REGULAR ARTICLE

Surfactant-assisted sacrificial template-mediated synthesis, characterization and photoluminescent properties of $\text{LaPO}_4 : \text{Eu}^{3+}$ phosphor

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Abstract. In this paper, we report a surfactant-assisted self-sacrificing route for synthesis of Eu^{3+} doped LaPO_4 nanostructures under hydrothermal conditions using the $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ precursor as a template and $\text{NH}_4\text{H}_2\text{PO}_4$ as the phosphate source. The synthesis was carried out in the absence and presence of surfactant [cetyltrimethyl ammonium bromide (CTAB)] and two different solvents (water and ethylene glycol). The precursor and products were characterized by powder X-ray diffraction, fourier transform infrared spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy and photoluminescence studies. Influence of surfactant and solvents on morphology and luminescence of the final product in sacrificial template-assisted method has been investigated in detail.

Keywords. Sacrificial template; nanorods; luminescence; phosphor.

1. Introduction

Lanthanide ion based nanomaterials have gained much attention due to their wide range of applications in the lighting devices, biological labels, catalysts and magnets.^{1–10} The properties of these nanomaterials mostly depend on their size, shape and dimensionality.^{11–13} Thus, the designing of nanoparticles with well-defined morphologies, dimensionality and sizes is an important and challenging issue. A remarkable advancement has been made in exploring the methods for the production of luminescent lanthanide phosphate nanoparticles with controllable morphology, size and dimensionality aspects.^{14–18} It has been observed that three dimensional (3D) nanomaterials possess more remarkable electrical, magnetic, optical and catalytic properties than the 1D and 2D structured nanomaterial due to presence of more active sites.¹⁹ Therefore, assembly of 1D and 2D nanobuilding blocks into ordered 3D structures is of great interest. A number of studies on the synthesis and characterization of 1D and 2D rare earth phosphate nanomaterials has been reported,^{20–23} but few reports appeared on 3D superstructures.²⁴ Assembly of nanoparticles can be achieved by use of various surfactants and chelating agents.^{13,25,26} Another way for

the preparation of three dimensional nanostructures is the template-directed synthesis. Template can be hard templates such as carbon spheres, silica and metal colloids^{27–29} or soft templates including emulsion droplets, vesicles and micelles.^{30–32} Sacrificial template is one of the hard templates, which act as a precursor for synthesis of hollow nanomaterials. The hydroxycarbonate sacrificial template method appears to be an effective and promising approach for morphology controlled synthesis of various nano- and micro- materials. A very important application of hydroxycarbonate compounds is their use as precursors for the formation of rare-earth oxide materials.^{33–35} Rare-earth carbonate precursors can be easily transformed into rare-earth oxides by thermal decomposition without any significant change in their shape and size. Thus, they provide good control on morphology of rare oxide nanoparticles. Besides this, rare-earth carbonate particles have been employed as sacrificial templates for the synthesis of other lanthanide compounds. Huang *et al.*, have employed amorphous $\text{Y}(\text{OH})\text{CO}_3$ nanospheres as a sacrificial template for the synthesis of 3D flower-like $\text{NaY}(\text{WO}_4)_2$ materials.³⁶ Z Yi *et al.*, have successfully synthesized $\text{GdPO}_4:\text{Ce}/\text{Tb}$ hollow microspheres with uniform morphology using the $\text{Gd}(\text{OH})\text{CO}_3 : \text{Ce}/\text{Tb}$ precursor as self-sacrificing template.³⁷

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Sacrificial template-assisted method for synthesis of nanoparticles is widely used and studied. However, effect of surfactant and solvent on morphology and properties of nanoparticles prepared by this method has not been explored. Nature of the surfactant and the solvent play an important role in deciding the morphology and crystal structure of final product and consequently affects the optical properties of the phosphor. Study of influence of surfactant (CTAB) and non-aqueous solvent (ethylene glycol) on morphology, crystal structure and optical properties of product in sacrificial template-assisted synthesis is the aim of present work. In this work, Eu^{3+} doped LaPO_4 nanostructures were prepared *via* typical sacrificial template-assisted hydrothermal route^{38,39} in the absence and presence of surfactant CTAB and in two different solvent media (water and ethylene glycol). In literature, various reports are available for Eu^{3+} doped LaPO_4 nanostructures with different doping concentration such as 1 mol%, and 5 mol% by using different synthetic methods.^{40–42} In the present work, 10 mol% Eu^{3+} doped LaPO_4 nanostructures have been synthesised by sacrificial template-assisted synthesis method. The crystal structure, morphology, formation process, the luminescent properties and lifetime measurements of the product have been investigated.

2. Experimental

2.1 Materials

Lanthanum(III) nitrate hexahydrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and europium(III) nitrate hexahydrate $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) were purchased from Alfa Aesar and used as received without further purification. Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), urea and cetyltrimethyl ammonium bromide (CTAB) were supplied by Sigma Aldrich. Deionized (DI) water was used throughout the experiment.

2.2 Synthesis

2.2a Synthesis of $\text{La}(\text{OH})\text{CO}_3 : 10 \text{ mol}\% \text{Eu}^{3+}$ template: $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ (S1) nanorods were prepared by urea-based homogeneous precipitation process. In a typical synthesis, 0.9 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.1 mmol of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL deionized water. Then, 2.0 g of urea was added into the prepared lanthanide aqueous solution with vigorous stirring. The solution was stirred for 2 h at room temperature and then heated to 90°C for another 2 h in an oil bath. A milky-white suspension was obtained. The precipitated $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ were centrifuged and washed with ethanol and deionised water three times. Precursor $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ (S4) was also synthesized in ethylene glycol solvent using same experimental protocol.

2.2b Synthesis of $\text{LaPO}_4 : 10 \text{ mol}\% \text{Eu}^{3+}$: In a typical synthesis, the as-prepared sample of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ rods acting as template was dispersed into 15 mL deionized water by ultrasonic treatment for 30 min, labelled as solution A. A separate solution B was prepared by dissolving 1 mmol (0.115 g) of $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.1 g of cetyltrimethyl ammonium bromide (CTAB) in 15 mL DI water and mixed with solution A with vigorous agitation. Finally, 30 mL of the resulting mixture was transferred into a Teflon lined bottle held in stainless steel autoclave, sealed and maintained at 180°C for 18 h. Once the autoclave cooled to room temperature naturally, the precipitate of $\text{LaPO}_4 : \text{Eu}^{3+}$ (CTAB) (S3) was collected and washed with DI water and ethanol and then dried at 60°C for 24 h in air. $\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods (S2) were also synthesized without surfactant using similar reaction conditions from same $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ precursor. In the third experiment, $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ precursor synthesised in ethylene glycol was used to prepare $\text{LaPO}_4 : \text{Eu}^{3+}$ (S5) nanorods by using same experimental protocol in aqueous medium. The scheme of the preparation process is shown in Figure 1.

2.3 Sample characterization

The phase structures of the samples was determined from powder X-ray diffraction (PXRD) using SmartLab 9 kV rotating anode X ray diffractometer with $\text{Cu} - \text{K}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$) at 45 kV and 40 mA and 2θ ranging from 10° to 70° . The infrared spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrometer (FT-IR) over the range of wavenumber $4000 - 400 \text{ cm}^{-1}$ and the standard KBr pellet technique was employed. Transmission Electron Microscopy (TEM) was recorded on Tecnai G² S-Twin Transmission Electron Microscope with a field emission gun operating at 200 kV. The energy spectra were obtained by energy-dispersive X-ray spectrum (EDS, Oxford Instruments) equipped on a Transmission Electron Microscope. Scanning electron micrographs (SEM) were collected on Nova Nano SEM-450 field emission scanning electron microscope at an accelerating voltage of 5.0 kV. The photoluminescence (PL) spectra of the samples were recorded on a Varian Cary Eclipse spectrophotometer with a Xenon lamp as the excitation source. Photoluminescence lifetimes of the prepared samples were calculated from the decay curves using Time-resolved cum Steady State Luminescence Spectrometer, Edinburgh Instruments, Model: FSP920. All the measurements were performed at room temperature.

3. Results and Discussion

3.1 Crystalline structure and morphology

The crystal phase and purity of the as-prepared samples were analysed by PXRD. Figure 2 shows PXRD pattern of the $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ precursors and $\text{LaPO}_4 :$

Figure 1. Scheme for the preparation process of $\text{La(OH)CO}_3 \cdot \text{Eu}^{3+}$ template and $\text{LaPO}_4 \cdot \text{Eu}^{3+}$ nanorods and flowers.

Figure 2. PXRD pattern of samples. (a) **S1**, (b) **S2**, (c) **S3**, (d) **S4** and (e) **S5**.

Eu^{3+} products. As shown in Figure 2a, the PXRD pattern of the precursor (**S1**) agrees well with the crystalline orthorhombic phase of La(OH)CO_3 ⁴³ whereas

S4 exhibits broad bands ranging from 10° to 70° representing the amorphous structure of the precursor³⁷ (Figure 2d). PXRD patterns of **S2** and **S3** correspond to hexagonal phase LaPO_4 nanostructures (Figures 2 b, c) (JCPDS 04-0635).^{44,45} However, PXRD pattern of **S5** (Figure 2e) indexed to the pure monoclinic phase of LaPO_4 (JCPDS no. 84-0600). Moreover, no other impurity peaks were detected from the PXRD pattern, which implied the formation of the pure phase Eu^{3+} doped LaPO_4 .

To gain more insight into the composition of the products, Fourier transform infrared (FTIR) spectra of samples were recorded and are shown in Figure 3. In the FT-IR spectra of the precursors (**S1** and **S4**), the strong bands in the range of $1400\text{--}1550\text{ cm}^{-1}$, 1075 cm^{-1} and $750\text{--}900\text{ cm}^{-1}$ are attributed to asymmetric, symmetric and bending modes of C-O group of carbonate confirming the composition of the precursor as $\text{La(OH)CO}_3 \cdot \text{Eu}^{3+}$.^{46,47} The FT-IR spectra of **S2** and **S3** show two absorption bands in the range of $500\text{--}650\text{ cm}^{-1}$ which correspond to the bending modes of O=P-O and O-P-O groups. A broad band at 1050 cm^{-1} is attributed to the stretching vibration of the $(\text{PO}_4)^{3-}$ groups.^{48,49} In the IR spectra of **S5**, P-O bending and stretching peaks are splitted which is characteristic of the monoclinic LaPO_4 phase. Characteristic absorption peaks at 542 cm^{-1} , 581 cm^{-1} and 610 cm^{-1} are ascribed to bending and broad band at 1075 cm^{-1} along with shoulder at 950 cm^{-1} correspond to stretching modes of $(\text{PO}_4)^{3-}$. The bands around 1650 cm^{-1} and $3200\text{--}3700\text{ cm}^{-1}$ correspond to the bending and stretching vibrations of

Figure 3. FTIR spectra. (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5.

adsorbed H₂O or -OH groups present on the surface of the materials. In the IR spectra of products (S2, S3 and S5), presence of characteristic peaks of phosphate group and absence of peaks of C-O group of the carbonate confirms successful conversion of the precursor La(OH)CO₃ : Eu³⁺ into the product LaPO₄ : Eu³⁺.

The morphology of the as-prepared precursor and final products was characterized by FE-SEM and HR-TEM analysis, as shown in Figures 4, 5, 6. La(OH)CO₃ : Eu³⁺ precursor was prepared *via* a general urea-based homogeneous precipitation method in two different solvent (water and ethylene glycol). Figure 4 shows TEM and SEM images of the as-synthesized La(OH)CO₃ : Eu³⁺ precursors. TEM and SEM images show rods and sheet-like structures of the S1 and S4, respectively. Further, TEM images of the precursors show that microrods and sheets have smooth surfaces which are

in agreement with the presented SEM images. However, after hydrothermal treatment of the precursor with PO₄³⁻ source, the surface of S1 became somewhat rough because of the aggregated LaPO₄ : Eu³⁺ nanorods formed on the surface. The hydrothermal treatment of S1 nanorods with PO₄³⁻ source in the presence of CTAB resulted into sacrificial conversion of precursor microrods into 3D flower-like morphology of LaPO₄ : Eu³⁺. Thus, CTAB leads to the assembly of precursor nanorods and their conversion into LaPO₄ : Eu³⁺ flowers. Hydrothermal treatment of S4 with PO₄³⁻ source in ethylene glycol solvent leads to the complete breakdown of sheet structure and change into LaPO₄ : Eu³⁺ 1D nanorods. The length and width of the rod-like precursor and product obtained from TEM are given in Table 1.

Outcomes of the EDS analysis (Figure 7) support that precursors consist of carbon, lanthanum, europium and

Figure 4. TEM image (a) and SEM image (b) of **S1**. TEM image (c) and SEM image (d) of **S4**.

oxygen. In the EDS spectra of products, presence of peaks corresponding to phosphorus further confirms the composition of the product as $\text{LaPO}_4 : \text{Eu}^{3+}$. Compositional % of elements present in the prepared samples are given in Table 2.

3.2 Photoluminescent properties

Figure 8 shows the excitation and emission spectra of $\text{LaPO}_4 : \text{Eu}^{3+}$ samples. The excitation spectra consist of several characteristic excitation lines of Eu^{3+} . A broad band centred at 256 nm can be ascribed to the oxygen-to-europium charge transfer (CT) band, arising due to transfer of an electron from the filled 2p shell of oxygen to a partially filled 4f shell of Eu^{3+} ion. Other characteristic peaks appeared at 317, 361, 377 and 393 nm originating from its 4f⁶ configuration and attributed to $^7\text{F}_0 - ^5\text{H}_6$, $^7\text{F}_0 - ^5\text{D}_4$, $^7\text{F}_0 - ^5\text{G}_2$, and $^7\text{F}_0 - ^5\text{L}_6$ transitions.

These peaks are of lower intensity due to the forbidden nature of f-f transitions. The emission spectra under excitation wavelength of 393 nm show characteristic peaks at 594 nm and 614 nm corresponding to $^5\text{D}_0 - ^7\text{F}_1$ and $^5\text{D}_0 - ^7\text{F}_2$ transitions of Eu^{3+} , respectively.⁵⁰ Apart from these prominent peaks, other weak emission peaks observed at 653 nm and 697 nm correspond to $^5\text{D}_0 - ^7\text{F}_3$ and $^5\text{D}_0 - ^7\text{F}_4$ transitions, respectively. The transition $^5\text{D}_0 - ^7\text{F}_1$ is magnetic dipole allowed and is not sensitive to the local site symmetry around Eu^{3+} ion. This transition is characterized by an orange-red emission. Transition $^5\text{D}_0 - ^7\text{F}_2$ is a hypersensitive forced electric dipole transition and its intensity is strongly affected by local site symmetry and the strength of electric field around the Eu^{3+} ions. This transition is responsible for the typical red luminescence observed in Eu (III) phosphors. The other transition $^5\text{D}_0 - ^7\text{F}_3$ has both electric

Figure 5. TEM images at low and high magnification. **S2:** (a), (b); **S3:** (c), (d); **S5:** (e), (f).

dipole and magnetic dipole character while transition $^5D_0 - ^7F_4$ is an electric dipole transition. If Eu^{3+} occupies a crystal site with inversion symmetry, $^5D_0 - ^7F_1$ (magnetic dipole transition) is usually the dominant emission line. If Eu^{3+} occupies a crystal site without inversion symmetry, the intensity of the $^5D_0 - ^7F_2$ (electric dipole transitions) is higher. The emission intensity ratio of magnetic dipole transition ($^5D_0 - ^7F_1$) relative to electric dipole transition ($^5D_0 - ^7F_2$), called symmetry ratio, is an important parameter for understanding the symmetry around the Eu^{3+} in the crystal lattice. It gives a measure of the degree of distortion from the inversion symmetry of the local environment surrounding the Eu^{3+} ions in the matrix. The symmetry ratio is related to the colour of phosphor also. Increase in symmetry ratio shows a marked decrease in R/O (red to orange ratio).

For **S3**, electric dipole transitions $^5D_0 - ^7F_2$ is more intense than that of the other two samples, indicating Eu^{3+} occupied the position with the non-inversion symmetry in host lattices and presents red emission. This can be due to the difference in morphology of **S3**. The $^5D_0 - ^7F_1$ magnetic dipole transition of Eu^{3+} is intense for **S5** indicating the Eu^{3+} ions in LaPO_4 is located at site with inversion symmetry and presents orange-red emission. The magnetic and electric dipole transitions are almost equally intense in **S2**. The luminescence decay lifetimes of $\text{LaPO}_4 : \text{Eu}^{3+}$ were measured at emission wavelength of 594 nm.^{44,51} The photoluminescence lifetimes of Eu^{3+} in **S2**, **S3** and **S5** are 4.619, 5.619 and 5.579 ns, respectively, as shown in Figures 9a–c. The luminescence intensity and decay lifetime are found to be highest for $\text{LaPO}_4 : \text{Eu}^{3+}$ flowers synthesised in presence of CTAB.

Figure 6. SEM images at low and high magnification. **S3:** (a), (b); **S5:** (c), (d).

Table 1. Length and width of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ micro-rods and $\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods.

	S1	S2	S3	S4
Length	1–2 μm	10–20 nm	20–30 nm	100–150 nm
Width	200–300 nm	5 nm	5–10 nm	10–20 nm

3.3 Growth mechanism

Formation process of $\text{LaPO}_4 : \text{Eu}^{3+}$ from $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ can be explained by using PXRD and TEM results as evidence. The PXRD pattern of the precursor **S1** shows the orthorhombic phase of $\text{La}(\text{OH})\text{CO}_3$. When the reaction of precursor **S1** was carried out

with $\text{NH}_4\text{H}_2\text{PO}_4$ in presence and absence of surfactant, all diffraction peaks of the as-obtained samples can be indexed to the hexagonal phase of $\text{LaPO}_4 : \text{Eu}^{3+}$. However, the XRD pattern of **S4** corresponds to the amorphous structure of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ and upon its reaction with $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods were obtained having monoclinic structure. Further, TEM images of the precursors (**S1**) show that microrods have smooth surfaces which are in agreement with presented SEM images. On hydrothermal treatment of the precursor with $\text{NH}_4\text{H}_2\text{PO}_4$, the surfaces of the rods get rough due to accumulation of $\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods. These observations can be described through solid-state diffusion phenomenon known as Kirkendall effect, which states that in a diffusing system, each chemical species has its own diffusion rate. The formation process of

Figure 7. EDS spectra. (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5.

Table 2. Atomic and weight % of the elements present in prepared samples.

	S1		S2		S3		S4		S5	
	Wt. %	At. %	Wt. %	At. %	Wt %	At. %	Wt %	At. %	Wt %	At. %
C	10.05	26.44	11.60	26.69	8.56	26.22	12.08	23.02	23.37	29.41
O	30.41	60.06	35.36	61.08	23.83	54.78	28.08	55.10	74.31	70.23
P	-	-	2.44	2.18	1.27	1.51	-	-	0.33	0.16
La	55.72	12.67	49.84	9.91	64.48	17.07	53.59	11.39	56.20	10.23
Eu	3.72	0.72	1.73	0.13	1.85	0.42	3.40	0.68	1.99	0.198

Figure 8. Excitation and emission spectra. (a) S2; (b) S3; (c) S5.

Figure 9. Photoluminescence decay curves. (a) S2; (b) S3; (c) S5.

$\text{LaPO}_4 : \text{Eu}^{3+}$ from $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ can be divided into three steps:

Due to ionisation of $\text{NH}_4\text{H}_2\text{PO}_4$ in aqueous solution, there are many H^+ ions present in the reaction mixture around the solid $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$. The H^+ ions then react with $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ causing the ionisation of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ as shown in eq. 2, leading to presence of a number of La^{3+} ions around the surface of the $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ microstructures. Then, the released La^{3+} react with PO_4^{3-} in the solution to form $\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods (eq. 3). The layers of

$\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods were formed over the surface of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ microrods. As the reaction continues, the $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ is consumed and the layers of $\text{LaPO}_4 : \text{Eu}^{3+}$ nanorods gradually grow. The outer $\text{LaPO}_4 : \text{Eu}^{3+}$ shell prevents a direct chemical reaction between La^{3+} and PO_4^{3-} and a concentration gradient of La^{3+} ions and PO_4^{3-} ions exists outside the $\text{LaPO}_4 : \text{Eu}^{3+}$ shell to the inner surface of the $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$. Due to high concentration of the PO_4^{3-} ions in the solution, PO_4^{3-} ions will diffuse inward to the inner surface of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ through the $\text{LaPO}_4 : \text{Eu}^{3+}$ shell while the La^{3+} ions will diffuse outward in the solution through the $\text{LaPO}_4 : \text{Eu}^{3+}$ shell. However, La^{3+} ions diffuse faster than PO_4^{3-} ions, and so, the production of $\text{LaPO}_4 : \text{Eu}^{3+}$ on the outside of the shell is faster than

that on the inside of the shell. The higher consumption rate of the $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ core than the production rate of $\text{LaPO}_4 : \text{Eu}^{3+}$ on the inside of the shell leads to the formation of $\text{LaPO}_4 : \text{Eu}^{3+}$ through the Kirkendall effect.

Surfactants play a key role in the self-assembly and in directing the growth and the morphology of the prepared nano/micromaterials. CTAB has been selected as the surfactant for the purpose. The dual role of CTAB molecules effectively leads to the formation of $\text{LaPO}_4 : \text{Eu}^{3+}$ flower architecture in sacrificial template-assisted synthesis. Nature of the solvent appears to play a crucial role in the crystal structure of nanoparticles. In general, LaPO_4 exists in three forms: hexagonal, monoclinic and tetragonal. The hexagonal phase of LaPO_4 appears to be the most stable structure in aqueous medium because of the higher stabilization energy of water. However, in non-aqueous medium, monoclinic phase $\text{LaPO}_4 : \text{Eu}^{3+}$ has been formed.

4. Conclusions

In summary, $\text{LaPO}_4 : \text{Eu}^{3+}$ flowers and nanorods have been successfully synthesized by sacrificial template-assisted route by employing $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ as the template and $\text{NH}_4\text{H}_2\text{PO}_4$ as PO_4^{3-} ion source. The XRD and FTIR results demonstrated the successful conversion of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ into $\text{LaPO}_4 : \text{Eu}^{3+}$. The SEM and TEM observations evidenced that the flower-like nanostructures were built in the presence of CTAB. It was found that CTAB plays an important role in the assembly of the precursor microrods and conversion of $\text{La}(\text{OH})\text{CO}_3 : \text{Eu}^{3+}$ into $\text{LaPO}_4 : \text{Eu}^{3+}$. In the absence of surfactant, rod-like $\text{LaPO}_4 : \text{Eu}^{3+}$ have been synthesized in both aqueous and non-aqueous medium. Solvent appears to play a key role in deciding the crystal structure of product. The hexagonal phase of $\text{LaPO}_4 : \text{Eu}^{3+}$ is obtained in aqueous medium whereas in non-aqueous medium leads to monoclinic phase of $\text{LaPO}_4 : \text{Eu}^{3+}$. The investigation of the luminescent properties showed that flower-like architectures exhibit an intense luminescence as compared to nanorod counterparts. The good luminescence property indicated that this product can be used in optoelectronic devices.

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References

- Huang X, Han S, Huang W and Liu X 2013 Enhancing solar cell efficiency: the search for luminescent materials as spectral converters *Chem. Soc. Rev.* **42** 173
- Singh A K, Singh S K, Kumar P, Gupta B K, Prakash R and Rai S B 2014 Lanthanide doped dual-mode nanophosphor as a spectral converter for promising next generation solar cells *Sci. Adv. Mater.* **6** 1
- Bunzli J C G, Comby S, Chauvin A S and Vandevyver C D B 2007 New opportunities for lanthanide luminescence *J. Rare Earths* **25** 257
- Ryu J, Park H Y, Kim K, Kim H, Kim K, Yoo J H, Kang M, Grailhe R and Song R 2010 Facile synthesis of ultrasmall and hexagonal $\text{NaGdF}_4 : \text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles with magnetic and upconversion imaging properties, *J. Phys. Chem. C* **114** 21077
- Gautam A and van Veggel F C J M 2011 Blue electroluminescence from Eu^{2+} -doped GaN@SiO_2 nanostructures tuned to industrial standards *Chem. Mater.* **23** 4817
- Singh N S, Sahu N K and Bahadur D 2014 Multicolor tuning and white light emission from lanthanide doped YPVO_4 nanorods: energy transfer studies *J. Mater. Chem.* **2** 548
- Park J Y, Baek M J, Choi E S, Woo S, Kim J H, Kim T J, Jung J C, Chae K S, Chang Y and Lee G H 2009 Paramagnetic ultrasmall gadolinium oxide nanoparticles as advanced T1 MRI contrast agent: account for large longitudinal relaxivity, optimal particle diameter and, in vivo T1 MR images *ACS Nano* **3** 3663
- Liu T C, Cheng B M, Hu S F and Liu R S 2011 Highly stable red oxynitride $\beta - \text{SiAlON} : \text{Pr}^{3+}$ phosphor for light-emitting diodes *Chem. Mater.* **23** 3698
- Wang F, Deng R, Wang J, Wang Q, Han Y, Zhu H, Chen X and Liu X 2011 Tuning upconversion through energy migration in core-shell nanoparticles *Nat. Mater.* **10** 968
- Wang W, Jiang X and Chen K 2012 $\text{CePO}_4 : \text{Tb}, \text{Gd}$ hollow nanospheres as peroxidase mimic and magnetic-fluorescent imaging agent *Chem. Commun.* **48** 6839
- Yang Y, Synthesis and luminescent properties of $\text{LaPO}_4 : \text{Eu}^{3+}$ microspheres 2013 *Mater. Sci. Eng. B* **178** 807
- Grzyb T, Gruszczyńska A, Włuski R J and Lis S 2013 The effects of down- and up-conversion on dual-mode green luminescence from Yb^{3+} and Tb^{3+} doped LaPO_4 nanocrystals *J. Mater. Chem. C* **1** 5410
- Yang M, You H, Huang Y, Jia G, Song Y, Guo N, Liu K, Zheng Y and Zhang H 2010 Facile synthesis and luminescent properties of flower-like $\text{LaPO}_4 : \text{Ln}^{3+}$ ($\text{Ln} = \text{Ce}, \text{Tb}$) hierarchical architectures *CrystEngComm* **12** 2865
- Yang M, You H, Song Y, Huang Y, Jia G, Liu K, Zheng Y, Zhang L and Zhang H 2009 Synthesis and luminescence properties of sheaflike TbPO_4 hierarchical architectures with different phase structures *J. Phys. Chem. C* **113** 20173
- Yang R, Qin J, Li M, Liu Y and Li F 2011 Redox hydrothermal synthesis of cerium phosphate microspheres with different architectures *CrystEngComm* **13** 7284

16. Pusztai P, Kukovecz A and Konya Z 2014 Green synthesis of biomimetic CePO_4 : Tb nanostructures using the simplest morphology control *RSC Adv.* **4** 49879
17. de Sousa F P C and Serra O A 2009 Red, green, and blue lanthanum phosphate phosphors obtained via surfactant-controlled hydrothermal synthesis *J. Lumin.* **129** 1664
18. Yang P, Quan Z, Li C, Hou Z, Wang W and Lin J 2009 Solvothermal synthesis and luminescent properties of monodisperse LaPO_4 : Ln (Ln = Eu^{3+} , Ce^{3+} , Tb^{3+}) particles *J. Solid State Chem.* **182** 1045
19. Wu C Z, Xie Y, Lei L Y, Hu S Q and Ouyang C Z 2006 Synthesis of new-phased VOOH hollow “dandelions” and their application in lithium-ion batteries *Adv. Mater.* **18** 1727
20. Huong D T M, Trang L T, Vu L V and Long N N 2014 Structural and optical properties of terbium doped lanthanum orthophosphate nanowires synthesized by hydrothermal method *J. Alloys Compd.* **602** 306
21. Di W, Li J, Shirahata N, Sakka Y, Willinger M G and Pinna N 2011 Photoluminescence, cytotoxicity and in vitro imaging of hexagonal terbium phosphate nanoparticles doped with europium *Nanoscale* **3** 1263
22. Li G, Li L, Li M, Song Y, Zou H, Zou L, Xu X and Gan S 2012 Facile synthesis and luminescent properties of LaPO_4 : Eu^{3+} , Sm^{3+} nanorods via a designed two-step hydrothermal method *Mater. Chem. Phys.* **133** 263
23. Yan B and Xiao X 2010 Hydrothermal synthesis, microstructure and photoluminescence of Eu^{3+} -doped mixed rare earth nano-orthophosphates *Nanoscale Res. Lett.* **5** 1962
24. Zhong S L, Luo L F, Wang L and Zhang L F 2012 DyPO_4 flower-like superstructures and macroporous microstructures from dysprosium-based coordination polymer wires *Powder Technol.* **230** 151
25. Xu Z, Li C, Cheng Z, Zhang C, Li G, Peng C and Lin J 2010 Self-assembled 3D architectures of lanthanide orthoborate: hydrothermal synthesis and luminescence properties *CrystEngComm* **12** 549
26. Lu G, Li C and Shi G 2007 Synthesis and characterization of 3D Dendritic Gold Nanostructures and their use as substrates for surface-enhanced Raman scattering *Chem. Mater.* **19** 3433
27. Qian H, Lin G, Zhang Y, Gunawan P and Xu R 2007 A new approach to synthesize uniform metal oxide hollow nanospheres via controlled precipitation *Nanotechnol.* **18** 1
28. Son K J, Yoon H J, Kim J H, Jang W D, Lee Y and Koh W G 2011 Photosensitizing hollow nanocapsules for combination cancer therapy *Angew. Chem. Int. Ed.* **50** 11968
29. Tang S, Huang X, Chen X and Zheng N 2010 Hollow mesoporous zirconia nanocapsules for drug delivery *Adv. Funct. Mater.* **20** 2442
30. Yang D P, Chen S, Huang P, Wang X, Jiang W, Pandoli O and Cui D 2010 Bacteria-template synthesized silver microspheres with hollow and porous structures as excellent SERS substrate *Green Chem.* **12** 2038
31. Liu J, Hartono S B, Jin Y G, Li Z, Lu G Q and Qiao S Z 2010 A facile vesicle template route to multi-shelled mesoporous silica hollow nanospheres *J. Mater. Chem.* **20** 4595
32. Feng S, Ren Z, Wei Y, Jiang B, Liu Y, Zhang L, Zhang W and Fu H 2010 Synthesis and application of hollow magnetic graphitic carbon microspheres with/without TiO_2 nanoparticle layer on the surface *Chem. Commun.* **46** 6276
33. Wang L, Zhang L F, Zhong S L and Xu A W 2012 Highly uniform CeO_2 hierarchical microstructures: Facile synthesis and catalytic activity evaluation *Appl. Surf. Sci.* **263** 769
34. Jia G, You H P, Liu K, Zheng Y, Guo N and Zhang H 2010 Highly uniform Gd_2O_3 hollow microspheres: Template-directed synthesis and luminescence properties *Langmuir* **26** 5122
35. Riccardi C S, Lima R C, dos Santos M L, Bueno P R, Varela J A and Longo E 2009 Preparation of CeO_2 by a simple microwave-hydrothermal method *Solid State Ion.* **180** 288
36. Huang S, Wang D, Wang Y, Wang L, Zhang X and Yang P 2012 Self-assembled three-dimensional $\text{NaY}(\text{WO}_4)_2$: Ln^{3+} architectures: Hydrothermal synthesis, growth mechanism and luminescence properties *J. Alloys Compd.* **529** 140
37. Yi Z, Lu W, Qian C, Zeng T, Yin L, Wang H, Rao L, Liu H and Zeng S 2014 Urchin-like Ce/Tb co-doped GdPO_4 hollow spheres for in vivo luminescence/X-ray bioimaging and drug delivery *Biomater. Sci.* **2** 1404
38. Natarajan S, Mandal S, Mahata P, Rao V K, Ramaswamy P, Banerjee A, Paul A K and Ramya K V 2006 The use of hydrothermal methods in the synthesis of novel open-framework materials *J. Chem. Sci.* **118** 525
39. Gangu K K, Dadhich A S and Mulkamala S B 2015 Hydrothermal synthesis, crystal structure and luminescence property of a three dimensional $\text{Sm}(\text{III})$ coordination polymer with 2,5-pyridinedicarboxylic acid *J. Chem. Sci.* **127** 2225
40. Ghosh P and Patra A 2008 Crystal Phase, shape and luminescence properties of LaPO_4 : Eu^{3+} nanocrystals *J. Nanosci. Nanotechnol.* **8** 3458
41. Yu C, Yu M, Li C, Liu X, Yang J, Yang P and Lin J 2009 Facile sonochemical synthesis and photoluminescent properties of lanthanide orthophosphate nanoparticles *J. Solid State Chem.* **182** 339
42. Runowski M, Grzyb T, Zep A, Krzyczkowska P, Gorecka E, Giersig M and Lis S 2014 Eu^{3+} and Tb^{3+} doped LaPO_4 nanorods, modified with a luminescent organic compound, exhibiting tunable multicolour emission *RSC Adv.* **4** 46305
43. Lee M H and Jung W S 2013 Hydrothermal Synthesis of LaCO_3OH and Ln^{3+} -doped LaCO_3OH powders under ambient pressure and their transformation to $\text{La}_2\text{O}_2\text{CO}_3$ and La_2O_3 *Bull. Korean Chem. Soc.* **34** 3609
44. Gupta S K, Ghosh P S, Sahu M, Bhattacharyya K, Tewari R and Natarajana V 2015 Intense red emitting monoclinic LaPO_4 : Eu^{3+} nanoparticles: host-dopant energy transfer dynamics and photoluminescence properties *RSC Adv.* **5** 58832
45. Han J, Wang L and Wong S S 2014 Morphology and dopant-dependent optical characteristics of novel composite 1D and 3D- based heterostructures of CdSe nanocrystals and LaPO_4 : Re (Re = Eu, Ce, Tb) metal phosphate nanowires *RSC Adv.* **4** 34963

46. He F, Yang P, Wang D, Li C, Niu N, Gai S and Zhang M 2011 Preparation and up-conversion luminescence of hollow La_2O_3 : Ln (Ln = Yb/Er, Yb/Ho) microspheres *Langmuir* **27** 5616
47. Wei F, Cao C, Huang P and Song W 2015 A new ion exchange adsorption mechanism between carbonate groups and fluoride ions of basic aluminum carbonate nanospheres *RSC Adv.* **5** 13256
48. Ferhi M, Naifer K H and Ferid M 2009 Combustion synthesis and luminescence properties of LaPO_4 : Eu (5%) *J. Rare Earths* **27** 182
49. Begun G M, Beall G W, Boatner L A and Gregor W J 1981 Raman spectra of the rare earth orthophosphates *J. Raman Spectrosc.* **11** 273
50. Ladol L, Khajuria H, Sheikh H N and Khajuria Y 2016 Synthesis and characterization of bi-functional magneto luminescent $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{NaLuF}_4$: Eu^{3+} hybrid core/shell nanospheres *J. Chem. Sci.* **128** 1149
51. Yang M, You H, Liang Y, Xu J, Lu F, Dai L and Liu Y 2014 Morphology controllable and highly luminescent monoclinic LaPO_4 : Eu^{3+} microspheres *J. Alloys Compd.* **582** 603