MASE BIOACTIVE DE TIP VITROCERAM DIN SISTEMUL $CaO-SiO_2-P_2O_5-CaF_2-MgO$ OBȚINUTE PRIN METODA SOL-GEL

BIOACTIVE GLASS-CERAMIC IN THE $CaO-SiO_2-P_2O_5-CaF_2-MgO$ SYSTEM OBTAINED BY SOL-GEL METHOD

SORIN ION JINGA, GEORGETA VOICU*, IONELA VASILE, ALINA IOANA BĂDĂNOIU

[2]*Universitatea Politehnica Bucureşti, Str. Ghe. Polizu nr. 1, sector 1, 011061, Bucureşti, România*

Synthesis of vitreous material which was the basis for the obtaining the glass-ceramic type masses was performed by sol-gel method at normal temperature; its composition corresponds to the system $CaO-SiO_2-P_2O_5-CaF_2-MgO$. Tetraethyl orthosilicate ($C_6H_{16}O_3Si$ - TEOS), calcium nitrate tetra hydrate ($Ca(NO_3)_2 \cdot 4H_2O$), triethyl phosphate ($C_6H_{15}O_4P$ - TEP), magnesium acetate ($(CH_3-COO)_2Mg$) and calcium fluoride (CaF_2) were used as raw materials. The glass-ceramic masses were obtained by the thermal treatment at 700°C of dry gel resulted in sol-gel synthesis, followed by calcination at different temperatures- 700°C, 800°C and 1000°C. The obtained glass-ceramic materials were characterized by thermal analysis (DTA-TG), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The glass-ceramics were also characterized from the point of view of bioactivity by an in-vitro test, which consists in soaking the samples in simulated body fluid (SBF) for a period of 14 days at a temperature of 37°C; the resulted materials were characterized from the point of view of their mineralogical composition (by XRD) and morphology (by SEM). At the surface of the specimens was observed the formation of a brittle layer containing mainly fluoroapatite with a spherical morphology i.e. agglomerations of spherical shaped crystals and rods, as well as the presence of fluoroapatite with "raspberry" type morphology.

Sinteza materialului vitros care a stat la baza obținerii de mase de tip vitroceram a fost realizată prin metoda sol-gel la temperatură normală, compoziția sa fiind plasată în sistemul $CaO-SiO_2-P_2O_5-CaF_2-MgO$. Ca materii prime s-au utilizat: tetraetil ortosilicat ($C_6H_{16}O_3Si$ - TEOS), azotat de calciu tetrahidrat ($Ca(NO_3)_2 \cdot 4H_2O$), trietil fosfat ($C_6H_{15}O_4P$ - TEP), acetat de magneziu ($(CH_3-COO)_2Mg$) şi fluorură de calciu (CaF_2). Masele de tip vitroceram au fost obținute prin tratarea termică a gelului uscat şi calcinat la 700°C la diferite temperaturi- 700°C, 800°C şi 1000°C, palier 2h. Materialele sintetizate au fost caracterizate prin tehnici de analiză termică complexă (ATD-TG), difracție de raze X (XRD) şi microscopie electronică de baleiaj (SEM). Vitroceramicile au fost caracterizate din punctul de vedere al bioactivității, prin testări in-vitro, prin imersarea în lichid fiziologic simulat (SBF) timp de 14 zile la temperatura de 37°C şi caracterizate din punct de vedere al compoziției mineralogice (prin analiza XRD) şi sub aspect morfologic (prin analiza SEM). În urma analizelor efectuate s-a putut observa formarea unui strat friabil format în principal din fluoroapatită care prezintă aglomerări cu morfologie sferică alcătuite din cristale rotunjite sau alungite precum şi prezența fluoroapatitei cu morfologie de tip „zmeură".

Keywords: *sol-gel method, glass-ceramic, apatite phases, fluoroapatite, in-vitro test*

1. Introduction

Bioglass and glass-ceramics with different chemical compositions can be produced in a wide range in order to serve various functions in the body (e.g. to repair damaged and diseased bones) [1-12]. These materials have a good bioactivity and can be both osteoconductive and osteoproductive.

When these materials come into contact with body fluid or tissue, they develop reactive layers at their surfaces resulting in a chemical bond between implant and tissue [1, 2, 6, 7]. Hench and co-workers have described a sequence of five reactions that result in the formation of a hydroxyl-carbonate apatite layer [1]. Also, the dissolution of the glass network leads to the formation of a silica-rich gel layer and subsequent deposition of an apatite-like layer on the glass surface.

Glass can be synthesised using two processing methods: the traditional melt-quenching route and sol-gel route. Sol-gel method was used in the production of a wide variety of biomaterials [6, 9-15]. By sol-gel method bioactive glasses can be obtained as nanoporous powders or monoliths with high surface area formed by assembling nanoparticles. Also, the synthesis of glasses by the sol-gel method assumes thermal treatment temperatures that are smaller than the ones involved in traditional method for glass preparation i.e. melt-quenching route. Therefore the glasses obtained by the sol-gel method have a high dissolution rate.

Literature reports the sol-gel synthesis of bioglasses with compositions corresponding to the $CaO-SiO_2-P_2O_5-MgO$ system [9, 11]. The novelty of this study consists in the sol-gel synthesis of a

* Autor corespondent/Corresponding author,
Tel.: +40214023884, e-mail: getav2001@yahoo.co.uk

composition with a supplementary component i.e. CaF_2. The presence of F ion in the mixture should determine the formation of floroaptite (FAp) which is a more chemical stable phase as compared with hydroxiaptite (HAp) [16-19].

This vitreous material obtained by sol gel was used as a precursor for the preparation of glass-ceramic masses, which were obtained by its calcination at different temperatures (700°C, 800°C and 1000°C) folllowed by slow cooling in the furnace. The in-vitro behaviour of the glass-ceramics was then evaluated by soaking in simulated body fluid (SBF) for a period of 14 days at a temperature of 37°C.

2. Experimental

2.1. Synthesis of glass-ceramics

Synthesis of the vitreous material which forms the basis for the preparation of glass-ceramic type masses was made at normal temperature by sol-gel method. The main steps of this synthesis are presented in Figure 1. The raw materials used were: tetraethyl orthosilicate ($C_6H_{16}O_3Si$ – TEOS; Fluka, >98%), calcium nitrate tetra hydrate ($Ca(NO_3)_2{\cdot}4H_2O$), triethyl phosphate ($C_6H_{15}O_4P$ – TEP; Sigma-Aldrich, >99.8%),magnesium acetate ($(CH_3\text{-}COO)_2Mg$; Sigma-Aldrich, >99%) and calcium fluoride (CaF_2; Sigma-Aldrich, >99.9%). As solvent was used distilled water. The designed composition of vitreous material is presented in Table 1.

TEOS was hydrolysed by mixing it with water and in this solution was dissolved CaF_2 under vigorous magnetic stirring. TEP was also hydrolysed by mixing it with water (under magnetic stirring) and the calcium nitrate and magnesium acetate were dissolved in water until a clear solution was obtained. These three solutions were homogenised for 1 h under vigorous magnetic stirring. After 24 h of curing at normal temperature, a viscous gel was formed. This gel was kept for maturation process at room temperature for five days. The gel was then dried at 100°C for 24 hours resulting a white powder.

Based on thermal analysis (DTA-TG) assessed on the dried gel, the thermal treatment temperature of 700°C was chosen. The thermal treatment at 700°C for 2h determines the dissociation of polymer network, burning of the

Table 1

The composition of vitreous material/ *Compoziția chimică a materialului vitros.*

Composition	SiO_2	CaO	P_2O_5	CaF_2	MgO
% mol.	35.3	56	7.2	0.5	1

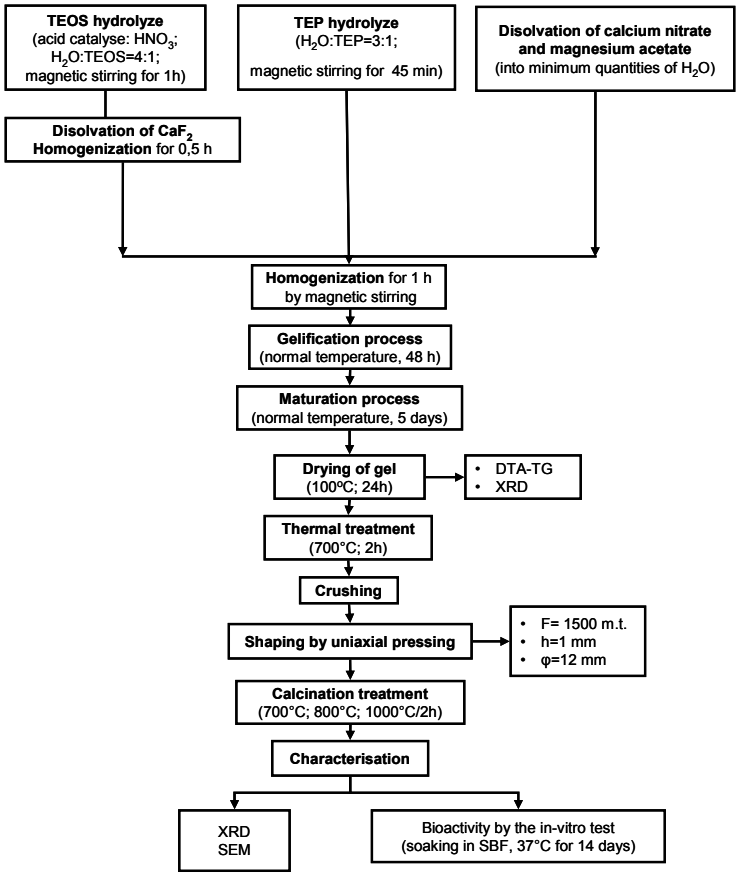


Fig. 1 - Flow chart of the synthesis of vitreous material by sol-gel method and the preparation of glass-ceramic masses/ *Schema de obținere a materialului vitros prin metoda sol-gel din care s-au obținut materialele de tip vitroceram.*

organic material and completion of all decomposition processes. The synthesized powder was then crushed and shaped in cylinders (hxφ=1 mm x12 mm) by uniaxial pressing. These specimens were then calcined in different conditions: 700°C, 800°C and 1000°C for 2h and then slowly cooled in the furnace, in order to obtain the final glass-ceramic masses. The resulted glass-ceramic materials were investigated by XRD and SEM.

2.2. Characterization methods

The thermal analysis (DTA/TG) was performed in air, in the 20-1000°C temperature range with a heating rate of 10°C/min, using a Shimadzu DTG-TA-60.

For the identification of crystalline phases, X-ray diffraction analysis was carried out on a Shimadzu diffractometer XRD 6000 - Ni-filtered CuKα (λ = 1.5406 Å) radiation, scanning speed of 2 deg./min in 2θ range of 10 - 70 deg.

SEM images were obtained by using a HITACHI S2600N equipment coupled with EDX probe, the samples being covered with a thin silver layer.

Glass-ceramics materials were characterized from the point of view of bioactivity by an in-vitro test. This consists in soaking the samples in simulated body fluid (SBF) for a period of 14 days at a temperature of 37°C. After that their mineralogical composition was assessed by XRD and their morphology was evaluated by SEM using a scanning electron microscope Quanta Inspect F (1.2 nm resolution). The SBF had a similar composition with human blood plasma- Kokubo solution [20] (see Table 2). The cylindrical specimens calcined at different temperatures were soaked in SBF solution (total area of sample/SBF ratio of 0.1 cm^{-1}) for 14 days at 37°C at a, without refreshing the SBF. After soaking the samples were softly washed and dried at 60°C for 24 h. After drying XRD and SEM analyses were performed.

3. Results and discussion

Figure 2 shows the DTA, TG and DTG curves of the dried gel. The total weight loss of the sample is 64.43% (w/w). Two small exothermic effects accompanied by mass loss recorded on the DTA-TG curves can be attributed to the following processes: dissociation of polymer network (333°C) and burning of the organic material (298°C). The five endothermic effects accompanied by mass loss recorded also on the DTA-TG curves can be attributed as follows: the effect at aprox. 60°C is due to loss of water, the ones at 160°C, 557°C and 587°C are determined by the dehydroxilation processes and the one from 640°C is due to the decomposition of carbonate phases formed by accidental carbonation during the synthesis.

Table 2

SBF Composition / *Compoziția lichidului fiziologic simulat* (SBF).

Ionic concentration / *Concentrația ionică* (mM)										
Solution	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}	Buffer	pH
Soluție SBF	142	5	1.5	2.5	147.8	4.2	1	0.5	*Soluție tampon*	7.25

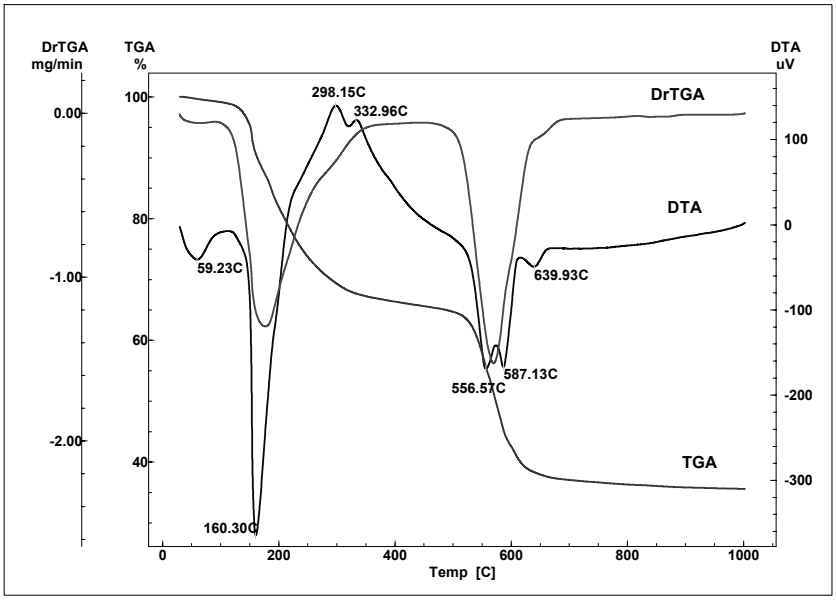


Fig. 2 - Thermal analysis of dried gel/ *Analiză termică caracteristică pentru gelul uscat.*

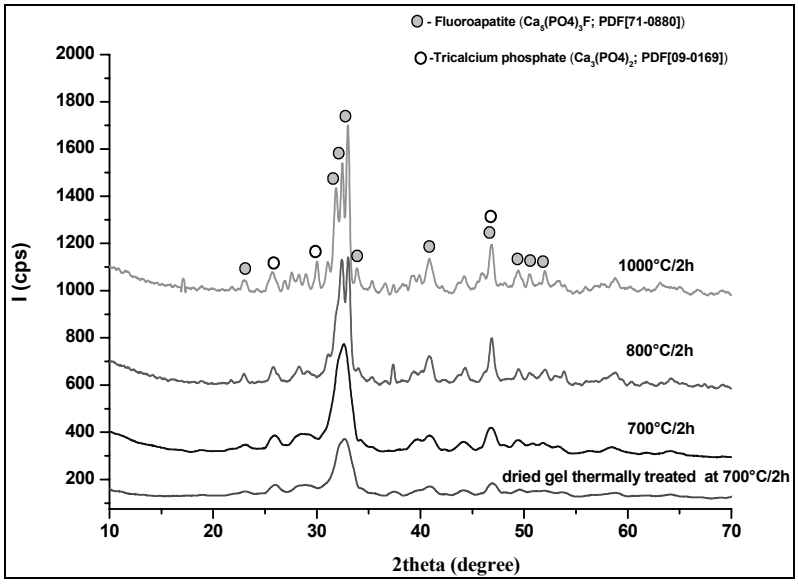
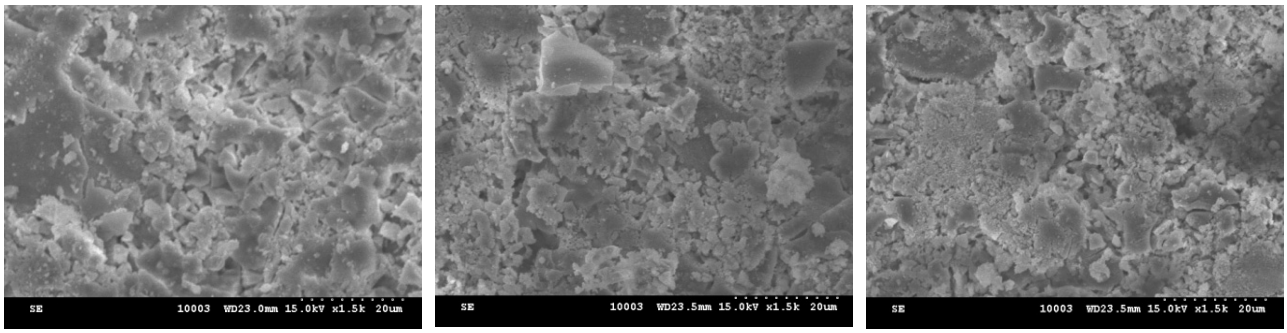


Fig. 3 - The XRD patterns of dried gel thermally treated at 700°C/2h and of glass-ceramics./ *Imaginile de difracție de raze X caracteristice gelului uscat tratat termic la 700°C/2h şi maselor de tip vitroceram.*



a b c

Fig. 4 - SEM micrographs for glass-ceramic masses obtained at: a – 700°C/2h; b- 800°C/2h and c -1000°C/2h./ *Imagini de microscopie electronică de baleiaj pentru mase de tip vitroceram obținute la: a – 700°C/2h; b- 800°C/2h şi c -1000°C/2h.*

The X-ray diffraction of dried gel thermally treated at 700°C/2h and of the glass-ceramics masses obtained by calcination at different temperatures are presented in Figure 3. It can be noticed the specific XRD peaks for fluoroapatite (FAp, PDF [71-0880]) in all samples. The calcination at different temperatures (700°C, 800°C and 1000°C/2h) of dried and thermally treated gel, determines the increase of the intensity of fluoroapatite XRD peaks and the formation of a new phase i.e. tricalcium phosphate (TCP, PDF [09-0169]). As expected, the increase of calcination temperature determines the increases of crystallinity degree of these phases.

From the point of view of microstructure (see Figure 4) it can be seen that the increase of calcination temperature leads to densification of the glass-ceramic mass.

These glass-ceramic masses were soaked for 14 days at 37°C in SBF. Fluoroapatite (PDF [03-0736]) is the crystalline mineralogical phase identified at the surface of these specimens (see Figure 5) and results by the interaction of glass-ceramic masses with the ions from SBF. The lower crystallinity degree assessed for the FAp formed in

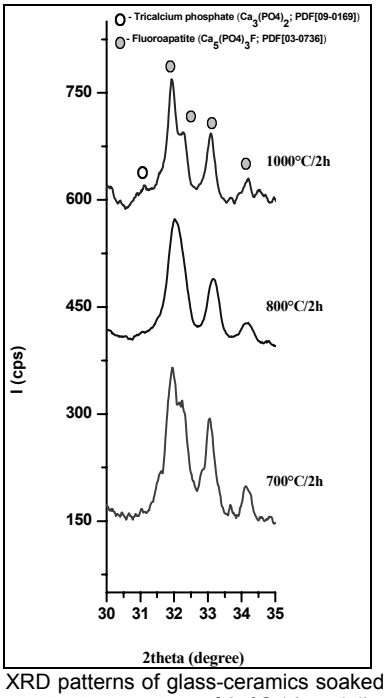
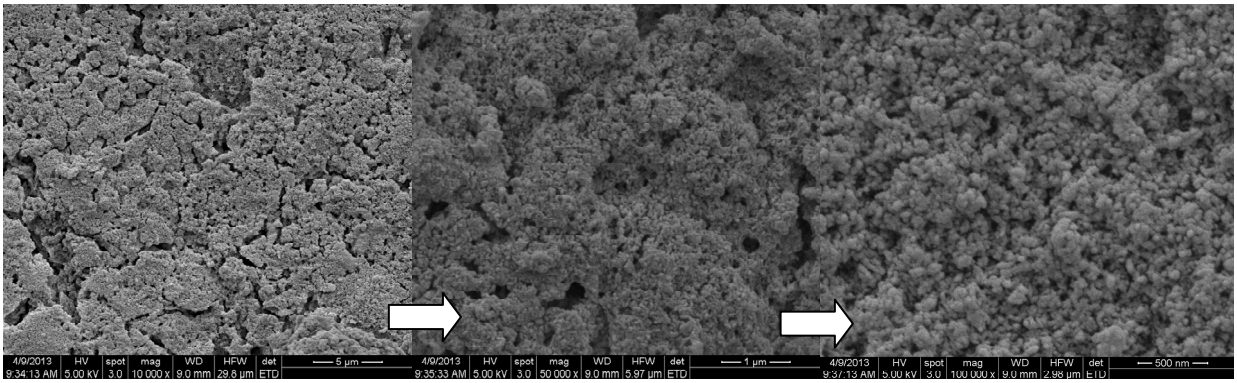


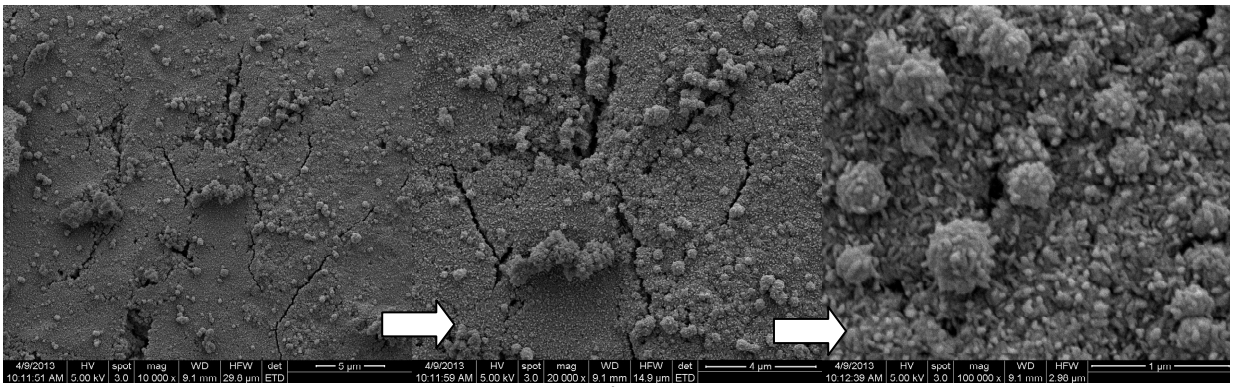
Fig. 5 - The XRD patterns of glass-ceramics soaked in SBF for 14 days at a temperature of 37°C./ *Imaginile de difracție de raze X caracteristice maselor de tip vitroceram scufundate în SBF 14 zile la 37°C.*

glass-ceramics soaked in SBF for 14 days (Figure 5) as compared with the one specific for the specimens before SBF immersion (Figure 3) supports the above mentioned mechanism.

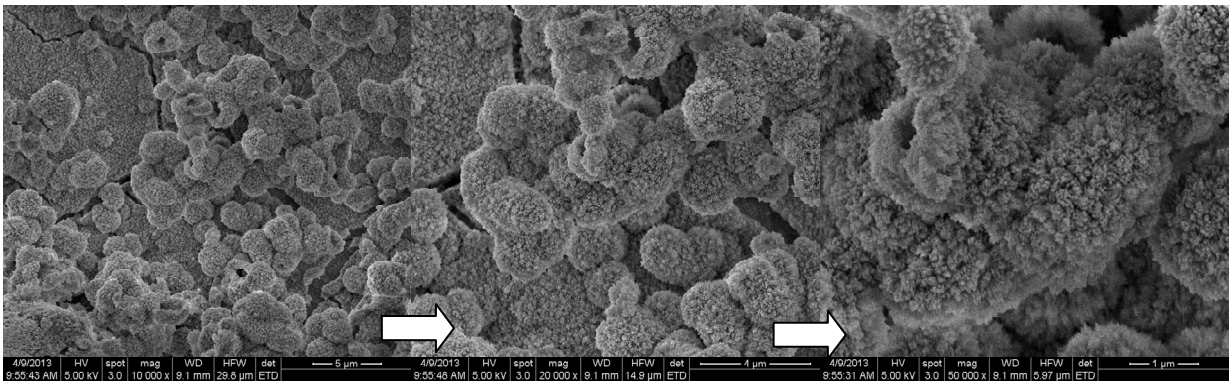
The SEM images, of the surface of glass-ceramic specimens soaked in SBF, shows the presence of a brittle layer consists mainly of fluoroapatite phase (FAp); FAp has a specific morphology consisting in spherical agglomeration of spherical shaped crystals (Figure 6a) and rods (Figure 6b). In case of glass-ceramic obtained at 1000°C/2h (Figure 6c), a „raspberry" type morphology, specific also for fluoroapatite phase, can be assessed. These different morphologies, assessed by SEM, can be explained by the amount and/or crystallinity degree of FAp and TCP formed in glass-ceramic masses calcined at different temperatures. As previously shown, the increase of claiming temperature determined the increase of amount and/or crystallinity degree of FAp and TCP and these phases plays the role of a crystallization substrate for the fluoroapatite formed by the interaction of glass-ceramic masses with SBF; this explains the different morphology of FAp layer formed at the surface of glass-ceramic materials, and the advanced structuration observed for the glass-ceramic materials obtained by calcination at 1000°C for 2h.



a



b



c

Fig. 6 - SEM micrographs for glass-ceramic masses obtained at : a- 700°C/2h; b-800°C/2h and c- 1000°C/2h soaked in SBF for 14 days at a temperature of 37°C./ *Imagini de microscopie electronică de baleiaj pentru mase de tip vitroceram obținute la: a-700°C/2h, b-800°C/2h şi c-1000°C/2h scufundate în SBF 14 zile la 37°C.*

4. Conclusions

The sol-gel synthesis represents a better approach for synthesis of bioactive glass-ceramics in the CaO-SiO_2-P_2O_5-CaF_2-MgO system. The sol-gel method assumes thermal treatment temperatures smaller than the traditional melt-quenching route and the resulted glasses have a high reactivity.

The gel obtained by the sol-gel method, dried and thermally treated at 700°C/2h, was the precursor for the preparation of glass ceramics masses. The calcination of this gel at 700, 800 and 1000°C, with a plateau of 2 h followed by slow cooling, lead to the crystallization of fluoroapatite and tricalcium phosphate. As expected, the increase of calcination temperature determines the increase of crystallinity degree of these phases. The SEM analysis pointed out also a densification of the glass-ceramic masses with the increase of the calcination temperature.

The obtained glass-ceramics masses were characterized from the point of view of their bioactivity by an in-vitro test, which consists in soaking the samples in simulated physiological fluid (SBF) for a period of 14 days at a temperature of 37°C. The surface of these specimens was analysed by XRD and showed the presence of a brittle layer consisting mainly of fluoroapatite. The morphology of this layer, assessed by SEM, is different and depends on the composition and morphology of glass-ceramics masses. For the specimens treated at lower temperatures (700^{o}C and 800^{o}C) the fluoroapatite phase consists in spherical agglomeration of spherical shaped crystals and rods. In case of glass-ceramic obtained at 1000°C/2h (Figure 6c), a „raspberry" type morphology, specific also for fluoroapatite phase was noticed.

Acknowledgements

This paper is supported by the Sectoral Operational Programme Human Resources Development, financed from the European Social Fund and by the Romanian Government under the contract number POSDRU/86/1.2/S/58146 (MASTERMAT).

REFERENCES

1. L.L. Hench; The story of Bioglass; Journal of Materials Science: Materials in Medcine, 2006, **17** (11), 967.
2. L.-C. Gerhardt and A.R. Boccaccini, Bioactive Glass and Glass-Ceramic Scaffolds for Bone Tissue Engineering, Materials, 2010, **3** (7), 3867.
3. C. Vitale-Brovarone, E. Verne, L. Robiglio, P. Appendino, F. Bassi, G. Martinasso, G. Muzio and R. Canuto, Development of glass-ceramic scaffolds for bone tissue engineering: characterisation, proliferation of human osteoblasts and nodule formation, Acta Biomaterialia, 2007, **3** (2), 199.
4. O. Bretcanu, S. Spriano, C.B. Vitale and E. Verne, Synthesis and characterization of coprecipitation-derived ferrimagnetic glass-ceramic, Journal of Materials Science, 2006, **41** (4), 1029.
5. D.G. Li, D.L. Zhou, Y. Lin, T.H. Pan, G.S. Chen and Q.D. Yin, Synthesis and characterization of magnetic bioactive glass-ceramics containing Mg ferrite for hyperthermia, Materials Science Engineering C, 2010, **30** (1), 148.
6. J.R. Jones, Review of bioactive glass: From Hench to hybrids, Acta Biomaterialia, 2013, **9** (1), 4457.
7. M.N. Rahaman, D.E. Day, B.S. Bal, Q. Fu, S.B. Jung, L.F. Bonewald and A.P. Tomsia, Bioactive glass in tissue engineering, Acta Biomaterialia, 2011, **7** (6), 2355.
8. R. Ravarian, F. Moztarzadeh, M. Solati Hashjin, S.M. Rabiee, P. Khoshakhlagh and M. Tahriri, Synthesis, characterization and bioactivity investigation of bioglass/hydroxyapatite composite, Ceramic International, 2010, **36** (1), 291.
9. A. Saboori, M. Rabiee, F. Moztarzadeh, M. Sheikhi, M. Tahriri and M.. Karimi, Synthesis, characterization and in vitro bioactivity of sol–gel derived SiO_2-CaO-P_2O_5-MgO bioglass, Materials Science Engineering C, 2009, **29** (1), 335.
10. L. Radev, V. Hristov, I. Michailova and B. Samuneva, Sol-gel bioactive glass-ceramics. Part. I: Calcium phosphate silicate/wollastonite glass-ceramics, Central European Journal of Chemistry, 2009, **7** (3), 317.
11. L. Radev, V. Hristov, I. Michailova and B. Samuneva, Sol-gel bioactive glass-ceramics. Part. II: Glass-ceramics in the CaO-SiO_2-P_2O_5-MgO system, Central European Journal of Chemistry, 2009, **7** (3), 322.
12. A. Balamurugan, G. Balossier, S. Kannan, J. Michel, A.H.S. Rebelo and J.M.F. Ferreira, Development and in vitro characterization of sol–gel derived CaO–P_2O_5–SiO_2–ZnO bioglass, Acta Biomaterialia, 2007, **3** (2), 255.
13. G. Voicu, A. I. Bădănoiu, E. Andronescu and C.M. Chifiruc, Synthesis, characterization and bioevaluation of partially stabilized cements for medical applications, Central European Journal of Chemistry, 2013, **11** (10), 1657.
14. G. Voicu, A.I. Bădănoiu, C.D. Ghițulică and E. Andronescu, Sol-gel synthesis of white mineral trioxide aggregate with potential use as biocement, Digest Journal of Nanomaterials and Biostructures, 2012, **7** (4), 1639.
15. G. Voicu, C. D. Ghițulică, E. Dinu and E. Andronescu, In-vitro behaviour of dicalcium silicate obtained through the sol-gel method, Romanian Journal of Materials, 2011, **41** (3), 229.
16. B. Nasiri-Tabrizi, A. Fahami, R. Ebrahimi-Kahrizsangi, A. Khazraei, M.R. Yazdani and M.J. Kajbafzadeh, A study on mechanochemical behavior of CaO–P_2O_5–CaF_2–ZrO_2 system to produce fluorapatite–zirconia composite nanopowders, Powder Technology, 2013, **243**, 59.
17. A. Bianco, I. Cacciotti, M. Lombardi, L. Montanaro, E. Bemporad and M. Sebastiani, F-substituted hydroxyapatite nanopowders: Thermal stability, sintering behaviour and mechanical properties, Ceramics International, 2010, **36** (1), 313.
18. Y. Chen and X. Miao, Thermal and chemical stability of fluorohydroxyapatite ceramics with different fluorine contents, Biomaterials, 2005, **26** (11), 1205.
19. F. Bir, H. Khireddine, A. Touati, D. Sidane, S. Yala and H. Oudadesse, Electrochemical depositions of fluorohydroxyapatite doped by Cu^{2+}, Zn^{2+}, Ag^{+} on stainless steel substrates, Applied Surface Science, 2012, **258** (18), 7021.
20. T. Kokubo and H. Takadama, How useful is SBF in predicting in vivo bone bioactivity?, Biomaterials, 2006, **27** (15), 2907.

****