Interplay between electronic and structural effects on the photoluminescence decay mechanisms in $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Tb}^{3+}$ and $\text{LaPO}_4:\text{Tb}^{3+}$ single-crystal nanorods

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Abstract

A novel High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) study at the Tb L₃-edge for the rhabdophane-type $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Tb}^{3+}$ and the monazite-type $\text{LaTbPO}_4:\text{Tb}^{3+}$ nanorods is reported. We have observed that the changes in the white-line intensity follow a similar trend to that previously observed in the photoluminescence behaviour of these materials. Those changes have been assigned to the localization of the terbium 5*d* states and the modification induced by the hybridization with the next neighbours as the terbium content is varied. The interplay between electronic (*d*-states localization) and structural (local disorder) effects is used to explain the different optical behaviour between the two series of nanorods. XAS results indicate that the local ordering is a key factor influencing the different emission efficiency, quenching effect and decay lifetimes observed experimentally for both series

of nanorods. The present results indicate that the long lifetime decay process is accounted within a standard single Tb^{3+} ion scenario, where the structural disorder, favoured by the presence of water molecules in the structure, aids the non-radiative recombination processes. Implications for future use of the white-line intensity in the HERFD-XAS spectra in characterizing other luminescent materials are also discussed.

Keywords: rare-earth phosphates; Photoluminescence; Nanorods; X-ray Absorption Spectroscopy; local structure.

Introduction

Luminescent oxide materials based on $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ or LaPO_4 doped with lanthanide ions (Ln) such as terbium, europium, and cerium, or codoped with terbium and europium, offer outstanding optical properties together with a high chemical/thermal stability,¹⁻⁶ at an affordable cost that makes them viable. They are then promising active components in functional applications as diverse as light-emitting devices, low-threshold lasers, optical amplifiers, markers for biomolecules, and colour television cathode ray tubes, to name but a few.⁷⁻¹¹ Moreover, luminescence efficiency is expected to increase when the size of the particles decreases to the nano-scale.⁴ Consequently, Ln-doped luminescent nanomaterials attract ever greater technological interest, and not surprisingly are currently being the focus of extensive research due to the enhanced luminescent quantum efficiency and display resolution.¹²

The properties of the luminescent nanomaterials depend largely on their particular morphologies and sizes. This justifies the great interest in the development of nanostructured

$\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Ln}^{3+}$ and $\text{LaPO}_4:\text{Ln}^{3+}$ with well-controlled size and shape in general, and in the production of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Ln}^{3+}$ and $\text{LaPO}_4:\text{Ln}^{3+}$ nanorods by microwave-assisted hydrothermal synthesis in particular. The nanorods obtained using this synthetic method present a high morphological uniformity since microwave radiation induces a rapid, homogeneous, and volumetric heating up to the crystallization temperature. This results in the wholesale nucleation of uniform seeds throughout the entire bulk of the solution and in their subsequent fast growth to give crystals with a narrower size distribution and greater uniformity. However, there must be taken into account that the short penetration depth of microwave irradiation into the liquid medium limits the size of the reactors, which is a problem for scale-up.

The synthesis and optical properties of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Tb}^{3+}$ and $\text{LaPO}_4:\text{Tb}^{3+}$ nanorods have been the subject of active research lately.^{6-9,13-15} However, despite the various studies investigating the relationship between synthesis and optical properties of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Tb}^{3+}$ and $\text{LaPO}_4:\text{Tb}^{3+}$ nanorods,^{14,15} a good understanding of their photoluminescent behaviour is still missing. Moreover, the dependence of photoluminescence on their local electronic and geometrical structures, and on terbium content in solid solution, also remains elusive. Shedding light on these gaps is however critical to guide the future controlled design of these, and other, enticing photoluminescent nanomaterials. Innovative studies in this field are thus needed to turn our aspiration into reality.

It is known at least that the normalized photoluminescence intensity due to the terbium f-f transitions, with both continuous and pulsed excitations, increases with increasing terbium content, and eventually reaches a maximum for the compositions $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\sim\text{La}_{0.83}\text{Tb}_{0.07}\text{PO}_4$, respectively.¹⁴ Importantly, the photoluminescence decay curves revealed a long lifetime (τ_1) which differs markedly for both $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ series (for $x=0.1$

τ_1 is ~ 3.5 and ~ 4.5 ms, respectively), and a short lifetime (τ_2) which shows similar values in both series of compounds (~ 1 ms for $x = 0.1$).¹⁴ The long lifetime decay was attributed to single terbium ions, whereas the short decay time was tentatively attributed to the formation of dimers, trimers, or clusters of terbium atoms.¹⁴ Both, the emission efficiency of the monazite-type nanorods and the A_1/A_2 ratio, where A_1 and A_2 are the weights of the long and short time components, respectively, are in general higher than that of the rhabdophane-type nanorods, likely due in part to the higher crystallinity degree induced by the calcination. The physical interpretation of these experimental observations could however be too sophisticated, and is then still a paradigm that needs reconsideration and further clarification.

Stimulated by determining the origin of the different optical performance of these materials, here we have performed a novel High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) study at the Tb L_3 -edge for both the rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and the monazite-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods with different terbium contents. It is anticipated that the simultaneous sensitivity of XAS to the local electronic and geometrical structure will provide the deeper understanding demanded before on the relationship between the electronic and structural effects and the different photoluminescence behaviour observed in $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods. Not less importantly, here we also demonstrate for the first time that a direct correlation exists between the intensity of the white-line in the X-ray Absorption Near Edge Structure (XANES) region of the HERFD-XAS spectra and the photoluminescence behaviour. The existence of correlation seems generic, and in principle could then be applicable to a broad palette of other photoluminescent nanomaterials, thus representing a new fertile characterization tool of this type of functional materials. It is for this reason that the

present study is likely to have relevant implications for the photoluminescence materials community in general.

Experimental

$\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods with different terbium content in solid solution ($x = 0.02, 0.05, 0.10, 0.15, 0.20$, and 1) were prepared by microwave-assisted hydrothermal synthesis. $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods were obtained after calcination. The as-synthesized products crystallize as rhabdophane-type substitutional solid solutions in the space group $P6_222$ (i.e., hexagonal $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$), with terbium atoms substituting lanthanum centres at Wyckoff positions 3d. In these compounds, the lattice parameters a and c decrease with increasing terbium content¹³ as listed in Table 1. Regardless of the terbium content in solid solution, the rhabdophane-type crystal structure transforms to the monazite-type crystal structure, monoclinic $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$, at $\sim 715^\circ\text{C}$. The space group of these monoclinic substitutional solid solutions is $P2_1/n$ (with terbium atoms substituting lanthanum centres at Wyckoff positions 4e), and the lattice parameters a , b , and c decrease while the lattice parameter β increases with increasing terbium content¹³ as also listed in Table 1. Specific details of sample preparation and characterization for the present $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Ln}^{3+}$ and $\text{LaPO}_4:\text{Ln}^{3+}$ compounds can be found elsewhere,^{13,14} whereas more general structural information for both $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ and LnPO_4 compounds is given elsewhere.¹⁶ The nanorod morphology of the as-synthesized $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and calcined $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ products can be seen in the representative Transmission Electron Microscopy (TEM) images in Figure 1. These observations were conducted with a JEM-2100F, JEOL microscope (Tokyo, Japan) at 200 keV.

Table 1. Lattice parameters and unit-cell volume of both the as-prepared $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods with rhabdophane-type crystal structure and the calcined $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods with monazite-type crystal structure, as a function of Tb^{3+} content in solid solution.

Rhabdophane-type crystal structure (hexagonal)				Monazite-type crystal structure (monoclinic)					
Composition	Lattice parameters		Cell volume ($\text{\AA}^3$)	Composition	Lattice parameters				Cell volume ($\text{\AA}^3$)
	a ($\text{\AA}$)	c ($\text{\AA}$)			a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	β ($^\circ$)	
$\text{La}_{0.98}\text{Tb}_{0.02}\text{PO}_4 \cdot n\text{H}_2\text{O}$	7.126 [#]	6.518 [#]	286.66 [#]	$\text{La}_{0.98}\text{Tb}_{0.02}\text{PO}_4$	6.855 [#]	7.086 [#]	6.518 [#]	103.36 [#]	308.0 [#]
$\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4 \cdot n\text{H}_2\text{O}$	7.120(7)	6.512(7)	285.9(7)	$\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$	6.847(5)	7.077(5)	6.513(5)	103.38(2)	307.0(4)
$\text{La}_{0.9}\text{Tb}_{0.1}\text{PO}_4 \cdot n\text{H}_2\text{O}$	7.113(8)	6.508(7)	285.2(7)	$\text{La}_{0.9}\text{Tb}_{0.1}\text{PO}_4$	6.840(8)	7.070(9)	6.509(9)	103.41(2)	306.2(7)
$\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$	7.103 [#]	6.500 [#]	284.02 [#]	$\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$	6.831 [#]	7.063 [#]	6.503 [#]	103.44 [#]	305.2 [#]
$\text{La}_{0.8}\text{Tb}_{0.2}\text{PO}_4 \cdot n\text{H}_2\text{O}$	7.094(9)	6.492(9)	283.0(9)	$\text{La}_{0.8}\text{Tb}_{0.2}\text{PO}_4$	6.823(8)	7.055(8)	6.497(8)	103.46(2)	304.2(6)
$\text{TbPO}_4 \cdot n\text{H}_2\text{O}$	6.951 ^{&}	6.381 ^{&}	267.003 ^{&}	TbPO_4	6.679 ^{&}	6.911 ^{&}	6.404 ^{&}	103.96 ^{&}	286.43 ^{&}

[#]Magnitudes (without error) obtained by interpolation. [&]Magnitudes (without error) obtained by extrapolation.

Figure 1. Representative TEM micrographs of the as-prepared $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (a) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ (b) powders, respectively.

The $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods were pressed into pellets to measure the PL spectra at room temperature. They were collected under 488 nm excitation light of an Ar⁺ laser (Melles-Griot, 35-LAP-431) focused with a microscope (Olympus, BX60M), using a x20 objective and a spot diameter of ~5 μm . The emission signal was collected with the same objective, and filtered by a Notch filter (Super-Notch-Plus Filters from Kaiser) at 488 nm to eliminate the elastic light. For the prepared nanorods the normalized photoluminescence (PL) intensity to the Tb^{3+} concentration reveals the occurrence of quenching (Fig. 2). It can be seen that the emission efficiency first decreases rapidly with increasing doping up to $x = 0.05$ or $x \approx 0.07$ for the as-prepared and calcined samples, respectively. A plateau is reached for Tb^{3+} content above these values. In addition, the emission efficiency of the $\text{TbPO}_4 \cdot n\text{H}_2\text{O}$ and TbPO_4 compounds is found to be significantly lower than that of $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ counterparts. Furthermore, the emission efficiency of the monazite-type nanorods is higher than that of the rhabdophane-type nanorods for the same doping content, likely due in part to the higher crystallinity degree in the former induced by the calcination and the presence of water in the latter, which would be favouring non-radiative recombination. Specific details of PL characterization for the present $\text{LaPO}_4 \cdot n\text{H}_2\text{O}:\text{Ln}^{3+}$ and $\text{LaPO}_4:\text{Ln}^{3+}$ compounds can be found elsewhere.¹⁴

Figure 2. PL intensity of the $^5D_4$ to $^7F_5$ transition for both the rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods and the monazite-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods after normalisation by Tb^{3+} concentration.

The Tb L_3 -edge (~ 7484 eV) HERFD-XAS data were collected at beamline I20-Scanning^{17,18} at Diamond Light Source (UK), operating at 3 GeV and 300 mA ring current. HERFD-XAS is essential¹⁹ within the confines of the present study because the spectra recorded at the lanthanide L-edges by conventional XAS exhibit too broad spectral features since they are intrinsically limited by the large (> 4 eV) core-hole lifetime. The HERFD-XAS experiment was performed at room temperature using the 1 m diameter X-ray emission spectrometer available at the beamline based on the Johan configuration.²⁰ The Tb $L\alpha_1$ emission line (6273 eV) was selected by using three Ge(440) spherically bent crystals. The incident intensity was measured by an ionization chamber filled with the appropriate gas mixture to absorb 15% of the radiation at the terbium L_3 -edge energy, while the fluorescence energy was measured using a medipix pixel

detector.²¹ Harmonic rejection was performed through the use of two silicon mirrors operating at 3.5 mrad incident angle. The samples were prepared as pressed pellets of 9 mm diameter.

The experiment was optimized to collect HERFD-XANES data, but additionally limited range ($k_{max} \sim 10 \text{ \AA}^{-1}$) Extended X-ray Absorption Fine Structure (EXAFS) data were measured as part of the collection procedure (Fig. S1). XAS data processing (i.e., spectra averaging, background subtraction, and amplitude normalization required to obtain the normalized XANES and EXAFS signals) was performed according to standard procedures²² by using the ATHENA program included in the Demeter package.²³ Data processing was made by using the default values calculated by the ATHENA program: k^2 weight, edge step equal to unity and spline range 0 to 10 $\text{\AA}^{-1}$ were used. The range used for the pre-edge polynomial was from -150 to -30 eV from the edge position, and that used for normalisation was from 150 to 282.3 eV. In our case, the absorption edge position, E_0 , was determined to be 7517.7 eV, and this was defined as the first inflection point of the absorption spectrum. No shift in E_0 was observed over the spectra collected for both series of compound (Fig. S1).

Results and discussion

Figure 3 compares the normalized Tb L_3 -edge HERFD-XAS spectra for the rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods as a function of their terbium content in solid solution. Four main features can be seen: (i) a weak pre-peak (labelled A) at ~ 7.5 eV below the threshold; (ii) a main absorption peak (B), usually referred as the white-line, at ~ 1.8 eV above the edge; (iii) a small peak (C) and (iv) a broad absorption maximum (D) centred, respectively, at ~ 12.5 eV and ~ 34.3 eV above the edge. Some differences can be seen in the absorption spectra when varying

the terbium content through the series. The intensity of both the white-line and peak C decreases as the terbium content increases, while the energy position of peak C is shifted towards higher values; the energy position of peak C shifts by ~ 1 eV between the two extreme terbium contents investigated (i.e., $x=0.02$ and $x=0.2$). The combination of both effects (i.e., intensity and position) produces the smearing out of peak C. It is interesting to highlight that the intensity of the white-line decreases linearly with the terbium content until the concentration reaches 15 mol%. Above this value the intensity of the white-line varies only marginally with increasing the terbium content. In contrast, the modification of the intensity and energy position of peak C vary linearly with the terbium content. Only in the case of the 2 mol% compound the changes of the intensity of peak C departs from the linearity.

Figure 3. (Color online) Comparison of the Tb L₃-edge spectra of the rhabdophane-type La_{0.98}Tb_{0.02}PO₄·*n*H₂O (black, solid line) and La_{0.80}Tb_{0.20}PO₄·*n*H₂O (red, dot-dash) compounds. In the insets a detailed comparison of the variations of the white-line intensity and of the spectral feature C with terbium content is given (see text for details): *x*=0.02 (black), 0.05 (red), 0.10 (green), 0.15 (blue), 0.20 (magenta), and 1 (cyan).

Similar behaviour is found in the case of the monazite-type La_{1-*x*}Tb_{*x*}PO₄ nanorods. As shown in Figure 4, the highest white-line is found for the lowest terbium content compound investigated in the series (i.e., 2 mol%). As observed previously for the rhabdophane-type La_{1-*x*}Tb_{*x*}PO₄·*n*H₂O nanorods, the intensity of the white-line decreases linearly when increasing the terbium content until it reaches saturation. In this series, however, the saturation is reached when the terbium content is 10 mol%, and not 5 mol% as in the previous series investigated. It is interesting to notice that the white-line intensity of the nanorods in the La_{1-*x*}Tb_{*x*}PO₄ series is significantly greater than that of the TbPO₄ end-member, independently of the terbium content. As can be seen in Figure 4, neither the intensity nor the energy position (~14.3 eV above the edge) of peak C vary when increasing the terbium content in this series, in contrast with the behaviour observed of peak C for the as-synthesized compounds.

Figure 4. (Color online) Comparison of the Tb L₃-edge spectra of the monazite-type La_{0.98}Tb_{0.02}PO₄ (black, solid line) and La_{0.80}Tb_{0.20}PO₄ (red, dot-dash) nanorods. In the insets a detailed comparison of the changes of the white-line intensity and of the spectral feature C with terbium content is given (see text for details): $x=0.02$ (black), 0.05 (red), 0.10 (green), 0.15 (blue), 0.20 (magenta), and 1 (cyan).

The absorption spectra of the La_{1-x}Tb_xPO₄·*n*H₂O and La_{1-x}Tb_xPO₄ series of nanorods for the two extreme compositions are shown in Figure 5. As mentioned above, the intensity of the white-line decreases by increasing the terbium content in both series. However, for all compositions, the intensity of the white line increases notably after calcination. While in the case of the La_{1-x}Tb_xPO₄·*n*H₂O series this intensity of the white-line for 20 mol% matches the white-line

intensity of the $\text{TbPO}_4 \cdot n\text{H}_2\text{O}$ end-member, this is not the case for the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods, where the intensity of the white-line is significantly greater than the end-member independently of the terbium content. As mentioned above, the behaviour of peak C is different for both series. In the case of the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ series this peak decreases in intensity and shifts towards higher energy as the terbium content increases. However, no significant changes in peak C intensity or position are observed in the case for the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods. This different behaviour suggests that peak C is related to the presence of water molecules in the structure. It can also be observed that peak D shifts towards lower energy after calcination, thus indicating that the nearest-neighbour distance to the terbium ions is larger in the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods than in the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ series.

Figure 5. (Color online) Comparison of the Tb L₃-edge spectra of the monazite-type La_{0.98}Tb_{0.02}PO₄ (black, solid line), La_{0.80}Tb_{0.20}PO₄ (red, dot-dash) and TbPO₄ (magenta, short dash-dot) nanorods and those of the rhabdophane-type series with the same terbium concentration: La_{0.98}Tb_{0.02}PO₄·*n*H₂O (blue, dashes) and La_{0.80}Tb_{0.20}PO₄·*n*H₂O (green, dots). In the inset a detailed view of the post-edge region showing peak C. For the sake of completion, the spectrum of TbPO₄·*n*H₂O (grey, short dash-dot) has been also included although it is practically identical to that of TbPO₄ (see text for details).

The differences found in the EXAFS region of the spectra as a function of Tb content in both series are small, in contrast to the changes found in the XANES region. The k-weighted extracted EXAFS signals reflects for the two series of nanorods are shown in Figure 6, top panel. The comparison of the EXAFS signals reflects the different local structure around the terbium ions in the La_{1-x}Tb_xPO₄·*n*H₂O and the La_{1-x}Tb_xPO₄ series, as expected from their different crystal structures. Within each series, the EXAFS spectra recorded for compounds of different terbium content show no appreciable difference and they resemble that of the corresponding TbPO₄·*n*H₂O and TbPO₄ end-members. This result underlines the different impact of Tb substitution in both the threshold and EXAFS regions as previously observed in different systems.²⁴ These two well-defined regions of the spectra carry, information about the electronic state and local structural environment of the absorbing atom, respectively. Consequently, the large differences observed in the edge region allows us to address the origin of the change in the photoluminescence properties of the studied series to an electronic-induced effect instead that to structural modifications exclusively.

For both series, the amplitude of the EXAFS signal decreases as a function of k , and for values of $k \geq 7 \text{ \AA}^{-1}$ the signal is completely damped. This is indicative of a highly disordered environment around the terbium ions, which is mainly dominated by Tb-O interactions. It is however interesting to highlight that all the spectra shown in Figure 6 exhibit, regardless the different local structure, a sharp feature at $k \sim 6.3 \text{ \AA}^{-1}$ that is attributable to a multi-electron excitation. This spectral feature has been identified as being due to the simultaneous excitation of $2p$ and $4d$ electrons ($2p4d \rightarrow 5d^2$ double-electron transition) in the case of the L_3 and L_2 -edges of the lanthanides.^{25,26,27} These excitations exhibit an atomic-like character and, consequently, their intensity and spectral shape do not depend of the local structure. The present experimental findings are in agreement with theoretical calculations which predict the occurrence of such a transition at $k \sim 6.7 \text{ \AA}^{-1}$ with a ratio of the main $2p \rightarrow 5d$ absorption line (i.e. the white-line) to the double electron $2p4d \rightarrow 5d^2$ cross section of 1.58×10^2 .²⁴ In the present case, the intensity ratio between the white-line to the aforesaid feature is 1.63×10^2 . Earlier studies have demonstrated that the presence of these anomalous features superimposed to the structural EXAFS oscillatory signal alters the structural signal, hampering an accurate extraction of the structural parameters from the EXAFS spectra even in crystalline systems.^{26,28}

Figure 6. (Color online). Top panel: Comparison of the Tb L₃-edge EXAFS extracted signal for the La_{1-x}Tb_xPO₄·*n*H₂O and La_{1-x}Tb_xPO₄ compounds: *x*=0.02 (black), 0.05 (red), 0.10 (green), 0.15 (blue), and 0.20 (magenta), and those of their end-members TbPO₄·*n*H₂O and TbPO₄. Bottom panel: EXAFS extracted signal, non-weighted, for the La_{0.98}Tb_{0.02}PO₄·*n*H₂O (black) and La_{0.98}Tb_{0.02}PO₄ (red) compounds.

The arrow marks the $2p4d \rightarrow 5d^2$ multi-electron excitation. The spectra have been vertically shifted for the sake of clarity.

Despite the limitations indicated above, the qualitative analysis of the EXAFS data might offer some additional information to our problem, especially regarding the presence of different Tb aggregates. Figure 7 shows the Fourier transform of the two extreme compositions for the two series of nanorods under investigation. It can be seen in the figure that the position of the first maximum, corresponding to the interatomic distance from the absorbing terbium to the nearest oxygen neighbours, is approximately 0.06 Å longer in the calcined La_{1-x}Tb_xPO₄ nanorods when compared with the La_{1-x}Tb_xPO₄·*n*H₂O nanorods, in agreement to the crystallographic data. It is interesting to highlight that both the electronic state and the next-neighbouring environment around the terbium atoms would be drastically changed in case of terbium clustering, contrary to the present results, and this would be reflected in both the XANES and the EXAFS parts of the absorption spectra. These XAS results provide a deeper insight into the origin of the optical properties exhibited by both the La_{1-x}Tb_xPO₄·*n*H₂O and La_{1-x}Tb_xPO₄ nanorods.¹⁴

Figure 7. (Color online). (a) Raw EXAFS data, k-weighted, of $\text{La}_{0.98}\text{Tb}_{0.02}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (black, solid circles) and $\text{La}_{0.80}\text{Tb}_{0.20}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (black, solid line), and those of the calcined $\text{La}_{0.98}\text{Tb}_{0.02}\text{PO}_4$ (red, open circles) and $\text{La}_{0.80}\text{Tb}_{0.20}\text{PO}_4$ (red, solid line). (b) Magnitude part of the Fourier transform of the EXAFS spectra included in part a.

Figure 8 shows the changes in the terbium L_3 -edge white-line intensity as a function of the terbium content for both the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ series. The intensity of the white-line is higher for the monazite-type nanorod series, independently of the terbium content. This is in good agreement with the photoluminescence behaviour exhibited by these compounds as the emission is greater in the monazite-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods than in the rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods for any terbium-doping content.¹⁴ It has also been found that for both series the normalized emission decreases when increasing the terbium content,¹⁴ also in good agreement with the XAS results; the larger the terbium content, the lower the intensity of the white-line for both series of nanorods, as shown in Figure 8. The maximum intensity of the white-line thus corresponds to the sample with 2 mol% terbium content for both series (i.e., $\text{La}_{0.98}\text{Tb}_{0.02}\text{PO}_4$ and $\text{La}_{0.98}\text{Tb}_{0.02}\text{PO}_4 \cdot n\text{H}_2\text{O}$). In the case of the calcined series (i.e., monazite-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods), the white-line intensity decreases until the terbium content reaches 10 mol% ($x = 0.10$). Above this value, the intensity remains constant within the error. Similar behaviour is observed in the rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods, although in this case a first saturation occurs for a terbium content of 5 mol% ($x = 0.05$). As shown in Figure 2, the emission efficiency (per terbium atom) for both series follows this same trend when increasing the terbium content.¹⁴

Figure 8. Comparison of the evolution of the maximum of the white-line intensity of the Tb L₃-edge HERFD-XAS spectra white line intensity with the terbium content through both La_{1-x}Tb_xPO₄·nH₂O (red, open circles) and La_{1-x}Tb_xPO₄ (black, solid circles) series. The dotted lines are an aide for the eyes.

The behaviour exhibited by the white-line intensity can be correlated with the localization of the terbium 5*d* states and its modification induced by the hybridization with the neighbouring atoms as the terbium content is increased. The X-ray absorption coefficient ($\mu(E)$) is related to the angular momentum-projected density of states ($\rho(E)$) through the expression $\mu(E)=f_{at}(E)\cdot\rho(E)$, where $f_{at}(E)$ is a smoothly-varying function of the probed atom that does not depend on its local

environment.²⁹ In the case of the rare-earth (RE) L₃-edge, the absorption of X-rays by excitation of the 2*p* electrons is a simple and sensitive probe of the local unoccupied lanthanide 5*d* states.³⁰⁻
³² According to the expression above, the intensity of the L₃ white-line can be directly related to the localization of the 5*d* states. According to the present data, the calcination process (i.e., the transformation from La_{1-x}Tb_xPO₄·*n*H₂O to La_{1-x}Tb_xPO₄) enhances the local structural order around the terbium atoms, leading to the localization of the 5*d* states on terbium sites and therefore to the increase of the white-line intensity. A similar effect has been observed in the case of RE-Fe intermetallics, where the increase of the RE white-line intensity upon hydrogen uptake is ascribed to the weakening of the RE-Fe hybridization as hydrogen enters the metallic framework, thus leading to the localization of the 5*d* states on the RE sites.³³ Also, Choi et al.^{34,35} have discussed the relationship between the covalence of chemical bonds of rare earth ions embedded in glasses with the L₃-edge white-line intensity of the rare earth ions.

The interplay between the electronic (*d*-states localization) and the structural (local disorder) effects can also explain the differences in the magnitude and evolution with time of the normalized photoluminescence on both series of nanorods, as described earlier.¹⁴ The decay curves have been fitted by using two exponentials, and two different lifetimes were then obtained. The relative weighting ratio of the long and the short lifetimes obtained, and its dependence with the terbium content, differ for each series. This ratio remains near constant in the case of the La_{1-x}Tb_xPO₄·*n*H₂O nanorods for all compositions, and in all cases is smaller than for the calcined La_{1-x}Tb_xPO₄ series, for which the ratio decreases as the terbium content increases.¹⁴ The long lifetime has been tentatively attributed to single terbium ions in the lattice, and the short lifetime to the formation of dimers, trimers, or clusters of terbium atoms. The XAS results reported here suggest that the long lifetime decay process is due to the standard mechanism associated to isolated Tb³⁺ ions, as

previously proposed. In this respect the higher intensity of the white-line for the monazite-type than rhabdophane nanorods series indicates a higher atomic-like character of the Tb^{3+} ions in the former nanorods that is reflected in the increased long lifetime value. Indeed, τ_1 is ~ 4.5 ms for the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ series, whereas it decreases to ~ 3.5 ms in the case of the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods showing an increased local structural disorder. The data suggest that the local ordering is the key factor influencing the quenching effect, and more specifically that the structural disorder favours the non-radiative recombination. The presence of water molecules in the structure increases both the local structural disorder, thus favouring the delocalization of the d -states, and the hybridization with neighbouring atoms, thus causing non-radiative recombination. This explains why the photoluminescence decay curves were found to be almost identical for the as-synthesized nanorods regardless the terbium content, and why it decays more rapidly than in the calcined samples. In addition, the presence of defects in the host-matrix acting as non-radiative de-excitation paths for the terbium ions cannot be disregarded.³⁶ The calcination induces a higher crystallinity and it increases the d -states localization, thus leading to an isolated-like terbium ion scenario. Moreover, the analysis of the XAS data precludes the formation of dimers, trimers, or clustering of terbium atoms as the explanation for the short lifetime component. It should be noted in this respect that contrary to the long lifetime, this short lifetime is similar for both monazite-type and rhabdophane-type nanorods, i.e. for compounds showing different disorder and 5d-states localization properties. Indeed the only variation regarding the short lifetime observed between both series of nanorods is its relative weight with respect to the long lifetime. This result suggests that short decay times are related to Tb^{3+} ions at the nanoparticle surface either the involvement of surface states in the carrier recombination process, in agreement with previous assignments.^{14,37} The reduction of the relative

weighting of the short time decay processes observed upon calcination should be addressed to the greater chemical homogeneity achieved.

Conclusion

We have performed a HERFD-XAS study at the Tb L₃-edge for both the rhabdophane-type La_{1-x}Tb_xPO₄·nH₂O and the monazite-type La_{1-x}Tb_xPO₄ nanorods with different terbium content. We found that the white-line intensity of the Tb L₃-edge XANES spectra decreases by increasing the terbium content through the La_{1-x}Tb_xPO₄·nH₂O and La_{1-x}Tb_xPO₄ series of nanorods. This variation is not linear with the terbium concentration, but shows a saturation effect at 5 and 10 mol%, respectively. In addition, the white-line intensity, related to the localization of the terbium 5*d* states, is larger for the La_{1-x}Tb_xPO₄ than for the La_{1-x}Tb_xPO₄·nH₂O nanorods, independently of the terbium concentration.

Contrary to the case of the near edge region, the differences found in the EXAFS region of the absorption spectra as the Tb content increases in both series are small, which points out the low impact of Tb substitution in the local structural environment of the absorbing atom. Moreover, the comparison of the EXAFS signals does not provide indication of terbium clustering. Consequently, the large differences observed in the edge region allows us to address the origin of the change in the photoluminescence properties of the studied series to an electronic-induced effect instead that to structural modifications exclusively.

Additionally, we observed that the changes of the Tb L₃-edge white-line intensity as a function of the terbium content for both La_{1-x}Tb_xPO₄·nH₂O and La_{1-x}Tb_xPO₄ series reproduce the behaviour exhibited by their photoluminescence. The XAS results are in agreement with the reported emission efficiency (per terbium atom), greater for the La_{1-x}Tb_xPO₄ than for the La_{1-x}Tb_xPO₄·nH₂O nanorods for all the compositions investigated. According to the present data, the

calcination process enhances the local structural order around the terbium atoms, leading to the localization of the $5d$ states on the rare-earth (RE) sites as reflected in the white-line intensity.

The present results thus suggest that the local ordering is a key factor influencing the quenching effect as well as the occurrence of two different decay lifetimes. Both the XANES and the EXAFS results support a hypothesis in which the long lifetime decay process is accounted within a single Tb^{3+} ions scenario for both series of nanorods. The results also indicate that the structural disorder, favoured by the presence of the water molecules in the structure, enhances the non-radiative recombination decay processes, while no evidence of terbium clustering influencing the decay processes has been found.

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References

- 1 W. Di, X. Wang and H. Zhao, Synthesis and characterization of $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ (Ln = La, Ce, Gd, Tb, Dy) Nanorods and nanowires, *J.Nanosci. Nanotechn.*, 2007, **7**, 3624-3628.
- 2 K. Mi, Y. Ni, Y. Xu, X. Ma and J.A. Hong, A simple mixed-solvothermal route for LaPO_4 nanorods: synthesis, characterization, affecting factors and PL properties of $\text{LaPO}_4\text{:Ce}^{3+}$, *J. Colloid and Interf. Sci.*, 2011, **356**, 490-495.
- 3 H. Lai, A. Bao, Y. Yang, Y. Tao and H. Yang, Selective synthesis and luminescence property of monazite- and hexagonal-type $\text{LaPO}_4\text{:Eu}$ nanocrystals, *CrystEngComm*, 2009, **11**, 1109-1113.
- 4 G. Bühler and C. Feldmann, Microwave-assisted synthesis of luminescent $\text{LaPO}_4\text{:Ce,Tb}$ nanocrystals in ionic liquids, *Angew. Chem. Intern. Edit.*, 2006, **45**, 4864-4867.
- 5 V. Pankratov, A.I. Popov, S.A. Chernov, A. Zharkouskaya and C. Feldmann, Mechanism for energy transfer processes between Ce^{3+} and Tb^{3+} in $\text{LaPO}_4\text{:Ce,Tb}$ nanocrystals by time-resolved luminescence, *Spectr. Phys. Stat. Sol. B-Basic Solid State Phys.*, 2010, **247**, 2252-2257.
- 6 M.T. Colomer, L. Zur, M. Ferrari, A.L. Ortiz, Structural-microstructural characterization and optical properties of $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 Nanorods Hydrothermally Synthesized with Microwaves, *Ceram. Intern.*, 2018, **44**, 11993-12001.
- 7 L. Ma, L.-M. Xu, W.-X. Chen, Z.-D. Xu, Microwave-assisted synthesis and characterization of $\text{LaPO}_4\text{:Re}$ (Re = Ce^{3+} , Eu^{3+} , Tb^{3+}), *Nanorods Mater. Lett.*, **63**, 1635-1637.
- 8 D.T. Lien, D.T.M. Huong, L.V. Vu, N.N. Long, Structure and photoluminescence characterization of Tb^{3+} -doped LaPO_4 nanorods prepared via the microwave-assisted method, *J. Lumin.*, 2015, **161**, 389-394.

- 9 G. Phaomei, R.S. Ningthoujam, W.R. Singh, N.S. Singh, M.N. Luwang, R. Tewari and R.K. Vatsa, Low temperature synthesis and luminiscence properties of re-dispersible Eu^{3+} doped LaPO_4 nanorods by ethylene glycol route, *Optical Mater.*, 2010, **32**, 616-622.
- 10 L. Yu, H. Song, Z. Liu, Yang, S. Lu, Z. Zheng, Remarkable improvement of brightness for the green emissions in Ce^{3+} and Tb^{3+} Co-activated LaPO_4 nanowires, *Solid State Commun.*, 2005, **134**, 753-757.
- 11 M. Ferhi, K. Horchani-Naifer, M. Férid, Hydrothermal synthesis and photoluminescence of the monophosphate $\text{LaPO}_4\text{:Eu}$ (5%), *J. Lumin.*, 2008, **128**, 1777-1782.
- 12 R.N. Bhargava, D. Gallagher, X. Hong, A. Nurmikko, Optical properties of manganese-doped nanocrystals of ZnS , *Phys. Review Lett.*, 1994, **72**, 416-419.
- 13 M.T. Colomer, A.L. Ortiz, Effect of Tb^{3+} Doping and self-generated pressure on the crystallographic/morphological features and thermal stability of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ single-crystal nanorods obtained by microwave-assisted hydrothermal synthesis, *Ceram. Intern.*, 2016, **42**, 18074-18086.
- 14 M.T. Colomer, J. Bartolomé, A.L. Ortiz, A. de Andrés, Raman characterization and photoluminescence properties of $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ phosphor nanorods prepared by microwave-assisted hydrothermal synthesis, *Ceram. Intern.*, 2017, **43**, 10840-10847.
- 15 D. Hou, X. Guo, C. Liu, T.-K. Sham, H. Liang, J. Gao, X. Sun, B. Zhang, F. Zhan, Y. Huan and Y. Tao, Hydrothermal synthesis, X-ray absorption and luminiscence properties of Tb^{3+} doped LaPO_4 , *J. Lumin.*, 2015, **165**, 23-29.
- 16 M.R. Rafiuddin, A.P. Grosvenor, A structural investigation of hydrous and anhydrous rare-earth phosphates, *Inor. Chem.*, 2016 55, 9685-9695.

- 17 S. Diaz-Moreno, S. Hayama, M. Amboage, A. Freeman, J. Sutter, G. Duller, The versatile X-ray absorption spectroscopy beamline at diamond light source, *J. Phys.: Conference Series*, 2009, **190**, I20; No article 012038.
- 18 S. Diaz-Moreno, M. Amboage, M. Basham, R. Boada, N. Bricknell, G. Cibir, T.M. Cobb, J. Filik, A. Freeman, K. Geraki, D. Gianolio, S. Hayama, K. Ignatyev, L. Keenan, I. Mikulska, J.F.W. Mosselmans, J. Mudd, S.A. Parry, The spectroscopy village at diamond light source, *J. Synchr. Rad.*, <https://doi.org/10.1107/S16005775180006173>.
- 19 P. Glatzel, U. Bergmann, High resolution 1s core hole X-ray spectroscopy in 3d transition metal complexes-electronic and structural information, *Coord. Chem. Rev.*, 2005, **249**, 65-95.
- 20 H. H. Johann, The production-aperture X-ray spectra with the help of concave crystals, *Zeitschrift für Physik*, 1931, **69**, 185-206.
- 21 R. Plackett, I. Horswell, E.N. Gimenez, J. Marchal, D. Omar, N. Tartoni, A. Merlin, Fast versatile readout system for medipix3, *J. Inst.*, 2013, 8, No article C01038.
- 22 D. E. Sayers and B. Bunker, in X-Ray Absorption: Principles, applications, techniques of EXAFS, SEXAFS, and XANES, ed. D. C. Koningsberger and R. Prins, Wiley, New York, chapter 6, 1988.
- 23 B. Ravel and M. Newville, Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchr. Rad.*, 2005, **12**, 537-541.
- 24 J. Chaboy, A. Marcelli, M.R. Ibarra, A. del Moral, Electronic instability in YMn₂ driven by Ni substitution: an X-ray absorption investigation, *Solid State Commun.*, 1994, **91**, 859-864.
- 25 J. Chaboy, J. García, A. Marcelli, M.F. Ruiz López, An experimental and theoretical study of multielectron excitations at the L₃ absorption edge in some rare earth alloys and their hydrides, *Chem. Phys. Lett.*, 1990, 174, 389-395.

- 26 J. Chaboy, T.A. Tyson, Relative cross sections for bound-state double-electron $LN_{4,5}$ -edge transitions, *Phys. Rev. B*, 1994, **49**, 5869-5875.
- 27 J. Chaboy, A. Marcelli, T.A. Tyson, Influence of double-electron transitions on the EXAFS L edges of rare-earth systems, *Phys. Rev. B*, 1994, **49**, 11652-11661.
- 27 J. Chaboy, T.A. Tyson and A. Marcelli, Relative cross sections for bound-state double-electron $LN_{4,5}$ -edge transitions of rare earths and non radioactive elements of the sixth row, *Prensas Universitarias de Zaragoza*, 1995.
- 28 J. Chaboy, J. Garcia, A. Marcelli, T.A. Tyson, Multielectron excitations at the L absorption edge of rare earths, *Jpn. J. Appl. Phys.*, 1993, **32** (Suppl. 32-2), 61-63.
- 29 J.E. Müller, Band-structure approach to the X-ray spectra of metals, *Acta Crystallograph. Sect. A*, 1984, **40**, C394-C394.
- 30 G. Materlik, B. Sonntag, M. Tausch, Experimental atom-to-solid L-level shifts for Ce, Sm, Gd, and Er, *Phys. Rev. Lett.*, 1983, **51**, 1300-1303.
- 31 J.I. Espeso, J.C. Gómez-Sal, J. Chaboy, Role of the electronic state of cerium in the magnetic properties of $CeNi_xPt_{1-x}$ compounds, *Phys. Rev. B*, 2001, **63**, No article 014416.
- 32 J. Chaboy, A. Marcelli, L. Bozukov, The influence of interstitial solutions (H, N) on the cerium electronic state in Ce-Fe intermetallic compounds: An x-ray absorption spectroscopy (XAS) study, *J. Phys.: Condensed Matter.*, 1995, **7**, 8197-8210.
- 33 J. Chaboy and C. Piquer, Modification of the magnetic properties of the $R_2Fe_{14}B$ series (R=rare earth) driven by hydrogen absorption, *Phys. Rev. B*, 2002, **66**, No article 104433.
- 34 Y. G. Choi, K. H. Kim, H. D. Park, Tb L3-edge x-ray absorption near-edge structure spectroscopic analysis of terbium-doped phosphor compounds for plasma display panel applications, *J. Mater. Res.*, 2002, **17**, 31-35.

- 35 Y. G. Choi, Covalence of chemical bonds and white-line intensity of an L3-edge X-ray absorption near-edge structure of rare earth elements embedded in glass, *Met. Mater. Int.*, 2009, **15**, 993-999.
- 36 M.M. Klak, G. Zatoryb, J. Wojcik, J. Misiewicz, P. Mascher and A. Podhorodecki, Mechanism of enhanced photoluminescence of Tb ions in hydrogenated silicon-rich silicon oxide films, *Thin Solid Films*, 2016, **611**, 62-67.
- 37 X. Wang, L. Qu, J. Zhang, X. Peng, M. Xiao, Surface-related emission in highly luminescent CdSe quantum dots, *Nano Letters*, 2003, **3**, 1103-1106.