CRYSTALLIZATION MECHANISM AND BIOACTIVITY OF LITHIUM DISILICATE GLASSES IN RELATION TO CaO, P_2O_5, CaF_2 ADDITION

EVA KUZIELOVÁ, MARTIN PALOU, JANA KOZÁNKOVÁ

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

E-mail: eva.kuzielova@stuba.sk

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The present investigation reports the results of P_2O_5, CaO and CaF_2 (in stechiometric ratio corresponding to fluoroapatite) effect upon the controlled crystallization of grain-sized particles of lithium disilicate (LS_2) glass and upon the bioactivity of given glasses, that have been investigated by means of DTA and by in vitro testing after 4 weeks, respectively. The crystallization of pure lithium disilicate glass as well as that of glass containing the above components proceeds by surface and internal mechanism as function of particle size. The onset of internal crystallization, which substitutes the surface one is found at about 0.3 mm for pure lithium disilicate glass, while this change occurred at size of 0.9 mm approximately in glass containing CaO, P_2O_5 and CaF_2. The addition of different amount of "apparent fluoroapatite" enhances the bioactivity of bioglasses as confirmed by SEM and EPMA.

INTRODUCTION

Li_2O-SiO_2 systems with composition close to lithium disilicate (LS2) are ones of the most studied systems regarding the control crystallization in glass ceramic synthesis. In fact, the first prepared glass ceramics were developed by Stookey [1] by heat treatment of glass from this system. The research on lithium disilicate glass ceramics can by classified into two categories in general. The first one deals with the study of binary system. In this case, the fundamental interest is focused on nucleation mechanisms and identification of the primary phases, which prevent the lithium disilicate precipitation [2-6]. The second field deals with the multicomponent systems in which some oxides are added to binary Li_2O-SiO_2 systems in order to develop new glass ceramic materials with extended applications. Thermal, optical and mechanical properties of these new materials, deduced from their microstructure and phase composition, can be obtained by controlled nucleation and grain growth processes. Many of these glass ceramic materials prepared by controlled crystallization have found applications in medicine, mainly in stomatology.

The well-known materials are the lithium disilicate glass ceramics in SiO_2–Al_2O_3–La_2O_3–MgO–ZnO–K_2O–Li_2O–P_2O_5 system for example, which excel in translucency, high strength (flexural strength: 300-400 MPa) and can be tailored by compressing [7]. High-strength and machinable glass ceramics were formed in the ZnO-free SiO_2–Li_2O–Al_2O_3–K_2O–P_2O_5 system (flexural strength 740.8 MPa, fracture toughness: 3.3 MPa $m^{1/2}$) [8]. Glass ceramics with natural optical properties were developed in SiO_2–Li_2O–K_2O–ZnO–CaO–P_2O_5–F system. Microstructure of this glass ceramic type contains the apatite crystals with needle-like morphology (like in natural teeth) [9]. All of these glass ceramics are applied as dental restorative materials, such as crowns or bridges.

Also, the glass ceramics from Li_2O–SiO_2–CaO–P_2O_5–F system are used in clinical applications. Because of high strength, opalescence, thermal stability and chemical resistance, the glass ceramics of this type are applied as dental bridges, crowns or veneers. The demonstration of bioactive properties, which are initiated by CaO, P_2O_5, CaF_2 contents, brings out the new application possibilities. CaO, P_2O_5 and CaF_2 as nucleation agents are frequently added in small portions to lithium disilicate glasses, in which they initiate the internal nucleation through the phase separation [8, 10, 11]. However, when using in larger amounts, these oxides cannot yet be considered to provide nucleation sites. Then the properties of the glass change and nucleation data for both the basic and modified glasses are not comparable. The knowledge of the effect of these substance additions on mechanism and on crystallization kinetics provides the facilities how to influence the properties of final materials by a controlled crystallization process. Consequently it brings the possibility to optimize the composition and heat treatment history, which would lead to additional improvement of material properties.

However, the overall crystallization process that occurs in glasses during reheating is a complex structural reorganization that is hard to classify uniquely into the so-called internal (bulk) or surface mechanism. In most glasses, crystallization by internal and surface mechanisms proceeds simultaneously and competitively. The specific mechanism which would dominate the crystallization of particular glass is generally determined by its kinetic and thermodynamic properties (such as diffusion coefficient, molar volume, entropy of fusion etc.), which depend upon the glass composition [12]. In addition, the mechanical damage of surface, dust particles, annealing atmosphere and other parameters play the significant role [13].

The rapid and convenient method that aids to identify and distinguish surface and internal crystallization is based on differential thermal analysis and has been developed by Ray and Day [14]. 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 width of the DTA peak at half-maxima are determined as a function of size of the glass particles used for DTA measurements. The past mentioned dependency is derived from Equation (1), which expresses the crystal growth dimension, n, (also known as Avrami parameter) [15].

$$n = [2.5/(\ T)_P]/(E/RT_P^2) \quad (1)$$

where R is the gas constant.

If E (J/mol) (activation energy for crystal growth) is assumed to be 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, the value close to 3 signifies internal crystallization and intermediate values between 1 and 3 are indicative of both surface and internal crystallization [16].

The goal of the present work is in advance to resolve the influence of CaO, P_2O_5 and CaF_2 additions on mechanism of crystallization in lithium disilicate glasses by using the above method and on bioactivity of these glasses.

EXPERIMENTAL

The samples of bioactive glass with different P_2O_5 content (Table 1) were prepared by mixing Tosil (SiO_2, w = 30.93 wt.% SiO2), Li_2CO_3 (pure), CaF_2 (dried) and $Ca_3(PO_4)_2$ (dried). The ratio of CaF_2 and $Ca_3(PO_4)_2$ responsed to stechiometric fluoroapatite composition. Pure lithium disilicate glass without P_2O_5 and CaF_2 content was prepared as a reference sample. The resulted suspensions were stirred by using the magnetic blender at current heating for 1 h. After partial evaporation of water, the drying under IR lamp and in the oven followed. The as prepared powdered samples were melted in a Pt-crucibles in a supercanthal furnace at a temperature of 1450°C (2 h, 10°C/min). Subsequently, the enamel was poured onto anticorrosive board, where it supported by ice rapidly cooled down.

In order to investigate the crystallization mechanism in relation to the chemical composition, the DTA analysis of two samples (without P_2O_5 content and with 14 wt.% P_2O_5) with different particle sizes were performed (DTA - Derivatograph Q - 1500D). For that purpose, the samples were subjected to grinding and subsequently separated to particular fractions by means of sieves. The following fractions were chosen: 0.071-0.125, 0.25-0.355, 0.355-0.5, 0.8-1.0, 1.6-2.0, 3.0-4.0, 4.0-6.3 (mm). The arithmetic average for each size range is represented by the numbers: 0.098, 0.3025, 0.4275, 0.9, 1.8, 3.5, 5.15 (mm). The powdered glasses were heated from room temperature until the crystallization was complete at 10°C min^{-1} rate and DTA measurements were realized in the atmosphere of nitrogen.

The bioactivity of the glasses with different contents of CaO, P_2O_5 and CaF_2 was studied by in vitro testing. The simulated body fluid (SBF), which ion concentrations are almost identical with inorganic ion concentrations of human blood plasma (Table 2), was prepared according to literature [17].

The calculated volumes of SBF (Equation (2)) were poured in the plastic containers and heated up to the temperature of 36.5 °C

$$V_S = \frac{S_a}{10} \quad (2)$$

where V_S is the volume of SBF (ml) and Sa is the apparent surface area of specimen (mm^2).

Carefully cleaned samples were immersed and stored in the incubation apparatus (Binder BD 115) for four weeks at the temperature of 37.5 °C.

Surface microstructures of glasses before and after soaking in SBF were studied by SEM (TESLA BS 300). The microprobe (EPMA JEOL JXA-840A) was used to examine the surface layer formed on the samples during exposure in SBF.

Table 1. The composition of mixtures designated for preparation of glasses (wt.%).

	P_2O_5 content (wt.%)			
	0	5	10	14
SiO_2 - Tosil	84.00	80.54	76.33	72.87
Li_2CO_3	16.00	15.32	14.52	13.51
CaF_2	0.00	0.32	0.71	1.05
$Ca_3(PO_4)_2$	0.00	3.82	8.44	12.57

Table 2. The ion concentrations of SBF in comparison with those in human blood plasma.

	Ion concentrations (10^{-3} mol/l)							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5
SBF	142.0	5.0	1.5	2.5	148.8	4.2	1.0	0.5

RESULTS AND DISCUSSION

The results of DTA analysis

For the purpose to determine the effect of CaO, P_2O_5 and CaF_2, below referred by P_2O_5 addition only, on crystallization mechanism, DTA thermograms of pure lithium disilicate glass and the glass containing 14 wt.% P_2O_5 were compared. The mechanism of crystallization by usage of DTA is predicted from the dependency of three parameters on particle size: (1) the temperature corresponding to the maximum of the DTA crystallization peak T_P, (2) the maximum height of the DTA crystallization peak $(\delta T)_P$, and (3) the ratio $T_P^2/(\Delta T)_P$.

The temperature corresponding to the maximum of the DTA crystallization peak, T_P, increases with increasing particle size as well in the case of LS_2 reference glass as in the case of glass with 14 wt.% P_2O_5 (Figure 1). This indicates that crystallization becomes increasingly difficult with increasing particle size. The pure LS_2 glass`s plot lies above the plot of glass containing P_2O_5. Consequently, the addition of P_2O_5 results in displacement of crystallization towards lower temperatures and hence promotes it.

The dependence of the maximum height of the DTA crystallization peak, $(\delta T)_P$, on particle size is shown in the Figure 2 ($(\delta T)_P$ is reduced to the unit weight). $(\delta T)_P$ decreases with increasing average particle size for both glasses until the particle size equals 0.9 mm, which indicates the surface mechanism of crystallization [14]. In the case of higher particle sizes, the course of dependency changes. $(\delta T)_P$ as a function of particle size of pure LS_2 glass returns to increasing, while the same dependency of glass with P_2O_5 content appears as independent on particle size. For all particle sizes, the maximum height of exothermic peak corresponded to the crystallization in pure lithium disilicate glass is higher as $(\delta T)_P$ belonging to the glass with P_2O_5 content.

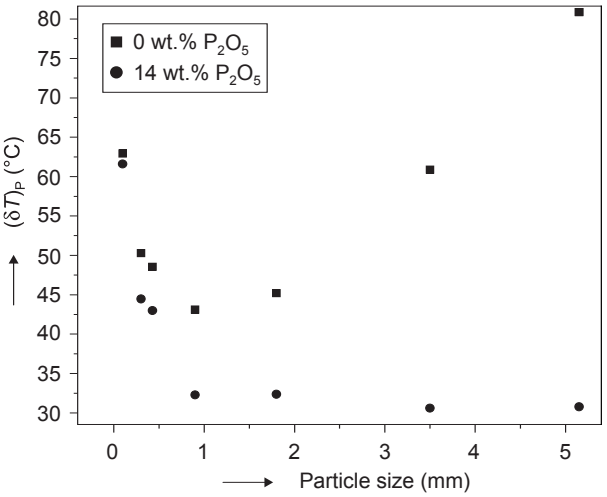

Figure 2. The dependence of the maximum height of the DTA crystallization peak, $(\delta T)_P$, on particle size for glass without P_2O_5 addition and for glass containing 14 wt.% P_2O_5.

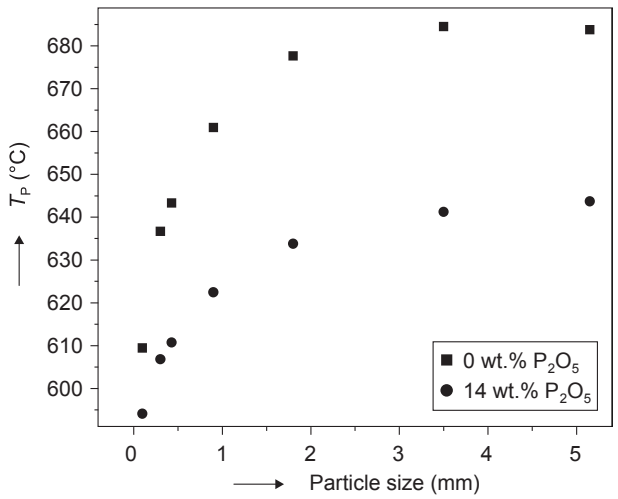

Figure 1. The temperature at the maximum height of the DTA crystallization peak, T_P, as a function of particle size for glass without P_2O_5 addition and for glass containing 14 wt.% P_2O_5.

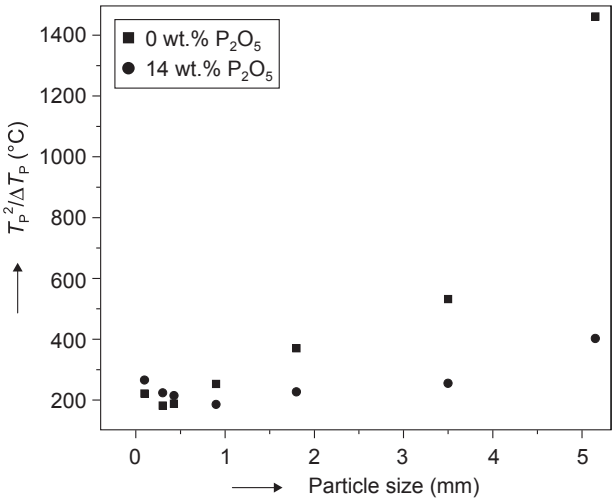

Figure 3. The ratio of the square of the peak temperature, T_P, to peak half-width, $(\Delta T)_P$, as a function of particle size for glass without P_2O_5 addition and for glass containing 14 wt.% P_2O_5.

The course of $T_P^2/(\Delta T)_P$ dependence on particle size of glass without and with P_2O_5 addition (Figure 3) differs one from other. Whereas the dependence of glass with 14 wt.% P_2O_5 demonstrates the decreasing feature until the particle size equals 0.9 mm, in the case of pure LS_2 glass this dependence is decreasing with increasing particle size up to 0.3 mm. After particle size exceeds 0.9 mm and 0.3025 mm, respectively, $T_P^2/(\Delta T)_P$ increases with increasing particle size for both glasses. However the slope of rising function is different. The function of LS_2 glass increases rapidly, while the glass containing P_2O_5 exhibits only smooth rising of $T_P^2/(\Delta T)_P$ dependence on particle size.

Considering the activation energy E = 299 kJ/mol [16] for pure lithium disilicate glass and that we calculated in [18] (E = 253 kJ/mol) for glass containing 14 wt.% P_2O_5, the value of n lower than 1 is obtained for all values of $T_P^2/(\Delta T)_P$ according the Equation (1). $T_P^2/(\Delta T)_P$ decreasing with increasing particle size ensures the decrease of n and consequently indicates the tendency to surface crystallization. On the contrary, increasing values of $T_P^2/(\Delta T)_P$ should imply the rising importance of internal crystallization mechanism. However, a decrease and an increase of with increasing particle size is not quite reasonable, because if E does not change appreciably with particle size, $T_P^2/(\Delta T)_P$ for all the particle sizes should be nearly the same. The cause purpose of this phenomenon is not yet clear up, but the similar findings have been noticed also by other authors 14, 16, 18-20 .

By comparing the $T_P^2/(\Delta T)_P$ dependency of both glasses and also in association with preliminary results it can be deduced that the reason for the change in dependency of two glasses can be explained by increasing internal crystallization, which substitutes the previous surface crystallization after the glass particles reach certain size. In the case of glass containing P_2O_5 the effect of internal crystallization is appeared after the bigger fractions of glass are used, on which it is clearly shown that the addition of P_2O_5 results in support of surface crystallization, which may play a role in bioactive behavior of this glass as will be suggested later.

The results of in vitro bioactivity testing

The surfaces of glasses without and with different contents of P_2O_5 (5, 10 and 14 wt.%) after immersion in SBF for a period of four weeks are demonstrated by Figures 4-7. To compare with smooth initial glass surfaces, the surfaces underwent marked change as consequence of SBF acting. The scattered regions comprised of small particles of new phases can be seen on the surface of reference LS_2 glass, whereas the surfaces of all samples containing P_2O_5 are covered by continual new layer. While the layer created on surface of glass with 5 wt.% P_2O_5 is fine, the higher contents of P_2O_5 resulted in growth of surface phases and the formed layers appear like coarser.

The surface layers of glass without P_2O_5 content and glass containing 14 wt.% P_2O_5 before and after SBF acting were analyzed by EPMA. Besides silicon which was only detected on the initial surface of pure LS_2 glass, the small amount of calcium and phosphorus was

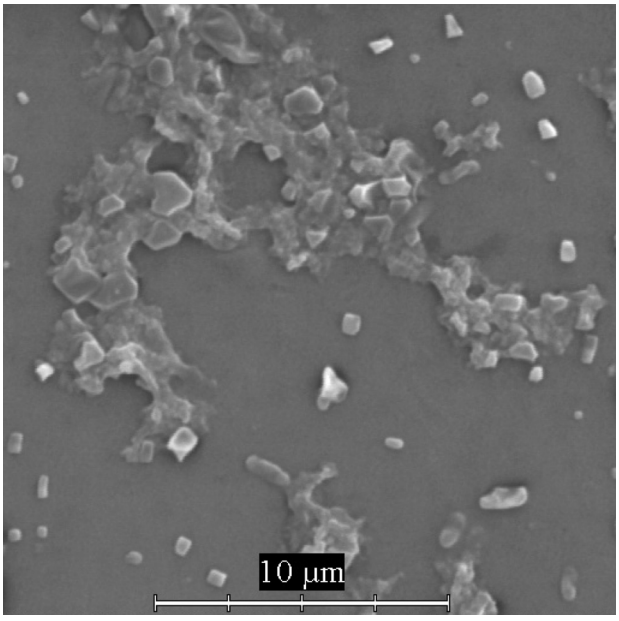

Figure 4. Surface microstructure of glass without P_2O_5 addition after 4 weeks in SBF.

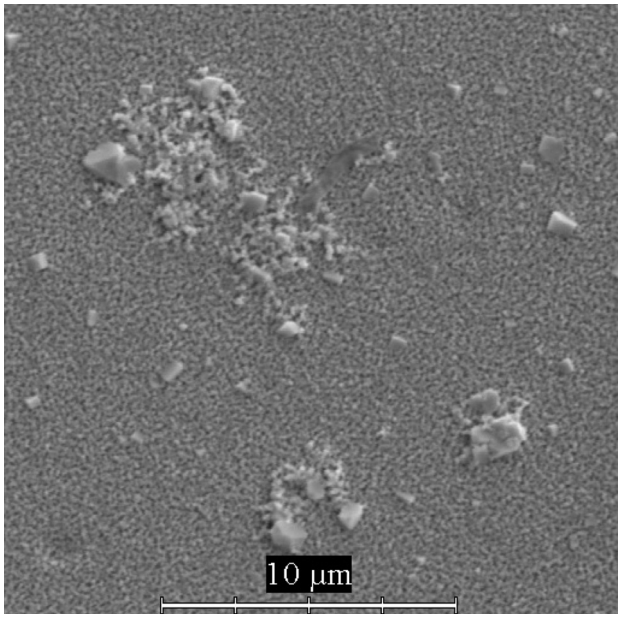

Figure 5. Surface microstructure of glass sample containing 5 wt.% P_2O_5 after 4 weeks in SBF.

revealed on the surface after bioactivity testing (Figure 8). In the case of glass with 14 wt.% P_2O_5, the microanalysis indicated only the presence of Ca and P without any amount of silicon, consequently the new created apatite layer covers whole initial surface (Figure 9). Thus, the results confirm the bioactivity of these glasses, which is promoted chiefly by P_2O_5 addition and is manifest by forming a calcium phosphate-rich layers on their surfaces. It should be noticed that the limits of device make impossible to detect the fluorine. Besides these major elements the presence of small amount of Na, Mg and Cl was detected in the samples after immersion in SBF. The above components descended from the simulated body fluid (see Table 2).

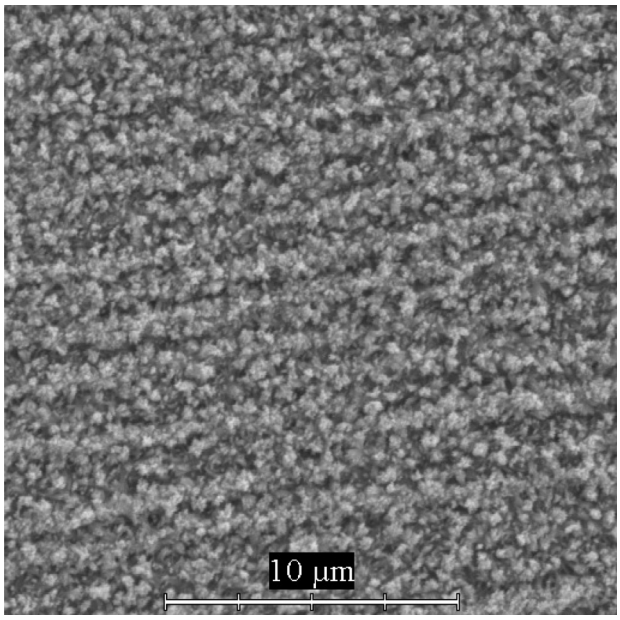

Figure 6. Surface microstructure of glass sample containing 10 wt.% P_2O_5 after 4 weeks in SBF.

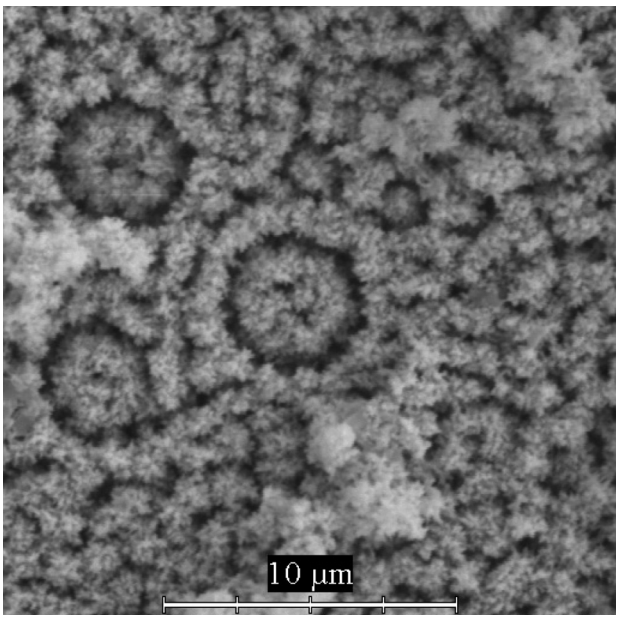

Figure 7. Surface microstructure of glass sample containing 14 wt.% P_2O_5 after 4 weeks in SBF.

CONCLUSIONS

In the present work a DTA method has been used to design the crystallization mechanism of glasses in the Li_2O–SiO_2–CaO–P_2O_5–CaF_2 system in correlation with chemical composition. The dependence of three DTA parameters, T_P, $(\delta T)_P$ and $T_P^2/(\Delta T)_P$, on particle size showed that the pure lithium disilicate glass as well as glass containing CaO, P_2O_5 and CaF_2 (in relative ratio corresponding to fluoroapatite composition) preliminary crystallize by surface mechanism. While the bigger particle sizes of LS_2 glass allow the internal crystalliza-

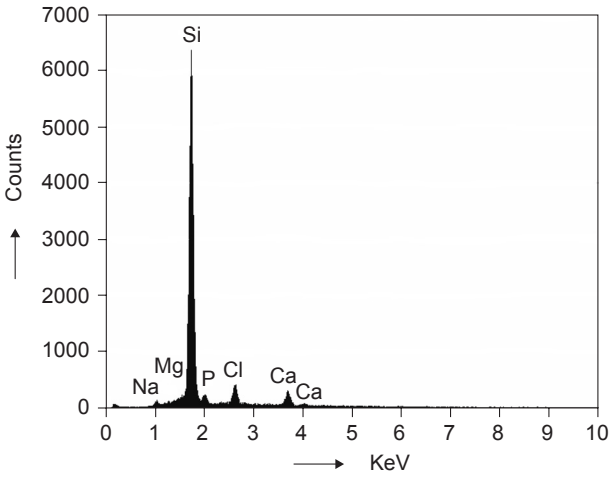

Figure 8. The result of element microanalysis of glass surface without P_2O_5 addition after soaking in SBF for 4 weeks.

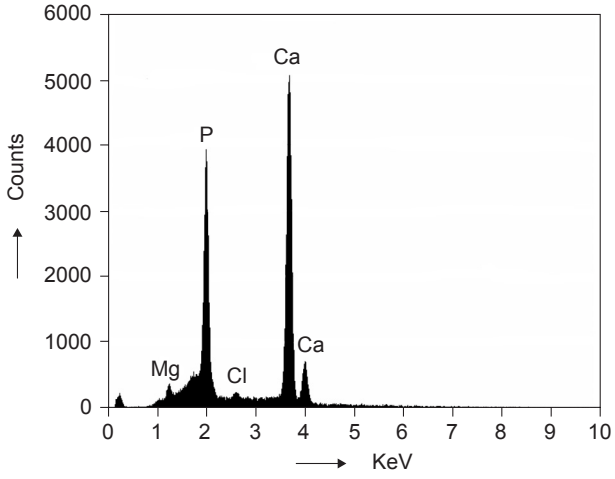

Figure 9. The result of element microanalysis of glass surface containing 14 wt.% P_2O_5 after soaking in SBF for 4 weeks.

tion to proceed, the addition of above components supported the crystallization by surface mechanism. The bioactivity of glasses was exhibited by in vitro testing. The addition of CaO, P_2O_5 and CaF_2 promoted the bioactive properties of glasses and the created calcium phosphate-rich layer covering the whole surface of them already 5 wt.% P_2O_5 was added to primary composition. The layer of new phases was formed in four weeks, which is the time that could satisfy the clinical requirements.

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MECHANIZMUS KRYŠTALIZÁCIE A BIOAKTIVITA LÍTIUM DISILIKÁTOVÝCH SKIEL V ZÁVISLOSTI OD OBSAHU CaO, P_2O_5, CaF_2

EVA KUZIELOVÁ, MARTIN PALOU, JANA KOZÁNKOVÁ

Ústav anorganickej chémie, technológie a materiálov, Slovenská technická univerzita, Radlinského 9, 812 37 Bratislava, Slovenská Republika

Prezentovaný výskum referuje o vplyve P_2O_5, CaO a CaF_2 (v stechiometrickom pomere zodpovedajúcom zloženiu fluórapatitu) na kontrolovanú kryštalizáciu rôznych frakcií lítium disilikátového skla, študovanú pomocou DTA, a na bioaktivitu príslušných skiel, ktorá bola študovaná prostredníctvom in vitro testovania. Kryštalizácia čistého lítium disilikátového skla rovnako ako skla obsahujúceho vyššie zmienené zložky prebieha v závislosti od veľkosti častíc mechanizmom povrchovej alebo objemovej kryštalizácie. V prípade čistého lítium disilikátového skla sa objemová kryštalizácia, ktorá nahrádza povrchovú kryštalizáciu, prejavila u častíc s veľkosťou okolo 0.305 mm, zatiaľ čo u skla obsahujúceho P_2O_5, CaO a CaF_2 bola zmena mechanizmu kryštalizácie detekovaná u častíc s veľkosťou okolo 0.90 mm. Prídavok rôznych množstiev „fluórapatitu" zlepšuje bioaktivitu týchto bioskiel, čo bolo potvrdené REM i EPMA.