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Evaluation of europium-doped HA/ β -TCP ratio fluorescence in biphasic calcium phosphate nanocomposites controlled by the pH value during the synthesis



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ABSTRACT

Europium-doped hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP) and biphasic phosphate nanopowders were synthesized by co-precipitation method and their crystal structures and fluorescence properties were investigated depending on the pH of the starting solution. In the range of pH 6–10, HA and β -TCP phases coexist. The β -TCP proportion increased as the pH of the solution decreased, while HA yields decreased. At pH below 6, monophasic β -TCP powder was obtained after thermal treatment. In particular, HA and β -TCP can be used as luminescent materials when activated by Eu^{3+} ions in substitution of Ca^{2+} ions. Herein, the Eu^{3+} ions doped HA and β -TCP phase composition were analyzed in order to investigate the fluorescence emission of the HA, β -TCP and biphasic compounds. Eu-doped HA exhibited a red-orange emission at 575 nm with several minor peaks at 610–640 nm, while Eu-doped β -TCP had an unexpected strong red emission at 610–620 nm and a secondary band at 590–600 nm. In fact, the Eu: β -TCP integrated emission area is almost 20-fold higher than Eu:HA for the same europium ion concentration. These results demonstrate the potential of Eu: β -TCP as biomarker for medical applications, as drug release and targeting based on their luminescent properties.

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1. Introduction

Calcium phosphates, including hydroxyapatite [HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] and beta-tricalcium phosphate [β -TCP, $\text{Ca}_3(\text{PO}_4)_2$], are the main mineral component of bone tissue and teeth [1]. The synthetic calcium phosphates are of special interest in medicine because of their biocompatibility, bioactivity and non-toxicity [1]. Different phases of calcium phosphates can be obtained by varying the atomic ratio. The stability of calcium phosphates in a body fluid generally varies with the Ca/P ratio, with the highest being the HA, while β -TCP is rather soluble [1].

Among these bioceramics, the developing HA/ β -TCP biphasic calcium phosphate (BCP) as more effective biomaterials is of great interest in bone repairing or regeneration, besides being a controlled loading and releasing drug delivery system optimized, by their controllable bioresorption rate [2].

Owing to its chemical nature, calcium phosphate allows the replacement of calcium for several ionic species in order to alter the morphology, stability, chemical, physical and biological properties of the bioceramics. For instance, europium ion substitution is known to be an important probe element in biological fluorescent labeling. Eu^{3+} has a simple electronic energy level scheme, emitting in the red region of the visible spectrum [3]. Furthermore, because of the hypersensitive transition the europium ion has been used as a local structure probe in determining the site microscopic symmetry, since it depends strongly on the chemical surroundings [2].

The excitation and emission characteristics of hydroxyapatite have been extensively studied and it is well known to be greatly influenced by the method of preparation and the thermal treatment [4,5]. Europium emissions depend on the calcium site substitution on HA: when europium ion is located at site I, the emission bands are observed at 579 nm ($^5\text{D}_0\text{--}^7\text{F}_0$), 592 nm ($^3\text{D}_0\text{--}^7\text{F}_1$) and 616 nm ($^5\text{D}_0\text{--}^7\text{F}_2$ transition) [4]. However, after the thermal treatment at higher temperatures europium ion migrates to site II, and the several new emissions bands originated from the $^5\text{D}_0\text{--}^7\text{F}_0$ (574 nm), $^5\text{D}_0\text{--}^7\text{F}_1$ (602 nm) and $^5\text{D}_0\text{--}^7\text{F}_2$ (610–630 nm)

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transitions are exhibited, under 394 nm excitation [3]. Another important effect of the temperature treatment is the enhancement of europium emission intensity, through increased mean crystallite size [4].

On the other hand, little attention has been given to the assessment of europium ion, with regard to tricalcium phosphate biomaterial. Regarding concerns to europium-doped β -TCP emissions, the literature is scarce and inconclusive. Wang H. et al synthesized Eu-doped HA, β -TCP and BCP with a maximum emission peak at 614 nm and other weak bands at 575 nm, 590 nm, 655 nm and 697 nm [6]. Chang et al. have produced europium-doped calcium phosphate with and without magnesium, and they observed an Eu: β -TCP emission spectra similar of those reported for europium doped HA, although the DRX patterns

confirm the presence of β -TCP, and HA as secondary phase [7]. The maximum intensity peaks were detected at 574 nm, 621 nm and 627 nm, and a decline in the emission intensity was observed when the temperature raise, in contrast with the literature reports [3,8]. Kim et al have produced HA and β -TCP doped with various europium ion concentration, up to 12% [6]. They detected the formation of β -Ca₂P₂O₇, CaO and Eu₂O₃, EuPO₄ in that samples with more than 1% of Eu. No significant difference between HA and β -TCP emission intensity was found by the authors. In all cases, the precipitation method was employed as a convenient biomaterial synthesis, by altering the (Ca+Eu)/P ratio to obtain either HA, β -TCP or a mixture of them.

Herein, the Eu³⁺-doped HA (Eu:HA), β -TCP (Eu: β -TCP) and biphasic calcium phosphates BCP (Eu:BCP) nanoparticles were synthesized by co-precipitation method, fixing the (Ca+Eu)/P ratio at 1.67 and altering the pH of the solutions. The luminescence properties of these calcium phosphates were investigated, particularly focusing on the effects of Eu emission depending on the phase structure and composition. For the first time, an unexpected strong emission of europium-doped β -TCP is being reported in comparison of Eu-doped HA, almost 20 times higher, improving the bioimaging applications.

2. Materials and methods

HA, biphasic BCP and β -TCP powders, pure and doped with Europium (1.5%, 3%, 6% and 12%) were synthesized by co-precipitation method, wherein the phosphoric acid (H₃PO₄, Synth – Brazil) diluted in deionized water (0.3 M) was slowly added drop by drop (8 ml/min rate) into a suspension of calcium hydroxide (Ca(OH)₂, Synth- Brazil) and europium nitrate (EuNO₃·5H₂O, Sigma Aldrich) (0.5 M). The initial (Ca+Eu)/P ratio was fixed at 1.67 for all compositions. The pH values of the solutions were varied from 5.9 to 10.3 during precipitation procedure by adding either NH₄OH or HNO₃. After the precipitation, the solutions were aged at room temperature for 24 h. The precipitates were filtered and washed several times with deionized water to remove free ions. Finally, they were dried at 60 °C for 24 h.

The dried powders were heated at 1000 °C for 3 h. Samples were characterized by X-ray diffraction (XRD) using a Multiflex Rigaku diffractometer using the Cu α radiation. The program GSAS was used to refine the structures with form factors for neutral atoms. The background was modeled using Chebyshev

Table 2

The final (Ca+Eu)/P molar ratio analyzed by ICP OES technique.

	Ca (mg g ⁻¹)	P (mg g ⁻¹)	Eu (mg g ⁻¹)	(Ca+Eu)/P
HAEu pH 10.28	406 ± 7	196 ± 2	11.60 ± 0.1	1.66
HAEu pH 9.32	407 ± 3	202 ± 1	10.93 ± 0.03	1.58
HAEu pH 7.76	400 ± 3	207 ± 1	11.32 ± 0.03	1.52
HAEu pH 6.66	421 ± 2	225 ± 1	12.11 ± 0.03	1.46
HAEu pH 5.89	391 ± 2	220 ± 2	11.96 ± 0.03	1.40

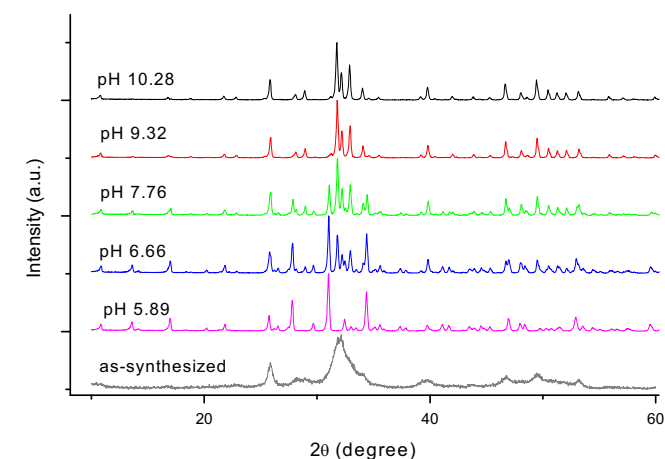


Fig. 1. X-ray diffraction pattern of Eu:HA monophasic (pH 10.28), Eu: β -TCP monophasic (pH 5.89) and Eu:BCP powders, depending on the pH during the synthesis, after thermal treatment (TT=1000 °C/3 h). All as-synthesized dried powders show the same poor crystalline hydroxyapatite diffraction pattern.

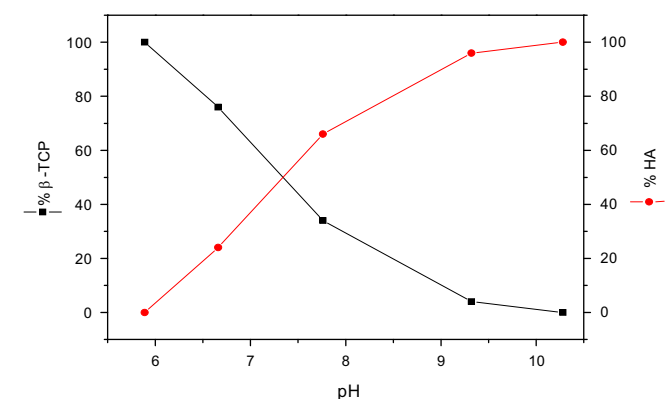


Fig. 2. Eu doped HA versus β -TCP rates depending on the pH solution during the co-precipitation synthesis.

Table 1

Rwp and lattice parameters for samples with standard deviations in brackets.

Sample	Rwp	Eu:HA			Eu: β -TCP		
		a (nm)	c (nm)	% Phase(wt)	a (nm)	c (nm)	% Phase(wt)
pH 10.28	3.65	0.9422 (2)	0.6884 (1)	100	–	–	0
pH 9.32	4.88	0.9420 (2)	0.6883 (1)	96	1.0364 (2)	3.7180 (1)	4
pH 7.76	3.98	0.9415 (2)	0.6883 (1)	66	1.0415 (2)	3.7369 (1)	34
pH 6.66	4.67	0.9418 (2)	0.6882 (1)	24	1.0424 (2)	3.7406 (1)	76
pH 5.89	4.13	–	–	0	1.0429 (2)	3.7445 (1)	100

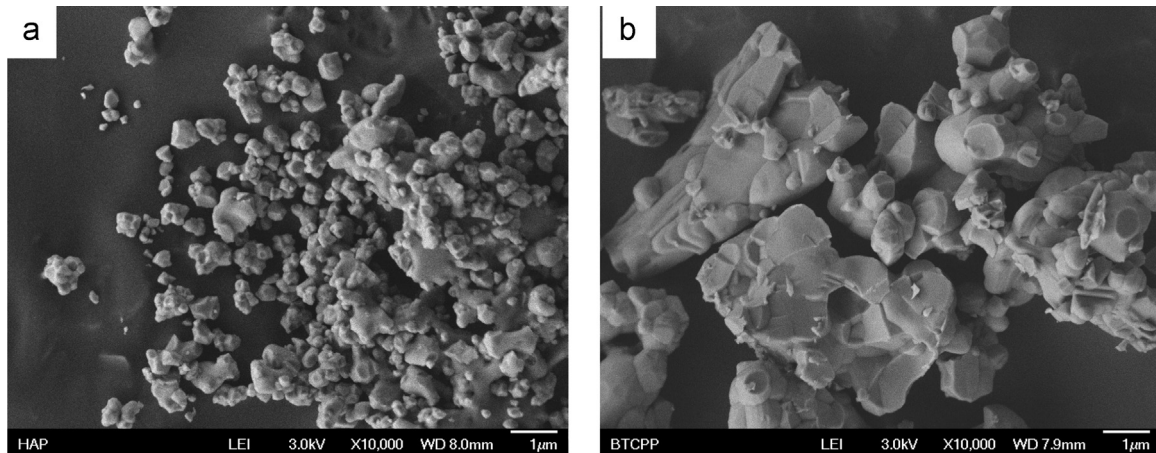


Fig. 3. SEM-FEG micrographs obtained for nanopowders after thermal treatment A) HA pure and B) β -TCP pure.

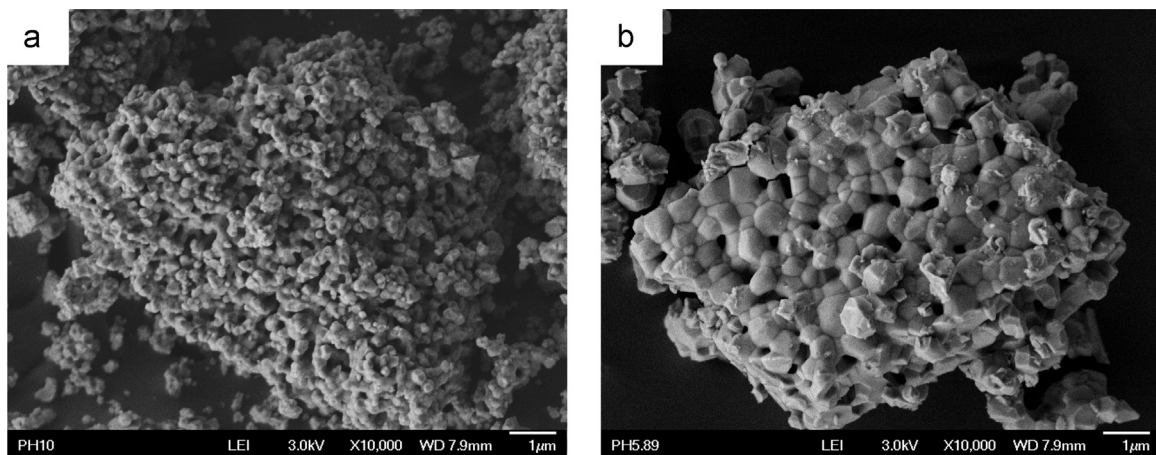


Fig. 4. SEM-FEG micrographs obtained for Nano-powders after thermal treatment A) Eu:HA and B) Eu: β -TCP.

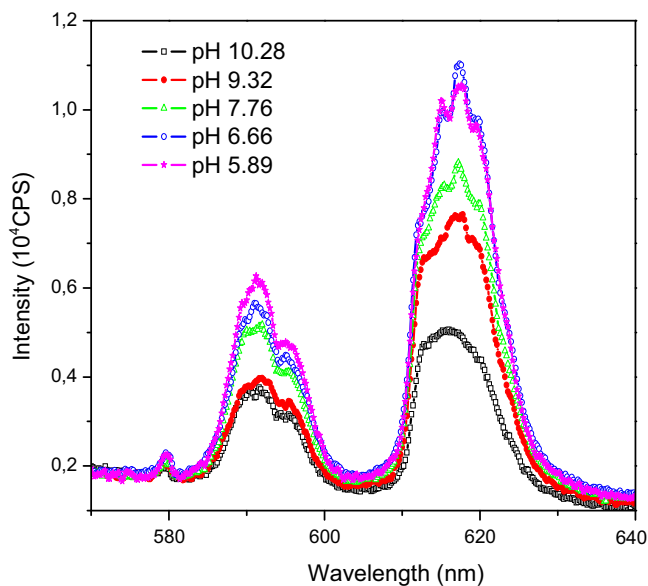


Fig. 5. Emission spectra of hydroxyapatite and Ca-deficient HA doped with europium ion synthesized at different pH values. Excitation at 394 nm.

polynomials of the first kind. The peak shape used was type 3 varying GU, GW, LX and trns. Apatite starting atomic parameters came from the refinement based on neutron data in $P6_3/m$ of Holly

Springs OHAp [9]. The occupancies, atom positions, unit cell peak profile, sample displacement and background parameters were varied. Following the previously used procedure [9], the Ca1 site occupancy was fixed at one, giving a total of four Ca1 per unit cell. Anisotropic atomic displacement parameters from the Holly Springs refinement [9] were used and kept constant. In the Rietveld refinements, the relative quantities of the two phases, lattice parameters, peak parameters and instrument zero were allowed to vary, but did not for structural parameters.

The morphology of the powders was investigated using a Field Emission Gun scanning electron microscopy (FEG JSM 6701F – JEOL). Fluorescence spectroscopy was carried out, at room temperature, in the Fluorolog 3 Fluorometer from Jobin Yvon that uses an optical bundle to excite and collecting the luminescence signals for analysis.

An inductively coupled plasma optical emission spectrometer (ICP OES) Spectro Arcos^{CCD} (Spectro Analytical Instruments Co, Kleve, Germany) was used for the determination of Ca, P and Eu in the calcium phosphate thermally treated samples. The spectrometer is equipped with axially viewed plasma and an air-cooled radio frequency generator based upon a free-running 27.12-MHz. An end-on gas interface was used to minimize interference caused by self-absorption and recombination, providing a wide linear dynamic range and low background. All solutions were prepared using reagents of analytical grade and ultrapure water. Standard multi-element (Ca, P and Eu) calibration solutions ranging from 0.01 to 10 mg L⁻¹ in a 1% (v v⁻¹) nitric acid aqueous solution were prepared using ICP OES Merck standard solutions traceable to NIST

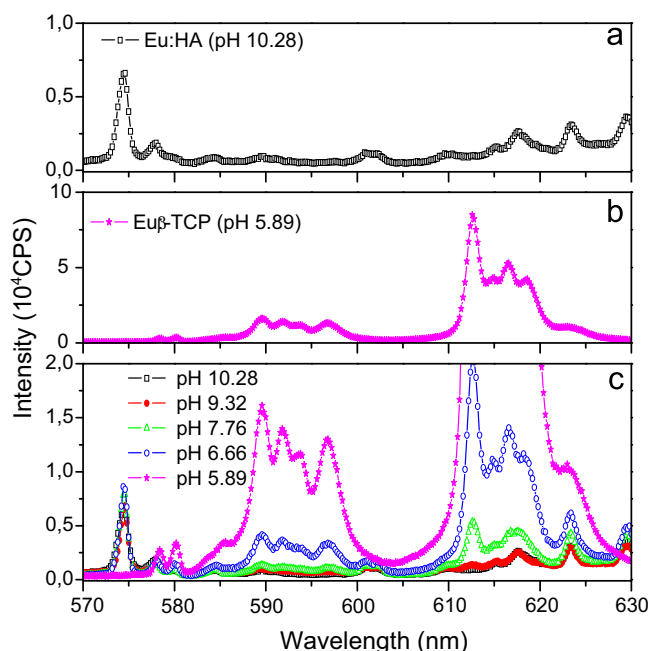


Fig. 6. Shows the emission spectrum of Eu:HA (a), Eu:β-TCP (b) and for Eu:BCP with various Eu:HA/ Eu:β-TCP rates(c), after thermal treatment at 1000 °C for 3 h, under excitation at 394 nm.

(Merck, Darmstadt, Germany). The samples were weighted and dissolved in a 50% (v v⁻¹) nitric acid aqueous solution and introduced into the system through a double pass spray chamber and a crow-flow nebulizer. All samples were analyzed in triplicates.

3. Result and discussion

Fig. 1 shows the XRD patterns of the thermal treated 1.5% Eu-doped calcium phosphate powders, depending on the pH of the solution during the synthesis procedure. At pH below 6, the synthesized powder showed well characterized peaks of pure β-TCP (JCPDS 09-0169), and at pH above 10 it shows just HA phase, the peaks were indexed according to the standard pattern (JCPDS 09-0432). Between these pH values (6 and 10), the diffractograms showed a mix of Eu:β-TCP and Eu:HA phases (biphasic). The percentage of each phase on biphasic phosphate calcium, shown in Fig. 2, was calculated from the relative intensity of constituent phases obtained by Rietveld refinements. Increasing the pH value caused a gradually decrease in the lattice parameter of Eu: β-TCP phase, while no significant variation in the Eu:HA lattice parameter were observed. The Rwp (weighted residual), the lattice parameters and phases contents are given in Table 1.

The yield of Eu:HA and Eu:β-TCP contents depends on the pH of the synthesis solution. For the intermediate pH values, a biphasic powders with 76 wt% Eu:β-TCP, 24 wt% Eu:HA for pH=6.66 and 34 wt% Eu:β-TCP, 66 wt% Eu:HA for pH=7.76 were obtained. At pH 9.32, the main phase was Eu:HA (96 wt%) and only a small amount of Eu:β-TCP (4 wt%) was contained in the mixture of powders, as it is demonstrated in Fig. 2.

One could notice that all the dried powders present the same poor crystalline hydroxyapatite diffraction peaks, since the technique does not distinguish between hydroxyapatite and Ca-deficient hydroxyapatite (Fig. 1). After the thermal treatment at 1000 °C for 3 h, the Ca-deficient hydroxyapatites of different (Ca+Eu)/P ratios, depending on pH of the starting synthesis, transforms into β-TCP or BCP with different Eu:HA/ Eu:β-TCP rates

and exhibit sharp diffraction peaks indicating a higher crystallinity. All powders were obtained without any tertiary phase.

The Ca, Eu and P contents in the samples (pH 5.89; 6.66; 7.76; 9.32 and 10.28) were determined by ICP-OES, and the results are showed in Table 2. The molar ratios of (Ca+Eu)/P varied from 1.4 (Eu:β-TCP pH 5.89) to 1.67 (Eu:HA pH 10.28). Although 1.4 molar ratio for β-TCP was lower than the theoretical one (1.5), no other phase was observed in Eu:β-TCP sample (see Fig. 1). Moreover, these results were consistent with previews literature reports [8].

The morphologies of HA and β-TCP pure and 1.5% Eu-doped powders calcined at 1000 °C are shown in Figs. 3 and 4, respectively. Both present an initial sintering and the grain growth processes, which one is even more pronounced to β-TCP than HA. The particles' size of the calcined powders decreased as the pH of the solutions increased, and the Eu doping also seems to affect the particle size, because the undoped β-TCP particle coarsening resulted in micrometer-sized powders (Fig. 3b).

The luminescence properties of all powders as-synthesized and after thermal treatment were characterized by fluorescence technique and the results are shown in Figs. 5–7 and Figure 8 as emissions and excitation spectra, respectively.

Efficient emissions of Eu³⁺ substituting calcium ion in the HA and Ca-deficient HA were observed. Although the emission intensity of as-synthesized samples is weak when compared to those after thermal treatment, the absence of calcium leads to an increasing of almost fifty percent in Eu-emission in powders without treatment, for the same europium ion concentration of 1.5 mol%. The spectrum emission comprises two broad emission bands centered at 592 nm and 617 nm corresponding to the typical ⁵D₀–⁷F₁ (magnetic dipole transition) and ⁵D₀–⁷F₂ (electric dipole transition), respectively (Fig. 5). The relative intensity of electric dipole transition and magnetic dipole transition ratio depends strongly on the local symmetry of europium ions occupancy [10]. The large ratio of the fluorescence intensities for the transitions implies a low symmetry field at the europium site

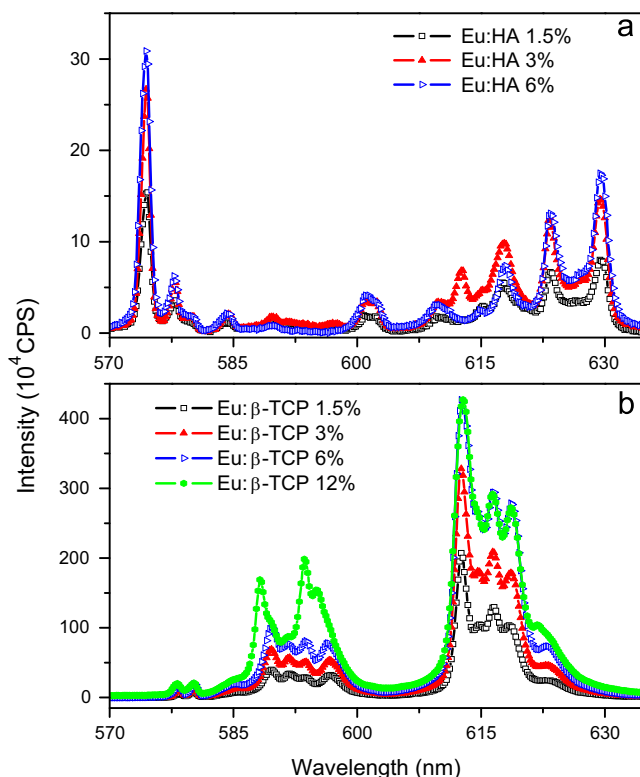


Fig. 7. Influence of Eu doping concentration in HA (1.5%, 3% and 6%) (a) and β-TCP (1.5%, 3%, 6% and 12%) (b) emission intensities.

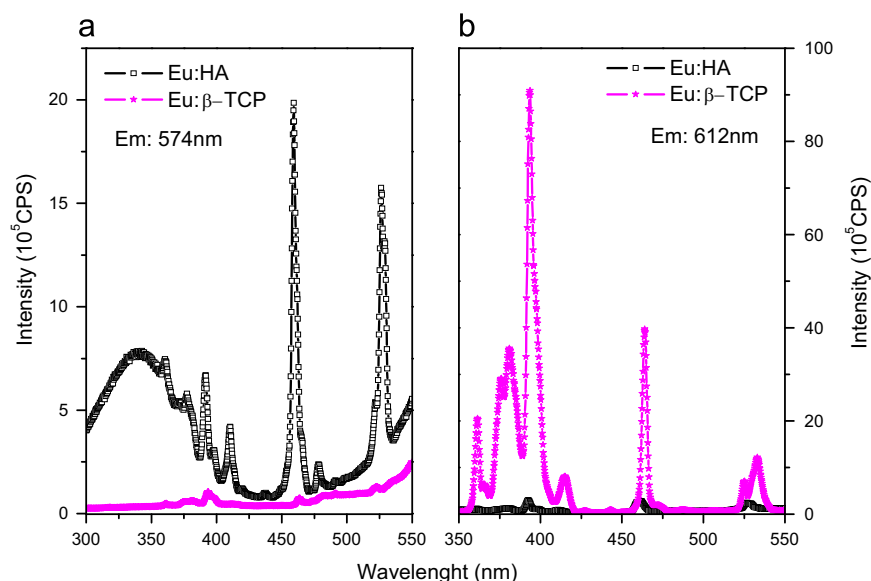


Fig. 8. Differences in the excitation spectra of 1.5 mol% Eu^{3+} in Eu:HA and Eu:β-TCP by monitoring the emission wavelength at 574 nm ($^5\text{D}_0\text{--}^7\text{F}_1$) and 612 nm ($^5\text{D}_0\text{--}^7\text{F}_2$).

surrounding [11]. In comparison with Eu^{3+} ion in Ca-deficient HA, Eu^{3+} ions in the HA structure have a relatively lower intensity ratio of $^5\text{D}_0\text{--}^7\text{F}_2$ to $^5\text{D}_0\text{--}^7\text{F}_1$.

However, after thermal treatment at 1000 °C for 3 h, the emission spectra and the intensity of them is completely distinguishable, under excitation at 394 nm.

The influence of thermal treatment in the HA fluorescence (Fig. 6a) was thoroughly discussed in our previous article [3]. For HA, the best temperature to obtain the maximum emission intensity was found to be 1200 °C and it is related to europium migration from CaI to CaII by a diffusion process and the subsequently increased mean crystallite size. Nevertheless, as Eu:β-TCP particle is bigger than Eu:HA, at 1000 °C it has already reached the maximum emission intensity, and for this reason 1000 °C was chosen as the treatment temperature in order to compare the performance between them.

Heated Eu:HA exhibits (Fig. 6a) the strongest emission peak at 574 nm ($^5\text{D}_0\text{--}^7\text{F}_0$), and weaker bands at 601 nm ($^5\text{D}_0\text{--}^7\text{F}_1$) and 610–630 nm ($^5\text{D}_0\text{--}^7\text{F}_2$), characteristics for europium ion occupying CaII in HA (the thermal treatment induces the europium migration from CaI to CaII [4]).

Eu-Deficient HA submitted at this temperature transforms into Eu:β-TCP structure, which one exhibits intense bands at 587–600 nm ($^5\text{D}_0\text{--}^7\text{F}_1$) and 610–620 nm ($^5\text{D}_0\text{--}^7\text{F}_2$) transitions splitted on four sharper bands. And, in fact, the unexpected strongest emission of Eu: β-TCP can be almost 20-fold higher than Eu:HA for an equal europium mol percentage (Fig. 6b).

This result also confirms that β-TCP presents just one spectroscopic site for europium ion, whose emission is exactly at the same region as europium ion substituting calcium at site I in HA or Ca-deficient-HA. The biphasic samples emission shows, in Fig. 6c, a mixture of both characteristic emissions spectra, and it is sensitive enough to detect low concentrations of Eu:β-TCP phase, as it is shown in pH 9.32 sample represented by a small, but well distinguishable, band at 612.5 nm. The higher the Eu:β-TCP amounts in the biphasic compounds, the higher the red emission of the samples.

Fig. 7 shows the influence of Eu doping concentration in HA (a) and β-TCP (b) emission intensities. HA doped with 3% europium showed higher emission intensity than those doped with 1.5% Eu ion, with the presence of β-TCP emission as secondary phase. For 6 mol% Eu, the HA emission intensity is the same as 3%

Eu, indicating the lower solubility limit of Europium ion in the HA structure. β-TCP allows an increasing Eu doping concentration up to 6%, as can be seen in Fig. 7b, which is consistent with literature reports [6]. The excess of europium ion (12%) leads to the presence of EuPO_4 phase (confirmed by XRD analysis) and it emits at 585–600 nm region. None of them has presented α-TCP phase.

The excitation spectra of Eu^{3+} by monitoring $^5\text{D}_0\text{--}^7\text{F}_1$ and $^5\text{D}_0\text{--}^7\text{F}_2$ emission in Eu:HA and Eu:β-TCP, at 574 nm and 612 nm, respectively, are shown in Fig. 8. When emission wavelength is fixed at 574 nm, the excitation spectrum of Eu:HA is composed by a broad absorption band at 300–380 nm region, which one is originated from the charge transfer (CT) transition of the $\text{Eu}^{3+}\text{--O}_2$ bonding [12] and narrow bands at 393 nm, 410 nm, 460 nm and 525 nm. The CT transition occurs when a valence electron is transferred from a delocalized ligand orbital toward the incompletely filled orbital of 4f of Eu^{3+} . The presence of CT band is determined by the oxidizing nature of the host matrices [13,14], and it appears in Eu:HA spectrum when the emission ion is fixed at 574 nm, but it is not observed for Eu:β-TCP. In contrast, for emission fixed at 612 nm, the excitation spectra reveal an intense absorption at 370–400 nm region, for Eu:β-TCP, and a weak one for Eu:HA, as it was already expected based in the fluorescence intensities (Figs. 6 and 7). These results give us evidence as how the differences in the central metal ion surrounding in the host lattices can directly influences the europium emission.

Such co-precipitation synthesis method was shown efficient and easy for obtaining calcium phosphates at different ratios of Eu: HA and Eu:β-TCP, since the lower the pH the more favorable is the formation of β-TCP phase [15]. This technique can be applied to obtain various ratios of Eu:HA and Eu:β-TCP phases composition, which one can be used to control the rate of biodegradation of the ceramics and the emission features of the samples. There are many reports on Eu:HA emission patterns, but up till now the Eu:β-TCP emission intensity has been underestimated. It may be expected that higher luminescent phosphors may be of great help in a further explanation of *in vivo* and *in vitro* biomaterial interaction phenomena and for luminescence-trackable drug delivery system.

Further studies are being developed to elaborate more on this matter, in order to obtain the most appropriate nanoparticle size distribution and the best fluorescence efficiency for bioimaging application.

4. Conclusion

The nanocrystalline HA, β -TCP and BCP doped with europium ion were successfully synthesized. Solution pH value during crystal growth was found to have a profound effect on particle composition and post-sintered phases, despite constant europium, calcium and phosphate ions starting solution concentration, $(Ca+Eu)/P=1.67$, for all powders synthesis. Different phase compositions can be easily achieved by simply changing the pH of the solution during the synthesis. The excess of free calcium ion for the different final molar ratios of $(Ca+Eu)/P$ is eliminated during the filtration and by washing thoroughly with de-ionized water several times procedures. Although it is not required to start the synthesis with an excess of Calcium, the pH controlling revealed to be the most important parameter to obtain the β -TCP structure.

The influence of the pH synthesis value on emission spectra is dealt with. PH values below 10 favor the formation of Ca-deficient Eu:HA powder, which turns into Eu: β -TCP structure after thermal treatment. The lower the pH the higher the concentration of Eu: β -TCP and lower the Eu:HA in the compound. The lowest pH, near to 6, leads to the formation of monophasic beta-tricalcium phosphate, that is stable even after thermal treatment at 1000 °C for 3 h. Europium ion doping β -TCP nanoparticles have shown a surprising strong emission, it may be expected that higher fluorescence intensity may also be of great interesting in further applications of luminescent properties.

Comparing the integrated Eu: β -TCP versus Eu:HA emission area, europium-doped tricalcium phosphate exhibits an unexpected strong emission that, to the best of our knowledge, has never been achieved. From the same Ca+Eu/P initial ratio (1.67),

varying only the pH of the solution, we were able to obtain various ratios of Eu: β -TCP/Eu:HA and the Eu: β -TCP with the highest red emission, almost 20-fold higher than Eu:HA, for the same lanthanide concentration.

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References

- [1] S.V. Dorozhkin, *Materials* (2009) 399.
- [2] Hassna R.R. Ramay, M. Zhang, *Biomaterials* 25 (2004) 5171.
- [3] N. Lakshminarasimhan, U.V. Varadaraju, *J. Solid State Chem.* 177.10 (2004) 3536.
- [4] Flávia R.O. Silva, et al., *Opt. Mater.* 47 (2015) 135.
- [5] Flávia R.O. Silva, et al., *Mater. Sci. Forum* 820 (2015).
- [6] H. Wang, J. Yu, J. Li, X. Cheng, Z. Huang, *J. Mater. Sci.* 45 (2010) 1237.
- [7] T.-Y. Chang, L. Hsiu-Mei, L. Tai-Yuan, *Photonics Asia. Int. Soc. Opt. Photonics* (2012).
- [8] E.J. Kim, S.-W. Choi, S.-H. Hong, *J. Am. Ceram. Soc.* 90 (9) (2007) 2795.
- [9] K. Sudarsanan, R.A. Young, *Acta Cryst.* B25 (1969) 1534.
- [10] Z. Wei, L. Sun, C. Liao, J. Yin, X. Jiang, C. Yan, *J. Phys. Chem. B* 106 (2002) 10610.
- [11] R. Reisfeld, *Rare Earths Struct. Bond.* 13 (1973) 53.
- [12] H.E. Hoefdraad, *J. Inorg. Nucl. Chem.* 37.9 (1975) 1917.
- [13] A.N. Belsky, J.C. Krupa, *Displays* 19.4 (1999) 185.
- [14] Yuhua Wang, et al., *J. Solid State Chem.* 177.7 (2004) 2242.
- [15] B.-T. Lee, et al., *Mater. Chem. Phys.* 104 (2007) 249.