

**Using Eu<sup>3+</sup> as an atomic probe to investigate the local environment in  
LaPO<sub>4</sub>–GdPO<sub>4</sub> monazite end-members**

Huittinen, N.; Arinicheva, Y.; Schmidt, M.; Neumeier, S.; Stumpf, T.;

Originally published:

August 2016

**Journal of Colloid and Interface Science 483(2016), 139-145**

DOI: <https://doi.org/10.1016/j.jcis.2016.08.027>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-24093>

Release of the secondary publication  
on the basis of the German Copyright Law § 38 Section 4.

CC BY-NC-ND

## Accepted Manuscript

Using  $\text{Eu}^{3+}$  as an atomic probe to investigate the local environment in  $\text{LaPO}_4$ – $\text{GdPO}_4$  monazite end-members

Nina Huittinen, Yulia Arinicheva, Moritz Schmidt, Stefan Neumeier, Thorsten Stumpf

PII: S0021-9797(16)30582-3  
DOI: <http://dx.doi.org/10.1016/j.jcis.2016.08.027>  
Reference: YJCIS 21495

To appear in: *Journal of Colloid and Interface Science*

Received Date: 27 May 2016  
Revised Date: 5 August 2016  
Accepted Date: 10 August 2016

Please cite this article as: N. Huittinen, Y. Arinicheva, M. Schmidt, S. Neumeier, T. Stumpf, Using  $\text{Eu}^{3+}$  as an atomic probe to investigate the local environment in  $\text{LaPO}_4$ – $\text{GdPO}_4$  monazite end-members, *Journal of Colloid and Interface Science* (2016), doi: <http://dx.doi.org/10.1016/j.jcis.2016.08.027>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



**Using  $\text{Eu}^{3+}$  as an atomic probe to investigate the local environment in  
 $\text{LaPO}_4\text{-GdPO}_4$  monazite end-members**

Nina Huittinen<sup>1\*</sup>, Yulia Arinicheva<sup>2</sup>, Moritz Schmidt<sup>1</sup>, Stefan Neumeier<sup>2</sup>, Thorsten Stumpf<sup>1</sup>

<sup>1</sup>Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner  
Landstraße 400, 01328 Dresden, Germany

<sup>2</sup>Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Nuclear Waste  
Management and Reactor Safety (IEK-6), 52425 Jülich, Germany

E-mail addresses of all authors in order of appearance : n.huittinen@hzdr.de,  
y.arinicheva@fz-juelich.de, moritz.schmidt@hzdr.de, s.neumeier@fz-juelich.de,  
t.stumpf@hzdr.de

\*Corresponding author :

Nina Huittinen / n.huittinen@hzdr.de

Phone : +49 351 260 2148

Fax : +49 351 260 13233

Abbreviations used in the article:

Time-resolved laser fluorescence spectroscopy (TRLFS)

**Abstract**

In the present study, we have investigated the luminescent properties of  $\text{Eu}^{3+}$  as a dopant in a series of synthetic lanthanide phosphates from the monazite group. Systematic trends in the spectroscopic properties of  $\text{Eu}^{3+}$  depending on the size of the host cation and the dopant to ligand distance have been observed. Our results show that the increasing match between host and dopant radii when going from  $\text{Eu}^{3+}$ -doped  $\text{LaPO}_4$  toward the smaller  $\text{GdPO}_4$  monazite decreases both the full width at half maximum of the  $\text{Eu}^{3+}$  excitation peak, as well as the  ${}^7\text{F}_2/{}^7\text{F}_1$  emission band intensity ratio. The decreasing  $\text{Ln}\cdots\text{O}$  bond distance within the  $\text{LnPO}_4$  series causes a systematic bathochromic shift of the  $\text{Eu}^{3+}$  excitation peak, showing a linear dependence of both the host cation size and the  $\text{Ln}\cdots\text{O}$  distance. The linear relationship can be used to predict the energy band gap for  $\text{Eu}^{3+}$ -doped monazites for which no  $\text{Eu}^{3+}$  luminescent data is available. Finally, mechanisms for metal-metal energy transfer between host and dopant lanthanides have been explored based on recorded luminescence lifetime data. Luminescence lifetime data for  $\text{Eu}^{3+}$  incorporated in the various monazite hosts clearly indicated that the energy band gap between the guest ion emission transition and the host ion absorption transition can be correlated to the degree of quenching observed in these materials with otherwise identical geometries and chemistries.

keywords :  $\text{Eu}^{3+}$ , monazite, incorporation, TRLFS, luminescence, quenching

## 1 Introduction

Crystalline lanthanide orthophosphates ( $\text{LnPO}_4$ ) doped with other elements of the lanthanide group have recently gathered substantial attention due to the favorable electronic properties of the  $4f$  elements that can be employed for applications ranging from light display systems<sup>1</sup> and nanoelectronic devices<sup>2</sup>, medical and biological labels for in vitro imaging<sup>3</sup> to applications in targeted drug release<sup>4</sup>. Orthophosphates offer an easily synthesized and robust solid matrix for the dopants, and  $\text{LnPO}_4$  nanoparticles can be tailored for a variety of purposes. The chemical durability and structural flexibility of  $\text{LnPO}_4$  make lanthanide phosphates crystallizing in the monazite structure attractive as host phases for the conditioning of long-lived radionuclides produced during the nuclear fuel cycle or in the dismantling of nuclear weapons.<sup>5-10</sup> The monazites are known to incorporate large quantities of actinides ( $> 20\%$ )<sup>6,11</sup>, and several studies report on the structural incorporation of actinides such as U, Th, Pu, Am, and Cm, within the monazite structure either through direct substitution by a trivalent actinide on the host cation site<sup>12,13</sup>, or through coupled substitution of an actinide of higher oxidation state with a mono- or divalent cation to preserve charge neutrality<sup>14,15</sup>.  $\text{Eu}^{3+}$  is often chosen as dopant in the investigated phosphates mainly due to its luminescent properties.  $\text{Eu}^{3+}$  is a preferred choice as an activator ion in the development of red-emitting phosphors due to its strong, long-lived luminescence emission.<sup>16,17</sup> Furthermore, crystal-field perturbation results in a fine structure in the luminescence spectra that depends on the site symmetry of the  $\text{Eu}^{3+}$  ion which, thus, can be used as a local structure probe for the determination of site symmetries in a host lattice.<sup>18</sup> In general, luminescent properties of lanthanide ions depend on the host composition and structure as well as the concentration (i.e. interatomic distance) of luminescent centers present in the materials.<sup>19-22</sup> Therefore, local changes in the host material and the concentration range of dopants used will alter the spectroscopic properties of the luminescent probe and, depending on the application, may affect the suitability of the material.

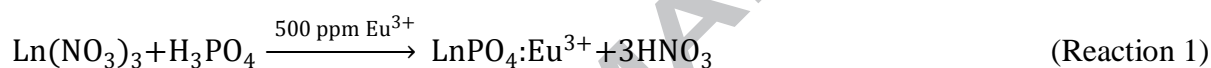
In the present work we have studied  $\text{Eu}^{3+}$  incorporation and the impact of systematic trends within the host crystal structure on the dopant luminescence in a series of  $\text{LnPO}_4$  end-members ( $\text{LaPO}_4$ - $\text{GdPO}_4$ ) crystallizing in the monazite structure. The ionic radius of the host cation in these monazite end-members decreases systematically from  $\text{La}^{3+}$  ( $r_{\text{ion}}^{\text{IX}} = 1.216 \text{ \AA}$ )<sup>23</sup> toward  $\text{Gd}^{3+}$  ( $r_{\text{ion}}^{\text{IX}} = 1.107 \text{ \AA}$ )<sup>21</sup> by ~10 %. A preferential incorporation of  $\text{Eu}^{3+}$  in monazites with a host cation radius similar to Eu's ( $r_{\text{ion}}^{\text{IX}} = 1.120 \text{ \AA}$ )<sup>23</sup>, e.g.  $\text{SmPO}_4$  or  $\text{GdPO}_4$ , could be expected. In addition, the systematic decrease of the  $\text{Ln}\cdots\text{O}$  bond distance in the series of monazite hosts with otherwise identical symmetry and chemistry provides an opportunity to study the impact of bond distance on the ligand field effect and the luminescent properties of the  $\text{Eu}^{3+}$  ion. Finally, by comparing the  $\text{Eu}^{3+}$  doped monazites with isolated fluorescent centers ( $c_{\text{Eu}} = 500 \text{ ppm}$ ) with pure  $\text{EuPO}_4$ , the influence of the lanthanide concentration in terms of metal-metal concentration quenching effects can be evaluated.

## 2 Experimental section

### 2.1 Lanthanide phosphate synthesis and characterization

The lanthanide phosphates  $\text{LaPO}_4$  to  $\text{GdPO}_4$  crystallizing in the monazite structure were synthesized by precipitation (excluding the redox sensitive  $\text{CePO}_4$  and radioactive  $\text{PmPO}_4$ ) similar to the procedure described in Roncal-Herrero et al.<sup>24</sup>

Lanthanide nitrate salts were dissolved in deionized water (MilliQ) in concentrations of 0.3-0.5 M. A 14.8 M aqueous solution of  $\text{H}_3\text{PO}_4$  was slowly added to the solution, causing precipitation of  $\text{LnPO}_4:\text{Eu}^{3+}$  according to Reaction 1. Details on the reagents used in the synthesis can be found in the supporting information (S.I.).



The suspension was heated in an oven at  $90^\circ\text{C}$  for 1 week to complete the precipitation. The solid was recovered by centrifugation (10,000 rpm, 10 min) and washed with MilliQ water. The washing step was repeated several times until the supernatant was free of nitrate ions ( $\text{NO}_3^-$  test strips). Subsequently the powders were dried in an oven at  $90^\circ\text{C}$  for 12 h. The dry powders were milled in an agate mortar and calcined for 2h at  $600^\circ\text{C}$  in order to remove any nitrate residues. As a final step, sintering of  $\text{LnPO}_4$  was carried out at  $1450^\circ\text{C}$  for 5h to obtain the crystalline monazite solids. Characterization of the synthetic monazites was done with X-ray powder diffraction (XRD), using a D4 Endeavor diffractometer with a  $\theta$ - $2\theta$  geometry (Bruker AXS GmbH) operating at 50 kV and 30 mA with a  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the range  $2\theta = 10$ – $100^\circ$ . The XRD patterns of all synthesized monazites are in a perfect agreement with the corresponding data from the ICDD database, confirming the sole presence of highly crystalline, monoclinic monazite. XRD patterns for pure  $\text{EuPO}_4$  and  $\text{Eu}^{3+}$ -doped  $\text{GdPO}_4$  are shown in Figure 1. For the XRD patterns of all synthetic monazites the reader is referred to the S.I., Figure S1.

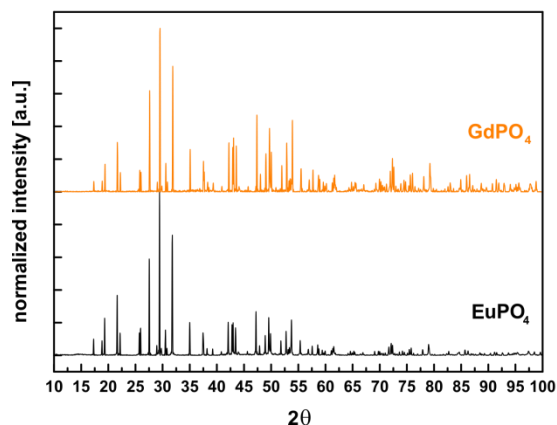


Figure 1: XRD patterns of synthetic  $\text{EuPO}_4$  monazite and  $\text{Eu}^{3+}$ -doped  $\text{GdPO}_4$  monazite.

## 2.2 Time-resolved laser fluorescence spectroscopy TRLFS

The  $\text{Eu}^{3+}$  ion exhibits many favorable luminescence properties, such as a non-degenerate ground state ( ${}^7\text{F}_0$ ) as well as emitting state ( ${}^5\text{D}_0$ ) and an even number of  $f$ -electrons ( $4f^6$ ) for which the number of crystal field levels is dependent on the site symmetry of the ion.<sup>25</sup> Therefore,  $\text{Eu}^{3+}$  is ideally suited for systematic studies of the structural incorporation of  $\text{Eu}^{3+}$  in crystalline solid phases, such as this series of synthetic monazites.

Detailed information on the  $\text{Eu}^{3+}$  environment in crystalline solids can be obtained by combining the luminescence data obtained from recorded excitation spectra, emission spectra, and luminescence lifetimes, as discussed below. Selective excitation of the  $\text{Eu}^{3+}$  ion from the  ${}^7\text{F}_0$  ground state to the  ${}^5\text{D}_0$  excited state, which both are non-degenerate due to their  $J = 0$  nature, allows for the determination of the number of non-equivalent species present in the solid matrix. In an excitation spectrum (integrated luminescence intensity as a function of excitation energy) of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition, one singlet signal is obtained for every  $\text{Eu}^{3+}$  species present in the system. The signal position, gives a first indication of the local environment of the respective  $\text{Eu}^{3+}$  species, where a stronger ligand field generally results in a lower energy transition and consequently in a stronger bathochromic shift of the signal.<sup>26,27</sup>



For  $\text{Eu}^{3+}$  incorporation in the synthetic monazites only one singlet species corresponding to the structural incorporation of the dopant on the host lanthanide site is expected.

Selective excitation of the  $\text{Eu}^{3+}$  species in the solid matrix yields emission spectra and luminescence lifetimes of the single species. The emission spectrum allows for identification of the site symmetry in the host by making use of the splitting pattern of especially the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions. The crystal-field perturbation splits up the  $^7\text{F}_J$  terms in a number of crystal field levels that depends on the symmetry class. For crystal fields of orthorhombic or lower symmetries, the  $2J+1$  degeneracy is completely lifted.<sup>18</sup> Thus, the monazite cation lattice site with a monoclinic ( $C_1$ ) symmetry would result in a full 3-fold and 5-fold splitting of the  $^7\text{F}_1$  and  $^7\text{F}_2$  bands, respectively, for  $\text{Eu}^{3+}$  incorporation.

The  $\text{Eu}^{3+}$  luminescence lifetime,  $\tau$ , has been correlated with the number of coordinating water molecules around the ion in solution through a linear empirical relationship, the so-called Horrocks equation<sup>28,29</sup>, Equation 1.

$$n(\text{H}_2\text{O}) [\text{water molecules}] = 1.07 [\text{water molecules} \cdot \text{ms}] \times \tau^{-1} [\text{ms}^{-1}] - 0.62 \quad (1)$$

For an incorporated ion without hydration water molecules in the first coordination sphere and in the absence of other quench processes (e.g. metal-to-metal energy transfer) the expected luminescence lifetime according to Eq. 1 is  $\sim 1.7$  ms. However, significantly longer lifetimes ( $> 3$  ms) have been reported for incorporated  $\text{Eu}^{3+}$  species.<sup>30-32</sup>

In the present work time-resolved laser fluorescence spectroscopy (TRLFS) for the collection of  $\text{Eu}^{3+}$  excitation and emission spectra was performed with a pulsed Nd:YAG (Spectra Physics) pumped dye laser set-up (Radiant Dyes Narrow Scan K) by directly exciting the  $\text{Eu}^{3+}$  ion from the ground  $^7\text{F}_0$  state to the emitting  $^5\text{D}_0$  state. The emitted luminescence emission light was directed into a monochromator (Acton SpectraPro 300i) with a 300- or 1200 lines/mm grating and the emission was monitored with an intensified CCD camera (Princeton Instruments) 10  $\mu\text{s}$  after the exciting laser pulse in a time window of 10 ms. The laser pulse

energy and the exact excitation wavelength were monitored in every measurement with optical power meter (Newport 1918-R) and wavelength meter (High Finesse WS-5), respectively. To achieve the desired spectral resolution the solid samples were cooled to approximately 10 K in a helium refrigerated cryostat. Luminescence lifetime measurements were performed at two temperatures (10 K and at room temperature, RT) by monitoring the luminescence emission as a function of delay time (up to 12 ms) between the laser pulse and the camera gating. Lifetime measurements at 10 K were conducted with the laser set-up described above. The room temperature TRFLS measurements were performed with a Nd:YAG pumped OPO laser system (Powerlite Precision II 9020 - PANTHER EX OPO, Continuum).  $\text{Eu}^{3+}$  was excited at 394 nm and the time-resolved emission signal was directed into a monochromator (Oriel MS 257) with a 300 lines/mm grating followed by detection with an intensified CCD camera (Andor iStar).

### 3 Results and discussion

#### 3.1 $\text{Eu}^{3+}$ incorporation in $\text{LnPO}_4$ monazites

Excitation spectra of  $\text{LaPO}_4$ ,  $\text{SmPO}_4$ , and  $\text{GdPO}_4$  monazites doped with 500 ppm  $\text{Eu}^{3+}$  are presented in Figure 2 together with the excitation spectrum of pure  $\text{EuPO}_4$ .  $\text{PrPO}_4$  and  $\text{NdPO}_4$  doped with  $\text{Eu}^{3+}$  did not yield any detectable europium luminescence signal due to strong metal-metal quenching induced by the host lanthanides. The  $\text{Eu}^{3+}$  luminescence quenching phenomenon observed in some of the investigated solids will be discussed separately in the following section.

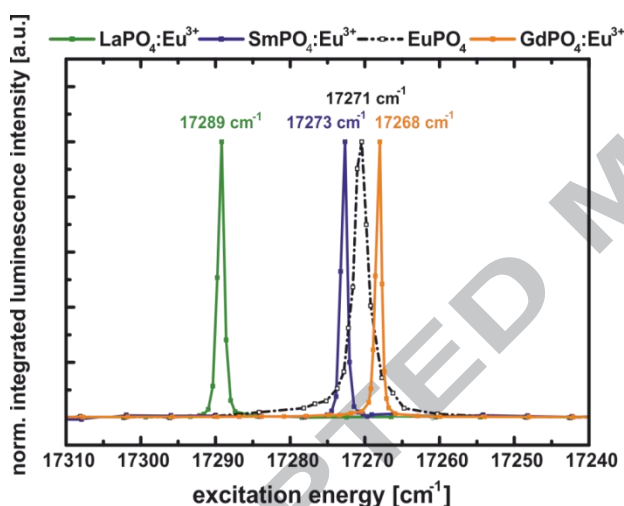


Figure 2:  $\text{Eu}^{3+}$  excitation spectra of the  ${}^7F_0 \rightarrow {}^5D_0$  transition in  $\text{LaPO}_4$ ,  $\text{SmPO}_4$ , and  $\text{GdPO}_4$  monazites doped with 500 ppm  $\text{Eu}^{3+}$  (colored lines) and pure  $\text{EuPO}_4$  (black line).

The  $\text{Eu}^{3+}$ -doped monazites show one narrow excitation peak with a half width of around  $1 \text{ cm}^{-1}$ , corresponding to  $\text{Eu}^{3+}$  incorporation on the host lattice sites in the crystalline monazite structure. The size of the host cation can be seen to influence the recorded  $\text{Eu}^{3+}$  luminescence signal in two ways: A slight excitation line narrowing can be seen across the monazite series (excluding  $\text{EuPO}_4$ ) with a FWHM of  $1.03 \text{ cm}^{-1}$ ,  $0.95 \text{ cm}^{-1}$ ,  $0.92 \text{ cm}^{-1}$  for  $\text{Eu}^{3+}$ -doped  $\text{LaPO}_4$ ,  $\text{SmPO}_4$ , and  $\text{GdPO}_4$ , respectively. This can be explained by slight local distortions of the monazite crystal lattice around the incorporated  $\text{Eu}^{3+}$  ion, which is more pronounced for larger differences between the host and dopant cation radii, see Table 1.

Table 1: Host lanthanide radii and average Ln...O bond distances in monazites.

Monazite	Ln <sup>3+</sup> radius $r_{\text{Ln(III)}}^{\text{IX}}$ [Å]*	Average Ln...O distance [Å]**
LaPO <sub>4</sub>	1.216	2.5787
CePO <sub>4</sub>	1.196	2.5554
PrPO <sub>4</sub>	1.179	2.5396
NdPO <sub>4</sub>	1.163	2.5242
PmPO <sub>4</sub>	1.144	2.5106 <sup>†</sup>
SmPO <sub>4</sub>	1.132	2.4988
EuPO <sub>4</sub>	1.120	2.4878
GdPO <sub>4</sub>	1.107	2.4760

\*from Shannon<sup>23</sup>\*\*calculated from the refined monazite structures in Ni et al.<sup>33</sup>

†predicted value from spectroscopic data, this study.

Furthermore, as the Ln...O bond length decreases from LaPO<sub>4</sub> toward GdPO<sub>4</sub> (Table 1) the ligand field effect that the oxygen atoms exert on the incorporated Eu<sup>3+</sup> ion increases, leading to a visible bathochromic shift of the excitation signal. This shift follows a linear trend as a function of both ionic radius of the host cation and Ln...O bond distance (Figure 3), with excellent accuracy ( $R^2 = 0.99999$  and  $R^2 = 0.99984$ , respectively). The average bond distances are calculated from the nine Ln...O distances in the LnO<sub>9</sub> polyhedron obtained from the refined monazite structures in Ni et al.<sup>33</sup>.

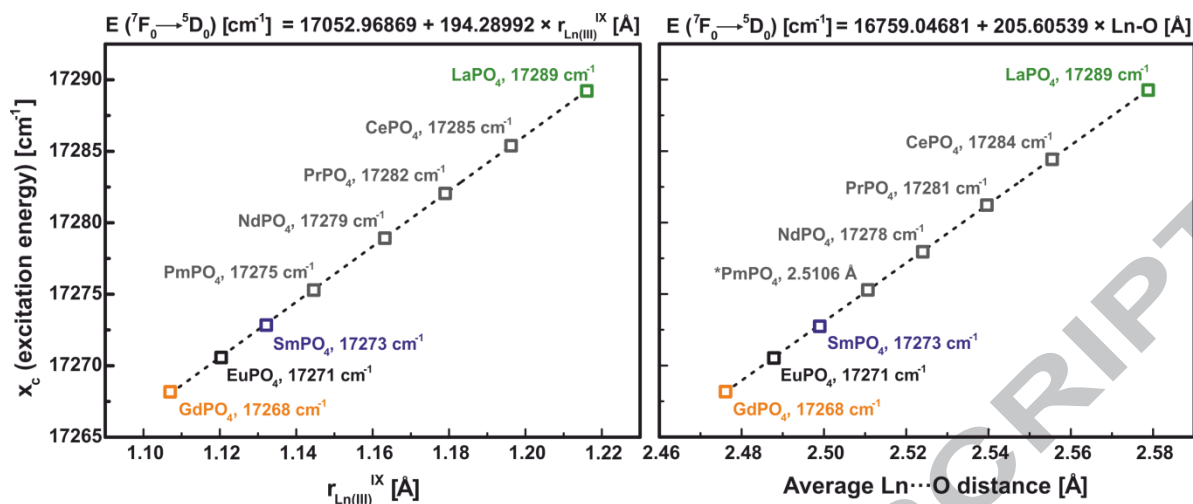


Figure 3: The  $\text{Eu}^{3+}$  excitation energy plotted as a function of the host cation radius (left) and average  $\text{Ln}\cdots\text{O}$  distance in the monazite structure (right). Colored and black squares represent experimental data. Gray squares represent predicted values for the  $\text{Eu}^{3+}$  excitation energy or average  $\text{Pm}\cdots\text{O}$  distance (\*).

The linear fit of the experimental data (colored squares for  $\text{Eu}^{3+}$ -doped monazites, black square for pure  $\text{EuPO}_4$  monazite) yield an expression for the excitation energy which can be calculated when either the lanthanide cation radius (Equation 2) or the average  $\text{Ln}\cdots\text{O}$  distance in the monazite (Equation 3) is known.

$$E(^7F_0 \rightarrow ^5D_0)[\text{cm}^{-1}] = 17052.96869 + 194.28992 \cdot r_{\text{Ln(III)}}[\text{Å}] \quad (2)$$

$$E(^7F_0 \rightarrow ^5D_0)[\text{cm}^{-1}] = 16759.04681 + 205.60539 \cdot \text{Ln}\cdots\text{O}[\text{Å}] \quad (3)$$

Provided that the linear trend is valid throughout the monazite series these equations can be used to predict the excitation energies for  $\text{Eu}^{3+}$  incorporation in monazites for which no experimental data is available ( $\text{CePO}_4$ ,  $\text{PrPO}_4$ ,  $\text{NdPO}_4$ ,  $\text{PmPO}_4$ ). In addition, we can apply the results to predict the  $\text{Pm}\cdots\text{O}$  distance for  $\text{PmPO}_4$ , for which no crystallographic structure has been reported. The predicted excitation energy for  $\text{Eu}^{3+}$ -doped  $\text{PmPO}_4$  can be calculated with the known ionic radius of  $\text{Pm}^{3+}$  using Equation 2. Subsequently, a  $\text{Pm}\cdots\text{O}$  bond distance of

2.5106 Å can be calculated using that excitation energy and Equation 3. The predicted values are indicated in Figure 3 in gray. For a summary of all determined and predicted excitation energies the reader is referred to the S.I. (Table S1).

When exciting europium at the excitation peak maximum in Figure 2, the emission spectra and luminescence lifetimes of the incorporated  $\text{Eu}^{3+}$  ion can be recorded, Figure 4.

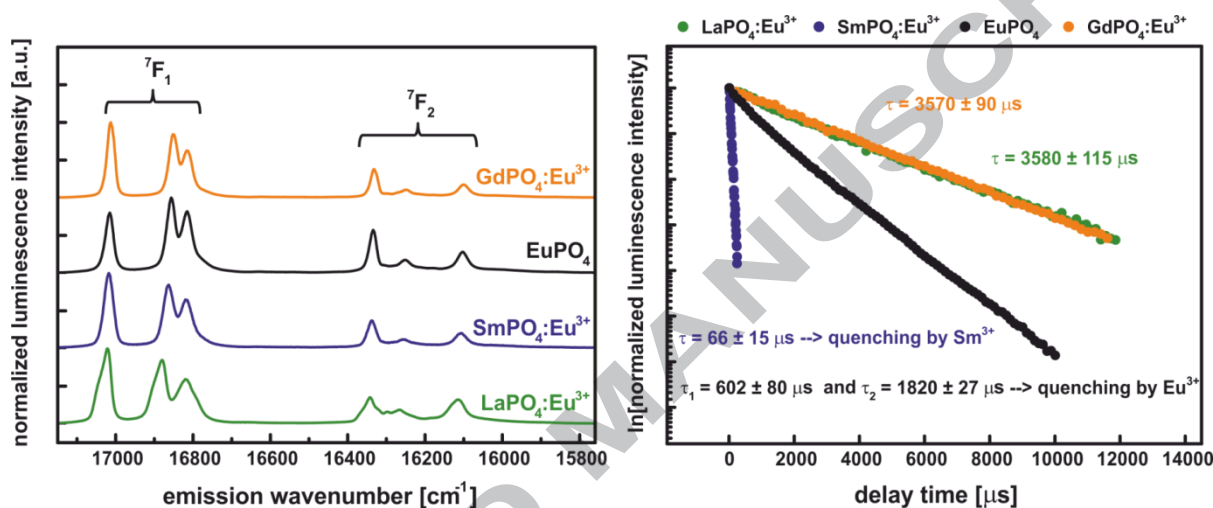


Figure 4:  $\text{Eu}^{3+}$  emission spectra (left) and luminescence lifetimes (right) in  $\text{LnPO}_4$  monazites.

The emission spectra show a full 3-fold and 5-fold splitting of the  ${}^7\text{F}_1$  and  ${}^7\text{F}_2$  bands, respectively, corresponding to  $\text{Eu}^{3+}$  incorporation on a low symmetry site, in accordance with the monoclinic ( $\text{C}_1$ ) lattice site in the monazites. The relative intensities of these bands reflect the coordination symmetry around the  $\text{Eu}^{3+}$  ion.<sup>34,35</sup> The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition has a predominant electric dipole character that is sensitive to changes in the ligand environment. In contrast, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition retains its magnetic dipole character even in low symmetry systems and its intensity is not significantly influenced by the ligand environment.<sup>36</sup> Thus, when the site symmetry decreases, the relative intensity of the hypersensitive transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) increases, resulting in a larger  ${}^7\text{F}_2/{}^7\text{F}_1$  ratio. For the  $\text{Eu}^{3+}$  doped monazites a decrease in the  ${}^7\text{F}_2/{}^7\text{F}_1$  ratio can be seen when going from  $\text{LaPO}_4$  toward  $\text{GdPO}_4$  with a ratio of 0.50 for  $\text{LaPO}_4$ , 0.41 for  $\text{SmPO}_4$ , and 0.37 for  $\text{GdPO}_4$ . This behavior can be explained by

the slight distortion of the crystal lattice accommodating a dopant with a dissimilar cation radius and the subsequent lowering of the site symmetry, as already explained above in connection to the observed excitation line narrowing. The largest difference of approximately 8%, between the size of the host and dopant cation radii, is observed for  $\text{Eu}^{3+}$  incorporation in  $\text{LaPO}_4$ , while a difference of just above 1 % applies for  $\text{Eu}^{3+}$  incorporation in  $\text{SmPO}_4$  and  $\text{GdPO}_4$ .

The luminescence lifetimes recorded at 10 K of  $\text{Eu}^{3+}$  incorporated in  $\text{LaPO}_4$  and  $\text{GdPO}_4$  decay monoexponentially with lifetimes of  $3580 \pm 115 \mu\text{s}$  and  $3570 \pm 90 \mu\text{s}$ , respectively. The long lifetimes speak for a full loss of the  $\text{Eu}^{3+}$  hydration sphere upon incorporation in the monazite lattice, as can be expected after sintering of the samples at  $1450^\circ\text{C}$ . The lifetime recorded for  $\text{Eu}^{3+}$  incorporation in  $\text{SmPO}_4$  ( $66 \pm 15 \mu\text{s}$ ) and the lifetimes obtained for pure  $\text{EuPO}_4$  ( $602 \pm 80 \mu\text{s}$  and  $1820 \pm 27 \mu\text{s}$ ) are significantly shorter than  $3600 \mu\text{s}$ , pointing toward quenching of the luminescence signal by e.g. the lanthanide neighbor atoms. As we can exclude quenching by water molecules due to the thermal treatment of the lanthanide phosphates,  $\text{Eu}^{3+}$  luminescence must be quenched through a different mechanism. This quenching behavior will be discussed in detail in the following section.

### 3.2 $\text{Eu}^{3+}$ luminescence quenching in $\text{LnPO}_4$ monazites

As discussed in the previous chapter, no  $\text{Eu}^{3+}$  luminescence could be detected in  $\text{Eu}^{3+}$ -doped  $\text{NdPO}_4$  and  $\text{PrPO}_4$  monazites, while significantly shortened lifetimes in  $\text{SmPO}_4$  and  $\text{EuPO}_4$  were recorded in comparison to the non-quenched  $\text{Eu}^{3+}$ -doped  $\text{LaPO}_4$  and  $\text{GdPO}_4$  hosts (Figure 4, right).

Various phenomena causing luminescence quenching of  $\text{Eu}^{3+}$  in a solid matrix have been reported, ranging from e.g. lattice defects in the solid structure<sup>37</sup> to excitation energy transfer to impurity ions present in the solid phase or metal-metal energy transfer between the dopant

and host cations<sup>38</sup>. In the present study, the monazite synthesis was carried out under controlled conditions where the chemicals, synthesis steps, sintering conditions and sample handling have been kept constant. Thus, lattice defects and the presence of impurity ions should be very comparable within the monazite end-member series, which would imply that other quench mechanisms such as metal-metal energy transfer between  $\text{Eu}^{3+}$  and the lanthanide host cations are responsible for the observed differences in the luminescence properties of  $\text{Eu}^{3+}$ . Metal-metal energy transfer can take place either via radiative energy transfer or through interionic processes involving direct excitation energy transfer between the two lanthanide ions without absorption or emission of photons.<sup>39</sup> Radiative energy transfer is only possible when one of the europium emission transitions  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  overlap with the absorption transition of another lanthanide, and in this case it is only the emission of the overlapping transition that is affected. The non-radiative relaxation process can be divided into resonant and non-resonant excitation energy transfer induced by either multipolar or exchange interactions between the interacting ions.<sup>39</sup> Resonant multipolar energy transfer occurs when the amount of energy delivered by the  $\text{Eu}^{3+}$  dopant is reasonably close to the amount of energy accepted by the host lanthanide. In the non-resonant case a fraction of excitation energy is either exchanged with the phonon field of the host lattice or transferred to a third ion. The extent of quenching through multipolar energy transfer has been shown to decrease exponentially with increasing energy mismatch, i.e. a larger band gap between donor and acceptor states.<sup>40,41</sup> The band gap in the present case is defined as the energy difference between the  $\text{Eu}^{3+}$   ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  emission transitions and the closest matching absorption transition of the accepting lanthanide. An exponential correlation cannot be deduced from our luminescence data but it is evident that the quenching of the  $\text{Eu}^{3+}$  luminescence is dependent on the size of the band gap  $\Delta E$ , according to:

$$\Delta E(\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}) \sim \Delta E(\text{Eu}^{3+} \rightarrow \text{Pr}^{3+}) < \Delta E(\text{Eu}^{3+} \rightarrow \text{Sm}^{3+}) < \Delta E(\text{Eu}^{3+} \rightarrow \text{Eu}^{3+})$$



The corresponding transitions are indicated in Figure 5, using identically colored arrows to indicate the  $^5D_0$  to  $^7F_6$  (purple),  $^7F_5$  (orange), and  $^7F_0$  (green) emission transitions and the closest matching absorption transitions. The arrow length is adapted to the individual band gaps, i.e. the length of the arrow indicating an emission transition does not necessarily match the arrow length of the closest matching absorption transition. For the corresponding transition energies the reader is referred to the S.I., Table S2. For  $\text{Eu}^{3+}$ , the absorption transition is assumed to be  $^7F_0 \rightarrow ^7F_6$ , which plays an important role in e.g. the quenching of  $\text{Tm}^{3+}$  luminescence<sup>42,43</sup>. It is however, clear that for every europium  $^5D_0 \rightarrow ^7F_J$  emission transition a perfectly matched  $^7F_J \rightarrow ^5D_0$  absorption transition is available and the energy band gap is, thus, zero. Energy transfer between matching transitions, however, does not lead to the observed quenching of the  $\text{Eu}^{3+}$  luminescence.

$\text{La}^{3+}$  is omitted from the figure due to the absence of  $f$  electrons and consequently  $f$ - $f$  transitions. In addition, electronic transitions in  $\text{La}^{3+}$  from  $5p$  to  $4f$  or  $5d$  states require substantially higher energies to occur and they will, thus, not interfere with the electronic transitions under consideration in the present study.

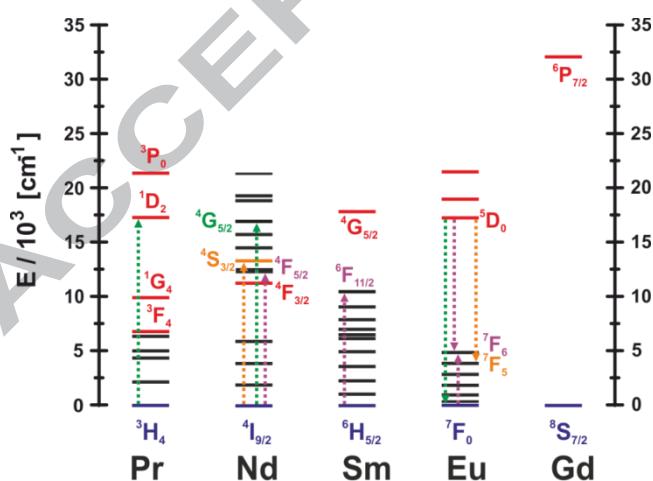


Figure 5: Partial energy level diagram of the lanthanides investigated in the present study. Emitting states are denoted in red. The colored arrows denote potential non-radiative transitions between donor and acceptor atoms, respectively. The figure is adapted from Bünzli and Piguet<sup>44</sup>.

In both NdPO<sub>4</sub> (transitions indicated with purple and orange arrows) and PrPO<sub>4</sub> (green arrow) the energy gap difference is small, i.e. approximately 10 cm<sup>-1</sup> in NdPO<sub>4</sub> and 60 cm<sup>-1</sup> in PrPO<sub>4</sub>. In neither of these solids any detectable luminescence from Eu<sup>3+</sup> was observed. In SmPO<sub>4</sub> the band gap is approximately 1900 cm<sup>-1</sup> and in EuPO<sub>4</sub> 7400 cm<sup>-1</sup>. In these solids Eu<sup>3+</sup> luminescence was visible but luminescence lifetimes were reduced. The effect is significantly stronger in SmPO<sub>4</sub> ( $\tau = 66 \pm 15 \mu\text{s}$ ) than in EuPO<sub>4</sub> ( $\tau_1 = 602 \pm 80 \mu\text{s}$ ,  $\tau_2 = 1820 \pm 27 \mu\text{s}$ ). In LaPO<sub>4</sub> and GdPO<sub>4</sub> non-radiative quenching is unlikely due to the absence of accepting energy levels below and close to the emitting <sup>5</sup>D<sub>0</sub> term and the decay constants determined in these systems can be treated as entirely radiative deexcitation. In NdPO<sub>4</sub> and PrPO<sub>4</sub> where the energy band gap is very small, it is reasonable to assume that Eu<sup>3+</sup> luminescence could be completely quenched by resonant multipolar energy transfer. In SmPO<sub>4</sub> and EuPO<sub>4</sub> non-resonant excitation energy transfer induced by either multipolar or exchange interactions should be considered due to the larger differences between the emission and absorption transitions. For the Sm<sup>3+</sup> - Eu<sup>3+</sup> couple, several studies reporting phonon assisted multipolar energy transfer between the lanthanide cations can be found<sup>45-47</sup>. Thus, it is reasonable to assume that the same energy transfer mechanism applies to Eu<sup>3+</sup>-doped SmPO<sub>4</sub> monazite.

For multipole interactions the rate of energy transfer,  $k_{ET}$ , between a donor and acceptor atom can be correlated with their interatomic distance  $R_{DA}$ , according to equation 4:<sup>48</sup>

$$k_{ET} = k_D \left[ \frac{R_0}{R_{DA}} \right]^s = \frac{1}{\tau_D} \left[ \frac{R_0}{R_{DA}} \right]^s \quad (4)$$

Here,  $s = 6, 8,$  and  $10,$  respectively, for  $dd, dq,$  and  $qq$  interactions.  $R_0$  is the critical distance (also known as the Förster radius for  $dd$ -interactions in (bio)organic systems)<sup>49</sup>, i.e. the distance at which the rate of energy transfer equals the reciprocal value of the lifetime of the donor level in the absence of acceptor ions,  $\tau_D$ . In case of dipole-dipole interactions that usually feature large interaction lengths of several tens of angstroms<sup>50,51</sup>, a critical distance  $R_0$  can be calculated when both the quenched ( $\tau_{DA}$ ) and unquenched lifetimes are known:

$$R_0^6 = R_{DA}^6 \left( \frac{\tau_D}{\tau_{DA}} - 1 \right) \quad (5)$$

Using the unquenched lifetime of 3570  $\mu\text{s}$  found for  $\text{Eu}^{3+}$  incorporation in  $\text{GdPO}_4$ , the average interatomic distance of 4.13  $\text{\AA}$  between two adjacent samarium atoms (connected to one another through an oxygen atom of a phosphate anion), and the quenched lifetime of 66  $\mu\text{s}$  for  $\text{Eu}^{3+}$ -doped  $\text{SmPO}_4$  the critical distance  $R_0$  is found to be 8.02  $\text{\AA}$ . This distance is similar to reported critical distances for  $\text{Eu}^{3+}$  incorporation in solid matrices such as  $\text{KGdTiO}_4$  ( $R_0 = 8.46 \text{\AA}$ )<sup>52</sup> or  $\text{Y}_2\text{O}_3$  ( $R_0=8.4 \text{\AA}$ )<sup>53</sup>.

In order to assess the self-quenching mechanism in  $\text{EuPO}_4$ , a critical distance should be calculated. Equation 6<sup>54,55</sup> provides a simple way of obtaining an estimate for the critical distance  $R_0$  below which no concentration quenching of  $\text{Eu}^{3+}$  occurs.

$$R_0 \approx 2 \times \left( \frac{3V}{4\pi x_c N} \right)^{1/3} \quad (6)$$

Here  $N$  is the number of  $\text{Eu}^{3+}$  cations in the  $\text{EuPO}_4$  unit cell ( $N = 4$ ),  $V$  is the volume of the unit cell ( $2.902 \times 10^{-28} \text{ m}^3$  derived from the  $\text{EuPO}_4$  unit cell parameters reported in Ni et al.<sup>33</sup>), and  $x_c$  is the critical concentration ( $\text{Ln}_{1-x}\text{Eu}_x\text{PO}_4$ ) beyond which concentration quenching is observed. As the focus of this paper has not been on resolving the quench mechanisms occurring in the  $\text{Eu}^{3+}$  doped monazites, we have not conducted a  $\text{Eu}^{3+}$  concentration dependent series for one of the monazites where a critical concentration could have been extracted. However, preliminary luminescence data on a  $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$  solid solution series indicates a slight deviation from the unquenched lifetime obtained for  $\text{Eu}^{3+}$  doped  $\text{LaPO}_4$  for an  $x$  value of 0.1<sup>56</sup>. Thus, by assuming a  $x_c$  value of 0.1 (also often encountered for  $\text{Eu}^{3+}$  in various solid matrices<sup>53,57-58</sup>) a critical distance of 11.2  $\text{\AA}$  is obtained. This value is much larger than expected for the exchange interaction<sup>18,59</sup>, indicating that electric multipolar interactions would be responsible for the observed self-quenching in  $\text{EuPO}_4$ . For a definite

assessment of the quench mechanism, however, a series of  $\text{Ln}_{1-x}\text{Eu}_x\text{PO}_4$  solids should be synthesized for the extraction of a more accurate critical concentration.

Finally, in  $\text{EuPO}_4$  the non-resonant energy transfer must be accompanied by a significant involvement of the phonon field or third party (impurity) ions to account for the excess excitation energy that is not dissipated through the acceptor absorption transition ( ${}^7\text{F}_0 \rightarrow {}^7\text{F}_6$ ). To get an idea of the significance of lattice vibrations in the monazite solids and their impact on the luminescence lifetimes, room temperature lifetime measurements were conducted and compared to the lifetimes obtained at 10 K, Figure 6. In  $\text{SmPO}_4$  no  $\text{Eu}^{3+}$  signal was obtained at RT, thus, a comparison cannot be made.

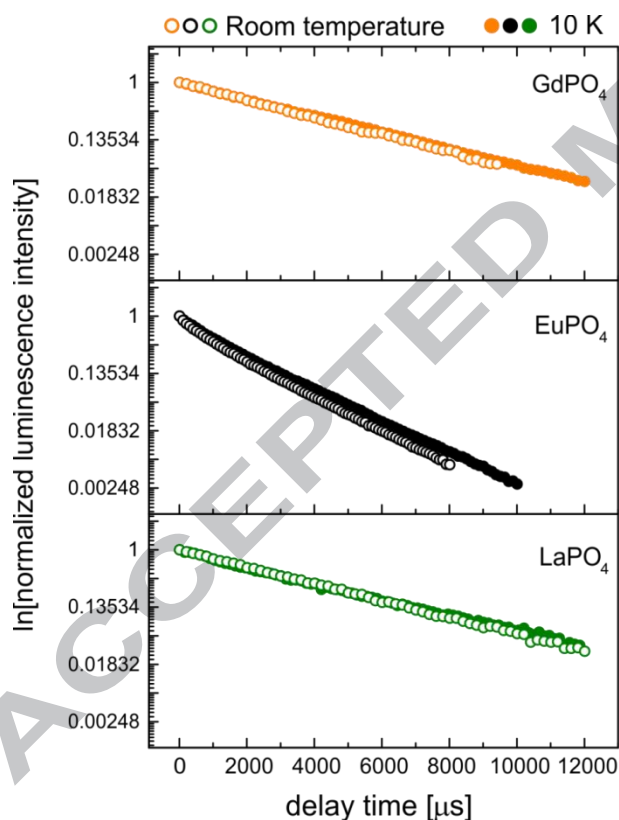


Figure 6: Comparison of lifetimes collected at room temperature (open symbols) and at 10 K (solid symbols) for  $\text{LaPO}_4$ ,  $\text{EuPO}_4$ , and  $\text{GdPO}_4$ .

The difference between RT and 10 K lifetimes is in general very small. The absolute reduction of the lifetime in these solids lies between 130  $\mu\text{s}$  and 285  $\mu\text{s}$ , leading to a relative difference of 5-8 % in  $\text{LaPO}_4$ ,  $\text{GdPO}_4$ , and for the longer component in  $\text{EuPO}_4$ . The largest

relative difference is observed for the shorter lifetime in  $\text{EuPO}_4$  which is reduced from  $602 \pm 80 \mu\text{s}$  at 10 K to  $465 \pm 60 \mu\text{s}$  at RT, i.e. a decrease of around 20%. Due to the overall low influence of temperature on the lifetimes, however, phonon assisted energy transfer dissipating an excess energy equivalent to  $7400 \text{ cm}^{-1}$  is not very likely. Thus, for  $\text{EuPO}_4$  impurities are expected to play a role in the deexcitation process. For  $\text{Eu}^{3+}$ -doped  $\text{SmPO}_4$  with a lifetime of  $66 \mu\text{s}$  at 10 K a similar absolute decrease of the lifetime as observed for the other monazite solids would be enough to completely quench the  $\text{Eu}^{3+}$  luminescence signal. It is not likely that the phonon field in  $\text{SmPO}_4$  would behave very differently to the other monazites, however, for a definite assessment of the phonon contribution to the quenching of the  $\text{Eu}^{3+}$  luminescence signal and the subsequent contribution of third party ions,  $\text{Eu}^{3+}$  luminescence lifetimes in the  $\text{SmPO}_4$  solid should be recorded at additional temperatures between RT and 10 K.

## 4 Conclusions

The systematic decrease of the  $\text{Ln}^{3+}$  host cation radius and  $\text{Ln}\cdots\text{O}$  bond distance in the series of synthesized  $\text{Eu}^{3+}$ -doped monazites ( $\text{LaPO}_4\text{-GdPO}_4$ ) has enabled the study of  $\text{Eu}^{3+}$  luminescence properties related to size differences between host and dopant cation radii and the ligand field effect, in this case exerted by the oxygen ligands, in the monazite solids. We have shown that the slight distortion of the monazite crystal lattice around the  $\text{Eu}^{3+}$  dopant, when going from very similar host- and dopant cation radii (such as  $\text{Eu}^{3+}$  doped in  $\text{GdPO}_4$ ) towards larger differences ( $\text{Eu}^{3+}$  doped in  $\text{LaPO}_4$ ) causes a slight broadening of the  $\text{Eu}^{3+}$  excitation peak and an increase of the  ${}^7\text{F}_2/{}^7\text{F}_1$  emission peak ratio. Furthermore, the increasing influence of the oxygen ligand field on the  $\text{Eu}^{3+}$  dopant as the  $\text{Ln}\cdots\text{O}$  bond distance decreases across the monazite series, results in a systematic shift of the  $\text{Eu}^{3+}$  excitation peak position. This trend shows a linear dependence of both the  $\text{Ln}^{3+}$  host cation radius and the  $\text{Ln}\cdots\text{O}$  bond distance. This dependence was used to predict the energy band gap of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_0$  transition for those  $\text{Eu}^{3+}$ -doped monazites that were not synthesized in the present study ( $\text{CePO}_4$  and  $\text{PmPO}_4$ ) or the monazites that did not show any  $\text{Eu}^{3+}$  luminescence due to strong metal to metal induced quenching ( $\text{NdPO}_4$  and  $\text{PrPO}_4$ ). In addition, we could apply the predicted excitation peak position for  $\text{Eu}^{3+}$ -doped  $\text{PmPO}_4$  to further predict the average  $\text{Pm}\cdots\text{O}$  distance in  $\text{PmPO}_4$ , for which no crystallographic structure has been reported. To our knowledge, a perfect linear relationship between the dopant to ligand distance and the energy band gap has not been observed previously for  $\text{Eu}^{3+}$  incorporation in solid materials with different host cations. If a linear trend can be found to apply for other solid materials, the possibility for energy band gap predictions based on the known host to oxygen ligand distance could open new possibilities in the construction and tailoring of luminescent materials for various applications. For such predictions, however, the presence and proximity of other luminescent centers around the dopant ion must be accounted for as shown in the present study. Due to the absence of structural or chemical differences in the series of investigated monazites, we can

attribute the degree of  $\text{Eu}^{3+}$  luminescence quenching by neighboring lanthanide cations to the size of the energy band gap between the donor atom emission transition and the acceptor atom absorption transition alone. However, it has to be noted that the quenching behavior in the present study applies to a doping of 500 ppm (0.05%)  $\text{Eu}^{3+}$  in the synthetic monazite solids. A different degree of quenching is likely to be obtained when increasing the dopant concentration in the monazites. Finally, the observed phenomena and the lack of  $\text{Eu}^{3+}$  luminescence in certain monazites do not influence the performance of the solid phases as suitable hosts for the trivalent dopant. A perfect substitution of the  $\text{Eu}^{3+}$  dopant for the host cation sites in all investigated monazites was obtained, independent of the size of the host cation, promoting the use of these ceramic phases as hosts phases, for example for the immobilization of trivalent dopants, such as the minor actinides  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ .

## Acknowledgements

The authors would like to thank Jacqueline Holthausen for the synthesis of the monazites. Dr. Gerhard Geipel is thanked for his assistance related to the laser set-up. This work was supported by the German Federal Ministry of Education and Research (BMBF) [grant number 02NUK021] and the Helmholtz Gemeinschaft Deutscher Forschungszentren by supporting the Helmholtz-Nachwuchsgruppe “Structures and Reactivity at the Water/Mineral Interface” [grant number VH-NG-942].

**Supporting Information:** Details on the reagents used for the monazite synthesis are given. XRD spectra of all synthesized monazite end-members are presented in Figure S1. The experimental and predicted excitation energies as well as the predicted Pm···O distance are compiled in Table S1. Table S2 summarizes the transition energies of the  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_j$  emission transitions and various absorption transitions of the host lanthanides.



## 5 References

- 1 P. Yang, Z. Quan, C. Li, Z. Hou, W. Wang and J. Lin, *J. Solid State Chem.*, 2009, **182**, 1045–1054.
- 2 M. Guan, J. Sun, M. Han, Z. Xu, F. Tao, G. Yin, X. Wei, J. Zhu and X. Jiang, *Nanotechnology*, 2007, **18**, 415602.
- 3 S. Rodriguez-Liviano, A. I. Becerro, D. Alcántara, V. Grazú, J. M. de la Fuente and M. Ocaña, *Inorg. Chem.*, 2013, **52**, 647–654.
- 4 L. Zhang, G. Jia, H. You, K. Liu, M. Yang, Y. Song, Y. Zheng, Y. Huang, N. Guo and H. Zhang, *Inorg. Chem.*, 2010, **49**, 3305–3309.
- 5 I. W. Donald, B. L. Metcalfe and R. N. J. Taylor, *J. Mater. Sci.*, 1997, **32**, 5851–5887.
- 6 R. C. Ewing and L. Wang, *Rev. Mineral. Geochem.*, 2002, **48**, 673–699.
- 7 G. Deissmann, S. Neumeier, G. Modolo and D. Bosbach, *Mineral. Mag.*, 2012, **76**, 2911–2918.
- 8 N. Dacheux, N. Clavier and R. Podor, *Am. Mineral.*, 2013, **98**, 833–847.
- 9 F. Brandt, S. Neumeier, T. Schuppik, Y. Arinicheva, A. Bukaemskiy, G. Modolo and D. Bosbach, *Prog. Nucl. Energy*, 2014, **72**, 140–143.
- 10 Y. Arinicheva, A. Bukaemskiy, S. Neumeier, G. Modolo and D. Bosbach, *Prog. Nucl. Energy*, 2014, **72**, 144–148.
- 11 C. M. Gramaccioli and T. V. Segalstad, *Am. Mineral.*, 1978, **63**, 757–761.
- 12 D. Bregiroux, R. Belin, P. Valenza, F. Audubert and D. Bernache-Assollant, *J. Nucl. Mater.*, 2007, **366**, 52–57.

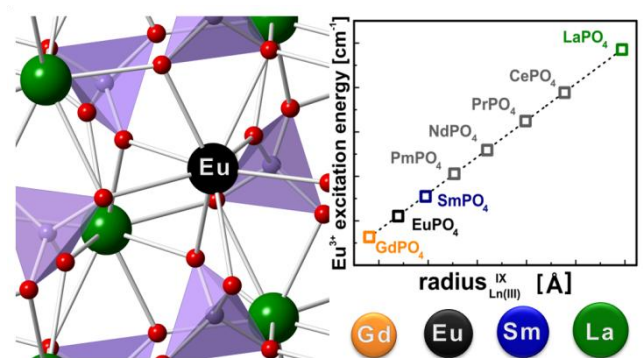
- 13 K. S. Holliday, C. Babelot, C. Walther, S. Neumeier, D. Bosbach and T. Stumpf, *Radiochim. Acta*, 2012, **100**, 189–195.
- 14 O. Terra, N. Dacheux, F. Audubert and R. Podor, *J. Nucl. Mater.*, 2006, **352**, 224–232.
- 15 D. Bregiroux, O. Terra, F. Audubert, N. Dacheux, V. Serin, R. Podor and D. Bernache-Assollant, *Inorg. Chem.*, 2007, **46**, 10372–10382.
- 16 R. P. Rao and D. J. Devine, *J. Lumin.*, 2000, **87–89**, 1260–1263.
- 17 F. Du, R. Zhu, Y. Huang, Y. Tao and H. J. Seo, *Dalton Trans.*, 2011, **40**, 11433–11440.
- 18 K. Binnemans, *Coord. Chem. Rev.*, 2015, **295**, 1–45.
- 19 L. G. Van Uitert, *J. Electrochem. Soc.*, 1960, **107**, 803–806.
- 20 A. Rapaport, V. David, M. Bass, C. Deka and L. A. Boatner, *J. Lumin.*, 1999, **85**, 155–161.
- 21 L. Li and S. Zhang, *J. Phys. Chem. B*, 2006, **110**, 21438–21443.
- 22 C. C. Santos, I. Guedes, C.-K. Loong, L. A. Boatner, A. L. Moura, M. T. de Araujo, C. Jacinto and M. V. D. Vermelho, *J. Phys. D: Appl. Phys.*, 2010, **43**, 025102.
- 23 R. D. Shannon, *Acta Cryst.*, 1976, **A32**, 751–767.
- 24 T. Roncal-Herrero, J. D. Rodríguez-Blanco, E. H. Oelkers and L. G. Benning, *J. Nanopart. Res.*, 2011, **13**, 4049–4062.
- 25 K. Binnemans and C. Görller-Walrand, *J. Rare Earths*, 1996, **14**, 173–180.
- 26 M. Albin and W. D. Horrocks, *Inorg. Chem.*, 1985, **24**, 895–900.
- 27 G. R. Choppin and Z. M. Wang, *Inorg. Chem.*, 1997, **36**, 249–252.
- 28 W. D. Horrocks and D. R. Sudnick, *J. Am. Chem. Soc.*, 1979, **101**, 334–340.

- 29 T. Kimura, G. R. Choppin, Y. Kato and Z. Yoshida, *Radiochim. Acta*, 1996, **72**, 61–64.
- 30 M. Marques Fernandes, M. Schmidt, T. Stumpf, C. Walther, D. Bosbach, R. Klenze and T. Fanghänel, *J. Colloid Interface Sci.*, 2008, **321**, 323–331.
- 31 M. Schmidt, T. Stumpf, M. Marques Fernandes, C. Walther and T. Fanghänel, *Angew. Chem. Int. Ed.*, 2008, **47**, 5846–5850.
- 32 M. Schmidt, T. Stumpf, C. Walther, H. Geckeis and T. Fanghänel, *Dalton Trans.*, 2009, **33**, 6645–6650.
- 33 Y. Ni, J. M. Hughes and A. N. Mariano, *Am. Mineral.*, 1995, **80**, 21–26.
- 34 R. Reisfeld, E. Zigansky and M. Gaft, *Mol. Phys.*, 2004, **102**, 1319–1330.
- 35 Z. Zhao, Q. G. Zeng, Z. M. Zhang and Z. J. Ding, *J. Lumin.*, 2007, **122-123**, 862–865.
- 36 F. S. Richardson, *Chem. Rev.*, 1982, **82**, 541–552.
- 37 T. Aitasalo, P. Dereń, J. Hölsä, H. Jungner, J.-C. Krupa, M. Lastusaari, J. Legendziewicz, J. Niittykoski and W. Stręk, *J. Solid State Chem.*, 2003, **171**, 114–122.
- 38 L. G. Van Uitert and L. F. Johnson, *J. Chem. Phys.*, 1966, **44**, 3514–3522.
- 39 A. Richter, *Laser parameters and performance of Pr<sup>3+</sup>-doped fluorides operating in the visible spectral region*, Cuvillier Verlag, Göttingen, 2008.
- 40 N. Yamada, S. Shionoya and T. Kushida, *J. Phys. Soc. Jpn.*, 1972, **32**, 1577–1586.
- 41 T. Miyakawa and D. L. Dexter, *Phys. Rev. B*, 1970, **1**, 2961–2969.
- 42 J. T. Vega-Durán, L. A. Díaz-Torres, M. A. Meneses-Nava, J. L. Maldonado-Rivera and O. Barbosa-García, *J. Phys. D: Appl. Phys.*, 2001, **34**, 3203–3208.
- 43 R. Lisiecki, W. Ryba-Romanowski and T. Łukasiewicz, *Appl. Phys. B*, 2006, **83**, 255–259.

- 44 J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048–1077.
- 45 D. Kouyate, J. C. Ronfard-Haret and J. Kossanyi, *J. Lumin.*, 1993, **55**, 209–216.
- 46 Y.-C. Fang, S.-Y. Chu, P.-C. Kao, Y.-M. Chuang and Z.-L. Zeng, *J. Electrochem. Soc.*, 2011, **158**, J1–J5.
- 47 H.-Y. Lin and S.-Y. Chu, *ECS J. Solid State Sci. Technol.*, 2013, **2**, R121–R125.
- 48 M. Inokuti and F. Hirayama, *J. Chem. Phys.*, 1965, **43**, 1978–1989.
- 49 T. Förster, *Ann. Physik*, 1948, **2**, 55–75.
- 50 N. Felorzabihi, P. Froimowicz, J. C. Haley, G. Rezanejad Bardajee, B. Li, E. Bovero, F. C. J. M. van Veggel and M. A. Winnik, *J. Phys. Chem. B*, 2009, **113**, 2262–2272.
- 51 M. Lunz, A. L. Bradley, V. A. Gerard, S. J. Byrne, Y. K. Gun'ko, V. Lesnyak and N. Gaponik, *Phys. Rev. B*, 2011, **83**, 115423.
- 52 N. Zhang, C. Guo, J. Zheng, X. Su and J. Zhao, *J. Mater. Chem. C*, 2014, **2**, 3988–3994.
- 53 M. K. Chong, K. Pita and C. H. Kam, *J. Phys. Chem. Solids*, 2005, **66**, 213–217.
- 54 G. Blasse, *Phys. Lett. A*, 1968, **28**, 444–445.
- 55 G. Blasse, *Philips Res. Repts.*, 1969, **24**, 131–144.
- 56 own unpublished data<sup>†</sup>
- 57 X. Zhang and H.-J. Seo, *J. Alloys Compd.*, 2010, **503**, L14–L17.
- 58 A. Yousif, S. Som, V. Kumar and H. C. Swart, *Mater. Chem. Phys.*, 2015, **166**, 167–175.
- 59 D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836–850.

<sup>†</sup>data provided to reviewers

## Graphical abstract



ACCEPTED MANUSCRIPT

**Supporting Information****Using  $\text{Eu}^{3+}$  as an atomic probe to investigate the local environment in  $\text{LaPO}_4\text{-GdPO}_4$  monazite end-members**

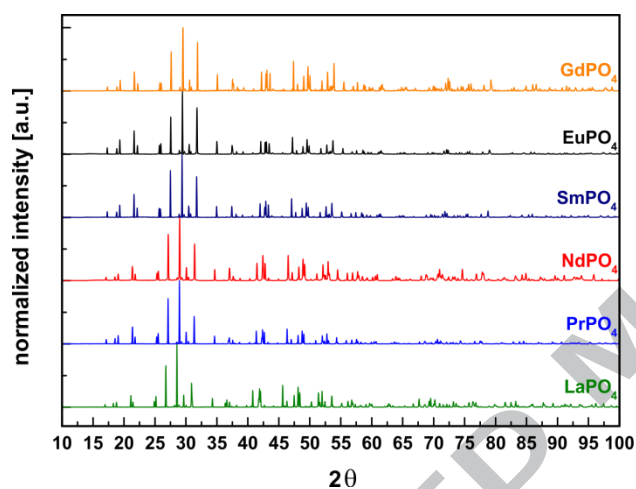
Nina Huittinen<sup>1</sup>, Yulia Arinicheva<sup>2</sup>, Moritz Schmidt<sup>1</sup>, Stefan Neumeier<sup>2</sup>, Thorsten Stumpf<sup>1</sup>

<sup>1</sup>Helmholtz-Zentrum Dresden - Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany

<sup>2</sup>Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Nuclear Waste Management and Reactor Safety (IEK-6), 52425 Jülich, Germany

As starting materials for the monazite synthesis the following reagents were used:  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar),  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar),  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich) and analytical grade 85%  $\text{H}_3\text{PO}_4$  (Merck).

The crystallinity and phase purity of the synthesized products were characterized by XRD. All measured XRD spectra are compiled in Figure S1.



**Figure S1:** XRD spectra of all synthesized monazite end-members

From the linear equations obtained by plotting the  $\text{Eu}^{3+}$  excitation peak position as a function of host cation radius or average  $\text{Ln}\cdots\text{O}$  distance, the excitation energies for  $\text{Eu}^{3+}$  incorporation in monazites for which no experimental data could be obtained ( $\text{CePO}_4$ ,  $\text{PrPO}_4$ ,  $\text{NdPO}_4$ ,  $\text{PmPO}_4$ ) have been calculated. In addition, the excitation peak position for  $\text{Eu}^{3+}$ -doped  $\text{PmPO}_4$  could be further used to predict the average  $\text{Pm}\cdots\text{O}$  distance in  $\text{PmPO}_4$ , for which no crystallographic structure has been reported. The experimentally derived and predicted values for the excitation energies and the  $\text{Pm}\cdots\text{O}$  distance are tabulated in Table S1 below.

**Table S1:** Experimentally derived and predicted values for the  $\text{Eu}^{3+}$  excitation energies and the  $\text{Pm}\cdots\text{O}$  distance in the synthetic monazite end-members.

Monazite	Experimental data $\text{Eu}^{3+}$ excitation energy [ $\text{cm}^{-1}$ ]	Predicted data* Equation 2 / Equation 3
$\text{LaPO}_4$	17289	-
$\text{CePO}_4$	-	17285 / 17284
$\text{PrPO}_4$	-	17282 / 17281
$\text{NdPO}_4$	-	17279 / 17278
$\text{PmPO}_4$	-	$E = 17275 / R = 2.5106$
$\text{SmPO}_4$	17273	-
$\text{EuPO}_4$	17271	-
$\text{GdPO}_4$	17268	-

\* $\text{Eu}^{3+}$  excitation energies are given in  $\text{cm}^{-1}$  and  $\text{Pm}\cdots\text{O}$  distance in  $\text{\AA}$ .



The band gap, i.e. the energy difference between the  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$  emission transitions and the closest matching absorption transition of the accepting lanthanide has been calculated from available data in Martin et al. 1978. For the sake of consistency, the calculations have been done with the published emission transition energy of  $17270 \text{ cm}^{-1}$  for the  $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_0$  transition of the  $\text{Eu}^{3+}$  ion despite the experimentally derived values for this transition ranging from  $17268$  to  $17289 \text{ cm}^{-1}$  in the various  $\text{Eu}^{3+}$ -doped monazites in the present study. The transition energies and energy gap differences are compiled in Table S2.

**Table S2:** Transition energies for the  $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$  emission transitions, chosen monazite host lanthanide absorption transitions and the energy difference ( $\Delta E$ ) of the emission- and absorption transitions.

Emission transition $\text{Eu}^{3+}$	Transition energy [ $\text{cm}^{-1}$ ]*	
$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_6$	12330	
$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_5$	13360	
$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_0$	17270	
Absorption transition $\text{Pr}^{3+}$	Transition energy [ $\text{cm}^{-1}$ ]*	$\Delta E$ (emission–absorption) [ $\text{cm}^{-1}$ ]
$\ ^3\text{H}_4 \rightarrow \ ^1\text{D}_2$	17334	$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ (17270) – 17334 = –64
Absorption transition $\text{Nd}^{3+}$	Transition energy [ $\text{cm}^{-1}$ ]*	$\Delta E$ (emission–absorption) [ $\text{cm}^{-1}$ ]
$\ ^4\text{I}_{9/2} \rightarrow \ ^4\text{F}_{5/2}$	12320	$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_6$ (12330) – 12320 = 10
$\ ^4\text{I}_{9/2} \rightarrow \ ^4\text{S}_{3/2}$	13370	$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_5$ (13360) – 13370 = –10
$\ ^4\text{I}_{9/2} \rightarrow \ ^4\text{G}_{5/2}$	16980	$\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_0$ (17270) – 16980 = 290

Absorption transition $\text{Sm}^{3+}$	Transition energy [ $\text{cm}^{-1}$ ]*	$\Delta E$ (emission–absorption) [ $\text{cm}^{-1}$ ]
${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{11/2}$	10470	${}^5\text{D}_0 \rightarrow {}^7\text{F}_6$ (12330) – 10470 = 1860
Absorption transition $\text{Eu}^{3+}$	Transition energy [ $\text{cm}^{-1}$ ]*	$\Delta E$ (emission–absorption) [ $\text{cm}^{-1}$ ]
${}^7\text{F}_0 \rightarrow {}^7\text{F}_6$	4940	${}^5\text{D}_0 \rightarrow {}^7\text{F}_6$ (12330) – 4940 = 7390

\*The transition energies are taken from Martin, W. C., Zalubas, R., and Hagan, L. 1978 Atomic Energy Levels – The Rare-Earth Elements: The Spectra of Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium. Institute for Basic Standards, National Bureau of Standards, Washington D.C. 20234.