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Photoluminescent properties of $LaPO_4$: Gd^{3+} phosphor

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ABSTRACT

Pure $LaPO_4$ and $LaPO_4$:Gd^{3+}(0.5 mol%) phosphor was synthesized by the conventional solid-state reaction method. Scanning electron microscopy (SEM),Fourier transform infrared spectroscopy (FT-IR), and photoluminescence (PL) spectra were used to characterize the pure $LaPO_4$ and $LaPO_4$:Gd^{3+} phosphor.The excitation spectrum of $LaPO_4$:Gd^{3+}phosphor monitored under 400nm wavelength was characterized by a broad band ranging from 220-280nm with a maximum intensity peak at 249nm(4.96 eV).Upon excitation at 254nm wavelength, the emission spectrum of $LaPO_4$:Gd^{3+} phosphor emits a broad band range from 400-565nm with maximum intensity peak at 469(blue)nm(2.64eV) with the full width at half maximum (1nm). The color coordinates for the $LaPO_4$:Gd^{3+}(0.5 mol%) phosphor are x=0.1726 and y=0.0048.This phosphor is having excellent colour tunability of blue light.

Keywords: Photoluminescence;SEM; FTIR; phosphor; rare-earth ions; solid state reaction technique.

INTRODUCTION

Rare-earth orthophosphates($REPO_4$) are a very interesting class of host lattices of activator ions due to their physic-chemical inercy(high insolubility, high thermal stability), thus providing durable phosphors[1]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. Lanthanide orthophosphate ($LnPO_4$) belongs to two polymorphic types, the monoclinic monazite type (for La to Gd) and quadratic xenotime type (for Tb to Lu).The $LaPO_4$ 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 $LaPO_4$ nanoparticles.Lanthanide orthophosphate ($LaPO_4$) 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]. 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]. It is known that the $LaPO_4$ has a monoclinic phase of monazite structure crystallographically,wherein La^{3+} ion is nine coordinated two oxygen atoms, four oxygens forming a distorted tetrahedron interpenetrating a quasiplanar pentagon formed by another five [7-10]. The La^{3+} 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 applied, such as solid state reactions, sol-gel techniques, hydroxide precipitation, hydrothermal synthesis, spray pyrolysis, laser-heated evaporation, and combustion synthesis[11-13].

In this paper pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor was prepared by the solid state reaction method in air at 1200^0C, 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 RE^{3+} doped nanocrystalline phosphors as well as for the growth of grain particles. Photoluminescence studies and CIE co-ordinates of $LaPO_4$:Gd^{3+} phosphor reveals that the emission colour having excellent colour tunability of blue light So this material may be a potential luminescent material.

MATERIALS AND METHODS

Synthesis:

The pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor was synthesized by using the conventional solid-state reaction method. The formation of the phosphor powder occurs according to the following chemical equation.

$La_2O_3 + 2\ (NH_4)\ H_2PO_4 \rightarrow 2LaPO_4 + 2NH_4OH \uparrow + H_2O\uparrow$

$La_2O_3 + 2\ (NH_4)H_2PO_4 + Gd_2O_3 \rightarrow 2LaPO_4$: Gd (0.5%)

The starting materials were lanthanum oxide (La_2O_3), Diammonium Hydrogen Phosphate [$(NH_4)_2$ H_2 PO_4)Gadolinium oxide(Gd_2O_3) 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^oC 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:

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 spectroflurophotometer(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).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].

RESULTS AND DISCUSSION

Photoluminescence Study of pure $LaPO_4$ and $LaPO_4$:Gd^{3+} phosphor

Fig.1(a,b) shows PL excitation and emission spectra of pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor recorded at room temperature. The excitation spectrum of pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor monitored under 400nm wavelength was characterized by a broad band ranging from 220-280nm with a maximum intensity peak at 249nm.The La^{3+} ion site in the monazite structure can be easily substituted by any other lanthanide ions. The La^{3+} 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 $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor emits a broad band range from 400-565nm with maximum intensity peak at 469(blue)nm with the full width at half maximum (1nm).

Fourier Transforms Infrared(FTIR) Spectroscopy analysis of $LaPO_4$:Gd^{3+} phosphor

In order to determine the chemical bonds in a molecule, FTIR analysis was carried out. Fig.2(a,b) shows the FTIR spectrum of pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor heated at 1200^oC. Most of the bands are characteristic of the vibrations of phosphate groups

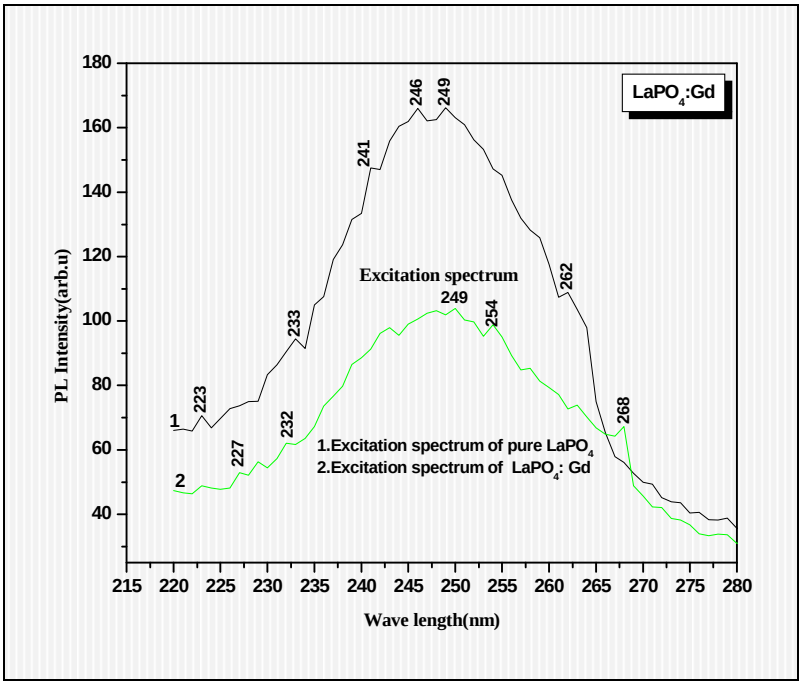

Figure.1(a) Excitation spectra of pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor

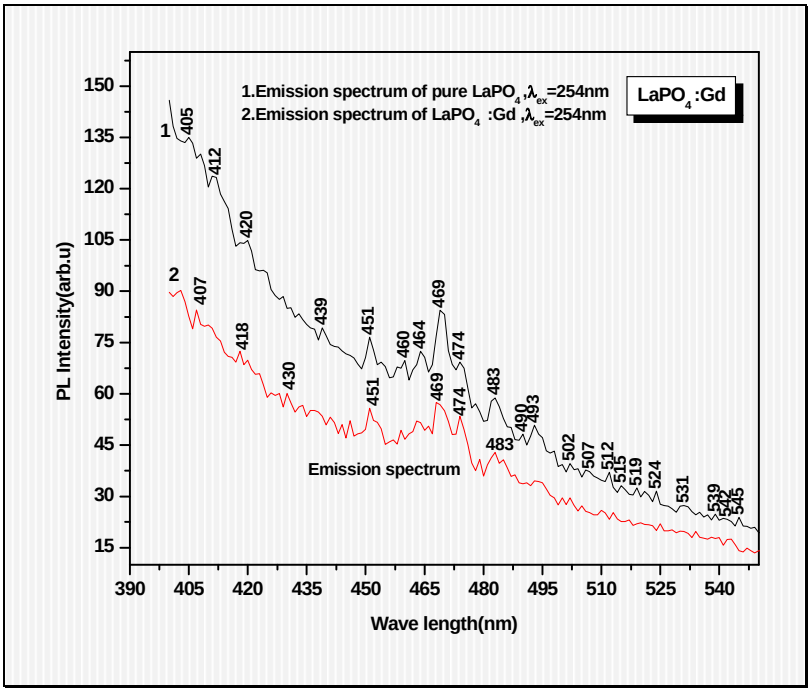

Figure.1(b) Emission spectra of pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor

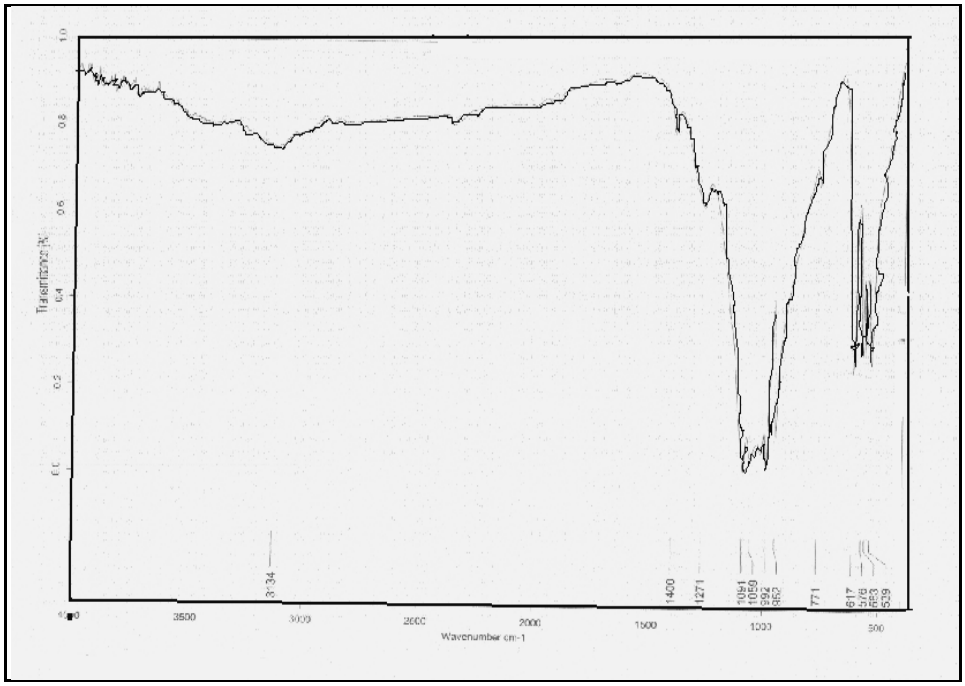

Figure 2(a). FTIR spectrograph of $LaPO_4$ phosphor

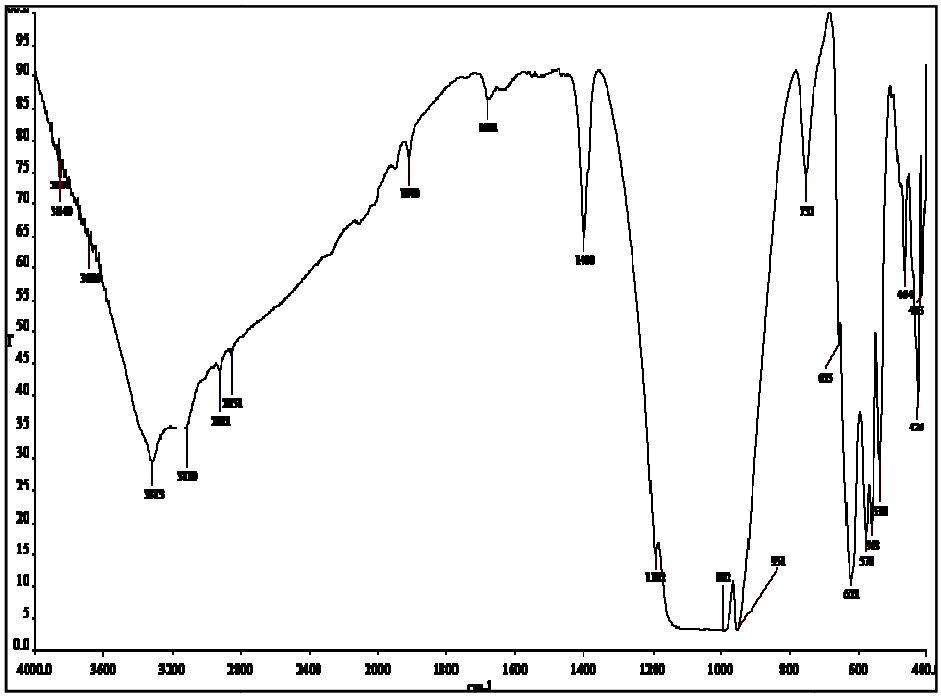

Figure.2(b) FTIR spectrograph of $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor

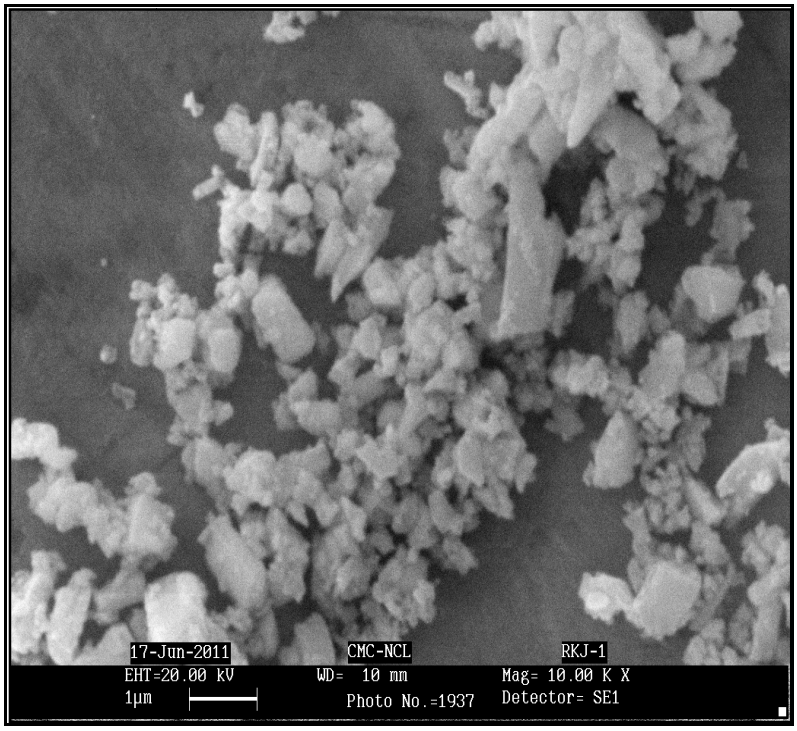

Figure 3(a) SEM of pure $LaPO_4$ phosphor

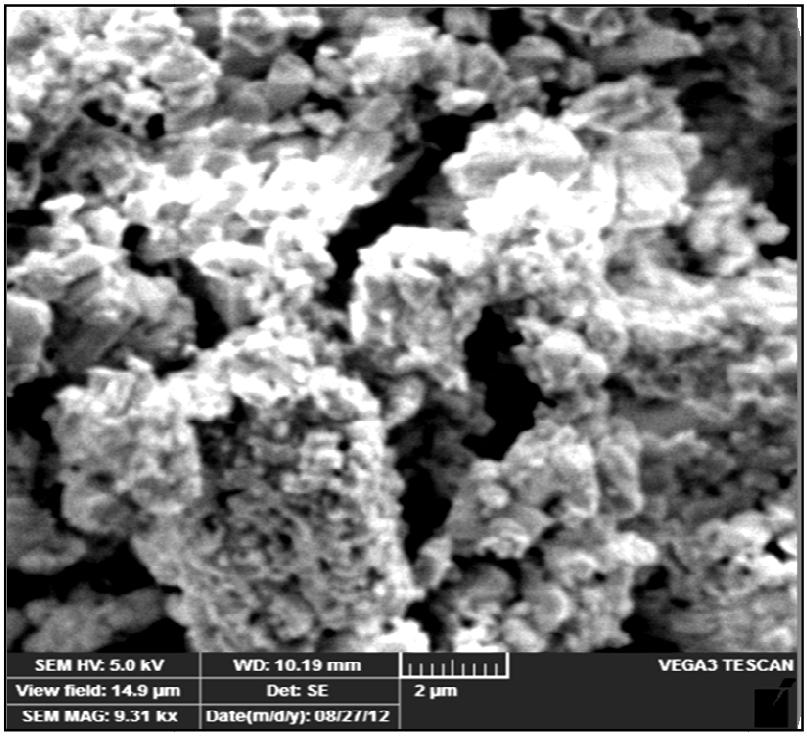

Figure.3(b) SEM Image of $LaPO_4$: Gd^{3+}(0.5%) phosphor

PO_4^{3-}[21]. It had been reported that the PO_4^{3-} should have C_1 symmetry including two (v_3 and v_4) vibration regions in the monoclinic $LaPO_4$ structure [22]. The v_3 vibration corresponds to the phosphate P- O stretching. The v_4 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 538,563,578,621,655,752 cm^{-1} were clearly observed in the v_4 region(bending vibration) of PO_4^{3-} groups vibration. The characteristic bands at 992, 1192 cm^{-1} belong to the v_3 vibration region. Split bands in the *v*3 region are characteristic of the monoclinic $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor phase[23].The vibration spectra give a conclusive evidence for monoclinic-phase formation in lanthanum phosphate.The peaks at

1400,1681,1910,3119,3313,3686,3849cm^{-1}can be attributed to the presence of water (stretching vibration of the O-H bond)adsorbed by KBr during the pellet formation.

Scanning Electron Microscopy Analysis of Pure $LaPO_4$ and $LaPO_4$:Gd^{3+} phosphor

Fig.3(a,b) shows the SEM micrograph of pure $LaPO_4$and $LaPO_4$:Gd^{3+} particles at 1200 ^{O}C. From fig.3(a,b) it is noted that the synthesized pure $LaPO_4$ powder is formed by spherical shape particles with some hundred nanometer grain size in the order of 0.2-2.0µm.The grain size of the sample estimated from SEM image is larger than that calculated from the Schrrer equation. Wang Ruigang et al[9] reported the grain size of the pure $LaPO_4$ particle as 0.2µm.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 and high surface tension of ultrafine nanoparticles.

CIE (1931-Chart) Coordinates of Pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor

Most lighting specifications refer to color in terms of the 1931 CIE chromatic colour coordinates which recognizes that the human visual system uses three primary colours: red, green, and blue. In general, the color of any light source can be represented on the (*x*, *y*) coordinate in this color space. The color purity was compared to the 1931 CIE Standard Source C (illuminant *C*s (0.3101, 0.3162)). The chromatic coordinates (*x*, *y*), was calculated using the color calculator program radiant imaging.

Fig.5 shows the CIE co-ordinates of (chart -1931) of Pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor. The color co-ordinates for the pure $LaPO_4$ are x= 0.1609 and y=0.0305 and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor are = 0.1726 and y= 0.0048.The location of the colour coordinates of the monophosphate powder on the CIE chromaticity diagram presented in Fig.5 indicates that the colour properties of the phosphor powder prepared by solid state reaction method are approaching those required for field emission displays. This phosphor is having excellent colour tunability of blue light.

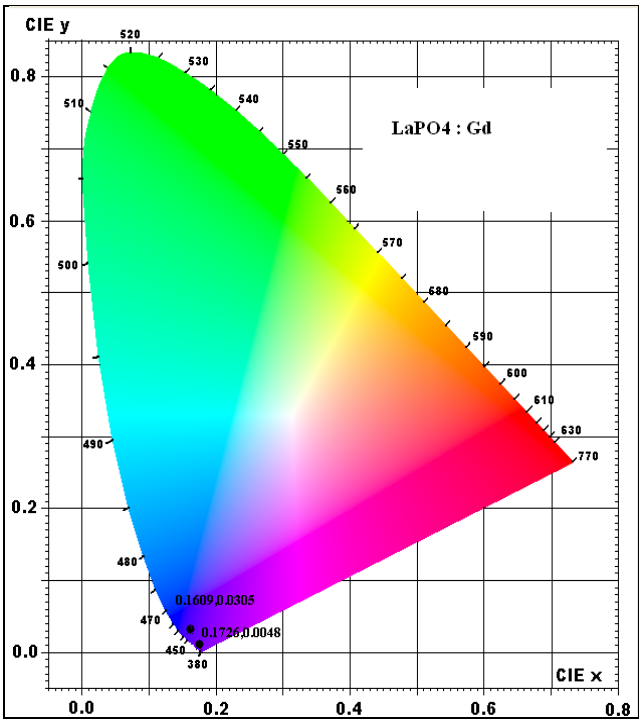

Figure. 4 CIE Co-ordinates of Pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor depicted on 1931 chart

.CONCLUSION

Pure $LaPO_4$ and $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor powder were successfully synthesized through solid state reaction method at high temperature(1200^{0}C) and the luminescent properties of sample was studied.The PL characterization demonstrates that the $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor shows the most intense emission.The Commission International de 1'Eclairage [CIE] co-ordinates of $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor exhibit the excellent colour tunability of blue.Therefore, the $LaPO_4$:Gd^{3+} (0.5 mol%) phosphor can be easily applied in various types of lamp and display due to its morphologies and good PL performance.

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