Preparation and Optical Properties of La₃PO₇:Eu³⁺ Nanophosphors Synthesized by Combustion Method

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Eu³⁺ doped La₃PO₇ nanoparticles were successfully synthesized under facial combustion method. The nano-phosphors then were characterized by some techniques including X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), photoluminescence spectrum (PL), and lifetime decay. SEM and TEM micrographs reveal exhibit of the La₃PO₇: Eu³⁺ nanophopwers in spherical morphology with an average size of about 20 nm, matching with Scherrer’s formula calculation. Otherwise, the influence of annealing temperature and concentration of Eu³⁺ ions on optical characteristics of Eu³⁺ was doped La₃PO₇, and optical properties were investigated too. The photoluminescence shows the strong red emission originating from the 5D₀ → 7F₂ transition of Eu³⁺ and the 614 nm emission from the ⁵D₀ → ⁷F₂ electronic dipole transition is dominant. [doi:10.2320/materials.MT-MN2019027]

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1. Introduction

Phosphates of rare-earth ions have a wide range of potential applications because of their unique properties such as excellent luminescence and potential applications in luminescent devices. Primarily, applications focus on display equipment including lighting, field emission display (FED), cathode ray tubes (CRT), plasma display panels (PDP), biochemical probes, and catalysts. In recent studies about these materials, many factors affect to the luminescence including particular size, morphology, crystallization, local symmetry, growth mechanism, doped proportion, and synthesis methods. In the La₅O₇-P₂O₃ system, there are seven intermediate compounds were suggested, i.e., La₅PO₁₀, La₃PO₇, La₃P₂O₁₈, LaPO₄, La₃P₄O₁₃, La₅P₂O₉, and La₅P₄O₁₄. Among them, nano La₃PO₇ materials are of great interest. In 2004, LiXinYu and HongweiSong incorporated Eu³⁺ on LaPO₄ by the hydrothermal method. On the other way, Ivice Vujcic and Tarama Gavrilovic prepared this material by the solid-state way in 2018. As an activator, the Eu³⁺ ion has been investigated frequently due to its excellent fluorescent properties. In practical applications, the characteristic emission from La(NO₃)₃: Eu³⁺ is composed of almost equal contributions from the ⁵D₀ → ⁷F₁ and the ⁵D₀ → ⁷F₂ transitions. Therefore, La₅PO₇: Eu³⁺ is an orange-red emission material instead of red colour purity. This changing depends on the crystal symmetry of the matrix. If the Eu³⁺ ions occupy the sites together inversion centers such as La₅PO₇: Eu³⁺, orange emission transition from ⁵D₀ → ⁷F₁ of Eu³⁺ is dominant. As a result, pure red luminescence of ⁵D₀ → ⁷F₂ can obtain when Eu³⁺ occupies a site without an inversion center. Similarily, S. Lu and Y. Jin has demonstrated these special properties of La₅PO₇: Eu³⁺ nanomaterial. Compound La₅PO₇ is a monoclinc structure, and the Eu³⁺ ion in this host lattice has no inversion symmetry. This phosphor warrants strong red fluorescence derived from ⁵D₀ → ⁷F₂ transition of Eu³⁺ upon UV excitation 266 nm.

However, there has been lacking the number of research on La₅PO₇ material until now. For a deeper understanding of this compound, we did an overcome of study in La₅PO₇: Eu³⁺ nanoparticles. In that, there are some methods for making the materials such as solid phase and co-precipitation and combustion method also were completion. In the study, red phosphor La₅PO₇: Eu³⁺ has been prepared by the combustion method. The photoluminescence (PL) emission intensity of Eu³⁺ ions depended on annealing temperature and concentration of the Eu³⁺ ions. All the results reveal that La₅PO₇: Eu³⁺ is a promising red-emitting phosphor for potential applications.

2. Experimental

La₅O₇ (Aldrich 99.99%), Eu₂O₃ (Aldrich 99.99%), HNO₃ (Merck, PA), (NH₄)₂HPO₄ (Merck, PA) were used as starting materials. La(NO₃)₃ and Eu(NO₃)₃ were prepared by dissolving La₂O₃ and Eu₂O₃ in nitric acid. LA₅O₇(NO₃)₃ was obtained from La(NO₃)₃ and Eu(NO₃)₃, with an appropriate ratio. Meanwhile, (NH₄)₂HPO₄ is a phosphorus source. The ratio of La(NO₃)₃ to (NH₄)₂HPO₄ was undoubtedly controlled to prevent the formation of other phases during the combustion process. Urea has been used as an organic fuel for combustion. Firstly, the mixing of La(NO₃)₃ and Eu(NO₃)₃ in a suitable ratio was heated at 80°C until drained condition. Then, add 5 mL distilled water and the appropriate amount urea, stirring for 30 min. Secondly, (NH₄)₂HPO₄ was added, vigorously stirring for 60 min at 50°C. Finally, the solution was heated until a lot of white gel. This precursor was calcined at 500, 600, 700,
800, and 900°C for 1 h in the air. In this process, the urea was oxidized by nitrate ions.

The crystalline structure was obtained on an Advance Bruker D8 X-ray diffractometer using Cu Kα radiation resource (λ = 1.5406 Å), and the scan range was set from 20° to 80° (2θ) with a step of 0.03°. The thermal decomposition of precursor samples was investigated by simultaneous thermogravimetry and differential thermal analysis (TG-DTA) on a TG-DTA/DSC (France) instruments in the air with a heating rate of 10°C min⁻¹ from room temperature to 900°C in Vietnam Academy of Science and Technology. The morphology of the final product was examined using a scanning electron microscope (SEM) (HITACHI S-4800). Excitation and emission spectra were determined by a Cary Eclipse fluorescence spectrophotometer equipped with an 80 Hz xenon lamp as the excitation source.

3. Results and Discussion

For understanding the chemical reaction occurring during the calcination, thermal decomposition of the precursor samples was recorded by TG-DTA technique. Figure 1 demonstrated four weight-loss stages in the TG curve from 20 to 1000°C, indicated degradation of the precursor samples and the formation of La₃PO₇. In details, in range of 20–130°C, the first weight loss of 10.8 mass% due to the evaporation of water, similar to endothermal peak, recorded at 122.3°C on the DTA curve. Otherwise, the second step of weight loss (9.4 mass%) with an exothermal peak at 150°C revealed excessive urea burning with oxygen. Finally, the third step of weight loss (52.5 mass%) with two endothermal peaks at 240 and 321.7°C can be contributed by the decomposition of ammonium dihydrogen phosphate, ammonium nitrate, respectively. Beside, an exothermal peak at 340°C was observed as a result of the burning reaction of the nitrate, (NH₂)₂CO, and oxygen.

The crystal phase of La₃PO₇:Eu³⁺ nanoparticles was investigated by X-ray diffraction (XRD) using a Cu target radiation resource (λ = 1.5406 Å). Figure 2 shows the XRD pattern of La₃PO₇: Eu³⁺ phosphors particles using various annealing temperatures at 500, 600, 700, 800, and 900°C. The results pointed out that nanopowders showing in good crystallinities with a pure monoclinic phase, according to the results of JCPDS card 49-1023. Their lattice parameters are a = 13.085 Å, b = 13.585 Å, and c = 12.429 Å, respectively. When annealing temperature increased, the diffraction peaks became little by little narrow, sharp, and increased. There were no unwanted diffraction peaks in the XRD patterns. This proved that Eu³⁺ ions incorporated into La₃PO₇ completely. This result was perfectly agreement with reports of Bing Yan and Jianfeng Gu (2009).¹²) The grains size (D) of La₃PO₇: Scherrer’s formula calculated Eu³⁺ nanoparticles:

\[
D = \frac{0.891}{\beta \cos \theta}
\]

Where β is the full width in radians at half-maximum (FWHM) of the peak at 2θ = 29.04°, and θ is the Bragg angle of the XRD peak.
The grain size of La$_3$PO$_7$: Eu$^{3+}$ phosphors particles slightly increased when annealing temperatures increased. These sizes were 7, 9, 11, 18, and 23 nm for annealing temperatures of 500, 600, 700, 800, and 900°C, respectively.

The surface morphology of La$_3$PO$_7$: 5 mol% Eu$^{3+}$ nano-crystals annealing at 500, 800, and 900°C were recorded by the SEM images (Fig. 3). It can be seen the La$_3$PO$_7$: 5 mol% Eu$^{3+}$ particles prepared by the combustion method have an almost spherical shape, smooth surface, well-order in the range of 10–20 nm. The morphology of La$_3$PO$_7$: 5 mol% Eu$^{3+}$ with monoclinic phase is present similar characteristics to La$_3$PO$_7$: Eu$^{3+}$ particles like works of Ye Jin and co-worker.\(^\text{11}\)

Figure 4 showed the representative HR-TEM images of La$_3$PO$_7$: 5 mol% Eu$^{3+}$ nanoparticles. In that, Fig. 4(a) showed an aggregate composed of many nanoparticles. The sample was composed of relatively well-order monoclinic particles while the size of the average nanoparticles is about 18–20 nm. This matches the average crystallite with the XRD line profile analysis. The crystal planes of the nanoparticle found in Fig. 4(b). The interplanar distance is determined to be 0.306 nm, which corresponds to the (411) crystal plane of monoclinic La$_3$PO$_7$. This result confirms that the samples are of high purity, and the material obtained in nanometer size.

The photoluminescence excitation spectrum (PLE) by monitoring the emission at 614 nm was performed in Fig. 5. All of the curves behave very similar characters. The PLE spectra revealed broadband and some sharp peaks. A band extended from 200 to 300 nm comes from the transition induced by charge transfer. On the other hand, the broad group is assigned to electron delocalization from an oxygen 2p orbital to an empty 4f orbital of Europium ions. The sharp lines are attributed to the f-f transitions of Eu$^{3+}$ ion corresponding to $^7F_0 \rightarrow ^5D_1$ at 319 nm, $^7F_0 \rightarrow ^5D_2$ at 382 nm, $^7F_0 \rightarrow ^5D_3$ at 413 nm, $^7F_0 \rightarrow ^5D_4$ at 532 nm, $^7F_0 \rightarrow ^5D_5$ at 465 nm and $^7F_0 \rightarrow ^5D_6$ at 532 nm.\(^\text{13}\)

**Annealing temperature dependence of La$_3$PO$_7$ phosphor emission**

Under 266 nm laser excitation, emission spectra of the annealed samples were recorded at different temperatures 500, 600, 700, 800, 900°C (see in Fig. 6). Collected spectra are composed of several sharp lines, ascribed to the $^5D_0 \rightarrow ^7F_0$ 578 nm, $^5D_0 \rightarrow ^7F_1$ 591 nm, $^5D_0 \rightarrow ^7F_2$ 614 nm, $^5D_0 \rightarrow ^7F_3$ 653 nm and $^5D_0 \rightarrow ^7F_4$ 702 nm. Although the main peak positions are identical to each other, the intensity peaks are different. In these samples, the intensity of emission transition $^5D_0 \rightarrow ^7F_2$ of Eu$^{3+}$ is stronger than $^5D_0 \rightarrow ^7F_1$. It was well known that Eu$^{3+}$ is sensitive to local symmetry. According to the rules of selection, the magnetic dipole transition is permitted, and the electric dipole transition is forbidden. The red emission at 614 nm from $^5D_0 \rightarrow ^7F_2$ transition is a typical electronic dipole transition, while the orange emission at 591 nm from $^5D_0 \rightarrow ^7F_1$ transition indicates an ideal magnetic dipole transition. When Eu$^{3+}$ ion occupies the site with the inversion center, the $^5D_0 \rightarrow ^7F_1$ transition would be relatively strong, whereas the $^5D_0 \rightarrow ^7F_2$ transition is forbidden and very weak. As shown in Fig. 6, the $^5D_0 \rightarrow ^7F_1$ transition is prominent in all change, that means Eu$^{3+}$ ion occupied at the site without inversion symmetry. As a consequently, the study all matches to previous publications (Wei-Ning Wang\(^\text{14}\) and Bing Yan\(^\text{12}\)).
Concentration dependence of La$_3$PO$_7$ phosphor emission

Figure 7 indicated the emission intensities’ dependence on different Eu$^{3+}$ concentrations in La$_3$PO$_7$: Eu$^{3+}$ samples annealed at 800°C. The red emission intensity increases with increasing Eu$^{3+}$ level from 1 to 7 mol\% and then begins to decrease with the Eu$^{3+}$ increasing concentration to 9 mol\%.

In the initial stage, an increase in doped concentration, the number of luminescent centers increases. However, when the Eu$^{3+}$ concentration continues increasing, the internuclear distance of Eu$^{3+}$–Eu$^{3+}$ is reduced. In other words, the distance of luminescence centers decreases, that causes the non-radiative energy migration. Since the non-radiative transition occurred, the concentration of Eu$^{3+}$ ions has reached a value of 9 mol\%. That changing is called the concentration quenching. The dependence of the ratio of the relative intensity of $^5$D$_0$ → $^7$F$_2$ (614 nm) to $^5$D$_0$ → $^7$F$_1$ (591 nm) on Eu$^{3+}$ concentrations points out inset of Fig. 7. This ratio rises with increasing Eu$^{3+}$ concentration from 1 to 5 mol\% and then begins to decrease with the Eu$^{3+}$ concentration approaching 7 mol\%.

The normalized luminescence decay curves for $^5$D$_0$ → $^7$F$_2$ of Eu$^{3+}$ in La$_3$PO$_7$:5 mol\% Eu$^{3+}$ excited at 266 nm and monitored at 614 nm are shown in Fig. 8. It can be well fitted into double-exponential function with the equation:

$$I = A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right).$$

Where, $I$ present to the emission intensity at time $t$, $\tau_1$ and $\tau_2$ are respectively the fast and slow constituent of luminescence lifetimes, $A_1$ and $A_2$ are the fitting parameters. The fitting results are listed in Table 1.

The equation $\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$ was applied to calculate the average lifetime of Eu$^{3+}$ for $^5$D$_0$ → $^7$F$_2$ emission. It can also see that there is a decrease in the emission lifetime value from 0.826 ms to 0.760 ms when the Eu$^{3+}$ ions concentration increases from 1 to 9 mol\%. This is explained that, if the Eu$^{3+}$ ions concentration increases in the lattice, the distances of Eu$^{3+}$–Eu$^{3+}$ internuclear will be reduced; leading to the extent of Eu$^{3+}$–Eu$^{3+}$ interaction would be increased. Thus, in the excited state, the energy transfer among different Eu$^{3+}$ ions follows by non-radiative decay. It causes a decrease in the excited state lifetime corresponding to $^5$D$_0$ level of Eu$^{3+}$ ions.

4. Conclusion

In summary, La$_3$PO$_7$: Eu$^{3+}$ nanoparticles were success-
fully obtained via sample synthesis by a facial combustion method. Size and morphology characteristics of the La$_3$PO$_7$: Eu$^{3+}$ nanoparticles were studied using X-ray, TEM, HR-TEM, and luminescence spectroscopy. The diffraction peaks of XRD are in good agreement with the results of JCPDS card No 49-1023 analysis with the monoclinic phase. The average size of nanoparticles, which is investigated by XRD, SEM, HR-TEM, is about 20 nm. Under 266 nm wavelength excitation, the emission intensities considerably improved with increase the annealing temperature of samples. The samples gained under 800°C exhibit a strong red emission at 614 nm, attributing to the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$. The red emission intensity of samples rose when the concentration of Eu$^{3+}$ ions increased from 1 to 7 mol% then decreased for the higher concentrations. The intensity ratio of $^5D_0 \rightarrow ^7F_2$ transition and $^5D_0 \rightarrow ^7F_2$ transition reached the maximum for 5 mol% Eu$^{3+}$-doped La$_3$PO$_7$ sample. Therefore, the best doping concentration of Eu$^{3+}$ in La$_3$PO$_7$ is determined to be 5 mol%. The lifetime curve of La$_3$PO$_7$: Eu$^{3+}$ nanophosphors can be well-fitted into a single exponential function. The lifetime of $^5D_0 \rightarrow ^7F_2$ transition decreased gradually with the increase of Eu$^{3+}$ ions concentration.

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**REFERENCES**


**Table 1** Decay lifetime of La$_3$PO$_7$:x mol%Eu$^{3+}$ nanopowders (x = 1, 3, 5, 7, 9).

<table>
<thead>
<tr>
<th>x (%)</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
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<td>$\lambda_1$</td>
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<tr>
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