

Synthesis and characterization of apatite silicated powders with wet precipitation method

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Abstract. The synthesis of apatite silicated $\text{Ca}_{10}(\text{PO}_4)_6-x(\text{SiO}_4)_x(\text{OH})_{2-x}$ (SiHA) with $0 \leq x \leq 2$ was investigated using a wet precipitation method followed by heat treatment using calcium carbonate CaCO_3 and phosphoric acid H_3PO_4 and silicon tetraacetate $\text{SiC}_8\text{H}_{20}\text{O}_4$ (TEOS) in medium of water ethanol, with three different silicate concentrations. After drying, the samples are ground and then characterized by different analytical techniques like X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning electron Microscopy (SEM) and chemical analysis

1 Introduction

The Synthetic apatite (HA) is one of the most important bioceramics used in orthopedic and dental surgery. Its composition, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is very similar to biological apatite that forms the mineral fractions of bone tissue [1]. The apatite is commonly used as a bioceramic due to its biological properties of biocompatibility and bioactivity [2]. The latter can be improved and one way to increase them, would be to use the ability of the apatite to accept a multi- ion of substituting. The calcium phosphate apatites are a family of ionic compounds described by the chemical formula $\text{Me}_x(\text{XO}_4)_y(\text{Y})_z$ wherein Me is a bivalent metal (Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} ...), XO_4 is a trivalent anion (PO_4^{3-} , AsO_4^{3-} , SiO_4^{4-} ...) and Y is a monovalent anion (F^- , Cl^- , Br^- , I^- , OH^- ...) [3].

The bioactive behavior of the apatite may be improved by approximating the general formula of the bone that is: $1.7 \text{Ca}_{8.3}(\text{PO}_4)_{4.3}(\text{CO}_3)_{1.0}(\text{HPO}_4)_{0.7}(\text{CO}_3, \text{OH})_{0.3}$. This approach can be achieved by incorporating as component (Si, Mg, V, As ...). To this end, we are interested in the insertion of Silicate on phosphocalcic apatite. The model chosen for this substitution is according to the following theoretical formula [4]:

$$\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-x} \text{ with } 0 \leq x \leq 2 \quad (1)$$

The man has always sought to improve their quality of life with more comfort, our bone system remain an effective way to keep man healthy, since it ensures many functions like support, movement, protection, minerals storage and formation of red blood cells. For all these reasons the science of biomaterials remains the first solution for saving lives and this justifies the development of synthetic bone substitutes [5]. According to the physicochemical properties of these synthetic

biomaterials, we choose those used for filling bone defects [6]

The incorporation of silicium into the apatitic structure gives significant results on the mechanical properties, as well as the bioactive behavior. The Bioactivity promotes the reaction between the bone and the implant, leading to an excellent osteointegration and ensuring the success of the implant [6].

This increase in biological performance can be attributed to Si-induced changes in the material properties and also to the direct effects of Si on physiological processes of the bone and connective tissue systems, after our synthesis, we introduce our biomaterials in bone, for studying its effects in biological processes [6].

The silicium (Si) is one of the essential elements. Its importance on bone formation and calcification has been demonstrated through in vitro and in vivo studies [7]. The Si-HA structure corresponds to substitution of phosphate ions (PO_4^{3-}) by Silicate SiO_4^{4-} ion in the HA crystal structure. Different mechanisms for charge compensation have been suggested [8,9]. The most cited was proposed by Gibson et al. with the creation of anionic vacancies at OH^- sites [10]. This mechanism leads to Si-HA with the general formula $\text{Ca}_{10}(\text{PO}_4)_6-x(\text{SiO}_4)_x(\text{OH})_{2-x}(\text{VOH})_x$, where x is the molar number of silicate groups introduced into the apatitic structure ($0 \leq x \leq 2$) and VOH represents vacancies to maintain the charge balance [11]. Si-substituted HA (Si-HA) has been synthesized using different methods such as the sol-gel route [12], solid state reactions [13], hydrothermal techniques [14], microwave irradiation [15] and precipitation from aqueous solutions [4,10]. Two reagents are primarily encountered in the literature for the preparation of a silicated apatite: silicon tetraacetate ($\text{Si}(\text{CH}_3\text{COOH})_4$) [4,10], and

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tetraethylorthosilicate called "TEOS" ($\text{Si}(\text{CH}_3\text{OCH}_2)_4$) [16,17]

The advantages and the disadvantages of aqueous precipitation methods are already described in the literature; it is the most talented route owing to its ease in experiment operations, low working temperature, high percentages of pure products and inexpensive equipment requirement [18]. The objective of this work is to synthesize the pure apatite silicated with controlled silicate portions by aqueous precipitation method.

2 Material and Methods

2.1 Materials /numbering

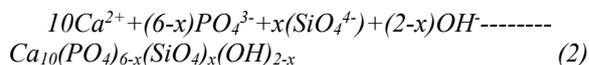
The objective of this work is to synthesize the pure apatite silicated with controlled silicate portions by aqueous precipitation method. The principle of synthesis by this method is to add an anionic solution (phosphate and silicate) to another ionic solution initially present in the reactor such as calcium solution. The reaction is maintained in aqueous ethanol medium.

We have to respect the experimental conditions such as temperature, the pH of reaction and the time of maturation. For all these reasons the precipitation reactions were carried at 80°C and the pH was maintained at 10 by the addition of ammonia solution. After a complete mixing of the reactants, the suspensions were shaken for 4 h. The resulting precipitates were filtered, washed and dried at 900°C for 4 h. After drying, the samples were ground and then characterized by different analytical techniques like X-ray Diffraction (XRD), Fourier Transform IR Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Chemical analysis.

In the first time, a pure HA $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ was prepared to be used as a reference material for further SiHA syntheses and analyses. The powders were prepared by aqueous precipitation method using calcium

carbonate CaCO_3 , phosphoric acid H_3PO_4 and $\text{Si}(\text{CH}_3\text{CH}_2\text{O})_4$ TEOS as reagents, and solvents.

The quantities of reagents were calculated assuming that one mole of phosphate was substituted by one mole of silicate (table1), while maintaining our stoichiometric apatite, reagent molar ratio of 10/6 was used $\text{Ca/P+Si}=1.67$, and the substitution mechanism (equation1) proposed for this synthesis depends on this equation:



The ratio Ca/P is determined in the first time by the dosage of calcium, the latter is carried out by complexometry with Ethylene Diamine Tetraacetic Acid (EDTA) in the presence of ammonia [19]. The excess EDTA is then dosed with a standard solution of zinc chloride. The turn/hue indicator is Eriochrome black. The error margin on the calcium content is of the order of 0.5%.

In the second time the dosage of the phosphore, in the solids studied, the phosphorus may be present in the form of orthophosphoric groups PO_4^{3-} or hydrogenphosphoric groups HPO_4^{2-} . The ions (PO_4^{3-}) are usually measured by color colorimetry [20, 21]. The principle of this method consists in measuring, in an acid medium, the optical density (absorbance) of the yellowish coloration of the phosphovanadomolybdic complex ($\text{VO}_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$) at $\lambda = 460 \text{ nm}$. (Table1).

The principle of synthesis by precipitation in aqueous solution of calcium phosphates apatite is to add an ionic solution like phosphate and silicate solution to another ionic solution initially present in the reactor like calcium solution. The choice of reagents is important in order to ensure a good homogeneity of the reaction. All the solutions must be mixed together.

However, the dissolution of a silicate precursor is complicated, for this reason we chose work in an aqueous ethanol medium.

Table 1. The quantities of reagents

Sample	X	CaCO_3 (mol)	H_3PO_4 (mol)	TEOS (mol)	pH	Ca/P	Ca/ P+Si	Ca/P cal	Chemical formula of xSiHA	Chemical formula of xSiHAcAl
HA	0	0.100	0.059	0	10	1.67	1.67	1.65	$\text{Ca}_{10}(\text{PO}_4)_6$ OH_2	$\text{Ca}_{9.8}(\text{PO}_4)_{5.94}$ $(\text{OH})_{1.85}$
0.5 Si HA	0.5	0.100	0.055	0.005	10	1.81	1.67	1.79	$\text{Ca}_{10}(\text{PO}_4)_{5.5}$ $(\text{SiO}_4)_{0.5}$ $(\text{OH})_{1.5}(\text{VOH})_{0.5}$	$\text{Ca}_{9.74}(\text{PO}_4)_{5.44}$ $(\text{SiO}_4)_{0.56}(\text{OH})_{0.44}$
1 Si HA	1	0.100	0.051	0.009	10	2	1.67	1.95	$\text{Ca}_{10}(\text{PO}_4)_{4.5}$ $(\text{SiO}_4)_1(\text{OH})$ $(\text{VOH})_1$	$\text{Ca}_{9.71}(\text{PO}_4)_{4.96}$ $(\text{SiO}_4)_{1.04}(\text{OH})$
2 Si HA	2	0.100	0.04	0.02	10	2.5	1.67	2.35	$\text{Ca}_{10}(\text{PO}_4)_4$ $(\text{SiO}_4)_2(\text{OH})_0(\text{VOH})_2$	$\text{Ca}_{9.7}(\text{PO}_4)_{4.09}$ $(\text{SiO}_4)_{1.91}(\text{OH})_{0.09}$

2.2 Methods of characterization

The X-ray diffraction (XRD) patterns of sintered Ha and SiHa is achieved using by a D8 advance Eco de Brucker diffractometer. Data were collected over the 2θ range $5^\circ\text{C}-70^\circ\text{C}$ with step size of 0.06° and count time of 1s, are shown in (figure 1). The XRD for the materials appeared to be similar; the incorporation of Silicium into the Ha did not have a direct effect on the phase composition, and we notice that we don't have secondary phase.

The first observation on X-Ray diffraction shows that the diffraction peaks lose intensity with increasing silicate content, and we also observe in the peaks a decrease of crystallinity and crystallite size (Figure 2).

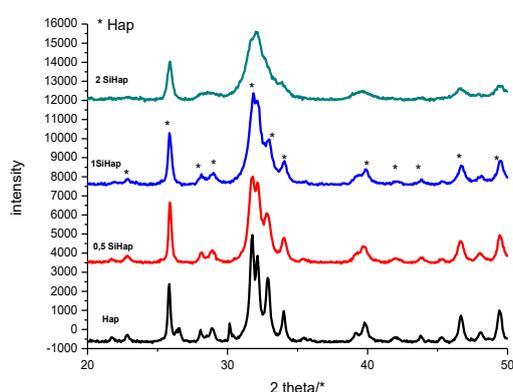


Fig. 1. X-ray powder diffraction patterns of HA and Si-HA powders calcined at 900°C

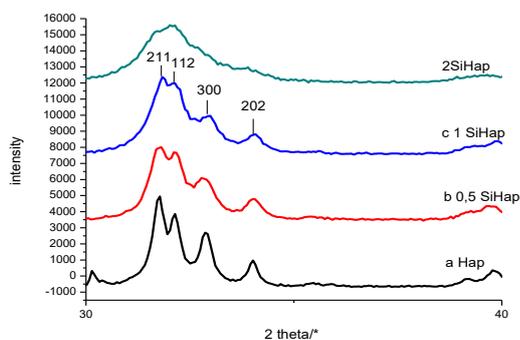


Fig. 2. Peak shift for Si-HA samples with increasing silicon content (a) pure HA, (b) 0.5 SiHA, (c) 1SiHA and (d) 2SiHA calcined at 900°C

The lattice parameters of pure Ha and Si substituted apatite sample are listed in table 2. The crystalline phases of samples were determined using X-ray diffraction (XRD). They were identified by means of the expert proof. We observe that the parameters of Si Hap are larger than those of pure Ha.

The substitution of PO_4^{3-} by SiO_4^{4-} is assumed to contribute to the increase in the lattice parameters of the Si-HA materials. Parameters a and c increase when the Si substitution increases. This increase of parameters can be explained to appear logical considering that the

ionic radius of Si^{4+} (0.042 nm) is larger than that of P^{5+} (0.035 nm) [22]. However, the observed variations in the lattice parameters and crystallite sizes did not change the intensity of the XRD peaks. This can also be understood considering that apparent intensity changes in the XRD peaks are only expected when there is an extensive atomic substitution of fairly different sized ions. In the present case, Si and P are adjacent to each other in the periodic table; differing only by one atomic number and the Si levels are relatively low. This could be attributed to different charge compensation mechanism for isomorphous substitution of PO_4^{3-} by SiO_4^{4-} .

Table 2. Crystallite sizes along a-axis and c-axis of calcined HA and SiHA using Scherrer's equation

Crystallite sizes	Space Groupe	a(nm)	c(nm)	V(nm ³)
HA	P63/m	9.4180	6.8842	528.81
0.5SiHA	P63/m	9.4282	6.8846	529.98
1SiHA	P63/m	9.4285	6.8862	530.14
2SiHA	P63/m	9.4288	6.8871	530.24

The Fourier Transform Infrared (FTIR) spectra is fulfilled using the iraffinity-1s spectrometer, at resolution of 4 cm^{-1} averaging 100 scans. Figure (3) shows the FTIR spectra of powders calcined at 900°C for 4 h. The FTIR was used to study the effect of the silicate substitution on the different functional groups such as phosphate and hydroxyl. The intense bands at 1092, 1036, and 964 cm^{-1} correspond to P-O stretching vibration modes. The doublet at $605-560\text{ cm}^{-1}$ and the band at 469 cm^{-1} corresponds to O-P-O bending modes. The bands at 3560 and 632 cm^{-1} were assigned to the stretching and vibration modes, respectively, of the hydroxide groups $1370-1600\text{ cm}^{-1}$ were assigned to the vibrations of CO_3^{2-} groups. In the 2SiHa we observe new band appearing at 880 cm^{-1} this was assigned to Si-O in the SiO_4^{4-} . (Figure 3).

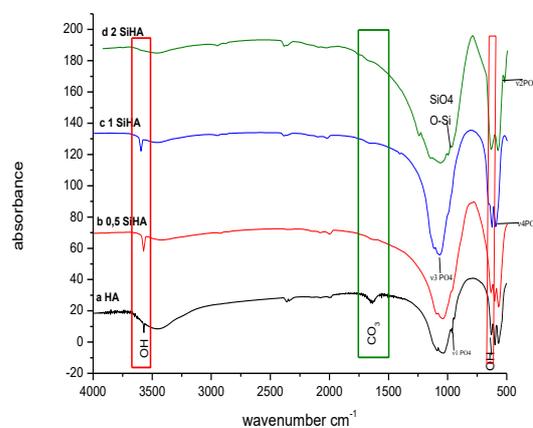


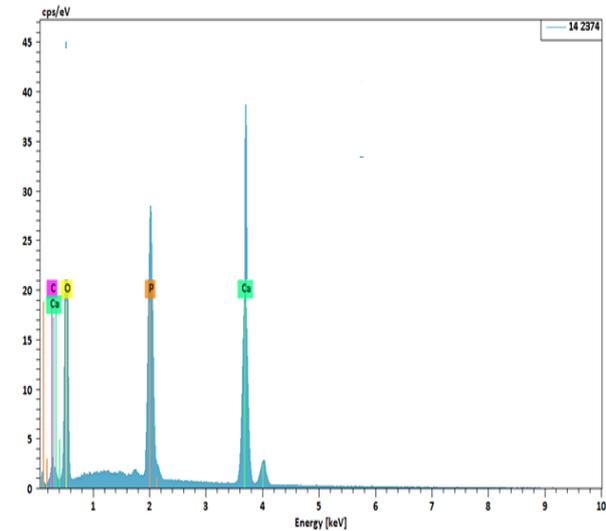
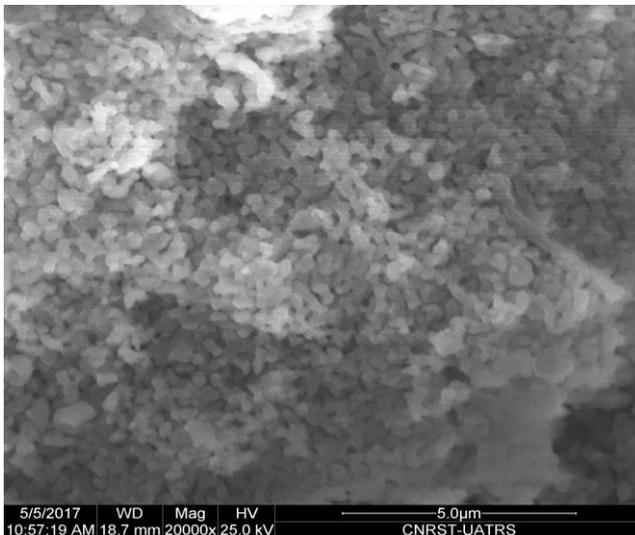
Fig. 3. FTIR spectra of the powders: (a) pure HA, (b) 0.5 SiHA, (c) 1SiHA and (d) 2SiHA calcined at 900°C .

SEM micrographs data and EDS (Energy Dispersive X-ray Spectroscopy) of the HA and SiHA powders

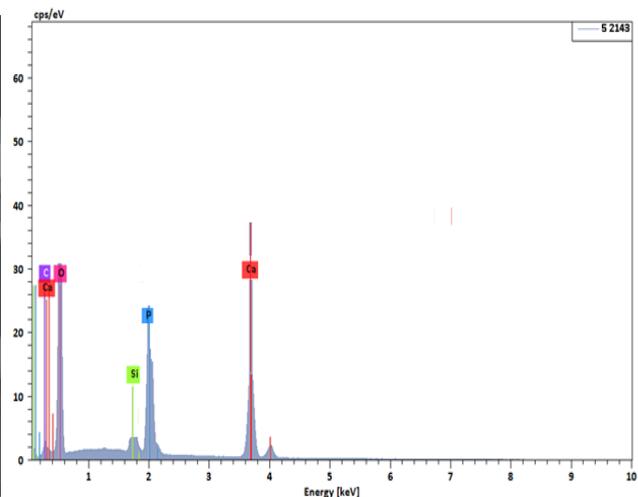
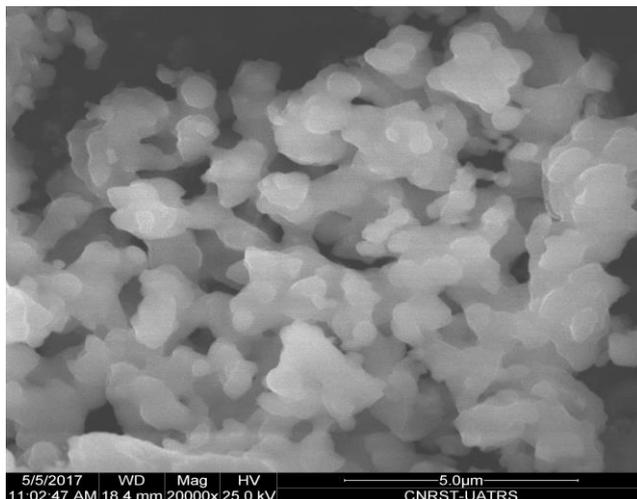
calcined at 900°C are given in figure 4. This shows the morphology of the substituted apatites (figure 4-b). The crystals of Si substituted apatite became larger than those of hydroxyapatite. Figure 4 shows that HA is spheroidal-shaped crystallites. However, increase with the Si content, the crystals started elongating and SiHA powder shows ellipsoidal shape morphology. This form

facilitates its insertion into the bone tissue for the filling of bone defects, suggesting that the growth perpendicular to the c-axis is easier in the presence of Si.

The EDS shows that our samples are constituting from calcium and phosphore and silisium.



a. EDS revealed that our Ha have 39.61 wt % of Calcium, 23.8 wt % of Phosphate.



b. EDS revealed that our Si Ha have 39.61 wt % of Calcium, 21.8 wt % of Phosphate and 3.2 wt % of silicium

Fig. 4. SEM micrographs and EDS (Energy Dispersive X-ray Spectroscopy) of the powders: (a) HA, (b) 0.5 SiHa

3 Conclusion

This paper presents the synthesis of silicate apatite with precipitation wet method using carbonate calcium CaCO_3 and phosphoric acid H_3PO_4 and TEOS. Silicate is incorporated in the apatite lattice and its stoichiometry was controlled, in the objective of obtaining biomaterials having an improved biocompatibility for the insertion in the bone. This special morphology observed in SEM micrographs and the results obtained in XRD and FTIR and chemical analysis, all these results are essential for the biological application of our biomaterial.

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