2012

Structural evolution of Eu-doped hydroxyapatite nanorods monitored by photoluminescence emission

JOURNAL OF ALLOYS AND COMPOUNDS, LAUSANNE, v. 531, n. 4, suppl. 1, Part 3, pp. 50-54, AUG 5, 2012
http://www.producao.usp.br/handle/BDPI/32587

Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo
Structural evolution of Eu-doped hydroxyapatite nanorods monitored by photoluminescence emission


**Abstract**

This paper reports the synthesis of Eu-doped hydroxyapatite (HA:Eu) resulting in particles with nanorod diameters from 9 to 26 nm using the microwave hydrothermal method (HTMW). Eu³⁺ ions were used as a marker in the HA network by basic hydrolysis followed by the HTMW treatment. The crystalline HA:Eu nanorod nature in a short-range order was detected by photoluminescence (PL) measurements from Eu³⁺ emission into the HA matrix. Thus, it was possible to verify that HA crystallization is favored in a short structural order when the HTMW treatment time was increased from 0 to 40 min and that the Eu³⁺ substitution in the HA lattice is site-selective.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂, (HA) is a bioceramic material, which constitutes 65% of the human bone mineral component [1]. The trivalent europium ion has been used as a luminescent probe in the investigation of crystallographic structure of activator centers, as well as a tool to probe the local symmetry and occupancy of cationic sites in apatite structures [2]. The luminescent emission of the organic probes degrades rapidly, and since the Eu³⁺ ion luminescence is photostable, the Eu-doped apatite can be employed as a biological probe. In addition, Eu³⁺ ion luminescence can be obtained under visible irradiation, which makes it suitable for prolonged examination of living cells [2].

The substitution of Ca²⁺ by a Eu³⁺ ion has been studied by a mechanical alloying technique [3], a combination of sol–gel and electropinning processes [4], a solvothermal method [5] and the thermal decomposition of precursors [6]. Yang and co-workers [6] obtained Eu-doped HA by the solvothermal process which showed uniform rod-like morphology. The authors observed that PL intensities increased with the solvothermal temperature due to enhanced crystallinity. According to Hou et al. [4] HA:Eu composites with mesoporous structures are suitable for drug release as a drug carrier which can easily be tracked and monitored in the drug-release process by changes in PL emission intensity. Long and co-workers [6] obtained different particle sizes of Eu-doped HA synthesized by the thermal decomposition of precursors. These authors verified that Eu³⁺ ions occupy Ca(II) sites in the bulk, while Eu³⁺ ions tend to occupy Ca(I) sites in doped HA as the particle size decreases. The use of rare earth ions has been shown to efficiently monitor lattice characteristics in a short range order for different inorganic systems such as Y₂O₃:Eu [7], PbTiO₃:Er or Sm [8,9] and CaTiO₃:Nd [10].

In this work, HA:Eu with 1 mol% Eu³⁺ was obtained by the HTMW method at 140 ºC for 0, 1, 20 or 40 min. Eu³⁺ ions were added to the HA as a marker during the matrix crystalline evolution in the HTMW process. The characteristics of the HA:Eu nanorods obtained and the influence of HTMW treatment are discussed in terms of X-ray diffraction (XRD), Raman spectroscopy, emission PL measurements and electronic microscopy.

2. Experimental details

The Eu-doped hydroxyapatite (HA:Eu) synthesis was produced with 1 mol% of Eu³⁺ by considering the charge compensation for divalent Ca and trivalent Eu (3Ca²⁺:2Eu³⁺). Initially, two aqueous solutions were prepared: a calcium nitrate tetrahydrate solution 1 M (Mallinckrodt, 99.9%) and an ammonium phosphate anhydrous 0.6 M solution (Mallinckrodt, 99.4%). The ammonium phosphate solution was dripped into calcium nitrate solution. For the Eu³⁺ source, a stoichiometric amount of Eu₂O₃ (99% purity, Aldrich) solubilized in nitric acid, which was added to the precursor solution of calcium nitrate tetrahydrate. Eu³⁺ was chosen as a marker...
because this ion possesses a simple electronic energy level scheme and hypersensitive transitions. Furthermore, the hydroxyapatite proved to be an efficient host of Eu\(^{3+}\) doping, since Eu\(^{3+}\) has an ionic radius similar to Ca\(^{2+}\) in this compound [6].

The pH solution was maintained at approximately 11 with the addition of ammonium hydroxide under N\(_2\) flow.

The suspension containing the white solid precipitate was placed in a 100 mL Teflon autoclave, which was sealed and loaded in a noncommercial HTMW system, using 2.45 GHz microwave radiation with 800 W of power. The system was heated to 140 °C and maintained at this temperature for 0, 1, 20 or 40 min by applying a heating rate of 140 °C/min\(^{-1}\) under constant pressure (approximately 3.0 bar). At the end of the treatment time, the autoclave was naturally cooled to room temperature. The resultant product was washed several times with deionized water to a neutral pH, and then dried in an oven.

For comparative purposes, pure HA was obtained without the addition of Eu\(^{3+}\) at room temperature. The experimental procedure was the same as described above except for the addition of Eu\(_{2}O_{3}\).

All Eu-doped and pure HA samples were characterized by XRD, using a Rigaku DMax 2500PC diffractometer at 40 kV and 150 mA with Cu K\(_{\alpha}\) radiation, a graphite monochromator and a rotary anode. In the analysis, the 2θ range from 10\(^{\circ}\) to 110\(^{\circ}\) in a step-scanning mode was used with a step width of 0.02° s\(^{-1}\) and a fixed time of 1 s. The divergence slit was fixed at 1°, and the receiving slit was established at 0.3 mm. Rietveld refinements for the samples were conducted using the General Structure Analysis System (GSAS) program of Larson and Von Dreele [11,12]. The peak profile function was modeled by using a convolution of the pseudo-Voigt with the asymmetry function described by Finger et al. [13]. To obtain the best fit, the CIF number 151414 (ICSD – Inorganic Crystal Structure Database) was used.

Raman spectra were recorded on a RFS/100/S Bruker Fourier transform Raman (FT-Raman) spectrometer with a 1064 nm excitation wavelength using a Nd:YAG laser in a spectral resolution of 4 cm\(^{-1}\). Ultraviolet–visible (UV–vis) absorption was recorded using the Cary 5G spectrometer in total reflection mode by the integration cell. PL spectra were collected with a Thermal Jarrell–Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350 nm exciting wavelength of a krypton ion laser (Coherent Innova) was used, with the nominal output power of the laser kept at 250 mW. All measurements were taken at room temperature.

To simplify the reading, samples were named according to the Eu\(^{3+}\) addition and HTMW treatment time. Thus, pure HA obtained at room temperature is identified as HA\(_{RT}\), and the Eu-doped HA samples submitted to the HTMW treatment for 0 (room temperature), 1, 20 and 40 min are described as HA:Eu\(_{0}\), HA:Eu\(_{1}\), HA:Eu\(_{20}\), HA:Eu\(_{40}\), respectively.

3. Result and discussion

The characterization in a long-range order of the pure and Eu-doped hydroxyapatite samples was analyzed by XRD (see Fig. 1). Fig. 1 illustrates XRD patterns for pure HA obtained at room temperature and Eu-doped HA powders submitted to the HTMW treatment at 140 °C for 0, 1, 20 or 40 min. This figure shows the formation of a HA single phase having a hexagonal structure with a

P 63/m space group for all synthesis conditions. Secondary phases, such as calcium carbonate and/or europium oxide were not found in the XRD results. It is also verified that the HTMW treatment at 140 °C for different times favors the crystallization process of the HA compared with samples obtained at room temperature which can mainly be observed by the better definition of the (3 0 0) reflection.

The hexagonal structure of the HA:Eu was analyzed using the Rietveld refinement method to obtain lattice parameters and the unit cell volume. Thus, the ICSD cif number 151414 was used for the refinement from XRD results (see Fig. 2) for the sample treated for 40 min.

The R-values are depicted in Table 1 to evaluate the fit. Table 1 shows that all R-values have good correlation which indicates the adequacy of the model used for the actual

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Chi(^{2})</th>
<th>R(_{\text{wp}}) (%)</th>
<th>R(_{\text{wp}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.78</td>
<td>1.95</td>
<td>6.56</td>
</tr>
<tr>
<td>1</td>
<td>1.90</td>
<td>1.99</td>
<td>6.95</td>
</tr>
<tr>
<td>20</td>
<td>1.85</td>
<td>1.64</td>
<td>6.70</td>
</tr>
<tr>
<td>40</td>
<td>1.91</td>
<td>1.14</td>
<td>6.83</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns for HA:Eu samples with 1 mol% of Eu\(^{3+}\) undergoing HTMW treatment at 140 °C for 0, 1, 20 and 40 min, and for pure HA obtained at room temperature.

Fig. 2. Rietveld refinement data of a HA:Eu sample treated at 140 °C during 40 min.

Fig. 3. Lattice parameters a and c obtained from Rietveld refinement as a function of the HTMW treatment time (a) and the unit cell volume (b).
structure and diffraction conditions. A decreasing in the $R_B$ values indicates a better fit of Bragg positions which agrees with the enhanced crystallization and the increase HTMW treatment time.

Fig. 3a illustrates the behavior of lattice parameter $a$ and $c$ obtained from Rietveld refinement for samples undergoing HTMW treatment. An analysis of this figure reveals that parameter $a$ decreases smoothly, and an inverse behavior occurs with parameter $c$ when the HTMW treatment is completed. Indeed, for samples undergoing the HTMW process, a diminishing of both cell parameters ($a$ and $c$) is visualized if the treatment time is increased from 0 up to 40 min which results in a decrease in the unit cell volume (see Fig. 3b). This behavior demonstrated in Fig. 3b suggests an increase of the HA structure densification with a consequent improvement in the lattice crystallization and the minimization of structural defects.

Han et al. [14] synthesized undoped HA nanoparticles from phosphoric acid and calcium hydroxide using the same method employed in the present work. These authors verified that the HA phase formation is totally dependent on the microwave power since the HA single phase was obtained using only 550 W without secondary phases. This result is in agreement with results obtained
in the present work where 800 W of energy was employed in the HTMW process.

HA with a nanorod structure has gained much attention for its biocompatibility and bioactivity due to good adsorbability, since the Van der Waal’s interactions are proportional to the large area of the rods [15]. Wiglus et al. [16], showed that particles of HA doped with Eu³⁺ with an average size between 20 and 50 nm were obtained when annealed at 600 °C. In this work, nanorods were obtained with diameter variations from 9 to 26 nm (see Fig. 4a–d) for both HA and HA:Eu samples when annealed at 140 °C. When the HTMW treatment time is increased, an increase in particle sizes with larger diameter occurs as well as a diminution of the population of the smaller particles.

The influence of Eu³⁺ in the HA structure in a short-range order was performed by FT-Raman analyses as a complementary study for XRD data. Raman spectra at room temperature in the frequency range of 400–1200 cm⁻¹ for HA:Eu powders processed in the HTMW system during 0, 1, 20 or 40 min, and for HA_RT are listed in Fig. 5. According to Penel et al. [17], all Raman modes are related to the HA phase which indicates that all samples contain only this phase. From Raman studies on carbonated apatite [17] two distinct wavenumbers of the ν₁ carbonate mode have been suggested according to OH⁻ or PO₄³⁻ site substitution at 1108 and 1070 cm⁻¹, respectively. A variable number of bands in the ν₁PO₄³⁻ domain were also detected by the authors [17]. Because none of these characteristics were found in the Raman spectrum (see Fig. 5), it is possible to deduce that the HA:Eu obtained by the HTMW method does not represent the concurrent calcium carbonate phase and is in agreement with XRD results which indicate the formation of the HA single phase.

As no significant structural alteration was observed in FT-Raman results with increased HTMW treatment time (see Fig. 5), PL emission was used to analyze the short range order in HA:Eu nanorods. Fig. 6a shows PL spectra of the HART and HA:Eu samples undergoing HTMW treatment at 140 °C for 0, 1, 20 or 40 min under excitation of 350 nm of a krypton ion laser. A broad intense luminescence in the visible region for all these samples can be observed in the luminescence response. Fig. 6a verifies that the pure HA sample has a broad band luminescent emission with a center position at 500 nm. This broad band luminescent is attributed to the shallow and deep defects of the HA matrix synthesized and reported in this paper. This HA PL behavior persists with the addition of Eu³⁺ which confirms the HA matrix effect for all HA:Eu samples. Emission spectra of all doped samples undergoing HTMW treatment show Eu³⁺ ⁵D₀→⁷F₂ (j = 0, 1 and 2) transitions at 575, ~600 and ~620 nm, respectively [18]. With an increase in the treatment time, broad bands become narrower, and a blue-shift is observed in all the samples. This displacement to lower wavelengths indicates
that shallow traps of the electrons and holes are promoted with an increase in the HTMW time. Nevertheless, deep defects are unfavorable with increased time, since the bands are narrowed, and the centers are displaced to a more energetic range which agrees with XRD results that show an improvement in HA crystallization with a time increase from 0 to 40 min. Thus, the Eu$^{3+}$ substitution is suggested to be a marker in the crystallization improvement of the HA:Eu system which indicates short-range alterations in the matrix lattice. This ordering was undetected by FT-Raman and XRD measurements (see Figs. 1 and 5, respectively).

Therefore, PL measurements are an important tool to analyze Eu$^{3+}$ substitution sites in the HA lattice obtained by the HTMW method. Furthermore, this technique provides detailed information about alterations in a short-range order in the HA lattice structure which facilitates an understanding of the crystallization behavior of the HA:Eu system.

4. Conclusions

Eu-doped hydroxyapatite was obtained by using HTMW process with a nanorod structure without a secondary phase which occur with a small increase in the nanoparticle diameters when the hydrothermal treatment is employed. The PL broad band and the increment of Eu$^{3+}$ emission can be effective in monitoring the HA structural evolution during the HTMW process since it provides information about the evolution of defects. A blue-shift and a narrowing of HA broad band PL spectra were detected with increase in the HTMW time which suggests a crystalline organization in the short order of the HA lattice. In this way, shallow defects were promoted with the HA crystalline structure improvement while deep defects were not advantaged. Eu$^{3+}$ substitution in the HA lattice obtained by the HTMW method is site-selective and prefers Ca(II) over Ca(I) sites. Hence, it is verified that Eu$^{3+}$ emissions are an important tool to monitor structural modifications in the HA lattice crystallization obtained by the HTMW process.

Acknowledgments

The authors would like to acknowledge the Brazilian agencies FAPESP/CEPID, CAPES, CNPq and FINEP/PRONEX for the financial support.

References