

# TRANSFORMATION OF GLASS TO GLASS-CERAMICS IN $\text{LiO}_2\text{-SiO}_2$ SYSTEM

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*The mechanism and kinetics of crystallization of  $\text{Li}_2\text{O-SiO}_2$  glass as function of grain size and fluorapatite content were investigated using non-isothermal DTA method. Two samples of glass based on lithium disilicate ( $\text{LS}_2$ ) without and with fluorapatite (FA) were synthesised. Then, glass-ceramics were obtained by thermal treatment of parent glasses. Activation energy of glass transformation calculated according to Kissinger ( $299 \pm 1 \text{ kJ mol}^{-1}$  for pure  $\text{LS}_2$  glass and  $288 \pm 7 \text{ kJ mol}^{-1}$  for glass containing FA) or according to Ozawa ( $313 \pm 1 \text{ kJ mol}^{-1}$  for pure  $\text{LS}_2$  glass and  $303 \pm 8 \text{ kJ mol}^{-1}$  for glass containing FA) indicates that the presence of FA in glass reduces its stability against crystallization. It was found that grain size determines the mechanism of crystallization. The smaller particles crystallize preferably through surface mechanism, while the coarser ones undergo the crystallization via internal volume process. The onset point of internal crystallization, which substitutes the surface one is found at about 0.3 mm for pure  $\text{LS}_2$  glass, while this change occurs at size of 0.9 mm approximately in glass containing FA. The addition of FA into  $\text{LS}_2$  glass-parent supports the crystallization by surface mechanism.*

## INTRODUCTION

The crystallization of glass has been extensively studied, especially in silicate glasses, considering the multi-stage thermal process [1-3]. Foremost, crystals are nucleated at lower temperatures and then grown to a well-detectable size at higher temperatures. Therefore, the nucleation and crystallization are considered as two linked stages of the same continuous thermal process. Indeed, the crystallization is continued growth of primary stable nuclei, i.e., of the clusters on molecular level, to their macroscopic crystal size. The „transition“ between nucleation and crystallization depends only on the thermodynamically critical size of nuclei-crystals [2,3]. It is generally accepted that the crystallization process occurs through two mechanisms: volume (internal) and surface crystallization. In most cases, crystallization by volume and surface mechanisms proceeds simultaneously and competitively [2,3], leading thus to the precipitation of two or more crystal phases with different sizes, morphology and distribution.

Authors [4] have applied differential thermal method (DTA) to study the nucleation and crystal growth rate as well as to determine the number of nuclei in glass. The most commonly suitable method used to investigate surface and volume crystallization is based on differential

thermal analysis developed by Ray and Day [5]. The method considers the temperature corresponding to the maximum of the DTA crystallization peak  $T_p$ , the maximum intensity of the DTA crystallization peak  $(\delta T)_p$  and the ratio  $T_p^2/(\Delta T)_p$ , where  $(\Delta T)_p$  is the peak half-width as a function of size of the glass particles. Then the crystal growth dimension  $n$ , also considered as Avrami parameter is defined by Equation (1)[6].

$$n = \left[ \frac{2.5R}{E} \right] \left[ \frac{RT_p^2}{\Delta T_p} \right] \quad (1)$$

where  $R$  is the gas constant,  $E$  (activation energy for crystal growth) independent from particle size,  $T_p^2/(\Delta T)_p$  would be proportional to  $n$ . A value of  $n$  close to 1 indicates the surface crystallization, while  $n$  close to 3 signifies internal crystallization and intermediate values between 1 and 3 are indicative of both surface and internal crystallization [7].

The stability of glass against crystallization and the knowledge of the mechanism by which the crystallization occurs are very important to find the suitable thermal treatment in production of glass-ceramics with specific properties. This thermal stability is evaluated by determining the characteristic temperatures from DTA or DSC curves and also by determining activation energy values [8,9].

In [9], the new criterion for evaluation the thermal stability of glass is determined from the induction period of crystallization and based on so-called single-kinetics

approximation.

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (2)$$

Indeed, equations describing the kinetics of processes occurring during the overall crystallization are substituted by the sole single-step kinetic equation. This single-kinetic approximation is based on the assumption that the temperature,  $k(T)$ , and conversion,  $f(\alpha)$ , functions are independent [10,11].

Under non-isothermal conditions, the temperature function is expressed by Arrhenius equation

$$k(T) = A_k \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where  $A_k$  is the pre-exponential factor, and the furnace temperature represents  $T = T_0 + \beta t$  ( $T_0$  is the temperature at time  $t = 0$ ,  $\beta$  is the heating rate). Then, Equation (4) can be obtained after some manipulations [12]:

$$\beta = \int_0^{\alpha_i} \frac{dT}{A \exp[E_a/RT]} \quad (4)$$

where  $T_i$  is the temperature at which the fixed conversion,  $\alpha_i$ , is reached. The parameter  $A$  is given as:

$$A = \frac{F(\alpha_i) - F(0)}{A_k} \quad (5)$$

where  $F(\alpha_i)$  and  $F(0)$  are the values of primitive function to  $1/f(\alpha)$  at  $\alpha = \alpha_i$  and  $\alpha = 0$ , respectively. The starting temperature in Equation (4) is set as  $T = 0$  K since the rate of the process at the starting temperature is negligible. Equation (4) expresses the integral isoconversional method.

The temperature dependence of induction period can be expressed for a special case of isothermal processes, where the denominator in Equation (5) is a constant equal to the induction period at the given temperature, as [12]:

$$t_i = A \exp\left[\frac{E_a}{RT}\right] \quad (6)$$

We have recently developed a variety of glass ceramics containing fluorapatite with appropriated mechanical and bioactive properties for biomedical and dental applications [13,14]. The present work is the continuation of the latest ones aimed at determination of the influence

Table 1. The composition of mixtures for preparation of glasses .

Raw materials	Content (wt.%)	
	<i>a</i>	<i>b</i>
SiO <sub>2</sub> - quartz	61.93	44.76
Li <sub>2</sub> CO <sub>3</sub>	38.07	27.52
CaF <sub>2</sub>	0.00	2.15
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.00	25.58
P <sub>2</sub> O <sub>5</sub> -equivalent	0	14

of fluorapatite on the mechanism and kinetics of LS<sub>2</sub> glass transformation and on the thermal stability of glass against crystallization using differential thermal method (DTA). The stability of glass will be evaluated by means of the kinetic parameters (the values of activation energy) and the length of induction period.

## EXPERIMENTAL

The samples of pure lithium disilicate glass (further denoted as glass *a*) and of glass with fluorapatite (reported as glass with 14 wt. % of P<sub>2</sub>O<sub>5</sub> and denoted as glass *b*) having the composition summarized in Table 1 were prepared as reported in our previous works [13,14]. The crystallization mechanism of samples was investigated using the DTA analysis (DTA - Derivatograph Q - 1500D). Grinded samples were sieved and the following mean sizes: 0.098, 0.3025, 0.4275, 0.9, 1.8, 3.5, 5.15 (mm) were used in the experiment. Then, samples with different particle size were heated from room temperature to the crystallization temperature at 10 °C min<sup>-1</sup> rate in the atmosphere of nitrogen. Also, the thermal stability of pure LS<sub>2</sub> glass and glass containing FA was performed by a TA INSTRUMENT 2860 SDT. The samples were subjected to grinding and sieving, and the fraction 0.71-0.125 mm (mean size 0.098 mm) was used for thermal analysis. The powdered glasses of about 20 mg stored in platinum crucibles were heated from room temperature until the crystallization was completed at 2, 4, 6, 8 and 12 °C min<sup>-1</sup> rates and DTA measurements were realized in the atmosphere of nitrogen.

## RESULTS AND DISCUSSION

The mechanism of crystallization from DTA measurements is predicted from the dependency of three parameters on particle size: (1)  $T_p$ , (2)  $(\delta T)_p$  and (3) the ratio  $T_p^2 / (\Delta T)_p$ . These parameters are reported in Table 2.

Temperature corresponding to the maximum of the DTA crystallization peak,  $T_p$

The temperature corresponding to the maximum of the DTA crystallization peak  $T_p$  of both samples increases with increasing particle size. This indicates that crystallization becomes increasingly difficult with increasing particle size.  $T_p$  of samples *b* are lower than that of sample *a* for all grain size, proving thus that the presence of FA promotes crystallisation of LS<sub>2</sub> glass.

The maximum intensity of the DTA crystallization peak,  $(\delta T)_p$

The values of the maximum intensity of the DTA crystallization peak  $(\delta T)_p$  with particle size decreases

with increasing average particle size for both glasses until the particle size equals 0.9 mm, that indicates the surface mechanism of crystallization. After this,  $(\delta T)_p$  of pure LS<sub>2</sub> glass returns to increasing, while the values of  $(\delta T)_p$  of sample containing FA appears as independent from particle size. For all particle sizes, the maximum intensity of exothermic peak corresponding to the crystallization of pure lithium disilicate glass is higher than that of to the glass with P<sub>2</sub>O<sub>5</sub> content.

#### The ratio $T_p^2/(\Delta T)_p$

The values of  $T_p^2/(\Delta T)_p$  of glass without and with P<sub>2</sub>O<sub>5</sub> addition according to particle size differ. Whereas the values of  $T_p^2/(\Delta T)_p$  of glass with FA demonstrate the decreasing tendency until the particle size equals 0.9 mm without exception, those of LS<sub>2</sub> glass have the same feature to 0.3025 mm. Considering Equation (1), which expresses the crystal growth dimension ( $n$ ) with activation energy for crystal growth ( $E$ ) independent from particle size, then the value of  $n$  depends only on  $T_p^2/(\Delta T)_p$ . Correspondingly,  $T_p^2/(\Delta T)_p$  decreasing with increasing particle size ensures the decrease of  $n$  and consequently indicates the tendency to surface crystallization. On the contrary, increasing values of  $T_p^2/(\Delta T)_p$  imply the internal crystallization mechanism. By comparing the dependency of both glasses and also in association with preliminary results it can be deduced that the reason for the change in dependency of pure LS<sub>2</sub> glass can be explained by internal crystallization, which substitutes the previous surface crystallization mechanism after the glass particles achieve certain size. On the other hand, the addition of P<sub>2</sub>O<sub>5</sub> enhances bioactive behaviour of these glasses [13,14] which may

support crystallization via surface mechanism.

#### Activation energy and thermal stability

The characteristic temperatures,  $T_x$  (the onset temperature of the crystallization peak) and  $T_p$  (temperature corresponding to the maximum intensity of the DTA crystallization peak), directly determined from all DTA curves recorded at different heating rates are summarized in Table 3.

The values of activation energies were calculated according to Equations (7) and (8) developed by Kissinger [15] and Ozawa [16], respectively.

$$\ln(\beta/T_p^2) = -E(T_p)/RT_p + \text{const.} \quad (7)$$

and

$$\ln\beta = -E(\beta)/(RT_p) + \text{const.} \quad (8)$$

The values of  $E(T_p)$  and  $E(\beta)$  determined from the slopes of mentioned dependencies are listed in Table 2.

The parameters  $A$  and  $E_a$  in Equation (4) were calculated by program KINPAR developed by Šimon et al. [11,12]. The program minimizes the squared deviations between experimental and theoretical values of temperature for various heating rates by the simplex method. When the induction period is assumed,  $T_i$  represents the temperature of the end of induction period  $T_x$ .  $T_x$  is the only temperature falling to the induction period which is detected. This is the reason why the kinetics of induction period can be described only by integral method and not by differential or incremental isoconversional methods. If the overall crystallization process is taken into account, then  $T_i$  is substituted by  $T_p$ .

Table 2. Parameters determining crystallisation mechanism.

Grain size (mm)	Maximum of the DTA crystallization peak, $T_p$ (°C)		Intensity of the DTA crystallization peak, $(\delta T)_p$		ratio $T_p^2/(\Delta T)_p$	
	Glass <i>a</i>	Glass <i>b</i>	Glass <i>a</i>	Glass <i>b</i>	Glass <i>a</i>	Glass <i>b</i>
0.098	609.43	594.09	62.927	61.61	221.33	265.97
0.3025	636.68	606.86	50.276	44.46	181.77	223.606
0.4275	643.33	610.75	48.558	43.00	187.86	214.377
0.9	660.94	622.45	43.113	32.28	252.80	185.646
1.8	677.65	633.81	45.194	32.38	370.33	226.96
3.5	684.5	641.22	60.868	30.612	532.43	363.81
5.15	683.78	643.69	80.873	30.783	1461.11	402.27

Table 3. Characteristic parameters to evaluate thermal stability of glasses a and b heated at different heating rates and activation energy  $E$  according to Kissinger or Ozawa.

Heating rate (°C/ min)	Glass <i>a</i>					Glass <i>b</i>				
	2	4	6	8	12	2	4	6	8	12
$T_x$ (K)	794	801	807	811	813	791	796	802	805	810
$T_p$ (K)	853	868	877	883	893	830	838	848	853	861
$E(T_p)$ (kJ/mol)	299 ± 1					288 ± 7				
$E(\beta)$ (kJ/mol)	313 ± 1					303 ± 8				

Table 4. Characteristic parameters of crystallization process of glasses *a* and *b*.

Parameters	Glass <i>a</i>		Glass <i>b</i>	
	<i>A</i> (min)	<i>E<sub>a</sub></i> (kJ/mol)	<i>A</i> (min)	<i>E<sub>a</sub></i> (kJ/mol)
Induction period	9.04 ± 10 <sup>-27</sup>	407 ± 12	4.21 ± 10 <sup>-24</sup>	365 ± 10
Crystal growth	2.89 ± 10 <sup>-16</sup>	270 ± 2	2.33 ± 10 <sup>-15</sup>	264 ± 11
Crystallization	1.53 ± 10 <sup>-16</sup>	275 ± 2	8.98 ± 10 <sup>-16</sup>	253 ± 11

Besides this, the value of activation energy for the crystal growth was also determined. In this case, the conversion reached between  $T_x$  and  $T_p$  was assumed.

The values of parameter *A* together with the values of activation energy estimated according to isoconversional method are listed in Table 4. The standard deviations of  $E_a$  and *A* were calculated.

### CONCLUSIONS

The addition of CaO, P<sub>2</sub>O<sub>5</sub> and CaF<sub>2</sub> to the pure lithium disilicate glass resulted in the higher tendency of glass sample to crystallize. The value of parameter *A* varies and is probably responsible for the difference in the stabilities of glasses. The smallest values of *A* and the highest values of  $E_a$  were achieved for the case of induction period evaluation as well for the glass *a* as glass *b*. As it was expected, the evaluation of crystal growth and overall crystallization gave the smaller values of activation energy.

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### References

1. Majling J.: *Solid State Phenomenon* 90-91, 75 (2003).
2. Durschang B. R., Carl G., Rüssel C., Roeder E.: *Glastech. Ber. Glass Sci. Technol.* 67, 171 (1994).
3. Höland W., Rheinberger V., Apel E., Hoen Ch.: *J. Eur. Ceram. Soc.* 27, 1521(2007).
4. Ranasinghe K. S., Wei P. F., Kelton K. F., Ray C. S., Day D. E.: *J. Non-Cryst. Solids* 337, 261 (2004).
5. Ray C. S., Day D. E.: *Thermochim. Acta* 280 163(1996).
6. Augis J.A., Bennett J.E.: *J. Therm. Anal.* 13, 283 (1978).
7. Ray C. S., Day D. E., Huang W., Narayan K. L., Cull T. S., Kelton K. F.: *J. Non-Cryst. Solids* 204, 1 (1996).
8. Guedes M., Ferro A. C., Ferreira J. M. F.: *J. Eur. Ceram. Soc.* 21, 1187(2001).
9. Jóna E., Šimon P., Nemčeková K., Pavlík V., Rudinská G.: *Jour. Therm. Anal. Cal.* 84, 673 (2006).
10. Branda F., Marotta A., Buri A.: *J. Non-Cryst. Solids* 134, 123 (1991).
11. Šimon P., Nemčeková K., Jóna E., Pliško A., Ondrušová D.: *Thermochim. Acta* 428, 11(2005).
12. Šimon P.: *J. Therm. Anal. Cal.* 82, 651(2005).
13. Kuzielová E., Hrubá J., Palou M., Smrčková E.: *Ceramics-Silikáty* 50, 159(2006).
14. Kuzielová E., Palou M., Kozánková J.: *Ceramics-Silikáty* 51, 136 (2007).
15. Kissinger H. E.: *Analytical Chemistry* 11, 1702 (1957).
16. Ozawa T.: *Jour. Therm. Anal.* 2, 301 (1970).