

INFLUENCE OF P₂O₅ UPON THE CRYSTALLIZATION OF LITHIUM DISILICATE AND FLUOROAPATITE IN BIO-GLASS CERAMICS

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Referred work is a preliminary investigation of the lithium disilicate (LS₂) and the fluoroapatite (FA) crystallization in bio-glass ceramics. Composite glass-ceramics with various content of P₂O₅ in oxide system SiO₂-Li₂O-CaO-CaF₂-P₂O₅ were prepared by heat treatment of glass at different temperatures. Two crystalline phases lithium disilicate (LS₂) and fluorapatite (FA) were developed in the samples depending on P₂O₅ content and temperature. The increase of temperature as well as the content of P₂O₅ promote the crystallization of FA. XRD measurements supplemented by DTA results showed that LS₂ crystallization at lower temperature is inhibited because of the present of amorphous FA. On the contrary, crystalline phase of FA promoted the crystallization of LS₂. Phase separation of the samples is well observed in scanning electronic micrograph. The Vickers hardness values of prepared bio-glass ceramics are higher than the average hardness of biological tooth and these materials could be applied as mechanically loaded biomedical implants.

INTRODUCTION

The reason and the interest for the development of bio-glass ceramics in SiO₂-Li₂O-CaO-CaF₂-P₂O₅ system are their possible applications as biomaterials in clinical surgery. The applications of biomaterials depend on their phase composition, mechanical properties and microstructure, which are designed mainly by original composition and by heat treatment. The method of heat treatment leading to formation of glass ceramic material is not groundless. It promotes the ability to cast components in glassy state directly to the required shape of implants, the crystalline phases dispersed into the basic glass increase the mechanical strength of materials [1]. The fluoroapatite is noted as bioactive material [2, 3], it is thermally stable and used to prevent dental caries in acidic environment containing bacteria [4]. Anion F⁻ promotes the nucleation and the crystal growth of calcium phosphate in the bone regenerating process [5]. Despite of these well-known facts the role of individual components remains uncertain.

Single lithium disilicate glass is the subject of various controversies related to discrepancy between classical nucleation theory predictions and experimental results [6-8]. A possible explanation of the anomalous nucleation behavior is the formation of one or several metastable phases in the early stages prior to the appearance of equilibrium phase. According to Soares and co-workers [9], the first phase is probably formed by homogenous nucleation. The occurrence of traces of metastable lithium metasilicate after crystallizing LS₂

glass was reported for example by Kinser and Hench [10], Hench et al. [11]. On the other hand, in different investigations [12,13] the crystallization of lithium disilicate or solid solution of LS₂ was only observed.

P₂O₅ is used as a nucleating agent initiating heterogeneous nucleation of a major phase in Li₂O-SiO₂ glasses. The authors [14,18] have reported that the nucleation rate of lithium disilicate is much higher in the presence of P₂O₅. In the James [15] work the nucleation rate in a 33.3 Li₂O × 65.7 SiO₂ × 1 P₂O₅ (mol %) glass was 1000 times greater than in a LS₂ base glass at 500°C. Firstly, one can attribute the rate increase to the amorphous phase separation in the glass containing P₂O₅. However, it is more possible that this effect is caused by reduction of thermodynamic barrier of nucleation or by precipitation of fine crystallites of a phosphate phase in the glass (probably Li₃PO₄), which acted as heterogeneous sites for nucleation of lithium disilicate crystals. The last possibility was indicated by the presence of cores in the LS₂ crystals observed by TEM [16,17]. Because of instability of the fine crystals in the electron beam, distinct evidence of Li₃PO₄ crystals existence was not obtain by TEM. Thus, P₂O₅ influence as nucleating agent is not yet clarified and requires further study.

The present work carries out the additional step to knowledge of this system, aids to clarify the relations between P₂O₅ content, the conditions of thermal processing and the final properties of material, which define the possible applications of synthesized biomaterials.

EXPERIMENTAL

The samples of bioglass with different P_2O_5 content (table 1) were prepared by mixing ground quartz sand (99.6 wt.% SiO_2), Li_2CO_3 (technical), CaF_2 (dried) and $Ca_3(PO_4)_2$ (dried). The shots of CaF_2 and $Ca_3(PO_4)_2$ responded to stoichiometric fluoroapatite composition. Pure lithium disilicate glass without P_2O_5 content was prepared as a reference sample. The mixtures were melted in a Pt-crucibles in a superkanthal furnace for 1 h at a temperature of $1400^\circ C$ after homogenization. Subsequently, the enamel was poured onto anticorrosive board, where it cooled down. The temperatures of $550^\circ C$, $650^\circ C$ and $750^\circ C$ for heat treatment, so for preparation of glass ceramics, were chosen on the base of DTA measurement (heating rate $10^\circ C/min$, holding time 6 h).

Microstructures of glass ceramics were studied by SEM (TESLA BS 300). Samples were etched with 2 % HF (for 30 s) to emphasize the grain boundaries. Their phase composition was identified by XRD analysis (STOE, type theta/theta diffractometer). Samples were

subjected to DTA (DTA - Derivatograph Q - 1500D) and hardness measurement according to Vickers (VICKERS HARDNESS TESTER FV-1). Before the hardness measurements the samples were polished.

RESULTS AND DISCUSSION

DTA thermograms of the sample of lithium disilicate glass without P_2O_5 content and of the samples with addition of 4 - 8 wt.% P_2O_5 show one exothermic peak (figure 1). Two exothermic peaks appeared till on the record of sample containing 10 wt. % P_2O_5 . By comparing DTA and XRD results the exothermic effect at lower temperature could be attributed to LS_2 crystallization and the exothermic effect at higher temperature to crystallization of FA. The addition of 4 wt. % and 6 wt. % P_2O_5 caused the displacement of LS_2 crystallization maximum towards higher temperatures, more increase of P_2O_5 content results in shift towards lower temperatures. At the 14 wt. % P_2O_5 content, the exothermic effect of FA crystallization is higher than the effect of LS_2 crystallization.

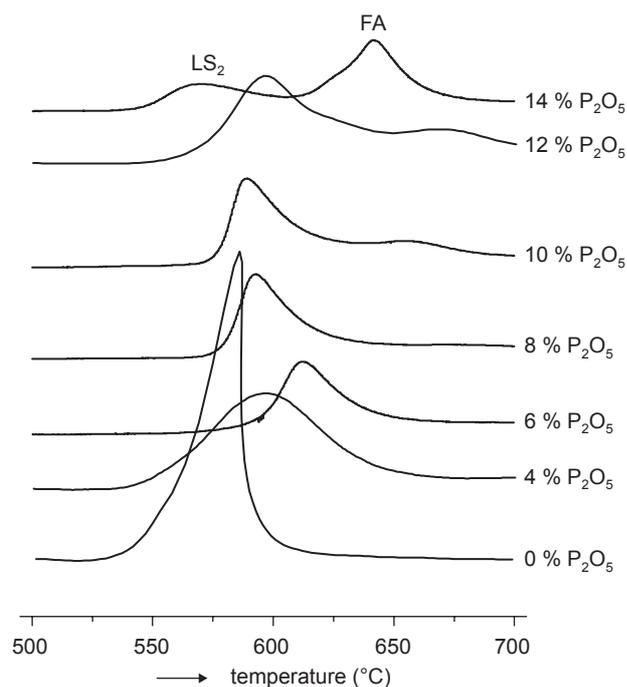


Figure 1. DTA thermograms of samples with different P_2O_5 content.

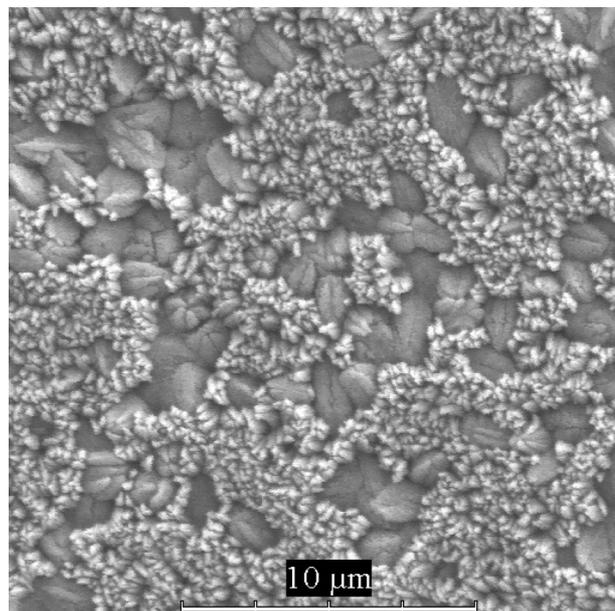


Figure 2. Microstructure of polished and etched surface of sample with 6 wt.% P_2O_5 heated at $650^\circ C$ for 6 h.

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

	P_2O_5 content (wt.%)						
	0	4	6	8	10	12	14
SiO_2 - quartz sand	61.93	57.29	54.89	52.45	49.94	47.38	44.76
Li_2CO_3	38.07	35.22	33.75	32.24	30.71	29.13	27.52
CaF_2	0.00	0.58	0.88	1.18	1.50	1.82	2.15
$Ca_3(PO_4)_2$	0.00	6.91	10.48	14.13	17.86	21.67	25.58

SEM micrographs revealed phase separation in the samples containing 6 and more wt.% P_2O_5 heated at 650°C and 750°C (figure 2).

The presence of crystalline phases in the samples depends on P_2O_5 content and also on temperature of heat treatment. It can be seen on XRD patterns that lithium disilicate crystallizes in these systems after heat treatment at 550°C, but increasing P_2O_5 inhibits its crystallization. For example, at P_2O_5 content of 12 wt.% only traces of LS_2 crystalline phase were detected (figure 3).

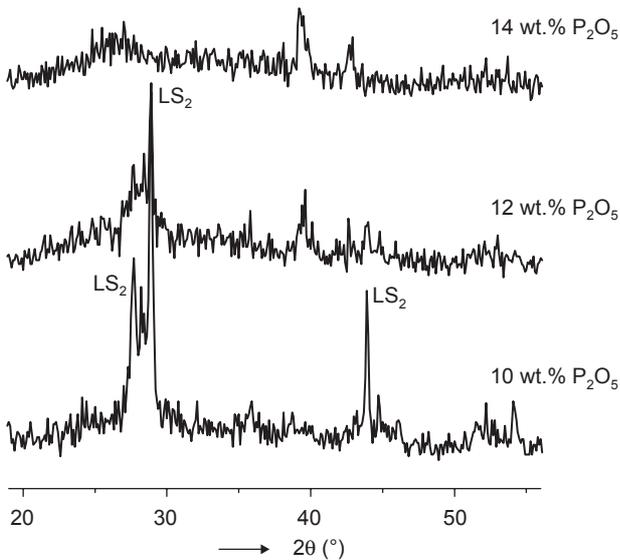


Figure 3. XRD diffraction patterns of samples with different P_2O_5 content heated for 6 h at 550°C.

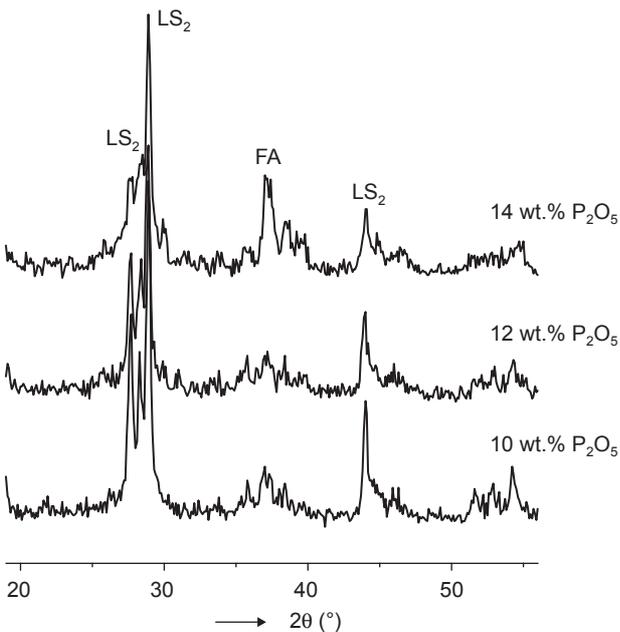


Figure 4. XRD diffraction patterns of samples with different P_2O_5 content heated for 6 h at 650°C.

In the case of higher treatment temperatures (650°C and 750°C) crystalline LS_2 is present in all samples. Besides crystalline LS_2 the crystalline FA appeared in the samples heated at 650°C and 750°C from P_2O_5 content of 10 wt.% (the trace since 8 wt.% P_2O_5).

With increasing P_2O_5 content the ratio of crystalline FA increased and peak intensity attributed to LS_2 decreased (figure 4). Upon this finding it could be deduced, that P_2O_5 reacts with CaO to form FA, that is in amorphous form after heat treatment at 550°C and inhibits the crystallization of LS_2 . This assumption is also in agreement with conclusions from DTA analysis. The higher temperatures promoted the crystallization of both phases (figure 5).

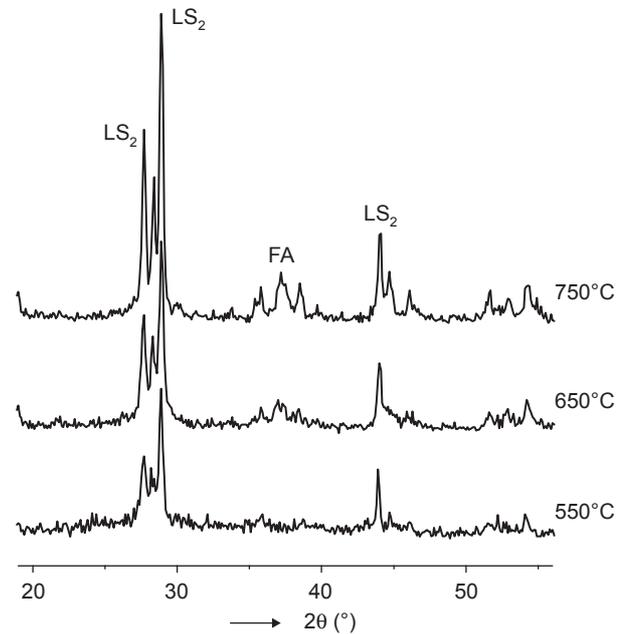


Figure 5. XRD diffraction patterns of samples containing 10 wt.% P_2O_5 heated for 6 h at different temperatures.

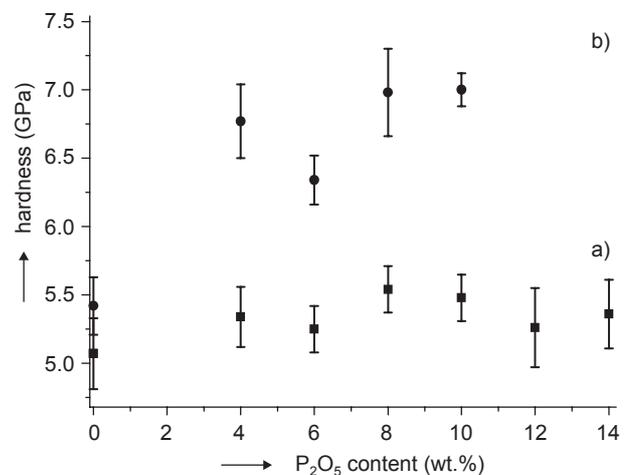


Figure 6. Hardness (GPa) of a) non heated and b) heated (650°C) samples with different P_2O_5 content at a load 9.81 N.

The results of hardness measurements are displayed in figure 6. The pure LS₂ glass showed minimum hardness value 5.07 GPa (load 9.81 N). Hardness of all other samples is higher. Depending on P₂O₅ content the hardness of glasses without subsequent heat treatment does not change markedly. The hardness values increased after heat treatment (about 20 % comparing with glasses of the same composition). In the samples without P₂O₅ addition hardness did not increase significantly. Nevertheless, hardness of all samples is higher than average hardness of teeth (3.6 GPa) as reported in [1].

CONCLUSION

Bio-glass ceramics without and with different P₂O₅ content were prepared by heat treatment of bio-glasses at three different temperatures (550°C, 650°C and 750°C). The crystallization of LS₂ occurs at lower temperature than the crystallization of FA. The lower P₂O₅ contents result in shift of LS₂ crystallization maximum towards higher temperatures, from 8 wt.% it shifted to lower temperatures and the intensity of the peak attributed to LS₂ on XRD patterns decreased. In the samples heated at 550 °C only LS₂ is crystallized, but the crystallization is inhibited by P₂O₅ addition. Crystalline FA was identified by XRD method in the samples heated at 650°C and 750°C with P₂O₅ content above 10 wt.%. The rise of temperature promoted the crystallization of both phases. It was evidenced by DTA and XRD results that addition of P₂O₅ has caused the formation of fluoroapatite. Whereas the amorphous FA inhibited the crystallization of LS₂, the crystalline FA promoted it. Hardness of materials satisfies the requirements set on implants used in loading parts of human organism.

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VPLYV P₂O₅ NA KRYŠTALIZÁCIU LÍTIUM DISILIKÁTU A FLUÓRAPATITU V BIO-SKLOKERAMICKOM SYSTÉME

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Prezentovaná práca je predbežným výskumom kryštalizácie lítium disilikátu (LS₂) a fluórapatitu (FA) v bio-sklokeramickom systéme. Kompozitná sklokeramika s rôznym obsahom P₂O₅ s oxidovým zložením SiO₂-Li₂O-CaO-CaF₂-P₂O₅ bola pripravená tepelným spracovaním skiel pri rôznych teplotách. Vo vzorkách kryštalizovali v závislosti od obsahu P₂O₅ a teploty dve kryštalické fázy: lítium disilikát a fluórapatit. Zvýšenie teploty rovnako ako obsahu P₂O₅ podporilo kryštalizáciu FA. RTG merania spolu s výsledkami DTA analýzy naznačili, že kryštalizácia LS₂ je pri nižšej teplote inhibovaná prítomnosťou amorfného FA. Kryštalický FA kryštalizáciu LS₂ naopak podporil. Fázová separácia vo vzorkách je dobre pozorovateľná na snímkach REM. Hodnoty Vickersovej tvrdosti pripravených bio-sklokeramik, vyššie ako hodnota priemernej tvrdosti biologických zubov, umožňujú aplikácie materiálov ako implantátov i v mechanicky zaťažených oblastiach organizmu.