Effect of Tb³⁺ doping and Self-generated Pressure on the Crystallographic/Morphological Features and Thermal Stability of LaPO₄·nH₂O Single-Crystal Nanorods Obtained by Microwave-Assisted Hydrothermal Synthesis

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Abstract

The effect of Tb³⁺-doping content (in the range 0–20 mol.%) and autogeneous/self-generated pressure (in the range 2.3–3.4±0.1 bar) on the crystallographic/morphological features and thermal stability of single-crystal nanorods of LaPO₄·nH₂O obtained by a simple and fast microwave-assisted hydrothermal synthesis was investigated. It is shown that high-quality (that is, well-shaped and linear/planar defect free) rhabdophane-type single-crystal La_{1-x}Tb_xPO₄·nH₂O ($x=0-0.20$) nanorods, with a high morphological uniformity, are obtained in all cases. In addition, it is shown that the Tb³⁺ solutes are incorporated into the LaPO₄·nH₂O host, forming substitutional solid solutions (*i.e.*, partial substitution of La³⁺ by Tb³⁺) with progressively smaller unit-cell volume but with identical thermal stability. Morphologically Tb³⁺ doping however results in the formation of nanorods with lower aspect ratio, and in particular in nanorods that are much shorter but essentially equally thick. With respect to the self-generated pressure during the microwave synthesis, it is shown that its increase does not affect to crystallographic aspects, but however results again in nanorods with lower aspect ratio. It is also demonstrated that monazite-type single-crystal La_{1-x}Tb_xPO₄ nanorods can be obtained by calcining their rhabdophane-type La_{1-x}Tb_xPO₄·nH₂O counterparts at ~700 °C in air, with a higher Tb³⁺-doping content and self-generated pressure leading as well to lower aspect-ratio calcined nanorods. Consequently, in the present study important guidelines have been identified for the controlled synthesis of functional La_{1-x}Tb_xPO₄·nH₂O nanorods with tailored morphology.

Keywords: Lanthanum orthophosphate; single-crystal nanorods; microwave synthesis; rare-earth doping.

1. Introduction

One-dimensional (1D) nanostructures such as nanorods, nanotubes, and nanowires are currently being the focus of extensive research, mainly because their unique set of properties with respect to their bulk counterparts make them to be technologically very attractive for functional applications as interesting as nanoscale sensors, generators, and actuators, photonic, (opto)electronic, and magnetic nanodevices, advanced catalysis, and energy conversion and storage, to name but a few. In addition, from the scientific point of view the shape anisotropy of the 1D nanostructures provides an ideal model system to investigate the dependence of the electronic transport, optical, and mechanical properties on the size confinement and dimensionality.^{1,2}

According to the open literature, lanthanide cations such as Tb^{3+} , Eu^{3+} , and Ce^{3+} offer outstanding optical, magnetic, and bio-affinity properties, and not surprisingly are being widely used for example as up conversion materials, catalysts, and fluorescence labels for biological detection.³⁻⁵ Also, the optical properties of lanthanide-doped materials are normally characterized by narrow emissions and large stokes shifts, and are therefore excellent phosphors.⁶ Interestingly, if fabricated in the form of nanorods, their luminescent quantum efficiency and display resolution is further enhanced as a result of both their marked shape-specific and quantum-confinement effects.⁷ Among various possible hosts for lanthanide dopants, LaPO_4 is noteworthy due to the high melting temperature,⁸ elevated chemical stability, and high light yields of the resulting doped materials.⁹

Several methods are nowadays available for the synthesis of rhabdophane-type undoped and doped 1D $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (*i.e.*, nanorods and nanowires), namely aqueous sol-gel,¹⁰⁻¹² aqueous precipitation,^{13,14} mechanical milling,^{15,16} and solvothermal¹⁷ and hydrothermal treatments.¹⁸⁻²¹ Nonetheless, these synthesis methods have certain drawbacks, as for example that they involve long times and/or multiple step reactions, require a precise pH control, and need stabilizing or chelating agents. This underscores the need of exploring and developing alternative methods for the preparation of high-quality nanorods of undoped and Tb^{3+} -doped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, such as for example the microwave-assisted hydrothermal synthesis. This is because the hydrothermal synthesis is a low-temperature, soft chemical route particularly suitable for obtaining nanoparticles, especially when combined with microwave radiation which offers rapid, selective, and volumetric heatings, highly-desirable attributes as well for the synthesis of inorganic nanocrystals.^{22,23,24} Indeed, earlier studies

have confirmed the feasibility of the microwave-assisted synthesis of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and LaPO_4 nanorods doped with different rare earth.²⁵⁻³¹ However, within that set of studies, only those by Ma *et al.*³⁰ and by Lien *et al.*³¹ have reported the microwave-assisted synthesis of Tb^{3+} -doped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods with hexagonal structure (*i.e.*, rhabdophane phase). In addition, these two studies are mainly focused on the photoluminescence properties of the resulting materials, and miss other type of important information such as for example the dependence of the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ lattice parameters on the Tb^{3+} -doping content, the evolution of the rhabdophane phase as a function of the calcination temperature, and the influence of the self-generated pressure during the synthesis on the features of the resulting products.

With these premises in mind, in the present study we have investigated for the first time, to the best of our knowledge, these three pending questions on $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods prepared by microwave-assisted hydrothermal synthesis in a closed vessel, whose use has the advantages of enabling to monitor the temperature and pressure with the help of a thermocouple and a pressure sensor inserted in its interior. The crystallographic study of the Tb^{3+} -content effect has been conducted on both $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ with varied concentrations of Tb^{3+} in the range $x=0-0.20$. The investigation of the self-generated pressure influence, which is crucial for protocoling this type of synthesis, has been performed via modification of the autogeneous pressure in the range $2.3-3.4 \pm 0.1$ bar during the synthesis, achieved by filling the microwave vessel up to different volumes in the range 40–70%. Finally, the effect of Tb^{3+} content on the thermal stability of the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods has been assessed with *in-situ* experiments as a function of the temperature, on nanorods without and with high-doping content. The set of the three studies involved the microwave synthesis tasks under different conditions, followed by the exhaustive characterization of the resulting powders using a wide battery of analytical techniques. The details of the experiments and the major findings are described next.

2. Experimental

2.1. Synthesis

A microwave oven (Milestone ETHOS 1, Sorisole, Italy) operating at 2450 MHz and capable of programming and adjusting the most important reaction parameters (*i.e.*, temperature, pressure, and time) was used for the synthesis. This multimode instrument

consists of a built-in magnetic stirrer, automatic temperature and pressure control for direct monitoring of vessel content, and software that enables on-line temperature/pressure control by regulation of the microwave power output. The microwave oven is equipped with two magnetrons. Installed power is 1600 W (800 W x 2), and delivered power is 1500 W in 1 W increments. The magnetrons work in conjunction with a premixing chamber in the rear of the cavity where the output of the two magnetrons is combined, and a pyramid-shaped rotating microwave diffuser which ensures homogeneous microwave distribution throughout the entire cavity, preventing both localized hot and cold spots. The reactions were carried out in sealed vessels (100 mL capacity) made of high-purity TFM (a PTFE polymer) and lined with safety shields made of a new, high-performance polymer.

All chemical reagents were of analytical grade and used as received without further purification. All aqueous solutions were prepared with deionized water with a resistivity of $>18\text{ M}\Omega\text{ cm}$, produced by a Milli-Q Plus pure water generating system from Millipore (Bedford, MA, USA). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% trace metals basis; Merck, Darmstadt, Germany), H_3PO_4 (85 wt.% concentration and 1.71 g/cm^3 density; Merck, Darmstadt, Germany) and $\text{C}_6\text{H}_9\text{O}_6\text{Tb} \cdot x\text{H}_2\text{O}$ (99.9% trace metals basis; Sigma-Aldrich, Saint Louis, USA) were used as starting materials. Stock solutions $\approx 0.50\text{ M}$ of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\approx 0.05\text{ M}$ of $\text{C}_6\text{H}_9\text{O}_6\text{Tb} \cdot x\text{H}_2\text{O}$ were prepared, and standardized via total reflection X-ray fluorescence (TXRF) by using a spectrometer (TXRF S2 PicoFox, Bruker, Berlin, Germany).

For the synthesis of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods, 10 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and H_3PO_4 at a molar ratio of 0.40 were used, and different quantities of milli Q water were added in such a way that the total volume of the microwave vessel was eventually filled up to 40, 50, 60 or 70% to intentionally achieve different autogeneous pressures during the reaction; the self-generated pressure was monitored by a pressure sensor. Once the 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 $50\text{ }^\circ\text{C}$. Then, the precursor solution was poured into a microwave vessel, and was heated in the microwave oven at $120\text{ }^\circ\text{C}$ for 20 min using a heating rate of $5\text{ }^\circ\text{C/min}$. Next, the resulting product was first centrifuged, filtered, and washed several times with milli Q water, and then dried at $60\text{ }^\circ\text{C}$ for 12 h. Finally, part of the powders was also calcined at $700\text{ }^\circ\text{C}$ in air for 2 h using a heating rate of $5\text{ }^\circ\text{C/min}$. The dried materials were crushed using an agate mortar and pestle. The same procedure was followed for the synthesis of Tb^{3+} -doped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, in which case $\text{C}_6\text{H}_9\text{O}_6\text{Tb} \cdot x\text{H}_2\text{O}$ was also incorporated to the solutions in the appropriate amounts.

2.2. Characterization

The as-synthesized undoped and Tb^{3+} -doped $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ powders were investigated using a wide battery of characterization techniques, as described next. In particular, X-ray diffraction (XRD) patterns were collected (D8 Advance, Bruker AXS, Karlsruhe, Germany) at room temperature in a zero-background holder using $\text{CuK}\alpha_1$ incident radiation ($\lambda = 1.5406 \text{ \AA}$) in the step-scanning mode over the angular range 10° – 70° 2θ with step width of 0.02° 2θ and counting time of 3 s per step. Phase identification was performed with the aid of the PDF2 database, and the lattice parameters of the phases present were calculated using the Pawley method. Additionally, X-ray thermo-diffraction (XRTD) patterns were also collected using a high-resolution diffractometer (D8 Advance, Bruker AXS, Karlsruhe, Germany) equipped with a linear ultra-fast detector and with a micro-furnace high-temperature chamber.³² The XRTD patterns were acquired *in-situ* in the temperature range 30 – 950°C with a temperature step of 3°C , heating ramp of 3°C/s , and delay time of 2 s, and the acquisition was done using $\text{CuK}\alpha_1$ incident radiation and with the detector operating in snapshot mode (fixed 2θ mode) for 60 s with its window being opened at $11^\circ 2\theta$ to register simultaneously the angular range 21 – $32^\circ 2\theta$. The XRTD patterns were interpreted to elucidate the thermal stability of the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0$ or 0.15) nanorods.

Fourier transform infrared (FTIR) spectra were recorded (FT-IR 1760X, Perkin Elmer Inc., Waltham, MA, USA) in the range 400 – 4000 cm^{-1} using the typical KBr pellet method. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves were acquired (DTA7 and TGA7, respectively, Perkin Elmer Inc., Waltham, MA, USA) in air in the temperature range 25 – 900°C under a heating rate of 5°C/min , and were used to infer mass and structural change processes. Contents of N and C were determined using a LECO CHNS-932 elemental analyzer, St. Joseph, MI, USA).

Field-emission scanning electron microscopy (FE-SEM) observations were made (Hitachi S-4700 type I, Tokyo, Japan) at 20 keV using secondary electrons. Transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM) observations were also conducted (JEM-2100F, JEOL, Tokyo, Japan) at 200 keV, and were complemented with the collection of selected area electron diffraction (SAED) patterns. The image processing was done using the ImageJ 1.45 software (Wayne Rasband, NIH, Bethesda, Maryland, USA), utilizing the standard diffraction lines of hexagonal $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (PDF card

00-046-1439) and monoclinic LaPO_4 (PDF card 01-083-0651) for the interpretation of the HREM images. The average dimensions of nanorods were determined by quantitative image analysis of FE-SEM and TEM micrographs: low-magnification images for the determination of the nanorod lengths and high-magnification ones for the determination of the nanorod diameters, using in the calculations at least 200 different, well-resolved nanorods.

3. Results and Discussion

3.1. Self-generated pressure

As mentioned above, with the microwave system employed in the present study it was possible to monitor and control the temperature thanks to a shielded thermocouple inserted directly into the vessel, while the self-generated pressure was measured with a pressure transducer sensor connected to the vessel and was continuously recorded as a function of time during each experiment synthesis as shown by way of example in Fig. 1 for the case of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$. As can be observed in Figs. 1 and 2, the self-generated pressure during the synthesis depends on the extent of water filling the microwave vessel. In particular, the maximum pressure reached was 2.3 ± 0.1 , 2.5 ± 0.1 , 3.0 ± 0.1 , and 3.4 ± 0.1 bar for filling volumes of 40, 50, 60, and 70%, respectively (Fig. 2), whereof it is inferred that an exponential dependence (or linear in first approximation) exists between both magnitudes at least for the water filling volumes used here. It is also convenient to mention that both the profiles and maximum values of the self-generated pressures were experimentally observed to be unaffected by the Tb^{3+} doping content.

Figure 1. Evolution of the autogenous pressure during the synthesis of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ using microwave vessel filling volumes of 40, 50, 60, and 70%.

Figure 2. Dependence of the self-generated pressure (maximum value achieved) during the synthesis of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ on the extent of water filling of the microwave vessel.

3.2. XRD and XRTD characterization

Fig. 3a and b show the XRD patterns of the as-prepared $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.20$) powders synthesized at 2.3 ± 0.1 bar self-generated pressure. There are various interesting features in this figure. First, the XRD patterns can all be ascribed to the rhabdophane phase (hexagonal symmetry, space group $P6_222$) of $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ according to the standard PDF card of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (JCPDS 46-1439); no diffraction peaks from $\text{La}(\text{PO}_3)_3$, which could have existed as a second phase, or Tb-rich phases, are observed. Second, there is an increasing peak shifting towards higher 2θ degrees as the Tb^{3+} content in $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ increases, which reflects the shrinkage of the unit cell. This observation and the absence of Tb-rich phases or amorphous phases indicate the formation of substitutional solid solutions with Tb^{3+} solutes in the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ host (*i.e.*, partial substitution of La^{3+} by Tb^{3+}). The same conclusion was reached by XRD for the powders of $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.20$) synthesized at 3.4 ± 0.1 bar (not shown), thus covering the entire range of self-generated pressures investigated here.

Figure 3(a) XRD patterns of the as-prepared $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.2$) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure), and (b) detailed comparison of the 102 peak position (normalized to the same peak intensity).

As an example, note in Fig. 4 (a and b) that the comparison of the XRD patterns of both $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ synthesized at 2.3 ± 0.1 and 3.4 ± 0.1 bar self-generated pressures reveals no differences. Thus, it can be concluded that the self-generated pressure during the synthesis does not condition the formation of these substitutional solid solutions.

Figure 4. Indexed XRD patterns of the as-prepared (A) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (B) $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized using microwave vessel filling volumes of 40 and 70%, respectively (*i.e.*, 2.3 ± 0.1 and 3.4 ± 0.1 bar self-generated pressures).

Progressive replacement of La^{3+} by Tb^{3+} is favored by the fact that both cations have the same valence (so oxygen vacancies are not generated), which must come accompanied by the reduction of the unit cell volume because the radius of $\text{Tb}^{3+}(\text{IX})$ is smaller than that of $\text{La}^{3+}(\text{IX})$ (*i.e.*, 1.095 vs. 1.216 Å).³³ The lattice parameters and unit cell volumes determined

by the Pawley refinement of the XRD patterns are shown in Fig. 5, whereof it is confirmed that the lattice parameters a and c of the rhabdophane phase decrease both linearly, and so does too the unit cell volume, with increasing Tb^{3+} -doping content, at least within the composition range investigated in the present study. It should be mentioned that these results are in good concordance with earlier observations by Lien *et al.*³¹ on nanorods of similar compositions, although they did not provide crystallographic data as however has been done here.

Figure 5. Lattice parameters and unit cell volume of the rhabdophane-type as-prepared $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.2$) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure).

Fig. 6 a and b shows the two-dimensional intensity contours generated from the indexed XRTD patterns collected *in-situ* as a function of temperature for the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized at 2.3 ± 0.1 bar self-generated pressure. These two powders cover the scenarios of no-doping and high content of Tb^{3+} doping, reason why have been chosen for the comparative studies of thermal stability. There are various interesting features in these figures. First, the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders are both formed by rhabdophane phase, which has smaller lattice parameters if doped with Tb^{3+} , as was already deduced by XRD. Second, initially the only visible effect in the XRTD patterns as the temperature increases is the peak shifting

towards lower 2θ degrees, which is not a surprise because it simply reflects the expected thermal expansion of the unit cell. Third, at about 200 °C the lattice parameters changed more abruptly, which is attributed to the dehydration of the rhabdophane phase (*i.e.*, $\text{LaPO}_4 \cdot n\text{H}_2\text{O} \rightarrow \text{LaPO}_4$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O} \rightarrow \text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$). And third, at about 715 °C the rhabdophane phase transforms to monazite phase (monoclinic symmetry, space group $\text{P2}_1/\text{c}$), which has a smaller unit cell volume if doped with Tb^{3+} . It is noted that the temperatures for the dehydration of the rhabdophane phase and for the phase transformation rhabdophane $\rightarrow$ monazite are not affected by the content of Tb^{3+} doping. Consequently, it can be concluded that the thermal stability of $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ is independent of the content of Tb^{3+} doping. In turn, this indicates that Tb^{3+} is not involved in the rate-limiting mechanism in the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ compounds, which is reasonable considering that Tb^{3+} is not likely to represent an obstacle for the diffusion/mobility of cations and anions due to its smaller ionic radius in relation to La^{3+} and to the fact that it occupies substitutional positions in the lattice, not interstitial positions. Lastly, an interesting difference between both sets of XRTD patterns is the greater peak broadening observed for the $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powder, which in principle indicates that the Tb^{3+} doping, apart from causing possible lattice microstrains, promoted the formation of smaller crystallites, although definitively this is something that has to be directly corroborated by electron microscopy observations.

Fig. 6. 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-prepared (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressures). The peak indexing for the phase identification is included; R and M denote rhabdophane and monazite, respectively.

Finally, Fig. 7a shows the XRD patterns of $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.20$) synthesized at 2.3 ± 0.1 bar self-generated pressure and then calcined at 700 °C in air for 2 h. As expected from the XRTD patterns shown in Fig. 6, the XRD patterns can all be ascribed to the monazite phase. The corresponding lattice parameters and unit cell volumes determined by the Pawley refinement of the XRD patterns are shown in Fig. 7b. Once again, it can be seen that the lattice parameters a , b and c of the monazite phase decrease linearly, and so does too the unit cell volume, with increasing Tb^{3+} -doping content, whereof it is concluded that the substitutional solid solutions developed during the microwave synthesis are preserved with the calcinations.

Fig 7. (a) XRD patterns and (b) lattice parameters and unit cell volume of the monazite-type calcined $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ ($x=0-0.2$) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure). The vertical line in (a) is to facilitate the observation of the progressive peak shifting towards higher 2θ degrees as the Tb^{3+} content in $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ increases.

3.3. FTIR and DTA-TG characterization

Figs. 8a and b show the FTIR spectra of both the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized at 2.3 ± 0.1 bar self-generated pressure in their as-prepared and calcined conditions, respectively. According to the literature, the site symmetry of tetrahedral PO_4^{3-} anions in the hexagonal, hydrated $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ structure is C_2 , and therefore the fundamental vibrational modes allowed are only ν_1 , ν_3 , and ν_4 . As can be seen in Fig. 8a, these three active vibrational modes are experimentally detected, thus confirming the conclusion reached by XRD that the as-synthesized powders crystallize as rhabdophane phase; specifically, ν_1 (that is, the P–O symmetric stretching) is located at $\sim 970 \text{ cm}^{-1}$, ν_3 (that is, the P–O asymmetric stretching) is located at $\sim 1093 \text{ cm}^{-1}$, and ν_4 (that is, the O–P–O asymmetric bending vibrations) are located at $\sim 541, 579$, and 617 cm^{-1} . Distinctively, in the FTIR spectra of Fig. 8b four bands, and not only three, located at $\sim 541, 564, 579$, and 617 cm^{-1} , respectively, appeared in the vibration region ν_4 of the phosphate groups. In addition, at low frequencies five characteristic bands in the region ν_3 (located at $\sim 1093, 1060, 1024, 993$, and 954 cm^{-1} , respectively) are clearly observed, and not only one, which reflects the distortion of the tetrahedral phosphate groups in the IX-fold coordinated lanthanide cations.^{24,34-37} Consequently, this set of observations corroborates the occurrence of the phase transformation rhabdophane $\rightarrow$ monazite with the calcination already detected by XRD. It is also convenient to mention that the bands at $\sim 3470, 3180$, and 1620 cm^{-1} ascribed to presence of H_2O and the band located at $\sim 1384 \text{ cm}^{-1}$ associated to the presence of nitrates,^{26,38} respectively, disappeared with the calcination, as expected. Also, as already occurred in the

case of XRD, no difference were either observed when comparing the FTIR spectra of powders prepared under different self-generated pressures (not shown).

Fig 8. FTIR spectra of the (a) as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders and (b) calcined LaPO_4 and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure).

Figs. 9a and b show the DTA-TG analyses conducted on the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized both at 2.3 ± 0.1 and 3.4 ± 0.1 bar self-

generated pressure, respectively. As can be seen, the total weight loss is ~8–9 wt.% for heat-treatments up to 900 °C. Specifically, there is a first weight loss in the temperature range ~25–170 °C, which corresponds to the desorption of physisorbed water as a consequence of an incomplete drying of the powders. This is followed by a second weight loss extending up to ~200 °C, accompanied by an endothermic event, which is associated with the elimination of chemisorbed water, that is, to the dehydration of the hexagonal, hydrated $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ phase;^{15,39} this is consistent with the XRTD analyses. Next there is a third weight loss with an exothermic peak at ~375 °C which is attributable to the removal of residual acetates from the precursors.^{38,40–42} And finally, a fourth weight loss accompanied by an exothermic peak occurs from 400 to 700°C, which is ascribed to various concurrent events including the oxidation of residual organics, the removal of residual nitrates from the precursors and the phase transformation rhabdophane→monazite; once again, this is in good agreement with the XRD and XRTD analyses.

Fig 9. Thermogravimetric analysis and differential thermal analysis curves of the as-prepared (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized using microwave vessel filling volumes of 40 and 70%, respectively (*i.e.*, 2.3 ± 0.1 and 3.4 ± 0.1 bar self-generated pressures).

The amounts of C and N present in the powders synthesized under different self-generated pressures have also been measured. Specifically, in the as-prepared powders the contents were found to vary in the ranges $\sim 0.09\text{--}0.11 \pm 0.01$ wt.% C and $\sim 0.87\text{--}0.91 \pm 0.01$ wt.% N, values that decreased down to the ranges $\sim 0.04\text{--}0.06 \pm 0.01$ wt.% and $\sim 0.05\text{--}0.07 \pm 0.01$ wt.%, respectively, after the calcination at 700 °C in air for 2 h. The comparison between ranges before and after the calcination confirms the removal of the acetates and nitrates from the precursor used in the synthesis, which is entirely consistent with the FTIR and DTA-TG analyses.

3.4. Electron microscopy characterization

Figs. 10a-c and 10d-f show representative electron microscopy images at different magnifications of the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized at 2.3 ± 0.1 bar self-generated pressure, respectively. It can be observed that the powder particles have the nanorod shape, and that they are certainly homogeneous both in shape and size. Also, macroscopically both powders possess a bundle-like morphology due to the uniform self-assembly of axially aligned nanorods. The nanorod proneness to agglomerate is due to that in this type of particle the van der Waals attractive forces predominate over the electrostatic repulsive forces,^{41,43} so that the bundled appearance is developed because the nanorods can thus maximize their entropy by minimizing the excluded volume per block in the array.^{18,44}

Fig. 10. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (d-f) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

It is convenient to mention that the high morphological uniformity of the nanorods derives from their synthesis with microwave radiation. It is well known that in conventional synthetic reactions crystals nucleate preferentially on the container walls and dust particles, and then undergo a slow growth due to the reduced number of crystal seeds and to the inhomogeneous, slow heating. On the contrary, microwave radiation induces a rapid, homogenous, and volumetric heating up to the crystallization temperature that 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 morphological uniformity,⁴⁵ as is indeed the case of the present $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.2$) nanorods.

The dimensions of the nanorods have been determined by quantitative image analysis of multiple FE-SEM and TEM images, as explained in the experimental section. In doing so for the synthesis under 2.3 ± 0.1 bar self-generated pressure, the average length and diameter of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods was found to be $\sim 154 \pm 25$ and $\sim 11 \pm 1$ nm, respectively, giving an aspect ratio of $\sim 14 \pm 1$; the corresponding length and diameter values for the $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods are $\sim 45 \pm 8$ and $\sim 9 \pm 1$ nm, respectively, giving an aspect ratio of $\sim 5 \pm 1$. Thus, it can be concluded from the morphology comparison between $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ that the Tb^{3+} doping clearly leads to much shorter nanorods but essentially equally thick, which should be borne in mind if morphological control of the nanorods is a key factor for the desired application. The underlying mechanism responsible for the slowed-down kinetics of nucleation and/or crystal growth with the Tb^{3+} doping is not entirely clear at this moment. However, it is reasonable to think that if crystal growth obeys to the same mechanisms of nucleation-aggregation-recrystallization proposed elsewhere for $\alpha\text{-Fe}_2\text{O}_3$ nanorods,⁴⁵ then the justification lies in the steric hindrance caused by the adsorption of Tb^{3+} ions and acetate groups onto the surface of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ gel, already formed when H_3PO_4 was added.

Additionally, the HREM images and the SAED patterns confirm that the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods synthesized at 2.3 ± 0.1 bar self-generated pressure are high-quality single-crystals with no linear or planar defects. Also importantly, the measurement of fringe spacing of planes using the HREM images of these $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods confirms the conclusion reached by XRD, XRTD, and FTIR, indicating that they crystallize as rhabdophane phase. Note for instance that the (100) plane is oriented parallel to the axial direction of the nanorods. Also, the fringe spacing of the (100) and (102) planes are 0.61 and 0.28 nm, respectively, which is in excellent agreement with those reported for hexagonal rhabdophane-type $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ (PDF card 46-1439; interplanar spacing values $d_{100}=0.61149$ nm and $d_{102}=0.2868$ nm). Additionally, it can also be inferred from the HREM images that the nanorods have grown anisotropically along the crystallographic direction dictated by their c -axis, which according to Wulff's theorem is the equilibrium shape for the crystal growth controlled by surface energy anisotropy with the basal plane having higher surface energy.^{38,46-48} The growth direction identified agrees with the results of earlier independent studies where $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods were prepared by precipitation followed by conventional heating.^{38,49,50}

Figs. 11a-c and 11d-f show representative electron microscopy images at different magnifications of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized at 2.3 ± 0.1 bar self-generated pressure and then calcined at 700 °C in air for 2 h. It can be seen that the as-prepared nanorods retained their anisotropic morphology with the calcination, but also that they shrunk. In particular, the average length and diameter of the calcined LaPO_4 nanorods was found to be $\sim 68 \pm 14$ and $\sim 11 \pm 1$ nm, given an aspect ratio of 6 ± 1 nm, while those of the calcined $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ nanorods are $\sim 57 \pm 10$ nm and $\sim 11 \pm 1$ nm, respectively, giving an aspect ratio of $\sim 5 \pm 1$. Thus, the aspect ratio of the undoped nanorods decreases notably with the calcination, an effect that however is not observed for the Tb^{3+} -doped nanorods. Once again, nanorods are shorter but equally thick if doped with Tb^{3+} , which is the same effect observed for the as-prepared nanorods. Previous results in $\text{LaPO}_4\text{:Ce}^{3+}/\text{Tb}^{3+}$ nano and microrods have shown that the brightness of the green $^5\text{D}_4\text{-}^7\text{F}_5$ emission in nanorods increases 3-5 times relative to that of the microrods,⁵¹ which was attributed to the hindrance of more boundary in nanorods. Consequently, within the set of powder prepared here, higher brightness is comparatively expected for the shortest Tb^{3+} -doped nanorods. Additionally, the measurement of fringe spacing of planes using the HREM images of the LaPO_4 and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ nanorods confirms that they are monoclinic single-crystals, which is in

perfect agreement with the conclusion reached by XRD, XRTD and FTIR indicating that at these calcination conditions the rhabdophane phase has transformed to monazite phase.

Fig. 11. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the calcined LaPO_4 (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ (d-f) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

Finally, Fig. 12 shows representative electron microscopy images at different magnifications of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized at 3.4 ± 0.1 bar self-generated pressure, while Fig. 13 are the corresponding to the same LaPO_4 and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ powders after calcination at 700°C in air for 2 h. It can be seen that the dependence with the Tb^{3+} doping is the same as observed before for lower self-generated pressure of 2.4 ± 0.1 bar, with the doping always leading to single-crystal nanoparticles of lower aspect ratio. The effect of the calcination does not change either, causing the shrinkage of the nanorods and therefore yielding lower aspect ratios. Also importantly, it is evident that the increase in self-generated pressure up to 3.4 ± 0.1 bar resulted in a considerable decrease in both the length and the diameter of the nanorods, so pronounced in the $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ case that even the nanorods shape is lost in favor of the equiaxed nanoparticles. It seems reasonable to think that a higher self-generated pressure during the synthesis favors the formation of a greater quantity of smaller primary $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nuclei (intensively produced by the rapid microwave-induced hydrolysis of La^{3+}) while restraining their subsequent anisotropic growth, a combination that leads to shorter nanorods or even to the loss of the nanorod shape. Whichever the exact underlying reason, it can nonetheless be concluded that an important variable to be controlled during the synthesis is the extent of water filling the microwave vessel because it markedly conditions the aspect ratio of the nanorods and even the nanoparticle morphology. The self-generated pressure however does not affect to crystallographic aspects because the HREM, SAED, XRD and FTIR analyses confirmed that the as-prepared products crystallize as rhabdophane phase and the calcined products transformed to monazite phase.

Fig. 12. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (d-f) powders synthesized using a microwave vessel filling volume of 70% (*i.e.*, 3.4 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

Fig. 13. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the calcined LaPO_4 (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ (d-f) powders synthesized using a microwave vessel filling volume of 70% (*i.e.*, 3.4 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

The present study has therefore very interesting practical implications, as explained next. It is well-known that monazite-type rare-earth-orthophosphates with nanorods morphology, as those prepared here using microwave-assisted synthesis, exhibit attractive photoluminescence properties. A highly-desired attribute for their possible use in functional applications such as for example laser technology, special glasses, fluorescence lamps, and plasma display panels⁵² is that these nanorods possess a high morphological stability. In this context, it emerges from the present experimental results that optimization of the self-pressure during the microwave synthesis is required to obtain high aspect ratio, morphologically stable nanorods, with the higher self-generated pressures leading to less-quality nanorods.

4. Conclusions

$\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods with different Tb^{3+} concentrations ($x=0-0.20$) has been prepared by microwave-assisted hydrothermal synthesis using various extents of water filling the microwave vessel, which have been characterized in detail both in their as-prepared and calcined (700 °C in air for 2 h) conditions using a wide battery of analytical techniques to investigate the dependence of the crystallographic/morphological features and thermal stability on the Tb^{3+} -doping content and self-generated pressure. The experimental results allow the following conclusion to be drawn:

1. Regardless of the Tb^{3+} -doping content and self-generated pressure, the synthesis results in the formation of high-quality single-crystal $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods of rhabdophane type. In particular, these nanorods not only are well-shaped and contain no linear or planar defects, but have also a high morphological uniformity.
2. Tb^{3+} cations enter as solutes into the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ host, thus forming substitutional solid solutions (*i.e.*, partial substitution of La^{3+} by Tb^{3+} without generation of oxygen vacancies for charge compensation). The lattice parameters, and therefore unit volume,

of the rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ solid solutions decrease progressively with increasing Tb^{3+} -doping content, as was to be expected from its smaller cationic size.

3. Tb^{3+} doping does not affect the thermal stability of the nanorods, indicating that Tb^{3+} cations, consistently with their smaller size and localization at substitutional positions in the lattice, are not involved in the rate-limiting mechanism of ion diffusion/mobility in the $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$. Tb^{3+} doping however conditions the nanorod morphology, in particular shortening the length without affecting the thickness. It can be due to the steric hindrance caused by the adsorption of Tb^{3+} ions and acetate groups onto the surface of the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ gel, already formed when H_3PO_4 was added.
4. By calcination at appropriate conditions (*i.e.*, 700 °C or higher) monazite-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods can be obtained from the corresponding rhabdophane-type $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ nanorods. These are also substitutional solid solutions, whose unit-cell volume decreases progressively with increasing Tb^{3+} -doping content. Once again, smaller aspect ratio nanorods are obtained as the Tb^{3+} -solute concentration in $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ increases.
5. The self-generated pressure during the microwave synthesis does not affect to crystallographic aspects of 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. However, it conditions the morphology of the nanorods in the sense that their aspect ratio decreases with increasing self-generated pressure. Indeed, depending on the self-generated pressure and calcination condition, the resulting nanoparticles can even lose the nanorod shape in favor of the equiaxed shape.
6. It emerges that the Tb^{3+} -doping content and the self-generated pressure are two important synthesis variables to be controlled with a view to obtaining functional $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ nanorods with tailored morphology.

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Figure captions

Figure 1. Evolution of the autogenous pressure during the synthesis of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ using microwave vessel filling volumes of 40, 50, 60, and 70%.

Figure 2. Dependence of the self-generated pressure (maximum value achieved) during the synthesis of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ on the extent of water filling of the microwave vessel.

Figure 3. (a) XRD patterns of the as-prepared $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.2$) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure), and (b) detailed comparison of the 102 peak position (normalized to the same peak intensity).

Figure 4. Indexed XRD patterns of the as-prepared (A) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (B) $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized using microwave vessel filling volumes of 40 and 70%, respectively (*i.e.*, 2.3 ± 0.1 and 3.4 ± 0.1 bar self-generated pressures).

Figure 5. Lattice parameters and unit cell volume of the rhabdophane-type as-prepared $\text{La}_{1-x}\text{Tb}_x\text{PO}_4 \cdot n\text{H}_2\text{O}$ ($x=0-0.2$) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure).

Figure 6. 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-prepared (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressures). The peak indexing for the phase identification is included; R and M denote rhabdophane and monazite, respectively.

Figure 7. (a) XRD patterns and (b) lattice parameters and unit cell volume of the monazite-type calcined $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ ($x=0-0.2$) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 bar self-generated pressure). The vertical line in (a) is to facilitate

the observation of the progressive peak shifting towards higher 2θ degrees as the Tb^{3+} content in $\text{La}_{1-x}\text{Tb}_x\text{PO}_4$ increases.

Figure 8. FTIR spectra of the (a) as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders and (b) calcined LaPO_4 and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure).

Figure 9. Thermogravimetric analysis and differential thermal analysis curves of the as-prepared (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ powders synthesized using microwave vessel filling volumes of 40 and 70%, respectively (*i.e.*, 2.3 ± 0.1 and 3.4 ± 0.1 bar self-generated pressures).

Figure 10. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (d-f) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

Figure 11. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the calcined LaPO_4 (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ (d-f) powders synthesized using a microwave vessel filling volume of 40% (*i.e.*, 2.3 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

Figure 12. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (d-f) powders synthesized using a microwave vessel filling volume of 70% (*i.e.*, 3.4 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.

Figure 13. Representative (a,d) FE-SEM, (b,e) TEM, and (c,f) HREM micrographs of the calcined LaPO_4 (a-c) and $\text{La}_{0.85}\text{Tb}_{0.15}\text{PO}_4$ (d-f) powders synthesized using a microwave vessel

filling volume of 70% (*i.e.*, 3.4 ± 0.1 bar self-generated pressure). The inset in the TEM micrographs shows the corresponding SAED pattern.