

Study on bioactivity of phosphocalcic glasses

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In this research bioactive capacity in case of three phosphocalcic glass compositions from ternary system $\text{SiO}_2 - \text{CaO} - \text{P}_2\text{O}_5$ was analyzed. For their synthesis sol-gel technique was used. The elemental composition of the initial samples was demonstrated by the X-ray fluorescence analysis using sequential wavelength dispersive spectrometer ARL Advent X Intelli Power. Study of bioactivity was performed after soaking of the samples in human simulated body fluid from 3 to 14 days. Phosphocalcic glasses bioactivity was confirmed by X-ray diffraction analysis using X-ray diffractometer Rigaku – Ultima IV and infrared spectroscopy analysis, by FTIR spectrometer Bruker - Vertex 80. By the analysis performed was observed the synthesis of apatite on phosphocalcic glasses surfaces.

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1. Introduction

Phosphocalcic glasses with bioactive capacity were designed to induce specific biological activity. In the most cases, this activity involves obtaining of interactions at the surface tissue - implant [1].

Bioactive glasses and vitroceraamics are among the most promising systems for bone reconstruction due to their excellent biological and particular mechanical properties. A common characteristic of the oxide materials with bioactive properties is to modify the reactivity of its surface immediately after implantation. This phenomenon consists in the formation of a carbonated hydroxyapatite layer, biologically active, which leads to the formation of the interfacial bond between the implant and the hard tissue (bone). The newly formed structure is chemically and structurally equivalent with mineral phase of bone [2].

In the recent decades, the interest in bioactive oxide materials has increased steadily. Research has shown that the bioactivity of the glasses and other compounds derived from the sol-gel technique is superior by comparison to the materials synthesized by melting of oxid mixtures [3, 4].

Related to the classical method of glass synthesis by melting of comonents, the sol-gel tehniue show the advantage of lower reaction temperature and a homogeneous composition, without solid impurities from the raw materials and crucible used for melting.

The published studies regarding investigations into the sol-gel synthesis technique showed that both glass

powders and glass-ceramics obtained thereby, have been used successfully in prosthetics and bone reconstruction and also showed a high bioactivity [5, 6].

The aim of this study is the characterization of three glass compositions in the ternary systems $\text{SiO}_2 - \text{CaO} - \text{P}_2\text{O}_5$ obtained by the sol-gel technique [7] in terms of the bioactivity exhibited in vitro. The characterization of new material compositions was achieved by various investigative techniques before and after soaking of samples in simulated body fluid (SBF), for different periods of time.

2. Experimental procedure

2.1 Synthesis of sol-gel glasses

Three glasses compositions from $\text{SiO}_2 - \text{CaO} - \text{P}_2\text{O}_5$ systems were synthesized by using sol-gel tehniue. Oxide compositions of sol-gel glasses obtained in this study are presented in Table 1.

Table 1. Oxide compositions of sol-gel glasses.

Sample	Composition [% wt]		
	SiO_2	CaO	P_2O_5
S ₁	50	45	5
S ₂	55	40	5
S ₃	50	41	9

The glass synthesis involved four basic stages: the hydrolysis and condensation of raw materials to obtain sol, gelation and aging of the gel (Fig. 1), drying of gel (xerogel) at temperatures below 180 °C, for 48 and 72 hours (fig. 1b), followed by stabilization of xerogels by calcination at 600 °C for at least 8 hours. (Fig. 1c) [8].

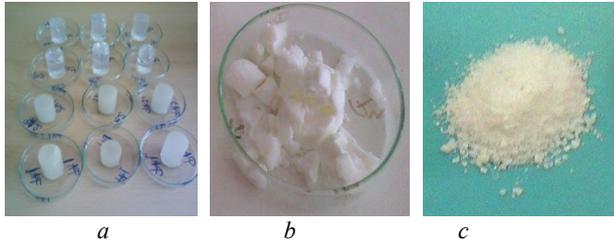


Fig. 1 Sol-gel glasses synthesis: a - aged gels, b - xerogels, c - glass powders.

2.2 Characterization of the samples

The oxide chemical compositions (CaO-SiO₂-P₂O₅) were determined by Wavelength Dispersive X-ray fluorescence spectroscopy (WD-XRF) by using Thermo Scientific ARL Advant'X with X-ray tube of 2400W, 60kV and 80 mA using the diffraction LiF 200 crystal [8].

The structural changes accrued in the glass surface synthesized by sol-gel and soaked in simulated body fluid (SBF) between 3 and 14 days were studied by X-ray diffraction analysis (XRD) [9, 10].

Structural characterization of bioactive glass powders were achieved by using Rigaku Ultima IV diffractometer, with the following features: $Cu_{k\alpha} = 1.5405 \text{ \AA}$ source of radiation generated at voltage 40 kV and current of 40 mA. Data were collected in scan range 20-60 °(2θ) with a scan speed of 0.04° (2θ) /sec.

XRD analysis was used to assess the unsoaked amorphous glass powders and the formation of apatite phase on their surface after immersion in simulated body fluid.

The chemical groups in the structure of the glass were emphasized by Fourier transform infrared spectroscopy (FTIR) by using a Bruker Vertex 80 spectrometer equipped with ATR crystal. The data were collected at room temperature in the range of wavelengths 4000 - 400 cm⁻¹ and spectral resolution of 2 cm⁻¹.

2.3. Preparation of SBF

Simulated body fluid was used to assess in vitro behavior of the prepared bioactive glass powders. This liquid is a solution of cell-free, non-protein with chemical composition similar to human blood plasma. It was reported by Kokubo et al. [13, 14, 15].

Tests conducted in vivo involve reproducibility difficulties which error level is involved, high costs, long periods of evaluation and especially ethics issues. For these reasons, products destined for implantation are initially tested in vitro.

The choice of solution used for the invitro study, respectively reactions that occur on the surface of the

material is very important in order to reproduced as closely biological conditions post-implantation.

The composition of the SBF with 1.5 N concentration used in the study is presented in Table 2.

Table 2. Composition and ionic concentration 1L SBF concentration of 1.5 N.

Reagent	Quantity [g]	Ionic concentration [mmol/l]	
		Cations	Anion
NaCl	11.994	Na ⁺	-
NaHCO ₃	0.525	213.0	HCO ₃ ⁻ 6.3
KCl	0.336	K ⁺	-
K ₂ HPO ₄	0.342	7.5	HPO ₄ ²⁻ 1.5
MgCl ₂	0.458	Mg ²⁺ 2.3	-
HCl 1M	60 cm ³	-	Cl ⁻ 221.7
CaCl ₂	0.417	Ca ²⁺ 3.8	-
Na ₂ SO ₄	0.107	-	SO ₄ ²⁻ 0.8
(CH ₂ OH) ₃ -C-NH ₂	9.086	-	-
HCl 1M	pH= 7.2-7.4	pH= 7.25	

The glass powders were soaked between 3 and 14 days in SBF, by using static immersion method, at 37 °C and an initial pH of 7.2.

In this paper, has been chosed the static immersion method of samples in order to stimulate the reactivity of materials. The glass powders are soaked in SBF without refreshing solution. In the case of dynamic method, the fluid is changed periodically for refreshing environment in which the bioactivity in vitro assay [9, 11, 12].

3. Results and discussion

3.1 WD – XRF analysis

WD-XRF analysis results for the three samples of glass synthesized are shown in Table 3. Also, it have been determined the yield of the glass synthesis process and the oxygen released during the analysis.

Table 3. Chemical composition and yield of the glasses

Sample	Oxides [% wt]			Yield [%]	Total O ₂ stripped [%]
	SiO ₂	CaO	P ₂ O ₅		
S1	47.83	45.73	5.60	92.4	41.033
S2	52.97	40.69	5.76	91.7	42.475
S3	49.55	38.87	10.62	94.6	43.663

These results confirm the correctness of the chosen method of synthesis. At the same time, the yield of the glass synthesis shows that procedure and adopted technological route were accurate, because the hydrolysis and condensation processes are considered optimal yields over 85% [16, 17].

3.2 XRD analysis

By soaking in simulated body fluid, bioactivity of glasses were tested, particularly the ability to generate nucleation of apatite crystals on their surface, the phenomenon being revealed by X-ray diffraction analysis [14, 15].

Fig. 2 shows the X ray diffraction patterns of sol-gel glasses S1 S2 and S3 before and after soaking in simulated body fluid.

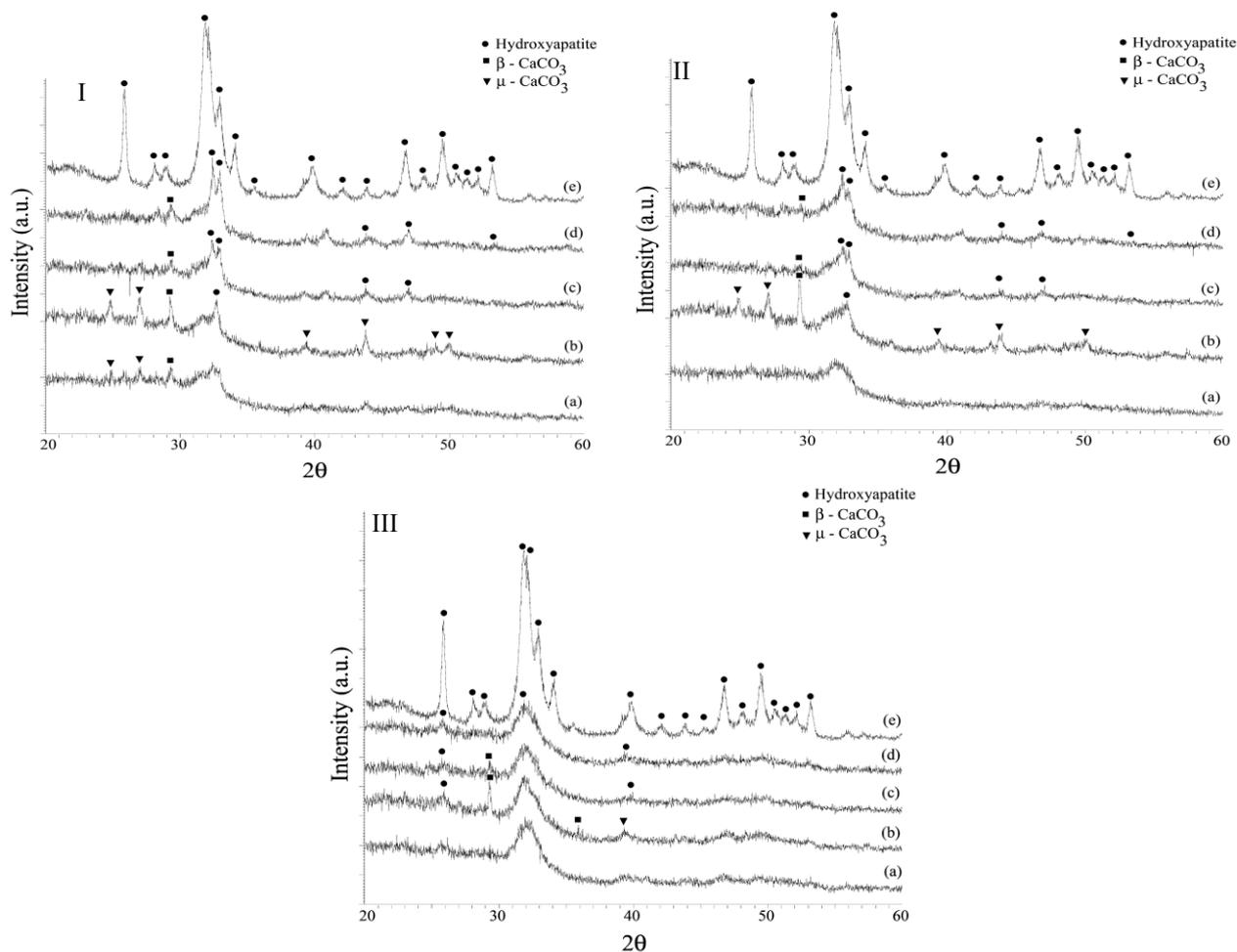


Fig. 2. X-ray diffraction patterns for sol-gel glasses (I) S1, (II) S2 and (III) S3
a) unsoaked and soaked in simulated body fluid for: b) 3days, c) 7 days and d) 14 days, e) hydroxyapatite.

In the case of sample unsoaked in simulated body fluid (Fig. 2.Ia), XRD analysis reveals the presence of some crystalline structure in the glass composition assigned to calcium carbonate β - CaCO_3 (calcite) and μ - CaCO_3 (vaterite). These two phases of calcium carbonate have been found at 2θ of 29.33, respectively 27.06 and 24.96 according to ICDD - PDF 2: 00-005-0586 - for β - CaCO_3 and 00-033-0286 for μ - CaCO_3 .

After 3 days of soaking in simulated body liquid, it can be seen an increase of the calcium carbonate formation on the glass surfaces, Fig. 2.Ib. Although vaterite has the highest water solubility compared to other forms of calcium carbonate (calcite and aragonite), the formation of

μ - CaCO_3 on the soaked glass surface is attributed to the presence of carbonate ions (CO_3^{2-}) found in simulated body fluid. By using NaHCO_3 as reagent in SBF solution synthesis of vaterite on the glass surface have been favored. An increase of CO_3^{2-} concentration in solution leads to a greater tendency of vaterite formation, rather than its transformation in calcite β - CaCO_3 [18].

Regarding the synthesis of apatite on the glass surface, the presence of the first crystals of the compound based on calcium and phosphorus have been identified by X-ray diffraction and ICDD-PDF2 standard: 00-009-0432 at $32.9\ 2\theta$ ($2.71\ \text{\AA}$).

By increasing the time of soaking in simulated body fluid from 7 to 14 days (Fig 2.Ic, 2.Id), the formation of apatite on the glass surface S1 has been observed. This aspect is revealed by the presence of new peaks located at $32.2\ 2\theta$ (2.71 Å), $43.05\ 2\theta$ (2.14 Å), $46.53\ 2\theta$ (1.94 Å), $53.24\ 2\theta$ (1.72 Å).

The XRD patterns of sol-gel glass S2, before and after soaking in SBF solution are shown in Figure 2.II.

X ray diffraction spectra presented in Fig. 2.IIa is specific to amorphous material such as glass, in this case, no crystalline phase was not identified.

After soaking for 3 days in simulated body fluid, apatite formation is found on the surface of the prepared glass powders S2, Fig 2.IIb. In this regard, it was found diffraction peak located at $32.8\ 2\theta$ (2.72 Å). Also, calcium carbonate phases were identified on the glass surface, by diffraction line present at $24.96\ 2\theta$, $27.06\ 2\theta$, $39.33\ 2\theta$, $39.5\ 2\theta$ and $50.11\ 2\theta$

In case of powders soaked for 7 days (Fig. 2.IIc), XRD analysis reveals an increase of bioactivity on the glass surface. New peaks assigned to apatite formation have been identified at $32.2\ 2\theta$ (2.77 Å), $43.86\ 2\theta$ (2.06 Å) and $46.68\ 2\theta$ (1.94 Å).

The reactivity of glass surface S2 after soaking for 14 days (Fig. 2.IId) increased. The rate of apatite formation on the glass surface grows continuously. This phenomenon is highlighted by increasing intensity of the peak located at $32.2\ 2\theta$ and appearance of a new peak located at $53.14\ 2\theta$ (1.72 Å).

It can also be seen a decrease in the proportion of calcium carbonate on the surface of the glass powders, after soaking of samples for 7 and 14 days, the only peak being identified and associated with calcite, is located $29.33\ 2\theta$.

Fig. 2.III presents the X ray diffraction patterns for sample S3 before and after testing in SBF solution at 37°C and $\text{pH} = 7.25$, between 3 and 14 days [17]. In the case of unsoaked sol-gel glass S3, XRD spectra is specific to amorphous material, as shown in Figure 2.IIIa. By soaking powders in simulated body fluid for 3 days (Fig. 2.IIIb) calcite (β - CaCO_3) on the glass surface was found. This phase are revealed by the diffraction lines located $29.33\ 2\theta$, $35.8\ 2\theta$. Also, μ - CaCO_3 was identified at $39.25\ 2\theta$. At the same time has been identified first apatite formations on the glass surface, by peak located at $25.85\ 2\theta$, (3.44 Å).

The change of soaking time to 7 and 14 days (Fig. 2.IIIc and 2.IIIId), leads to increase of apatite formation on the glass surface, the aspect highlighted by the new diffraction peaks located at $31.77\ 2\theta$ (2.81 Å), $39.7\ 2\theta$ (2.26 Å). In the case of SiO_2 - CaO - P_2O_5 glass S3 degree of apatite formation is inferior to the other two compositions.

By comparison has been presented X - ray diffraction pattern for raw hydroxyapatite (Fig. 2.Ie, 2.IIe, 2.IIIe).

3.3 FT-IR analysis

In the case of the three glass compositions, the study bioactivity, ie the formation of apatite on the surface of these amorphous powders revealed by Fourier transform IR spectroscopy analysis.

The aim of FTIR analysis was to indicate the formation and development, in a period between 3 and 14 days, of specific molecular groups common for SiO_2 - CaO - P_2O_5 glass system and hydroxyapatite.

On this subject, was taken into account the formation and development of molecular groups such as Si-O, Si-O-Si or Si-OH common by found in sol-gel glass structure and carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) and hydroxyl (HO^{\cdot}) groups present in the carbonated hydroxyapatite structure [19, 20, 21, 22, 23].

In figure 3.I is shown the FTIR spectra for the sample S1 before and after soaking the glass powder in simulated body fluid at $\text{pH} 7.25$ at 37°C for 3, 7 and 14 days.

The FTIR spectrum presented in Figure 3.Ia, for glass composition S1, highlights the formation of molecular groups such as Si-O and Si-O-Si, that are specific to silicate network in the glass structure. The peak located at $451\ \text{cm}^{-1}$ is characteristic to bending vibration mode of Si - O, and the peak at $1014\ \text{cm}^{-1}$ corresponding to asymmetric stretching vibration of Si - O - Si bridges.

The presence of silanol groups Si-OH emphasized by the broadened band located at $3350\ \text{cm}^{-1}$ corresponds to the stretching vibration of hydroxyl (O-H) common especially in case of Si - OH groups and chemically bound water presents in the phosphocalcic glass structure. The peaks at $1639\ \text{cm}^{-1}$ and $2361\ \text{cm}^{-1}$ confirm the presence of H_2O molecules in SiO_2 - CaO - P_2O_5 glass structure.

The peaks located at $569\ \text{cm}^{-1}$, $606\ \text{cm}^{-1}$ highlighted the presence of phosphate (PO_4^{3-}) in glass structure. These two peaks correspond to P - O - P bending vibrations of PO_4^{3-} structure.

At the same time, FTIR analysis emphasized the presence carbonate groups (CO_3^{2-}) in the glass structure by the peaks located at $1447\ \text{cm}^{-1}$ and $877\ \text{cm}^{-1}$.

Apatite formation on the S1 glass surface has been emphasized by the increase of intensity for the peaks common for phosphate groups placed at $569\ \text{cm}^{-1}$ and $606\ \text{cm}^{-1}$ after soaking of powders from 3 to 14 days (Fig. 3.Ib, 3.Ic and 3.Id). The presence of carbonate groups (CO_3^{2-}) is typical for apatite structure being confirmed by peaks from $1469\ \text{cm}^{-1}$ and $877\ \text{cm}^{-1}$, in the case of samples soaked up to 14 days in SBF solution.

By comparison a spectrum of a raw hydroxyapatite is shown (Fig.3.Ie) in order to indicate the molecular groups of this phosphocalcic compound.

For the composition S2, FTIR spectrum (Fig. 3.IIa) reveals the formation of three dimensional silicate network in the glass structure by peaks located at $447\ \text{cm}^{-1}$ and $1021\ \text{cm}^{-1}$ corresponding to the bending vibration modes and asymmetrical stretching vibration of Si - O and Si - O - Si bridges.

Phosphate groups (PO_4^{3-}) are identified by the presence of the peaks located at $569\ \text{cm}^{-1}$ and $606\ \text{cm}^{-1}$, which correspond to bending vibration of P - O - P bonds.

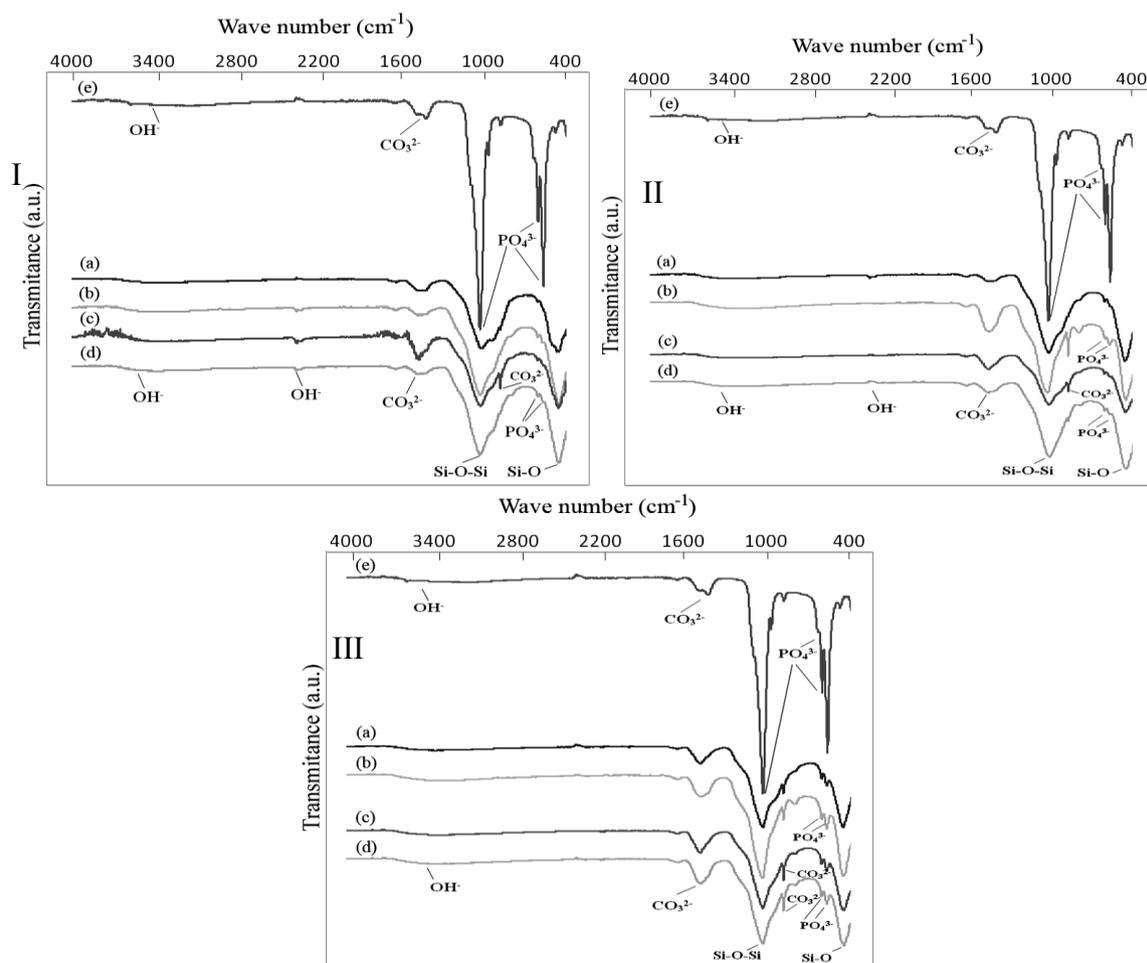


Fig. 3. FTIR spectra of sol-gel glasses S1(I), S2(II) and S3(III): a) unsoaked and after soaked in simulated body fluid for: b) 3 days, c) 7 days and 14 days, e) hydroxyapatite.

The hydration water existing in glass structure is emphasized by peaks located at 2365 cm^{-1} and 1636 cm^{-1} . More than that, the peaks posted at 1428 cm^{-1} and 877 cm^{-1} show the presence of carbonate groups (CO_3^{2-}) in the phosphocalcic glasses structure.

In the case of glass powders soaked for 3 days in simulated body fluid (Fig. 3.IIb) an increase of intensity for the peaks located at 569 cm^{-1} and 606 cm^{-1} characteristic of phosphate groups (PO_4^{3-}) typical for apatite structure has been observed.

By increasing of soaking time at 7 and 14 days (Fig 3.IIc and 3.IId), a diminish of the intensity in case of the PO_4^{3-} peaks can be seen, a phenomenon attributed to the decrease of apatite formation process on the surface S2 glasses.

The presence of silicate groups in glass structure after soaking of powders for 3 days in simulated body fluid is emphasized by the peaks located at 447 cm^{-1} and 1036 cm^{-1} specific to bending vibrational modes of Si-O and asymmetric stretching vibration of Si - O - Si bridges. Also, the peak located at 799 cm^{-1} corresponds to the flexural vibration of Si - O bond.

In case of the same sample formation of carbonate groups (CO_3^{2-}) are highlighted by peaks located at 1465 cm^{-1} and 877 cm^{-1} .

For samples soaked for 7 and 14 days in simulated body fluid, it can be noticed a decrease in the intensity of peaks for CO_3^{2-} groups. At the same time, band located at 3350 cm^{-1} , corresponding to hydroxyl groups (HO^-) and water molecules in the glass structure is assigned to peak located at 2365 cm^{-1} both being present in the structure of the apatite.

FTIR analysis, on glass composition S3, unsoaked in SBF solution (Fig. 3.IIIa) reveals a typical spectrum for this material. Thus, the peaks located at 447 cm^{-1} and 790 cm^{-1} correspond to the bending and flexural vibration modes of Si - O bonds. Moreover, presence of the silicate network in glass structure was confirmed by the peak located at 1025 cm^{-1} usually assigned to asymmetric stretching vibration of Si - O - Si bridges.

FTIR analysis reveals the presence of carbonate groups (CO_3^{2-}) through peaks found at 1469 cm^{-1} and 875 cm^{-1} . The presence of crystalline water in the the structure of glass is emphasized by the peaks at 1640 cm^{-1} and 2365 cm^{-1} .

Phosphate groups (PO_4^{3-}) are highlighted by peaks at 565 cm^{-1} and 603 cm^{-1} typical bending vibration of P - O - P bonds.

In the case of glass S3, peaks intensity of carbonate groups increases with soaking time from 3 and 14 days, as

it can be seen from Fig. 3.III.b, 3.III.c and 3.III.d. The same phenomenon is can be specified in the case of phosphate groups, intensity peaks being located at 447 cm^{-1} and 603 cm^{-1} , grow with increasing of soaked time.

Hydroxyl groups (HO^-) commonly found in glass and apatite structure are highlighted by broad band located at 3350 cm^{-1} .

Silica network found in glass structure has been revealed for all samples soaked in SBF solution by the peaks located at 447 cm^{-1} , 790 cm^{-1} , 1025 cm^{-1} and 1032 cm^{-1} corresponding to bending and flexural vibration modes of Si-O bonds and asymmetric stretching vibration of Si - O - Si bridges, as can be seen from Fig. 3.III.b, 3.III.c and 3.III.d.

4. Conclusions

In this paper bioactivity of glass powders from SiO_2 - CaO - P_2O_5 ternary system, synthesized by sol-gel technique was successfully tested.

The bioactivity of the glass powder has been determined by in vitro study, through soaking the samples in simulated body fluid at pH = 7.25 for 3, 7 and 14 days at 37°C . Structural changes on the glass surface has been demonstrated by XRD and FTIR analysis.

WD-XRF analysis shows that all glasses were synthesized with satisfactory results by the comparison with theoretical composition. Also, the yield of the sol-gel glasses synthesis was between 91.7-94.6%, higher than those in the literature.

XRD analysis in the case of samples unsoaked in simulated body fluid highlighted characteristic diffractograms typical for amorphous material. As a result of soaking in SBF solution, apatite growths on glass surface. This compounds based on calcium and phosphorus was identified after three days. The rate of apatite formation increases with the duration of soaking from 7 to 14 days. This phenomenon is revealed by increasing of intensity of apatite peaks.

Calcium carbonate has been found at the surface of all tested sol-gel glass. The proportion of CaCO_3 decrease with soaking time of glass powders in SBF solution.

The compositional changes occurred on glasses surface were analysed by FTIR analysis. After soaking in SBF solution, the most significant changes observed on the sol-gel glass powders surface has been revealed by increasing of intensity in case of the peaks associated with PO_4^{3-} groups found in the range of at 565 cm^{-1} and 606 cm^{-1} . Apatite growth on the glass surface has been confirmed by the presence of carbonate (CO_3^{2-}) and hydroxyl (HO^-) groups.

S1 sample shows two forms of calcium carbonate, even before soaking in SBF due to large amounts of calcium oxide present in glass composition and the process of carbonation occurred during thermal stabilization of glass into the air.

The lowest bioactivity was identified in S3 sample. This phenomenon is due to the reduced content of calcium, by comparison with the S1 and S2 compositions.

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