

FLUOROAPATITE - MATERIAL FOR MEDICINE Growth, morphology and thermoanalytical properties

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Abstract

Fluoroapatite containing glass-ceramics were prepared from $\text{Li}_2\text{O}-\text{CaO}-\text{CaF}_2-\text{P}_2\text{O}_5-\text{SiO}_2$ system. The glass was melted at 1480°C for 1 h. The object of observation was the preparing crystal phase of fluoroapatite in amorphous glass matrix. The morphology of lithium disilicate glass-ceramics was studied by SEM. The crystal growth and thermal properties of fluoroapatite were studied by X-ray diffraction and DTA. The more the content of P_2O_5 , the more the presence of fluoroapatite particles. SEM investigation clearly indicated the phase separation and formation of a primary crystalline phase of fluoroapatite in the studied glass-ceramics. DTA curves of the fluoroapatite samples exhibit exothermic effects in the temperature range $337-694^\circ\text{C}$ depending on the composition of the materials. The position of *exothermic peak* for lithium disilicate on DTA curves moves with increasing *specific surface* towards lower temperatures which points on its preferential surface crystallization. As far as physical qualities are concerned, mainly color and gloss, the best qualities of all observed materials belong to glass-ceramics with 10% P_2O_5 .

Keywords: DTA, fluoroapatite, growth, morphology, P_2O_5 , SEM, synthesis, XRD

Introduction

Bulk single phase apatite ceramics suffer from the insufficient mechanical strength that prevents its direct application, e.g. in dentistry. Composites including glass ceramics, containing dispersed biocompatible hydroxyapatite or fluoroapatite phases, are therefore the solution of the problem. The fluoroapatite as a thermally more stable phase in comparison to hydroxyapatite offers increased possibilities in preparing the glass ceramics by the convenient melting/crystallization processes. The formation of fluoroapatite with randomly oriented, or aligned prolonged crystals has been studied in a number of chemically more simple, or complex glassy systems. Natural fluoroapatite can have different colors, makes column-like or table-like crystals and it is also known in the form of

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granulous or fibrous aggregates [1]. Fluoroapatite can be found also in bones and teeth and for its good qualities is used as a substitute for dental enamel. Dental enamel is the hardest substance in bodies of vertebrates and about 96% its composition is $\text{Ca}(\text{PO}_3)_2$ [2]. In bones, the fluoroapatite is accompanied by hydroxyapatite and therefore its research is important for another field of medicine: orthopedics and bone surgery [3]. More attention has focused to development of new materials containing fluoroapatite and hydroxyapatite [4–7]. Höland *et al.* [4] studied the mechanism of nucleation and crystallization of fluoroapatite glass-ceramics in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--K}_2\text{O--CaO--P}_2\text{O}_5$ system. Moiescu *et al.* [5] studied the orientation of fluoroapatite crystals with needle morphology in fluoroapatite glass-ceramics. They have discovered that extrusion of semi-crystal samples with fluoroapatite if exposed to high temperatures can result in the creation of highly oriented glass-ceramics in which the needles are oriented in the direction of extrusion. Likewise in another study where Yue *et al.* [6] studied the morphology of two types of fluoroapatite glass-ceramics different in extrusion rate. They claim the extrusion rate to have a significant influence on its morphology. Fluoroapatite is a very important biomaterial. It is not surprising, therefore, that many authors have investigated biomaterials including fluoroapatite and also examined their structural, thermal, electrical and biological properties [8–21]. The scope of the present work is a preliminary investigation on the fluoroapatite crystallization in the basic lithium disilicate glass. Lithium disilicate glass provides the resulting material with desired properties in dentistry. The aim of this work is to analyze the structural changes of fluoroapatite glass-ceramics with different percentage of P_2O_5 .

Experimental

Synthesis

The examined glasses with different composition (Table 1) were melted in a Pt-crucible in a superkanthal furnace for 1 h at a temperature of 1480°C. It took 8 h until the temperature reached 1480°C and subsequently the enamel was poured onto an anticorrosive board. Glasses with varying contents of P_2O_5 were then thermally processed. After the temperature reached 1150°C and sustained for 4 h, the platinum

Table 1 Chemical composition of basic and $\text{P}_2\text{O}_5\text{--CaO--F}^-$ enriched glasses (mass%)

Sample	A	B	C	D
Oxide/mass%	P_2O_5 0%	P_2O_5 5%	P_2O_5 10%	P_2O_5 15%
Li_2O	19.91	17.55	15.20	12.84
CaO	–	5.93	11.85	17.78
P_2O_5	–	5.00	10.00	15.00
SiO_2	80.09	70.60	61.12	51.63
CaF_2	–	0.92	1.83	2.75

base was put on a ceramic base to slow down the process of cooling and promote the formation of crystals. The cooling time was 30 min.

Measurements

The values of micro-hardness according to Vickers were gained by measurements on device Vickers Hardnesstester, Future-tech. Corp.

Samples of the glasses for SEM examination were prepared in form of fragments. After coating of fracture surfaces by laying a layer of Au in sputter coater Balzers SCD 050 the samples were examined in SEM Tesla BS-300 with digital unit Tescan. In all cases we compared the microstructure of non-etched fracture surfaces of samples with samples of glasses after etching with 2% HF, like in the works of Moisescu and Yue [5, 6]. The samples were etched at a laboratory temperature for 10, 20 and 30 s. Etching with HF is based on a fact that the amorphous phase is etched faster and therefore the crystal phase is emphasized [22]. The inner structure of glass and glass-ceramics is then uncovered.

DTA measurements were carried out on a Q1500D device. Glass samples with 10% P₂O₅ (sample C) and without P₂O₅ (sample A) were prepared in two fractions: fraction 1.00–3.15 mm and fraction under 0.063 mm to study the surface and volume crystallization in observed systems of crystallizing glasses.

For XRD analysis the samples A, B, C and D were prepared in a form of a powder and the measurements were carried out on a RTG STOE device.

Results and discussion

The oxide chemical composition of prepared glasses is given in Table 1. The basic lithium disilicate glass (A) contains 19.91 mass% Li₂O and 80.09 mass% SiO₂. Three other glasses were prepared with the addition of CaO, P₂O₅ and CaF₂ in proportions to form fluoroapatite. While assessing the physical qualities, the prepared samples were different in color, gloss and cleavability. Glass without addition of P₂O₅ is clear and transparent. Glass containing 5% P₂O₅ is transparent similarly to the primary glass without P₂O₅ and other oxides taking part in formation of fluoroapatite crystals. The sample of glass with 10% P₂O₅ is white opaque, with high gloss. Sample with 15% P₂O₅ is white, opaque with corrugated surface. First three samples containing 0, 5 and 10% P₂O₅ are liable to produce chips with glossy fracture surfaces when broken. The sample with 15% P₂O₅ has granulated fracture surface, which corresponds with higher amount of crystal phases, especially fluoroapatite. The gradual change of fraction surface character is shown on SEM images taken from fracture surfaces (Fig. 1a, b, c, d).

Besides the color, gloss and cleavability another important quality of the examined materials is their hardness. The results of the microhardness measurements are shown in Table 2 [7].

According to literature, the hardness of a tooth is 3.6 GPa, materials developed for dental purposes: 6.2 GPa – enamel, 5.7 GPa – Dentin porcelain, 3.4 GPa – (Ca-P) glass, 3.8 GPa – (Ca-P) glass-ceramics [23]. The hardness of glass-ceramics with a

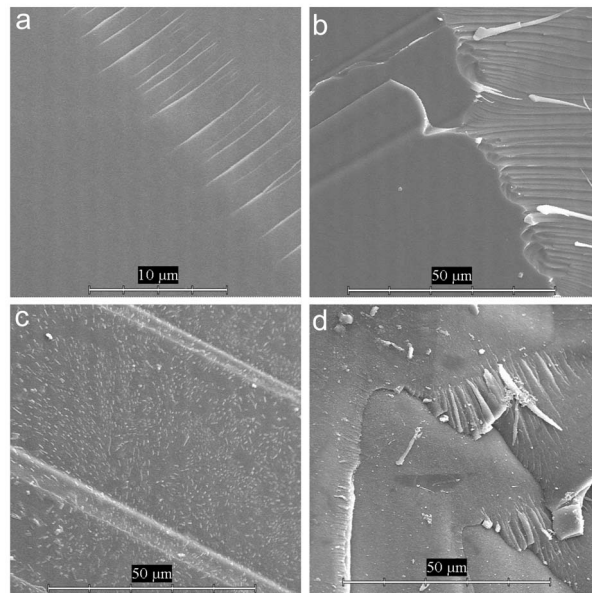


Fig. 1 Microstructure of the fracture surface of samples: a – basic glass of lithium disilicate, sample A; b – fluoroapatite glass-ceramics, sample B, 5% P_2O_5 ; c – fluoroapatite glass-ceramics, sample C, 10% P_2O_5 ; d – fluoroapatite glass-ceramics, sample D, 15% P_2O_5

Table 2 Micro-hardness according to Vickers in examined glass and glass-ceramic systems

Sample	% P_2O_5 /Mass	Hardness/Gpa
A	0	5.759
B	5	5.794
C	10	5.832
D	15	5.822

main crystal phase of lithium disilicate (5.7 GPa) is high compared to the hardness of a tooth and is even greater with the presence of a crystal phase of fluoroapatite (5.8 GPa). Color, gloss and hardness of this kind of glass-ceramics are suitable for use in medicine, especially in stomatology.

In our study we also focused on observing the microstructure and crystallization of fluoroapatite in Li_2O-SiO_2 (LS) system. The basic system was enriched with other substances of $P_2O_5-CaO-F$ to form crystals of fluoroapatite after thermal processing (Table 1 for composition). A crystalline phase of fluoroapatite can be seen on SEM records along with a significant increase in growth of glass-ceramic volume with increasing amount of P_2O_5 . Fracture surface of the basic LS glass system, sample A, has a typical character of fragile fracture (Fig. 2a). By etching with 2% HF the pres-

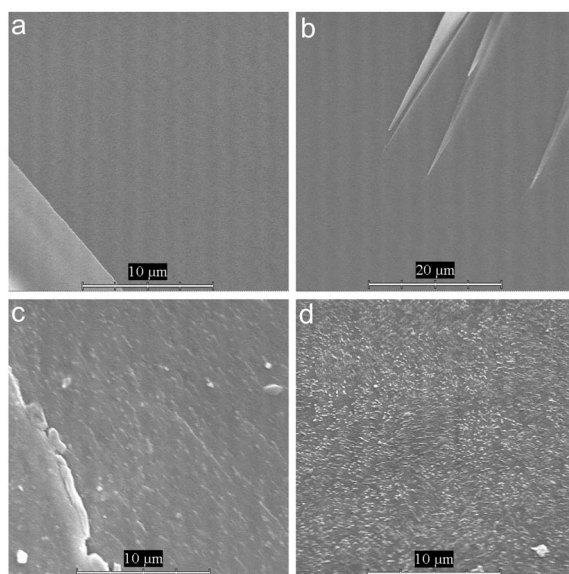


Fig. 2 Microstructure of the fracture surface of LS-P₂O₅-CaO-F⁻ system samples: a – basic glass of lithium disilicate, sample A; b – fluoroapatite glass-ceramics, sample B, 5% P₂O₅; c – fluoroapatite glass-ceramics, sample C, 10% P₂O₅; d – fluoroapatite glass-ceramics, sample D, 15% P₂O₅

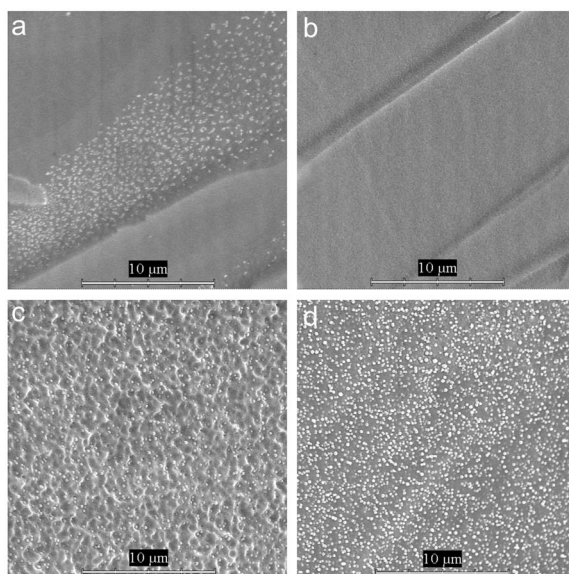


Fig. 3 Microstructure of the fracture surface of samples etched in 2% HF: a – basic glass of lithium disilicate, sample A; b – fluoroapatite glass-ceramics, sample B, 5% P₂O₅; c – fluoroapatite glass-ceramics, sample C, 10% P₂O₅; d – fluoroapatite glass-ceramics, sample D, 15% P₂O₅

ence of a crystal phase of lithium disilicate can be emphasized (Figs 3a, 4a). Sample B with 5% P_2O_5 has a similar fracture surface to basic glass (Fig. 2b). Only etching has revealed the microstructure of a new crystal phase of fluoroapatite in a form of soft particles under $0.1 \mu\text{m}$ (Figs 3b, 4b). In sample C (10% P_2O_5), a significant change in microstructure can be seen, while on the non-etched fracture surface, we can see a presence of fluoroapatite crystal phase in form of needles (Fig. 2c). Etching has emphasized the presence of spherical particles of fluoroapatite crystal phase cca $0.3 \mu\text{m}$ of size (Figs 3c, 4c). An image of a hole-like surface of matrix is typical for this sample. It is also described in work [4]. In sample D (fluoroapatite glass-ceramic with 15% P_2O_5), we have observed a microstructure with a certain texture caused by higher amount of fluoroapatite (Fig. 2d). The presence of spherical particles under $0.3 \mu\text{m}$ of size was emphasized by etching (Figs 3d and 4d) similar to particles in sample C. The hole-like surface disappeared on an etched surface of sample D (was not observed); however, the frequency of fluoroapatite particles has increased. Upon these observations we may say that P_2O_5 supports the phase separation in observed glass-ceramics. With its increasing volume the volume of fluoroapatite crystal phase is increased.

Crystallization of the glass-ceramics observation was carried out by slow cooling (crystallization from above), starting at 1150°C because the crystals would not be able to form if the temperature would have raised gradually (crystallization from below) as a result of preferential crystallization of lithium disilicate. Its production was

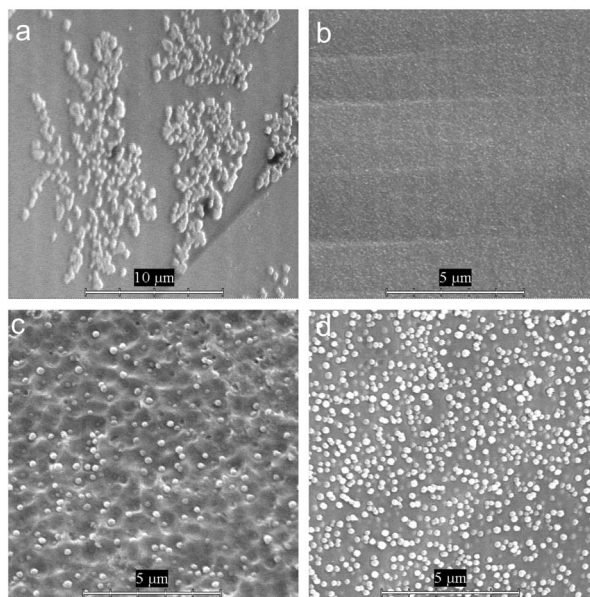


Fig. 4 Microstructure of the fracture surface of $LS-P_2O_5-CaO-F^-$ system samples etched in 2% HF: a – basic glass of lithium disilicate, sample A; b – fluoroapatite glass-ceramics, sample B, 5% P_2O_5 ; c – fluoroapatite glass-ceramics, sample C, 10% P_2O_5 ; d – fluoroapatite glass-ceramics, sample D, 15% P_2O_5

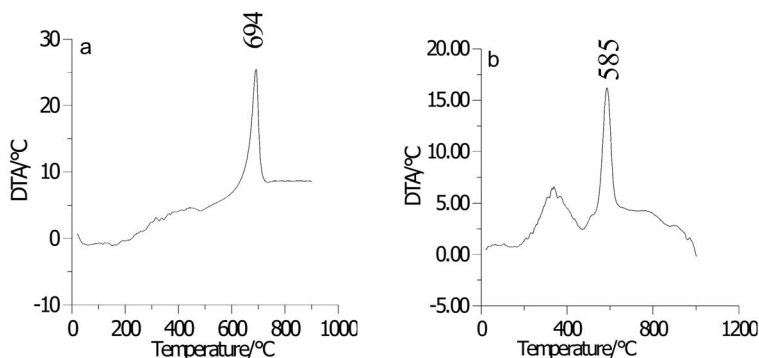


Fig. 5 DTA curves of basic $\text{Li}_2\text{O}\cdot\text{SiO}_2$ glass, heating rate $10^\circ\text{C min}^{-1}$, prepared in two fractions: a – 1.00–3.15 mm and b – under 0.063 mm for study the surface and voluminous crystallization in observed systems of crystallizing glasses

also observed using DTA. On DTA curves the *exothermic* peaks corresponding with lithium disilicate crystallization are present whereas the exothermic peaks for fluoroapatite crystallization are absent. Comparing DTA curves of two similar samples (sample A and C) different size of particles, we can say that with increasing *specific surface* the exothermic peak corresponding to lithium disilicate moves towards lower values (by 109°C , in case of sample A), which represents the superficial crystallization. The DTA curve for the fraction of 1.00–3.15 mm (Fig. 5a) has a sharp exothermic maximum at a temperature of 694°C , which corresponds with the crystallization of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. The DTA curve for a softer fraction under 0.063 mm (Fig. 5b) has this exothermic maximum at 585°C . Exothermic peak on Fig. 5b at 337°C most likely represents the nucleation of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ which was not significantly expressed on DTA curve (Fig. 5a). Exothermic peak corresponding to formation of fluoroapatite was not observed which is related to preferential crystallization of lithium disilicate at

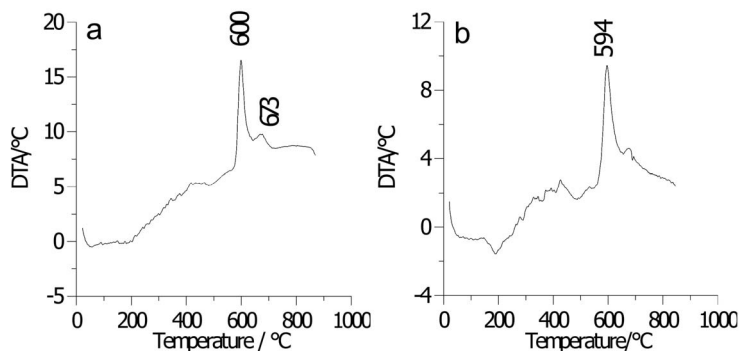


Fig. 6 DTA records of glass-ceramics with addition of 10% P_2O_5 , heating rate $10^\circ\text{C min}^{-1}$, prepared in two fractions: a – 1.00–3.15 mm and b – under 0.063 mm for study the surface and voluminous crystallization in observed systems of crystallizing glasses

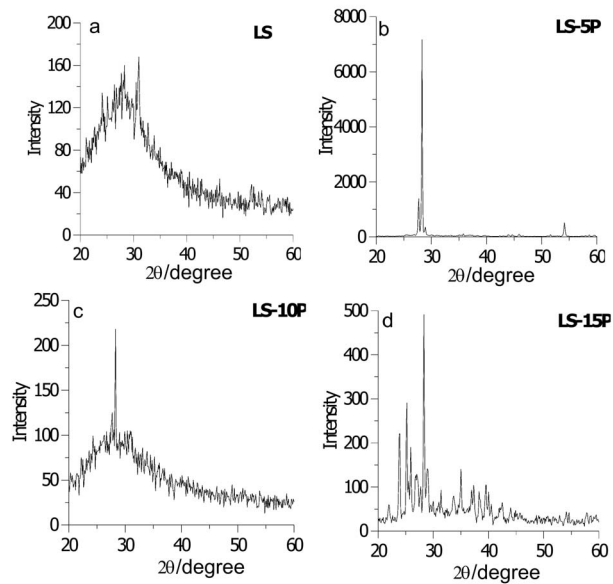


Fig. 7 XRD patterns of glass-ceramics samples: a – A - basic glass $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$, b – B - 5% P_2O_5 , c – C - 10% P_2O_5 and d– D - 15% P_2O_5

gradual heating of the ceramics. DTA curves of sample C for a fraction of 1.00–3.15 mm (Fig. 6a) and fraction under 0.063 mm (Fig. 6b) show the influence of P_2O_5 on crystallization of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. The exothermic peak moves to 600 and 594°C, respectively. In this case the superficial crystallization of lithium disilicate was not observed. The exothermic peak position also did not change significantly.

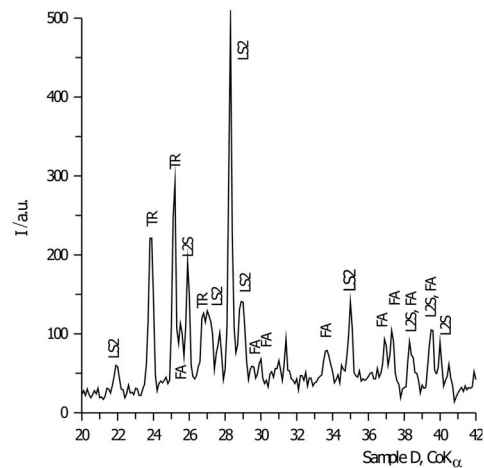


Fig. 8 XRD patterns of glass-ceramic sample D – 15% P_2O_5

Samples A, B, C, D (Figs 7a, b, c, d) was also studied by XRD. The results correspond to the changes of microstructure observed by SEM. There is a remarkable diffraction maximum corresponding to crystal phase of lithium disilicate. The presence of fluoroapatite crystal phase was confirmed by low diffraction maxima only on the XRD record of sample D with 15% P₂O₅ (Figs 7 and 8).

Conclusions

The studied system of lithium disilicate with precipitated fluoroapatite is important for development of new materials in medical field, mainly in dentistry and stomatology. The development of microstructure and physical qualities of glass are characterized in a system of Li₂O–SiO₂. Along with sustaining the stable ratio of these two components and addition of CaO, P₂O₅ and CaF₂. P₂O₅ was added to these systems in 0, 5, 10 and 15%. Precipitation of fluoroapatite in this system must be carried out from above, because the crystals would not be able to form if the temperature would have risen gradually (crystallization from below) as a result of preferential crystallization of lithium disilicate. This is the reason why there is only a peak corresponding to lithium disilicate crystallization and not to fluoroapatite on DTA curves. According to the SEM study of sample we can say that with an increasing volume of P₂O₅ the number of fluoroapatite particles is increased in studied glass-ceramics. Results of the X-ray powder diffraction correspond with the results from the SEM study. P₂O₅ supports the phase separation in glasses of the observed system and its increasing addition has an influence on an amount of crystal phase. Fluoroapatite is excreted in a form of soft particles (under 300 nm of size), especially in lower amounts of P₂O₅. According to this fact, its presence was not expressed at a volume of 5 and 10%, or its diffraction maximum merges with the very strong diffraction lines of Li₂O·2SiO₂ and are identified only with 15% P₂O₅. With an increasing amount of P₂O₅ in the studied LS system the optical qualities are changed from opaque to blue at 5% P₂O₅, to white with high gloss at 10% P₂O₅ to opaque white at 15% P₂O₅. The measurements of micro-hardness of the prepared materials show qualities suitable for use in the field of dental and bone medicine. In terms of physical qualities, especially color and gloss the most convenient are LS ceramics with 10% P₂O₅.

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