**Structural-microstructural characterization and optical properties of
Eu³⁺, Tb³⁺-codoped LaPO₄·nH₂O and LaPO₄ nanorods
hydrothermally synthesized with microwaves**

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Abstract

Rhabdophane-type Eu³⁺, Tb³⁺-codoped LaPO₄·nH₂O single-crystal nanorods with the compositions La_{0.99999-x}Eu_xTb_{0.00001}PO₄·nH₂O (x=0–0.030), La_{0.99999-y}Tb_yEu_{0.00001}PO₄·nH₂O (y=0–0.010), and La_{0.99999-z}Tb_zEu_{0.00007}PO₄·nH₂O (z=0–0.012) were hydrothermally synthesized with microwaves. It is shown that the Eu³⁺, Tb³⁺ codoping does not affect the thermal stability of these nanorods, which is due to the formation of substitutional solid solutions with both Eu³⁺ and Tb³⁺ replacing La³⁺ in the crystal lattice. Moreover, it is also shown that monazite-type Eu³⁺, Tb³⁺-codoped LaPO₄ single-crystal nanorods can be obtained by calcining their rhabdophane-type Eu³⁺, Tb³⁺-codoped LaPO₄·(n,n',n'')H₂O counterparts at moderate temperature in air, and that they are thermally stable. It is also observed that, for the same Eu³⁺, Tb³⁺-

codoping content, the monazite-type $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 nanorods exhibit higher photoluminescent efficiency than the rhabdophane-type $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods, as it is expected. Moreover, it is found that the highest photoluminescence emission corresponds to the monazite-type $\text{La}_{0.96999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ nanorods for the $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ system. However, for those compositions energy transfer from Tb^{3+} to Eu^{3+} does not occur. In addition, for an efficient energy transfer to occur, a content of at least 1 mol.% Tb^{3+} is needed in all the studied materials.

Keywords: **A. Processing:** Microwave processing; Powders: Chemical preparation.

C. Properties: Optical properties. **E. Applications:** Functional applications.

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1. Introduction

There are great efforts put on the search for novel phosphor materials that can be used as white light-emitting diodes (W-LEDs), and in general in the field of integrated optics [1,2]. Typically, W-LEDs are fabricated by combining red, green, and blue tri-phosphor powders, which can be excited by near ultraviolet light [3]. Unfortunately, W-LEDs prepared from mixed phosphor matrices have some disadvantages, such as low luminescence, little color reproduction, and unstable ratio control, to name but a few. Instead, single phosphor matrices have potential application as white light-emitting sources due to their high luminescence efficiency and lower cost. Lanthanide cations, and particularly Tb^{3+} and Eu^{3+} , exhibit notable luminescent properties, and hence the lanthanide-containing compounds have great potential as phosphors [4]. An attractive host to entrap Tb^{3+} or Eu^{3+} cations is LaPO_4 because of the high melting temperature ($> 2000^\circ\text{C}$) [5], elevated chemical stability, and high light yields of the resulting doped compounds [6]. Eu^{3+} , Tb^{3+} -codoped phosphors can even be more appealing than the corresponding single-doped phosphors since energy transfer between Tb^{3+} and Eu^{3+} is expected to occur [7]. Surprisingly however, to the best of our knowledge, Eu^{3+} , Tb^{3+} -codoped LaPO_4 phosphors have seldom been prepared and, consequently, investigated. These phosphors with narrow emission bands then merit greater attention, especially if synthesized in the form of nanorods because their luminescent quantum efficiency and display resolution would be even greater due to marked shape-specific and to quantum-confinement effects [8].

In earlier works, $\text{La}_{0.96}\text{Eu}_{0.02}\text{Tb}_{0.02}\text{PO}_4$ [9], $\text{La}_{1-x-y}\text{Eu}_x\text{Tb}_y\text{PO}_4$ ($x=0-0.05$, and $y=0$ or 0.2) [10] and $\text{La}_{0.93}\text{Eu}_x\text{Tb}_y\text{PO}_4$ ($x=0, 0.07, 0.006, 0.011$, and 0.017 , and $y=0, 0.07, 0.064, 0.059$, and 0.053) [11] were prepared. $\text{La}_{0.96}\text{Eu}_{0.02}\text{Tb}_{0.02}\text{PO}_4$ was obtained by solid-state reaction, $\text{La}_{1-x-y}\text{Eu}_x\text{Tb}_y\text{PO}_4$ by microwave-assisted co-precipitation method, and $\text{La}_{0.93}\text{Eu}_x\text{Tb}_y\text{PO}_4$ by a microwave-assisted solvothermal route, finding that $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 are novel phosphors due to the occurrence of energy transfer from Tb^{3+} to Eu^{3+} . Those earlier studies of photoluminescence (PL) properties are very encouraging, but missed other type of important information. For example, it seems convenient to investigate the influence of the codoping (i) on structural and crystallographic aspects, and (ii) on the thermal stability of the as-synthesized products. In addition, it also seems necessary to conduct studies on compounds with a lower concentration of codoping cations, since earlier work on both $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ demonstrates the occurrence of quenching effects for Tb^{3+} concentrations below 5 mol.% [12].

With these premises in mind, in the present study we, have prepared by microwave-assisted hydrothermal synthesis and characterized structural and microstructurally both rhabdophane-type $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.03$), $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$ ($y=0-0.01$), and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n''\text{H}_2\text{O}$ ($z=0-0.012$) nanorods. We have also prepared monazite-type $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$, $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4$, and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4$ nanorods by calcination of the rhabdophane-type counterparts, which have been characterized as well. Finally, we have measured and compared the optical properties of those $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 nanorods, and determined the minimum Tb^{3+} doping content required to have an efficient energy transfer from Tb^{3+} to Eu^{3+} .

2. Experimental procedure

2.1. Microwave-assisted hydrothermal synthesis

A microwave oven (Milestone ETHOS 1, Sorisole, Italy) operating at 2450 MHz and equipped with sensors for both temperature and pressure control was used for the synthesis. The chemical reagents were of analytical grade and used without further purification, and the corresponding aqueous solutions were prepared with deionized water (with a resistivity of $>18 \text{ M}\Omega\cdot\text{cm}$). $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (99.9% trace metals basis; Merck, Germany), H_3PO_4 (85 wt.% concentration and 1.71 g/cm^3 density; Merck, Germany), $\text{C}_6\text{H}_9\text{O}_6\text{Eu}\cdot u\text{H}_2\text{O}$ (99.9% trace metals basis; Sigma-Aldrich, USA) and $\text{C}_6\text{H}_9\text{O}_6\text{Tb}\cdot n\text{H}_2\text{O}$ (99.9% trace metals basis; Sigma-Aldrich, USA) were used as starting materials. Stock solutions 0.50 M of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, 0.05 and 0.00001 M of $\text{C}_6\text{H}_9\text{O}_6\text{Eu}\cdot u\text{H}_2\text{O}$, and 0.05 and 0.00001 M of $\text{C}_6\text{H}_9\text{O}_6\text{Tb}\cdot v\text{H}_2\text{O}$ were prepared, and standardized by inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo Jarrell Ash spectrometer, Model Iris Advantage Duo, USA). The precision of the results, as mean relative standard deviation (RSD%) for five replicative measurements, were about 0.1 for ^{139}La , 0.4 for ^{151}Eu , and 0.3 for ^{159}Tb . Analytical results obtained for each element showed good agreement with the nominal compositions. The calibration was performed with standard solutions of appropriate concentrations (SCP Science, Canada).

For the synthesis of the $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.03$) nanorods, adequate proportions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{C}_6\text{H}_9\text{O}_6\text{Eu} \cdot u\text{H}_2\text{O}$, $\text{C}_6\text{H}_9\text{O}_6\text{Tb} \cdot v\text{H}_2\text{O}$, and H_3PO_4 were used, and deionized water was added filling the TFM microwave vessel (with 100 mL capacity) up to 40 vol.%. Once the $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{C}_6\text{H}_9\text{O}_6\text{Eu} \cdot u\text{H}_2\text{O}$, and $\text{C}_6\text{H}_9\text{O}_6\text{Tb} \cdot v\text{H}_2\text{O}$ reagents were dissolved, H_3PO_4 was added dropwise, immediately observing the formation of a white colloidal gel. This mixing was performed under continuous stirring at 50 °C. Then, the precursor solution was poured into the microwave vessel, and was heated in the microwave oven at 120 °C for 20 min using a heating rate of 5 °C/min. Next, the resulting product was centrifuged, filtered, and washed several times with deionized water, and then dried at 60 °C for 12 h. Finally, part of the resulting powder was calcined at 700 °C in air for 2 h using a heating rate of 5 °C/min, to thus obtain $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ nanorods. The dried and calcined powders were crushed using an agate mortar and pestle. The same procedure was followed for the synthesis and obtaining of the $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$, $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4$ ($y=0-0.01$), and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n''\text{H}_2\text{O}$ and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4$ ($z=0-0.012$) nanorods (see Table 1, 2, and 3 where the compositions prepared in this study are registered).

Family	Nominal Compositions
$\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$	$\text{La}_{0.99999}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$
	$\text{La}_{0.98999}\text{Eu}_{0.01}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$
	$\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$
	$\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$
$\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$	$\text{La}_{0.99999}\text{Tb}_{0.00001}\text{PO}_4$
	$\text{La}_{0.98999}\text{Eu}_{0.01}\text{Tb}_{0.00001}\text{PO}_4$
	$\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$
	$\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4$

Table 1. Nominal composition corresponding to the $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ families prepared in this study.

Family	Nominal Compositions
$\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$	$\text{La}_{0.99999}\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$
	$\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$
$\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4$	$\text{La}_{0.99999}\text{Eu}_{0.00001}\text{PO}_4$
	$\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$

Table 2. Nominal compositions corresponding to the $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4$ families prepared in this study.

Family	Nominal Compositions
$\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n\text{H}_2\text{O}$	$\text{La}_{0.99999}\text{Eu}_{0.000007}\text{PO}_4 \cdot n\text{H}_2\text{O}$
	$\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.000007}\text{PO}_4 \cdot n\text{H}_2\text{O}$
	$\text{La}_{0.98796}\text{Tb}_{0.012}\text{Eu}_{0.00007}\text{PO}_4 \cdot n\text{H}_2\text{O}$
$\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4$	$\text{La}_{0.99999}\text{Eu}_{0.000007}\text{PO}_4$
	$\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.000007}\text{PO}_4$
	$\text{La}_{0.98796}\text{Tb}_{0.012}\text{Eu}_{0.00007}\text{PO}_4$

Table 3. Nominal compositions corresponding to the $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4$ prepared in this study.

2.2. Characterization techniques

The $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$, $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$, $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$, $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4$, $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n\text{H}_2\text{O}$, and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4$ nanorods were selectively characterized using a wide battery of analytical techniques. In particular, the as-synthesized nanorods were analyzed by both ICP-OES (for major and minor element concentrations) and ICP-MS (for trace element concentrations) to determine their experimental concentrations. The samples were dissolved by acid digestion in an open polypropylene tube in a Digiprep graphite block digestion system (JR Model, SCP,

Science, Canada). The precision of the results, as mean relative standard deviation (RSD%) for five replicative measurements, were about 0.2 (ICP-OES) for ^{139}La , 0.4 (ICP-MS)-0.7 (ICP-OES) for ^{159}Tb , 1.4 (ICP-MS)-0.9 (ICP-OES) for ^{151}Eu , and 0.3 (ICP-OES) for ^{31}P . Analytical results obtained for each element showed good agreement with the nominal compositions. The calibration was performed with standard solutions of appropriate concentrations (SCP Science, Canada).

X-ray diffractometry (XRD; D8 Advance, Bruker AXS, Germany) was used to determine the crystalline phase composition (identified with the PDF2 database) and lattice parameters of the phases present (calculated using the Pawley method). X-ray thermo-diffractometry (XRTD; D8 Advance, Bruker AXS, Germany) was used to investigate the thermal stability in air in the temperature range 30–950 °C (3 °C/min heating rate) [13]. The XRTD studies were complemented with a thermal characterization study by differential thermal analysis (DTA; DTA7 Perkin Elmer Inc., USA) and thermogravimetric analysis (TGA; TGA7, Perkin Elmer Inc., USA) in air in the temperature range 25–950 °C (5 °C/min heating rate), to thus infer mass and structural change processes.

Fourier transform infrared (FTIR) spectra were recorded (FT-IR 1760X, Perkin Elmer Inc., USA) in the range 400–1300 cm^{-1} using the typical KBr pellet method. Contents of N and C were determined for as-prepared and calcined at 700°C for 2 h powders (LECO CHNS-932 elemental analyzer, USA).

Raman spectra were recorded (Renishaw spectrometer, UK) with an excitation wavelength of 514 nm produced by Ar^+ laser. The 200–1100 cm^{-1} spectral range was evaluated using 10 scans for each measurement. The samples were focused with a Leica optical

microscope with a 50x magnification objective lens. A sharp line of silicon at 520 cm^{-1} was taken as a reference in the Raman shift scale.

Scanning electron microscopy (SEM) observations were made (Hitachi S-4700 type I, Tokyo, Japan) at 20 keV using secondary electrons. Transmission electron microscopy (TEM) observations were also conducted (JEM-2100F, JEOL, Japan), at 200 keV.

Absolute photoluminescence quantum yields (internal quantum efficiency) of prepared nanorods were measured on Hamamatsu Quantaurus-QY C11347-11 (150 W Xenon light source, Horiba Jobin Yvon, USA) under excitation in the range from 300 to 470 nm (every 10 nm). The emission spectra of obtained nanorods have been registered under excitation with DPSS 532 nm laser (Horiba Jobin Yvon, USA).

Additionally, the PL characterization was performed by a Horiba Jobin Yvon Fluorog-3 spectrofluorimeter (USA) under 345 nm excitation wavelengths (450 W Xenon lamp, OFR). The optical emission of the samples is analyzed by a single grating monochromator coupled to a suitable Hamamatsu PMT R928 detector (USA).

3. Results and discussion

3.1. XRD and XRTD characterization

Fig. 1 shows, as an example, the XRD patterns of the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders in their as-prepared condition. The two XRD patterns can be ascribed to the rhabdophane phase (hexagonal symmetry, space group $P6_222$) of $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$, without presence of other phases. Interestingly, the two XRD

patterns look nearly identical, except for subtle phenomena of peak shifting towards higher diffraction angles and of peak broadening as the Eu^{3+} content in $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ increases. Given the single-phase nature of the powders, the peak shifting observed reflects the formation of solid substitutional solutions (i.e., Eu^{3+} solutes in the $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ host) whose lattice parameters (and therefore unit cell volume) decrease with increasing Eu^{3+} content. In addition, the peak broadening observed indicates reduction of the crystallite sizes.

Progressive replacement of La^{3+} by Eu^{3+} in the $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ lattice is facilitated by the fact that they are isovalent cations, and entails the reduction of the unit cell volume because the $\text{Eu}^{3+}(\text{IX})$ has smaller radius than $\text{La}^{3+}(\text{IX})$ (i.e., 1.120 vs 1.216 Å) [14]. Certainly, the lattice parameters (a and c) and unit cell volumes (V) of the rhabdophane structure measured here by the Pawley refinement of the XRD patterns confirms this expectation, with the following values: $a=7.130(6)$ Å, $c=6.521(6)$ Å, and $V=287.1(5)$ Å³ for the reference, undoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$; $a=7.123(8)$ Å, $c=6.512(7)$ Å, and $V=286.2(7)$ Å³ for $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$; and $a=7.119(8)$ Å, $c=6.509(7)$ Å, and $V=285.7(7)$ Å³ for $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$. A recent study [15] on $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ has demonstrated that the lattice parameters, and then unit cell volume, of the rhabdophane structure decrease linearly with increasing Tb^{3+} -doping content in the range $x=0-0.2$, so that this is the expectation for $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($y=0-0.10$) and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($z=0-0.012$) as well. Whichever the case, the present results agree with earlier independent observations [16] comparing the unit cells of LaPO_4 and $\text{La}_{0.98}\text{Eu}_{0.02}\text{PO}_4$ with monazite structure (monoclinic symmetry, space group $P2_1/c$).

Figure 1. XRD patterns of the as-synthesized $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders. The vertical lines across some selected peaks are to facilitate the observation of the peak shifting phenomenon with increasing Eu^{3+} content in

Fig. 2 compares, as an example, the two-dimensional intensity contours generated from the indexed XRTD patterns collected in-situ as a function of temperature for the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders in their as-prepared condition. In concordance with the XRD patterns, it can be observed that the compounds crystallize as rhabdophane phase, with the Eu^{3+} , Tb^{3+} codoping reducing the lattice parameters and unit cell volume (note the slight peak

shifting towards higher diffraction angles). With increasing temperature the XRD peaks shift in both cases toward lower diffraction angles, which is due to expected thermal expansion of the unit cells. It can also be seen in Fig. 2 that the lattice parameters changed more markedly at ~200 °C (note the abrupt peak shifting), which reflects the dehydration of the rhabdophane phase (i.e., $\text{LaPO}_4 \cdot n\text{H}_2\text{O} \rightarrow \text{LaPO}_4$, and $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O} \rightarrow \text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$). At ~715 °C the rhabdophane phase transforms into the monazite structure (note the disappearance of the rhabdophane peaks and the appearance of the monazite peaks). The resulting monazite structure has also smaller unit cell volume as the $\text{Eu}^{3+}, \text{Tb}^{3+}$ codoping content increases. Very interestingly, the temperatures for the dehydration of the rhabdophane phase and for the rhabdophane $\rightarrow$ monazite transformation are unaffected by the $\text{Eu}^{3+}, \text{Tb}^{3+}$ codoping. Eu^{3+} and Tb^{3+} do not condition the thermal stability of the $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ compounds because none of the two is the rate-limiting species for the overall ion diffusion/mobility since both Eu^{3+} and Tb^{3+} (i) have smaller ionic radii than La^{3+} and (ii) occupy substitutional positions in the crystal lattice. Lastly, there is greater peak broadening in $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ than in $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, thus suggesting that the $\text{Eu}^{3+}, \text{Tb}^{3+}$ codoping promotes the formation of smaller crystallites (apart from causing possible lattice microstrains). This has been observed earlier for Tb^{3+} -doped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 [15].

Figure 2. Two-dimensional intensity contours extracted from the XRTD patterns collected in-situ as a function of the temperature in the range 30–950 °C for the as-synthesized (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders. Peak indexing (i.e., Miller indices) is provided to facilitate the phase identification; R and M denote rhabdophane and monazite, respectively.

Fig. 3 shows, as an example, the XRD pattern of the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ powder obtained by calcination at 700 °C for 2 h in air. In entire concordance with the XRTD patterns in Fig. 2, this XRD pattern is ascribed to monazite phase, without presence of other phases. The lattice parameters and unit cell volume determined by the Pawley refinement of the XRD pattern are $a=6.8426(4)$ Å, $b=7.0787(4)$ Å, $c=6.5109(4)$ Å, $\beta=103.320(8)^\circ$, and $V=306.9(3)$ Å³ for $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$, while the corresponding values reported previously for the reference LaPO_4 monazite are $a=6.860(7)$ Å, $b=7.093(7)$ Å, $c=6.522(6)$ Å, $\beta=103.34(2)^\circ$, and $V=308.7(5)$ Å³ [15]. Therefore, the unit cell volume of the monazite structure also decreases with the $\text{Eu}^{3+}, \text{Tb}^{3+}$ codoping, thus evidencing that the substitutional solid solutions prepared with the microwave synthesis are preserved during the calcination. There is not earlier work, to the best of our knowledge, reporting such crystallographic data for $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 .

Figure 3. XRD pattern of the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ powder obtained by calcination at 700 °C for 2 h in air.

Fig. 4 shows the two-dimensional intensity contours generated from the indexed XRTD patterns collected in-situ as a function of temperature for the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ and $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4$ powders obtained by calcination at 700 °C for 2 h in air. Clearly, the monazite phase achieved with the calcination is thermally stable. In addition, as occurs for rhabdophane-type $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$, the unit cell volume of the monazite-type $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ also becomes smaller with increasing Eu^{3+} doping content (note the peak shifting towards higher diffraction angles).

Figure 4. Two-dimensional intensity contours extracted from the XRTD patterns collected in-situ as a function of the temperature in the range 30–950 °C for the (a) $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ and (b) $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4$ powders obtained by calcination at 700 °C for 2 h in air. Peak indexing (i.e., Miller indices) is provided to facilitate the phase identification; M denotes monazite.

The observations described above for $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ are also qualitatively valid for $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$, $\text{La}_{0.99999-y}\text{Tb}_y\text{Eu}_{0.00001}\text{PO}_4$, $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n''\text{H}_2\text{O}$, and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4$. This has already been validated for $\text{La}_{1-y}\text{Tb}_y\text{PO}_4 \cdot n'\text{H}_2\text{O}$ and $\text{La}_{1-y}\text{Tb}_y\text{PO}_4$ in earlier work [15], and 0.001 mol.% or less of Eu^{3+} does not make any difference. To illustrate this latter, Fig. 5 shows the XRD pattern of the $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ powder obtained by calcination at 700 °C for 2 h in air. This XRD pattern is ascribed to the monazite phase, with the lattice parameters and unit cell volume determined by the Pawley refinement being $a=6.856(12)$ Å, $b=7.086(12)$ Å, $c=6.519(12)$ Å, $\beta=103.36(2)^\circ$, and $V=308.1(9)$ Å³. Thus, $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ has smaller unit cell than pure LaPO_4 , as anticipated.

Figure 5. XRD pattern of the $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ powder obtained by calcination at 700 °C for 2 h in air.

3.2. FTIR and TG-DTA characterization

Fig. 6 shows the FTIR spectra of the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder in both its as-prepared and calcined (700 °C for 2 h) conditions. Only the three fundamental vibrational modes (i.e., ν_1 , ν_3 , and ν_4) are observed for $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$, as expected for the site symmetry C_2 of the tetrahedral PO_4^{3-} anions in the rhabdophane structure. Thus, the P–O symmetric stretching (i.e., mode ν_1) is detected at $\sim 964\text{ cm}^{-1}$, the P–O asymmetric stretching

(i.e., mode ν_3) at $\sim 1052\text{ cm}^{-1}$, and the O–P–O asymmetric bending vibrations (i.e., mode ν_4) at $\sim 543, 570, \text{ and } 616\text{ cm}^{-1}$. Thus, the FTIR, XRD, and XRTD analyses are entirely consistent. The FTIR spectrum of the calcined $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ is different, as expected for the monazite structure [17-21]. In particular, there are (i) four bands at $\sim 542, 565, 580, \text{ and } 614\text{ cm}^{-1}$ in the vibration region ν_4 associated to the phosphate groups and (ii) five bands at $\sim 1093, 1061, 1026, 992, \text{ and } 954\text{ cm}^{-1}$ in the region ν_3 , and however there are no bands at $\sim 3470, 3180, 1620, \text{ and } 1384\text{ cm}^{-1}$ associated to water and nitrates [22-24]. Thus, the FTIR, XRD, and XRTD analyses are again entirely consistent.

The FTIR spectra collected for the rest of rhabdophane and monazite compounds are similar, and therefore not shown for the sake of brevity. However, increasing shifting to higher wavenumbers was observed in the FTIR bands as the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content in both $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 increased, which is consistent with the reduction of the unit cell volumes. The same trend has been observed independently for Eu^{3+} -doped LaPO_4 [25].

Figure 6. FTIR spectra of the as-synthesized $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder and of the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ powder obtained by calcination of the former at 700 °C for 2 h in air.

Fig. 7 shows the TG-DTA curves measured for the $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder in its as-prepared condition. The total weight loss is ~8.6 wt.% when calcined up to 950 °C. The weight loss in the temperature range ~25–150 °C (accompanied by an endothermic peak at ~67 °C) is due to desorption of physisorbed water. The weight loss in the range ~150–224 °C (accompanied by an endothermic peak at ~208 °C) is due to dehydration of the rhabdophane structure [24,26], which is consistent with the XRTD analyses. The weight loss in the range

~224–400 °C is essentially due to removal of the residual acetates and nitrates (from the precursors) which is associated to an exothermic peak centred at 277°C [5,23,27,28]. Lastly, the moderate weight loss in the range ~400–950 °C is due to oxidation of residual organics (also from the precursors). Note that in the DTA curve there is an exothermic peak at ~744 °C, which is in good agreement with the XRD and XRTD analyses and is ascribed to the rhabdophane → monazite transformation. The TG-DTA curves measured for the rest of rhabdophane and monazite compounds are similar, and therefore not shown for the sake of brevity.

Figure 7. TG-DTA curves of the as-synthesized $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder.

C and N contents were also measured for all the powders. The rhabdophane-type powders contain $\sim 0.09\text{--}0.11 \pm 0.05$ and $0.87\text{--}0.91 \pm 0.05$ wt.% C and N, respectively. The monazite-type powders contain however only $\sim 0.04\text{--}0.06 \pm 0.05$ and $\sim 0.05\text{--}0.07 \pm 0.05$ wt.% C and N,

respectively, which is due to the calcination at 700 °C for 2 h removing acetates and nitrates from the precursor used in the synthesis. Thus, the chemical analyses are consistent with the FTIR and TG-DTA analyses.

3.3. Raman characterization

Fig. 8 shows the Raman spectra of rhabdophane-type $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and of monazite-type LaPO_4 , $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$, and $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4$. $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ exhibits Raman bands at $\sim 220, 377, 411, 465, 541, 573, 625, 974, 1027, 1047$, and 1086 cm^{-1} . In this list, the 2nd, 3rd, and 4th bands are due to the PO_4 -bending ν_2 , the 5th, 6th, and 7th bands to PO_4 -bending ν_4 , the 8th band to the PO_4 -symmetric stretching ν_1 , and the 9th, 10th and 11th bands to the PO_4 -asymmetric stretching ν_3 . Lower frequency bands are due to normal modes associated mainly to the heavier ions (La^{3+} , Eu^{3+} , and Tb^{3+}) and to lattice vibrations [29-31]. LaPO_4 exhibits a greater number of Raman bands due to the symmetry loss (i.e., hexagonal $\rightarrow$ monoclinic), located at $\sim 214, 273, 393, 412, 463, 534, 568, 589, 616, 965, 988, 1022, 1053$, and 1070 cm^{-1} . In this list, 3rd, 4th and 5th bands are due to the PO_4 -bending ν_2 , the 6th, 7th, 8th, and 9th bands to PO_4 -bending ν_4 , the 10th and 11th bands to the PO_4 -symmetric stretching ν_1 , and the 12th, 13th, and 14th bands to the PO_4 -asymmetric stretching ν_3 . The Raman bands of LaPO_4 are better defined (i.e., the peaks have smaller width) than those of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$.

An interesting observation in Fig. 8 is that the Raman peaks shift to higher frequencies (the frequency of the most intense peak of each composition is indicated in Fig. 8), and slight broadened, with increasing $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content in LaPO_4 . These phenomena were also observed for $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ systems (not shown for the sake of brevity), and is

consistent with earlier independent observations on $\text{La}_{1-x}\text{Eu}_x\text{PO}_4$ [25]. The band shifting is due to the decrease of the unit-cell volume, and then bond lengths, whereas the slight band broadening is due to lattice disordering.

Figure 8. Raman spectra of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, LaPO_4 , and $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ ($x=0.02$ and 0.03) powders.

3.4. Electron microscopy characterization

Fig. 9 shows representative FEG-SEM and TEM images of the $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder in its as-prepared condition. The nanorod morphology is evident, with the individual nanorods having a high shape and size homogeneity. This is because the rapid, homogenous, and volumetric microwave-assisted heating promotes a wholesale nucleation of uniform seeds throughout the entire bulk of the solution and their fast growth into crystals with narrow size distributions and high morphological uniformity [32]. Due to the uniform self-assembly of axially aligned nanorods, the powder particles exhibit nonetheless a bundle-like morphology at the macroscopic scale, which maximizes the entropy by minimizing the excluded volume per block in the array [33]. This nanorod proneness to undergo agglomeration is not a surprise when the van der Waals attractive forces predominate over the electrostatic repulsive forces, which is the typical scenario in this type of particles [5].

Figure 9. Representative (a) FE-SEM and (b) TEM images of the as-synthesized $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder.

Fig. 10 shows representative TEM images of the as-synthesized $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4 \cdot n'\text{H}_2\text{O}$ and calcined $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ powders. It is worthy to note that the calcination does not destroy the nanorod morphology, although, logically, the nanorods shrink. This observation is also applicable to other $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping contents (Fig. 11). Thus, it is feasible to obtain monazite-type for $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 nanorods by calcination of the corresponding rhabdophane-type $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot (n, n', n'')\text{H}_2\text{O}$ nanorods.

Figure 10. Representative TEM images of the (a) as-synthesized $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder and (b) $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ powder obtained by calcination of the former at 700 °C for 2 h in air

Figure 11. Representative TEM images of the (a) $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ and (b) $\text{La}_{0.987993}\text{Tb}_{0.012}\text{Eu}_{0.000007}\text{PO}_4$.

3.5. Optical properties

Fig. 12 shows the emission spectra of the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$, $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$, and $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4$ powders under excitation at 532 nm and at room temperature. Clearly, there are sharp emission peaks attributable to the $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2,3,4}$ transitions of Eu^{3+} . However, the band due to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition is strictly forbidden according to the Judd-Ofelt theory [34,35], but it is observed for some Eu^{3+} doped materials. This transition demonstrates that Eu^{3+} ion occupies a site with C_{nv} , C_s , C_n centers [36]. The probability of the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition is generally quite weak due to its nature. Furthermore, for the systems with lower than C_2 symmetry, this transition may be allowed [37]. The presence of

this strongly forbidden transition indicates that Eu^{3+} ions occupy a low symmetry site without an inversion center.

The intensity of the emission peaks is higher for the compounds with monazite structure for a given composition, as it is expected due in part to the higher crystallinity degree induced by calcination. In addition, the presence of water in rhabdophane-type $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods, that can enhance non-radiative recombination, must be also taken into account for explaining the highest emission peaks for monazite nanorods. Moreover, the intensity of the emission peaks is the highest for Eu^{3+} -doping content equal to 2 mol.%. Thus, the monazite-type $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ nanorods are those maximizing the emission intensity. The measured internal quantum efficiency for the monazite-type $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ nanorods is about 7.6% (under excitation at 400 nm), showing the best results among the obtained nanorods.

Fig. 12. PL spectra (measured at room temperature under 532 nm excitation) for rhabdophane-type $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder and for the monazite-type $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$, and $\text{La}_{0.96999}\text{Eu}_{0.03}\text{Tb}_{0.00001}\text{PO}_4$ powders.

1. Fig. 13 shows the emission spectra of the $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ and $\text{La}_{0.987993}\text{Tb}_{0.012}\text{Eu}_{0.000007}\text{PO}_4$ nanorods under excitation at 345 nm and at room temperature. Emission peaks of both Tb^{3+} ($^5\text{D}_4 \rightarrow ^7\text{F}_{6,5,4}$ transitions) and Eu^{3+} ($^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2,3}$ transitions) are observed. In addition, it can be seen from the spectrum of $\text{La}_{0.987993}\text{Tb}_{0.012}\text{Eu}_{0.000007}\text{PO}_4$ that the intensity of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition increases as Tb^{3+} content increases and Eu^{3+} content

decreases, which confirms both the occurrence and efficiency of the energy transfer from Tb^{3+} to Eu^{3+} . This phenomenon has been reported earlier for $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 , but for larger Tb^{3+} and Eu^{3+} contents [11]. Emission peaks from the Tb^{3+} transitions were not observed for either $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ or $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ compounds, since the Tb^{3+} concentration is extremely low. In addition, for an efficient energy transfer to occur a minimum content of 1 mol.% Tb^{3+} is needed. According to Oliveira et al. [11] the presence of the emission peaks of both Tb^{3+} and Eu^{3+} ions, that are visible under excitation at 394, 376, and 255 nm (345 nm in this study), confirms the energy transfer from Tb^{3+} to Eu^{3+} . According to those authors the energy transfer process from Tb^{3+} to Eu^{3+} ions occurs from the ground state of terbium $4f^8$ ($^7\text{F}_6$) to the excited state $^5\text{D}_3$ upon ultraviolet light irradiation. Subsequently, the electron decays to the lower-localized terbium excited state $^5\text{D}_4$ via multiphonon relaxation. Finally, the electron returns to the ground state, generating the terbium emissions ($^5\text{D}_4 \rightarrow ^7\text{F}_{6,5,4}$) or transfers this energy to excited energy levels of Eu^{3+} by cross-relaxation followed by the relaxation to the emissive $^5\text{D}_0$ (Eu^{3+}) level.

Fig. 13. PL spectrum (measured at room temperature under 345 nm excitation) for the monazite-type $\text{La}_{0.98999}\text{Tb}_{0.01}\text{Eu}_{0.00001}\text{PO}_4$ and $\text{La}_{0.987993}\text{Tb}_{0.012}\text{Eu}_{0.000007}\text{PO}_4$ nanorods.

5. Conclusions

We have prepared by microwave-assisted hydrothermal synthesis $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods (i.e., $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods ($x=0-0.03$), $\text{La}_{0.99999-y}\text{Eu}_{0.00001}\text{Tb}_y\text{PO}_4 \cdot n'\text{H}_2\text{O}$ ($y=0-0.01$), and $\text{La}_{0.99999-z}\text{Tb}_z\text{Eu}_{0.000007}\text{PO}_4 \cdot n''\text{H}_2\text{O}$ ($z=0-0.012$), and also have $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 nanorods by calcination of the formers at 700 °C for 2 h in air. Both the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 nanorods have been characterized in detail using a wide battery of analytical techniques (namely, XRD, XRTD, FTIR, TG-DTA,

Raman spectroscopy, SEM, and TEM), which allowed to investigate the dependence on the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content of structural-microstructural features and of the thermal stability. The optical properties of the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 nanorods have also been measured. The experimental results allow the following conclusions to be drawn:

2. Microwave-assisted hydrothermal synthesis produces high-quality $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ single-crystal nanorods with rhabdophane structure.
3. $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping results in the formation of solid solutions with both Eu^{3+} and Tb^{3+} partially substituting to La^{3+} in the $\text{LaPO}_4 \cdot (n, n', n'')\text{H}_2\text{O}$ crystal lattices. These solid solutions have smaller lattice parameters, and therefore unit cell volume with increasing $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content, which is due to the smaller cationic size of Eu^{3+} and Tb^{3+} relative to La^{3+} .
4. $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content does not affect the thermal stability of the rhabdophane-type nanorods, which is due to the substitutional nature of these solid solutions with reduced unit cell volumes.
5. $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 single-crystal nanorods with monazite structure can be obtained by calcination of the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot (n, n', n'')\text{H}_2\text{O}$ single-crystal nanorods at appropriate conditions. $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 is also a substitutional solid solution, whose unit cell volume decreases progressively with increasing $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content. Unlike the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped $\text{LaPO}_4 \cdot (n, n', n'')\text{H}_2\text{O}$ nanorods, the $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoped LaPO_4 nanorods are thermally stable.
6. The presence of the strongly forbidden transition $^5\text{D}_0 \rightarrow ^7\text{F}_0$ indicates that Eu^{3+} ions occupy a low symmetry site in the monazite without an inversion center.
7. For the same $\text{Eu}^{3+}, \text{Tb}^{3+}$ -codoping content the monazite-type nanorods have higher photoluminescent efficiency than the rhabdophane-type nanorods. Moreover, the highest

photoluminescence emission corresponds to the $\text{La}_{0.97999}\text{Eu}_{0.02}\text{Tb}_{0.00001}\text{PO}_4$ nanorods. Furthermore, in $\text{La}_{0.99999-x}\text{Eu}_x\text{Tb}_{0.00001}\text{PO}_4$ energy transfer from Tb^{3+} to Eu^{3+} does not occur, while for an efficient energy transfer to occur in the codoped systems a minimum content of 1 mol.% Tb^{3+} is needed.

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