.e. both the nucleation and crystal growth, is taken into account, then T_i is substituted by T_p. The temperature of the peak maximum, T_p, corresponds to the maximum rate of the crystal growth. Besides this, the kinetic parameters for the crystal growth were also determined. In this case, the lower integration limit in Eq. (2) was set to T_x and the upper integration limit was set to T_p.

The calculated values of parameters A and E_a are listed in Table 3. The comparison of experimental and calculated values of temperatures for the induction period and overall crystallization is presented in Fig. 2 and shows a very good agreement. Likewise, the values of temperatures calculated for the crystal growth correspond well with the experimental ones.

The lengths of isothermal induction period, t_i, were determined from Eq. (3). The temperature dependence of t_i for both glasses is shown in Fig. 3A. The temperatures for which the lengths of induction period were calculated fall to the interval where the onset temperatures of crystallization has been observed; hence, the calculated induction periods can be considered realistic and the kinetic parameters ob-

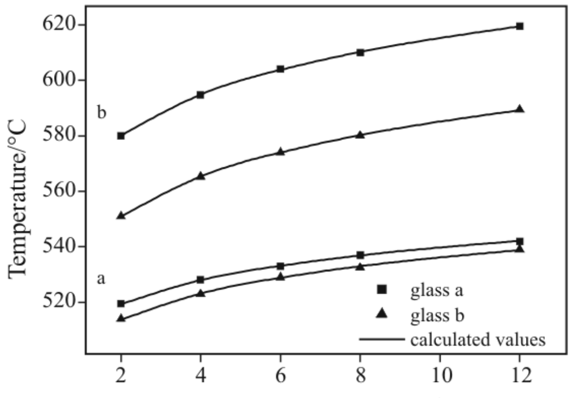

Fig. 2 Experimental and calculated values of A – the onset temperatures of glass crystallization, B – the temperatures corresponding to the maximum of the DTA crystallization peak for various heating rates

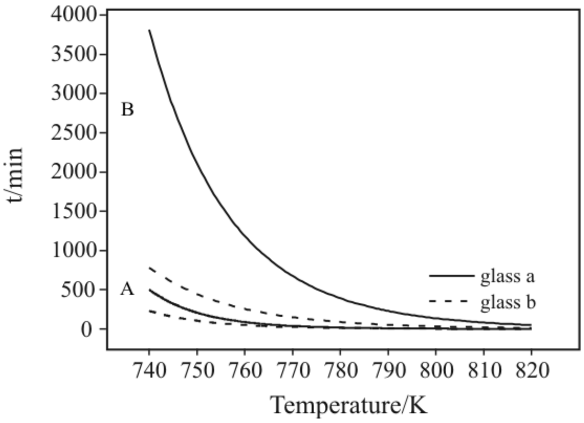

Fig. 3 The temperature dependence of the time of A – induction period and B – of overall isothermal crystallization for individual glass samples calculated using Eq. (3)

tained can be used to propose suitable thermal treatment regimes of these glasses for the production of the glass ceramics. The lengths of overall isothermal crystallization process were also calculated (Fig. 3B) that could be also helpful to choose the appropriate temperature/time regime. According to Fig. 3, the glass containing CaO, P_2O_5 and CaF_2 addition crystallizes in a shorter time period. The addition of CaO, P_2O_5 and CaF_2 thus accelerates both processes, i.e. the nucleation and crystal growth.

Consequently, the results obtained confirm that the glass containing CaO, P_2O_5 and CaF_2 exhibits the enhanced tendency to crystallize. However, it is necessary to emphasise that the obtained values of kinetic parameters, including the values of activation energy, are the apparent parameters without a real physical meaning. They can be used to evaluate the thermal stability of glasses or to model the crystallization process for other temperature regimes than those applied in the measurements.

Conclusions

In the present work the effect of CaO, P_2O_5 and CaF_2 addition on the tendency of lithium disilicate glass to crystallize has been evaluated by evaluating the length of induction period and the length of overall isothermal crystallization. The integral isoconversional method has been applied to obtain the kinetic parameters for the description of the length of the induction period, the times of the maximum rate of crystal growth and the overall crystallization, respectively. The results indicate that the addition of CaO, P_2O_5 and CaF_2 to the pure lithium disilicate composition leads to the enhanced tendency of the glass to crystallize and that the both processes, i.e. the nucleation and crystallization, are accelerated. The calculated lengths of isothermal induction period and of isothermal crystallization process could be used to propose the suitable heat treatment regimes.

Acknowledgements

This work has received a financial support from the Slovak Grant for Science and Technology APVT No. 20-015904.

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Received: August 6, 2007
Accepted: September 5, 2007

DOI: 10.1007/s10973-007-8681-8