HIGH TEMPERATURE PREPARATION OF SILICON CONTAINING APATITE

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Importanţa prezenţei siliciului in mineralizarea osoasă a fost studiată in mai multe lucrări recente. Hidroxiapatita fosfocalcică (HA: $Ca_{10}(PO_4)_6(OH)_2$) este principalul component mineral al osului.

Această lucrare studiază obţinerea apatitei dopate cu siliciu prin metoda "reacţie solid- solid". Compusul stabil la temperatură înaltă pare a fi silicocarnotita. Totuşi, o apatită dopată cu siliciu a fost obţinută prin incălzirea unui amestec de fosfat tricalcic, carbonat de calciu şi silice la 1200°C-1300°C. Materialul obţinut poate fi folosit in medicină ca substitut osos sau ca strat subţire depus pe suprafaţa protezelor sau implanturilor osoase.

Several studies have shown that silicon presence is beneficial in bone mineralization process. Phosphocalcium hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is the principal mineral component of bone.

This work studies the synthesis of silicon containing apatite by a high temperature method. The stable compound at high temperature seems to be the silicocarnotite. Nevertheless, a silicon containing apatite has been obtained by heating a mixture of tri-calcium phosphate, calcium carbonate and silicon dioxide at 1200°C-1300°C. The synthesized materials can be used in medicine as bone substitution or as proṭsthesis and implant coating.

1. Introduction

The calcium phosphate (Ca-P) ceramic family has been largely studied for its good biocompatibility and bioactivity. The research on processing of synthetic CaP started in the 70s [1] and comprehensive reviews on natural and synthetic calcium phosphates materials have been written since this date [2, 3].

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Phosphocalcium hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is the principal mineral component of bone and is already used in dental and medical applications [4]. In the bone, the hydroxyapatite presents different ionic substitutions, such as sodium, magnesium, carbonate or silicate [6, 7]. The in vivo behavior of the synthetic apatite and the influence of different substitutions have been studied by several authors [5, 8, 18]

The silicon effect in bone mineralization has been shown for the rat and the chicken since 1970 [8]. The benefits of silicon presence were also evidenced by the good bioactivity of the silicon based glasses [9, 10]. A study on the osteoblast response on the silicon substituted hydroxyapatite (HA-Si) has evidenced that silicon modifies the dissolution rate and plays a very important role in the biomineralization processes [11].

Lately, several synthesis methods have been studied, such as the wet chemical preparation or the hydrothermal process [12, 13, 14, 15, 16]. Previous studies were performed by Boyer and Lacout, in order to prepare silicon apatite by solid state reaction for various applications. In this case the electronic charge balance was realized by the introduction of secondary ions as La^{3+} or Nd^{3+}, which confers to the final product a high chemical stability [17].

This paper studies the silicoapatite (HA-Si) synthesis by a solid state route. In that way, SiO_4^{4-} replaces the PO_4^{3-} in the hydroxyapatite lattice sites and the charge balance is obtained by the formation of OH^- vacancies in the channel. Then, the expected general chemical formula is $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$.

Several initial mixtures and several silicon ratios were studied. The objective was to optimize the mixture composition and to describe the influence of the different parameters on the synthesis process.

The final powders can be used in biological applications like the filling or the replacement of bone defects or coatings on dental implants and bone prosthesis. In that last case, such a silicon apatite ceramic coating on the metallic surface can induce the biointegration phenomenon.

2. Materials and methods

The aim of this study is the HA-Si preparation by a solid state reaction method. The result of such a synthesis can be affected by the silicon ratio, the chemical composition of the mixture, the physicochemical properties of the different compounds, the temperature cycle of heating, and the rates of intermediate reactions which occur during the global synthesis.

Calcium, phosphorus and silicon can be provided by different mineral compounds. Therefore the following compounds were chosen:

-     $Ca_3(PO_4)_2$ (tricalcium phosphate) or $Ca_2P_2O_7$ (pyro calcium phosphate) providing the calcium and phosphorous
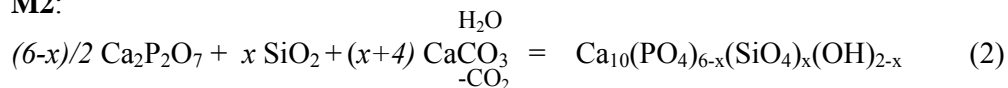
-        SiO_2 (silicon dioxide) or $CaSiO_3$ (calcium silicate) as silicon providers
-        $CaCO_3$ (calcium carbonate) in order to supply the calcium needed for the stoechiometry of the reaction.

The expected chemical reactions for the four mixtures, noted by M1, M2, M3 and M4 were:
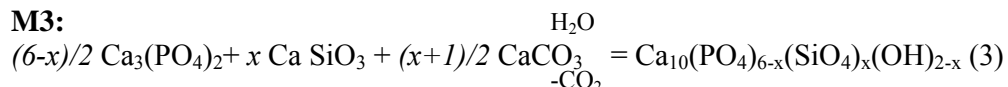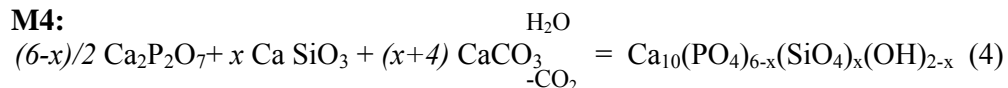
M1:

$$(6\text{-}x)/2\ Ca_3(PO_4)_2 + x\ SiO_2 + (3x+2)/2\ CaCO_3 \overset{H_2O}{\underset{-CO_2}{=}} Ca_{10}(PO_4)_{6\text{-}x}(SiO_4)_x(OH)_{2\text{-}x} \quad (1)$$

M2:

$$(6\text{-}x)/2\ Ca_2P_2O_7 + x\ SiO_2 + (x+4)\ CaCO_3 \overset{H_2O}{\underset{-CO_2}{=}} Ca_{10}(PO_4)_{6\text{-}x}(SiO_4)_x(OH)_{2\text{-}x} \quad (2)$$

M3:

$$(6\text{-}x)/2\ Ca_3(PO_4)_2 + x\ Ca\,SiO_3 + (x+1)/2\ CaCO_3 \overset{H_2O}{\underset{-CO_2}{=}} Ca_{10}(PO_4)_{6\text{-}x}(SiO_4)_x(OH)_{2\text{-}x} \quad (3)$$

M4:

$$(6\text{-}x)/2\ Ca_2P_2O_7 + x\ Ca\,SiO_3 + (x+4)\ CaCO_3 \overset{H_2O}{\underset{-CO_2}{=}} Ca_{10}(PO_4)_{6\text{-}x}(SiO_4)_x(OH)_{2\text{-}x} \quad (4)$$

The beta tri-calcium phosphate was prepared by heating at 900°C the commercial product. The calcium pyrophosphate was obtained by heating at 1000°C the di-hydrated di-calcium phosphate $CaHPO_4 \cdot 2H_2O$. $Ca_3(PO_4)_2$, and also calcium silicate $CaSiO_3$ were provided by Prolabo®. The calcium carbonate ($CaCO_3$) used was a Scoralite® precipitated calcium carbonate and the silicon dioxide was the Sipernat 50S powder from Degussa®.

Several compositions with different amounts of silicon were tested, with x in the range [0…2], where x is the number of PO_4^{3-} ions substituted by SiO_4^{4-}, as noticed in the general chemical formula. The charge balance made by the OH^- vacancies, so x value is limited to 2. The compound mixing was done by using a ceramic mortar with pestle. The heating cycles were made at different temperatures which varied between 1100°C and 1400°C, at a heating rate of 5°C/min, with maintaining time that varied between 60 minutes and 12 hours.

The reaction products were analyzed by X-ray diffraction using an INEL XRD apparatus fitted with a cobalt target. The patterns were compared with standard patterns from the Joint Committee and Powder Diffraction Standards database (JCPDS).

Infrared FTIR analyses were made with a Nicolet FTIR-ATR spectrometer. The spectra were obtained from 450 to 4500cm^{-1} after 64 successive scans averaged with OMNIC® software.

3. Results

The solid state reaction is influenced by several parameters:

-        The different initial compositions: M1, M2, M3, M4 as previously described.

-        The SiO_2 amount, between 0 and 12 weight percentage.

-        The temperature range between 1100°C and 1400°C;

-        The heating time between 60 minutes and 12 hours;

A first study was made for the x=1 mixtures heated at 1200°C during 3 hours. These temperature and duration treatments were chosen by taking account of previous results [17, 18]. In Fig. 1 are shown the X-ray diffraction patterns for the four final compounds obtained with the initial mixtures (M1, M2, M3, M4).
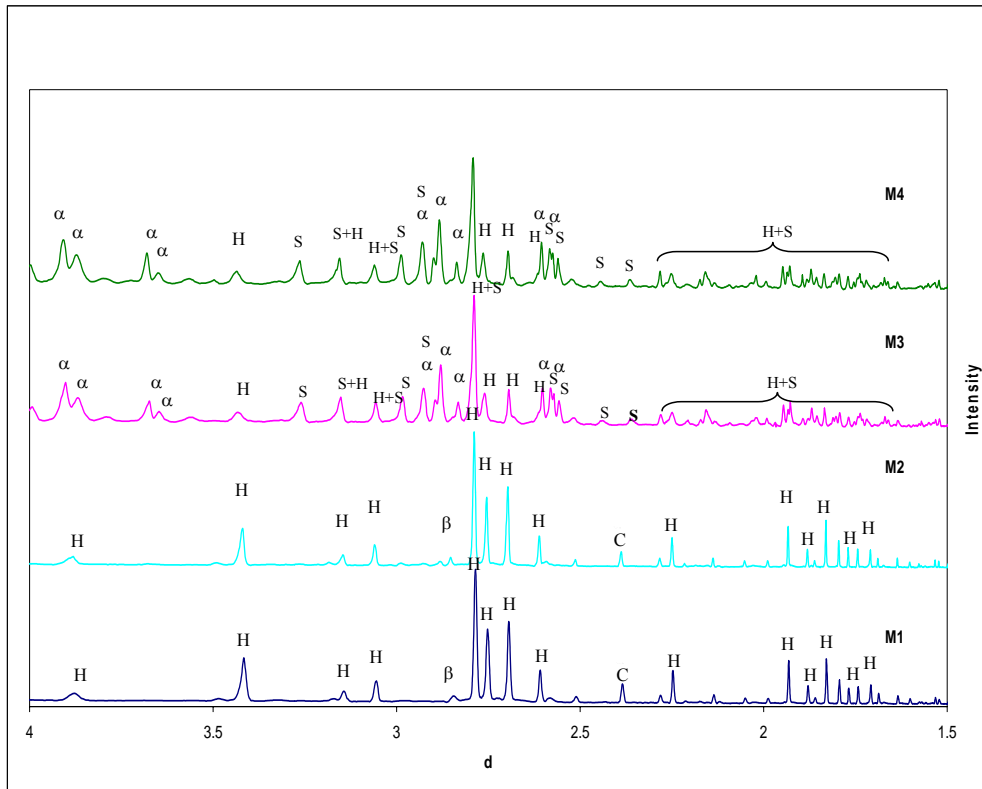

Fig 1: X-ray diffraction patterns of different mixtures with x=1 after heating at 1200°- 3hours
H-hydroxyapatite, S-silicocarnotite, α- α tri calcium phosphate, β-β tri calcium phosphate
C-calcium oxide

The results depend on the initial materials. For the mixtures M1 and M2, with SiO_2 as Si provider, the X-ray diffraction patterns correspond to a pure hydroxyapatite phase. Only some weak lines correspond to traces of β tricalcium phosphate and lime (CaO) which have not yet reacted. When $CaSiO_3$ is used as initial Si provider (M3, M4), the X-ray patterns show the presence of three different compounds: hydroxyapatite, silicocarnotite ($Ca_{10}(PO_4)_4(SiO_4)_2$) [23], and α tri-calcium phosphate. It clearly appears that a quasi pure apatite phase was only obtained for the mixtures M1 and M2.

In order to optimize the apatite synthesis conditions, only the M1 mixture was heated at different temperatures between 1100 and 1400°C. In table 1 are reported the different amounts of the initial compounds in the mixture M1. For the mixture M1 containing no silicon (x=0) the X-Ray diffraction patterns showed the presence of HA with β-TCP and CaO at 1100°C and a quasi pure HA pattern after heating at 1400°C during 1h.

Table 1

Weight percent of initial compounds for different silicon amounts in the mixture M1, with constant Ca/(P+Si) atomic ratio=1.667

x	Ca3(PO4)2	SiO2	CaO	CaCO3
0	94.3295	-	5.6795	9.9602
0,5	86,9454	3,0597	9,9949	17,8480
1	79,4872	6,1538	14,3590	25,6410
2	64.3153	12.4481	23.2365	41.4938

The mixture M1 containing different silicon amounts was heated between 1100°C and 1400°C.

Fig. 2 shows the X-ray diffraction patterns of M1 with x=1.

In all the temperature range the main compound formed after heating is the hydroxyapatite. At 1100°C the reaction is advanced, but is not completed even after a 12 hours heating period.

At 1200°C, after heating for 3 hours all the compounds mainly contain HA and small amounts of β-TCP and CaO. At 1300°C, the only difference which can be observed is crystalline phase transformation of β-TCP into α-TCP.
At 1400°C the formation of the silicocarnotite occurred.

No line corresponding to the high temperature form of silicon oxide (cristobalite) appears. Previous experiments showed that cristobalite presence is clearly evidenced for an amount of 3% in a mixture with apatite.
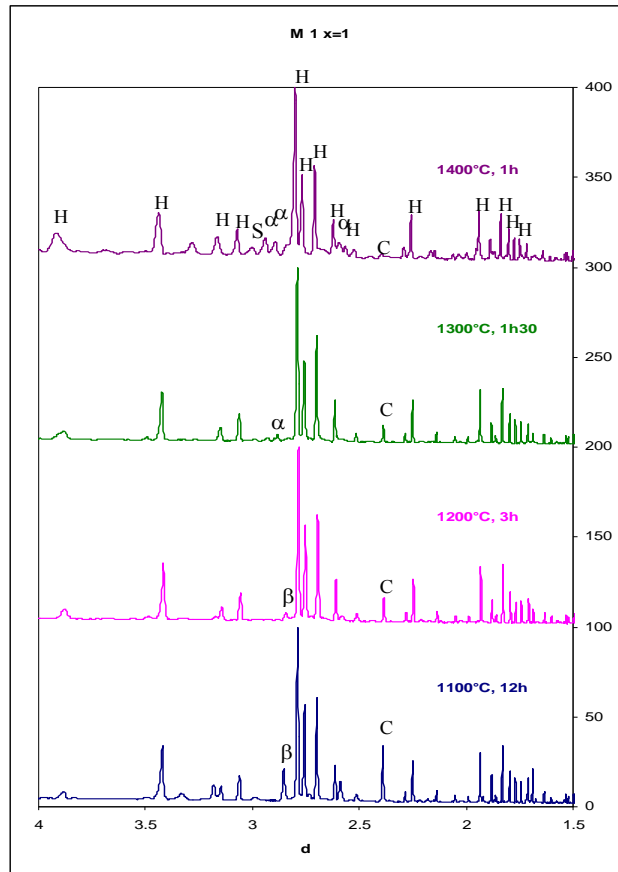
Fig. 2: X-Ray diffraction patterns of M1 with x=1 after heating at different temperatures; H-hydroxyapatite, S-silicocarnotite, α- α tri calcium phosphate; β-β tri calcium phosphate;C-calcium oxide (lime)

On the FTIR spectra (Fig. 3), the intense bands at 1086, 1015, 958 cm^{-1} correspond to P-O stretching vibration modes, as well as the bands at 597 and 560 cm^{-1} correspond to the O-P-O bending mode. The bands at $3570cm^{-1}$ and $630cm^{-1}$ are characteristic of OH^{-} in the hydroxyapatite. The band at 3642 cm^{-1} is due to OH^{-} into the extra-phase $Ca(OH)_2$.

Besides the HA bands, a new band appears at 880 cm^{-1}. This band can be assigned to Si-O vibration mode of SiO_4^{4-}. Effectively, on the zoom on the Fig. 5 one can see the infrared spectra for x=0, x=1, x=2 and note the increase of this band with the x value. No other compound, especially calcium silicate is evidenced on the X-ray diffraction pattern, and so these bands can be surely attributed to SiO_4^{4-} ions, in the apatite or silicocarnotite lattice [19].
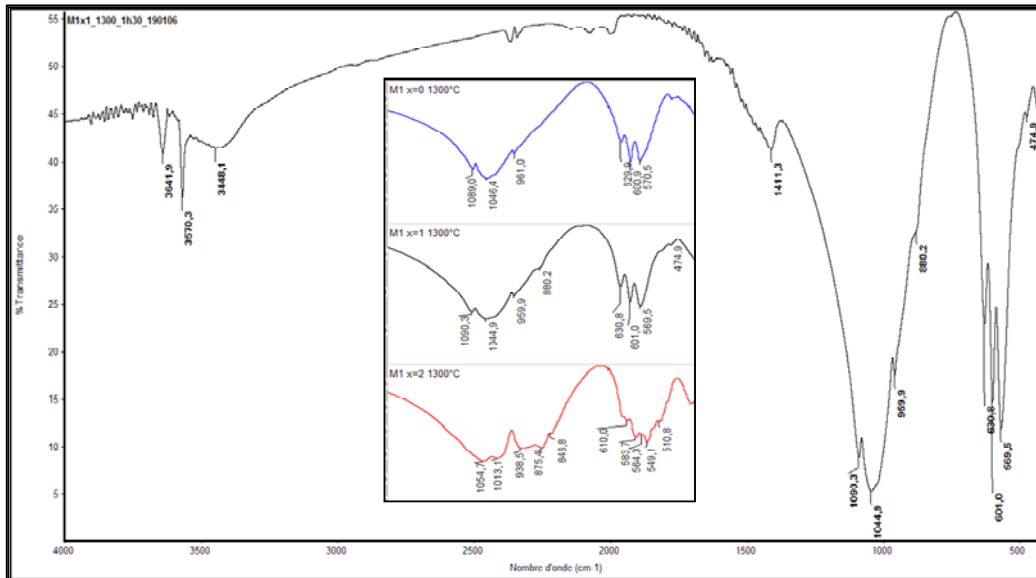
Fig. 3 : FTIR spectra after heating at 1300°Cof the M1 mixture

For the silicocarnotite (x=2), the presence of SiO_4^{4-} bands is associated with the absence of the OH^- bands. That corresponds to the coupled substitution $(PO_4^{3-}, OH^-) <=> (SiO_4^{4-})$. For silicon amounts lower than x=2, one can propose a coupled substitution in the apatitic lattice $(PO_4^{3-}, OH^-) <=> (SiO_4^{4-}, \square)$. This proposal is in direct correlation with the expected formula for silicoapatite $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$.

For the case x=2, when silicocarnotite was obtained, a displacement of the PO_4^{3-} and SiO_4^{4-} bands can be observed. This fact is due to the different environments in the crystalline structures between apatite (hexagonal) and silicocarnotite (orthorhombic).

4. Discussion

The behavior of hydroxyapatite during heating has been studied by many authors [20, 21, 22]. The reactions which occur are well-known. First, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is formed easily at 1000°C. Above 1000°C, one observes the structural water liberation with formation of oxyhydroxyapatite (HOA), following the reaction:

$$Ca_{10}(PO_4)_6(OH)_2 \Leftrightarrow Ca_{10}(PO_4)_6O_x(OH)_{2(1-x)} + x\ H_2O \qquad (5)$$
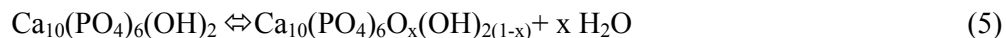
At 1320°C the thermal decomposition of HOA partially occurs and forms α-TCP and CaO,

$$Ca_{10}(PO_4)_6O_x(OH)_{2(1-x)} \Leftrightarrow 3\ Ca_3(PO_4)_2 + CaO + H_2O \qquad (6)$$
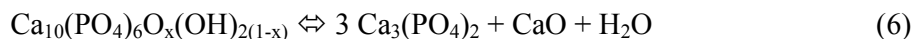
These reactions are reversible and the apatite can be decomposed at high temperature and recomposed during the cooling process due to the low cooling rate. Some high temperature phases, by example α-TCP, can be quenched during the cooling and remain at low temperature. Thereby, in the experimental conditions, for x= 0, a hydroxyapatite was obtained after heating the mixtures M1 or M2 at 1400°C.

When silicon is present in the mixture, silicocarnotite $Ca_{10}(PO_4)_4(SiO_4)_2$ can be formed. For the mixtures M1 and M2, when Si is provided by SiO_2, the silicocarnotite appears after heating at 1400°C, but for mixtures M3 and M4 when Si is provided by $CaSiO_3$, silicocarnotite appears at a lower temperature (1200°C).

So, the main difference between mixture (M1, M2) and (M3, M4) is the Si initial compound. The formation of silicocarnotite appears to be easier starting from calcium silicate than from silicon oxide. The existence of silicocarnotite at 1400°C, due certainly to the decomposition of a previous silicoapatite prepared at 1200°C (route with M1 and M2 mixture) and the existence at 1200°C due to the reaction with $CaSiO_3$, (route M3 and M4) show evidently the high stability of this compound. It clearly appears that, at high temperature, the silicocarnotite is the stable phase.

Summarizing:
- in the case x=0, the final product is hydroxyapatite;
- for x=2 the final product is essentially constituted by the silicocarnotite;
- between 0 and 2, the final compound is a mixture containing hydroxyapatite and silicocarnotite.

The synthesis of a pure silicoapatite by a solid state reaction can be observed. It is the case for the mixture M1, with x=1 at 1200 and 1300°C. One can suppose that the heating and cooling conditions, the initial compounds nature, the rate of the intermediate reactions allows the formation of this apatite. Nevertheless, when this silicoapatite is heated at higher temperature, the demixing in the two phases occurs: silicocarnotite and hydroxyapatite.

5. Conclusions

A silicon containing apatite $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$ was synthesized by a solid state reaction at 1200°C and 1300°C. Nevertheless, it is difficult to prepare a silicon substituted apatite at high temperature due to the fact that above

1300°C the thermodynamically stable phase is certainly the silicocarnotite $Ca_{10}(PO_4)_4(SiO_4)_2$.

The chosen initial mixture was: tri calcium phosphate, silicon dioxide and calcium carbonate. In these conditions, the rate of the intermediate reaction allows the formation of a quasi pure apatite.

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