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Sol-gel bioactive glass-ceramics Part I: Calcium Phosphate Silicate/Wollastonite glass-ceramics

Research Article

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Abstract: In this work we present experimental results about synthesis, structure evolution and *in vitro* bioactivity of new calcium phosphate silicate/wollastonite (CPS/W) glass-ceramics. The samples obtained were synthesized via polystep sol-gel process with different Ca/P+Si molar ratio (R). The structure of the materials obtained was studied by XRD, FTIR spectroscopy and SEM. XRD showed the presence of $Ca_{15}(PO_4)_2(SiO_4)_6$, β-$CaSiO_3$ and α-$CaSiO_3$ for the sample with R=1.89 after thermal treatment at 1200°C/2h. The XRD results are in good agreement with FTIR analysis. SEM denotes that apatite formation can be observed after soaking in simulated body fluid (SBF).

Keywords: *Sol-gel • Glass-ceramics • In vitro bioactivity*

1. Introduction

Hydroxyapatite (HA) closely resembles the mineralized phase of bone and tooth. Biological apatites differ chemically from stoichiometric HA in that they contain a number of additional trace elements substituted into the HA lattice. Some of the major substituents are CO_3^{2-} [1], CO_3^{2-} and Mg^{2+} [2], F^- [3], Ce^{3+} [4] and Fe^{2+} [5].

It is known that silicon has an important role in the bone calcification process [6,7]. However, by the term silicon substituted hydroxyapatite (SiHA) it is meant that silicon is substituted into the apatite crystal structure end and not simply added [8].

Several methods have been described in literature for the synthesis of SiHA structures.

Some authors [9-11] have prepared SiHA using TEOS (tetraethoxysilane) as a silicon source *via* sol-gel method. The materials obtained include other crystalline phases, such as α-$Ca_3(PO_4)_2$ (α-tricalcium phosphate, TCP) and CaO besides the HA phase. This kind of silicon precursor can lead to SiHA with different physicaland chemical properties [11].

By solid state reaction Arcos *et al*. [12] has obtained SiHA sample. $Ca_2P_2O_7$, $CaCO_3$ and SiO_2 treated at 1100°C/72 h can lead to the formation of TCP and/or $Ca_5(PO_4)_2SiO_4$ (silicocarnotite). Barba *et al*. [13] observed that the synthesized SiHA ceramics contain silicocarnotite as the main phase with $Ca_7(PO_4)_2(SiO_4)_2$ (calcium silicate phosphate) and $CaSiO_3$ (wollastonite). Other authors [14-16] investigated the phase formation and evolution in Si-TCP/HA (silicon-stabilized tricalcium phosphate/hydroxyapatite). They concluded that the loss of all OH from HA due to SiO_4 substitution results in silicocarnotite, a compound with a different crystal structure than that of HA. This observation was in good agreement with [17]. Silicon substitution in crystal structures of calcium phosphate ceramics such as HA and TCP bioceramics has also been discussed in [18].

Controlled crystallization route is the most common method used to prepare SiHA from silicon acetate, calcium salt or $Ca(OH)_2$ with H_3PO_4. The amount of silicon incorporated has an important influence on its thermal stability and phase composition [2,19-24]

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Magnetron co-sputtering method is used in [25,26] to prepare of SiHA materials with 0.8, 2.2 and 4.9 wt.% silicon content. The *in vitro* cellular response indicated an increase in the growth of human osteoblast (HOB) cell on the synthesized coatings, along with formation of extracellular matrix.

Many authors have extensively studied the possibility of preparation of HA structures in the presence of other phases. Obtained bioactive glass-ceramics are known to have good mechanical properties, such as high strength and fracture toughness and excellent biocompatibility.

In 1982, Kokubo *et al*. [27] developed apatite/β-wollastonite (A/W) glass-ceramic in MgO-CaO-SiO_2 glassy matrix. This bioactive glass-ceramic material has superior mechanical strength comparable to human cortical bone [28]. Calver *et al*. [29] observed that increasing of fluorine content in A/W glass also appears to promote the crystallization of apatite phase. On the other hand, Juhasz *et al*. [30] observed that apatite/wollastonite/polyethylene composite (AWPEX) with 50 vol% PE is the most promising for use as an implant material. Some authors observed that α-$CaSiO_3$ (wollastonite) and β-$CaSiO_3$ (pseudowollastonite) are bioactive materials which can induce HA formation on their surface after immersion in SBF [31-34].

In our previous work we have synthesized with the help of sol-gel technology some bioactive ceramics, containing HA and different other phases such as: mullite [3,35,36], anorthite-gehlenite [37]; HA and crystalline phases from the systems ZnO-SiO_2, ZnO-Al_2O_3-SiO_2, ZnO-CaO-2SiO_2 [38]; HA and crystalline phases from the MgO-SiO_2 and MgO-Al_2O_3-SiO_2 systems [39]. We have also shown that bioactive hybrid materials were synthesized in SiO_2-P_2O_5-TiO_2-CaO-PVA system. When Ca/P+Si was 1.96 two calcium phosphate silicate phases can be observed after thermal treatment at 1200°C/2 h [40].

The aims of this study were to obtain a ceramic material in the system CaO-SiO_2-P_2O_5 with higher silica content and to investigate its bioactivity in 1.5 SBF.

2. Experimental Procedures

The materials obtained have been synthesized by polystep sol-gel method. The first step was to prepare SiO_2 sol from tetraethoxysilane (TEOS). TEOS was stirred under the mixed solvent of C_2H_5OH and H_2O with a very small amount of HCl as catalyst in the volume ratio TEOS: C_2H_5OH: H_2O: HCl = 1:1:1:0.01. After recognizing transparent solution of above mixture in approximately 1 h the mixture of calcium and phosphate sources was added under intensive stirring. The calcium phosphate (CP) solution was prepared by mixing $Ca(OH)_2$ and H_3PO_4 at pH = 10 - 11. CP solution was added to SiO_2 sol under stirring for 20 h. The sol obtained was gelated at 120°C/12 h and thermal treated at different temperatures (1100°C, 1200°C) for 2 h.

Chemical compositions of the prepared materials are given in Table 1.

Table 1. Chemical compositions of the materials obtained

Samples	Composition of synthesized samples, wt%			Ca/P+Si, molar ratio (R)
	CaO	P_2O_5	SiO_2	
CPS-1	58.12	29.42	12.45	1.67
CPS-2	62.60	10.56	26.83	1.89

Bioactivity of the materials obtained was evaluated by examining the apatite formation on their surfaces in 1.5 SBF [41]. 1.5 SBF solution was prepared from reagents as follows: NaCl = 11.9925 g, $NaHCO_3$ = 0.5295 g, KCl = 0.3360 g, $K_2HPO_4 \cdot 3H_2O$ = 0.3420 g, $MgCl_2 \cdot 6H_2O$ = 0.4575 g, $CaCl_2 \cdot 2H_2O$ = 0.5520 g, Na_2SO_4 = 0.1065 g, and buffered at pH 7.4 at 36.5°C with tris (hydrohymethyl) aminomethane $(CH_2OH)_3CNH_2$ = 9.0075 g and 1M HCl in distilled water. Prepared and thermal treated samples were pressed at 50 MPa with PVA to disc (12 × 2 mm) specimens and immersed in 1.5 SBF at human body temperature (36.6°C) in polyethylene bottles in static conditions for different periods of time (one and tree days).

The structural evolution and phase formation of the hybrid materials obtained were studied using XRD (Bruker D8 Advance) with CuKα radiation, FTIR (MATSON 800 FTIR) and SEM (Philips-515).

3. Results and Discussion

As can be seen XRD patterns (Fig. 1) of the two synthesized samples (CPS-1 and CPS-2) are quite different due to their different R values.

In CPS-1 with R=1.67 (Fig. 1a), XRD shows the presence of pure $Ca_5(PO_4)_2SiO_4$ (PDF 40-0393). Its bioactive future has been established by [20]. In CPS-1 sample has not been observed the secondary phases of TCP and CaO. These phases have been detected in the sample, prepared with 3.75 wt% Si [9]. XRD analysis was in good agreement with [20]. In the CPS-2 sample, thermal treated at 1100°C/2 h with R = 1.89 (Fig. 1b), XRD showed the presence of wollastonite (PDF 84-0655) and $Ca_{15}(PO_4)_2(SiO_4)_6$ (calcium phosphate silicate) (PDF 50-0905). When the same sample was

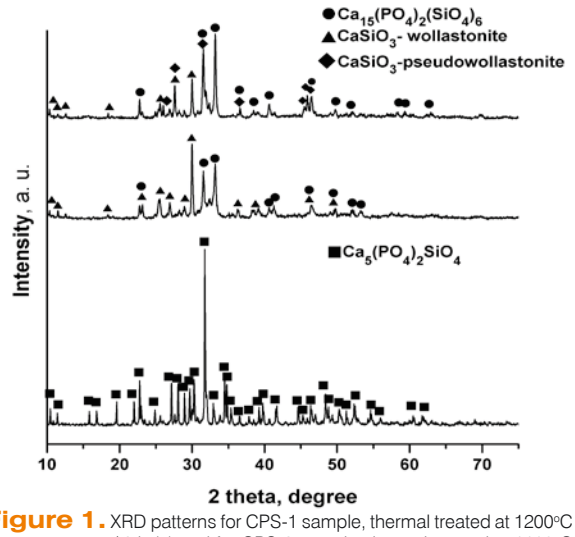

Figure 1. XRD patterns for CPS-1 sample, thermal treated at 1200°C / 2 h (a) and for CPS-2 sample, thermal treated at 1100°C / 2 h (b) and 1200°C / 2 h (c)

thermal treated at 1200°C/2 h (Fig. 1c), XRD proved the presence of $Ca_{15}(PO_4)_2(SiO_4)_6$, pseudowollastonite (PDF 74-0874) and wollastonite. Our XRD data for the synthesized $Ca_{15}(PO_4)_2(SiO_4)_6$ is in very good agreement with Mumme *et al*. [42]. It is possible that CaO and P_2O_5 might move to SiO_2 to form a Ca-Si-P-O glassy phase [43]. For HA/W = 25/75 wt% sample, after annealing at 1350°C/2 h, Ruy *et al*. [44] observed the presence of $Ca_{12}P_2Si_6O_{31}$ phase. Barba *et al*. established the presence of $Ca_7P_2SiO_{16}$ in calcium phosphate ceramics after thermal treatment at 1150°C/2 h.

FTIR spectroscopy was used to study the materials obtained after heat treatment state and to quantify the effect of silicon substitution.

FTIR spectra of thermal treated CPS-1 and CPS-2 samples are given in Fig. 2

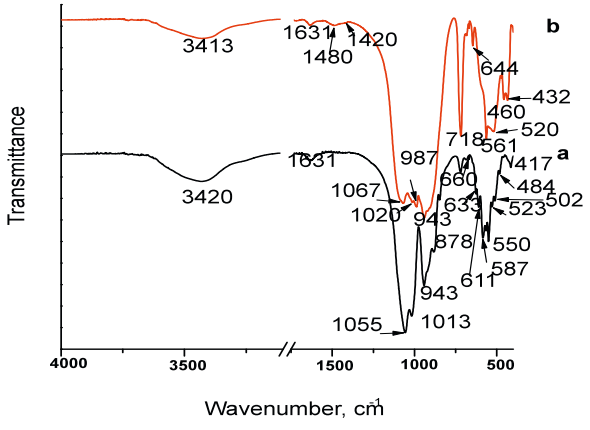

Figure 2. FTIR spectra of CPS-1 (a) and CPS-2 (b) samples, heat treated at 1200°C / 2 h

As can be seen, the obtained FTIR spectra are very complicated. From literature data, the intense bands at 568, 600, 960, 1043 and 1008 cm^{-1} correspond to ν_4, ν_1 and ν_3 P-O stretching vibration modes [23,45]. The FTIR spectra of thermal treated CPS-1 and CPS-2 samples had a characteristic ν_3 PO_4^{3-} and ν_1 PO_4^{3-} bands, identified by the three peaks at 1013, 1055 and 484 cm^{-1} (for CPS-1) and 1020, 1067 and 987 cm^{-1} (for CPS-2) sample [45]. On the other hand the absorption bands at 1013 (1055) cm^{-1} and 1020 (1067) cm^{-1} can be assigned to the vibration of the Si-O-Si bond [46,47]. The ν_4 PO_4^{3-} was identified by some peaks, centered at 523, 550, 587, 611 and 660 cm^{-1} (for CPS-1) and by 520, 561, 644 cm^{-1} (for CPS-2) [24,45]. In CPS-2 sample the presence of one peak can be observed at 460 cm^{-1}, which could be ascribed to ν_2 PO_4^{3-} [45]. For CPS-1 sample the absorption peaks centered at 502, 878 and 943 cm^{-1} were detected. For CPS-2 only one peak, centered at 943 cm^{-1} was observed. These peaks can be assigned to the presence of SiO_4^{4-} in the obtained samples [21,24]. We also see that in CPS-1 sample, silicon content leads to decrease in the intensity of the band at 633 cm^{-1} that correspond to the OH^-. This observation is consistent with the silicon substitution mechanism proposed as $SiO_4^{4-} \rightarrow PO_4^{3-}$, leading to loss of some OH^- groups so as to maintain the charge balance [23], *i.e.* the obtained CPS-1 sample may be partially dehydroxylated. In CPS-2 spectrum (Fig. 2b) the absorption band at 630 cm^{-1} was absent. In CPS-2 sample the peaks at 432, 561 and 718 cm^{-1} could be ascribed to the presence of wollastonite and pseudowollastonite [48-50]. As can be seen, the OH stretch at 3420 and 3413 cm^{-1} for the two samples dramatically decreases with the addition of silicon. A very surprising finding in the CPS-2 sample is the presence of slight CO_3^{2-} band, which is observed at 1420 and 1480 cm^{-1}. CO_3^{2-} presence in the samples is due to absorbance of CO_2 [19,23,51] from the air even after thermal treatment at 1200°C/2 h, this indicates that the CPS-2 sample must be kept out of atmosphere in a desiccator.

Fig. 3 shows the FTIR spectra of the apatite formed on CPS-2 sample after 1 and 3 days soaking in 1.5 SBF.

FTIR spectra depicts that the increase the intensity of CO_3^{2-} (~1420 cm^{-1} and ~1480 cm^{-1}) and PO_4^{3-} (~560 cm^{-1}) are associated with apatite formation on CPS-2 sample after only 1 day immersion in 1.5 SBF [30,52-54].

Fig. 4 illustrates the SEM micrographs of CPS-2 sample surfaces before and after 1 and 3 days of soaking in 1.5 SBF.

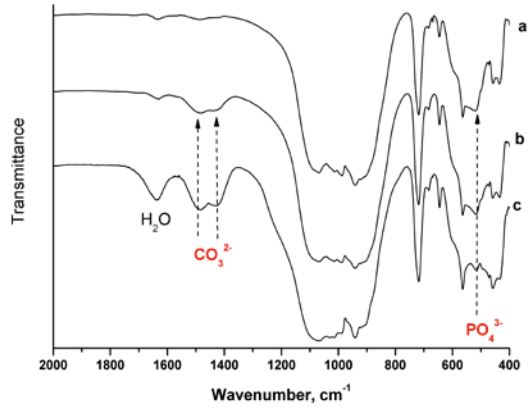

Figure 3. FTIR spectra obtained for CPS-2 before (a) and after 1 day (b) and 3 days (c) soaking in 1.5 SBF

SEM images show that the surface after 1 day immersion in 1.5 SBF of static *in vitro* test (Fig. 4b), was entirely covered with precipitate of apatite phase. On the other hand, "flower-like" irregular assemblies onto CPS-2 surface can be observed. The average granularity of these apatite "flower-like" assemblies is about 11 μm.

After soaking for 3 days, the apatite crystals covered the entire surface. Isolated aggregates of particles can also be observed on their surfaces.

4. Conclusions

A new calcium phosphate silicate/wollastonite bioactive glass-ceramics has been synthesized *via* polystep sol-gel process. The calcium phosphate solution was added to the prehydrolysed TEOS. The synthesized samples were prepared at 1.67 and 1.89 Ca/P+Si molar ratio (R). After thermal treatment of the sample with R = 1.67 at 1200°C/2 h, XRD showed the presence of only one crystalline phase - $Ca_5(PO_4)_2SiO_4$. For the sample with R = 1.89 thermal treated at 1100°C/2 h, XRD showed the presence of α-$CaSiO_3$ and $Ca_{15}(PO_4)_2(SiO_4)_6$. When the same sample was treated at 1200°C/2 h, XRD proved the presence of $Ca_{15}(PO_4)_2(SiO_4)_6$, β-$CaSiO_3$ and α-$CaSiO_3$. FTIR study indicates the conformation of the obtained XRD data. *In vitro* evaluation of bioactivity was carried out in static conditions in 1.5 SBF. FTIR spectra show that the increase the intensity of CO_3^{2-} and PO_4^{3-} are associated with apatite formation on sample with R = 1.89. SEM images demonstrate that the apatite phase covered the entire surface after 1 and 3 days immersion in 1.5 SBF.

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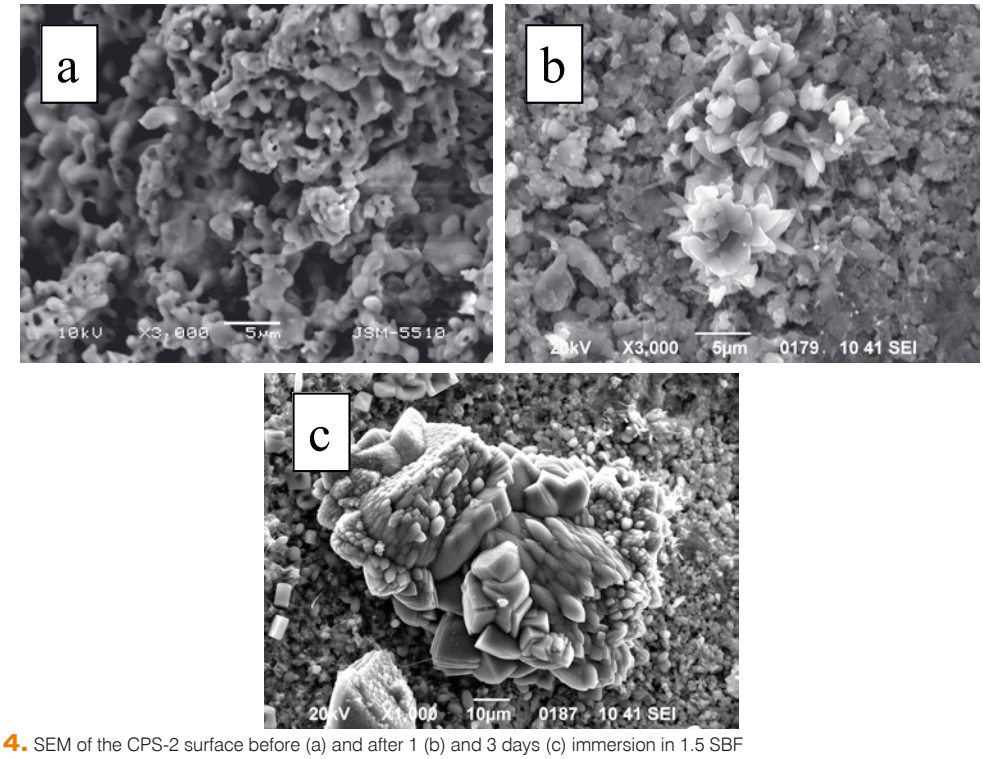

Figure 4. SEM of the CPS-2 surface before (a) and after 1 (b) and 3 days (c) immersion in 1.5 SBF

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