



## Effect of carbonates on hydroxyapatite self-activated photoluminescence response



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### ABSTRACT

The effect of carbonate impurities in the photoluminescence (PL) properties of hydroxyapatite has been studied. Different hydroxyapatite samples were synthesized by chemical precipitation with some differences in the purity of the precursors or the final neutralization treatment. All the materials were calcined in the temperature range of 200–800 °C. Calcination treatments in the range of 400–450 °C resulted in intense and broad luminescence spectra. Especially high PL intensity was obtained in samples HaB which was neutralized with phosphoric acid and in HaD a carbonated apatite. The band gap of these samples was in the range of 3.1–3.96 eV. The materials were characterized by Fourier Transformed Infrared spectroscopy, scanning and transmission electron microscopy, differential scanning calorimetry and x-ray diffraction. The time resolved luminescence decay was in the range from 500 to 980 ms in samples HaB, for calcination temperatures from 400 to 500 °C. The PL properties of these non-toxic materials made them very promising for new optical applications.

### 1. Introduction

Luminescence materials that do not contain toxic elements could have important applications in diagnostics and bioimaging for medical detection where toxicity plays a very critical role. Additionally, it is important to find environmental friendly and non-expensive stable materials, for other technological applications where nowadays toxic elements such as mercury, cadmium, or rare earths are used as emissive centers. Hydroxyapatite is a material with interesting optical properties and possible applications for bioimaging.

Hydroxyapatite (Ha) is a calcium phosphate,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , with a structure similar to the mineral constituent of bone. Therefore, it presents biocompatible and bioactive properties that induce osseointegration. This material presents an extraordinary structure flexibility that makes it able to accept more than half of the elements of the periodic table without breaking its crystal symmetry [1]. To accommodate the foreign ions structural defects form to neutralize the added charge. The defective structure of hydroxyapatite has been attributed to the OH groups along the c-axis being inherently disordered and responsible for many of the peculiar properties of this material. A few

works have reported photoluminescence of Ha and Ha substituted compounds [2–5], Machado et al. [2] reported the effect of heat treatments in the optical properties of Ha nanoparticles and attributed them to order-disorder changes induced by impurities, OH vacancies and the presence of  $\text{CO}_3^{2-}$  ions decomposing at 400 °C, contributing to additional energy levels. Zhang [3] studied the effect of particle morphology on luminescence properties of Ha synthesized at different pH, although a detailed analysis of the structural variation with pH was not given in such work. Bystrova [6] performed first principle calculations, and evaluated the effect of surface hydrogenation treatments and microwave irradiation on the photoluminescence properties of Ha, attributing the photoluminescence response to the increase on defects concentration.

Pure hydroxyapatite crystallizes at low temperature in the monoclinic structure ( $P2_1/b$  space group symmetry), and a reversible transformation to a non-stoichiometric hexagonal structure ( $P6_3/m$  space group) has been reported starting at around 207 °C and completely transforms at 400 °C [7]. Structural defects and the inclusion of carbonate ions from the atmosphere create vacancies also leading to the formation of the hexagonal structure ( $P6_3/m$  space group). Carbonate

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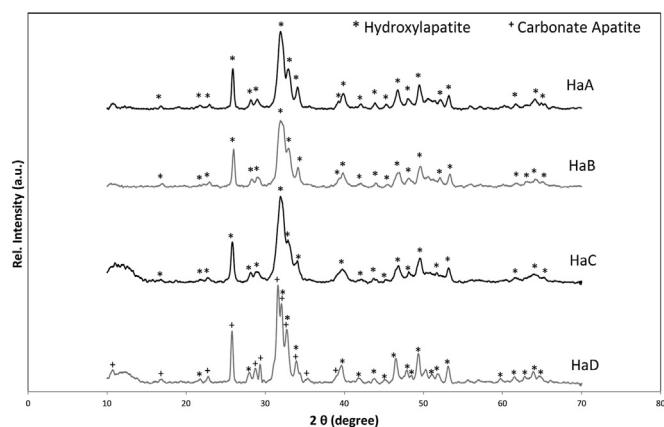


Fig. 1. XRD patterns of raw hydroxyapatites samples.

ions can substitute a hydroxide (OH) or a phosphate (PO<sub>4</sub><sup>3-</sup>) group. The carbonate content of hydroxyapatite results in calcium deficiencies, and it could be A-type (CO<sub>3</sub><sup>2-</sup> → OH) or B type (CO<sub>3</sub><sup>2-</sup> → PO<sub>4</sub><sup>3-</sup>) or a mixture of both (AB type), when substitution occurs in OH-sites it is called A-type and when it occurs in PO<sub>4</sub><sup>3-</sup> sites B-type, or a mixture of both AB-type.

The photoluminescence properties of hydroxyapatite have been attributed to its defective structure, mainly to OH<sup>-</sup> movement and reorientation in the c-channel, and CO<sub>3</sub><sup>2-</sup> content. The control of these ions could modify the electronic structure and charge distribution resulting in different energy levels with tunable colors. A detailed study of the effect of different impurities, such as carbonate content in the photoluminescence properties has not been reported up to now, as far as the author's knowledge. Therefore, in the present work the

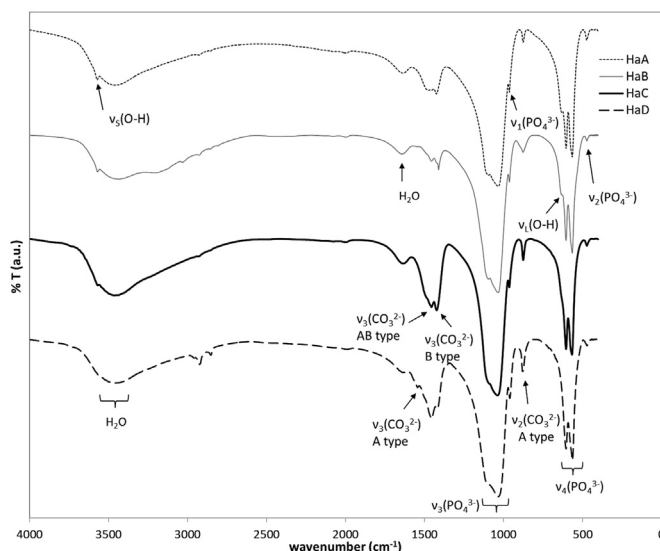


Fig. 2. FTIR of raw hydroxyapatites samples.

photoluminescence properties of four different hydroxyapatites with different carbonate content have been studied from room temperature to 800 °C, in order to understand the role of impurities and defects in these properties.

## 2. Experimental section

### 2.1. Synthesis of hydroxyapatite

Four different hydroxyapatites (Ha) have been studied with

Table 1  
FTIR band assignment of HA samples.

	OH stretch	CO <sub>3</sub> <sup>2-</sup> ν <sub>3</sub> – A type	CO <sub>3</sub> <sup>2-</sup> ν <sub>3</sub> – B type	CO <sub>3</sub> <sup>2-</sup> ν <sub>3</sub> – AB type	PO <sub>4</sub> <sup>3-</sup> ν <sub>3</sub>	PO <sub>4</sub> <sup>3-</sup> ν <sub>1</sub>	CO <sub>3</sub> <sup>2-</sup> ν <sub>2</sub> – A type and HPO <sub>4</sub> <sup>2-</sup> ions	OH ν <sub>L</sub>	PO <sub>4</sub> <sup>3-</sup> ν <sub>4</sub>	PO <sub>4</sub> <sup>3-</sup> ν <sub>2</sub>
HaA	3570		1424	1472	1033 1090	962	875	630	605 565	473
HaB	3570		1410	1456	1033 1091	962	875	630	605 565	471
HaC	3570		1420	1456	1033 1091	963	875	633	605 571	471
HaD	–	1545	1420	1454	1103 1033	959	879	–	605 565	471

All values correspond to the wavenumber (cm<sup>-1</sup>) of the different hydroxyl, carbonate and phosphate vibration bands.

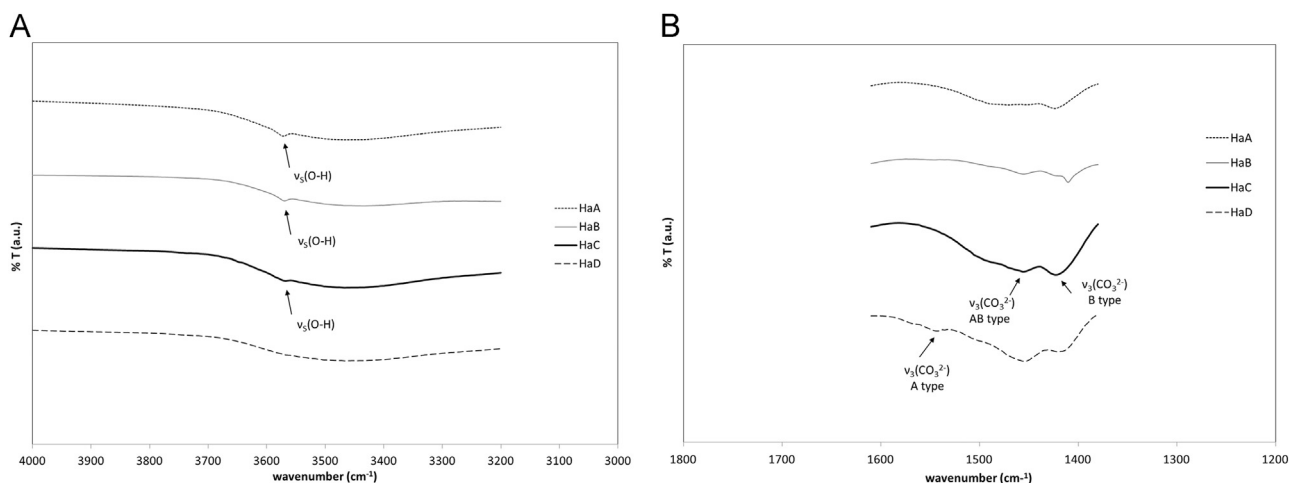


Fig. 3. a. FTIR of raw samples in the region of OH vibrational band (3000–3600 cm<sup>-1</sup>) b. FTIR of raw samples in the region of CO<sub>3</sub><sup>2-</sup> groups (1400–1500 cm<sup>-1</sup>, ν<sub>3</sub> carbonate region).

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