

SYNTHESIS AND CHARACTERIZATION OF CERAMIC HYDROXYAPATITE

Nicolae ANGELESCU, Dan UNGUREANU, Vasile BRATU, Violeta Anghelina
Valahia University of Targoviste

Abstract. *In this paper we present a synthesis method of calcium phosphate bioceramics such as hydroxiapatite, the mineral component of bones and hard tissue in mammals. Investigations carried out have confirmed obtaining of hydroxyapatite characterized by a high degree of crystallinity, purity, and a good stoichiometry.*

Keywords. *Hydroxyapatite, chemical co-precipitation, x – ray diffraction, X-ray fluorescence spectroscopy*

1. INTRODUCTION

In this paper we present a synthesis method of calcium phosphate bioceramics such as hydroxiapatite, the mineral component of bones and hard tissue in mammals. Hydroxyapatite ceramics are of considerable interest for clinical applications due to their high biocompatibility with hard tissues, particularly, bone and teeth tissue [1, 2]. Hydroxyapatite is the most stable calcium phosphate in an aqueous solution, they solubility depend on numerous factors such as: Ca/P ratio, crystallinity index, porosity, particle size and foreign ions such as carbonates, fluorine, chlorine or magnesium ions, which are often present in hydroxyapatite as impurities [3]. The production of synthetic ceramic hydroxyapatite powders may be classified under two main headings: processing of hard tissue from mammal or coral, and laboratory synthesis (chemical co precipitation, reactions in solid state, hydrothermal methods, sol – gel process) [4, 5, 6]. The proposed method is based on chemical co precipitation process. The hydroxyapatite powders are obtained after the chemical reaction of inorganic oxide solution. As the starting reagent, analytical grade calcium hydroxide and orthophosphoric acid were used. The choices of this method take account of the main advantages of wet chemical synthesis [7].

- use of aqueous solution
- probability of contamination during processing is very low.
- low processing costs

Also, the method chosen in this case is quite simple, non-polluting by nature and suitable for large scale production.

Disadvantages arising in the use of this procedure consist of relatively low solubility of calcium hydroxide and phosphoric acid addition rate, which must remain sufficiently low in order to avoid increasing acidity of the reaction environment. In this case the reaction products is formed, such as calcium hydrogen phosphate. The synthesis results show a hydroxyapatite with stoichiometry desired and highly crystallinity was obtained. The heat treatment applied was prevent decomposition of hydroxiapatite powders obtained by

this method in other calcim phosphate compounds, such as β - tricalcium phosphate. An important role in synthesis of hydroxyapatite powders with a stoichiometry as close as possible of theoretical value, ie a ratio $Ca / P = 1.67$, had the purity of reactants and main process parameters involved in the synthesis: pH level of reaction, reactants addition rate, stirring speed of reactants, reaction temperature.

2. EXPERIMENTAL PROCEDURE

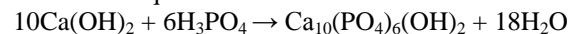
2.1. Hydroxyapatite synthesis

Hydroxyapatite was synthesized via the chemical precipitation method. As the starting reagent, analytical grade $Ca(OH)_2$, H_3PO_4 and NH_4OH were used. Properties of the chemicals used to produce hydroxyapatite powders are summarized in Table 1

Table1. Raw materials used for the processing of hydroxyapatite ceramics

Name	Features		Producer
	Chemical formula	Purity/ Solution in water, %	
Calcium hydroxide	$Ca(OH)_2$	99.4	Acros Organics, Belgia
Orthophosphoric acid	H_3PO_4	86.14	Fisher Chemical, S.U.A

The chemical equation that describes the reaction is :



A stoichiometric hydroxyapatite was prepared using the precipitation reaction between 0,3 moles calcium hydroxide, $Ca(OH)_2$ in 500 ml distilled water and 0,18 moles ortophosphoric acid, H_3PO_4 in 200 ml distilled water, as we present in figure 1.

In order to obtain a hydroxyapatite slurry, H_3PO_4 solution was added by dropwise, for the 1 - 4 hours over the alkaline solution based on $Ca(OH)_2$, in conditons of intense stirring.

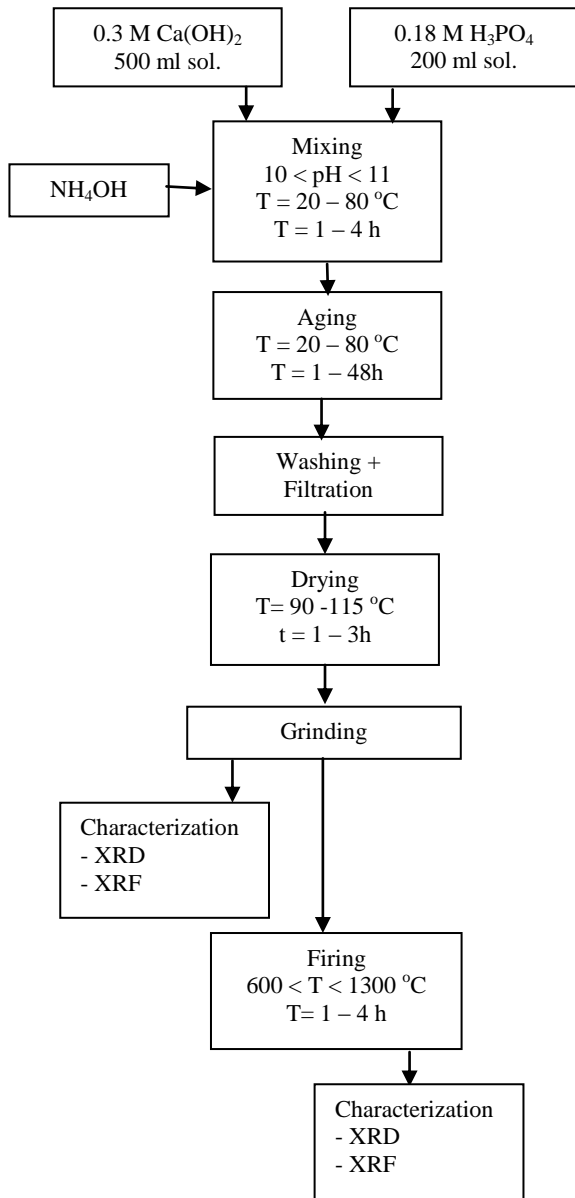


Fig. 2. Flow chart for synthesis of hydroxyapatite by chemical co-precipitation process

In order to obtain a stoichiometric hydroxyapatite, therefore $Ca / P = 1.67$, the pH of the solution was continuously adjusted, $pH > 7$, by the addition of NH_4OH [3].

The reaction mixture was stirred for several hours at a temperature between 20 and 80°C and then aged for up to 48 hours. In order to remove any impurities, the precipitate was filtered and washed with distilled water and / or ethanol. Precipitates were filtered by using a Buehler funnel and washed several times with distilled water. The filtered precipitate was oven dried at 80°C and then ground to a powder in an mortar and pestle. In the next step, hydroxyapatite powders was calcined at 800°C for 30 min. Finally, powders was then ball milled, using a porcelain mill pot with tungsten carbide balls, for 1 hour.

2.2 Characterization technique

Investigations of hydroxyapatite powder samples were made using a Seifert X – ray diffractometer with $Cu_{k\alpha} = 1.5405\text{\AA}$ radiation generated at a voltage of 40 kV and a current of 30 mA. The samples were examined from 20° to 60° with a step size of 0,05 ° 2θ/s. X - ray analysis was used to assess the present phases, the degree of crystallinity and size of crystallites, in case of hydroxyapatite studied. Identification of phases was achieved by comparing the diffraction patterns of hydroxyapatite with ICDD – PDF2 standards.

Table 2. Phases identifications present in the samples obtained by chemical co-precipitation

Calcium phosphate compound	Chemical formula	PDF files
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	9-432
Calcium Phosphate (Whitlockite)	$\beta-Ca_3(PO_4)_2$	9-169
Calcium Phosphate	$\alpha-Ca_3(PO_4)_2$	9-348
Calcium Oxide (Lime)	CaO	37-1497

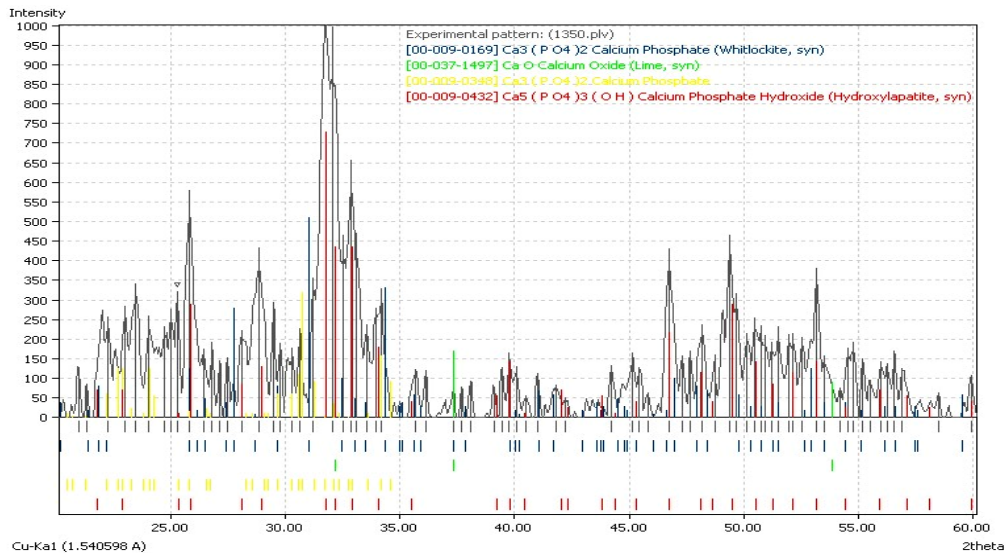
Also, the calcium and phosphorus contents of hydroxyapatite powders were determined by X-ray fluorescence (XRF) using a Panalytical Axios spectrometer. In order to produce high-quality samples, for a highly accurate and reproducible analysis an automated sample preparation system Pearl X`3 was used.

3. RESULTS

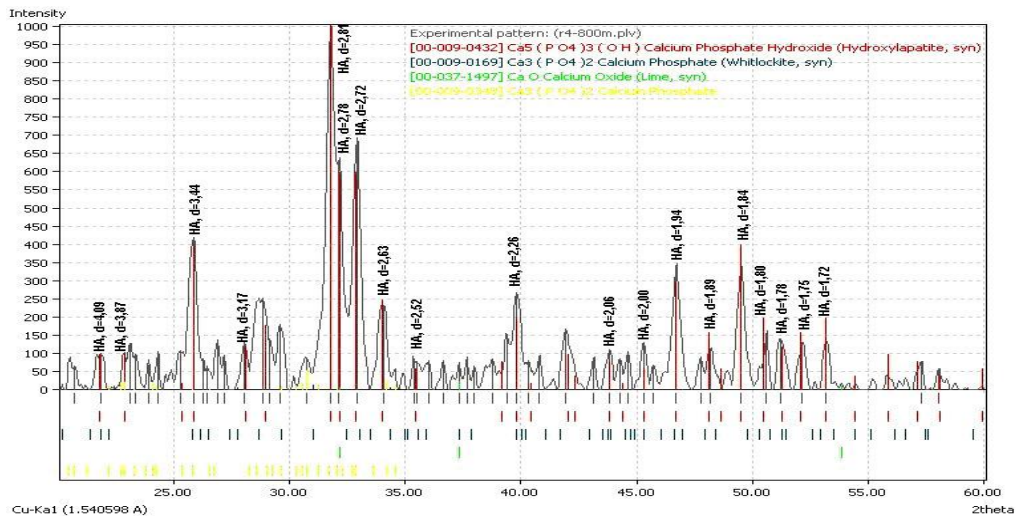
Figure 2 show the X - ray diffraction patterns for hydroxyapatite samples, according with experimental procedure above described, and the diffraction lines for file PDF 9 – 432.

All xrd patterns shows peaks characteristic of hydroxyapatite, both present in standards and in literature. The major phase, as expected, is hydroxyapatite, which is confirmed by comparing data obtained with the standard ICDD - PDF2 (The International Centre for Diffraction Data - Powder Diffraction File 2) and applications Match 1.9 - Crystal Impact Inc. and PowderX Ver 2004-04.72 Pro. In figure 2a are present xrd pattern for as dried hydroxyapatite sample. This pattern revealed the presence of an important amorphous phase.

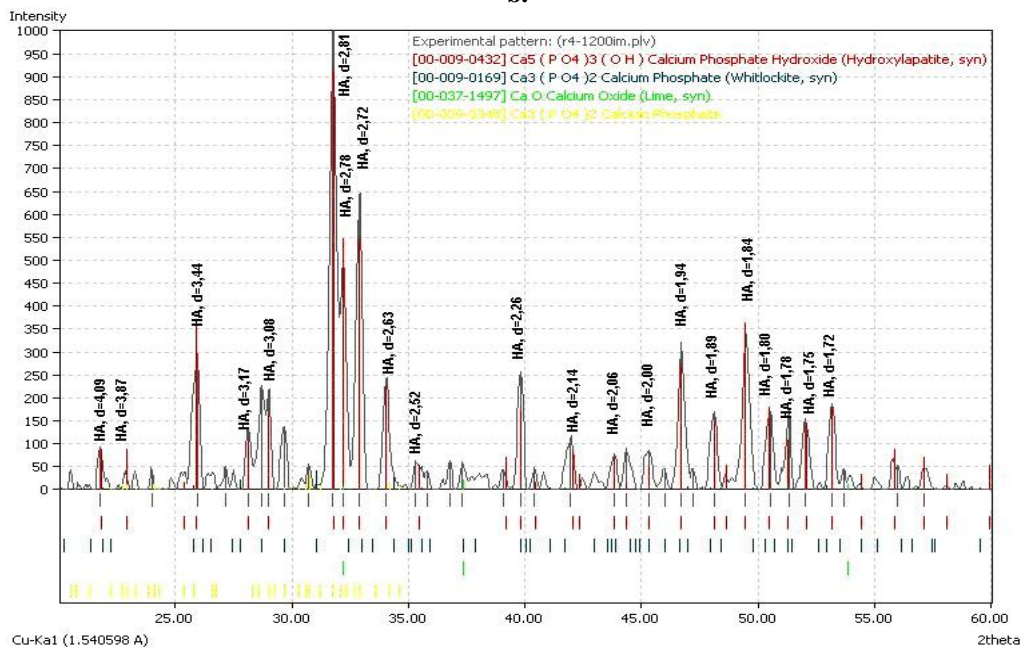
The proportion of amorphous phase decreases with increasing of heat treatment temperature at 800°C, respectively 1200°C, as are presented in figure 2b and figure 2c. In case of samples heat treated at temperatures above 800°C, hydroxyapatite peaks located at 25.88; 31.77; 32.19; 32.90; 34.04; 39.82; 46.71; 49.46; 53.14 (2θ) are clearly evidenced. The shape of these peaks become more sharper once the temperature of heat treatment increase at 1200°C.



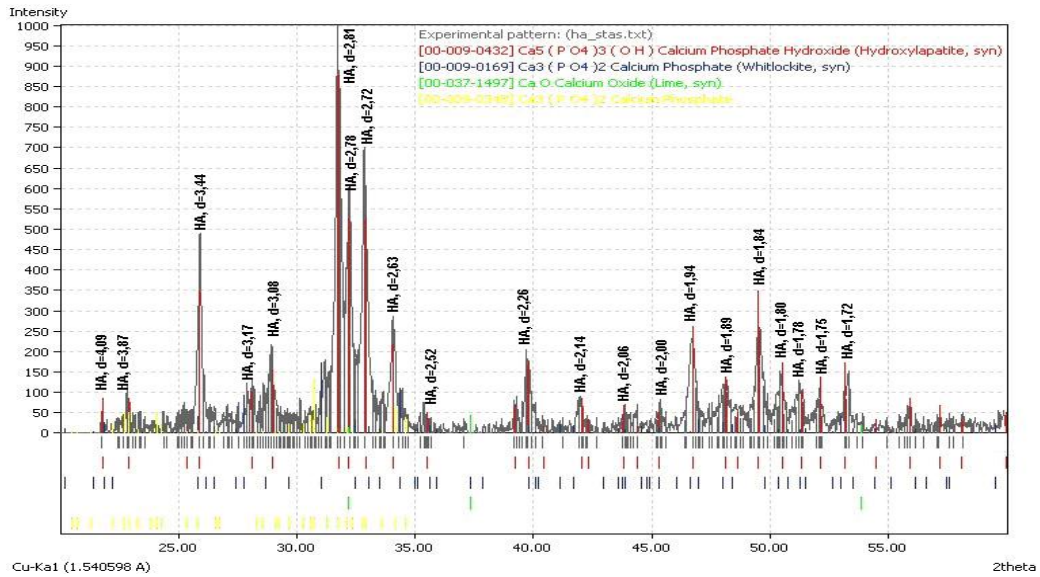
a.



b.



c.



d.

Figure 2. X- ray diffraction patterns of hydroxyapatite samples:

- a) samle as percipitated b) sample after heat treatment at 800°C; c) sample after heat treatment at 1200 °C; d) standard sample

This shape is attributed to increased size of hydroxyapatite crystallites. To estimate the size of crystallites is using Debye-Scherrer relationship:

$$\tau = \frac{K \cdot \lambda}{w \cdot \cos(\theta)}$$

where: w is defined as the a full width of the intensity distribution at half of the maximum intensity (FWHM – full width at half maximum) and give the difference between the two 2 theta values, in radians; $FWHM = w = 2\theta_{max} - 2\theta_{min}$ [20].

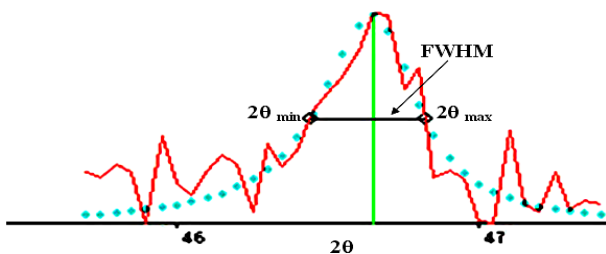


Figure 3. Generic example of full width at half maximum representation

K = constant dependent on crystallite shape, $0.8 < K < 1.1$; λ is the wavelength of monochromatic radiation, $\lambda_{CuK\alpha} = 1.5405 \text{ \AA}$, and θ is the Bragg angle, in degree.

Table 3. The estimated values of hydroxyapatite crystallites in the (002) plane

Sample	Plane	FWHM, °	□□□nm
HA-as dried	(002)	0.847	10.7
HA – 800		0.315	28.7
HA – 1200		0.155	58.42
HA- etalon		0.161	56.25

As shown in table 3, based on Debye-Scherrer relationship is in the range 10-58 nm. These data are consistent with those presented for the standard sample analysis and the literature. The estimated crystallites size of hydroxyapatite are in according with data obtained regarding the crystallinity degree. In terms of x-ray diffraction, the crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak (halo). The ratio between these intensities can be used to calculate the amount of crystallinity in the material.

An estimation regarding crystallinity degree and relative crystallinity, in case of hydroxyapatite samples, are presented in table 4. The relative crystallinity was calculated as a ratio between both crystallinity degrees of hydroxyapatite samples obtained in laboratory and standard sample.

Table 4. The estimated value of crystallinity degree and relative crystallinity in case of all hydroxyapatite samples

Samples	Crystallinity degree, %	Relative crystallinity, %
HA-as dried	54.3	61.63
HA – 800	68.3	77.52
HA – 1200	82.4	93.53
HA- standard	88.1	100

The XRD analysis results show that secondary phases such as β -tricalcium phosphate, $\beta - Ca_3(PO_4)_2$, and calcium oxide (CaO) were not found. The only relevant peak corresponding to secondary phases, in this case α -tricalcium phosphate, $\alpha - Ca_3(PO_4)_2$, was identified at 30.73 (2 θ). Relative intensity of the peak situated at 30.73 (2 θ) will decrease proportionally with heat treatment temperature applied to the hydroxyapatite powders studied.

Results of x-ray diffraction analysis are supported by the semi quantitative chemical analysis achieved by X-ray fluorescence (XRF). In table 5 are presented the results of XRF analysis for the sample as dried, heat treated at 1200°C and, for a commercial hydroxyapatite.

Table 5. Results of semi quantitative chemical analysis achieved by X-ray fluorescence (XRF) in case of both laboratory-synthesized and commercial hydroxyapatite

Sample	CaO, %	P ₂ O ₅ , %	Ca, %	P, %	Ca / P
HA-commercial	57,3	41,5	40,95	18,11	1,74
HA-as dried	52,35	37,9	37,41	16,53	1,74
HA-1200	55,93	42,69	39,97	18,62	1,66

The chemical analysis by X-ray fluorescence reveals a good stoichiometry, very close to the theoretical value, Ca / P = 1.67, for the sample heat treated at 1200°C. Thus, an important role in achieving these results had purity of reactants and the most important parameters involved in the synthesis process : pH level of reaction, reactants addition rate, stirring speed of reactants, reaction temperature. They play an important role in obtaining the proper products for their intended applications.

4. CONCLUSION

The proposed method for the synthesis of hydroxyapatite powders led to obtaining a product with a high degree of crystallinity and purity.

The crystallinity degree and the relative crystallinity was 82.5%, respectively 93.53%, in case of the sample heat treated at 1200°C.

The results above mentioned was compared with data obtained from hydroxyapatite X – ray diffraction patterns published in American Mineralogist Structure Database (AMCSD). The positive trend regarding crystallinity degree once with increasing of heat treatment temperature is confirmed by the estimated values of hydroxyapatite crystallites.

The X –ray diffraction analysis did not reveal the presence of calcium phosphate compounds such as: β – Ca₃(PO₄)₂, α – Ca₃(PO₄)₂, CaO as secondary phases. The results of semi quantitative chemical analysis achieved by X-ray fluorescence (XRF) confirm that a hydroxyapatite samples obtained in laboratory has a calcium phosphorous ratio between 1.66 and 1.74, very close to the stoichiometric value.

An essential role in obtaining this value was the heat treatment applied and the optimal choice of parameters involved in the synthesis process, such as: pH level of reaction, reactants addition rate, stirring speed of reactants and reaction temperature.

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