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Influence of sintering temperature on the structure, morphology and bioactivity of bioactive glass powders

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ABSTRACT — In this work, a ternary bioactive glass powders (SiO_2-CaO-P_2O_5) were prepared via sol-gel method. Initially, the bioactive glass (BG) powder was synthesized by heating the solution of precursors in ethanol at 60°C and dried at 130°C. In the other hand, the influence of the sintering temperature of the final products on the structure, morphology and bioactivity of bioactive glass powders were also investigated. After the synthesis of bioactive glass powders, the bioactivity test was confirmed and their structure and morphology were distinguished by different analyses methods. The X-ray diffraction (XRD) and SEM-EDS analysis showed the amorphous structure at low sintering temperature and a crystalline structure by increasing the sintering temperature. The bioactive glass powders obtained were bioactive and the formation of an apatite layer on their surface after immersion in SBF solution for 1, 3 and 7 days was improved by X-ray diffraction and SEM – EDS analysis.

***Keywords**: Biomaterials, Bioactive glasses, sol-gel methods, bioactivity.*

1. Introduction

One of the major stakes of our society is the improvement of the quality of life. This involves the widespread use of increasingly sophisticated medical systems designed to compensate an organ or deficient tissues in the context of pathology, trauma or aging tissues. The development of bioactive glasses is part of this multidisciplinary approach. This family of substitutes is particularly suited for filling bone defects and prosthetic coatings in orthopedic, maxillofacial and dental surgery [1, 2].

In fact, in contact with living tissues, bioactive glasses produce a series of physicochemical reactions at the material/bone tissue interface leading to the formation of a layer of calcium phosphate [3, 4].

Bioactive glasses must be provided with a set of mechanical and physicochemical properties as close as possible to the properties of the tissues at which it is implanted. Thus, bioactive glass must not introduce harmful toxicity or reactions.

L. L. Hench developed the first bioactive glass with a composition of 45% of SiO2, 24.5% of Na2O, 24.5% of CaO and 6% of P2O5, called 45S5 of L. L. Hench [5].

However, the method of synthesis of bioactive glasses has a great influence on the physicochemical properties of the final material. Bioactive glasses can be obtained by two method: the conventional one corresponds to a heat treatment at high temperature (1300-1500°C), comprising a decabonatation phase, melting and then quenching in water or air. The second known as sol-gel, allows the manufacture of the bioactive glass by simple chemical reactions (hydrolysis and condensation) at a low temperature (20 to 150°C) [6].

The heating conditions of the gel obtained by sol-gel method and the sintering temperature are also important factors in the evolution of the

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structure, morphology and bioactivity of the produced bioactive glasses.

The objective of this study is the development of 63S ternary bioactive glass powders via sol-gel method sintered at different temperatures, in case of studying the difference between their structures and morphologies. However, this work focuses on the comparative study of bioactive glass powders sintered at different temperatures in order to test their bioactivity by immersion in simulated body fluid (SBF) to analyze their feasibility as a biomaterial.

II. Materials and methods

II.1. Materials

Tetraethylorthosilicate (TEOS), calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$, triethyl phosphate (PET) as starting materials for the preparation of 63S bioactive glass, ethanol C_2H_5OH as solvent and hydrochloric acid HCl, 2N as a catalyst [7]. All the reagents needed to prepare the SBF solution according to Kokubo protocol [8] for the bioactivity test.

II.2. Synthesis of bioactive glass powders

Sol-gel process was used to prepare a ternary bioactive glasses (SiO_2-CaO-P_2O_5) [7]. Initially, tetraethylorthosilicate (TEOS) was added to ethanol as an alcoholic medium and stirred for 30 min. The other reagents were added in the following order, with 30 minutes stirring for each reagent to completely react: H_2O/ TEOS with a molar ratio of 4/1, triethyl phosphate (PET), calcium nitrates tetrahydrate and hydrochloric acid (2N, HCl) was used as the catalyst. After the final addition, the solution was stirred for an additional hour and then the final solution was heated at 60°C for 10 h, dried at 130°C for 20 h and then the gel obtained was sintered at different temperatures (400, 600 and 800°C). In order to determine the structural, physicochemical and morphological properties of our elaborated bioactive glass powders, different characterizations are used, namely X-ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscope coupled with elemental analysis (MEB-EDX).

II.3. In vitro bioactivity tests

In order to test the biological activity of the syntheses bioactive glass powders and their ability to form a layer of hydroxyapatite [9], pellets of 15 mm in diameter and 2 mm in thickness are designed using a Press. The pellets obtained were immersed in a simulated body fluid (SBF) prepared according to the protocol developed by Kokubo et al. [8] at a temperature of 37°C for 1, 3 and 7 days, with a surface to volume ratio of 0.1 cm^{-1} [10]. The pH of the SBF solution used is buffered to 7.4 with Tris $(CH_2OH)_3CNH_2$) and hydrochloric acid. The SBF solution of the submerged samples was refreshed every two days. After immersion, the pellets were extracted from the SBF solution, rinsed with deionized water and dried at room temperature. pellets without soaking in SBF are referred as zero-day specimens (0 d). The formation of an apatite layer on the surface of the samples is evaluated by XRD for phase analysis, SEM for morphology and energy dispersive spectroscopy (EDS) for elemental analysis.

II.4. Characterization

II.4.1. Scanning electron microscopy - microanalysis X (MEB-EDX)

The morphology of the bioactive glass powders and pellets were carried out using a high-resolution environmental scanning electron microscope equipped with EDX microanalysis and backscattered electron diffraction analysis of the Quanta 400 FEG ESEM type / EDAX Genesis X4M. The samples were coated with a thin Au / Pd film by spraying using the SPI Sputter Coater module equipment prior to their MEB-EDX assays.

II.4.2. X-ray diffraction

Structural characterization and the identification of the nature of the crystalline phases present in the bioactive glass powders obtained were carried out by X-ray diffraction with a sample-stage Epert plate-form diffractometer (Sample-Stage) using radiation Monochromatic copper (CuKα) of wavelength λ = 1.5406Å. The diffractograms were recorded in a range of angles 2θ between 10 and 60°.

II.4.3. Fourier Transform Infrared Spectroscopy

The structural characterization of the bioactive glass powders was carried out with an Affinity1 IR spectrometer SHIMADZU FTIR spectrometer, in spectral range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. 2 % (weight %) of bioactive glass powders were mixed with

98% KBr powder and pressed into pellets. The spectra were recorded in transmission mode.

III. Results and Discussions

III.1. Characterization of bioactive glass powders

The powders sintered at 400, 600 and 800°C were labelled as 63S1, 63S2 and 63S3 respectively were characterized with different methods of analysis (DRX, FTIR and MEB-EDX) before testing their bioactivities.

III.1.1. X-ray diffraction (XRD) of the bioactive glass powders

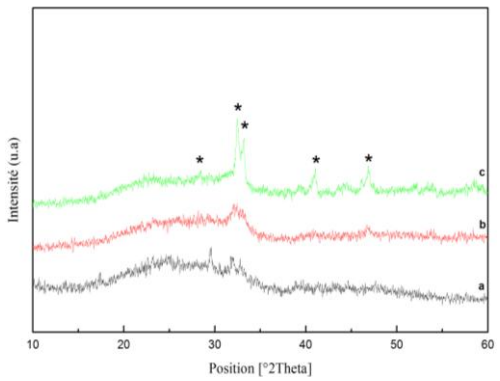

Fig. 1 The diffractograms of the bioactive glass powders: a-63S1, b-63S2 and c-63S3.

The phase formation behavior of the bioactive glass powders at different sintering temperature was invistegated by XRD (Fig.1) and the results patterns indicated that the bioactive glass powders 63S1 and 63S2 have an amorphous state. While the powder 63S3 illustrate a crystalline structure at positions 32, 41, 46 and 58° refered to the pseudo wollastonite (CaSiO3) or apatite [11 - 14]. This indicated that the crystallization process depend on the sintering temperature.

III. 1. 2. FTIR analysis of the bioactive glass powders

The formation of the bioactive glass powders was confirmed by FTIR spectral analysis (Fig.2). The spectra showed adsorption bands around 1055, 780 and 453 cm^{-1} assigned to the asymmetric, symmetric and bending vibrations of Si-O-Si bond respectively [11, 14-16, 17]. This proves that all the powders consist mainly of an Si-O-Si network. The spectra involve a band around 574 cm^{-1} attributed to the stretching vibrations of the Si-OH bonds [18-20]. The band at 1396 cm^{-1} is assigned to the vibrations of PO_2 and/or NO_3 groups. This band disappear in xerogel bioactive glass powders sintered at 600 and 800°C. The weak inflection at 1653 cm^{-1} and the broad band centered at 3468 cm^{-1} are assigned to O-H band of adsorbed water and structural hydroxyl group respectively [2, 15, 21]. Finally the band at 2372 cm^{-1} is attributed to the adsorption of CO_2 by the atmosphere [16].

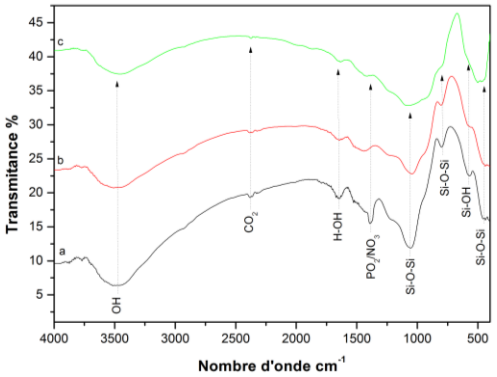

Fig. 2 FTIR spectra of the bioactive glass powders: a-63S1, b-63S2 and c-63S3**.**

III.1.3. SEM-EDS analyses of the bioactive glass powders

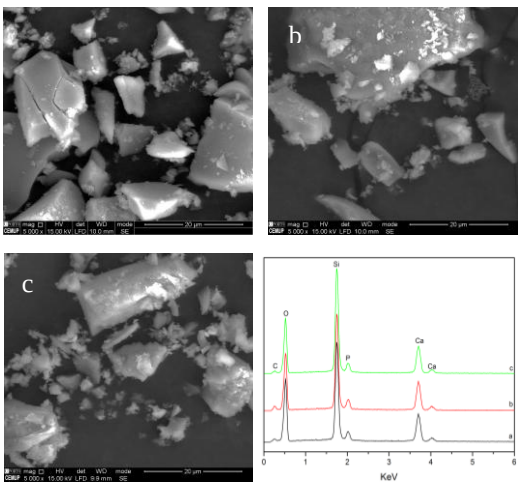

Fig.3 SEM morphologies and EDS analysis of the bioactive glass powders: a-63S1, b-63S2 and c-63S3.

Fig. 3 shows the surface and morphology of the bioactive glass powders as well as their EDS spectra. The micrographs revealed that the powders are constituted of dense and irregularly particles with the apparition of white particles in the powders 63S2 and 63S3 assigned to the crystalline phase.

The EDS analysis of the bioactive glass powders confirmed the presence of all the introduced species during the step of mixing in sol-gel process. The peaks observed at 1.75, 2 and 3.7 correspond to Si, P and Ca respectively indicating the constituent elements of ternary bioactive glasses [22-24].

III.2. Bioactivity test of bioactive glass powders

After having characterized the different bioactive glass powders, an in vitro bioactivity test in simulated body fluid SBF is carried out in order to analyze their feasibility as biomaterials. The formation of the apatite layer on the surface of the pellets are confirmed by SEM-EDS analysis.

III.2.1. Elemental analysis EDS of the bioactive glass pellets

Elemental analysis of the bioactive glass pellets before and after immersion in the SBF solution for 0, 1, 3 and 7 days was confirmed by EDS analysis (Fig.4).

The results show a significant increase in the intensity of the calcium and phosphorus elements and the decrease of the silica element in all the bioactive glass pellets from the first day of immersion in the SBF compared to the pellets without soaking. After 7 days of immersion, we noticed the almost total disappearance of peak Si and the appearance only of the peaks Ca and P which proves that the surface of the pellets are covered by an apatite layer.

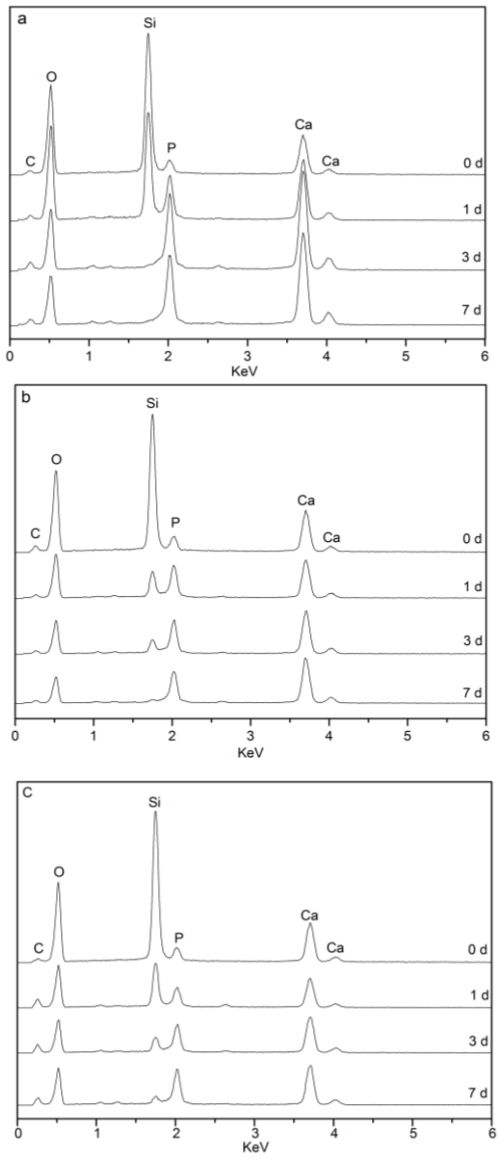

Fig.4 The EDS quantitative analysis spectra of the bioactive glass pellets before and after immersion in the SBF solution for 0, 1, 3 and 7 days: a-63S1, b-63S2 and c-63S3.

III.2.2. Morphology of bioactive glass pellets by SEM analysis

The formation of bone as an apatite layer during the bioactivity tests was also evaluated by examining the variation in the surface morphology of the bioactive glass pellets during incubation in the SBF solution. The results show that the surface morphology changes with incubation periods (Fig.5). After 1 day soaking in SBF compared to 0 day which is considered as control, the surface shows the formation of

individual spherical grains of apatite. But these spherical grains are numerous and well defined in the sample sintered at 600 °C [24]. With increasing incubation periods, the formation of apatite grains increases, after 3 days of incubati on, the bioactive glass pellet surface sintered at 400°C. is partially covered with apatite layer, in contrast to the sintered pellets at 600 and 800°C,

where the surface are totally covered by an apatite layer. However, the density of the precipitate (apatite layer) increased significantly after 7 days of immersion. The formation of the apatite layer can be explained by the exchange between the Ca^{2+} ions of the bioactive glass pellets and the $H3O^{+}$ of the SBF solution, which can give rise to the formation of Si-OH groups on the surface of the samples that induces the nucleation of apatite [21, 25]. We observed that the formation of an apatite layer is more important when the sintering temperature is increased.

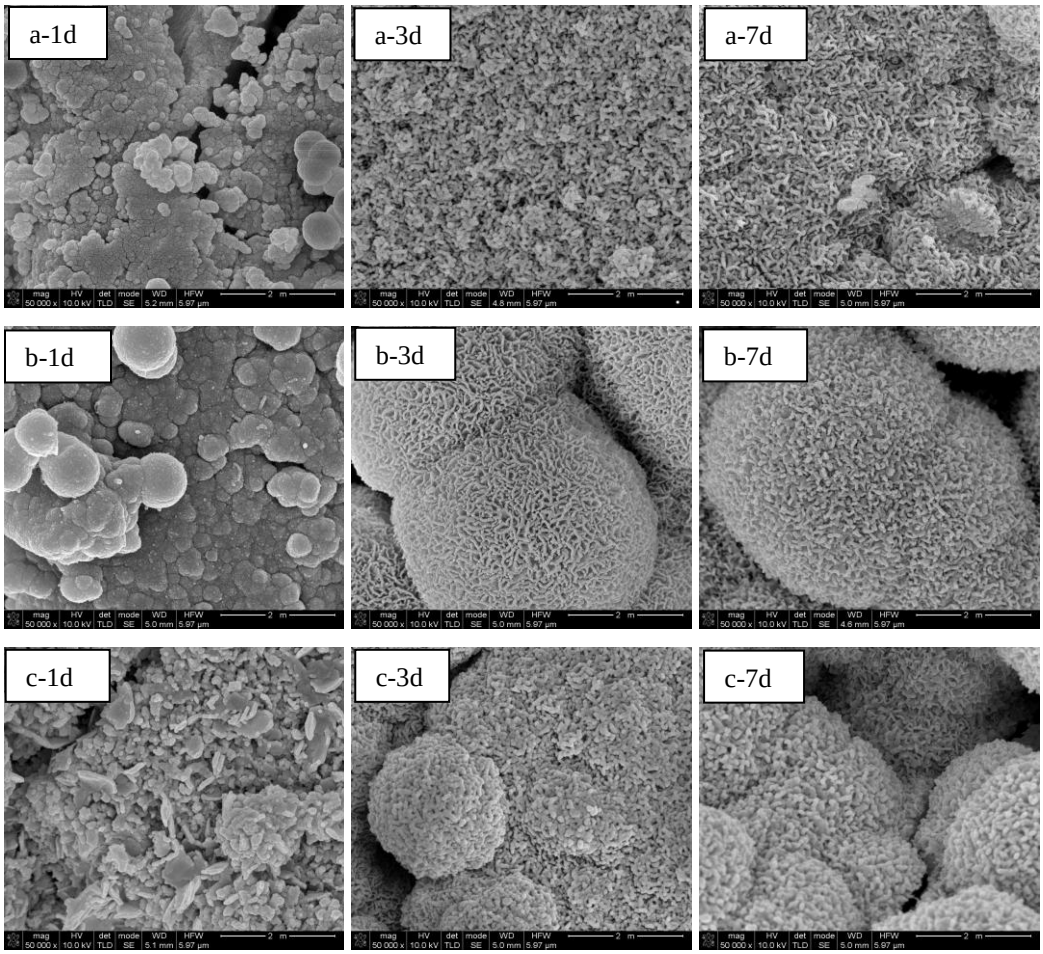

Fig. 5 The SEM micrographs of the bioactive glass pellets after immersion in the SBF solution for 1, 3 and 7 days: a-63S1, b-63S2 and c-63S3.

IV. Conclusion

In this study, bioactive glass powders in ternary system (CaO-P_2O_5-SiO_2) was successfully synthesized via sol-gel route. The results obtained show that the texture of the bioactive glass powders is strongly influenced by the sintering temperature. The XRD analysis shows that the powders are transformed from the amorphous state to the crystalline state by increasing the sintering temperature and SEM analysis is in agreement with XRD. The bioactivity test shows a surface covered by an apatite layer after three days of immersion in SBF solution. The powders sintered at 800°C present a good properties and the improvement of their biocompatibility tests will be interesting for this powder in order to improve its viability to be used in regenerative medicine: In filling bone defects, prosthetic coating in orthopidic surgry, maxillofacial and dental.

References

[1]. Ahmed Al-Noaman, Simon C.F. Rawlinson, Robert G. Hill. *The role of MgO on thermal properties, structure and bioactivity of bioactive glass coating for dental implants.* Journal of Non-Crystalline Solids. 2012, 358: 3019–3027.

[2]. M. Mehdipour, A. Afshar. *A study of the electrophoretic deposition of bioactive glass-chitosan composite coating*. Ceramics International. 2012, 38: 471-476.

[3]. Devis Bellucci, Valeria Cannillo, Antonella Sola. *Calcium and potassium addition to facilitate the sintering of bioactive glasses*. Materials Letters. 2011, 65: 1825–1827.

[4]. D. Zhitomirsky, J.A. Roether, A.R. Boccaccini, I. zhitomirsky. *Electrophorotic deposition of bioactive glass/polymer composite coating with and without HA nanoparticle inclusions for biomedical applications*. Journal of Materials Processing Technology. 2009, 209: 1853-1860.

[5]. L. L. Hench, R. J. Splinter, W. C. Allen; T. K. Greenlee. *Bonding mechanism at interface of ceramic prosthetic materials*. J. Biomed.Mater. Res. 1972, 2: 117-141.

[6]. H.C. Li, D.G. Wang, J.H. Hu, C.Z. Che. *Effect of various additives on microstructure, mechanical properties, and in vitro bioactivity of sodium oxide-calcium oxide-silica-phosphorus pentoxide glass–ceramics*. Journal of Colloid and Interface Science. 2013, 405 : 296–304.

[7]. A. Doostmohamadi, A. Monshi, M. H. Fathi, S. Karbasi, O. Braissant, Q. U. Daniels. *Direct cytotoxicity evaluation of 63S bioactive glass and bone-derived hydroxyapatite particles using yeast model and human chondrocyte cells by microcalorimetry*. J Mater Sci: Mater Med. 2011, 22: 2293-2300.

[8]. T. Kokubo. *Surface chemistry of bioactive glass-ceramics*. J Non-Cryst Solids. 1990, 120: 138-5.

[9]. I. B. Leonor, R. A. Sousa, A. M. Cunha; R. L. Reis. *Novel starch thermoplastic/Bioglass composites: Mechanical properties, degradation behavior and in-vitro bioactivity.* Journal of materials science: Materials in medicine. 2002, 13: 939-945.

[10]. W. Zhao, J. Wang, W. Zhai, Z. Wang, J. Chang. *The self-setting properties and in vitro bioactivity of tricalcium silicate*. Biomaterials. 2005, 26: 6113-6121.

[11]. J.Ma, C.Z. Chen, D.G. wang, X.G. Meng, J.Z. Shi. *Influence of the sintering temperature on the structural feature and bioactivity of sol-gel derived SiO_2-CaO-P_2O_5 bioglass.* Ceramics International. 2010, 36: 1911-1916.

[12]. A.L. Girot, F.Z. Mezahi, M. Mami, H. Oudadesse, A. Harabi, M.L. Floch.

Sol–gel synthesis of a new composition of bioactive glass in the quaternary system SiO2–CaO–Na2O–P2O5 Comparison with melting method. Journal of Non-Crystalline Solids. 2011, 357 : 3322–3327.

[13]. P. Jiang, H. Lin, R. Xing, J. Jiang, F. Qu. *Synthesis of multifunctional macroporous-mesoporous TiO_2-bioglasses for bone tissue engineering*. J Sol-Gel Sci Technol. 2011.

[14]. H.S. Costa, M.F. Rocha, G.I. Andrade, E.F. Barbosa-Stancioli, M.M. Pereira, R.L. Orefice, W.L. Vasconcelos, H.S. Mansur. *Sol-gel derived composite from bioactive glass-polyvinyl alcohol.* J Mater Sci. 2008, 43: 494-502.

[15]. S.H. Jun, E.J. Lee, S.W. Yook, H.E. Kim, H.W. Kim, Y.H. Koh. *A bioactive coating of a silica xerogel/chitosan hybrid on titanium by a room temperature sol-gel process.* Acta Biomaterialia. 2010, 6: 302-307.

[16]. H. Hajiali, S. Karbasi, M. Hossein. H.R. Rezaie. *Preparation of a novel biodegradable nanocomposite scaffold based on poly (3-hydroxybutyrate)/bioglass nanoparticles for bone tissue engineering.* J Mater Sci: Mater Med. 2010, 21: 2125-2132.

[17]. A.R. Boccaccini, M. Erol, W.J. Stark, D. Mohn, Z. Hong, J.F. Mano. *Polymer/bioactive glass nanocomposites for biomedical applications: A review.* Composites Science and Technology. 2010, 70: 1764-1776.

[18]. C.Y. Kim, A.E. Clark, L.L. Hench. *Early stages of calcium-phosphate layer formation in bioglasses.* Journal of Non-Crystalline Solids. 1989, 113: 195-202.

[19]. H.A. Elbatal, M.A. Azooz, E.M.A. Khalil, A.S. Monem, Y.M. Hamdy. *Characterization of some bioglass-ceramics.* Materials Chemistry and Physics. 2003, 80: 599-609.

[20]. A. Balamurugan, G. Balossier, S. Kannan, J. Michel, A.H.S. Rebelo, 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: 255-262.

[21]. O. Petil, E. D. Zanotto, L. L. Hench. *Highly bioactive P_2O_5- Na_2O- CaO-SiO_2 glass-ceramics.* J. Non-Cryst.Solids. 2011, 292: 115-126.

[22]. J.P. Nayak, S. Kumar, J. Bera. *Sol-gel synthesis of bioglass-ceramics using rice husk ash as a source for silica and its characterization.* Journal of Non-Crystalline Solids. 2010, 356: 1447-1451.

[23]. L. Radev, K. Hristova, V. Jordanov, M.H.V. Fernandes, I.M.M. Slvado. *In vitro bioactivity of 70 Wt.% SiO_2- 30 Wt.% CaO sol-gel glass, doped with 1,3 and 5 Wt.% NbF_5.* Central European Journal of Chemistry. 2012, 10: 137-145.

[24]. A. Rainer, S.M. Giannitelli, F. Abbruzzese, E. Traversa, S. Licoccia, M. Trombetta. *Fabrication of bioactive glass-ceramic foams mimicking human bone portions for regenerative medicine.* Acta Biomaterialia. 2008, 4: 362-369.

[25]. M. M. Pereira, A. E. Clark, L. L. Hench. *Effect of texture on the rate of hydroxyapatite formation on gel-silica surface.* J. Am. Ceram. Soc. 1995, 78: 463-468.