Synthesis, Structure and Photoluminescent properties of LaPO₄:Er³⁺ nanophosphor

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Abstract

LaPO₄:Er³⁺ (0.5 mol %) nanophosphor was synthesized by the conventional 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 the LaPO₄:Er³⁺ nanophosphor. The XRD results reveal that the synthesized LaPO₄:Er³⁺ phosphor is well crystalline and assigned to the base centered monoclinic structure with a main (120) diffraction peak. The calculated crystallite size of LaPO₄:Er³⁺ phosphor is 64.12nm. The excitation spectrum of LaPO₄:Er³⁺ nanophosphor monitored under 400nm wavelength was characterized by a broad band ranging from 220-400nm with a maximum intensity peak at 246nm (5.04eV). Upon excitation at 254nm wavelength, the emission spectrum of LaPO₄:Er³⁺ nanophosphor emits a broad band range from 400-650nm with maximum intensity peak at 469(blue) nm (2.64eV). The color coordinates for the LaPO₄:Er³⁺ (0.5 mol %) nanophosphor are x=0.1727 and y= 0.0048. This phosphor is having excellent colour tunability of blue light.

Key words: Photoluminescence; XRD; FTIR; nanophosphor; rare-earth ions; solid state reaction method; CIE.

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1. Introduction

The optical properties of the lanthanides in inorganic compounds, their preferred valence, and their electron donating or accepting properties are all determined by the electronic structure, i.e., by the relative and absolute level energies of the lanthanide impurity states and the host conduction and upper valence band states. Rare-earth orthophosphates (REPO₄) are a very interesting class of host lattices of activator ions due to their physical-chemical inercy (high insolubility, high thermal stability), thus providing durable phosphors [1]. Lanthanide ortho-phosphate (LaPO₄) belongs to two polymorphic types, the monoclinic monazite type (for La to Gd) and quadratic xenotime type (for Tb to Lu). The LaPO₄ crystalline matrix is widely used for development of phosphors for compact fluorescent lamps, plasma display panels, field emission display, optical amplifiers, laser active mediums and electrical conduction. Process ability of this material and resistance for atmospheric influence caused the interest to study of the luminescent properties of LaPO₄ nanoparticles. Monoclinic lanthanum phosphate is a compound with extremely low solubility in water, and high thermal and chemical stability; it has been proposed for use in broad applications. 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 [2-4]. Lanthanide orthophosphate (LaPO₄) and lanthanide (III)-doped lanthanide orthophosphate have attracted much attention due to their unique photoluminescent properties and various potential applications in various areas, including color displays, light sources, field-effect transistors, solar cells, and biomedical labels, nanoscintillators for radiotherapy [5,6]. It is known that the LaPO₄ has a monoclinic phase of monazite structure crystallographically, wherein La³⁺ ion is nine coordinated to oxygen atoms, four oxygens forming a distorted tetrahedron interpenetrating a quasiplanar pentagon formed by another five [7-10]. The La³⁺ ion site in the monazite structure can be easily substituted by any other lanthanide ions. To improve luminescent properties of nanocrystalline phosphors, many preparation methods have been used, such as solid state reactions, sol-gel techniques, hydroxide precipitation, hydrothermal synthesis, spray pyrolysis, laser-heated evaporation, and combustion synthesis[11-13].

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In this paper LaPO₄:Er³⁺ (0.5 mol%) nanophosphor was prepared by the solid state reaction method in air at 1200°C, and their luminescent properties were studied. 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 RE³⁺ doped nanocrystalline phosphors as well as for the growth of grain particles. Photoluminescence studies and CIE co-ordinates of LaPO₄:Er³⁺ nanophosphor reveals that the emission colour having excellent colour tunability of blue light so this material may be a potential luminescent material.

2. Experimental

Synthesis:
The LaPO₄:Er³⁺ (0.5 mol %) nanophosphor was synthesized by using the conventional solid-state reaction method. The formation of the phosphor powder occurs according to the following chemical equation.

La₂O₃ + 2 (NH₄)H₂PO₄ + Er₂O₃ → 2LaPO₄: Er (0.5%)

The starting materials were lanthanum oxide (La₂O₃), Diammonium Hydrogen Phosphate [(NH₄)H₂PO₄] and erbium oxide (Er₂O₃) of 99.9% purity. They were weighed with a certain stoichiometric ratio. The composite powders were grinded 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. Finally, the powders were sieved again through 100 µm sieve.

Characterization:
Phase identification was carried out by X-ray diffraction (XRD) using a PAN alytical’s X-ray diffractometers X’Pert PRO, operating at 50 kV and 30mA with a Cu Kα radiation, λ=0.154nm and a Ni filter, in the range 2θ = 15–80°. The step size was 0.05° and the counting time 1.5 s. The morphology of the nanoparticles was observed by using a scanning electron microscope (TESCAN VEGA3 SEM) with a tungsten heated filament. The morphology and the excitation spectra of the synthesized powders were characterized with a spectrofluorophotometer (Shimadzu RF-5301 PC) with xenon lamp as excitation source. The frequencies of the absorption bands were analyzed through Fourier transform infrared spectroscopy (Bruker Vector 22 FT-IR Spectrometer) for the as-prepared material. The pellets used for analysis were made of 0.01 g of the sample powders and 0.3 g of KBr. Infrared spectra for the prepared solid nano powders were recorded in the range between 400 and 4000 cm⁻¹. The Commission International de l’Eclairage (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 [14].

3. Results and Discussions

Crystal structure of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor:
The crystal structure of the obtained product was identified by X-ray diffraction analysis (XRD). Fig.1 and 2 shows the typical X-ray diffraction (XRD) patterns of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor treated at 1200°C. The XRD spectra consist of three strong peaks and several weak peaks. The three main peaks occur at 2θ=26.82, 28.60 and 31°. These peaks correspond to the diffractions from the (200),(120), and (012) planes of LaPO₄:Er³⁺ respectively. The relatively weak multipeaks centered at 21.17, 34.33, 42 and 48.81° 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. All the diffraction peaks could be well indexed to International Centre for Diffraction Data (ICDD) database card number: 84-0600, which indicated a base centered monoclinic phase LaPO₄:Er³⁺ (space group P2₁/n) with a main diffraction peak (120). No spurious diffractions due to crystallographic impurities are found. The XRDA 3.1 software has been used to calculate the lattice parameters. Unit cell parameters values calculated from XRD are enumerated in the Table-1 and observed that the cell volume of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor is slightly more than standard volume [15,16]. Table-2 shows the calculated crystallite size of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor. However, the diffraction peaks are broad which indicating that the crystalline size is very small.

![Figure 1](image-url)
A nanophosphor is formed via solid state reaction method.

The crystallite size was determined by means of the X-ray line broadening method using the Debye-Scherrer equation:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of the X-ray (\( \lambda = 1.54 \text{Å} \) for CuK\( \alpha \)), \( \beta \) is the broadening of the diffraction line measured at half of its maximum intensity (FWHM: full width at half maximum), \( \theta \) is the Bragg's diffraction angle, and \( D \) is the crystallite size. The average crystallite size of LaPO\(_4\):Er\(^{3+}\) (0.5 mol%) nanophosphor 1200\(^\circ\)C is 64.12nm. This confirms the formation of nano crystalline size phosphor, via solid state reaction method. Fig. 3 (a,b) shows the crystal structure of LaPO\(_4\): Er\(^{3+}\) (0.5 mol%) nanophosphor [17-20].

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameters</th>
<th>Bond angle(( \beta ))(deg)</th>
<th>Unit Cell volume(V) (nm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICDD:84-0600</td>
<td>a (nm) 0.6825</td>
<td>0.7057</td>
<td>0.6482</td>
</tr>
<tr>
<td>Prepared Sample: LaPO(_4)</td>
<td>b(nm) 0.6811</td>
<td>0.7047</td>
<td>0.6503</td>
</tr>
<tr>
<td>LaPO(_4):Er(^{3+}) (0.5%) nanophosphor</td>
<td>c (nm) 0.6822</td>
<td>0.7059</td>
<td>0.6512</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>2( \theta ) of intense peak(deg)</th>
<th>(hkl)</th>
<th>FWHM of intense peak (( \beta ) radian)</th>
<th>Crystallite size of particle (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.96846</td>
<td>012</td>
<td>0.1503332</td>
<td>54.8583</td>
</tr>
<tr>
<td>28.60382</td>
<td>120</td>
<td>0.1279431</td>
<td>64.1278</td>
</tr>
<tr>
<td>21.17566</td>
<td>111</td>
<td>0.0879609</td>
<td>91.9183</td>
</tr>
<tr>
<td>26.82407</td>
<td>200</td>
<td>0.0586406</td>
<td>139.3311</td>
</tr>
<tr>
<td>25.21143</td>
<td>020</td>
<td>0.0506442</td>
<td>160.8065</td>
</tr>
</tbody>
</table>

In order to determine the chemical bonds in a molecule, FTIR analysis was carried out. Fig.4 shows the FTIR spectrum of LaPO\(_4\): Er\(^{3+}\) (0.5 mol%) nanophosphor heated.

Figure 2: X-ray powder diffraction pattern of LaPO\(_4\):Er\(^{3+}\) (0.5 mol %) nanophosphor

Figure 3 (a,b): Crystal structure of (a) pure LaPO\(_4\) and (b) LaPO\(_4\): Er nanophosphor

Figure 4: FTIR spectrograph of LaPO\(_4\):Er\(^{3+}\) (0.5 mol %) nanophosphor
The LaPO₄ crystal structure can be easily substituted by any other lanthanide ions. The LaPO₄:Er³⁺ (0.5 mol%) phosphor is having excellent colour tunability of blue light. Therefore, the LaPO₄:Er³⁺ (0.5 mol%) nanophosphor depicted on the 1931 chart shows the most intense emission.

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**Figure 5** Excitation and emission spectra of LaPO₄:Er³⁺ (0.5 mol%) nanophosphor at 1200°C. Most of the bands are characteristic of the vibrations of phosphate groups PO₄³⁻[21]. It had been reported that the PO₄³⁻ should have C₂ᵥ symmetry including two (v₁ and v₂) vibration regions in the monoclinic LaPO₄:Er³⁺ (0.5 mol %) nanophosphor [22]. The v₁ vibration corresponds to the phosphate P-O stretching. The v₂ vibration corresponds to the O= P- O is bending and O-P- O is bending modes. So the characteristics of the monoclinic phase of four bands located at about 538, 563, 577, 618 cm⁻¹ were clearly observed in the v₄ region (bending vibration) of PO₄³⁻ groups vibration. The characteristic bands at 952, 992, 1091 cm⁻¹ belong to the v₃ vibration region. Split bands in the v₃ region are characteristic of the monoclinic LaPO₄:Er³⁺ (0.5 mol%) phosphor phase[23]. The vibration spectra give a conclusive evidence for monoclinic-phase formation in lanthanum phosphate. The peaks at 1271, 1400, 3134 cm⁻¹ can be attributed to the presence of water (stretching vibration of the O-H bond) adsorbed by KBr during the pellet formation.

**Photoluminescence Study of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor:**
Fig. 5 shows PL excitation and emission spectra of LaPO₄:Er³⁺ (0.5 mol%) nanophosphor recorded at room temperature. The excitation spectrum of LaPO₄:Er³⁺ (0.5 mol%) phosphor monitored under 400nm wavelength was characterized by a broad band ranging from 220-400nm with a maximum intensity peak at 246nm. The La³⁺ ion site in the monazite structure can be easily substituted by any other lanthanide ions. The La³⁺ ion site in the monazite structure can be easily substituted by any other lanthanide ions. The luminescent characteristics of the particles depend on its size and other properties including the degree of crystallization, defects and the valence state of the doped activator ions. The shape of the emission spectra and emission peak wavelength is independent of the excitation wavelengths. Upon excitation at 254nm wavelength, the emission spectrum of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor emits a broad band range from 400-650nm with maximum intensity peak at 469 (blue) nm.

**Figure 6 CIE Co-ordinates of LaPO₄:Er³⁺ (0.5 mol %) Nanophosphor depicted on the 1931 chart**

**4. Conclusion**
LaPO₄:Er³⁺ (0.5 mol %) nanophosphor powder were successfully synthesized through solid state reaction method at high temperature (1200°C) and the luminescent properties of sample was studied. The prepared LaPO₄:Er³⁺ (0.5 mol %) nanophosphor in a single-phase monoclinic structure with average crystallite size of 64.12 nm. The width of diffraction peak is broadened because of the small size of the crystallites. The PL characterization demonstrates that the SLaPO₄:Er³⁺ (0.5 mol%) nanophosphor shows the most intense emission. The Commission International de l’Eclairage (CIE) co-ordinates of LaPO₄:Er³⁺ (0.5 mol %) nanophosphor exhibit the excellent colour tunability of blue. Therefore, the LaPO₄:Er³⁺ (0.5 mol %) nanophosphor can be easily applied in various types of lamp and display due to its morphologies and good PL performance.
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