

# Synthesis and characterization of LaPO<sub>4</sub>:Ho<sup>3+</sup> nanopowders

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## Abstract

LaPO<sub>4</sub> nanopowders doped with 1, 2, 3, 4 and 6 mol% Ho<sup>3+</sup> had been prepared by the co-precipitation technique. Transmission Electron Microscope (TEM) images indicated that the nanopowders were composed of nanowires. The XRD analysis showed that the nanopowders exhibited the hexagonal structure with lattice constants a=b= 7.07 ± 0.01 Å, and c= 6.52 ± 0.01 Å. The best adsorption wavelength was at 378 nm which provided the best emission light at the wavelength of 500 nm.

Keywords: Nanopowder, Holmium, Lanthanide Phosphate

## 1. Introduction

Rare earth phosphates have become a topic of growing interest during the past few years due to their potential applications in optical materials, phosphors, lasers, light-emitting diodes (LED), sensors, displays and luminescent lamps [1–3]. One of the present day actual tasks is the fabrication of relatively cheap rare earth phosphate nanopowders because their luminescence efficiency is expected to increase when the size of particles decreases to nanoscale [4, 5]. Recently, lanthanide phosphate (LaPO<sub>4</sub>) has been reported to act as an excellent host for cerium, terbium and europium ions, to synthesize phosphors emitting a variety of colors for development of photo luminescent materials with applications in optoelectronic devices, solid-state lasers, white LEDs, displays and phosphors [6–13].

Very recently, it has been found that rare earth doped LaPO<sub>4</sub> is one of the best candidates for biomedical applications such as fluorescence resonance energy transfer (FRET) assays, bio-labelling, optical imaging or phototherapy [14–16]. For synthesis of the rare-earth-doped LaPO<sub>4</sub>, various methods including sol–gel [16–18], hydrothermal synthesis [13,16,19,20], co-precipitation [21–23], polyol-mediated

synthesis [8] and microwave-assisted technique [9–12] have been developed. The LaPO<sub>4</sub> nanostructures with various morphologies such as nanowires [19, 23], nanorods [12, 17, 24, 25], thin films [18], nanoparticles [8-11, 13, 14, 16, 21, 22] and microspheres [20] were obtained.

Because of the mentioned above reasons, we chose the fluorescent materials LaPO<sub>4</sub>:Ho<sup>3+</sup> as the main research object of this project. In this report, we focus on the synthesis, research of properties and comparison between the properties of the LaPO<sub>4</sub> fluorescent materials doped with Ho<sup>3+</sup> ions. There are many fabrication methods of LaPO<sub>4</sub>:Ho<sup>3+</sup> such as hydrothermal method, co-precipitation method, and microwave method. An important reason to use the co-precipitation method because it is easy to fabricate, saves energy and time and does not require special conditions such as high temperature or vacuum. Moreover, the product of this method is quite abundant and good stability. Hence, we tried to use this method for synthesis of LaPO<sub>4</sub>:Ho<sup>3+</sup> nanopowders.

In this paper, we reported the preparation of LaPO<sub>4</sub> nanopowders doped with holmium (Ho<sup>3+</sup>) ions by co-precipitation method. Our studies were focused on the Ho<sup>3+</sup> concentration effect on XRD and PL properties of the LaPO<sub>4</sub>:Ho<sup>3+</sup> nanopowders.

## 2. Experimental

Undoped and Ho<sup>3+</sup>-doped LaPO<sub>4</sub> nanopowders were prepared by co-precipitation method from lanthanum oxide La<sub>2</sub>O<sub>3</sub>, Holmium nitrate Ho(NO<sub>3</sub>)<sub>3</sub> and ammonium dihydrogen phosphate NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> as precursors as shown in Figure 1. The lanthanum nitrate La(NO<sub>3</sub>)<sub>3</sub> solution were obtained by dissolving La<sub>2</sub>O<sub>3</sub>, respectively, in nitric acid HNO<sub>3</sub> (30%) solution under heating with agitation for 15 min. To prepare NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution, 0.5454 mg of

$\text{NH}_4\text{H}_2\text{PO}_4$  was dissolved in 50 mL of double distilled water under constant stirring for 15 min. In a typical synthesis, stoichiometric amounts of  $\text{La}(\text{NO}_3)_3$  and  $\text{Ho}(\text{NO}_3)_3$  aqueous solutions were mixed. The molar ratio of Ho:La was 0, 1, 2, 3, 4 and 5 mol%. In a typical synthesis, stoichiometric amounts of  $\text{La}(\text{NO}_3)_3$  and  $\text{Ho}(\text{NO}_3)_3$  aqueous solutions were mixed. Then appropriate amounts of  $\text{NH}_4\text{H}_2\text{PO}_4$  solution were added into the mixed nitrate solution under stirring for 3 h at room temperature. The resulting precipitate was filtered off and washed many times in water and ethanol to remove chemicals possibly remaining in the final products. The last products were dried in air at  $65^\circ\text{C}$  for 6 h, obtaining white fine powders.

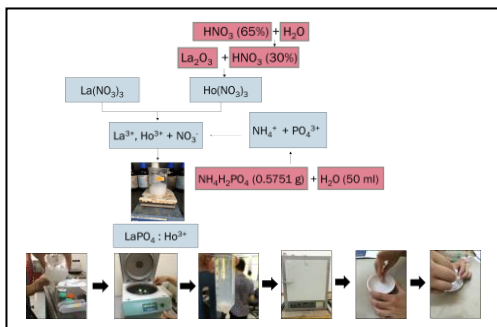


Fig. 1. Preparation of  $\text{Ho}^{3+}$ -doped  $\text{LaPO}_4$  nanopowders

The synthesized nanopowders were studied by X-ray Diffractometer SIEMENS D5005, Bruker with  $\text{CuK}\alpha_1$  irradiation ( $\lambda=1.54056 \text{ \AA}$ ), Transmission Electron Microscope JEOL JEM 1010, Spectrofluorometer Fluorolog FL3-22 Jobin-Yvon- Spex and X-ray Spectrometer OXFORD ISIS 300 attached to the JEOL-JSM5410 LV Scanning Electron Microscope.

### 3. Results and Discussion

The SEM images depicted in Figure 2 indicate that the Figure 2(a) showed that sample of 0 mol%  $\text{Ho}^{3+}$  composed nanopowders which image with 100k x Magnification. The Figure 2(b) showed that sample of 3 mol%  $\text{Ho}^{3+}$  composed nanopowders which image with 100k x Magnification. The Figure 2(c) showed that sample of 6 mol%  $\text{Ho}^{3+}$  composed nanopowders which image with 100k x Magnification.

Typical X-ray diffraction (XRD) pattern of the undoped  $\text{LaPO}_4$  was shown in the Figure 3. XRD spectrum of  $\text{LaPO}_4$  shows that the diffraction peaks at  $2\theta$  angles of  $11.09^\circ$ ,  $14.33^\circ$ ,  $19.91^\circ$ ,  $24.01^\circ$ ,  $29^\circ$ ,  $31.19^\circ$ ,  $37.50^\circ$ ,  $41.67^\circ$ ,  $48^\circ$  and  $53^\circ$  corresponding to (100), (101), (110), (200), (102), (112), (211), (212) and (302) planes were separated explicitly. All the peaks in the XRD pattern clearly indicated that the  $\text{LaPO}_4$  particles had simple hexagonal crystal structure. The lattice constants determined from the XRD patterns were  $a=b=7.07 \text{ \AA}$ , and  $c=6.52 \text{ \AA}$  which are in agreement with get standard values  $a=b=7.042 \text{ \AA}$  and  $c=6.445 \text{ \AA}$  (JCPDS card no.04-0635).

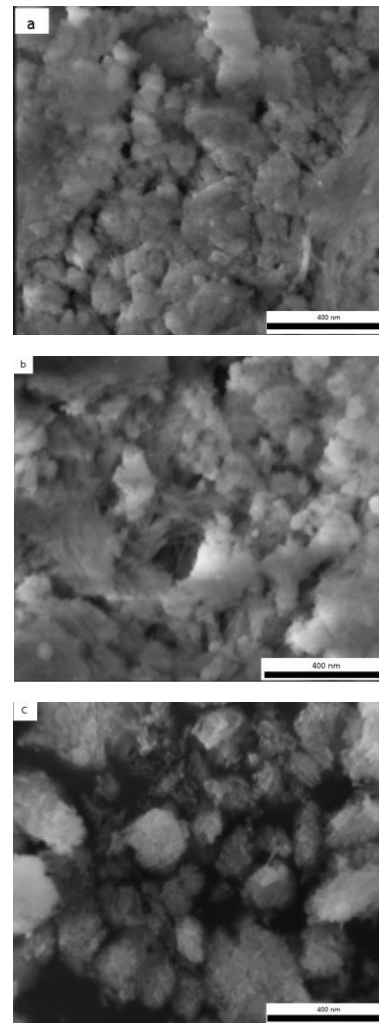


Fig. 2. (a) nano SEM image of 0 mol%  $\text{Ho}^{3+}$ , (b) nano SEM image of 3 mol%  $\text{Ho}^{3+}$ -doped  $\text{LaPO}_4$ , (c) nano SEM image of 6 mol%  $\text{Ho}^{3+}$ -doped  $\text{LaPO}_4$  prepared by the co-precipitation method.

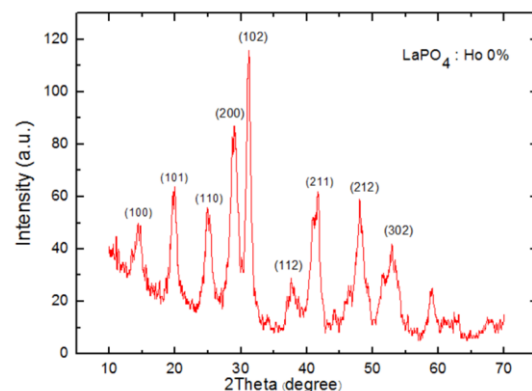


Fig 3. Typical XRD pattern of undoped  $\text{LaPO}_4$ .

Typical EDS spectra of the  $\text{LaPO}_4$  nanopowders undoped and doped 6 mol%  $\text{Ho}^{3+}$  were shown in Figure 4. The EDS analysis showed that the chemical composition for the undoped sample was 61.01 at.% O, 20.18 at.% P, 18.81 at.% La ; for the 6% Ho doped sample was 60.76 at.% O, 18.86 at.% P, 18.21 at.% La and 1 at.%  $\text{Ho}^{3+}$ .

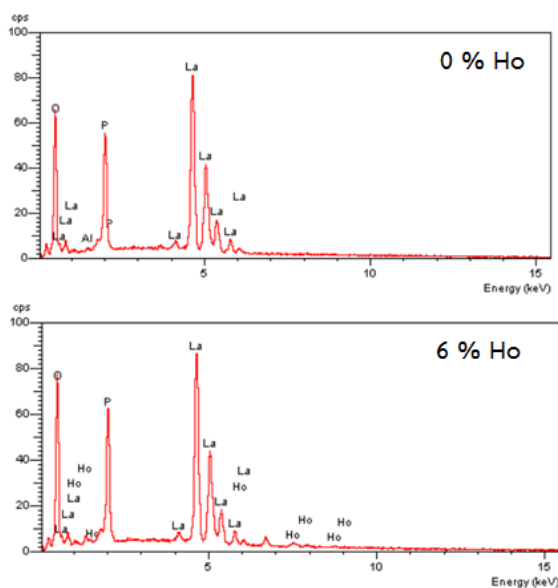


Fig 4. The EDS spectrum of the undoped and 6 % Ho<sup>3+</sup> doped LaPO<sub>4</sub> nanopowders.

The PL and PLE spectra of the 3 mol% Ho<sup>3+</sup> doped of LaPO<sub>4</sub> sample were shown in Figure 5. The PL spectrum under 378 nm excitation showed three peaks at 500, 573 and 659 nm, of which the peak at 500 nm had the strongest intensity. We chose this peak to measure the PLE spectrum. As shown by Figure 5 in the PLE spectrum monitored at 500 nm emission line seven peaks located at 357, 378, 397, 425, 438, 462 and 468 nm had detected. The excitation peak at 378 nm was the strongest. Consequently, it was used as excitation wavelength in the measurement of PL spectra.

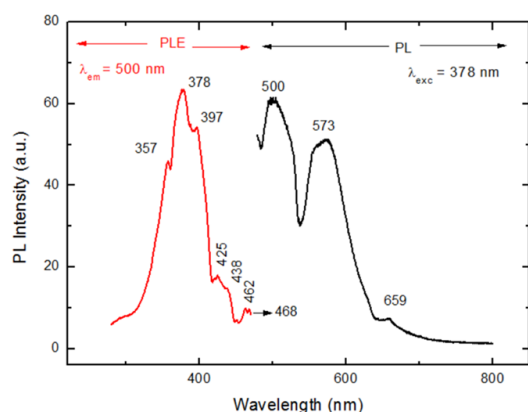


Fig 5. PL (with  $\lambda_{exc} = 378$  nm) and PLE (at  $\lambda_{em} = 500$  nm) spectra of the LaPO<sub>4</sub>:3 mol% Ho<sup>3+</sup> sample

#### 4. Conclusion

Undoped and doped LaPO<sub>4</sub> with 1, 2, 3, 4, and 6 mol% Ho<sup>3+</sup> had been synthesized by co-precipitation method. The XRD analysis showed that the sample of undoped and doped LaPO<sub>4</sub> exhibited a pure hexagonal structure with lattice constants  $a=b= 7.07 \pm 0.01 \text{ \AA}$ , and  $c= 6.52 \pm 0.01 \text{ \AA}$ . The best

adsorption wavelength was at 378 nm which provided the best emission light at the wavelength of 500 nm. LaPO<sub>4</sub>:Ho<sup>3+</sup> can be possibly used as the luminescence materials of LED

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