

# Wet chemical method for preparing high purity $\beta$ and $\alpha$ - tricalcium phosphate crystalline powders

M. Fathi, A. El Yacoubi, A. Massit, B. Chafik El Idrissi

**Abstract**— The object in the present study is to provide a simple route for synthesizing highly pure nano-sized  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) and  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP) powders. Apatitic -tricalcium phosphate (ap-TCP) powders were synthesized through wet chemical precipitation method using a diammonium phosphate solution  $(\text{NH}_4)_2\text{HPO}_4$  and a calcium nitrate tetrahydrate solution  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  as precursor materials, with a Ca/P molar ratio 1.50 from the initial reagents, calcining the powders at 800 and 1200°C to obtain single phase  $\beta$ -TCP and  $\alpha$ -TCP respectively. The synthesized powders were characterized by X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR). The results showed that high purity and well-crystallized  $\beta$ -TCP and  $\alpha$ -TCP powders could be obtained.

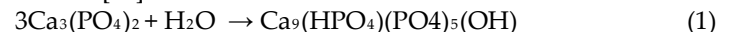
**Index Terms**—  $\beta$  and  $\alpha$ -Tricalcium phosphate, FTIR, wet chemical precipitation synthesis, X-ray diffraction.

## 1 INTRODUCTION

Apatitic tricalcium phosphate with the chemical formula of  $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$  is a calcium orthophosphate that transforms into  $\beta$ -tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  by heating above 750 °C. TCP is divided into three polymorphs ( $\alpha$ ,  $\beta$  and  $\alpha'$ ) according to their thermal stability [1]: the low-temperature  $\beta$ -TCP, and the high-temperature forms,  $\alpha$ - and  $\alpha'$ -TCP. The last one lacks practical interest because it only exists at temperatures > 1430°C and reverts almost instantaneously to  $\alpha$ -TCP on cooling below the transition temperature. In contrast,  $\beta$ -TCP is stable at room temperature and transforms reconstructively [2,3] above 1125°C to  $\alpha$ -TCP, which can be retained during cooling to room temperature [1].  $\alpha$ - and  $\beta$ -TCP are currently used in several clinical applications in dentistry, maxillo-facial surgery and orthopaedics:  $\beta$ -TCP is the component of several commercial mono- or biphasic bioceramics and composites, and  $\alpha$ -TCP is the major constituent of the powder component of various hydraulic bone cements [4,5]. In spite of having the same chemical composition,  $\alpha$  and  $\beta$ -TCP differ considerably in their structure, density and solubility which, in turn, determine their biological properties and clinical applications.

$\beta$ -TCP is used mainly for preparing biodegradable bioceramics shaped as dense and macro-porous granules and blocks, whereas the more soluble and reactive  $\alpha$ -TCP is used mainly as a fine powder in the preparation of calcium phosphate cements, although some commercial bioceramic granules and blocks made of  $\alpha$ -TCP may be found on the market. Both  $\beta$  and  $\alpha$ -TCP materials are used in clinics for bone repair and remodelling applications.

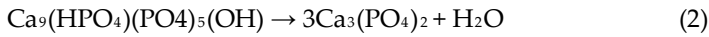
$\alpha$ -TCP crystallizes in the monoclinic crystal system and belongs to the space group  $P2_1/a$ , the  $\beta$ -TCP crystallizes in the rhombohedral space group  $R3c$ . Cell parameters ( $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ ), number of formula units per cell ( $Z$ ) and cell volume ( $V$ ) are displayed in Table 1 for  $\alpha$ -TCP and its polymorphs  $\beta$ -TCP and  $\alpha'$ -TCP [6,7]. The structural differences between  $\beta$ - and  $\alpha$ -polymorphs of TCP are responsible for their different chemical and biological properties, among them, solubility and biodegradability. The high dissolution rate of  $\beta$ -TCP in the human biological environment advances bone growth during the progressive degradation. This property imparts significant advantage to  $\beta$ -TCP compared to other biomedical materials which are not easily resorbed and replaced by natural bone [8,9]. Therefore,  $\beta$ -TCP is frequently used as bone repairing materials.  $\alpha$ -TCP with high solubility has been applied as a component of bone cements and other bone substitutes [10–12].  $\alpha$ -TCP with the liquid phase forms a very hard material that can be used for filling bone defects as well as joining another biomaterial with bone tissue. Moreover, according to Eq. (1),  $\alpha$ -TCP reacting with water leads to calcium deficient apatite, which imparts high biocompatibility to the cement [13].



The synthesis of pure TCP powders is not so much reported in the literature compared with that of hydroxyapatite (HA)  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . The synthesis of  $\alpha$ -TCP is accomplished by thermal transformation of a precursor with molar ratio Ca/P~1.5 (calcium-deficient hydroxyapatite, CDHA; amorphous calcium phosphate, ACP; or  $\beta$ -TCP) previously obtained [14, 15], or by solid-state reaction of a mixture of solid precursors at high temperatures [16, 17]. Self-propagating high-temperature synthesis [18] and combustion synthesis [19] have also been employed.

TCP powders are synthesized via wet-chemical method slightly modified. This method is most commonly used to form the Ap-TCP. The molar ratio of Ca/P in ApTCP is the same as that in TCP, and the ApTCP is usually calcined above 700–800°C to transform into  $\beta$ -TCP, as described by the following equation (2):

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Then  $\beta$ -TCP is reconstructively transforms at 1125°C into  $\alpha$ -TCP.

Property	$\text{Ca}_3(\text{PO}_4)_2(\text{TCP})$ $\beta$ -TCP	polymorph $\alpha$ -TCP	$\alpha'$ -TCP
Symmetry	Rhombohedral	Monoclinic	Hexagonal
Space group	R3c	P2 <sub>1</sub> /a	P6 <sub>3</sub> /mmc
a(nm)	1.04352(2)	1.2859(2)	0.53507(8)
b(nm)	1.04352(2)	2.7354(2)	0.53507(8)
c(nm)	3.74029(5)	1.5222(3)	0.7684(1)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	126.35(1)	90
$\gamma$ (°)	120	90	120
Z	21	24	1
V(nm <sup>3</sup> )	3.5272(2)	4.31(6)	0.19052(8)

## 2 EXPERIMENTAL PROCEDURE

Reaction conditions for the preparation of TCP using wet-chemical method slightly modified was initially optimized. Analytical grade calcium nitrate tetrahydrate [Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O] and diammonium hydrogen phosphate [(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>] were dissolved individually in distilled water preheated to 37°C. The Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution was added dropwise into (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solution under constant stirring to reach the Ca/P molar ratio of 1.50. The temperature of the opaque solution is maintained at 37°C. The pH was adjusted at once by the addition of concentrated ammonium hydroxide (NH<sub>4</sub>OH) solution to around 8.5. The milky solution is stirred for 2h at 37°C. Formed precipitates are then filtered out of the mother liquor, washed repeatedly with distilled water to remove NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, followed by drying in an air atmosphere at 60°C for 24h. The cake obtained after drying was powdered with agate mortar and pestle, and then calcined into alumina crucible at 800°C for 2 h. The product was determined to be pure  $\beta$ -TCP. Next, the as prepared  $\beta$ -TCP were calcined at 1200°C followed by quenching to room temperature (RT). The calcination is performed as follows:  $\beta$ -TCP powders are heated from RT to 1200°C in 4 hours, soaked at 1200°C for 3 hours, followed by quenching, in the furnace, from 1200°C to RT in 4 hours.

## 3 MATERIALS CHARACTERIZATION

Crystalline phases were identified by means of a XPERT-PROPW 3050/60 (Theta/Theta) X-ray diffractometer (XRD) using CuK $\alpha$  radiation and operating at 30 kV and 35 mA. XRD patterns were collected over the 2 $\theta$  range of 5-80° at a step size of 0.06°. Crystalline phases detected in the patterns were identified by comparison to the standard patterns from the ICDD-PDF (International Center for Diffraction Data-Powder Diffraction Files).

The functional groups present in the prepared powder

were recorded on FTIR spectrophotometer, VERTEX 70, Genesis Series (400–4000 cm<sup>-1</sup>, resolution 4, scans 20). For this 1% of the powder was mixed and ground with 99% KBr and the spectrum was taken in the range of 400 to 4000 cm<sup>-1</sup>.

## 4 RESULTS AND DISCUSSION

XRD patterns of as-prepared sample dried 24 h at 60°C is shown if Figure 1. It reveals that the powder exhibited a single apatitic phase can be indexed as CDHA phase according to JCPDS N°. 9-432, without a second phase as dicalcium phosphate anhydrous CaHPO<sub>4</sub> (DCPA, PDF 9-80). When the as-dried sample is calcined at 800°C (Fig. 2), all the diffraction peak positions match well with the standard XRD pattern of  $\beta$ -TCP (JCPDS NO.9-169). The diffraction peaks are high and narrow, implying that the  $\beta$ -TCP crystallizes well. In addition, no peaks of impurities are observed in the X-ray diffraction diagram of the obtained  $\beta$ -TCP. When the  $\beta$ -TCP is calcined at 1200°C (Fig. 3), all the diffraction peak positions match well with the standard XRD pattern of  $\alpha$ -TCP (JCPDS NO.9-348); There are no reflections characteristic for the crystalline phases of other calcium phosphates, such as  $\beta$ TCP or hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>.

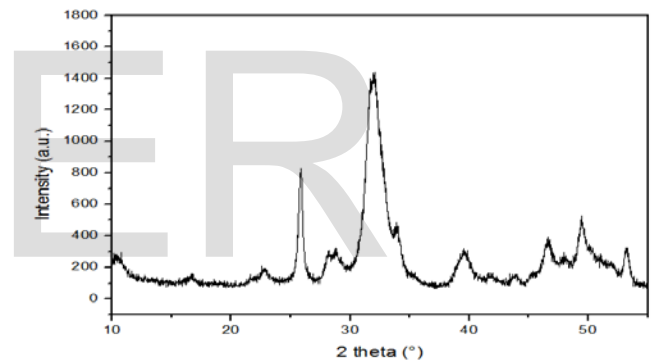


Fig. 1: XRD patterns of as-prepared sample dried 24 h at 60°C

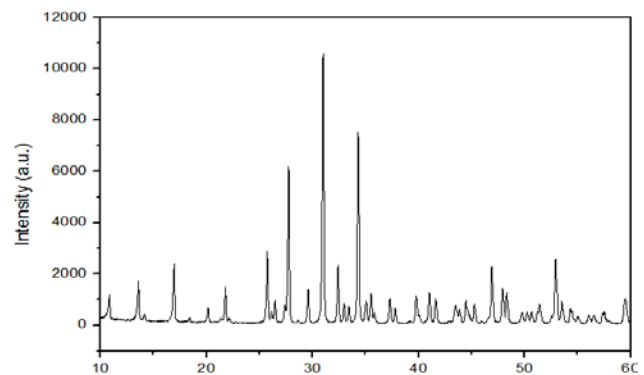


Fig. 2: XRD patterns of as-prepared sample calcined at 800°C ( $\beta$ -TCP)

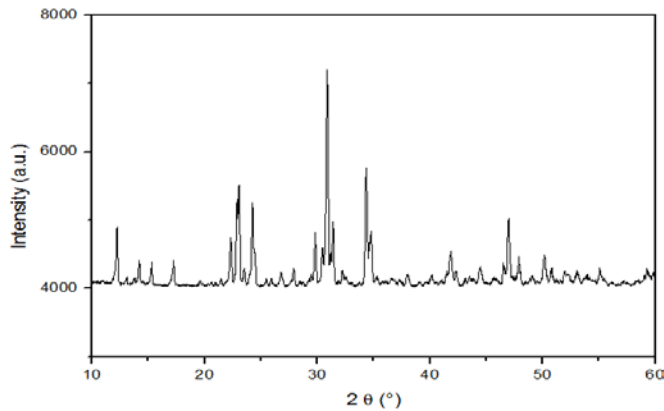


Fig. 3: XRD patterns of as-prepared sample calcined at 1200°C ( $\alpha$ -TCP)

The mean crystallite size ( $D$ ) was calculated from the XRD line broadening measurement from the Scherrer equation [20] Eq (3):

$$D = 0.9 \lambda / \beta \cos \theta \quad (3)$$

Where  $\lambda$  is the wavelength of the used Cu  $K\alpha$  radiation,  $\beta$  is the full width at the half maximum of the  $\beta$ -TCP line and  $\theta$  is the diffraction angle.

The values calculated of crystallites size, according to Scherrer's formula, are 10, 60 and 47 nm for TCPap,  $\beta$ -TCP and  $\alpha$ -TCP respectively.

The fraction of crystalline phase ( $X_c$ ) of the  $\beta$ -TCP powders was evaluated by the following Eq. (4) [21]:

$$X_c = 1 - v/I \quad (4)$$

Where  $I$  is the intensity of highest diffraction peak and  $v$  is the intensity of the hollow between two considered diffraction peaks of TCP.

The crystallinity degree of Ap-TCP is 10 %, while that of  $\beta$ -TCP and  $\alpha$ -TCP is 98 % and 92 % respectively.

Fig. 4a illustrates the FT-IR absorption spectra of the as-prepared samples. The bands at 1092 and 1040  $\text{cm}^{-1}$  are assigned to the components of the triply degenerate  $\nu_3$  anti-symmetric P-O stretching mode. The 962  $\text{cm}^{-1}$  band is assigned to  $\nu_1$ ; the non-degenerate P-O symmetric stretching mode. The bands at 601 and 571  $\text{cm}^{-1}$  are assigned to components of the triply degenerate  $\nu_4$  O-P-O bending mode and the bands in the range of 462–474  $\text{cm}^{-1}$  are assigned to the components of the doubly degenerate  $\nu_2$  O-P-O bending mode. The broad band between 3700 and 3000  $\text{cm}^{-1}$ , as well as the one at 1640  $\text{cm}^{-1}$ , corresponded to residual water adsorbed at the particle surface. A significant concentration of hydroxyl groups remains in the structure as observed from the intensity of the stretching and librational bands at 3572 and 632  $\text{cm}^{-1}$  [22–24]. From literature, the band at 875  $\text{cm}^{-1}$  was ascribed to hydrogenophosphate  $\text{HPO}_4^{2-}$  groups; can be associated with Ca-deficient apatite (CDAp)  $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$  and decomposition of CDAp after thermal treatment lead to formation of  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) or biphasic calcium phosphates (BCP) [25-29]. The absorption bands at 1456, 1413 confirm the presence of carbonate group  $\text{CO}_3$ ,  $\text{CO}_2$  has a very affinity to apatite crystal during the synthesis process.

In addition, the band at 1380  $\text{cm}^{-1}$  is attributed to nitrate  $\text{NO}_3^-$  and ammonium  $\text{NH}_4^+$  groups resulting from synthesis residuals was only observed in as-prepared samples. The presence of hydrogenophosphate and hydroxide ions confirms that the apatite phase is apatitic tricalcium phosphate  $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$ . Fig.2a and 2b gives the IR spectra of powders heat-treated at 800 and 1200°C respectively. They are in good agreement with the phases determined from XRD patterns of calcined powders. The  $\beta$ -TCP and  $\alpha$ -TCP peaks, in both of the powders heat-treated at 800 and 1200°C, were in good accordance with those reported in the literature [30, 31]. The peaks at 632  $\text{cm}^{-1}$  and 3572  $\text{cm}^{-1}$  represent the -OH group. These peaks appear as weak shoulders in the FT-IR curve of "as dried" sample which however, do not exist in the FT-IR curves of  $\beta$ -TCP and  $\alpha$ -TCP samples. This has proved the elimination of hydroxyl ion ( $\text{OH}^-$ ) ions from the structure of Ap-TCP. The band attributed to  $\text{HPO}_4^{2-}$  groups in the as-synthesized powder ( $\nu = 875 \text{ cm}^{-1}$ ) had disappeared. This is the most important change in the FTIR spectra of "as dried" sample, as it confirms the transformation of the Ap-TCP to TCP is completed after this heat treatment (800°C). The spectra bands between 1456 and 1413  $\text{cm}^{-1}$  in the spectra of "as dried" sample represent the carbonate groups that are not present in the  $\beta$  and  $\alpha$ -TCP sample

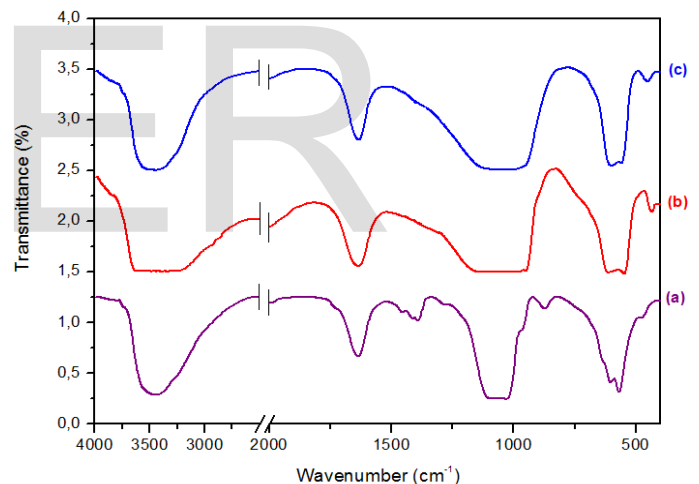


Fig. 4: FT-IR absorption spectra of the as-prepared samples: (a): dried at 60°C; (b): calcined at 800°C; (c): calcined at 1200°C ( $\alpha$ -TCP)

## 5 CONCLUSION

Based upon the experimental results, a quite fast, simple and efficient method has been set up for the preparation of high purity nano-sized  $\beta$ -TCP and  $\alpha$ -TCP powders with 47 and 60 nm respectively and high degree of crystallinity.  $\beta$  and  $\alpha$ -TCP are obtained from powders synthesized at relatively elevated synthesis temperature (37°C). From the FT-IR and the XRD analysis result, we confirmed that the tricalcium phosphate had a high phase purity.

## REFERENCES

- [1] Elliot JC. Structure and chemistry of the apatites and other calcium orthophosphates. Amsterdam: Elsevier Science; 1994.
- [2] Buerger MJ. The rôle of temperature in mineralogy. *Am Miner* 1948;33(3-4): 101-21.
- [3] Buerger MJ. Crystallographic aspects of phase transformations. In: Smoluchowski R, Meyer JE, Weyl WA, editors. *Phase transformations in solids*. New York: John Wiley; 1951. p. 183-211.
- [4] Bohner M. Calcium orthophosphates in medicine: from ceramics to calcium phosphate cements. *Injury* 2000;31 (Suppl. D):37-47.
- [5] Dorozhkin SV. Calcium orthophosphate cements for biomedical application. *J Mater Sci* 2008;43:3028-57.
- [6] Yashima M, Sakai A, Kamiyama T, Hoshikawa A. Crystal structure analysis of  $\beta$ -tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  by neutron powder diffraction. *J Solid State Chem* 2003;175:272-7.
- [7] Yashima M, Sakai A. High-temperature neutron powder diffraction study of the structural phase transition between  $\alpha$  and  $\alpha'$  phases in tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$ . *Chem Phys Lett* 2003;372:779-83.
- [8] B.Q. Chen, Z.Q. Zhang, J.X. Zhang, Q.L. Lin, D.L. Jiang, *Mater. Sci. Eng. C: Biomim. Supramol. Syst.* 28 (2008) 1052-1056.
- [9] J. Román, M.V. Cabanas, J. Pena, J.C. Doadrio, M. Vallet-Regí, *J. Biomed. Mater. Res.* A 84 (2008) 99-107.
- [10] D. Siek, J. Czechowska, W. Mróz, A. Zima, S. Burdyńska, R. Załączny, A. Ślósarczyk, *Bull. Pol. Acad. Sci. Technol. Sci.* 61 (2) (2013) 433-439.
- [11] K. Sakai, Y. Hashimoto, S. Baba, A. Nishiura, N. Matsumoto, *Dent. Mater. J.* 30 (6) (2011) 913-922.
- [12] G. Grandi, C. Heitz, L.A. dos Santos, M.L. Silva, M.S. Filho, R.M. Pagnocelli, D.N. Silva, *Mater. Res.* 14 (1) (2011) 11-16.
- [13] M.-K. Ahn, Y.-W. Moon, Y.-H. Koh, H.-E. Kim, *Ceram. Int.* 39 (2013) 5879-5885.
- [14] Döbelin N, Brunner TJ, Stark WJ, Fisch M, Conforto E, Bohner M. Thermal treatment of flame-synthesized amorphous tricalcium phosphate nanoparticles. *J Am Ceram Soc* 2010;93 (10):3455-63.
- [15] R.G. Carrodeguas, S. De Aza,  $\alpha$ -Tricalcium phosphate: Synthesis, properties and biomedical applications. *Acta Biomaterialia* 7 (2011) 3536-3546
- [16] Gibson IR, Akao M, Best SM, Bonfield W. Phase transformation of tricalcium phosphates using high temperature X-ray diffraction. In: Kokubo T, Nakamura T, Miyaji F, editors. *9th International Symposium on Ceramics in Medicine*. Otsu, Japan: Pergamon Press, Oxford; 1996. p. 173-6.
- [17] Camiré CL, Jegou Saint-Jean S, Hansen S, McCarthy I, Lidgren L. Hydration characteristics of  $\alpha$ -tricalcium phosphates: comparison of preparation routes. *J Appl Biomater Biomech* 2005;3(2):106-11
- [18] Burkes DE, Moore JJ, Ayers RA. US 20080112874 A1 Method for producing calcium phosphate powders using an auto-ignition combustion synthesis reaction. US 2008/0112874 A1 (Patent) 2008.
- [19] Volkmer TM, Bastos LL, Sousa VC, Santos LA. Obtainment of alpha-tricalcium phosphate by solution combustion synthesis method using urea as combustible. *Key Eng Mater* 2009;396-398:591-4.
- [20] L.A. Azaroff, *Elements of X-ray Crystallography*, McGraw-Hill, New York, 1968. pp. 38-42
- [21] E. Landi, A. Tampieri, G. Celotti, S. Sprio, Densification behaviour and mechanisms of synthetic hydroxyapatites, *J. Eur. Ceram. Soc.* 20 (2000) 2377-2387.
- [22] Slosarczyk A, Paluszkiwicz C, Gawlicki M, Paszkiewicz Z. The FTIR spectroscopy and QXRD studies of calcium phosphate bases materials produced from the powder precursors with different Ca/P ratios. *Ceram Intern* 1997;23:297-304.
- [23] Cheng ZH, Yasukawa A, Kandori K, Ishikawa T. FT-IR study on incorporation of CO<sub>2</sub> into calcium hydroxyapatite. *J Chem Soc Faraday Trans* 1998;94:1501-5.
- [24] Sz-Chian Liou, San-Yuan Chen. Transformation mechanism of different chemically precipitated apatitic precursors into  $\beta$ -tricalcium phosphate upon calcinations. *Biomaterials* 23 (2002) 4541-4547.
- [25] A. Destainville, E. Champion, D. Bernache-Assollant, E. Laborde, Synthesis, characterization and thermal behavior of apatitic tricalcium phosphate, *Materials Chemistry and Physics* 80 (2003) 269-277.
- [26] N. Rameshbabu, K. Prasad Rao, "Microwave synthesis, characterization and in-vitro evaluation of nanostructured bi-phasic calcium phosphates", *Curr. Appl Phys.*, 9 (2009) S29-S31.
- [27] Kristine Salma, Liga Berzina-Cimdina, Natalija Borodajenko. Calcium phosphate bioceramics prepared from wet chemically precipitated powders. *Processing and Application of Ceramics* 4 [1] (2010) 45-51.
- [28] Asmae Massit, Ahmed El Yacoubi, Brahim Chafik El Idrissi, Khalid Yamni. Synthesis and characterization of nano-sized  $\beta$ -Tricalcium phosphate: Effects of the aging time. *IOSR Journal of Applied Chemistry (IOSR-JAC)* Volume 7, Issue 7 Ver. I. (July. 2014), PP 57-61.
- [29] A. Massit, A. Yacoubi, B. Chafik El Idrissi, K. Yamni. SYNTHÈSE DE NANOPARTICULES DE POSPHATE TRICALCIQUE  $\beta$  PAR VOIE AQUEUSE. *Verres, Céramiques & Composites*, Vol. 4, N°1 (2015), 1-6.
- [30] Jillavenkatesa A, Condrate Sr RA. The infrared and Raman spectra of  $\beta$ - and  $\alpha$ -tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ). *Spectrosc Lett* 1998;31(8):1619-34.
- [31] L. Sha, Y. Liu, Q. Zhang, M. Hu, Y. Jiang, Microwave-assisted co-precipitation synthesis of high purity  $\beta$  tricalcium phosphate crystalline powders, *Mater. Chem. Phys.* 129 (2011) 1138-1141

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