

**Preparação e Caracterização de Hidroxiapatita pelo método de precipitação e
tratamento térmico**

**Preparation and Characterization of Hydroxyapatite by the precipitation method and
heat treatment**

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tratamiento térmico**

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Resumo

Hidroxiapatite é uma substância sintética em formato de microesferas compostas de cálcio e fosfato, presente nos ossos humanos e esmalte dos dentes. O objetivo do trabalho foi sintetizar a hidroxiapatita, a partir da solução de nitrato de cálcio e fosfato diamônico pelo método de precipitação e tratamento térmico, obtendo a hidroxiapatita em forma de pó. Para estudar sua evolução estrutural, utilizou-se a espectroscopia no infravermelho com transformada de Fourier (FTIR), a difração de raios-X (DRX) e a espectroscopia Raman. Os resultados mostram que a nanocristalina de hidroxiapatita pode ser produzida com sucesso pela técnica de precipitação a partir de matérias-primas.

Palavras- Chave: Hidroxiapatita; Caracterização; Precipitação.

Abstract

Hydroxyapatite is a synthetic substance in the form of microspheres composed of calcium and phosphate, present in human bones and tooth enamel. The objective of the work was to synthesize hydroxyapatite, from the solution of calcium nitrate and diamonic phosphate by the method of precipitation and heat treatment, obtaining the hydroxyapatite in powder form. To study its structural evolution, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Raman spectroscopy were used. The results show that the hydroxyapatite nanocrystalline can be successfully produced by the precipitation technique from raw materials.

Keywords: Hydroxyapatite; Characterization; Precipitation.

Resumen

La hidroxiapatita es una sustancia sintética en forma de microesferas compuestas de calcio y fosfato, presente en los huesos humanos y el esmalte dental. El objetivo del trabajo fue sintetizar hidroxiapatita, a partir de la solución de nitrato de calcio y fosfato diamónico mediante el método de precipitación y tratamiento térmico, obteniendo la hidroxiapatita en forma de polvo. Para estudiar su evolución estructural, se utilizaron espectroscopía infrarroja

por transformada de Fourier (FTIR), difracción de rayos X (XRD) y espectroscopía Raman. Los resultados muestran que la hidroxiapatita nanocristalina se puede producir con éxito mediante la técnica de precipitación a partir de materias primas.

Palabras clave: Hidroxiapatita; Caracterización; Precipitación.

1. Introduction

The biomaterials have been getting one large attention by part of the scientific community. The hydroxyapatite (HAp), with its chemical formula of $(\text{Ca}_5(\text{PO}_4)_3\text{OH})$, and ratio of Ca/P equal to 1.67 (Santos, 2005). Is a bioceramic widely studied due to their chemical similarity to component mineral from bone. in addition, it is biocompatible, non exhibits effects cytotoxic, bioactive and thermodynamically stable in the fluid body, as well as with hard tissue, skin and muscle, which places as an attractive material for a wide range of applications in the field biomedical. Unfortunately, due to low stability, especially in environments wet, the HAp currently not can be used to load heavy applications, such as teeth or artificial bones (Suchanek, Yoshimura & Mater, 1998).

Various techniques have been used for the preparation of HAp powders. Two most used ways are wet methods and solid state reactions. The first method can be divided into three groups: precipitation, hydrothermal technique and hydrolysis of other calcium phosphates (Aoki, 1991).

It is possible to improve the properties of HAp ceramics, controlling important parameters of precursors in their preparation reaction, such as particle size and shape, particle distribution and agglomeration (Best & Bonfield, 1994). After nanocrystalline of HAp exhibit greater surface area (LeGeros. (1993). It can provide better density and reduced sintering temperature (Yeong, Wang & Ng, 1999). In addition, it is also expected that HAp when in nanometric character has better bioactivity than larger crystals (Stupp & Ciegler, 1992) . Recently, the use of precipitation processes for the synthesis of HAp has become an important research objective (Han, et al. 2004). The HAp pure crystallizes in the monoclinic form at temperatures up to 250 ° C; however, above this temperature, the phase transition to the hexagonal form occurs with space group P 63/m. Natural HAp crystals exhibit hexagonal conformation and have a single cell with network parameters: $a = b = 9.389 \text{ \AA}$ and $c = 6.869 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ (Brundavanam et al., 2013).

The objective of the work was to synthesize hydroxyapatite, from the solution of calcium nitrate and diamonic phosphate by the method of precipitation and heat treatment, obtaining the hydroxyapatite in powder form.

2. Methodology

The sample was prepared through the synthesis of nanocrystalline hydroxyapatite using the precipitation method, by the author Mobashenpour et al (2007). This method uses the hydrated calcium phosphate solution of hydrated calcium nitrate and diamonium by the method of precipitation and heat treatment of hydroxyapatite powders.

Such a technique involves wet reactions between calcium and phosphorus precursors with temperature and pH control of the solution. The precipitated powder is calcined at 400-600°C or even at higher temperatures, in order to obtain a stoichiometric apatite structure. Rapid precipitation during the titration of the phosphate solution in calcium solution can lead to a lack of chemical homogeneity in the final product. Slow titration and diluted solutions should be used to improve the chemical and stoichiometric homogeneity of the resulting HAP. Careful control of the solution conditions is critical in wet precipitation.

2.1. Sample characterization

2.1.1. Diffraction X-ray (DRX)

The X-ray diffraction technique is fundamental in the analysis of crystalline structures of powders and allows the identification of the material. The analysis is based on the identification of Bragg's reflections and comparison with an ICSD database (Inorganic Crystal Structure Database, Germany), where it is possible to identify the material and determine the possible phases formed by it (Lopes et al, 2015).

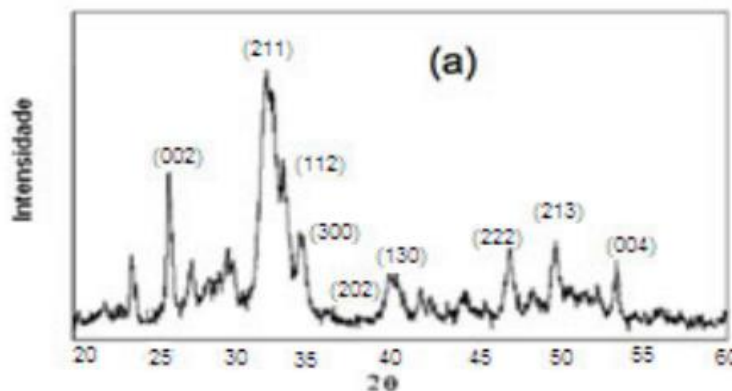
The identification of the sample synthesized by X-ray diffraction was carried out on a Panalytical diffractometer, in which experimental set up detections of 40 kV, current of 30 mA and observation range between $30^\circ \leq 2\theta \leq 90^\circ$ were used. The X-ray diffraction analysis was carried out in the design department of the Federal University of Pernambuco, campus agreste. The commercial software Origin was used, based on simulated X-ray diffraction data, to model the crystalline structure of the HAp powder .

The Scherrer equation is one of the most used ways of calculating particle size using X-ray diffraction data. This method takes into account the fact that the widening of the diffraction peak is caused by the size of the crystallite.

A single unit cell of HAp consists of 44 atoms, with 10 atoms of calcium (Ca), 6 atoms of phosphatotetrahedral (PO_4^{3-}), and 2 OH groups very well organized in the hexagonal atomic structure (Brundavanam et al, 2013). The network parameters of HAp, obtained from X-ray diffraction measurements, are $a = b = 9.389 \text{ \AA}$ and $c = 6.869 \text{ \AA}$. The hexagonal cell of the space group $P63/m$ has a cell volume of 528.79 \AA^3 (Tas, 2001).

Figure 1, the author Lopes et al (2015), shows diffraction X-ray d and sample HAp commercial, with spikes in expected positions. The characteristic peaks, referring to the crystalline planes 002, 211 and 300 of HAp are observed in the 2θ diffraction angles of $2\theta = 31.7, 32.2$ and 33° . It is also possible to observe some secondary peaks of lower intensity located at $2\theta = 26, 40, 46.5$ and 49° , and others less intense located at $2\theta = 29$ and 53.2° , which corroborates the existence of hydroxyapatite. It was concluded that the commercial powder used in the manufacture of foams did not present different phases from HA, being highly crystalline.

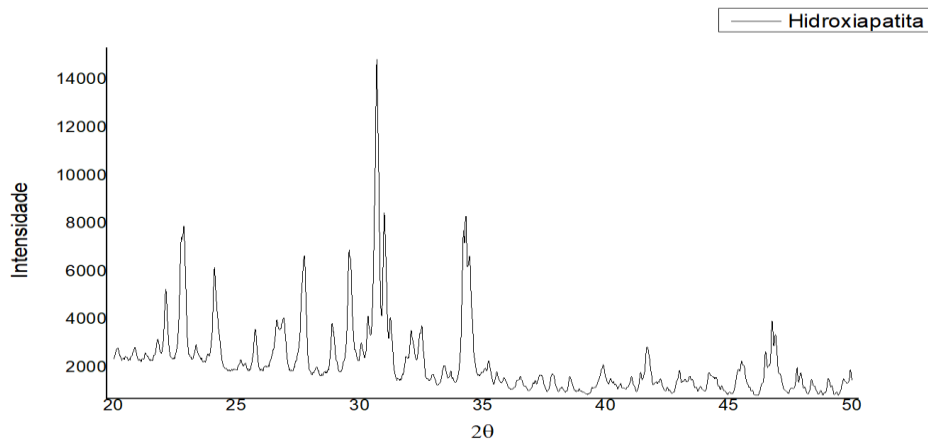
Figure 1: X-ray diffraction spectrum generated in the modeling using the PowderCell software.



Source: Lopes et al., 2015

In comparison with the sample of HAp sintered by precipitation, we could see peaks similar to those of the author Lopes et al. (2015), also in the 002, 211 and 300 plans, the values were not closer due to the difference in crystallinity of the HAp samples. Figure 2 shows the spectrum obtained from the sample, where its peaks are narrower compared to figure 1, thus characterizing the sample obtained as more crystalline.

Figure 2: X-ray diffraction spectrum of the sample obtained from HAp generated using Origin software.



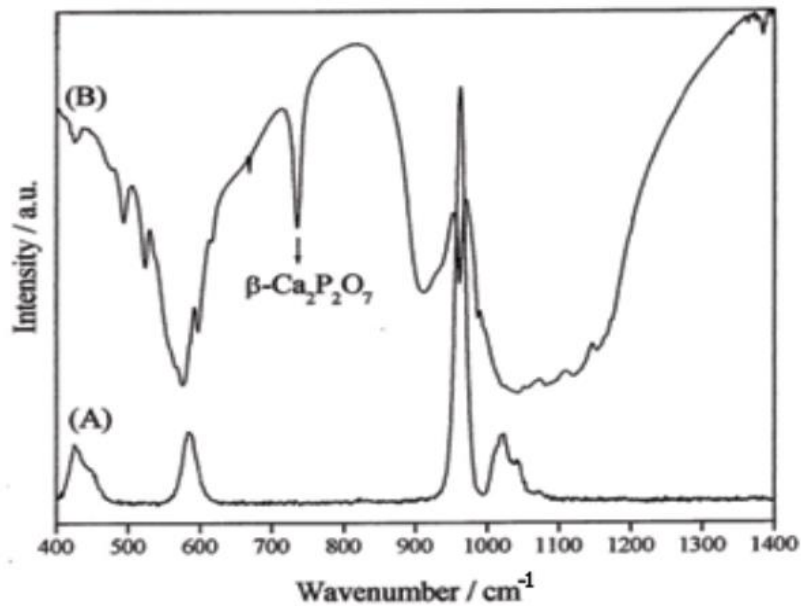
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2.1.2. RAMAN

The Raman spectroscopy technique determines the functional groups of the sample examined, thus ensuring that the synthesized material is exactly what is desired.

The Raman spectrum of HAp do Torres- Gallegos et al (2012) (Figure 3) shows a very strong band at 962 cm^{-1} , attributed to ν_1 ; the strong bands at 590 and 565 cm^{-1} and the peak at 571 cm^{-1} are attributed to a group of component factors of ν_4 ; the middle bands at 1070 and 1040 cm^{-1} are assigned to ν_3 ; the weak band at 470 cm^{-1} (in contrast to the previous assignments) can be assigned to ν_2 and the medium intensity range at 3570 cm^{-1} in an OH vibrational mode.

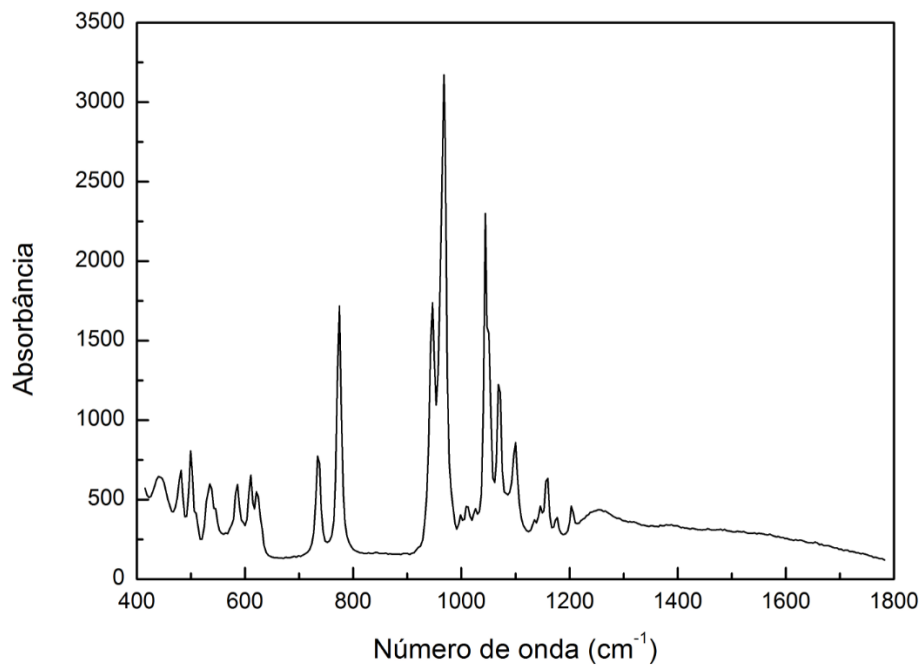
Figure 3: (a) Raman and (b) spectrum IV of the inorganic HAp replica.



Source: Torres- Gallegos et al., 2012

In the synthesized sample, the main peaks present in hydroxyapatite were identified, especially those obtained at points 400, 600 and in the range 900 to 1000. When comparing in the literature a Raman spectrum obtained from a hydroxyapatite of a dental enamel by studies of Torres- Gallegos et al. (2012) it was possible to identify a similar profile, as well as the signals 600 and 950. As well the requirement main scan as a positive identifier for identifying hydroxyapatite obtained using this analysis tool.

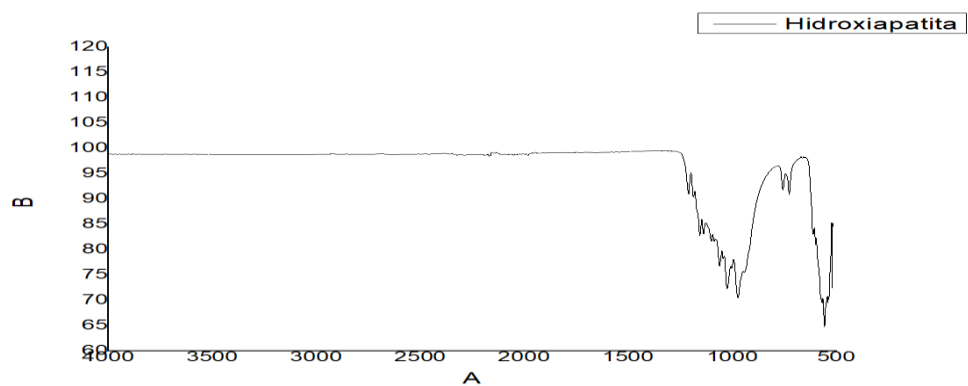
Figure 4: Raman spectroscopy of the sample obtained from HAp generated through Origin software.



Source: own

2.1.3- Fourier transform infrared (FTIR)

Figure 5. Spectroscopy IV of the sample obtained from HAp generated through Origin software



Source: own

The bands in the region of 474, 572, 601, 1032 to 1090 cm^{-1} can be attributed to changes in the connection distances (elongation) and to the change in the connection angle (flexion) of the PO_4^{3-} groups. It is observed how the strongest bands are in the regions of 1100 to 1000 cm^{-1} . The bands around 630 cm^{-1} and 3570 cm^{-1} correspond to the stretching of the hydroxyl groups, OH^- , of HA. The samples treated at (550, 650, 750 and 850) $^\circ\text{C}$ also have bands around 1458 cm^{-1} and 1412 cm^{-1} corresponding to phosphoric acid HPO_4^{2-} and not NH_4^+ , since the sample has already been calcined at temperatures above 700 $^\circ\text{C}$, this should not appear on the structure. Bands around 1630 cm^{-1} can be attributed to changes in the hydrogen bonding angle in crystallized water; this band also appears in samples treated at (550, 650, 750 and 850 and 950) $^\circ\text{C}$.

Small displacements are also observed in the bands corresponding to OH^- . The difference between treated samples at temperatures below 900 $^\circ\text{C}$ and treated at temperatures higher than those, present only in the samples treated below 900 $^\circ\text{C}$ (bands at 1458 cm^{-1} and 1413 cm^{-1}) should be noted, what with chance is the least crystalline. The presence of this ion, occluded within the structure and not as a phase, shows how it competes with OH^- and phosphates. In addition, at low calcination temperatures, its presence may be due to an inconclusive reaction, given the short time that the system has to achieve its stability.

3. Final Considerations

It can be concluded that the hydroxyapatite compound with nanoparticles can be successfully produced by the precipitation technique from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and solution $(\text{NH}_4)_2\text{HPO}_4$ as starting materials.

The powder consists of fine particles, forming uniform and dispersed agglomerates. Clinical cases have shown that this product is effective for causing bone tissue growth.

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