Characterization and Luminescence of Eu$^{3+}$- and Gd$^{3+}$-Doped Hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$

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Received: 21 August 2020; Accepted: 9 September 2020; Published: 11 September 2020

Abstract: Luminescence properties of europium-doped Ca$_{10-x}$Eu$_x$(PO$_4$)$_6$(OH)$_2$ ($x_{Eu}$ = 0, 0.01, 0.02, 0.10 and 0.20) and gadolinium-doped hydroxyapatite Ca$_{9.80}$Gd$_{0.20}$(PO$_4$)$_6$(OH)$_2$ (HA), synthesized via solid-state reaction at $T = 1300$ °C, were investigated using scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR), and luminescence spectroscopy. Crystal structure characterization (from unit cell parameters determination to refined atomic positions) was achieved in the $P6_3/m$ space group. FTIR analyses show only slight band shifts of (PO$_4$) modes as a function of the rare earth concentration. Structural refinement, achieved via the Rietveld method, and luminescence spectroscopy highlighted the presence of dopant at the Ca2 site. Strong luminescence was observed for all Eu- and Gd-doped samples. Our multi-methodological study confirms that rare-earth (RE)-doped synthetic hydroxyapatites are promising materials for bio-imaging applications.

Keywords: hydroxyapatite; rare earths; SEM; PXRD; FTIR; luminescence spectroscopy

1. Introduction

Synthetic hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (HA) is the calcium phosphate compound having the most close affinities with the mineral component of human bones and teeth, with excellent biocompatibility and bioactivity, due to its non-toxic and noninflammatory properties [1]. For these reasons, the most common applications of HA are in biomedical sciences, although a wide range of other applications, e.g., as material suitable for laser ablation [2], host for toxic substances [3], and gas sensors [4] have been explored.

Specifically, in biomedical sciences, HA is used in: orthopedics, such as coating for metallic prosthesis, bone filler [5] and as composite materials HA/poly (L-lactide) for bone tissue scaffolds [6]; orthodontics, e.g., cements and dental implants [7]; oncology (cancer treatments) [8]; carrier in drug delivery applications [9,10], and so on. In this context, in recent years there has been a growing
interest in rare-earth (RE) doped HA materials, due to the excellent luminescence properties of RE, which has induced a strong interest in these materials for applications exploiting light-emission properties [11,12]. These materials are more suitable than the common fluorescent organic molecules, since their luminescence properties are not affected by the exposure to irradiation [10]. Moreover, incorporation of RE into the HA matrix overcome the risk of toxicity deriving from RE ions in view of biomedical applications [13].

As a consequence, HA doped with RE ions is employed as cell labelling materials, owing to the strong luminescence under visible radiation, or as fluorescent probe, largely used for nondestructive observations both in vivo and in vitro [14]. The performance of the probe, in terms of luminescence intensity, typically depends on the crystallinity and crystal structure of the host material, and on the concentration of the RE used as dopant [14]. For these applications, the crystal chemical flexibility of HA allows the substitutions of many RE ions without any major modification at the two Ca1 and Ca2 sites; this feature has been also observed for all the most common Ca_{10}(PO_4)_{6}(F,OH,Cl)_2 apatite species [15]. This property is mainly due to the ionic radii similarity between Ca^{2+} and RE^{3+} [16] allowing their easy exchange in the structure.

Among all RE-doped hydroxyapatites, europium-doped HA revealed to be an interesting luminescent material, due to Eu^{3+} ion’s nondegenerate ground (7F_0) and emitting (5D_0) states, giving rise to luminescence spectra that provide valuable information about the local structure around the impurity ion [17]. As a consequence, there has been, in recent years, the production of a large number of Eu-HA systems employed as luminescent biomaterials [18–20]. We also point out that gadolinium-doped HA has been revealed to be a suitable specie for bioimaging applications [21–23], due to its magnetic properties, while its luminescence efficiency upon gamma ray radiation can in turn be useful for dosimetry devices [23]. In particular, its emission in the UV range can be used as sensitizer in co-doped systems [13,22], but applications in many other fields such as phosphor [24] or antibacterial materials [25] can also be interesting.

In this work, we investigate the luminescence behaviour of a set of Eu^{3+}-doped Ca_{10-x}RE_{x}(PO_4)_{6}(OH)_2 hydroxyapatite, with x = 0, 0.01, 0.02, 0.10 and 0.20, and of Ca_{9.80}Gd_{0.20}(PO_4)_{6}(OH)_2, through a multidisciplinary study based on scanning electron microscopy (SEM), powder X-Ray diffraction (PXRD), Fourier transform infrared (FTIR), and luminescence spectroscopies. This work is part of our ongoing investigation into the crystal chemistry and physical-chemistry of synthetic calcium phosphate materials [26–30]. The more profound investigation of the luminescence behavior of HA-Eu with respect to previous work concerning the luminescence of Eu^{3+} ion in HA-based materials is worth noting in the present work; this was accomplished by collecting well resolved spectra and lifetimes decays; in addition, the emission of Gd^{3+} ion in the compound Ca_{9.80}Gd_{0.20}(PO_4)_{6}(OH)_2 was investigated for the first time. In both cases, luminescence features were related to their structure. Moreover, the structural analysis was improved by means of the Rietveld method.

2. Materials and Methods

The Ca_{10-x}RE_{x}(PO_4)_{6}(OH)_2 samples under investigation in this study are labelled in the following way: HA = undoped hydroxyapatite, HA-Eu1 to HA-Eu4 = Eu-doped hydroxyapatite with x_{Eu} = 0.01, 0.02, 0.10 and 0.20, respectively, while HA-Gd = Gd-doped hydroxyapatite with x_{Gd} = 0.20. Gd-doped HA with x_{Gd} = 0.01, 0.02, 0.10 were also preliminary investigated with luminesce spectroscopy; since the did not show any appreciable luminescence, they were not considered for the present study. X-ray structures were refined only for HA-Gd and HA-Eu compounds at higher concentrations (i.e., samples HA-Gd and HA-Eu4), to examine the site preference for the RE substituting for Ca.

The HA-RE samples were synthesized by the solid-state route. Stoichiometric amounts of CaCO_3, CaHPO_4, and RE_2O_3 (RE = Eu, Gd) were mixed using an agate mortar for 1 h. The homogenized powders were then placed in alumina crucibles and calcinated at high temperature (T = 1300 °C) for 7 h [31].
Morphological analyses of the HA-RE samples were obtained by using a scanning electron microscope (SEM) JEOL-JSM 5310 (JEOL LTD, Tokio, Japan).

Powder XRD data of HA-Eu4 and HA-Gd samples were collected for structural analysis by using an automated Rigaku RINT2500 laboratory diffractometer (Rigaku Co., Tokio, Japan). Working at room temperature at 50 kV and 200 mA in Debye Scherrer geometry, the equipment uses an asymmetric Johansson Ge (111) crystal to select the monochromatic Cu Kα1 radiation (λ = 1.54056 Å) and the silicon strip Rigaku D/teX Ultra detector (Rigaku Co., Tokio, Japan).

The 2θ angular range 10–120° was scanned with a step size of 0.02° (2θ) and counting time of 4 s/step, by introducing the sample in a special glass capillary of 0.5 mm of diameter and mounted on the axis of the goniometer. To reduce the effect of possible preferred orientation, the capillary was rotated during measurement to improve the randomization of the orientations of the individual crystallites. The main acquisition parameters are reported in Table 1. All the powder structure solution steps: unit cell parameters calculation, identification of the space group, structure solution in reciprocal or direct space, and model refinement via the Rietveld method [32], were carried out by EXPO 2013 software [33].

Table 1. Main acquisition and structure refinement parameters for Eu-doped hydroxyapatite Ca_{10}(PO_4)_6(OH)_2 (HA-Eu4) and Gd-doped hydroxyapatite Ca_{10}(PO_4)_6(OH)_2 (HA-Gd) samples. FMLQ = full matrix least squares; Pearson VII [33].

| Crystal Formula | HA-Eu4 | HA-Gd |
|-----------------|--------|-------|
| Refined formula | (Ca_{4.86}Eu_{0.09})_2(PO_4)_6(OH)_2 | (Ca_{4.87}Gd_{0.11})_2(PO_4)_6(OH)_2 |
| Formula weight  | 1019.50 | 1024.20 |
| Color           | Colorless | Colorless |
| Temperature (K) | 293 | 293 |
| Wavelength (Å)  | 1.54056 | 1.54056 |
| 2θ range; step (°) | 10-120, 0.02 | 10-120, 0.02 |
| System, space group | Hex., P63/m | Hex., P63/m |
| a = b (Å)       | 9.41264(5) | 9.41284(6) |
| c (Å)           | 6.88038(..) | 6.88151(10) |
| V (Å³)          | 527.917(3) | 528.026(9) |
| Z; Density calc. (Mg·m⁻³) | 1, 3.207 | 1, 3.221 |
| Bragg refl., parameters | FMLQ | FMLQ |
| $R_\text{p}$; $R_\text{wp}$; $R_\text{exp}$ (%) | 4.34, 5.80, 4.87 | 7.00, 9.31, 5.33 |

FTIR powder samples spectra were collected using a Nicolet iS50 FTIR spectrometer equipped (Thermo Fischer Scientific, Waltham, MA, USA) with a deuterated triglycine sulfate (DTGS) detector and a KBr beam splitter; the nominal resolution was 4 cm⁻¹ and 64 scans were averaged for both sample and background. All samples were prepared as a KBr disk by mixing 1 mg of sample with 150 mg of KBr.

Room temperature luminescence spectra and decay curves were achieved by using a Fluorolog 3 (Horiba-Jobin Yvon) spectrofluorometer (Horiba Ltd., Kyoto, Japan), equipped with a Xe lamp, a double excitation monochromator, a single emission monochromator (Horiba Ltd., Kyoto, Japan) (mod. HR320) and a photomultiplier in photon counting mode for the detection of the emitted signal. The following set up was employed in order to obtain well resolved emission spectra: excitation at 393 nm; integration time: 0.5 s; slits: 5 (in)-2 (out) nm, filter 550 nm, step 0.2 nm. Integration time for HA-Eu4 was lowered to 0.2 s in order to avoid signal saturation. Lifetimes were measured using time-correlated single-photon counting technique (TCSPC), with a xenon microsecond pulsed lamp as excitation source. The decays curves were fitted by the Horiba Jobin Yvon DAS6 instrument software [34].
3. Results and Discussion

3.1. SEM Analysis

High-resolution SEM investigation of Eu-doped HA samples showed the presence of three different morphologies: compact and porous aggregates (Figure 1b,d,f,h), and massive fragments (Figure 1h). The porous aggregates are the most common, with the largest crystallite size of ~10 μm (Figure 1a,c,g). The massive fragments and compact aggregates have the largest dimension ~35 μm (Figure 1c,e,f) and ~5 μm (Figure 1e), respectively. In all cases, the crystallites show a rounded morphology, from elongated to sub-spherical, and the most common dimension is ~5 μm. SEM investigations also suggested the growth of porous morphologies on massive fragments (Figure 1d,f,h).

The shapes of Eu-doped HA crystallites synthesized in this study are similar to those described by [35], for the sample with Eu/Ca molar ratios of 7.5% in [36], and by [37] for the sample prepared at pH = 12. According to these papers, the spherical morphologies of the crystallites (phosphors) are ideal for enhancing brightness and resolution via the high packing density and the reduction of light scattering. This offers the possibility of brighter photoluminescence (PL) performance, higher definition, and improved screen packing [35,36]. This aspect is well-described by [35] that showed how the peak intensity of the PL spectra reached the maximum value for HA doped with 7.5 wt% of Eu³⁺, and consisting of crystallites having clearly sub-spherical shapes.

The morphologies of the synthetic samples obtained in this work show some correlations with those described for Eu- and Gd-doped tricalcium phosphates by [27]. For example, the porous aggregates are very similar to microcrystalline aggregates found in Ca₀RE(PO₄)₇ (RE = Eu and Gd),

![Figure 1. Scanning electron microscopy (SEM) images of Eu- and Gd–doped HA samples synthesized here. Detail of: HA-Eu1 at 5 μm (a) and 10 μm (b); HA-Eu2 at 5 μm (c) and 10 μm (d); HA-Eu3 at 5 μm (e) and 10 μm (f); HA-Eu4 at 5 μm (g) and 10 μm (h); HA-Gd at 5 μm (i).](image-url)
in terms of dimension and microcrystals shape, even if in the doped HA samples, the porosity of aggregates are higher.

SEM analyses of sample HA-Gd showed the presence of porous aggregates composed by elongated and rounded crystallites with an average size of 5 \( \mu \text{m} \) (Figure 1i). These type of compounds were not so exhaustively studied from the morphological point of view as the analogue Eu phases, therefore there is scarce information in the literature. We can only quote the work of [37], where Gd-HA nanoparticles of ~70 \( \mu \text{m} \) size were described, with a rounded morphology similar to the one observed in our HA-Gd synthetic product.

3.2. X-ray Structural Study

The crystal structure investigation was performed for Eu and Gd doped HA at highest concentration \( (x = 0.2), \) by using the EXPO software [33]. The indexing of the powder diffraction patterns by N-TREOR09 program [38], as integrated in EXPO, revealed a hexagonal unit cell typical of HA, with some unindexed diffraction peaks attributed to Ca$_3$(PO$_4$)$_3$ tricalcium phosphate (TCP) phase. The mixture is in agreement with [39] reporting a partial dissociation of HA into TCP at about 900°C.

The crystallinity of both HA-Eu4 and HA-Gd samples, calculated according to [40] was 97.07% and 99.03%, respectively, in agreement with the typical results for HA obtained from solid state synthesis [41,42].

The next step of the structure investigation revealed the hexagonal \( P6_3/m \) space group for the hydroxyapatite [43], while the structure solution was obtained via the direct methods procedure in EXPO, confirming the hexagonal \( P6_3/m \) model reported in [43]. The obtained structure was submitted to structural refinement by the Rietveld method, assuming both calcium sites as possible localizations of the dopant rare earth. Detailed crystallographic results are given in Table 1. The following refinement strategy was applied: in the sites shared by Ca and rare earth, the position and the thermal parameter of both occupants were constrained to be equal, and the sum of Ca and RE occupancies fixed according to the experimental crystal chemical formulas. Moreover, the thermal parameters of P and O atoms were constrained to be equal. Hydrogen atoms were not found by Fourier analysis. The main crystal structure refinements data are reported in Table 1. The agreement between the observed (blue line) and the calculated (red line) diffraction pattern is displayed, together with the background (green line) and the difference pattern plotted on the same scale (violet line), in Figure 2a,b for HA-Eu4 and HA-Gd samples, respectively.

![Figure 2. Cont.](image-url)
Table 2. Atomic position, isotropic thermal parameters, and site occupancy for HA-Eu4 and HA-Gd samples.

| Atom | Site | x    | y    | z     | Ueq | Occ. |
|------|------|------|------|-------|-----|------|
| Ca1  | 4f   | 2/3  | 1/3  | −0.0016(5) | 0   | 1    |
| Ca2  | 6h   | 1.0073(3) | 0.2513(2) | 1/4 | 0.0000(3) | 0.961(1) |
| Eu1  | 6h   | 1.0073(3) | 0.2513(2) | 1/4 | 0.0000(3) | 0.029(1) |
| P1   | 6h   | 1.0291(3) | 0.3978(3) | −1/4 | 0.0122 | 1    |
| O1   | 6h   | 0.8430(6) | 0.3261(6) | −1/4 | 0.0112 | 1    |
| O2   | 6h   | 0.8773(7) | 0.4111(7) | 1/4 | 0.0011 | 1    |
| O3   | 12i  | 1.0854(5) | 0.3385(5) | −0.0682(6) | 0.0112 | 1    |
| O4   | 4c   | 0    | 0    | 0.2000(18) | 0.0156(5) | 0.5  |

| Atom | Site | x    | y    | z     | Ueq | Occ. |
|------|------|------|------|-------|-----|------|
| Ca1  | 4f   | 2/3  | 1/3  | −0.0004(8) | 0   | 1    |
| Ca2  | 6h   | 1.0076(4) | 0.2518(4) | 1/4 | 0.0000(6) | 0.956(2) |
| Gd1  | 6h   | 1.0076(4) | 0.2518(4) | 1/4 | 0.0000(6) | 0.034(2) |
| P1   | 6h   | 1.0309(6) | 0.3990(5) | −1/4 | 0.0035 | 1    |
| O1   | 6h   | 0.8407(11) | 0.3240(11) | −1/4 | 0   | 1    |
| O2   | 6h   | 0.8788(12) | 0.4086(12) | 1/4 | 0.0096 | 1    |
| O3   | 12i  | 1.0869(8) | 0.3367(8) | −0.0647(9) | 0.0035 | 1    |
| O4   | 4c   | 0    | 0    | 0.197(3) | 0.0035(8) | 0.5  |

Figure 2. Rietveld plots of HA-Eu4 (a) and HA-Gd (b) samples. Observed diffraction profile (blue line), calculated profile (red line), background (green line) and difference profile (violet line).

Figure 3. Coordination environments around the Ca1 and Ca2 sites in hydroxyapatite. Dashed lines: Ca-O interactions >2.8 Å.
Table 3. Bond distances (Å) and bond valence parameters (valence units) for HA-Eu4 and HA-Gd samples. The Ca2-O values are calculated taking into account the refined occupancy parameters for Ca and Eu (Table 2).

| Distance | HA-Eu4 | bvp | HA-Gd | bvp |
|----------|--------|-----|-------|-----|
| 3xCa1-O1 | 2.406(5) | 0.30 | 2.404(8) | 0.31 |
| 3xCa1-O2 | 2.452(5) | 0.27 | 2.459(9) | 0.26 |
| 3xCa1-O3 | 2.830(4) | 0.10 | 2.833(7) | 0.10 |
| Ca2-O1   | 2.687(5) | 0.14 | 2.670(13) | 0.15 |
| Ca2-O2   | 2.367(9) | 0.34 | 2.332(5) | 0.37 |
| 2xCa2-O3 | 2.325(4) | 0.38 | 2.300(6) | 0.41 |
| 2xCa2-O3 | 2.486(4) | 0.25 | 2.479(9) | 0.25 |
| Ca2-O4   | 2.357(3) | 0.35 | 2.364(5) | 0.34 |
| P1-O1    | 1.530(6) | 1.26 | 1.562(14) | 1.16 |
| P1-O2    | 1.558(6) | 1.17 | 1.569(10) | 1.14 |
| 2xP1-O3  | 1.566(5) | 1.15 | 1.599(7) | 1.05 |

The Ca atoms are engaged in complex co-ordinations: Ca1 in a CaO$_6$ polyhedron (Figure 3), with three couples of bond distances related by symmetry, ranging from 2.406(5)–2.830(4) Å for HA-Eu4, and 2.404(8)–2.833(7) Å for HA-Gd (Table 3). The Ca1-O3 distance slightly exceeds the bonding sphere of Ca, providing a weak contribution to the bond valence [44] to Ca1, as discussed later (see also Table 3). Actually, based on the refined distances, we could describe the Ca1 site as a CaO$_6$ polyhedron, the Ca1···O3 being interpreted as relatively weak interactions. The Ca2 polyhedron displays a CaO$_6$(OH) coordination, resembling a distorted pentagonal bipyramid with five bonds (1xCa2-O1 and two couples of symmetry-related Ca2-O3 bonds) on the equatorial plane, and vertices consisting of one O2 atom and one OH group. The Ca2-O distances are in the range 2.325(4)–2.687(5) Å (HA-Eu4), and 2.300(10)–2.670(13) Å (HA-Gd).

For both compounds, all P-O and Ca-O bond distances are in good agreement with those observed in other HA structural investigations [45].

As observed in the work of Rossi et al. [46], the O4 hydroxyl atoms occupy the 4e sites, split above or below the mirror planes, with a disordered site-distribution (Table 2). This arrangement causes a local deviation from the P6$_3$/m symmetry, with a consequent lack of the mirror plane, being only one of the two mirror-related sites statistically occupied. However, because each mirror-related site is half occupied, the average P6$_3$/m symmetry is preserved [15].

To support the Rietveld refinement results for the distribution of RE dopants within the available sites, we examined the calculated bond valence parameters [44], testing the possible dopant localization at both Ca1 and Ca2 cationic positions: the occupancy refinements unambiguously converged into the presence of the rare earth cation at the Ca2 site for both samples (Table 2), in agreement with the substitution mechanisms described by Fleet et al. [47] and by Graeve et al. [48]. This conclusion was confirmed by the calculated excess charge converging to the Ca2 position, resulting in 2.09 v.u. for HA-Eu4 and 2.18 v.u. for HA-Gd, while Ca1 displayed values close to the ideal charge of 2.00 for both phases. For packing reasons, and to balance the excess charge at Ca2, the P site resulted under-bonded in both structures, with 4.73 v.u. and 4.40 v.u. for HA-Eu4 and HA-Gd, respectively. The final results of bond valence parameters analysis are given in Table 3.

Hexagonal P6$_3$/m hydroxyapatite, whose crystal formula can be written as [Ca$_1$$_4$Ca$_2$$_6$](PO$_4$)$_6$(OH)$_2$, shows a zeolitic character; it can be described as a framework of columns of face-sharing Ca1O$_6$ metaprisms (a polyhedron intermediate between an octahedron and a trigonal prism), corner-connected to PO$_4$ tetrahedra down [001]; such an arrangement indeed creates one-dimensional tunnels occupied by [Ca(2)$_6$(OH)$_2$]$^{10+}$ counter-ions (Figure 4). The Ca1O$_6$ metaprism is ideally built up by the six strongest Ca-O bond distances; those over 2.8 Å are not considered. The HA framework has the ideal stoichiometry [Ca$_1$$_4$(PO$_4$)$_6$]$_{10-}$, with the hexagonal channel containing [Ca$_2$$_6$(OH)$_2$]$_{10+}$ moieties acting as counter-ions [49], while the Ca1-O3 interactions further stabilize the framework.
HA framework has the ideal stoichiometry $[\text{Ca}_{14}(\text{PO}_4)_6]^{10-}$, with the hexagonal channel containing $[\text{Ca}_{26}(\text{OH})_2]^{10+}$ moieties acting as counter-ions [49], while the Ca1-O3 interactions further stabilize the framework.

Figure 4. Three-dimensional framework of HA-Eu4 sample, showing details of Ca1O6 metaprisms, and Ca26(OH)2 groups. The OH groups correspond to O4 atoms. Ca1-O3 bonds are dashed for clarity.

3.3. FTIR Spectroscopy

The powder FTIR absorbance spectra of HA-Eu and HA-Gd samples were collected in the 400–4000 cm$^{-1}$ wavenumber range and are shown in Figure 5, in comparison with the pattern of undoped HA. Measured band positions (wavenumbers, cm$^{-1}$) are listed in Table 4.

Figure 5. (a) Fourier transform infrared (FTIR) spectra of Eu-doped HA samples in comparison with undoped HA in the low-frequency (<1200 cm$^{-1}$) lattice mode region; (b) comparison between the spectra of samples HA-Gd and HA-Eu4 in the full range 4000–400 cm$^{-1}$.
Table 4. Measured absorption features in the FTIR spectra and relative assignments for HA samples.

|       | HA  | HA-Eu1 | HA-Eu2 | HA-Eu3 | HA-Eu4 | HA-Gd | Assignment   |
|-------|-----|--------|--------|--------|--------|--------|--------------|
| 3569  | 3570| 3569   | 3566   | 3569   | 3569   | ν\textsubscript{2}(OH) |
| 1633  | 1633| 1634   | 1633   | 1633   | 1633   | δ(H\textsubscript{2}O) |
| 1090  | 1090| 1090   | 1090   | 1091   | 1091   |        |
| 1047  | 1047| 1047   | 1047   | 1048   | 1048   | ν\textsubscript{3}(PO\textsubscript{4})\textsuperscript{3−} |
| 1015  | 1015| 1015   | 1015   | 1015   | 1015   |        |
| 960   | 960 | 960    | 960    | 961    | 961    | ν\textsubscript{1}(PO\textsubscript{4})\textsuperscript{3−} |
| 633   | 633 | 633    | 633    | 632    | 632    | ν\textsubscript{1}(OH) |
| 600   | 600 | 600    | 601    | 602    | 602    |        |
| 574   | 570 | 570    | 570    | 571    | 571    | ν\textsubscript{4}(PO\textsubscript{4})\textsuperscript{3−} |
| -     | -   | -      | -      | 518    | 518    | RE-O   |
| 472   | 472 | 472    | 472    | 473    | 473    | ν\textsubscript{2}(PO\textsubscript{4})\textsuperscript{3−} |

Interpretation of the spectra can be based on the vast literature for phosphate compounds [50–55]. Accordingly, in the higher wavenumber 4000–3000 cm\textsuperscript{−1} range the well resolved and relatively sharp peak at 3570 cm\textsuperscript{−1} is assigned to the (OH)\textsuperscript{−} stretching mode [56]. This peak is superimposed to a broad absorption extending from 3600 to 3000 cm\textsuperscript{−1} that is due to H\textsubscript{2}O (moisture) adsorbed on the KBr disk [57]. The bending mode of these moisture molecules occurs around 1600 cm\textsuperscript{−1} (Figure 5b).

In the lower wavenumber region, the most intense peaks in the 1090–1000 cm\textsuperscript{−1} range can be assigned to the triply degenerated antisymmetric stretching modes (ν\textsubscript{3}) of the phosphate group (PO\textsubscript{4})\textsuperscript{3−} [58], while the medium-intense peak at 960 cm\textsuperscript{−1} is due to the symmetric stretching of this anion. Two medium intense and very sharp peaks at 602 and 564 cm\textsuperscript{−1} can be related to the triple degenerate antisymmetric bending mode of the [PO\textsubscript{4}]\textsuperscript{3−} group [14]. Analysis of deuterated samples [56] shows that the relatively sharp peak at 663 cm\textsuperscript{−1} is due to the O-H libration. According to [59], the sharpness of selected bands in the phosphate region, especially 632 cm\textsuperscript{−1}, 602 cm\textsuperscript{−1}, and 564 cm\textsuperscript{−1}, are an experimental indication of good crystallinity of the hydroxyapatite, confirming the XRD results. Finally, the band at 475 cm\textsuperscript{−1} can be attributed to the ν\textsubscript{2}(PO\textsubscript{4})\textsuperscript{3−} mode [60]. It is worth noting that the presence, in samples with the higher concentration of dopant, of a peak at 518 cm\textsuperscript{−1} that could be assigned to the RE-O mode as proposed for La and by [58], for Gd-doped hydroxyapatites prepared at high annealing temperatures. Last, in HA-Eu3 sample, the weak peak at 460 cm\textsuperscript{−1} is attributed to trace amounts of Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} (TCP) that are occasionally associated with hydroxyapatite synthesized at high temperature [30].

For increasing concentration of the RE dopant no significant modifications of the spectra (Figure 5), except slight peak shift, are observed (Table 4).

3.4. Luminescence Spectroscopy

3.4.1. Eu\textsuperscript{3+} Dopant

The analysis of the luminescence revealed significant emission bands for all Eu-doped HA samples, and for the Gd-doped sample. It should be pointed out that while Eu\textsuperscript{3+} luminescence was clearly observed at all investigated concentrations, for Gd\textsuperscript{3+} only the highest concentration (2%) yielded an observable emission. At lower doping amounts, the intensity was too weak, thus all other samples with lower gadolinium concentrations were abandoned for the present study.

The room temperature excitation and emission spectra collected for the representative HA-Eu4 sample are displayed in Figure 6a,b, respectively.
Figure 6. (a) Normalized excitation spectrum of HA-Eu4, detecting the emission at 628 nm. (b) Emission spectrum of HA-Eu4, collected upon excitation at 393 nm.

The most striking feature that is worth noting, however, is the strong intensity of the emission peak at 573 nm that corresponds to the $^5D_0 \rightarrow ^7F_0$ forbidden transition of Eu$^{3+}$. This band acquires intensity only in the presence of a strong covalent bond involving the impurity ion [61,62]. This unusual behavior is addressed below. The profile of the $^5D_0 \rightarrow ^7F_0$ band for the present samples is Gaussian, with a full width at half maximum (FWHM) around 70 cm$^{-1}$, which is a high value for a crystalline material, and comparable with the one typically observed in glasses [63]. This observation is therefore compatible with the accommodation of Eu$^{3+}$ in a distribution of sites affected by the presence of significant disorder.

Inspection of the excitation spectra obtained at the 628 nm emission line (Figure 6a), shows that the most intense excitation peak is at 460 nm, corresponding to the $^7F_0 \rightarrow ^5D_2$ transition. In addition, a broad band occurs in the 260–350 nm range, that is due to Eu$^{3+}$−O$^{2−}$ charge transfer (CT band).

Decay curves were collected at room temperature in correspondence of maxima at 573 and 628 nm for all samples, upon excitation at 393 and 460 nm. Normalized decay curves obtained at $\lambda_{\text{exc}}$ = 393 nm and $\lambda_{\text{emiss}}$ = 628 nm are shown in Figure 7. In these conditions all the decay curves can be described by a single exponential. As a result, independently of the excitation wavelengths (in the range 320–530 nm) and of the Eu$^{3+}$ concentration, the decay times measured at 573 and 628 nm are close to 0.45 ms. This decay time is shorter than the one normally observed for anhydrous materials (≥1 ms) and is more typical of hydrated oxides.

Figure 7. Normalized decay curves in correspondence of $\lambda_{\text{exc}} = 393$ nm and $\lambda_{\text{emiss}} = 628$ nm.
As already pointed out, a remarkable feature of all HA-Eu doped samples is the strong intensity of the forbidden europium $^{5}D_0 \rightarrow ^{7}F_0$ transition. A similar behaviour was reported by [30,64] for samples treated at $T > 900^\circ$C, while for samples synthesized at 600$^\circ$C the same forbidden transition was reported to occur with less intensity [30]. The examined structure is that of HA; above a certain concentration of RE dopant we observe the formation of additional phases in the assemblage. According to [65], Ca phosphate and Ca oxide occur in low concentrations until Eu reaches about 5%. Ca$_3$(PO$_4$)$_2$ tricalcium phosphate (TCP) begins to appear in the assemblage at 600$^\circ$C in the presence of Eu at 4% [64]. The complete transformation of HA into β-TCP is observed for $T > 1000^\circ$C for different thermal treatments [48]. Moreover, the presence of Eu$^{3+}$ ions has been shown to inhibit the crystallization of nano-sized HA [64]. The loss of OH$^-$ group for higher $T$ is also feasible to induce a local structural distortion [48], that probably involves the anomalous appearance of the forbidden transition. This feature is unusual and was previously found in similar nano crystalline Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ doped with 3% of Eu$^{3+}$ [30], while the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition was otherwise dominant in HA-Eu materials [6,10,13].

For samples whose spectra were obtained under experimental conditions allowing high spectral resolution (i.e., low temperature, laser excitation, etc.), the $^5D_0 \rightarrow ^7F_0$ transition shows a single band [66], indicating the disorder of Eu$^{3+}$ at non-equivalent Ca$^{2+}$ sites, i.e., Ca1 (higher symmetry) and Ca2 (lower symmetry). In particular, Eu$^{3+}$ may enter preferentially the Ca2 site in order to better optimize the charge balance through the thermal diffusion mechanism occurring in these materials [10,66]. The mechanism can be described according to [64]

$$\text{OH}^- + \text{Ca}^{2+} \leftrightarrow \text{Eu}^{3+} + \text{O}^{2-}$$

(1)

On the other hand another charge compensation mechanism is possible [64]:

$$3\text{Ca}^{2+} \leftrightarrow 2\text{Eu}^{3+} + \Box \text{ (vacancy)}$$

(2)

implying the creation of Ca$^{2+}$ vacancies.

In the present samples, the first mechanism (Equation (1)) is undoubtedly active, given the close similarity of the luminescence spectra to the ones reported by [67] for the Eu$^{3+}$ in HA and oxyapatites, in particular for the unusually strong 0-0 transition [67]. The explanation of the abnormal intensity of the formally forbidden 0-0 transition was proposed on the basis of the strong covalence of the Eu$^{3+}$-O$^{2-}$ bond in the Ca2 sites [61,62,66,67]. However, the presence of a relatively short decay time of about 0.45 ms for the emission at 573 nm (corresponding to the 0-0 band) indicates that the $^5D_0$ level is also affected by multiphonon relaxation induced by the O-H vibrations (Equation (1)). It is worth to noting that the presence of vibronic sidebands ascribed to coupling between the Gd$^{3+}$ and O-H vibrations indicate that a fraction of the RE impurities enter the HA lattice also through the mechanism presented in Equation (2) (see below). It is, however, plausible that traces of the dopant can be present in Ca1 sites even for higher synthesis temperature, although they are not directly detected in the present study by luminescence spectroscopy, while being invisible to a long-range technique like X-ray diffraction.

### 3.4.2. Gd$^{3+}$ Dopant

The Gd-doped sample, HA-Gd showed strong UV luminescence. In fact, the bands are well resolved both in the excitation and in the emission spectra, displaying narrow peaks (Figure 8a), as it usual for 4f-4f transitions. However, this is the first time that the optical properties of Gd$^{3+}$ are studied in relation to the HA structure.

Upon excitation in the $^6I_J (J = 7/2-17/2)$ region, emission bands corresponding to $^6P_{5/2} \rightarrow ^8S_{7/2}$ and $^6P_{7/2} \rightarrow ^8S_{7/2}$ transitions are observed, with the stronger peak at 314 nm (31,806 cm$^{-1}$) as observed for Gd$^{3+}$ in different hosts [68–71], suitable for potential multimodal applications [23]. It is interesting to point out that weak, but clear vibronic bands are detected at 319.6, 325, and 351 nm in the emission spectrum, located respectively at energy differences from the purely electronic transition that
Correspond to features present in the FTIR spectrum [72], as reported in Figure 8b. We note that similar sidebands are also observed in the excitation spectrum (not shown here for brevity).

Figure 8. (a) HA-Gd excitation (detecting the emission at 314 nm) and emission (excitation at 274 nm) spectra; (b) vibronic bands and assignments in the HA-Gd emission spectrum.

The sharp purely electronic lines in the optical spectra of RE ions are often accompanied by other weak peaks, corresponding to the vibronic transitions [72]. The position and intensity of these transitions are strongly related to the surroundings of the ions, thus they can give information about the nature of the chemical environment and the vibrational coupling with the 4f0 electrons. [71,73]. For Gd3+, the vibronic intensity is mainly due to vibronically-induced forced electric dipole transitions [71]. To the best of our knowledge, this is the first time that vibronic sidebands of this type have been observed in the case of Gd3+ present as impurity in HA.

The energy of the vibronic peaks observed in HA-Gd suggests that the electronic levels of the impurity ion are coupled to local Gd-O vibrations in the first coordination sphere, and to vibrations in more distant phosphate and hydroxyl molecular ions. Indeed, we observe an intensity ratio between the O-H vibronic peak and the main electronic transition 6P7/2 → 8S7/2 of about 3%, confirming the presence of coupling of the Gd3+ ion to this high energy vibration [68]. In turn, this observation proves that not only the charge compensation mechanism reported in Equation (1) (for Eu3+) is present, but also the one presented in Equation (2). This should affect the non-radiative decay of the excited states of the impurity ions [68] (see below).

The excitation spectrum shows three main peaks in the region corresponding to 8S7/2 → 6I7/2 transition. The decay curve corresponding to the 314 nm emission peak, obtained upon pulsed 274 nm excitation, is characterized by an exponential profile with a decay time of 0.76 ms. This value is shorter than the typical decay times for the Gd3+ ion in phosphate hosts, which can be as long as 2.72 ms [73], so that non-radiative decay due to the interaction with O-H vibrations is likely to be operative. This results nicely agrees with the coupling of the Gd3+ ion with hydroxyl vibrations evidenced by the presence of relevant vibronic sidebands. In addition, it explains the short decay times observed for HA doped with Eu3+ (see above).

4. Conclusions

Luminescence properties of Eu-doped Ca10-xEu x(P2O7)6·(OH)2 (xEu = 0, 0.01, 0.02, 0.10 and 0.20) and Gd-doped Ca9.80Gd0.20(P2O7)6·(OH)2 hydroxyapatite powder samples, synthesized via solid state reaction at T = 1300 °C, were fully characterized through a multi-methodological approach based on SEM microscopy, powder X-ray diffraction, FTIR, and luminescence spectroscopy. SEM analysis showed the presence of three different morphologies (compact, porous, and aggregates), with the most common average size being ~10 μm; crystal structure refinement via the Rietveld method (P63/m space group) showed how the RE ions are strongly ordered at the Ca2 site, a feature that is in agreement with the high temperature of synthesis; FTIR showed slight band shifts of modes typical of the (PO4) moiety as a function of the rare earth concentration rate. Beside the strong luminescence observed for...
all of the samples investigated, the Gd-doped hydroxyapatite also showed interesting vibronic features that revealed information about the electron-phonon coupling in the HA-doped host. The results obtained are in agreement with the presence of RE ions at the Ca2 site as refined based on the XRD data; the short decay times and the presence of vibronic sidebands assigned to the coupling with hydroxyl anions indicate that two charge compensation mechanisms are present. One of these implies the formation of free oxide ions, and the other the creation of Ca$^{2+}$ vacancies. In conclusion, this work provides new insights into the luminescent properties and the local structure of hydroxyapatites doped with rare-earth ions and produced by high temperature synthesis. This information will be useful for the design of biocompatible synthetic materials for bio-imaging applications. This work also stresses the need for multi-methodological approaches for a full and detailed characterization of this class of materials.

**Author Contributions:** All the authors conceived and designed the main ideas together, supervised the whole work, and wrote the text; A.E.K. contributed in the synthesis; M.R. contributed in SEM-EDS analysis; R.R. and F.C. contributed in PXRD data collections and Rietveld refinements; G.D.V. contributed in FTIR spectroscopy; V.P. and M.B. contributed in luminescence spectroscopy. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding. G.D.V. was financially supported by MIUR-Italy Dipartimenti di Eccellenza, ARTICOLO 1, COMMI 314–337 LEGGE 232/2016.

**Acknowledgments:** Research developed within the activities of CNR (Italy)-CNRST (Morocco) bilateral project 2016–17 ‘Novel Ca$$_9$$RE(PO$$$_4$$)$$$_7$$ biomaterials: synthesis and multi-methodological characterization via X-ray techniques’ reference CNR 1588/16. The authors gratefully thank Erica Viviani (Verona University), Federico Galdenzi (Roma Tre University) and Francesco Baldassarre (IC-CNR) for expert technical assistance, and the Facility “Centro Piattaforme Tecnologiche” of the University of Verona for access to the Fluorolog 3 (Horiba-Jobin Yvon) spectrofluorometer. University of Verona is gratefully acknowledged.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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