

Silicon Substitution in Biphasic Calcium Phosphate Bioceramics: Preparation, Characterization and Dissolution Properties

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Abstract— Biphasic Calcium Phosphate bioceramics unsubstituted (BCP) and silicon substituted (Si-BCP) are prepared by solid-solid reaction. The prepared powders were characterized by Fourier Transform Infrared spectroscopy (FTIR) and X-ray Diffraction (XRD). The dissolution of the ceramics was carried out in a buffer solution (pH = 4.8). The results of FTIR and the structural refinement show the formation of Hydroxyapatite and Tricalcium phosphate mixtures and an incorporation of the silicon ion in the hydroxyapatite phase. The substitution of PO_4^{3-} by SiO_4^{4-} groups causes a reduction of the hydroxyl groups and increase the lattice distortion indice ($D_{\text{ind}} = 6.995$) compared to the unsubstituted hydroxyapatite value ($D_{\text{ind}} = 4.782$) and the theoretical value ($D_{\text{ind}} = 3.079$). This structural change increases the dissolution of BCP which enhances the biological activity of these bioceramics.

Index Terms— Bioceramics, hydroxyapatite, tricalcium phosphate, silicon, dissolution.

1 INTRODUCTION

APATITES based on calcium phosphates, are among the materials that have taken place in the research domain because of their important biological role. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: HAP, molar ratio Ca/P = 1,667) has some advantages as a biomaterial due to its structure similar to the mineral part of bone and human tissues, compared to other ceramics, such as bioglass and A-W glass [1],[2]. For this reason it is used in many medical and dental applications [3]. However, pure HAP is not resorbable in the body and may cause critical problems in orthopedic and dental clinics [4]. The resorbability of HAP can be improved by the combination of HAP with tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$: β -TCP, molar ratio Ca/P = 1.50) which has a high dissolution rate. This biphasic mixture HAP / TCP ($1,52 < \text{Ca/P} < 1,667$) are particularly suitable materials for synthetic bone substitute applications [5]. Furthermore, hydroxyapatite may be also doped with ions to improve their resorbability. Indeed, the structure of the Hydroxyapatite may be substituted with more ions such as strontium, magnesium, silicon... [6],[7],[8].

Silicon has been identified as an important element in the bone by Carlisle [9],[10]. The inclusion of silicates in the

apatite structure causes an acceleration of the dissolution and stimulates the action of osteoblasts and therefore plays a role in the calcification process [11],[12]. It has been reported that in vitro Si enhances and stimulates osteoblast-like cell activity [13] and in vivo induces a higher dissolution rate [14]. Moreover, several studies suggest better biological activity of Si-substituted calcium phosphates with respect to unsubstituted calcium phosphates [15],[16],[17].

Various methods of synthesis of hydroxyapatite doped with Si have been proposed as the sol-gel method, hydrothermal synthesis [18], the aqueous method [19],[20] and solid-state reaction [21]. Wet precipitation and hydrothermal preparation became more popular methods, but conventional precipitation has a poorer ability to control the Ca/P ratio. The introduction of silicates in calcium-hydroxyapatite is possible by solid-solid reaction generally yield stoichiometric and well crystallized products. However, the solid-solid reaction requires high temperatures between 1100°C and 1400°C with repeated calcinations cycles.

In this work, we prepared unsubstituted biphasic bioceramics (BCP) and silicon substituted biphasic bioceramics (Si-BCP) by a solid-solid reaction with single step at 900°C for 3 hours. We studied the incorporation effect of silicon on the structure of hydroxyapatite and on the solubility of biphasic bioceramics.

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2 MATERIALS AND METHODS

2.1 powders preparation

The preparation of Biphasic Calcium Phosphate bioceramics was performed from calcium carbonate (CaCO_3), tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) and silica (SiO_2). The powders were weighed and then mixed with molar ratio Ca/P (BCP) and Ca/P+Si (Si-BCP) constant and equal to 1.623. In order to have a homogeneous mixture, the initial powders were ground in ethanol for several hours. For each product the calcinations were carried out at 900 °C for 3 hours. The heating rate is selected from 5 °C / min to ensure even heating of the furnace.

2.2 Characterization of powders

The identification of different crystal phases were determined by X-ray diffraction (Siemens Diffractometer D5000) and Fourier Transform Infrared spectroscopy (KBr pellet method, Bio-Rad Win-IR Pro).

Structural characterization for the prepared samples was carried out with FullProf 2011 program. Calculating the distortion of the PO_4 tetrahedrons can provide an estimation of the structure distortion. The tetrahedral distortion index was obtained from the calculated data using the relation:

$$D_{ind} = \frac{\sum_{i=1}^6 (\text{OPO}_i - \text{OPO}_m)^2}{6} \quad (1)$$

Where OPO_i denotes the six angles between P and the four O atoms of the phosphate tetrahedron and OPO_m is the average angle (around 109.17°).

2.3 Dissolution tests

The dissolution tests were carried out under acidic medium (similar to the process of acidification of the extracellular environment of osteoclasts) at pH close to 4.8 ± 0.2 involved by the in vivo degradation of the phosphocalcic implants [22]. The calcined powder was manually ground, and the particles less than 125 μm were separated by sieving. 200 mg of each sample was individually soaked in 100 ml of buffer solution of acetic acid-sodium acetate ($\text{pH} = 4.8 \pm 0.2$) at constant temperature of $37.0 \pm 0.1^\circ\text{C}$ for fixed periods of time. The solution was kept under mechanical agitation and at sufficient speed to keep all the grains in suspension. At the end of each period, the liquid phase was separated and analyzed.

The ion concentrations of Ca^{2+} , PO_4^{3-} and SiO_4^{4-} were determined by atomic emission spectrophotometer, argon plasma and inductive coupling (ICPAES) (ThermoJarrel Ash. Atom Scan 16)

3. RESULTS AND DISCUSSION

3.1. Powder characterization

The XRD patterns recorded for the samples BCP and Si-BCP treated at 900°C/3hours are shown in Fig. 1. The result indicates: i) the samples are composed of the crystallized HAP and β -TCP phases and the phases α -TCP and SiO_2 are absent. This result indicates that the reaction between β -TCP, CaCO_3 and SiO_2 is total. It's due to the ethanol milling step included in the method of preparing. Indeed, and In agreement with the literature the absence of α -TCP indicates a relatively low silicon substitution in the TCP phase. ii) Unsubstituted powder from BCP presents an amount of β -TCP less than that Si-BCP contains. In agreement with the literature, the amount of β -TCP depends on the silicon substitution; the amount of β -TCP increases with the presence of silicon [23].

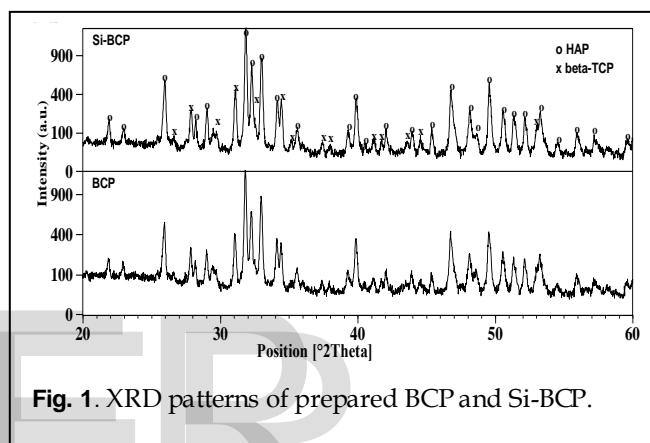


Fig. 1. XRD patterns of prepared BCP and Si-BCP.

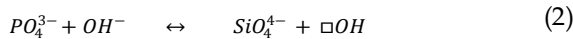
Fig. 2 shows the infrared spectra of the samples BCP and Si-BCP. The bands at 3574 cm^{-1} and 633 cm^{-1} corresponds to hydroxyl group stretching and vibrational modes, respectively. The intense bands at 962 cm^{-1} corresponds to P-O stretching vibration modes, while the doublet at 603-569 cm^{-1} corresponds to bending O-P-O mode. In addition, the broad band at 3468 cm^{-1} was attributed to the moisture in the samples.

The same four fundamental vibration modes are found in the SiO_4^{4-} group, with frequencies rather near to those of the PO_4^{3-} vibrations, so it is quite difficult to discriminate between them [26]. In addition, in the silicon containing samples, particularly for 10% SiO_2 , a weak absorption peak is observed at about 800 cm^{-1} , which could be assigned to a Si-O-Si vibration [24]. In our case, we have a very low content of Silicon that explains the absence of the band of SiO_4 groups.

The significant effect of the silicon addition was the decrease in the hydroxyl stretching bands at 3571 cm^{-1} and 631 cm^{-1} and phosphate stretching bands at 965 cm^{-1} . This can be related to the substitution of PO_4^{3-} by SiO_4^{4-} tetrahedrons, within the hydroxyapatite structure.

The incorporation of silicon ion in the hydroxyapatite phase induces a reduction of the amount of hydroxyl groups

to compensate for the extra negative charge of the silicates group. The proposed mechanism to explain these structural changes is:



($\square OH$ indicates a vacancy in the hydroxyl site)

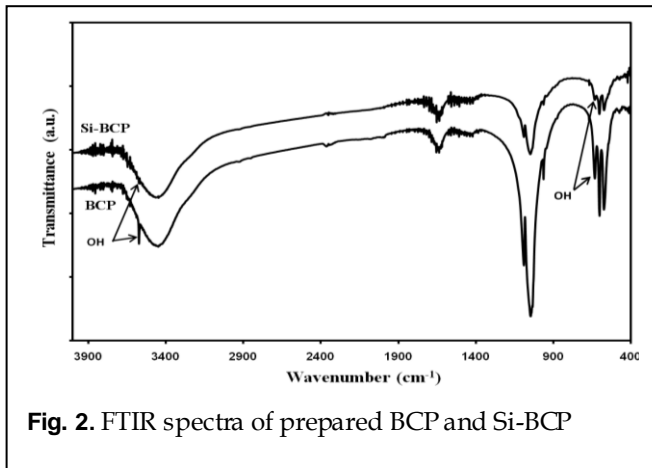


Fig. 2. FTIR spectra of prepared BCP and Si-BCP

3.2 Structural study results

The structural characterization of the BCP and Si-BCP was performed using the Fullprof program (2011). The lattice parameters and distortion of the hydroxyapatite phase are given in Table 1. The substitution of PO_4^{3-} by SiO_4^{4-} in the hydroxyapatite structure induces a decrease of the lattice parameter a-axis and the cell volume, and an increase of the following lattice parameter c-axis. Variations in the lattice parameters (a-c) and the cell volume from different previous studies are heterogeneous [28]. The results of this work are in accordance with the work of Gibson et al [13]. Substitution of the PO_4^{3-} by the SiO_4^{4-} group leads to a distortion in the network. The calculated index value ($D_{ind} = 6.995 \text{ \AA}$) is higher than the reference hydroxyapatite (BCP) distortion value ($D_{ind} = 4.782 \text{ \AA}$) and the theoretical value ($D_{ind} = 3,080 \text{ \AA}$) (Table 1).

Table 1: Structural refinement results: lattice parameters, unit cell volumes and tetrahedral distortion index (D_{ind}) of HAP.

Sample	a (Å)	b (Å)	c (Å)	V(Å ³)	D_{ind}
HAP(the)	9.4190	9.4190	6.8800	529.16	3.080
HAP (BCP)	9.4198	9.4198	6.8805	528.73	4.782
HAP(Si-BCP)	9.4170	9.4170	6.8820	528.56	6.995

3.3 Dissolution tests

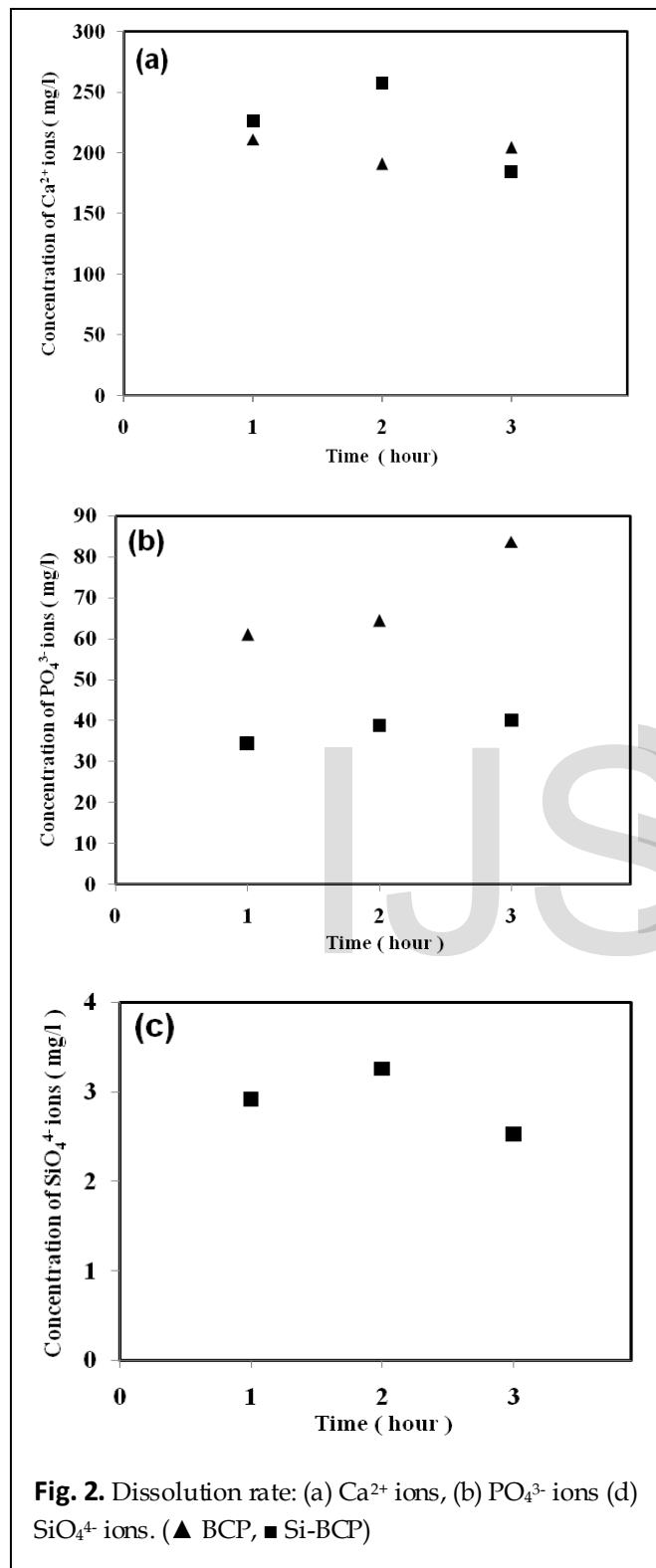
Fig. 3 show the results of ion concentrations of Ca^{2+} , PO_4^{3-} and SiO_4^{4-} with the immersion time of two samples Si-BCP and BCP. The ion concentrations of Ca^{2+} released by Si-BCP increase with the immersion time, and then decrease after 2 hours of immersion. However, the ions concentrations of Ca^{2+} released by BCP remain unchanged.

The ion concentrations of PO_4^{3-} released by BCP are higher than that released by Si-BCP, and has increased with time of immersion. However, the ion concentrations of PO_4^{3-} released by Si-BCP remain unchanged. The Si concentration released by Si-BCP increases until 2 hours then decreases.

This results show that dissolution of Si-BCP is higher compared to BCP without silicate, it's in agreement with previous studies. A.E. Porter and al observed that the dissolution of the substituted silicon ceramic increases with silicon increase. Dissolution was observed to follow the order 1.5wt% Si-HA > 0.8wt% Si-HA > pure HA, suggesting that silicate ions increase the solubility of HA [14]. Yu and al. found that the dissolution was observed to follow the order Si-HA1.6 > Si-HA0.8 > HA, suggesting that the silicate increased the solubility [29].

In this study, the results of Si-BCP dissolution show that the ion concentrations of Ca and Si released increase until 2 hours, then decrease. However, the concentrations of PO_4^{3-} released by Si-BCP remain unchanged. The changes of Ca^{2+} and SiO_4^{4-} concentration indicate that dissolution and precipitation of the samples occur simultaneously after immersion in buffer solution. We suggest that this decrease in concentrations of Ca^{2+} , and SiO_4^{4-} is the result of a phenomenon of precipitation of a complex to the surface of the grains. In agreement with Yu and al, the rapid decrease of Ca^{2+} and PO_4^{3-} concentrations is due to the new apatite layers formed on the surface of Si-HAP after a short time in SBF solution [29]. Porter proposed the dissolution-reprecipitation mechanism of apatite nucleation [30]. In this study the concentration of Ca decrease firstly as compared to PO_4^{3-} , it shows that there is an adsorption of Ca ions into the surface at first and then there is the adsorption of other ions after forming the complex. The limit of dissolution of the samples may be related to the formation of this complex at the surface of grains.

Some authors have described that the fast dissolution of Si-hydroxyapatite is due to the migration to the positioning of whether the grain boundary [27], and a smaller grain size with more triple-junctions per unit area, facilitating increased dissolution at the surface [14],[30]. The results of our work show that the substitution of PO_4^{3-} by SiO_4^{4-} groups leads to the formation of OH site vacancies and hydroxyapatite lattice distortion. This structural distortion could decrease the



stability of the hydroxyapatite structure and increase the solubility. The composition and the structure of the homogeneous biphasic mixtures (Si-BCP), prepared in this work by simple solid-solid reaction, appear very promising for biological applications.

4. CONCLUSION

Silicon substituted Si-BCP and BCP calcium phosphate bioceramics were prepared by simple solid-solid reaction at 900°C for 3 hours. The results show the formation of hydroxyapatite and tricalcium phosphate phases thus confirming the formation of homogeneous biphasic mixtures. The incorporation of Silicon ions in the hydroxyapatite lattice distorts its structure and promotes the dissolution. The silicon substituted BCP could be more bioactive material compared to the BCP.

REFERENCES

- [1] L.L. Hench, *J. Am. Ceram. Soc.* 74 (1991) 1487-1510.
- [2] S. H. Maxian, J. P. Zawadzsky and M. G. Dunn: *J. Biomed. Mater. RES.* 28 (1994) 1311.
- [3] E. L. Solla, J. P. Borrajo, P. Gonzalez, J. Serra, S. Chiussi, B. Leon and J. Garcia Lopez: *Appl. Surf. Sci.* 253 (2007) 8282.
- [4] M. Mastrogiacoma, A. Muraglia, V. Komlev, F. Peryin, F. Rustichelli, A. Crovace, et al, *Orthod. Craniofacial. Res.* 8 (2005) 277-284.
- [5] Yamada S, Heymann D, Bouler J-M, Daculsi G. *Biomaterials*; 18 (1997) 1037-41.
- [6] Zhang W et al. *Acta Biomater.* 7 (2011)800-8
- [7] Laurencin D et al. *Biomaterials* 32 (2011)1826-37
- [8] Mickaël Palard, Eric Champion, Sylvie Foucaud. *Journal of Solid State Chemistry* 181 (2008) 1950- 1960
- [9] Carlisle, E. M. *Science* (1970), 167, 179.
- [10] Carlisle, E. M. *Calc. Tissue Int.* (1981), 33, 27.
- [11] A.E. Porter et al. *J. Biomed Mater Res* 69A (2004) : 670-679.
- [12] N. Patel et al. *J. of Material Science* 16 (2005) : 429-440.
- [13] Gibson I, Best S, Bonfield W. *J Biomed Mater Res* (1999); 44:422-8.
- [14] A.E Porter, N. Patel, J.N. Skepper, S.M. Best, W. Bonfield. *Biomaterials* 24 (2003) 4609-4620
- [15] Pietak AM, Reid JW, Stott MJ, Sayer M. *Biomaterials* 28 (2007) 4023-4032
- [16] Patel N, Best S, Bonfield W, Gibson I, Hing K, Damien E, et al. *J Mater Sci Mater Med* (2002);13:1199-206.
- [17] Botelho C, Brooks R, Spence G, McFarlane I, LopesM, Best S, et al. *J Biomed Mater Res A* (2006);78:709-20.
- [18] X.L. Tang, X.F. Xiao, R.F. Liu, *Mater. Lett.* 59 (2005) 3841-3846.
- [19] A. Ruys, *J. Aust. Ceram. Soc.* 29 (1993) 71-80.
- [20] D. Arcos, J. Rodriguez Carvajal, M. Vallet-Regi, *Chem.Mater.* 16 (2004) 2300-2308.
- [21] L. Boyer, J. Carpena, J. Lacout, *Sol. State Ionics* 95 (1997) 121-129.
- [22] Frayssinet P, Rouquet N, Tourenne T, Fages J, Hardy D, Bonel G. *Cells and Materials*; 3(4):383-94 (1993).
- [23] S. Gomes, G. Renaudin, A. Mesbah, E. Jallot, C. Bonhomme, F. Babonneau, J.-M. Nedelec. *Acta Biomaterialia* 6 (2010) 3264-3274

- [24] Gheorghe Tomoaia, Aurora Mocanu, Ioan Vida-Simiti, Nicolae Jumate, Liviu-Dorel Bobos, Olga Soritau, Maria Tomoaia-Cotisel. *Materials Science and Engineering C* 37 (2014) 37-47.
- [25] Reid JW, Pietak A, Sayer M, Dunfield D, Smith TJN. *Biomaterials* (2005); 26:2887.
- [26] Gheorghe Tomoaia, Aurora Mocanu, Ioan Vida-Simiti, Nicolae Jumate, Liviu-Dorel Bobos, Olga Soritau, Maria Tomoaia-Cotise. *Materials Science and Engineering C* 37 (2014) 37-47.
- [27] Alexandra E. Porter, Claudia M. Botelho, Maria A. Lopes, Jose ´ D. Santos, Serena M. Best, William Bonfield. *J Biomed Mater Res* (2004) 69A: 670-679.
- [28] S. Gomes, G. Renaudin, A. Mesbah, E. Jallot, C. Bonhomme, F. Babonneau, J.-M. Nedelec. *Acta Biomaterialia* 6 (2010) 3264-3274
- [29] Huaguang Yu · Kejun Liu · Fengmin Zhang · Wenxian Wei · Chong Chen · Qingli Huang. *Silicon*, (2015) 1-11.
- [30] AE. Porter. *Micron* 37 (2006) 681-688.

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