

## Production and thermal stability of pure and Cr<sup>3+</sup>-doped hydroxyapatite

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**Abstract.** Hydroxyapatite (HAP) have been used as starting material for biomedical applications. The pure and Cr<sup>3+</sup>-doped hydroxyapatite were prepared by chemical precipitation reactions at 100, 500 e 800 °C in order to investigate the thermal stability of these materials. The characterization of the thermal behavior of this phosphate, especially on the structural changes with heating, is very important for production of sunscreens. The powders were characterized using chemical analysis: X-ray diffraction (XRD) and thermal analysis. The present study was successful in the preparation of pure hydroxyapatite and chromium substituted hydroxyapatites with good thermal stability and nanoparticles formation.

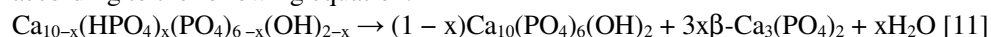
### 1. Introduction

In the last decade, synthetic hydroxyapatite (HAP) has been widely used in various clinical applications due to its compositional similarity to the mineral phase present in hard tissue of human body [1, 2]. Lately it has been studied for applications as active ingredients of inorganic sunscreens [3, 4]. The characterization of the thermal behavior of this phosphate, especially on the structural changes with heating, is very important for several applications. So it is very significant to reveal the thermal stability details of hydroxyapatite.

In the literature are found many methods to synthesize HAP crystals with different characteristics such as hydrolysis of other calcium phosphates, solid-state reactions [5] and various techniques of wet chemical synthesis [6, 7], etc. In this work the hydroxyapatite was prepared through aqueous precipitation processing. Unlike the synthesis for thermal processes, this method produces larger amounts of the material, besides being one of the most economical processes, simple with possibility of industrial application [8, 9]. The precipitation method makes possible the obtaining of homogeneous particles and the control of the concentration of the reactants [3, 9, 10].

Hydroxyapatite powders can be precipitated from conventional wet chemical methods and decomposed into a mixture of HAP and tricalcium phosphate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (TCP) by thermal treatment above 700 °C. This allows a direct processing of biphasic calcium phosphate ceramics HAP/TCP without the step of powder blending. The main interest in the last years is not only controlling the stoichiometry of synthetic HAP but also controlling the crystal size [11].

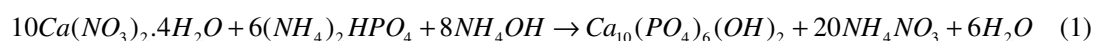
Considering calcium-deficient HAP change with thermal treatment to stoichiometric HAP and TCP according to the following equation:



The  $\text{Cr}^{3+}$  is a metal non toxicant that can be incorporate in HAP in order to produce fluorescence. For the measures of the fluorescence of the ions of  $\text{Cr}^{3+}$  in HAP is possible to identify the levels of HAP that are being incorporate to the human bone. The low toxicity of  $\text{Cr}^{3+}$  is partially due to the fact that many  $\text{Cr(III)}$  complexes are poorly soluble at physiological pH values and are not easily transported through the cell membranes. Complexes which are not able to penetrate into the cells may not induce toxic responses [2]. Besides  $\text{Cr}^{3+}$  is a metal that may generates optical absorption bands in the UV range when incorporated in a crystalline matrix. The biocompatibility HAP with the optical activity of the  $\text{Cr}^{3+}$  turn the HAP very interesting to be investigated as active ingredient for inorganic sunscreens. The objective of this work was to know the thermal behavior of pure and  $\text{Cr}^{3+}$ -doped HAP. To study the thermal stability of HAP is important in the determination of the great conditions of temperature for calcination of the obtained precipitate powders, as well as to know the thermal behavior of pure HAP and doped with  $\text{Cr}^{3+}$ . For example, producing pure and  $\text{Cr}^{3+}$ -doped HAP in a temperature of appropriate calcination the formation of species reactivates they can be avoided, and that will guarantee the success of your application in sunscreens.

## 2. Experimental procedure

Nanocrystalline HAP was prepared from an aqueous precipitation reaction using mixture of  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with  $\text{Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$ . The reaction can be written as follows [2, 3]:



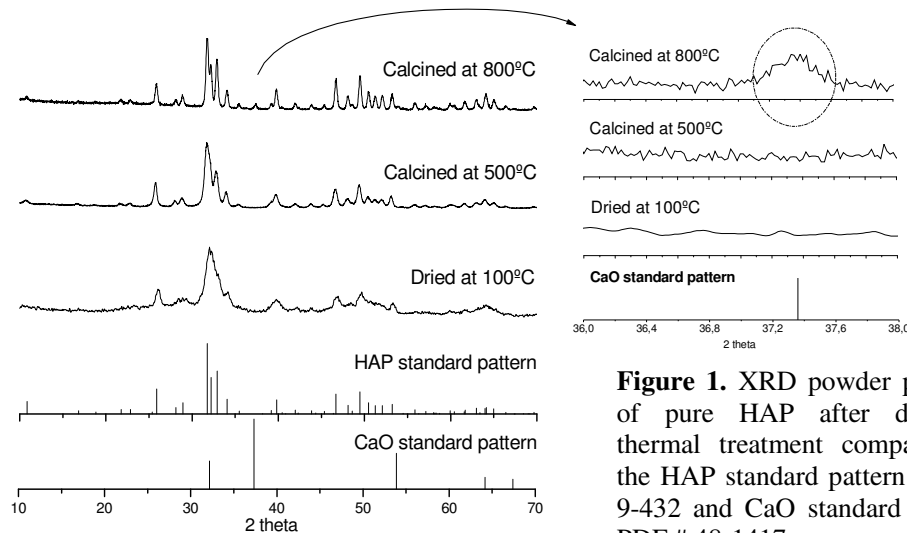
The aqueous solution of  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was slowly added to  $(\text{NH}_4)_2\text{HPO}_4$  at a rate of 1.5 ml/min, keeping the pH in 10.4. The pH was adjusted during the mixing using a solution of  $\text{NH}_4\text{OH}$  under a constant stirring condition at room temperature. After total addition of the  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with 0,01 mol/L  $\text{Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution, the suspension was matured during 30 min. Then, it was filtered and washed. The resulting precipitate received thermal treatment at 100 °C, 500 °C and 800 °C for 1 hour. It was varied the temperature of thermal treatment of the samples in order to verify the effects of the temperature in the thermal stability of the materials.

In this study the crystal behavior of the 100, 500 and 800 °C treated pure and  $\text{Cr}^{3+}$ -doped HAP powders were characterized by X-ray powder diffraction (XRD) and the thermal behavior was investigated by Differential thermal analysis (TG-DTA).

The XRD data were obtained on an X-ray diffractometer (Rigaku DMAX2000) with  $\text{CuK}\alpha$  radiation at 40 kV/40 mA with a spinning sample holder and a monochromator detector. The thermal decomposition of the samples was studied from 10 to 900 °C by TG, DTG and DTA using a TG-DTA apparatus of TA – Instruments, model SDT 2960, at a heating rate  $10^\circ\text{C min}^{-1}$ , synthetic air atmosphere, alumina crucibles and sample mass of approximately 9 to 13 mg.

## 3. Results and discussions

The XRD patterns of the pure HAP samples that received different thermal treatment are shown in figure 1. The standard HAP and CaO XRD patterns are also shown in the bottom part of the figures. The thermal treatment at 100 °C was sufficient to obtain the precipitate of HAP, however, broad diffraction peaks are observed indicating low crystallinity of the powders. It is possible to observe an increase of the crystallinity after calcination at 500 °C and a mixture of crystalline structures of HAP and calcium oxide (CaO) after calcination at 800°C. As this new phase is biocompatible [12], the material can be used in sunscreen. That shows that an extra amount of  $\text{Ca}^{2+}$  stayed in the mixture and reacted with the oxygen ( $\text{O}_2$ ) of the environment. Raynald et al [13] it observed the presence of a small amount of CaO and great amount of TCP in the HAP matrix when preparing HAP by aqueous precipitation method of  $(\text{NH}_4)_2\text{HPO}_4$  with  $\text{Ca(NO}_3)_2$  calcined at 1250 °C. In the literature the decomposition of HAP in temperatures above 700 °C is frequently found during the production of ceramic HAP [11, 13-15].



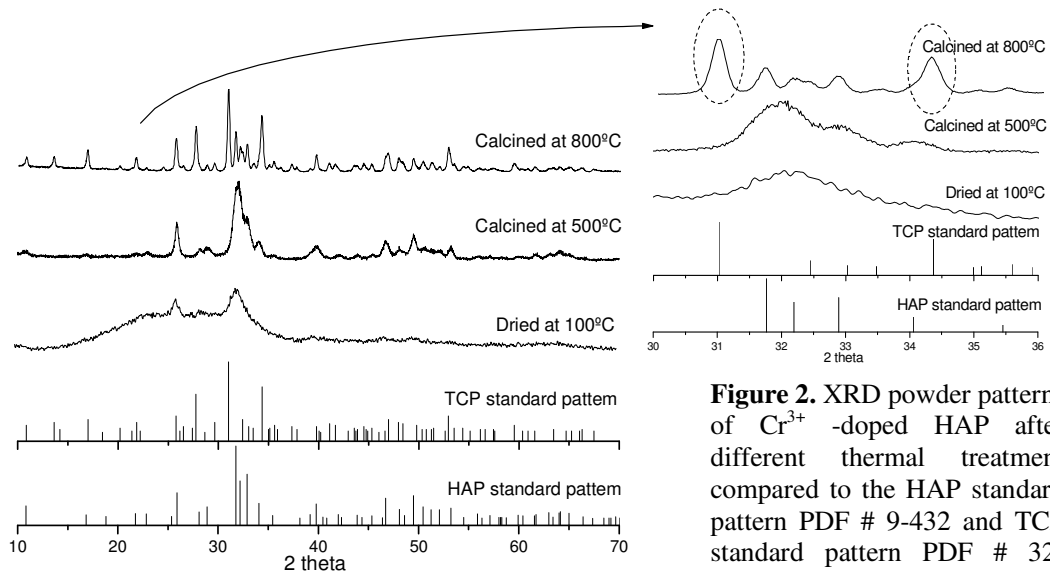
**Figure 1.** XRD powder patterns of pure HAP after different thermal treatment compared to the HAP standard pattern PDF # 9-432 and CaO standard pattern PDF # 48-1417.

Figure 2 compares the XRD patterns of the  $\text{Cr}^{3+}$ -doped HAP after different treatments of calcinations. All the patterns show only the peaks characteristic of HAP.

As shown in figure 2 the  $\text{Cr}^{3+}$ -doped HAP treated to 100 °C it presented an amorphous structure with only two picks crystalline of HAP. For the precipitate calcined at 800 °C there is the decomposition of the apatite to form TCP that is biocompatible.

Doped HAP show a significant correlation between the crystallinity and the thermal treatment. The crystallinity of the material decreases with the incorporation of the dopant. The correlation between crystallinity and thermal treatment is evident for pure and doped samples. That is more noted for dried at 100°C samples; the diffractograms of pure and doped calcined 500°C samples are very similar. The results of XRD patterns are compatible with the results of Wakamura et al [16].

The best definition of the powder XRD peaks as function of the calcination temperature is also related with the increase in the crystallite size. Comparing the pure sample and doped calcined 500 °C significant difference it is not observed as the crystallite size of the two samples. The table 1 presents the medium crystallite sizes calculated from Scherrer equation. The effect of the thermal treatment is well known from materials engineering studies. The results of crystallite size are very similar for pure and doped samples. The results indicate that a temperature increase favors the growth of the crystallites. Besides, the low values of crystallite sizes (<40 nm) indicates the formation of nanoparticles.

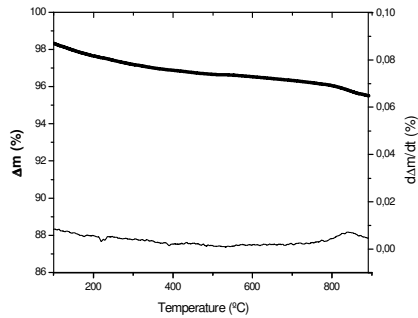


**Figure 2.** XRD powder patterns of  $\text{Cr}^{3+}$ -doped HAP after different thermal treatment compared to the HAP standard pattern PDF # 9-432 and TCP standard pattern PDF # 32-0176.

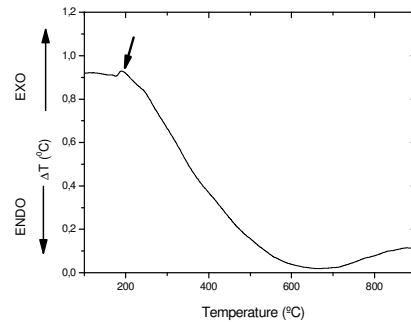
**Table 1.** Medium size crystallite obtained via XRD measurements using Scherrer's equation to HAP after different thermal treatment

| Temperature                 | Crystallite size<br>$\pm 1$ (nm) |
|-----------------------------|----------------------------------|
| Pure HAP                    |                                  |
| 100                         | 20                               |
| 500                         | 25                               |
| 800                         | 34                               |
| $\text{Cr}^{3+}$ -doped HAP |                                  |
| 100                         | 16                               |
| 500                         | 23                               |
| 800                         | 35                               |

TG, DTG and DTA curves of pure HAP calcined at 500 °C are shown in figure 3 and 4. The DTA curve shows a small exothermic peak in 191 °C, attributed to HAP of low crystallinity (Figure 4). In fact the powder XRD patterns showed formation of little crystalline HAP at the temperature of 100 °C. In fact the powder XRD patterns showed formation of little crystalline HAP at the temperature of 100 °C. The TG curve indicate a mass variation of 2.5% up to 800°C. The weight loss under 750 °C is attributed to the elimination of  $\text{H}_2\text{O}$  (Figure 3). As expected there are not peaks indicating phase transformation of the material in the temperature of 500 °C. The studies of XRD patterns showed that in 800 °C there is decomposition of the apatite into a mixture of HAP/CaO. Therefore, the mass loss starting from 770 °C refers to the decomposition of HAP in CaO.

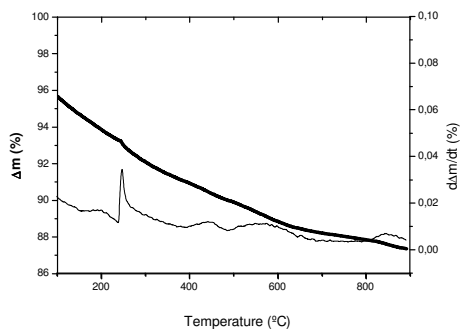


**Figure 3.** TG (bold line) and DTG of pure hydroxyapatite powder calcined at 500 °C.

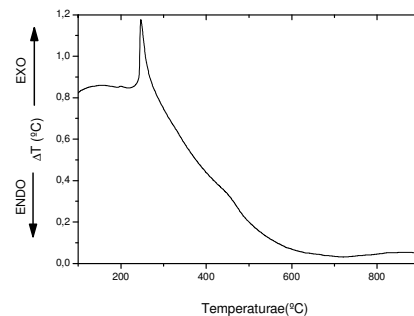


**Figure 4.** DTA of pure hydroxyapatite powder calcined at 500 °C.

In the figures 5 and 6 we can observe the thermal behavior of pure HAP dried at 100 °C. The results show an increase in the mass loss around 248 °C with relationship to the roasted sample (Figure 5). The existence of the exothermic process in approximately 230 °C probably indicates a crystallization of HAP starting from the amorphous phases (Figure 6). This result is in agreement with the analyses of XRD patterns that demonstrated a better crystallinity degree for samples that were calcined 500 °C than those that received thermal treatment at 100 °C, in other words, below the temperature of the exothermic pick.

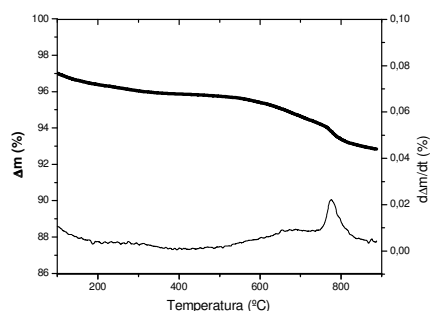


**Figure 5.** TG (bold line) and DTG of pure hydroxyapatite powder dried at 100 °C.

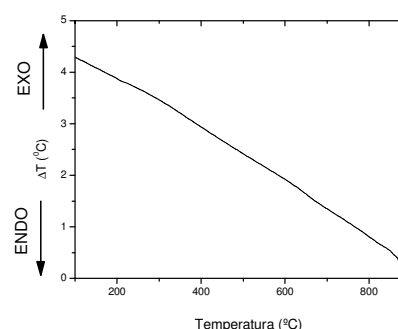


**Figure 6.** DTA of pure hydroxyapatite powder dried at 100 °C.

$\text{Cr}^{3+}$ -doped HAP calcined at 500 °C has good thermal stability, in agreement with figure 7 and 8. The crystallinity of the material is not altered along the process, being considered the absence of the exothermic pick (Figure 8). The mass loss starting from 750 °C is due to formation of TCP. This agreed with the research of Miyaji et al [17] when doping HAP with zinc, in which he indicated that Ca-deficient HAP tends to transform to TCP on heating at 800 °C depending on the deficiency of calcium.

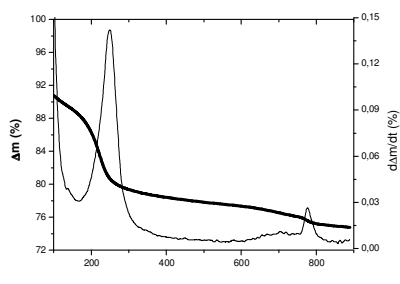


**Figure 7.** TG (bold line) and DTG of  $\text{Cr}^{3+}$  -doped hydroxyapatite powder calcined at 500 °C.

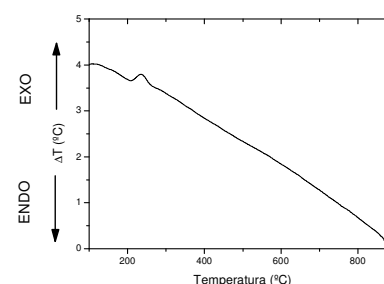


**Figure 8.** DTA of  $\text{Cr}^{3+}$  -doped hydroxyapatite powder calcined at 500 °C.

In  $\text{Cr}^{3+}$  -doped HAP dried to 100 °C the elimination of the molecules of water is larger than in the pure sample in the same temperature, because this sample has amorphous structure (Figure 9). For it is reason the exothermic pick that is associated to the crystallization of HAP it is smaller compared with the pure sample (Figure 10).



**Figure 9.** TG (bold line) and DTG of  $\text{Cr}^{3+}$  -doped hydroxyapatite powder dried at 100 °C.



**Figure 10.** DTA of  $\text{Cr}^{3+}$  -doped hydroxyapatite powder dried at 100 °C.

#### 4. Conclusions

Pure HAP and Cr-substituted Ca hydroxyapatites were synthesized by precipitation method under the specific conditions (pH 10.4, room temperature), and varying the temperature of thermal treatment of the samples, where the structural properties were investigated. The present study was successful in the preparation of chromium substituted hydroxyapatites. It was seen that in the production of pure and doped HAP using precipitation of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with  $(\text{NH}_4)_2\text{HPO}_4$  the best temperature of calcination of the samples in only phase nanocrystalline it is between 400 °C and 530 °C.

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