Spectroscopic and Structural Properties of β-Tricalcium Phosphates Ca$_9$RE(PO$_4$)$_7$ (RE = Nd, Gd, Dy)

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Abstract: Rare-earth-based Ca$_9$RE(PO$_4$)$_7$ (RE = Nd, Gd, Dy) materials were synthesized by solid-state reaction at T = 1200 °C. The obtained tricalcium phosphate (TCP) materials are efficient light emitters due to the presence of RE$^{3+}$ ions, although these ions are present at high concentrations. Moreover, in these host structures, these ions can be used as optical probes to study their local environments. Thus, photoluminescence (PL) emission spectra of the powder samples clearly indicated, for Dy$^{3+}$ and Gd$^{3+}$ ions, the presence of the RE$^{3+}$ ion in low-symmetry sites with some local structural disorder, and the spectra show the presence of vibrational features (in the case of Gd$^{3+}$). For the Nd$^{3+}$ phase, emission bands are present around 900, 1050, and 1330 nm, originating from the $^4F_{3/2}$ level. In general, these RE-TCP samples are interesting luminescent materials in the visible (Dy), UV (Gd), and NIR (Nd) regions, due to weak concentration quenching even for high concentrations of the emitting ion.

Keywords: TCP; rare-earth elements; luminescence spectroscopy; structural investigation

1. Introduction

Tricalcium phosphate (TCP)-based materials, such as Ca$_3$(PO$_4$)$_2$ and Ca$_9$RE(PO$_4$)$_7$ (RE = rare earth), are interesting as hosts for luminescent ions. They are isotypic with a whitlockite structure, and thus they are characterized by the presence of five different crystal sites having different coordination numbers and by intrinsic structural disorder [1–3]. These sites are suitable for substitution with several dopant ions [3–5]. The effects on the crystal structure after substitution of the Ca$^{2+}$ ions has been studied in relation to the doping amount and the ionic radius of the dopant [2,5]. The luminescence properties were found to be dependent on the site distribution and crystal structure [2]. Most of the studied materials involve the introduction of the emitting ion as an impurity. Structural and optical properties of RE$^{3+}$-doped calcium-phosphate-based materials have been investigated in several hosts and with different RE$^{3+}$ ions as dopants as well as bulk constituents [1–7]. The presence of multiple sites and their peculiar distribution in whitlockite-type structures have been shown to be suitable for obtaining light emission even in the presence of concentrated materials [3], mainly thanks to their inefficient concentration quenching [3,8,9].

Some of these compounds doped with RE$^{3+}$ ions have also shown applications as lighting emitting materials, scintillating materials [1,4], in vivo imaging [2,10], and thermoluminescent dosimeters (TLD) [11]. The study of absorption and emission characteristics...
of a phosphor enables the understanding of electronic energy levels in the host crystal and, consequently, the development of new phosphors of practical relevance [12].

Concentrated materials based on Eu$^{3+}$ and Tb$^{3+}$ have been employed, thanks to their efficient emission in the red and green, respectively, often with a high Tb$^{3+}$ concentration doped with Eu$^{3+}$ to obtain an energy transfer mechanism (ET) [3]. Moreover, due to the role of Eu$^{3+}$ as a structural probe, its luminescence has allowed the study of local symmetry in these materials [13].

In order to further expand the study of Ca$_9$RE(PO$_4$)$_7$ materials, Dy$^{3+}$, Gd$^{3+}$, and Nd$^{3+}$ ions were employed as bulk constituents and their luminescence properties were investigated in relation to their structure. Up to now, the luminescence of these specific ions has been investigated in TCP hosts only at low doping concentrations (lower that 10%) or in combination with other RE$^{3+}$ ions for several applications [14], but not as bulk constituents. Moreover, the lifetime analysis has generally been omitted [11,15].

In this work, the relative intensity of Dy$^{3+}$ emission bands, as well as its decay kinetics, were investigated to give more insight into the local disorder of the host, showing the possible presence of multiple emitting centers that are mutually interacting through non-radiative mechanisms.

However, the characteristic transitions of Gd$^{3+}$ are strongly related to the surrounding host vibrations and are dependent on the nature of the lattice. Comparison of the emission bands with the vibrational modes occurring in the FTIR spectrum also made this ion a good optical probe with which to investigate the structural features of the host materials [9,16,17].

The aim of the present work was to provide a study of the optical spectroscopy of Ca$_9$RE(PO$_4$)$_7$ (RE = Nd, Gd, Dy) TCP materials obtained from a solid state reaction and to relate the luminescence features to the structures of the materials.

2. Experimental

_Synthesis_. Ca$_9$RE(PO$_4$)$_7$ (RE = Nd, Gd, Dy) β–TCP were synthesized by solid state reaction from a mixture of reagent-grade CaCO$_3$, CaHPO$_4$, and pertinent rare-earth oxides RE$_2$O$_3$ (RE = Nd, Gd, Dy), according to the method of Lecointre et al., 2010 [18]:

$$4 \cdot \text{CaCO}_3 + 14 \cdot \text{CaHPO}_4 + \text{RE}_2\text{O}_3 \rightarrow 2 \cdot \text{Ca}_9\text{RE}(\text{PO}_4)_7 + 7 \cdot \text{H}_2\text{O} + 4 \cdot \text{CO}_2$$

After a first heating cycle at 400 °C for 6 h, performed in order to remove H$_2$O and CO$_2$ from the mixture, the different powder samples were ground in an agate mortar and calcined again in an alumina crucible for 12 h at 1200 °C [6].

_X-ray diffraction (XRD)._ The powder XRD data of the title compounds for qualitative and structural analysis were recorded at room temperature on a Bruker D8 diffractometer using Cu Kα radiation (λ$_{Kα}$ = 1.54056 Å) and equipped with a LYNXEYE detector. The measures were achieved in Bragg–Brentano geometry (angular range = 10–70° (2θ); step size of 0.06° (2θ); data collection time = 18 min). Main acquisition parameters are reported in [6].

_Fourier Transform Infrared (FTIR) spectroscopy._ Powder spectra of the title compounds were collected on a Nicolet iS50 FTIR spectrometer equipped with a DTGS detector and a KBr beamsplitter; the nominal resolution was 4 cm$^{-1}$; 64 scans were averaged for both sample and background. The samples were prepared as KBr disks, mixing ca. 1 mg of RE–TCP powder with 150 mg of potassium bromide. Experimental details are reported in [6].

_Photoluminescence spectroscopy._ Room temperature luminescence spectra were achieved by using a Fluorolog 3 (Horiba-Jobin Yvon) spectrofluorometer, equipped with a continuous Xe lamp as the excitation source for steady state measurements, a double excitation monochromator, and a single-emission monochromator (mod. HR320). A photomultiplier in photon counting mode was employed for the detection of the emitted signal up to 800 nm, while a CCD array detector Symphony II cooled by liquid nitrogen was used to measure in the NIR region.

Lifetimes were collected with the same instrument, with a xenon microsecond pulsed lamp as the excitation source. The decay curves were measured by means of a time-correlated single-photon counting technique (TCSPC) and were fitted by the instrument software [19].
3. Discussion
3.1. β–TCP Structural Arrangement
3.1.1. β-TCP and Related Phases

B-tricalcium phosphate, Ca$_3$(PO$_4$)$_2$ (β-TCP), is a high-temperature phase usually obtained by thermal decomposition at $T = 800 \, ^\circ C$ of Ca-deficient HA$p$, or by solid-state reaction of acidic Ca orthophosphate with a base, usually CaO. β-TCP is rhombohedral with space group R3c ($a = b = 10.4352(2) \, \AA$; $c = 37.4029(5) \, \AA$; $V = 3527.26 \, \AA^3$ [20]) and, at $T > 1125 \, ^\circ C$, changes into the polymorph phase α-TCP, monoclinic in $P2_1/a$ ($a = 12.887(2) \, \AA$; $b = 27.280(4)$; $c = 15.219(2) \, \AA$; $\beta = 126.20(1)^\circ$; $V = 4317.52 \, \AA^3$ [21]); the \( \beta \rightarrow \alpha \) transition in TCP may occur later at a higher temperature in the presence of $RE_2O_3$ reactants [6], as in the case of the present $RE$-TCP samples calcined at 1200° (see Synthesis paragraph) but displaying a β–TCP structure as described later. β-TCP has its natural counterpart in the isotypic mineral whitlockite, ideally Ca$_9$Mg(PO$_4$)$_6$[PO$_3$(OH)], rhombohedral in $R3c$ ($a = b = 10.357(3) \, \AA$, $c = 37.095(15) \, \AA$ and $V = 3446(2) \, \AA^3$ [22]); because of isotypicity among natural whitlockite and β-TCP, the latter is often indicated as synthetic whitlockite, and its structure is indicated as whitlockite-type. TCP presents a third polymorph, the high-pressure form known as γ-TCP, rhombohedral in $R3m$, usually coming from transformation both at high temperature and pressure of β-TCP [23]; it is also found with mineral name tuite in chondritic meteorites, as a result of shock impact of other calcium phosphate minerals [24]. Last, the occurrence of a trivalent cation ($RE^{3+}$, but also Fe$^{3+}$, Cr$^{3+}$) in the β-TCP structure leads to the present formula Ca$_9$RE$^{3+}$(PO$_4$)$_7$ [6].

3.1.2. XRD Qualitative Analysis

Qualitative analysis of the powder XRD profiles of the Ca$_9$RE(PO$_4$)$_7$ ($RE = \text{Nd, Gd, Dy}$) underlined the matching between the experimental profiles and undoped β-TCP, highlighting the single-phase behavior for all the three powder samples [6]. XRD spectra were deposited at the PDF-2 database [25] with card numbers 00-070-0125 (Nd), 00-070-0127 (Gd), and 00-070-0128 (Dy). Powder XRD patterns are reported in Figure 1a (Nd), Figure 1b (Gd), and Figure 1c (Dy).

![Figure 1. Powder X-ray spectra of Ca$_9$Nd(PO$_4$)$_7$ (a), Ca$_9$Gd(PO$_4$)$_7$ (b), and Ca$_9$Dy(PO$_4$)$_7$ (c).](image_url)

3.1.3. Polyhedral Environment

As a preliminary remark, structural features of Ca$_9$RE$^{3+}$(PO$_4$)$_7$ compounds are strongly dependent on the lanthanide contraction effect [26], a physical property of those particular rare-earth elements called ‘lanthanides’ (Ln), from La (Z = 57) up to Lu (Z = 71), i.e., the decrease in ionic radius. This causes in $RE$-bearing compounds a certain similarity in crystal-chemical features, such as lattice parameters and cell volume, which usually slightly decrease going across the $RE$ series (from La up to Lu), or in other words they decrease at the lowering of ionic radius of the replacing rare earth. In particular, in inorganic phosphates this is observed in $RE$(PO$_4$)$_3$ synthetic monazites ($RE = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$) and xenotime ($RE = \text{Tb, Dy, Ho, Er, Tm, Yb, Lu}$) [27], in $KLn$(P$_2$O$_7$)-2H$_2$O diphosphates ($Ln = \text{Gd, Tb, Yb}$) [28], and in hybrid diphosphates $Ln_2$(NH$_2$(CH$_2$)$_2$NH$_2$)$2$(HP$_2$O$_7$)$_2$·4H$_2$O ($Ln = \text{Eu, Tb, Er}$) [29]. In particular, for what concerns the present work, we will discuss...
X-ray powder structures, and thus unit cell parameters and bond lengths herein, coming from Rietveld refinements of available Ca$_9$RE(PO$_4$)$_7$ structures in the literature [6,30–32].

Interpretation of unit cell (u.c.) parameters reported for La-, Pr-, Nd-, Eu-, Gd-, Dy-, Tm-, Yb- [6], Ce- [30], Lu- [31], Tb-, and Ho- phases [32] shows a decreasing trend in the refined unit cell parameter values, ranging from $a = b = 10.4695(3)$ Å, $c = 37.500(3)$ Å (La) to $a = b = 10.4164(1)$, $c = 37.302(1)$ Å (Lu). The same trend is followed by the cell volumes: from 3559.7(2) (La) to 3505.1(1) Å$^3$ (Lu), while, as a consequence, the calculated density increases from 3.25 Mg·m$^{-3}$ (La) up to 3.41 Mg·m$^{-3}$ (Lu). Generally, only some small deviations are observed for such trends, as in the case of the Tb and Ho phase in the $a$ parameter, or for Lu in $a$, $c$, and $V$ parameters. Figure 2 reports u.c. parameters for available Ca$_9$RE$^{3+}$(PO$_4$)$_7$ structures, plotted as a function of RE ionic radius; in particular Figure 2a reports the $a$ parameter, Figure 2b reports the $c$ parameter, and Figure 2c depicts the volume trend.

![Figure 2](image-url). Unit cell parameters of RE β–TCP as a function of RE ionic radius (for 6-folded polyhedra). (a) $a$ parameter (Å); (b) $c$ parameter (Å); (c) Volume (Å$^3$). Data from [6], except Ce [30], Lu [31], Tb and Ho [32].

For better describing the Ca$_9$RE$^{3+}$(PO$_4$)$_7$ structure, the site notation proposed by Yashima et al. (2003) [20] in the neutron refinement model of β-TCP will be adopted across the work. Thus, five cationic sites are present in the structures, three in a general position (Wyckoff notation 18b) named M1, M2, and M3 sites, and two in a special position (6a), named M4 and M5. The M4 site is only partially occupied, being in β–TCP the site occupancy factor usually fixed at 1/2 for allowing the charge balance [20]. Two phosphorous and nine oxygen atoms are located on general positions, while a third phosphorous atom
and the O10 atom are placed on special positions (6a). The coordination environments of the single M1–M5 sites are usually respected in β–TCP structures. M1 displays irregular 7-fold coordination, while M2 and M3 display irregular 8-fold coordination, according to a Ca-O bonding sphere fixed at about 2.81 Å. M5 shows a fairly regular octahedral geometry, and M4 presents an uncommon triangular coordination, with three oxygen atoms related for symmetry.

In the isotypic mineral whitlockite, despite the presence of Mg$^{2+}$ replacing Ca$^{2+}$ at the M5 octahedral site, there are no substantial modifications in number and coordination of sites [22]. Eventually, M4 coordination number possibly increases up to six, due to a second group of three oxygen atoms related for symmetry found over 2.81 Å [22], providing very weak contributions in terms of valence bonds [33].

In Ca$_9$RE$^{3+}$(PO$_4$)$_7$ compounds, as for the case of present samples reported in this work, the most important structural modification compared to pure β–TCP and natural whitlockite is the M4 site resulting completely vacant, insofar as 6$^{3+}$ and three vacancies have been substituted for 9Ca$^{2+}$. The RE atoms are usually spread over three of the four remaining sites: in M1, M2, and M3, while M5 is fully occupied by Ca, according to [13], or in M1, M2, and M5 sites according to [31] as described later.

(PO$_4$)$_3$ groups in Ca$_9$RE$^{3+}$(PO$_4$)$_7$ compounds show tetrahedral coordination, which in most cases is quite regular, with P-O bond distances ranging between 1.43(4) (La) and 1.57(4) (Pr) Å for a P(1)O$_4$ tetrahedron, 1.23(6) and 1.74(6) Å (both in Yb phase) for P(2)O$_4$, and 1.43(5) (La) and 1.71(8) Å (Yb) for P(3)O$_4$, in good agreement with P-O bond values found for orthophosphate phases [34], even if some short P-O distances are observed in phosphate structural refinements from powder X-ray data [29,35], when compared with those observed from single-crystal X-ray data, they are usually not lower than 1.40 Å [34,36,37].

Ca and mixed Ca/RE cations are involved in complex coordinations: M1O$_8$, M2O$_7$, M3O$_8$, fixing the threshold M-O at 2.81 Å; the last cationic site is occupied by a fairly regular octahedron M5O$_6$ (Figure 3), owing to the site symmetry, which produces two terms of distances. Bond distances in different sites range between 2.28(8) (Tm) and 2.81(8) (Dy) Å for the M1 site, 2.21(10) (Eu) and 2.57(6) Å (Yb) for the M2 site, 2.29(8) (Gd) and 2.79(5) (Yb) for the M3 site, and 2.20(6) (Dy) and 2.38(6) (La) for the M5 site [31]. In addition, the average M-O values, reported in [6,31,32], show that bond distances are quite homogeneous among M1, M2, and M3 sites, while decreasing in the M5 site, for packing reasons. In a recent structural study on Ca$_9$Tb(PO$_4$)$_7$ TCP [32], the M2O$_8$ polyhedron is described as 7-fold coordinated by excluding the longest M2-O distance. In these compounds the possibility that a longer bond may change in an interaction is not unlikely, and the problem should be considered from a bond valence perspective [33], according to the single bond length values.

![Figure 3. Polyhedral environment in structural sites of Ca$_9$RE$^{3+}$(PO$_4$)$_7$ β–TCP.](image)

The rare-earth distribution within such compounds can occur with two different mechanisms: (1) RE in M1, M2, and M3 sites, with no occurrence in M5 [13]; (2) RE in M1, M2, and M5 sites, but not in M3 [6]. Analysis of the structure of available Ca$_9$RE(PO$_4$)$_7$ highlights that RE = La, Pr, Nd, Eu, Gd, Tb, and Dy enter sites M1, M2, and M3, and not site M5 for steric reasons due to the large RE ionic radius. Conversely, Ho, Tm, Yb, and Lu prefer the second mechanism, entering site M5 over M1 and M2 sites, and not M3, because of their lower ionic radius, giving results that are quite comparable to that of Ca$^{2+}$,
1.00 Å [38], in the 6-coordinated M5 site. The RE distribution in β-TCP within single M sites as a function of the atomic number, observed for most of RE comprised among La and Lu, is reported in [31,32]. In M1, the distribution initially increases for all RE from La3+ up to Ho3+, with a small deviation for the Tb-phase, and afterwards decreases in Tm, Yb, and Lu. In M2 a fairly irregular distribution occurs, increasing from La up to Tb; afterwards it decreases with deviations in Tm and Lu terms. In M3, the trend is regularly decreasing, becoming null in Ho, Tm, Yb, and Lu. Finally, in the M5 site, the RE does not occur for all phases up to Dy, except in the same phases that resulted in the M3 site being RE-free. The only deviation in those trends is represented by the Ce phase [30], where the RE dopant is fully refined in the M5 site. The RE distribution trends in β-TCP are reported in Figure 4.

Figure 4. Distribution of RE cations within M1, M2, M3, and M5 sites in available Ca9RE(PO4)7 structure refinements; data from [6], with the exception of Ce [30], Tb and Ho [32], and Lu [31].

3.1.4. Three-Dimensional Framework

The three-dimensional framework in Ca9RE(PO4)7 materials can be described as the repetition of two columnar arrays, indicated as ‘A’ and ‘B’, down the c-axis (Figure 5). The A array is made by the sequence of . . . P1O4 M5O6 P1O4 . . . polyhedra, while the B array displays the . . . P3O4 M1O8 M3O8 M2O8 P2O4 P3O4 . . . polyhedra repetition (Figure 5). The A array does not display sharing oxygen atoms among P1O4 and M5O6 groups. On the contrary, in the B array the single polyhedra are joined to each other via vertices or edges, i.e., the P2O4 group and M2O8 polyhedron share the O1 vertex, M2O8 and M3O8 polyhedra share the O9-O3 edge, and M3O8 and M1-O8 polyhedra share the O6-O7 edge, while M1O8 is joined with the P3O4 group through the O8 vertex (inset b of Figure 5). In some phases of the series, for example Ca9Tb(PO4)7, owing to the lack of the Ca3-O9 bond, the M2O8-M3O8 polyhedral sharing is described simply as O3 vertex sharing. Each A array is surrounded by six B columns, while each B column is surrounded by two A and four B columns (Figure 6).

The two arrays are joined among themselves via different mechanisms; the most important is that formed by the M5O6 octahedron through corner-sharing with P2 and P3 tetrahedra, the [M5(PO4)6] unit, depicted in Figure 5 (inset b). Such units assure the link between one A column and six B columns, being flat in the c direction and holding 6 different tetrahedra belonging to as many as B columnar arrays (Figure 6). Another important joining network among A and B arrays, in present Ca9RE(PO4)7 structures, is that formed by the P1O4 group, forced from site symmetry of P1 (6a site). The P1O4 tetrahedron can be described as a regular triangular pyramid, whose three base-vertices are the three O9 atoms, which in turn belong simultaneously to one M1O8 from an adjacent B array (inset a of Figure 6), and to M2O8 and M3O8 polyhedra belonging to another B array. Owing again to the site symmetry, the joining mechanism is repeated three times,
further helped by the O10 apical vertex of the P1O4 tetrahedron, which is joined to three M3O8 groups (inset (a) of Figure 6).

Figure 5. Ca9RE(PO4)7 packing: A and B arrays. Inset (a): detail of [M5(PO4)6] unit. Inset (b): joining mechanism among B arrays (M-O bonds dashed).

Figure 6. View down c of the RE β-TCP framework. Inset (a): (P1O4) group environment and joining mechanisms with M1-M2-M3 polyhedra from adjacent B arrays.

3.2. FTIR Spectroscopy

The infrared features of the studied compounds in the 1600–400 cm⁻¹ region (Figure 7) are consistent with the ones observed for pure β-TCP [6]. The phosphate ion has four vibrational modes active in the infrared, compatible with a C1 symmetry: the symmetric stretching (ν₁), the symmetric double degenerate bending mode (ν₂), and the triple degenerate asymmetric stretching (ν₃) and asymmetric bending (ν₄) modes [6]. The substitution of RE in Ca sites in the studied compounds only causes an increase in multiplicity, accompanied by a shift in some of the band positions dependent of the ionic radius of the RE [6,31]. The most intense ν₃ peak is, for example, slightly shifted to lower wavenumbers from Dy to Nd as the ionic radius increases (from 1033 cm⁻¹ to 1029 cm⁻¹ to 1027 cm⁻¹ for Ca₀Dy(PO₄)₇, Ca₀Gd(PO₄)₇, and Ca₀Nd(PO₄)₇, respectively) [6,31]. All the samples show the most intense group of components in the 1000–1200 cm⁻¹ region, corresponding to antisymmetric stretching ν₃ (P-O). The bands between 1000 and 900 cm⁻¹ can be assigned to the symmetric stretching bands ν₁ (P-O). The bending modes are located at lower wavenumbers. Two intense bands at about 610 cm⁻¹ (609 for Dy- and Gd-based materials, 607 for Nd) and 551 cm⁻¹ for all the samples are attributable to the O-P-O
antisymmetric bending. The symmetric bending mode $v_2$ ($PO_4^{3-}$) appears as a weak component around 440 cm$^{-1}$.

Figure 7. FTIR spectra of (a) Ca$_9$Dy(PO$_4$)$_7$, (b) Ca$_9$Gd(PO$_4$)$_7$, and (c) Ca$_9$Nd(PO$_4$)$_7$ in the 1600–4000 cm$^{-1}$ region.

3.3. Photoluminescence Spectroscopy

3.3.1. Dy$^{3+}$ TCP

As shown in Figure 8a, many bands are present in the excitation spectrum of Ca$_9$Dy(PO$_4$)$_7$ by monitoring the emission at the most intense emission band (571 nm, $^4F_{9/2} \rightarrow ^6H_{13/2}$). The spectral features can be attributed to absorption transitions from the ground state $^6H_{15/2}$ to $^4H_{13/2}$ + $^4G_{9/2}$ (294 + 299 nm), $^6P_{3/2}$ (324 nm), $^4F_{5/2}$ + $^4I_{9/2}$ (337 nm), $^4M_{15/2}$ + $^6P_{7/2}$ + $^4I_{11/2}$ (350 nm), $^4M_{19/2}$ + $^6P_{5/2}$ + $^4P_{3/2}$ (364 nm), $^4F_{7/2}$ + $^4I_{13/2}$ + $^4M_{21/2}$ + $^4K_{17/2}$ (387 nm), $^4G_{11/2}$ (426 nm), $^4I_{15/2}$ (452 nm), $^4F_{9/2}$ (472 nm) [8, 39, 40]. Among them, $^6H_{15/2} \rightarrow ^4M_{15/2} + ^6P_{7/2} + ^4I_{11/2}$ is the most intense one.

Figure 8. Excitation (a) and emission (b) spectra of Ca$_9$Dy(PO$_4$)$_7$.

No CT bands are observed in the excitation spectrum, in agreement with previous reports [9].

Excitation at 350 nm brings the Dy$^{3+}$ ion to the $^6P_{7/2}$ level, and that is followed by non-radiative relaxation to the $^4F_{9/2}$ level [41]. Thus, the visible emission spectrum upon excitation at 350 nm shows three main components around 480 nm, 570 nm, and 660 nm (Figure 8b), belonging to 4f-4f intraconfigurational transitions of Dy$^{3+}$ [9]. They correspond to $^4F_{9/2} \rightarrow ^4H_{15/2}$ (blue), $^6H_{13/2}$ (yellow), and $^6I_{11/2}$ (red) [42]. The observed features are rather broad and do not show a well-resolved Stark structure. This indicates that in the material under investigation the sites accommodating the dopant ion are affected by disorder.

No significant emission is detected around 400 nm, deriving from levels lying higher in energy than $^4F_{9/2}$. This indicates that thermal population of these high energy levels ($^4H_{15/2}$ and above) can be neglected. The strongest emission band ($^4F_{9/2} \rightarrow ^6H_{13/2}$), located in the yellow region, is of forced electric dipole nature ($|\Delta J| = 2$) and is therefore sensitive...
to the surrounding environment, whilst the $^4F_{9/2} \rightarrow ^6H_{15/2}$ (blue region) is of magnetic dipole nature ($|\Delta J| = 1$) and its intensity does not depend on the host [8,40,41].

The dominance of the yellow band above the blue one is compatible with a low-symmetry site for Dy$^{3+}$ without an inversion center [40,41].

The asymmetry ratio is defined as the ratio between the integrated emission intensity of the yellow to the blue bands and gives information about the local symmetry and the covalency of Dy$^{3+}$ ions in a crystal [40]. For Ca$_9$Dy(PO$_4$)$_7$, a very high value of 2.18 was obtained, indicating that the dopant ions are accommodated in low-symmetry sites, such as the ones available in the TCP structure [6,31]. The asymmetry ratio changes with Dy$^{3+}$ concentration, which is related to structural changes in the local environment of this ion [9]. By varying the ratio between the yellow and blue components, it is possible to tune the final colour of the material, potentially obtaining white light [41]. The prevalence of the yellow component obtained upon excitation at 350 nm is shown in the CIE diagram (Figure 9a).

![CIE 1931](image)

**Figure 9.** (a) CIE diagram for Ca$_9$Dy(PO$_4$)$_7$ material upon excitation at 350 nm. (b) Decay time obtained for the compound Ca$_9$Dy(PO$_4$)$_7$ upon excitation at 350 nm and by detecting the emission at 571 nm.

The decay curve of the $^4F_{9/2}$ level is non-exponential, with a short component of 19 ms and a long one of 97 ms (Figure 9b). This could indicate the presence of multiple emitting centers, such as two or more crystallographic sites occupied by the emitting species. This is in accordance with the presence of both Ca$^{2+}$ and RE$^{3+}$ in the same crystallographic sites [3] and with the occupancy of three of the four Ca-sites in Ca$_9$Eu(PO$_4$)$_7$ [13]. In particular, a preference for the 8-fold coordinated M1 and M2 sites for cations such as Eu$^{3+}$ and Tb$^{3+}$ was found in concentrated compounds [3]. These factors are both responsible for the disorder of the whitlockite structure. However, the non-exponential profile of the decay curve could also be ascribed to the presence of energy transfer processes, namely cross-relaxation, given the concentrated nature of the material under investigation.

The long component is definitely shorter compared to the values found in other matrices where Dy$^{3+}$ is present as a dopant. To give some examples, the lifetime was found to be greater than 370 ms in NaYF$_4$ microcrystals [40], or ranging from 150 up to 1022 ms in glasses [3], then again 305 ms in Y$_2$O$_3$:Dy$^{3+}$ nanophosphors [43]. Cross-relaxation between Dy$^{3+}$ pairs to the intermediate levels Dy$^{3+}$ ($^6F_{3/2}$) and Dy$^{3+}$ ($^6H_{9/2}$) is probably responsible for the observed decrease in decay time compared to the values reported for different compounds [42,43]. The process is enhanced when the ions are in close proximity according to the distance-dependence of the resonant energy transfer mechanism [9]. The pathways involved in Dy$^{3+}$-doped materials are as follows [8]:

\[
^4F_{9/2}, \ 6^H_{15/2} \rightarrow ^6H_{11/2} + ^6F_{11/2}, \ ^6F_{3/2}
\]

\[
^4F_{9/2}, \ 6^H_{15/2} \rightarrow ^6F_{3/2}, \ ^6H_{9/2} + ^6F_{11/2}
\]
and usually lead to concentration quenching [43]. Nevertheless, besides the particular multisite distribution of cations, the shorter distance between RE dopants in the analogous Eu$^{3+}$ compound is 3.67 Å, between M1 and M2 sites, which was found to be large enough to limit the Eu$^{3+} \rightarrow$ Eu$^{3+}$ energy transfer [3,13]. Moreover, a deep study of decay behaviour of concentrated and diluted Tb$^{3+}$ and Eu$^{3+}$ ions in Ca$_9$Eu(PO$_4$)$_7$ and Ca$_9$Tb(PO$_4$)$_7$ demonstrated that for RE$^{3+}$-concentrated whitlockite materials, the energy migration between ions is not efficient due to the energy mismatch between the Stark levels in neighbouring sites, preventing concentration quenching [3]. Furthermore, while low doping concentrations usually give single exponential decays, non-exponential behaviour can be related to a high dopant concentration, due to an increase in ion–ion interactions and consequent non-radiative pathways [9]; indeed, Ca$_9$Dy(PO$_4$)$_7$ presents a different and intense luminescence and only partial quenching despite Dy$^{3+}$ being a constituent of the matrix, confirming the low interaction between ions in whitlockites.

Due to the dependence of the site occupancy on the ion size, it is likely that the same structure-dependent luminescence behaviour occurs for Dy$^{3+}$ and Gd$^{3+}$. This explains the intense emission as well as a lifetime in the 100-μs region of Dy$^{3+}$ even as a full constituent in β-TCP, due to the similarity of this cation with the ones previously studied. This makes these materials very interesting for applications like thermoluminescence or phosphors [13].

3.3.2. Gd$^{3+}$ TCP

The excitation spectrum of Ca$_9$Gd(PO$_4$)$_7$ (Figure 10a) shows 3 bands, at 36,630, 36,563, and 35,842 cm$^{-1}$, attributable to the transitions $^6S_7/2 \rightarrow ^8I_{11/2}$, $^6S_7/2 \rightarrow ^6I_{17/2}$, and $^6S_7/2 \rightarrow ^6I_{17/2}$, respectively [44].

![Figure 10](image)

**Figure 10.** (a) Excitation spectrum of Ca$_9$Gd(PO$_4$)$_7$ (black line) at $\lambda_{\text{emis}} = 311$ nm. Emission spectrum of Ca$_9$Gd(PO$_4$)$_7$ (blue line) at $\lambda_{\text{exc}} = 273$ nm. (b) Decay time obtained for the compound Ca$_9$Gd(PO$_4$)$_7$ upon excitation at 273 nm and by detecting the emission at 311 nm.

The emission spectrum upon excitation at 273 nm is also shown in Figure 10a. The strongest band is located at 32,133 cm$^{-1}$ and corresponds to the $^6P_7/2 \rightarrow ^8S_7/2$ transition, and in particular is the zero-phonon line [45]. For Gd$^{3+}$-based samples, vibronic lines may also be visible besides electronic transitions that are due to the interaction between 4f electrons of RE$^{3+}$ and lattice vibrations [16]. These are due to electron–phonon coupling and have a strong influence on the spectroscopic features of a given material; for these reasons, they are important from the application point of view and they can give information about the local structure of rare-earth-based compounds [16]. These cooperative transitions involve electronic transitions on the metal together with vibrational transitions in the coordinating environment [46], with a consequent mixing of opposite parity wavefunctions [47]. This gives rise to Stokes and anti-Stokes structure in the emission spectrum [47]. Thus, in the emission spectrum of Ca$_9$Gd(PO$_4$)$_7$, vibronic features generated by the coupling of
the 4f electrons of the Gd$^{3+}$ ion with lattice vibrations are visible close to the zero-phonon transition [45]. At energies higher than the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition, only one band is observed at 32,679 cm$^{-1}$, corresponding to the thermally activated $^6P_{5/2} \rightarrow ^8S_{7/2}$ transition [45,46]. Two vibronic peaks at 31,908 and 31,094 cm$^{-1}$ are present at lower energies with respect to the most intense band (located at 32,133 cm$^{-1}$) and are characterized by a broad shape and a low intensity [45]. The band at 31,908 cm$^{-1}$ is 225 cm$^{-1}$ distant from the main peak, thus it is presumably associated with lattice vibrations (indicated as $\nu_L$ in Figure 10a). Indeed, the peak located at 31,094 cm$^{-1}$ is 1039 cm$^{-1}$ shifted with respect to the zero-phonon line, a value close to the peak located at 1029 cm$^{-1}$ in the FTIR spectrum of Ca$_9$Gd(PO$_4$)$_7$ (Figure 7b) corresponding to the symmetric stretching bands $\nu_1$ (P-O) (this band is indicated as $\nu_1$ in Figure 10a). The band located at 32,679 cm$^{-1}$ is 546 cm$^{-1}$ from the 0-0 line (32,133 cm$^{-1}$) and is also compatible with the O-P-O antisymmetric bending at 551 cm$^{-1}$ in the FTIR spectrum of Ca$_9$Gd(PO$_4$)$_7$ reported in Figure 7b.

Moreover, the zero-phonon line presents a not-resolved shoulder at 32,072 cm$^{-1}$ that probably belongs to the first coordination sphere, while the lower energy peaks are related to the second coordination sphere [45]. The integrated intensity of the second coordination sphere vibronic bands is 0.5% of the main transition, several times lower than the bands associated with the first coordination sphere [45]. In the Ca$_9$Gd(PO$_4$)$_7$ sample, the integrated area of $^6P_{7/2} \rightarrow ^8S_{7/2} + \nu$ vibronic peaks is lower than 7% with respect to the zero-phonon line, comparable with those found for Gd in other matrices [16,48].

The decay curve of the $^6P_{7/2}$ level, measured by observing in the zero-phonon band, is mono-exponential, characterized by a lifetime of 3.24 ms (Figure 10b). This value, together with the high intensity of Gd$^{3+}$ emission, indicates that concentration quenching due to energy migration among the Gd$^{3+}$ ions is negligible [48]. The lifetime value for Gd-based whitlockite is similar to that found in LaB$_3$O$_6$:Gd$^{3+}$ glass and crystal [16]. This corresponds to a decay rate constant of 308.6 s$^{-1}$, close the value found for the estimated radiative rate of Gd$^{3+}$ in a site without inversion symmetry [46]. This may suggest that non-radiative transitions are almost absent in the present material. Similar values are also found at low temperature for Gd-doped LaAlO$_3$, where the zero-phonon transition probability has been determined to be 297 s$^{-1}$, and the lifetime for the same compound is 3.6 ms [47].

3.3.3. Nd$^{3+}$ TCP

The Ca$_9$Nd(PO$_4$)$_7$ compound shows emission in the NIR region upon excitation at 520 nm. In detail, upon excitation in the $^4I_{9/2} \rightarrow ^4G_{9/2} + ^4G_{7/2} + ^2K_{13/2}$ [49], splitted but weakly resolved emission bands appear around 900 nm, 1050 nm, and 1350 nm, corresponding to $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{13/2}$, respectively (Figure 11). The probability of spontaneous emission from these transitions is dependent on the ratio between the Judd–Ofelt parameters $f_4$ and $f_6$, namely the spectroscopic quality factor $X = \Omega_4/\Omega_6$. In the present material, the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition is dominating, as usually occurs when $X$ is <1.15 [50]. A value in this region was found for Nd$^{3+}$ in alkali chloroborophosphate glasses [51] and in tetraborate glasses [50] and the lower the value, the higher the intensity for laser applications. Due to the available equipment, and to the poor crystallinity of the samples, it was not possible to collect the excitation spectrum, or to perform the lifetime analysis.
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earth dopants in structural sites of Ca9

tance analysis. According to previous structural investigations, distribution of rare-

cations. Due to the available equipment, and to the poor crystallinity of the samples, it

by solid state reaction at T = 1200°. The work aimed to study possible applications of such

4. Conclusions

Microcrystalline Ca9RE(PO4)7 (RE = Nd, Gd, Dy) phosphor materials were prepared

for all phases up to the Tb term, from which both the trends slightly decrease, while in

The PL emission spectra confirmed, for Dy3+ and Gd3+ phases, the presence of dopants

in the framework in a low-symmetry site with some local structural disorder, which still

allows the presence of vibrational features. For the Nd3+ phase, the location of RE dopant

in the sites was not achieved, due to the lack of excitation spectrum and lifetime analysis
due to the instrumental limitations and poor quality of the microcrystals. These materials
showed strong and well resolved luminescence spectra although the emitting RE3+ was
present as a bulk constituent, suggesting that energy migration between the luminescent
centers is minimal. These samples are also interesting as examples of materials emitting in
three different regions of the spectra: UV (Gd3+), visible (yellow) (Dy3+), and NIR (Nd3+).

Author Contributions: V.P., M.B. and F.C. conceived and designed the main ideas together, and
wrote and supervised the whole work; A.E.K. synthesized the samples and collected XRD data; F.C.
and D.M.T. contributed to the TCP structural description; V.P. contributed in luminescence and FTIR
spectroscopies. All authors have read and agreed to the published version of the manuscript.

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from structure solutions of the title compounds can be obtained from the Inorganic Crystal Structure
Database (ICSD, Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany,
Fax: +49-7247-808-666; email: crysdata@fiz-karlsruhe.de) [34] on quoting the following depository
numbers CSD432796 (Nd-TCP), CSD432793 (Gd-TCP), and CSD432791 (Dy-TCP). XRD spectra were
deposited at the PDF-2 (Powder Diffraction File-2) database of International Center for Diffraction
Data (ICDD, Newton Square, PA, USA, 2003 [25]) with card numbers 00-070-0125 (Nd-TCP), 00-070-
0127 (Gd-TCP), and 00-070-0128 (Dy-TCP).

4. Conclusions

Figure 11. Emission spectrum of Ca9Nd(PO4)7 at λexc = 520 nm.
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