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Short communication

Bioactive fluorapatite-containing glass ceramics

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Abstract

Fluorapatite-containing glass ceramics were synthesized on the basis of the glass-forming system SiO_2–Al_2O_3–P_2O_5–CaO–CaF_2. The introduction of phosphorus and fluorine containing materials, as well as the specific regime of heat treatment of the glasses gave glass ceramic materials with crystalline phases of the apatite group—fluorapatite ($Ca_{10}(PO_4)_6F_2$), apatite ($Ca_3(PO_4)_2$), vitlokite ($Ca_9P_6O_{24}$), etc. The X-ray phase analysis showed that the main phase in all the glass ceramic samples was fluorapatite. The phase composition, structure and some of the basic properties of the glass ceramic samples were determined.

Keywords: D. Glass; D. Glass ceramics; Fluorapatite; X-ray analysis; DTA; SEM

1. Introduction

The design of bioactive glass ceramic materials which are closely related to the glass technology is considered to be one of the main achievements in glass production. Recently, the interest towards the preparation of glasses and glass ceramic materials for stomatologic and orthopedic purposes significantly increased [1–6]. In stomatology, bioactive glass ceramics are widely used as an implant on which the denture is fixed and for manufacturing the denture itself [7–11]. The denture glass ceramics outperform the materials used not so long ago by its aesthetic look, mechanical strength, biological compatibility and functionality.

Both inert and bioactive materials are used since they can successfully replace the natural bones and teeth ensuring good functionality and biological compatibility. To make glass ceramic materials, i.e. materials with which the live bone tissue would interact, it should contain apatite phase $Ca_3(PO_4)_2$. This phase is part of the natural bones and provides strength and growth ability [12–17].

Apatite phase can be obtained by controlled crystallization where a melt of variable concentration could be separated into mica and apatite crystals [18–24].

Fluorapatite is a kind of hydroxyapatite where the hydroxylic groups (OH^-) are substituted by F^- ions which reduces the solubility, stimulates the formation of bone tissue and increases the compression strength. The extraction of ions in the surrounding bone forms stronger bonds since it strengthens the tissue next to the implanted one. Therefore, it could be supposed that the F^- ions stabilize the calcium-phosphate phase.

Taking into account the interest towards the preparation of non-metal implantants, the present paper is focused on the preparation of bioactive glass ceramics. The aim is to synthesize fluorapatite ($Ca_{10}(PO_4)_6F_2$)-containing glass ceramics by certain heat treatment of three glass compositions, as well as to determine some of their basic physicochemical properties.

2. Experimental

2.1. Materials

For the preparation of the glass ceramic materials, the glasses were selected so as to obtain crystalline phases of the apatite group after certain heat treatment. They were based on the system: SiO_2–Al_2O_3–P_2O_5–CaO–CaF_2.

2.2. Methods

The materials were studied by X-ray analysis, differential thermal analysis (DTA) and scanning electron microscopy (SEM).

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The X-ray analyses were carried out by the method of powder diffraction using X-ray apparatus equipped with goniometer URD-6 (Germany) with cobalt anode and Kα emission.

The DTA experiments were performed on a derivatograph OD-102 (MOM, Hungary) by heating to 1000 °C at a rate of 10 °C/min.

The micrographs were taken using scanning electron microscope Tesla BS 340 (Czech Republic).

The materials densities were determined by the method of hydrostatic weighing. Their chemical resistance was studied by the weight method using glass grains sized 0.40–0.50 mm where the weight difference before and after treatment with 0.1N HCl and 0.1N NaOH for 1 h was measured.

2.3. Composition and experimental procedure

The oxide compositions of the initial glasses are shown in Table 1. Aiming to obtain certain properties of the end product, components and additives in various percentages were introduced into the basic composition SiO_2–Al_2O_3–P_2O_5–CaO–CaF_2 and three compositions were prepared, as shown in Table 1 (BG_1, BG_1 и BG_1).

As initial materials, part of the oxides were introduced in the form of $Al(OH)_3$, $CaCO_3$, H_3PO_4, K_2CO_3, K_2SiF_6, $3MgCO_3{\cdot}Mg(OH)_2{\cdot}H_2O$ for better homogenization and degassing of the glass material. Taking into account that the glass composition contained some volatile components like: K_2O, CaF_2, K_2SiF_6, their quantities were increase proportional to the coefficient of volatility.

The glass compositions of the mixtures used are presented in Table 2.

The glass was melted, cast in a die and subjected to thermal treatment for phase separation and crystallization to obtain the main phase of fluorapatite. The material obtained is easily processed. The melting was carried out in an oven ‘‘Naber’’ at heating rate of 350 °C/h and 2 h isothermal treatment at 1450 °C. After that, the molten glass was cast into preliminarily heated graphite dies. The tempering was carried out at 680 °C for 12 h, followed by free cooling of the oven.

The samples prepared were then subjected to high temperature crystallization in a high temperature superkanthal oven on corundum support. The aim of this treatment was to form the necessary crystalline phases in the samples. The crystallization was performed at 850, 900 and 950 °C. When the required temperature was reached, 2 h isothermal periods were used to finalize the process of crystallization, followed by free cooling of the oven.

Table 1
Initial glass compositions for the preparation of glass ceramics

Component	Composition BG_1 (mass%)	Composition BG_2 (mass%)	Composition BG_3 (mass%)
SiO_2	–	15	9.5
MgO	–	–	7.2
CaO	50	25	37.5
Al_2O_3	–	25.35	3
K_2O	–	–	0.93
CaF_2	7.74	13.6	5.8
P_2O_5	42.23	21.1	31.7
K_2SiF_6	–	–	4.4

Table 2
Composition of glass mixtures for preparation of 100 g glass material

Raw materials	Composition BG_1 (mass%)	Composition BG_2 (mass%)	Composition BG_3 (mass%)
SiO_2	–	15.1	9.58
$Al(OH)_3$	–	39	4.63
K_2CO_3	–	–	1.37
K_2SiF_6	–	–	4.38
CaF_2	10.2	17.8	7.65
$MgCO_3{\cdot}Mg(OH){\cdot}3H_2O$	–	–	16.3
H_3PO_4	94	47	70.5
$CaCO_3$	89	45	67

3. Results and discussion

3.1. Differential thermal analysis (DTA)

DTA was used to determine the temperature intervals of crystallization of the glasses. The DTA curves for glasses with compositions BG_1 and BG_2 showed that characteristic endothermic reactions occurred in the interval 500–660 °C, corresponding to the generation of crystallization nuclei which grew with the highest rate at 700 °C. With the increase of temperature to 800–850 °C, as well as at higher temperatures about 905 °C, a new phase was formed. In glass composition BG_3, characteristic exothermic reactions were observed in the interval 720–740 °C, corresponding to formation of crystalline phases. New crystalline phases were formed at 940 °C.

Based on the results from the DTA analyses, the crystallization regime was selected to be 850 °C for BG_1, 900 °C for

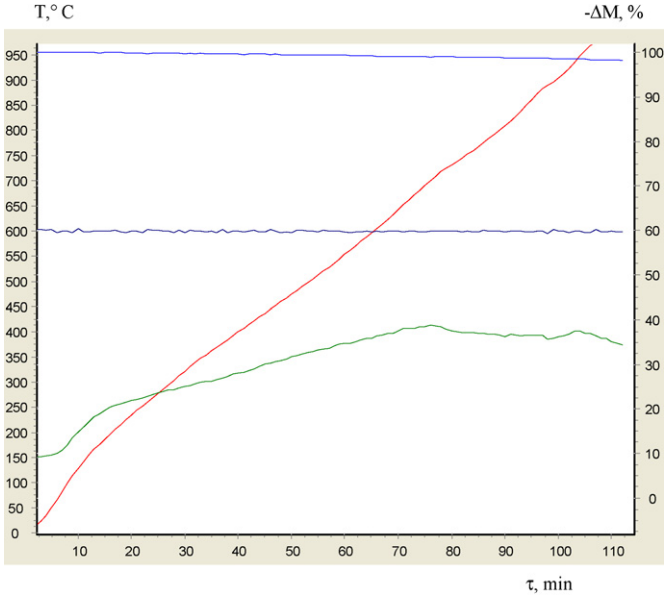

Fig. 1. DTA of glass with composition BG_1.

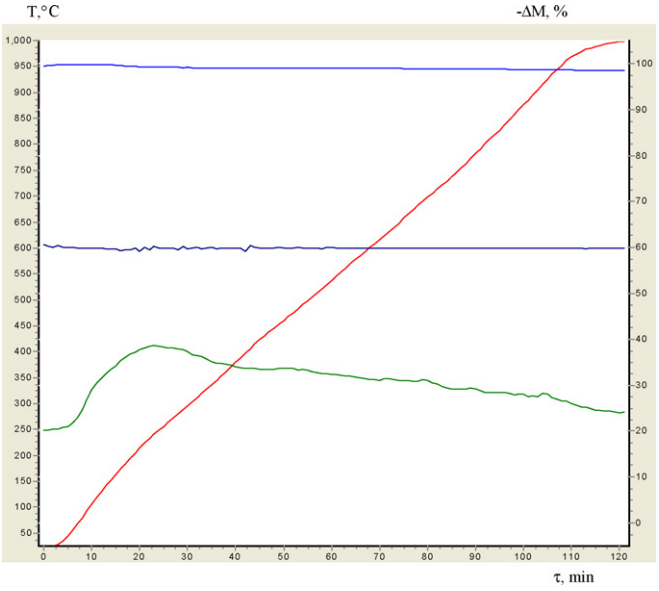

Fig. 2. DTA of glass with composition BG_2.

BG_2 and 950 °C for BG_3, with 2 h isothermal treatment for all the three regimes (Figs. 1–3).

3.2. X-ray analysis

The crystalline phases formed in the samples are quite important for their properties and possible fields of application. The type and distribution of the newly formed crystalline phases were determined by X-ray phase analysis.

The results obtained are presented in Table 3.

According to X-ray data, the predominating phases are these of the apatite group with fluorapatite being the largest phase in composition BG_1. In this sample, the amount of the initial components are the closest to the theoretical composition of fluorapatite. Peaks of two other phases—vitlokite ($Ca_9P_6O_{24}$) and fluormargarite ($CaAl_2(Al_2Si_2)O_{10}F_2$) were observed in the X-ray pattern for the BG_2 sample. Sample BG_3 showed the greatest versatility which was due to the introduction of MgO, K_2O and K_2SiF_6 along with the components participating in compositions BG_1 and BG_2. This stimulated the crystallization of several other phases: apatite ($Ca_3(PO_4)_2$), sellaite (MgF_2), norbergite ($Mg_3F_2SiO_4$) and fluorphlogopite ($KMg_{2.5}Si_4O_{10}F_2$).

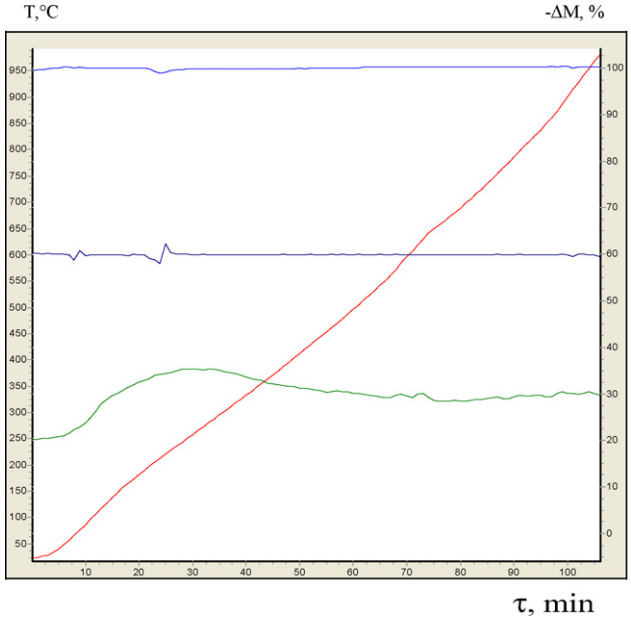

Fig. 3. DTA of glass with composition BG_3.

Table 3
X-ray phase analysis of glass ceramic materials

Composition	T_M (°C)	$T_{cr.}$ (°C)	Main crystalline phases
BG_1	1450	850	Fluorapatite, vitlokite
BG_2	1450	900	Fluorapatite, fluormargarite, vitlokite
BG_3	1450	950	Fluorapatite, vitlokite, apatite, sellaite, norbergite, fluorphlogopite

Further, the densities of the glasses were determined, as well as their alkali and acid resistance.

The data on glasses densities are presented in Table 4 and they showed different values due to the material type (glass or glass ceramics), different initial composition and different crystalline phases. The overall tendency observed was a density decrease from glasses to glass ceramics due to the somewhat denser formed crystalline phases.

Since bioactive materials are subjected to chemical reactions in human body, their more deep characterization requires a study on their behavior in alkali and acidic media. These chemical reactions lead to chemical and biological bonding with the tissue at the interface between human tissue and the bioactive implantant which was expected to be faster than the common growth of tissue into the implantant pores and providing mechanical fixation.

Glass grains sized 0.40–0.50 mm were used for the determination of their chemical resistance, measured by the weight difference before and after 1 h treatment with 0.1N HCl and 0.1N NaOH.

As can be seen from the data on chemical resistance (Table 5), the materials obtained were more resistant to alkali

Table 4
Densities of glasses and glass ceramic materials (g/cm^3)

Composition	BG_1	BG_2	BG_3
Glass	3.147	3.354	3.145
Glass ceramics	2.769	2.804	2.687

Table 5
Chemical resistance of glasses and glass ceramic materials (%weight loss)

Sample	Composition	Alkali resistance	Acid resistance
Glass	BG_1	3.8	10
	BG_2	1	15
	BG_3	5	10
Glass ceramics	BG_1	0	20
	BG_2	0.8	13
	BG_3	1.4	15

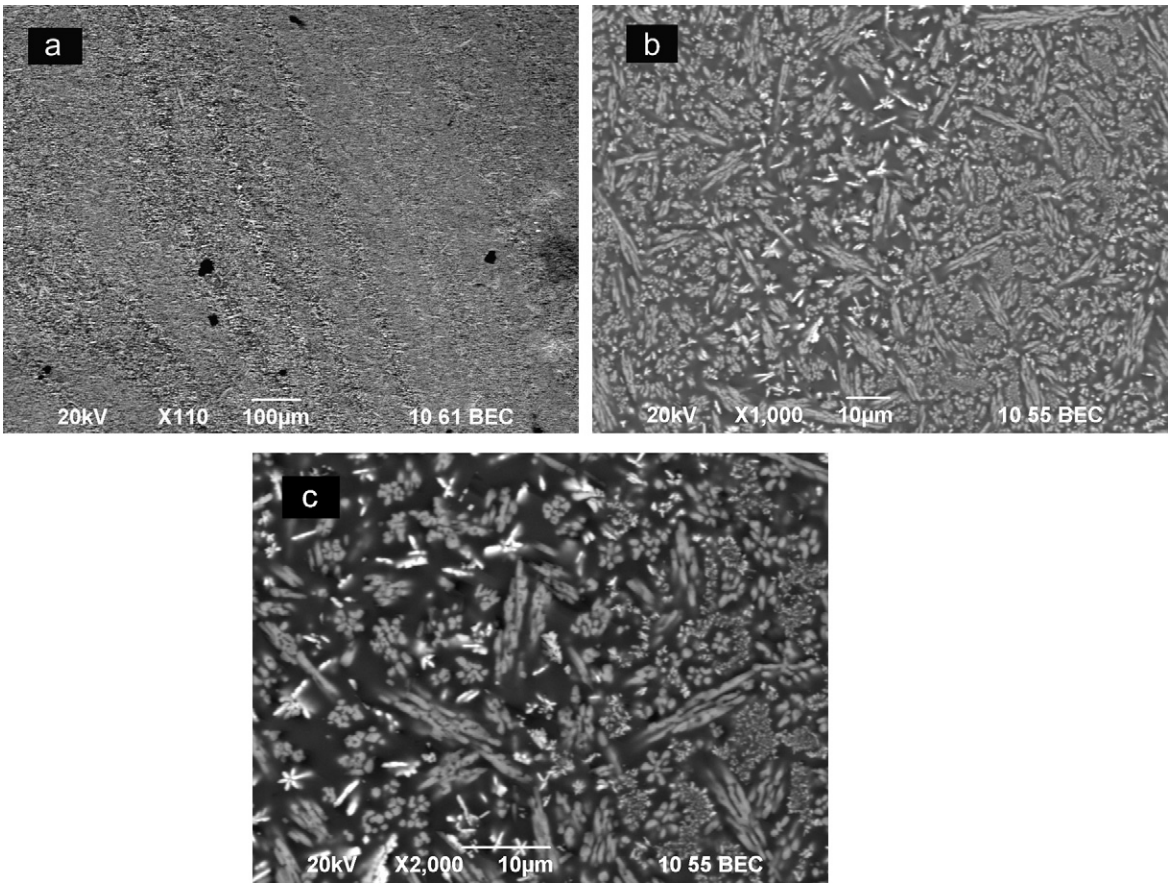

Fig. 4. SEM micrographs of glass ceramic samples of composition BG_2 at magnifications: (a) ×110, (b) ×1000, (c) ×2000.

media than to acidic ones. The highest alkali resistance was observed for the glass ceramic materials, which varied from 0 to 2%. A tendency to decrease of the values of certain properties from glasses to glass ceramic materials was also established.

3.3. Scanning electron microscopy

Fig. 4 shows electron micrographs of samples of composition BG_2.

Prismatic crystals characteristic for apatite structure are shown in Fig. 4. They, 10–20 μm in size, were evenly distributed throughout the native glass phase. Crystals of different habitus were also observed due to the presence of alloyed phases. Their sizes were in the range 5–10 μm.

4. Conclusions

Three kinds of glasses were obtained in the system SiO_2–Al_2O_3–P_2O_5–CaO–CaF_2 and the conditions for their crystallization were determined in order to synthesize glass ceramic materials. It was found that bioactive glass ceramic materials can be prepared under certain regime of thermal treatment of the glass mixture—melting at 1450 °C for 2 h and crystallization at 680 °C for 12 h. The X-ray phase analyses showed that the main crystalline phase in all the samples studied was fluorapatite. The additional phases found in some of the samples were: apatite, norbergite, vitlokite, fluorphlogopite, fluormargarite, sellaite. It was experimentally established that the density and the chemical resistance of the glass ceramics synthesized depend directly on the type and quantity of the crystalline phases.

References

[1] T. Kokubo, M. Shigernatsu, Y. Nagashima, M. Tashiro, T. Nakamura, T. Yaniamuro, Apatite- and wollastonite-containing glass-ceramics for prosthetic application, Bull. Inst. Chem. Res. 60 (1982) 260–268.
[2] T. Kokubo, H.M. Kim, M. Kawashita, T. Nakamura, Novel ceramics for biomedical applications, J. Aust. Ceram. Soc. 36 (2000) 37–46.
[3] K.H. Karlsson, Bioactivity of glass and its relation to glass structure, Glass Phys. Chem. 24 (1998) 280–284.
[4] T. Kokubo, S. Ito, M. Shigematsu, S. Sakka, T. Yamamuro, Fatigue and life-time of bioactive glass-ceramic A–W containing apatite and wollastonite, J. Mater. Sci. 22 (1987) 4067–4070.
[5] T. Kokubo, S. Ito, M. Shigematsu, S. Sakka, T. Yamamuro, Mechanical properties of a new type of apatite-containing glass-ceramic for prosthetic application, J. Mater. Sci. 20 (1985) 2001–2004.
[6] S. Likitvanichkue, W.C. Lacource, Apatite-wollastonite glass-ceramics, J. Mater. Sci. 33 (1998) 5901–5904.
[7] T. Nakamura, T. Yamamuro, S. Higashi, T. Kokubo, S. Itoo, A new glass-ceramic for bone replacement: evaluation of its bonding to bone tissue, J. Biomed. Mater. Res. 19 (1985) 685–698.
[8] J.B. Park, Biomaterials Science and Engineering, Plenum Press, New York, 1987.
[9] W. Suchanek, M. Yoshimura, Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants, J. Mater. Res. 13 (1998) 94–117.

[10] W. Vogel, W. Holand, Development of glass-ceramics for medical application, Angew. Chem. Int. Ed. Engl. 26 (1987) 527–544.
[11] T. Yanianiuro, L.L. Hench, J. Wilson, AAV Glass-ceramic: clinical applications, in: An Introduction to Bioceramics, World Scientific, Singapore, 1993, pp. 89–103.
[12] W. Holand, V. Rheinberger, E. Apel, C. van't Hoen, Principles and phenomena of bioengineering with glass-ceramics for dental restoration, J. Eur. Ceram. Soc. 27 (2007) 1521–1526.
[13] W. Holand, V. Rheinberger, E. Apel, C. van't Hoen, M. Hoeland, A. Dommann, M. Obrecht, C. Mauth, U. Graf-Husner, Clinical applications of glass-ceramics in dentistry, J. Mater. Sci. – Mater. Med. 17 (2006) 1037–1042.
[14] R. Hill, A. Calver, S. Skinner, A. Stamboulis, R. Law, A MAS-NMR and combined Rietveldt study of mixed calcium/strontium fluorapatite glass-ceramics, Key Eng. Mater. 309–311 (2006) 305–308.
[15] A. Stamboulis, R.G. Hill, A. Calver, N. Bubb, P. Manuel, Real time neutron diffraction studies of apatite glass ceramics, Key Eng. Mater. 309–311 (2006) 309–312.
[16] C.O. Freeman, I.M. Brook, A. Johnson, P.V. Hatton, K. Stanton, Crystallization modifies osteoconductivity in an apatite-mullite glass-ceramic, J. Mater. Sci. – Mater. Med. 14 (2003) 985–990.
[17] Y. He, W.M. Bao, C.L. Song, Microstructure and leach rates of apatite glass-ceramics as a host for Sr high-level liquid waste, J. Nucl. Mater. 305 (2002) 202–208.
[18] A. Clifford, R. Hill, A. Rafferty, P. Mooney, D. Wood, B. Samuneva, S. Matsuya, The influence of calcium to phosphate ratio on the nucleation and crystallization of apatite glass-ceramics, J. Mater. Sci. – Mater. Med. 12 (2001) 461–469.
[19] H. Robert, R. Aran, M. Patrick, W. David, The influence of glass composition on nucleation crystallisation microstructure and properties of apatite-mullite glass-ceramics, Glass Sci. Technol.: Glastech. Berichte 73 (Suppl. C1) (2000) 146–153.
[20] W. Holand, M. Schweiger, V. Rheiberger, Nucleation process in glass-ceramics, in: Proceedings of the International Congress on Glass, Extended Abstracts, vol. 2, Edinburgh, Scotland, (2001), pp. 11–12.
[21] Y.Z. Feng, Y.C. Wang, Y.N. Tan, Y. Liu, Q.J. Xian, X.X. Sheng, Bioactivity of mica/apatite glass ceramics, Trans. Nonfer. Met. Soc. China 17 (2007) 828–831.
[22] Y. Liu, X.X. Sheng, X.N. Dan, Q.J. Xiang, Preparation of mica/apatite glass-ceramics biomaterials, Mater. Sci. Eng. C—Biomim. Supramol. Syst. 26 (2006) 1390–1394.
[23] S. Taruta, K. Watanabe, K. Kitajima, N. Takusagawa, Effect of titania addition on crystallization process and some properties of calcium mica-apatite glass-ceramics, J. Non-Cryst. Solids 321 (2003) 96–102.
[24] S. Taruta, K. Mukoyama, S.S. Suzuki, K. Kitajima, N. Takusagawa, Crystallization process and some properties of calcium mica-apatite glass-ceramics, J. Non-Cryst. Solids 296 (2001) 201–211.