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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

# Hydrothermal synthesis and characterization of $LaPO_4$ for bio-imaging phosphors

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**Abstract** Rare earth orthophosphates, $RPO_4$ ($LaPO_4$ and Nd: $LaPO_4$) have been synthesized under hydrothermal conditions with an experimental temperature of 120 °C and duration of 16–30 h. Crystals were typically in the size range of 50–120 nm. The nanoparticles obtained were characterized using powder X-ray diffraction, infrared spectroscopy, photoelectron spectroscopy, SEM, and optical absorption spectroscopy. The typical morphology of the rare earth phosphate particles obtained was either rod-shaped or spherical depending upon the experimental conditions.

## Introduction

Recently, the bio-imaging potential of the rare earth's compound has been unearthed [1]. The current bio-imaging system uses organic fluorescent probes, which requires UV excitation light. One of the most serious problems in bio-imaging is the damage caused by the UV light on the biosystem and especially on the organic fluorescent probe itself recognized as color-fading. A solution for solving the UV damage on bio-imaging system is the use of IR excitation and emission [2, 3].

The preparation of these compounds carries peculiarities with respect to their qualities. The greatest requirement in the preparation of these compounds is the absence of hydroxyl molecules, which insists high temperature synthesis [4]. The presence of hydroxyl molecules heavily quenches the fluorescence in these compounds [5]. Very recently, great efforts have been made to develop new phosphor systems for white-LED [6], FED, and PDP applications [7, 8].

Several authors reported the synthesis of rare earth phosphate compounds via different methods. The physiochemical properties of the powders, which depend on the synthesis route, i.e., the chemical composition, the crystalline structure, the grain size, and the morphology that in turn influence the thermal behavior and the luminescent properties in these compounds. Hence, the preparation processes of these compounds are of prime importance.

In the present work, the authors report the preparation of $LaPO_4$ and $Nd^{3+}$ doped $LaPO_4$ using novel approaches of preparation. The effect of experimental temperature, solvents, ratio of the starting materials, stirring, and experimental duration has been studied in great detail with respect to the particle size, morphology, and crystallinity of the resultant products in order to obtain the optimum experimental conditions for the preparation of bio-photonic materials.

Also the concentration of optically active $Nd^{3+}$ has been varied from 1 wt.% to 6 wt.% in the experiments. The products obtained have been characterized using XRD, SEM, XPS, FTIR, and VIS–NIR absorption spectrophotometer, etc.

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## Experimental

### Preparation of $LaPO_4$ and $Nd^{3+}$: $LaPO_4$ nanomaterials

The experiments were carried out using Teflon lined General Purpose autoclaves, Tuttle-Roy autoclaves, and stirred autoclaves. In a typical synthesis operation, $La_2O_3$ and $H_3PO_4$ were taken in 1:1.2 molar ratio in a beaker containing water (14 mL) to prepare $LaPO_4$ and $Nd_2O_3$ (1–6 mol%) was added for the preparation of $Nd^{3+}$: $LaPO_4$. The mixture was stirred for about 15 min, forming a white colloidal solution. The pH of the solution was adjusted to 1.4–2 using ethanol. Then the solution was poured into a Teflon lined steel autoclave. The autoclave was maintained at 120 °C for about 16–30 h. After the specific time, autoclave was naturally cooled to room temperature and products were washed several times in water and alcohol. Then the products were collected and characterized by various techniques. A series of experiments were carried out by increasing the temperature, time, and Nd content as shown in Table 1.

### Characterization

X-ray powder diffraction (XRD) was performed on Rigaku X-ray diffractometer, Japan, equipped with graphite monochromatized CuK$\alpha$ radiation ($\lambda = 0.154068$ nm). The $2\theta$ range used was from 10° to 70° in steps of 0.02° with a count time 1 s. The FTIR spectra were recorded using FTIR Jasco-460 plus, spectrophotometer, Japan.

X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALABMKII-X-ray photoelectron spectrometer equipped with ultra-high-vacuum (UHV) system. X-ray spectroscopy (EDS) was obtained from an attached Oxford link ISIS energy-dispersive spectrometer fixed on a JEM-2010 electron microscope. The size and morphology of the products were measured using scanning electron microscopy (SEM) (JEOLJSM-6300). VIS–NIR Optical spectra were measured by using a spectrophotometer equipped with an integrating sphere.

**Table 1** Experimental conditions[a] of the synthesis of $LaPO_4$ and $Nd^{3+}$: $LaPO_4$

| Run No. | Nd (wt%) | Temp (°C) | Time (h) |
|---|---|---|---|
| 1 |  | 100 | 16 |
| 2 |  | 120 | 16 |
| 3 | 1 | 120 | 30 |
| 4 | 2 | 120 | 30 |
| 5 | 3 | 120 | 30 |
| 6 | 4 | 120 | 30 |
| 7 | 5 | 120 | 30 |

[a] pH was maintained in all experiments at <2, Molar ratio of La:P was maintained at 1:1.2

## Results and discussion

The overall crystallinity and purity of the as-synthesized sample prepared were examined by X-ray powder diffraction (XRD) measurements as shown in Fig. 1. All reflections could be easily indexed to the monoclinic $LaPO_4$ (JCPDS 280–515) (Fig. 1a) and $Nd^{3+}$: $LaPO_4$ (Fig. 1b). After calcination at 100 °C for 1 h, the monoclinic structure could be changed to tetragonal structure (Xenotime). The LaPO4 powder was also prepared by solid-state reaction in order to compare lattice parameters of as $LaPO_4$ nanoparticles. Figure 2 shows the FTIR spectra of $LaPO_4$ and Nd: $LaPO_4$ nanomaterials. The FTIR spectra of as-prepared particles show some $OH^-$ absorption bands probably because of the smaller particle size and also absorption of some moisture from the atmosphere. The IR

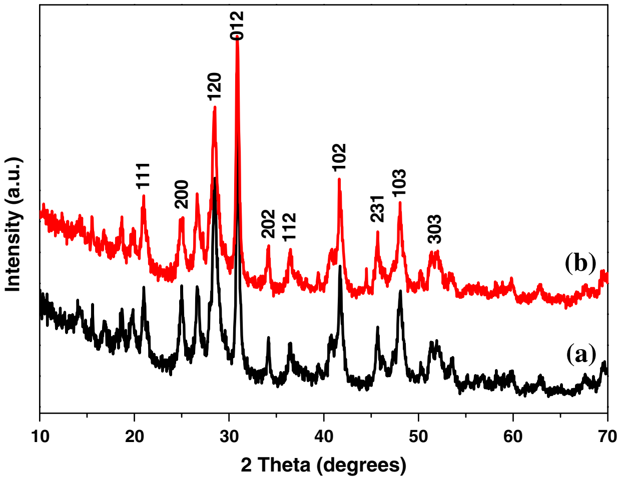

**Fig. 1** XRD pattern of rare earth phosphate (**a**) $LaPO_4$ and (**b**) $Nd^{3+}$: $LaPO_4$ nanocrystals

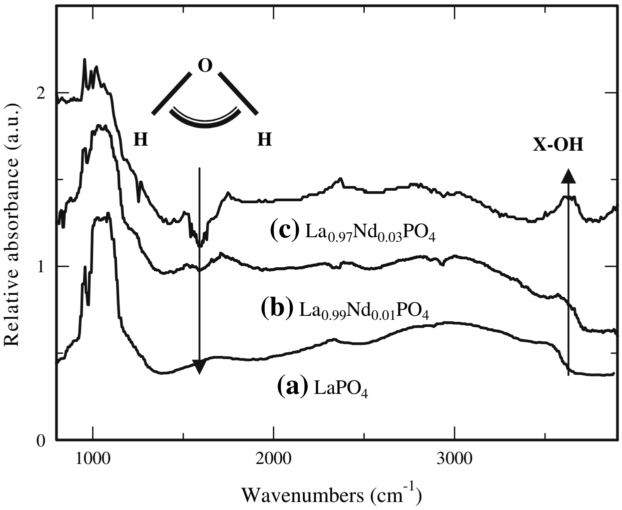

**Fig. 2** FTIR Spectra of (**a**) $LaPO_4$; (**b**) 1%Nd: $LaPO_4$ and (**c**) 3%Nd:$LaPO_4$

spectra recorded for the same samples after annealing at 100 °C did not show the $OH^-$ absorption bands. The characteristic IR absorption peaks at 536, 575, 614, 951, and 1060 $cm^{-1}$ in Fig. 2a–c are assigned to symmetric and asymmetric stretching of $PO_4$ groups [8–11]. The Fig. 2a represents the infrared spectrum of the monoclinic $LaPO_4$ synthesized at 120 °C with an experimental duration of 16 h. The band at 1600 $cm^{-1}$ corresponds to that of bending mode of structural water, which could be decreased by increasing the Nd content. The IR band at 3300–3700 $cm^{-1}$ is due to water molecules adsorbed on the surface of the particles. The X-OH band at 3700 $cm^{-1}$ is absent as seen in Fig. 2a and increased by increasing the Nd content as shown in Fig. 2b and c. The increase might be because of the replacement by rare earth element ($Nd^{3+}$).

The morphology and size of the $LaPO_4$ and Nd:$LaPO_4$ nanocrystals were examined using scanning electron microscopy and the respective electromicrographs are shown in Fig. 3a–e. The Fig. 3a and b show the SEM images of $LaPO_4$ synthesized at 120 °C with an experimental duration of 16 h and 30 h, respectively. The $LaPO_4$

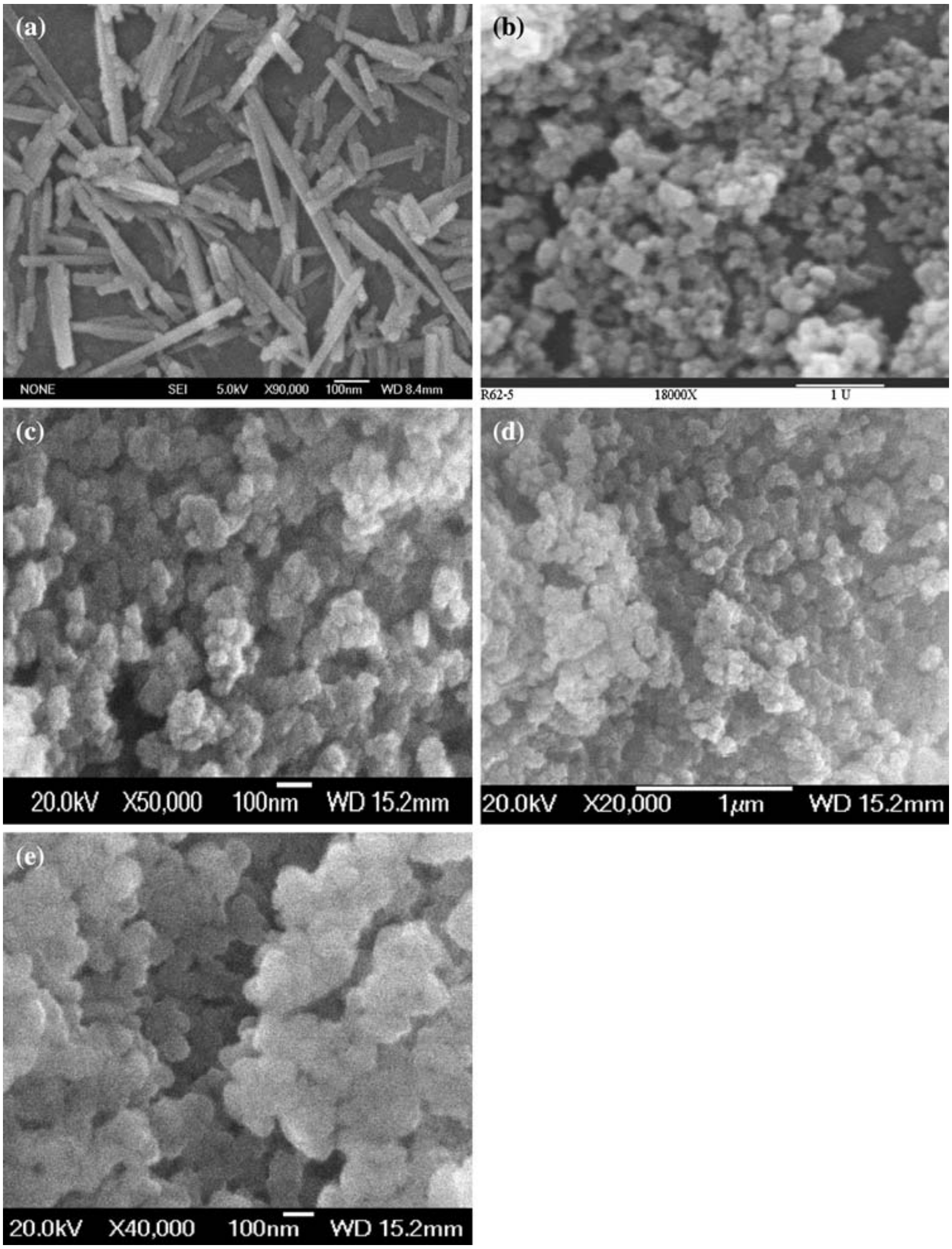

**Fig. 3** SEM of $LaPO_4$ and Nd:$LaPO_4$ nanomaterials: (**a**) $LaPO_4$ nanorods synthesized at 120 °C for about 16 h; (**b**) $LaPO_4$ nanoparticles synthesized at 120 °C for 30 h; (**c**) 1 mol%Nd:$LaPO_4$; (**d**) 2 mol%Nd:$LaPO_4$; (**e**) 3 mol%Nd:$LaPO_4$ nanoparticles

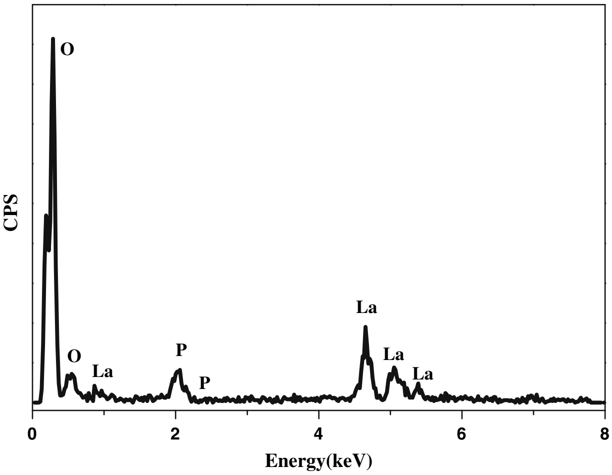

**Fig. 4** EDS Spectrum of $LaPO_4$ nanorods

synthesized at 120 °C for about 16 h exhibits nanorods like morphology with diameter ranging from 40 to 100 nm. Whereas the $LaPO_4$ synthesized at 120 °C for about 30 h exhibits sphere like morphology with diameter less than 100 nm. The Fig. 3c–e represent the SEM of (Nd:1–3 mol%):$LaPO_4$, respectively. They exhibit sphere like morphology and the particle diameter varies with Nd mol% present in lanthanum phosphate nanomaterials and the average particles size is approximately between 50 and 120 nm.

The Fig. 4 shows the EDS spectrum of $LaPO_4$ nanorods synthesized at 120 °C for about 16 h under hydrothermal conditions. The energy dispersive spectrum (EDS) of the as-prepared rare earth phosphates indicates the presence of La, P, and O elements (Fig. 4.) The Fig. 5 shows the XPS spectrum of $LaPO_4$ nanorods (Fig. 3a) synthesized at 120 °C for 16 h. All the peaks were calibrated by using C1s (284.8 eV) as the reference. The XPS spectrum indicates that phosphorus exists completely in the form of $PO_4^{3-}$ and La exists in trivalent state in $LaPO_4$ nanorods. The binding energy for the $La3d_{5/2}$ orbital of $La^{3+}$ is 835.10 eV and $P2P_{3/2}$ of $PO_4^{3-}$ is 133.10 [12–14]. Figure 6 shows the optical absorption spectrum of $Nd^{3+}$ ions in 5 mol%Nd:$LaPO_4$ nanoparticles together with a typical energy level diagram of $Nd^{3+}$ ions in YAG crystal. Absorption bands corresponding to the transition from ground state, $^4I_{9/2}$ to $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2,}$ and higher levels are observed. The absorption shows that $Nd^{3+}$ ions are homogeneously distributed or doped in the $LaPO_4$ particles and are optically active.

## Conclusions

Lanthanum phosphate and Nd doped Lanthanum phosphate nanomaterials were prepared successfully under hydrothermal conditions at 120 °C for 16–30 h.

As-prepared nanomaterials exhibit rod and sphere like morphology with average diameter less than 100 nm.

The elemental analysis of $LaPO_4$ nanorods was identified by EDS analysis. The valence state of La and P were detected by XPS analysis.

The FTIR spectra of Nd: $LaPO_4$ nanoparticles show the absence of hydroxyl in the Nd doped and annealed samples and this could be of great interest for their luminescence properties.

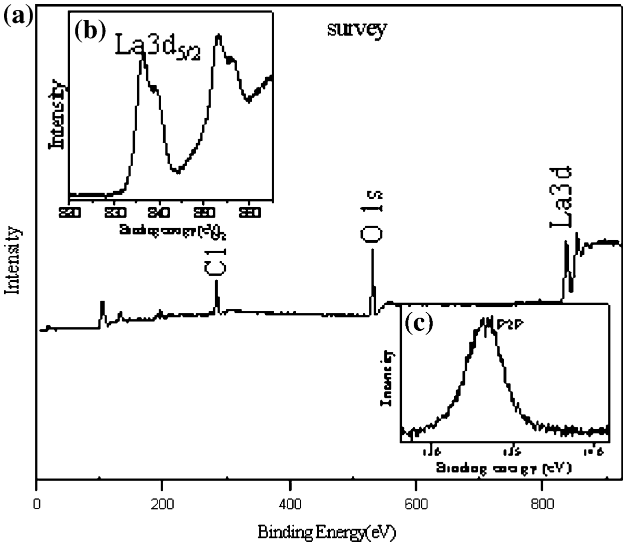

**Fig. 5** XPS Spectrum of $LaPO_4$ nanorods (**a**) XPS survey (**b**) La3d5/2 region and (**c**) P2P region

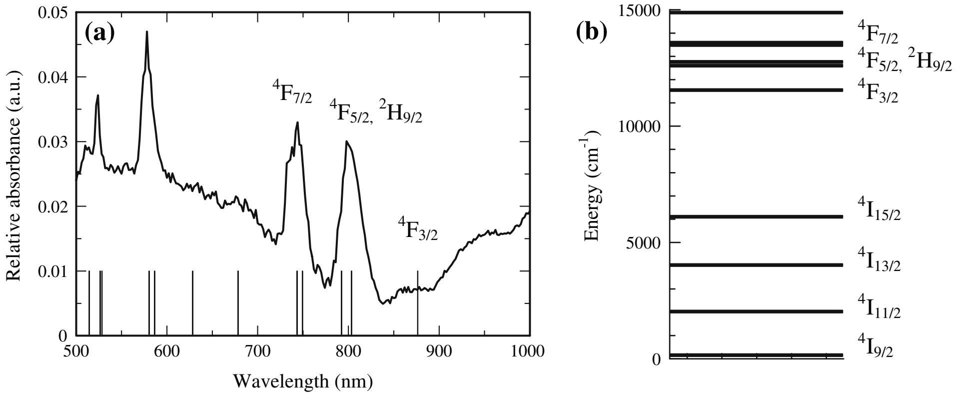

**Fig. 6** Optical absorption spectrum of $La_{0.95}Nd_{0.05}PO_4$ (**a**) and a typical energy level diagram of $Nd^{3+}$ in crystal (YAG) (**b**). The bars on the bottom of the fig (**a**) indicates the wavelength corresponds to the diagram (**b**)

The optical absorption spectra for Nd: $LaPO_4$ shows that $Nd^{3+}$ ions are homogeneously distributed in the $LaPO_4$ particles and are optically active.

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