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# Hydrothermal synthesis, X-ray absorption and luminescence properties of Tb<sup>3+</sup> doped LaPO<sub>4</sub>

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## ABSTRACT

Tb<sup>3+</sup> activated LaPO<sub>4</sub> nano-phosphors have been prepared by a hydrothermal method. Luminescence spectra in VUV–vis range as well as fluorescence decays were studied for bulk and nano-phosphors. Bulk sample exhibits a relatively fast decay time. The <sup>5</sup>D<sub>3</sub> emissions from Tb<sup>3+</sup> ions increase under X-ray excitation in comparison with that under ultraviolet light excitation. X-ray absorption near-edge structure (XANES) was employed to study the chemical environment and energy transfer efficiency to optical emission. XANES results across different element absorption edges indicate that the chemical environment does not change significantly, only oxygen contributes to luminescence negatively.

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## 1. Introduction

Lanthanum orthophosphate (LaPO<sub>4</sub>) is a useful host for doping rare earth ions with high quantum efficiencies. Much attention has been paid to LaPO<sub>4</sub> during the last decades [1–5]. Among them, Ce<sup>3+</sup> and Tb<sup>3+</sup> co-doped LaPO<sub>4</sub> is well known; it has been commercialized as a green component in fluorescent lamps and plasma display panels (PDPs) due to its excellent chemical and thermal stabilities and high quantum yield (> 70%) [6,7]. Recent research works show that rare earth ions based LnPO<sub>4</sub> nanoparticles are also promising for biological applications [8,9]. Thus, to better understand the luminescence processes and to develop more potential applications, the study of rare earth ions doped LaPO<sub>4</sub> phosphor remains urgent and important.

As we all know, the properties of luminescent materials have close relationship with their morphologies and sizes, the controlled synthesis of phosphors has been a hot topic in recent material chemistry [10]. Considerable efforts have been taken to fabricate nano-size LaPO<sub>4</sub> with controlled morphology. For example, Yang et al. successfully achieved nanowire, core–shell nanowire and

flower-like LaPO<sub>4</sub> through a precipitation method [10,11]; Oleic acid (OA) modified LaPO<sub>4</sub>:Eu<sup>3+</sup> nanorods can generate white light due to OA-related mid-gap state [12]. Oval spherical as well as mesoporous LaPO<sub>4</sub> nanostructures were also synthesized [13–15].

Wet chemistry methods such as precipitation, hydrothermal, sol-gel, etc. are usually employed to prepare micro/nano-materials. During the synthesis process, the surfactant, chelating agent, pH value and reaction temperature will influence the final results. Therefore, the size, shape, morphology, and structure of the synthesized materials can be effectively controlled [16]. In this study, Tb<sup>3+</sup> doped LaPO<sub>4</sub> nano-materials were synthesized through hydrothermal method. Using ethylenediamine tetraacetic acid disodium salt (Na<sub>2</sub>EDTA) as chelating agent, the nano-sizes could be successfully controlled with different chelating agent amounts.

X-ray absorption near edge structure (XANES) measures the absorption coefficient across an absorption edge of an atom by exciting electrons from the core-level of the atom in a chemical environment to previously unoccupied electronic states. Thus XANES is an element specific method, which is sensitive to the chemical surroundings and the oxidation states which modulate the absorption coefficient relative to that of a free atom. XANES measurements can be made in transmission or by the surface sensitive total electron yield (TEY) and bulk sensitive X-ray fluorescence yield (FLY) when transmission measurements are not feasible (e.g. a thin film on a

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substrate). For luminescence materials, photoluminescence yield (PLY) can also be measured, which is useful to determine the origin and radiative relaxation pathway for luminescence [17].

The luminescence properties can be expected to be different from those of bulk powder and nano-particle samples (or even between different nano-size samples) due to different distortion symmetry, surface to bulk atomic ratio and defects [15]. Hence, the main objective of this study is to investigate the luminescence property of  $\text{LaPO}_4:\text{Tb}^{3+}$  nano-phosphors and to compare the luminescence with bulk powder. XANES and the associated X-ray Excited Optical Luminescence (XEOL) technique are used to understand the luminescence processes.

## 2. Experimental

In a typical synthesis process for nano-samples reported here, 4.75 mL of  $\text{La}(\text{NO}_3)_3$  [0.2 mol/L], 0.25 mL of  $\text{Tb}(\text{NO}_3)_3$  [0.2 mol/L], 0.2 g of hexadecyl trimethyl ammonium bromide (CTAB) and a pre-determined amount (controlling factor) of  $\text{Na}_2\text{EDTA}$  were mixed together, then 5 mL of cyclohexane was added into the solution. After vigorous magnetic stirring for 1 h, 5 mL of  $\text{NH}_4\text{H}_2\text{PO}_4$  [0.2 mol/L] were added. The resulting solution was then transferred into a stainless Teflon-lined autoclave and heated at 180 °C for 12 h. After cooling down to room temperature (RT), the precipitates were separated by centrifugation and washed several times alternately with ethanol and distilled water, then dried at 60 °C for 12 h. Un-doped bulk  $\text{LaPO}_4$  and 5%  $\text{Tb}^{3+}$  doped bulk  $\text{LaPO}_4$  ( $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$ ) were synthesized by a traditional high-temperature solid-state reaction route [18].

The phase purity of the products was examined by X-ray diffraction (XRD) using a D8 ADVANCE powder diffractometer with  $\text{Cu K}\alpha$  radiation at RT. The TOPAS-Academic program was used to perform the structural refinement of XRD data [19].

Transmission electron microscopy (TEM) images were measured on FEI Tecnai G2 F20 S-TIWN. High resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) analysis were performed on a JEOL 2010 instrument with an accelerating voltage of 200 kV. Steady-state (excitation and emission) spectra in VUV–UV–vis range were measured at the VUV spectroscopy experimental station on 4B8 beam line of Beijing Synchrotron Radiation Facility (BSRF). The measurement details have been described previously [20]. For luminescence decay curves, an FLS 920 equipment with a 60 W  $\mu\text{F}$  flash lamp was used (pulse width 1.5  $\mu\text{s}$ , repetition rate 20 Hz).

Infrared (IR) spectra were measured with a Nexus 670 FT-IR spectrometer. The samples were measured as KBr pellets with a resolution of 2  $\text{cm}^{-1}$  at RT.

XANES measurements were performed using two beamlines at the Canadian Light Source (CLS) – the Tb, La  $L_3$ -edge and P K-edge XANES measurements were performed on the Soft X-ray Micro-characterization Beamline (SXRMB) in TEY, FLY and PLY modes; the InSb(1 1 1) crystals were used for the P K-edge XANES measurements while Si(1 1 1) was used for the La and Tb  $L_3$ -edge XANES; O K-edge XANES were performed on the Spherical Grating Monochromator (SGM) beamline in TEY, FLY and PLY modes. The optical luminescence was tracked using a CCD based Ocean Optics QE 65,000 spectrometer.

## 3. Results and discussions

### 3.1. Phase purity and morphology

The XRD patterns of bulk powder and three representative nano  $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$  samples are displayed in Fig. 1. The diffraction patterns are identical to each other, all peaks match well with the

Joint Committee on Powder Diffraction Standards File (JCPDF) 32-0493 [monoclinic  $\text{LaPO}_4$ ], indicating all samples are pure phase. The diffraction peaks for nano-samples are broader than that of bulk powder, which relates to smaller particle sizes.

The Rietveld refinements on XRD patterns of undoped bulk  $\text{LaPO}_4$ , nano  $\text{LaPO}_4$  (0 mol  $\text{Na}_2\text{EDTA}$  assisted) and  $\text{Tb}^{3+}$  doped nano  $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$  (0 mol  $\text{Na}_2\text{EDTA}$  assisted) were performed using the P2<sub>1</sub>/n structure model. The diffraction result of nano- $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$  is presented in Fig. 2 as an example, the lattice constants and cell volumes of the three samples are shown in Table 1. The cell volume shows a little increase for undoped nano- $\text{LaPO}_4$  in comparison with bulk  $\text{LaPO}_4$ , indicating that the crystal lattice expands when it is nano-crystallized. The lattice constants *a*, *b*, *c* all exhibit some changes and the cell volume of nano  $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$  decreases when compared with nano  $\text{LaPO}_4$ . For the monoclinic  $\text{LaPO}_4$  matrix, there is only one  $\text{La}^{3+}$  site with nine-coordination by oxygen atoms. The radius of nine-coordinated  $\text{Tb}^{3+}$  is 109.5 pm, a little smaller than that of  $\text{La}^{3+}$  (121.6 pm), therefore, the cell volume tends to decrease when  $\text{Tb}^{3+}$  ions substitute  $\text{La}^{3+}$  in the host as expected from lanthanide contraction. The refinement results demonstrate that  $\text{Tb}^{3+}$  ions have been effectively incorporated into the  $\text{La}^{3+}$  site.

Fig. 3a shows the TEM image of the nano-sample without  $\text{Na}_2\text{EDTA}$ , the sample exhibits uniform nanorod structure with 350–400 nm in length and 40–50 nm in width. An individual nanorod TEM image and a HRTEM image taken from a selected area are displayed in Fig. 3b and c. The interplanar spacing of 0.485 and

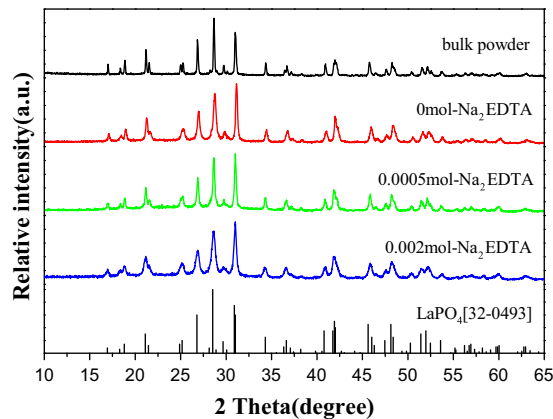


Fig. 1. XRD patterns of nano-phosphors with different amounts of  $\text{Na}_2\text{EDTA}$  and bulk sample at RT.

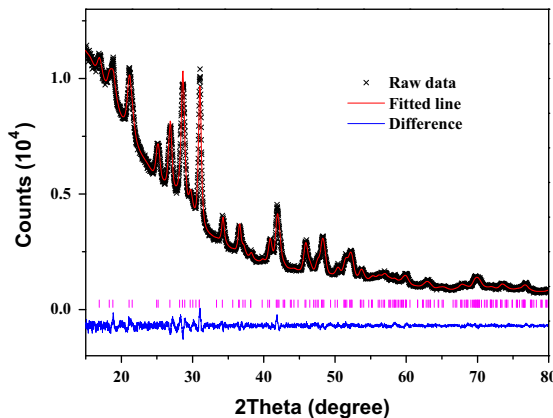


Fig. 2. The experimental (crosses) and calculated (red line) XRD patterns and the difference (blue line) for nano-sample  $\text{La}_{0.95}\text{Tb}_{0.05}\text{PO}_4$  (0 mol  $\text{Na}_2\text{EDTA}$  assisted). The ticks mark the Bragg reflection positions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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