Synthesis and Photoluminescent properties of Eu$^{3+}$ doped LaPO$_4$ nanophosphors

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Abstract
LaPO$_4$ and LaPO$_4$:xEu$^{3+}$ (x=0.1, 0.5, 1.0, 1.5, 2.0 mol %) phosphors were synthesized by the solid-state reaction method. X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL) spectra and the particle size analysis were used to characterize these samples. The XRD results reveal that the synthesized LaPO$_4$:Eu$^{3+}$ phosphors are well crystalline and assigned to the monoclinic structure with a main (120) diffraction peak. The crystallite size was estimated by using the Scherrer formula, and 62 nm size was obtained for LaPO$_4$:Eu$^{3+}$ phosphor and 67.6 nm for LaPO$_4$. Upon excitation at 254 nm, the LaPO$_4$: Eu$^{3+}$ phosphor emits the characteristic $^5$D$_{0}$$rightarrow$$^7$F$_{2}$ emission lines of Eu$^{3+}$. The emission spectra of LaPO$_4$:Eu$^{3+}$(1.5 mol %) phosphor under excitation at 254 nm exhibited two strong intense band at 589 nm and 594 nm with maximum intensity and the energy difference between the two peaks was 0.02 eV. From the emission spectra the emission transition $^5$D$_{0}$$rightarrow$$^7$F$_{2}$ has been found to be more prominent over the normal red emission transition $^5$D$_{0}$$rightarrow$$^7$F$_{1}$. The observed absorption frequencies are reported from the measured FTIR spectra. Scanning electron microscopic investigations are carried out to understand the surface morphological features and grain size. Commission international de l’éclairage (CIE) co-ordinates of samples revealed that the emission varies from blue to red with increasing of Eu concentration.

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Key words: Photoluminescence; XRD; SEM; FTIR; phosphor; rare-earth ions; solid state reaction technique; CIE; particle size analysis.

1. Introduction
Lanthanide compounds have been extensively used as optoelectronic devices, magnets, catalysts, and biological fluorescence labeling because of their special optical, electronic, and chemical properties resulting from the 4f electron configurations [1-5]. In recent years, lanthanide orthophosphates (LnPO$_4$) have attracted much interest in the potential applications as phosphors, proton conductors, sensors, catalysts, ceramic materials, and heat-resistant materials [6] based on their interesting properties, such as low water solubility [7], high thermal stability [8], a high index of refraction, and high concentrations of losing ions [9], and so on [10-13]. The luminescent properties of rare-earth phosphates can be conferred by the presence of lanthanide(III) ions as activators due to their intense and narrow emission bands arising from f-f transitions, which are proper for the generation of individual colours in multiphosphor devices [14-16]. So, the red $^5$D$_{0}$$rightarrow$$^7$F$_{2}$ (610 nm), green $^3$D$_{2}$$rightarrow$$^5$F$_{3}$ (545 nm) and blue $^1$D$_{2}$$rightarrow$$^5$F$_{4}$ (450 nm) emissions of Eu$^{3+}$, Tb$^{3+}$ and Tm$^{3+}$, respectively, can be used for the design of novel phosphors [17]. LaPO$_4$ is a well-known host used to elaborate the luminescent materials for lighting phosphors [18], optical amplifiers and lasers [19] as well as for the other applications. It is known that the LaPO$_4$ has a monoclinic phase of monazite structure crystallographically, wherein La$^{3+}$ ion is nine coordinated to oxygen atoms, four oxygens forming a distorted tetrahedron interpenetrating a quasiplanar pentagon formed by other five [20]. The La$^{3+}$ ion site in the monazite structure can be easily substituted by any other lanthanide ions. Several researchers have reported the syntheses of LaPO$_4$ particles via various methods such as solid-state reaction [21,22], spray pyrolysis [23] or hydrothermal methods [24,25].

In this article, we have studied on the synthesis, size, morphology and photoluminescence of Pure LaPO$_4$ and LaPO$_4$:xEu$^{3+}$ (x=0.1, 0.5, 1.0, 1.5, 2.0 mol %) phosphors prepared by the solid state reaction method in air at
1200°C. Optimization of the concentration of activator ions incorporated into the host lattice during the synthesis of the phosphor powders is essential for developing highly luminescent RE\(^3+\) doped nanoparticle phosphors as well as for the growth of grain particles. Photoluminescence studies and CIE co-ordinates of LaPO\(_4\):xEu\(^{3+}\) (x=0.1, 0.5, 1.0, 1.5, 2.0mol%) phosphors reveal that the emission colour varies from blue to red.

2. Experimental section

Pure LaPO\(_4\) and LaPO\(_4\):xEu\(^{3+}\) (x=0.1, 0.5, 1.0, 1.5, 2.0mol%) phosphor powders were synthesized by using the conventional solid-state reaction method. The formation of the phosphor powders occurs according to the following chemical equation.

\[
\text{La}_2\text{O}_3 + 2\text{NH}_4\text{H}_2\text{PO}_4 \rightarrow 2\text{LaPO}_4 + 2\text{NH}_3\text{OH} + \text{H}_2\text{O}
\]

The starting materials were lanthanum oxide (La\(_2\)O\(_3\)), Diammonium Hydrogen Phosphate (\(\text{NH}_4\text{H}_2\text{PO}_4\)), and Europium oxide (Eu\(_2\)O\(_3\)) of 99.9% purity. They were weighed with a certain stoichiometric ratio. The composite powders were ground in an agate mortar and then placed in an alumina crucible with the lid closed. After the powders had been sintered at 1200°C for 3 hr in a muffle furnace and then cooled to room temperature. All the samples were again ground into fine powder using an agate mortar and pestle about an hour.

The crystalline structure of the products was investigated by using an X-ray diffractometer (PANalytical’s X-ray diffractometers XPert PRO) with Cu Kα radiation. The morphology of the nanoparticles was observed by using a scanning electron microscope (TESCAN VEGA3 SEM) with a tungsten heated filament. The emission and the excitation spectra of the synthesized powders were characterized with a spectrofluorophotometer (Shimadzu RF-5301 PC) with xenon lamp as excitation source. Infrared spectra for the prepared solid nano powders were recorded in the range 400 and 4000 cm\(^{-1}\) on a Fourier-transform spectrometer (Bruker Vector 22 FT-IR Spectrometer). The Commission International de l’Éclairage (CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution. The chromatic coordinates (x, y) of prepared materials were calculated with colour calculator version 2, software from Radiant Imaging [26].

3. Results and Discussions

Fig.1 show the X-ray diffraction (XRD) patterns of synthesized samples of LaPO\(_4\):Eu\(^{3+}\) (1.5mol%) phosphor powder. The XRD spectra consist of three strong peaks and several weak peaks: The three main peaks occur at 2θ = 20=26.86, 28.65 and 31.5°. These peaks correspond to the diffractions from the (200), (120), and (012) planes of LaPO\(_4\) respectively. The relatively weak peak multiplets centered at 21.3, 34.3, 42 and 48.23° are attributed to the diffraction from the (111), (202), (311), and (132) planes, respectively. The intensity of peaks reflected the high degree of crystallinity of the nanoparticles. However, the diffraction peaks are broad which indicates that the crystalline size is very small. All the diffraction peaks could be well indexed to JCPDS, 84-0600, which indicated a monoclinic structure LaPO\(_4\) (space group P2\(_1\)/n) with a main diffraction peak (120). No spurious diffractions due to crystallographic impurities are found.

The average particle size has been estimated by using the Debye-Scherrer formula D = 0.9 λ / β cosθ, where λ is the wavelength of the X-ray (λ = 1.54A\(^{-1}\)), β is FWHM (full width at half maximum), θ is the diffraction angle and D is the particle diameter size. The average size of a particle of pure LaPO\(_4\) phosphor and LaPO\(_4\):Eu\(^3+\) phosphor is 67.6nm and 62nm respectively. This confirms the formation of nano crystalline size phosphor, via solid state reaction method. Unit cell parameters values calculated from XRD are enumerated in the table-land observed that the cell volume of pure and doped LaPO\(_4\) is slightly more than standard volume. Fig. 2(a) is a typical SEM image of the morphology of the synthesized nanoparticles. It was observed in the picture that the mean size of the pure LaPO\(_4\) is about 0.2-2.0µm and the shape is nearly spherical [18]. In addition, it indicates that the particles in powder form seem to cluster. The grain sizes of the samples estimated from the SEM picture is larger than that obtained from XRD analysis. The observation of some larger nanoparticles may be attributed to the fact that the nanoparticles have the tendency to agglomerate due to their high surface energy. From Fig. 2(b), the SEM micrograph, the mean size of LaPO\(_4\):Eu\(^{3+}\) phosphor is about 1.5µm.

FTIR analysis was carried out to determine the chemical bonds in a molecule. The FTIR spectrum of LaPO\(_4\):Eu\(^{3+}\) phosphor is shown in Fig.3. It had been reported that the PO\(^4\)\(_{3-}\) should have C\(_3\) symmetry, including two (v\(_3\) and v\(_4\)) vibrational modes, one in the monoclinic LaPO\(_4\) [27]. The v\(_3\) vibration corresponds to the phosphate P-O stretching. The v\(_4\) vibration corresponds to the O=P-O bending and O-P-O bending modes.

The peaks appearing at 534–613 cm\(^{-1}\) and 957–1096 cm\(^{-1}\) correspond to the bending vibrations (v\(_3\) region) and stretching vibrations (v\(_1\) region) of PO\(^4\)\(_{3-}\) group, respectively. Characteristic bands at 534cm\(^{-1}\) and 579cm\(^{-1}\) are evident in the v\(_1\) vibration region. Characteristic bands at 957cm\(^{-1}\), 993cm\(^{-1}\) and 1096cm\(^{-1}\) belong to the v\(_3\) vibration region [28]. Split bands in the v\(_3\) region are characteristic of the monoclinic LaPO\(_4\) phase [29]. The vibration spectrum gives a conclusive evidence for monoclinic-phase formation in lanthanum phosphate. The absorption bands at 3608 and 2009cm\(^{-1}\) can be assigned to physical adsorbed OH and H\(_2\)O.

The Particle size distribution histograms of LaPO\(_4\):Eu\(^{3+}\) phosphor particles synthesized using the solid state reaction method is illustrated in fig.4. The mean particle size is 1.69µm.

3.2. Photoluminescence behaviour of LaPO\(_4\) and LaPO\(_4\):xEu\(^{3+}\) (x=0.1, 0.5, 1.0, 1.5, 2.0mol%) phosphors

A series of LaPO\(_4\):xEu\(^{3+}\) (x=0.1, 0.5, 1.0, 1.5, 2.0mol%) phosphors heated at 1200°C were prepared and the effect of Eu\(^{3+}\) concentration on the emission intensity was investigated. Fig.5 (a) exhibits the PL excitation and emission spectra of pure LaPO\(_4\) phosphor. In the excitation spectrum monitored under 400nm wavelength, the broadband ranging from 220-390nm with peaks at 249nm and 362nm. The shape of the emission spectra and emission...
Figure 1. XRD of LaPO$_4$ and LaPO$_4$:Eu(1.5mol%)

Table1 Unit cell lattice constants of the sample powders

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>β angle (deg)</th>
<th>Cell volume (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JCPDS 84-0600</td>
<td>0.6825</td>
<td>0.7057</td>
<td>0.64822</td>
<td>103.210</td>
<td>0.3039</td>
</tr>
<tr>
<td>LaPO$_4$ phosphor</td>
<td>0.6827</td>
<td>0.70477</td>
<td>0.63968</td>
<td>103.210</td>
<td>0.3077</td>
</tr>
<tr>
<td>LaPO$_4$:Eu$^{3+}$ phosphor</td>
<td>0.6837</td>
<td>0.7074</td>
<td>0.6425</td>
<td>103.66</td>
<td>0.3107</td>
</tr>
</tbody>
</table>

Figure 2 SEM images of pure LaPO$_4$ and LaPO$_4$:Eu$^{3+}$(1.5mol%) phosphor
Figure 3  FTIR spectrum of LaPO$_4$:Eu$^{3+}$(1.5 mol%) 

Figure 4  Particle size distribution histogram of LaPO$_4$:Eu$^{3+}$ phosphors 

Figure 5(a)  Excitation and Emission spectrum of LaPO$_4$ phosphor 

Figure 5(b)  Excitation spectrum of LaPO$_4$:Eu$^{3+}$ phosphor
peak wavelength is independent of the excitation wavelengths. Upon excitation at 254 nm, the emission spectrum of pure LaPO₄ phosphor emits a broad band range from 400-760nm with a maximum intensity peak at 400nm, and other peaks at 437, 470, 494, 589, 612, and 727 nm as shown in fig. 5a. Fig.5(b) exhibits the PL excitation spectra of LaPO₄:Eu³⁺ phosphor. In the excitation spectrum monitored by the Eu³⁺ ⁵D₀→⁷F₂ transition at 612 nm wavelength, the broadband, ranging from 220-450 nm with maximum peak at 265 nm originates from the excitation of the oxygen-to-europium charge transfer band (CTB). The weak line at 396 nm may arise from f-f transitions within the Eu³⁺ ⁴f₆ electron configuration [30] which corresponds to the direct excitation of the Eu³⁺ ground state into higher levels of the 4f manifold (⁵F₀→⁷L₆).

Fig.5(c) show the emission spectrum of LaPO₄:xEu³⁺ (x=0.1, 0.5, 1.0, 1.5, 2.0 mol %) phosphor under 254 nm excitation wavelength. The shape of the emission spectra and emission peak wavelength is independent of the excitation wavelengths. Upon excitation at 252 nm, the emission spectra displays the bands associated with the ⁵D₀→⁷F₉ (J=1, 2, 3, 4) electronic transitions characteristics of the Eu³⁺ ion at a position. Among them, the ⁵D₀→⁷F₇ transitions are the strongest and is characterized by an orange–red emission. The ⁵D₀→⁷F₁ lines originate from the magnetic dipole transition, while the ⁵D₀→⁷F₂ lines originate from the electric dipole transition [31]. The electric dipole transition is allowed only on the condition that the Eu³⁺ ion occupies a site without inversion centre and is sensitive to local symmetry, which induces the relatively strong of ⁵D₀→⁷F₁ transition and the relatively weak of ⁵D₀→⁷F₂ transition. The emission spectra of LaPO₄:xEu³⁺ (x=0.1, 0.5, 1.0, 1.5, 2.0 mol %) particles, the exhibits lines in orange at 589 and 594 nm, both peaks correspond to the magnetic dipole transitions (⁵D₀→⁷F₁) and much stronger than the lines in red at 614 and 622 nm (⁵D₀→⁷F₂) emission. Therefore, it is inferred that the Eu³⁺ ions in samples located a site with inversion symmetry.

4. Conclusions
Pure LaPO₄ and LaPO₄:Eu³⁺ (x=0.1, 0.5, 1.0, 1.5, 2.0 mol %) phosphor powders were successfully synthesized by the high temperature solid state reaction method. The XRD results reveal that the synthesized samples phosphors are well crystalline and assigned to the monoclinic crystal structure with a main (120) diffraction peak. No spurious diffractions due to crystallographic impurities are found. The width of diffraction peaks is broadened because of the small size of the crystallites. The grain sizes of the samples estimated from the SEM picture is larger than that obtained from XRD data. This means that, the SEM picture indicates the size of polycrystalline particles. The mean particle size of the LaPO₄:Eu³⁺ 1.5 mol%Eu³⁺ phosphor samples determined from distribution histograms was 1.69 μm. LaPO₄:xEu³⁺ (x=0.1, 0.5, 1.0, 1.5, 2.0 mol %) phosphor powders exhibits the characteristic emission lines of Eu³⁺. And also exists energy transfer process between LaPO₄ and Eu³⁺ ion. The Stoke shift and the FWHM of the emission were characteristic of a ligand-to-metal charge transfer(CT) emission. The Commission International de l’Eclairage [CIE] co-ordinates of pure LaPO₄ phosphor exhibit the excellent colour tunability of blue, and LaPO₄: 1.5 mol%Eu³⁺ phosphor reveals that the emission varies from blue to red, making the material a potential candidate for advanced display devices.

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References

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