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Synthesis and Effect of Eu Dopant on PL and Crystallites size of lanthanum Phosphate: $\text{LaPO}_4:\text{Eu}^{3+}$

Y. S. Patil¹, K. G. Chaudhari¹, K. V. R. Murthy² and N. V. Poornachandra Rao

¹Applied Physics Department, MCT'S Rajiv Gandhi Institute of Technology, Versova, Andheri (w), Mumbai

²Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara

³Department of Physics, VSR & NVR College, Tenali, Guntur District, A.P

ABSTRACT

In present paper the effect of dopant on the crystallite size, morphology and the photoluminescence of the sample were also investigated with X-ray spectrometer (XRD), Fourier-transform infrared spectroscopy (FTIR). The phosphors were synthesized using the standard solid state reaction technique and ground using mortar and pestle, fired at 1200°C for 1 hour in a muffle furnace. We have studied the effect of dopants on the Photo luminescent properties of the samples using Spectrofluorophotometer at room temperature. PL emission of undoped LaPO_4 phosphor was observed at 470 nm. Under the excitation of 254nm wavelength, PL emission of doped LaPO_4 phosphor shows peaks at 589, 596, 614 and 622nm with good intensity.

Keywords: Photoluminescence, SEM ,XRD, Particical size, rare earth ions, solid state reaction.

INTRODUCTION

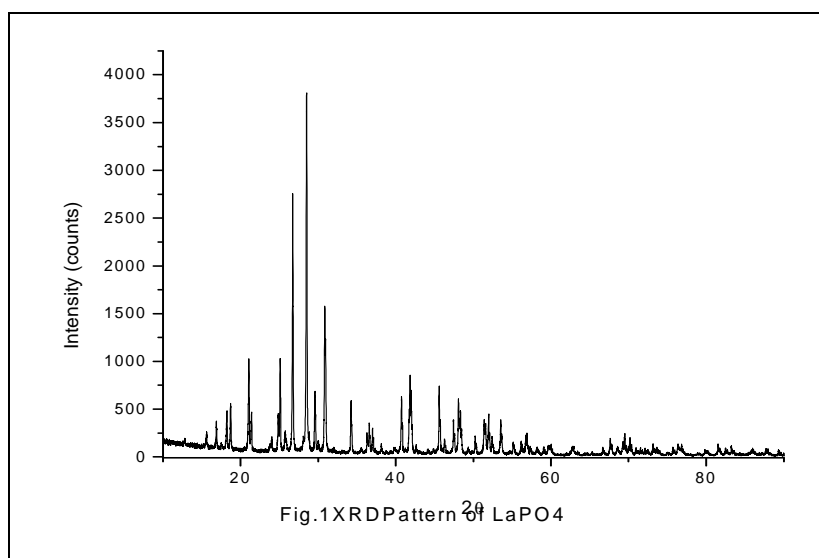
Recently there has been the great interest in the synthesis of various phosphors, because of the wide range of applications in optoelectronic fields. The morphology of the phosphor has an important effect on the emission intensity and the luminous intensity of the phosphors. The size and shape of the phosphors in growth becomes more and more important. Phosphors are widely used in displays and lighting devices. Over the past a few years, they have been applied in many fields, such as optical display panels, cathode ray tubes, optoelectronic, sensitive device, nanoscale electronic and plasma display panels[2-4]because of their excellent performance high density excitation and high energy quantum excitation. Various solution-phase routes, including solid state reaction, sol-gel, precipitation, water oil micro emulsion, polyol-mediated process, ultrasonification, hydrothermal, and mechano chemical method[6-9], have been tried to lower the reaction temperature and obtain high-quality LaPO_4 based nano particles. However, the simple and mass fabrication of LaPO_4 nanocrystals with narrow grain size distribution and uniform morphology still remains a challenge. Eu^{3+} doped LaPO_4 is a red phosphor widely used in fluorescent lamps due to its high quantum efficiency.[2] We adopted the standard solid state reaction technique to prepare LaPO_4 with good morphologies and fine crystal structures; and its emission and intensity of luminescence were also studied.

MATERIALS AND METHODS

The base sample LaPO₄ and LaPO₄ phosphor doped with Eu rare-earth ions, were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La₂O₃), Diammonium Hydrogen Phosphate [(NH₄)₂ H PO₄], Europium Oxide (Eu₂O₃) were grinded in an agate motor and mixed and compressed into a crucible and heated at 1200⁰C for 1 hour in a muffle furnace. The prepared samples were again powdered for taking the measurements.

The XRD patterns of the samples were obtained using Diffractometer system XPERT-PRO at NCL Pune and the excitation & emission spectra were recorded at room temperature using (SHIMADZU,make Spectrofluorophotometer RF – 5301 PC) using Xenon lamp as excitation source at display research Lab., Department of Applied Physics, M.S.U. Baroda.. The emission and excitation slit were kept at 1.5 nm.FT-IR measurements were carried out on BRUKER Make,Vector-22 spectrometer in transmittance mode. With KBr tablet cell as the background spectrum, spectra were collected in a vacuous environment at a resolution of 1 cm⁻¹ over the wave number of 4000-400 cm⁻¹.To record IR spectra, about 100 mg of the mixture of sample and pure and dry potassium bromide is grounded and heated .Then mixture was compressed into a sample cell at the pressure 12 ton for 1 min .

RESULTS AND DISCUSSION



The crystallinity and phase purity of the product were firstly examined by XRD analysis. Fig 1 and 2 for pure LaPO₄ and LaPO₄ dopped Eu reply shows the typical X-ray diffraction (XRD) patterns of synthesized samples. As shown XRD patterns of nanocrystals are in good agreement in the values from JCPDS no.32-0493 of LaPO₄, which shows that all the products are monazite LaPO₄ with monoclinic structure. This implies that the La ions in LaPO₄ system are replaced by Eu ions with smaller atomic radius. The diffraction patterns were obtained using CuK_α radiation ($\lambda = 1.540598 \text{ \AA}$) at 40 kv and 30 mA, and divergence slit fixed at 1.52 mm. Measurements were made from $2\theta = 10^{\circ}$ to 80° with steps of 0.008356° .

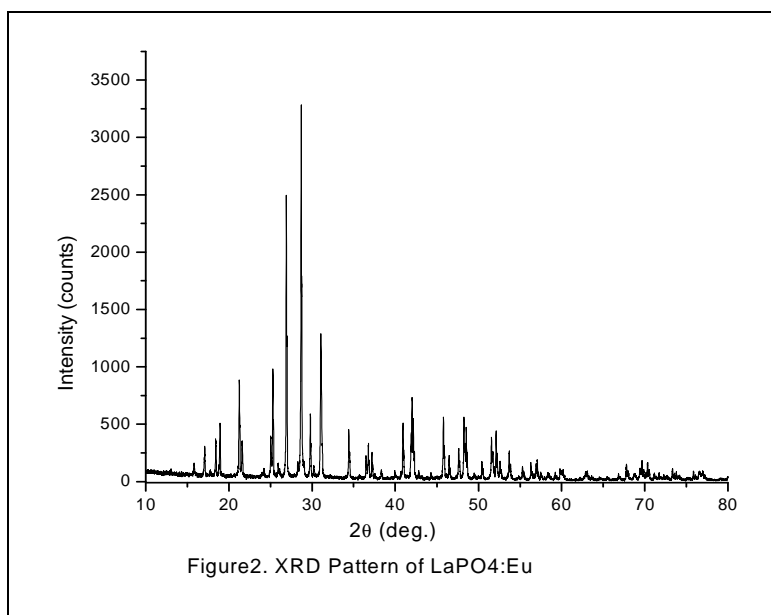
When crystallites are less than approximately 100 nm in size, appreciable broadening in X-ray diffraction lines occurs. The grain size of particles of powder sample were calculated by using Scherer equation

$$D = 0.9 \lambda / \beta \cos \theta$$

Where β represents full width at half maximum of XRD lines.

The main peak was found around 28.7° corresponding to a d- value of about 3.12 \AA , followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate.

The crystallite size of LaPO_4 is 59 nm. The crystallite size increases to 76 nm in LaPO_4 doped with Eu^{3+}



Energy Dispersive X-Ray Analysis (EDAX):

An elemental analysis of base sample lanthanum phosphor (LaPO_4) was carried out by employing the energy dispersive X-ray analysis technique which provides local information of concentration of different elements. Fig.3 shows the EDAX spectra of LaPO_4 in which the presence of La, O, and P are clearly identified from table 1. Here the element N is may be present due to the atmospheric nitrogen.

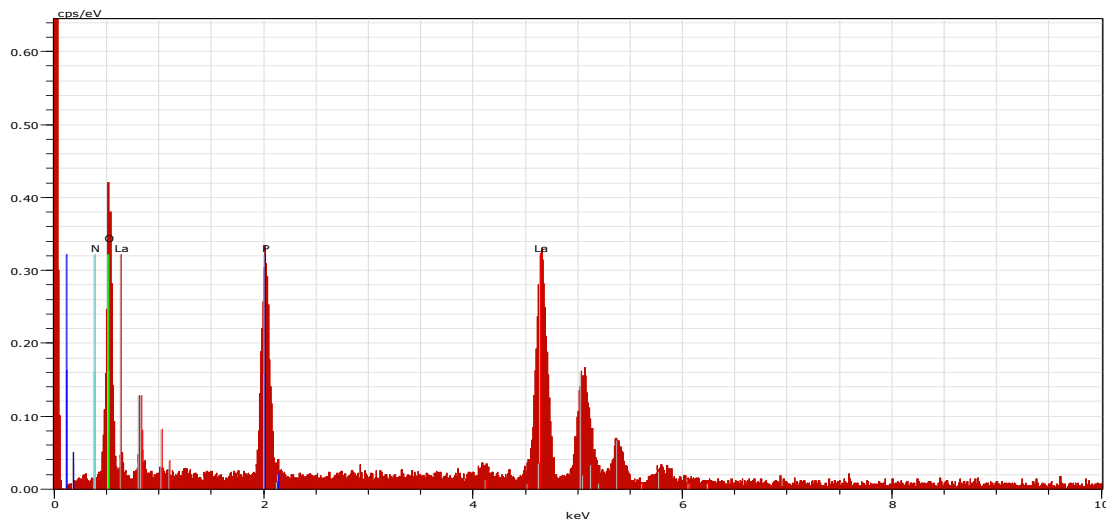


Fig.3. EDAX spectra of LaPO_4

Fourier transform infrared spectroscopy (FT-IR):

The technique has been used to identify the reaction between solids, by monitoring the vibrational and rotational motion of the molecules during the reaction. The FTIR spectrum of LaPO_4 and LaPO_4 doped Eu heated at 1200°C has been depicted in fig. 4 and fig.5 resply.

Table 1. Quantitative analysis of LaPO₄

	El AN Series	unn. C norm.	C Atom.	C Error
	[wt.%]	[wt.%]	[at.%]	[%]
La	57 L-series	46.58	45.14	9.09 1.4
O	8 K-series	42.24	40.93	71.54 7.4
P	15 K-series	7.96	7.71	6.96 0.4
N	7 K-series	6.41	6.22	12.41 2.9

Total: 103.19 100.00 100.00				

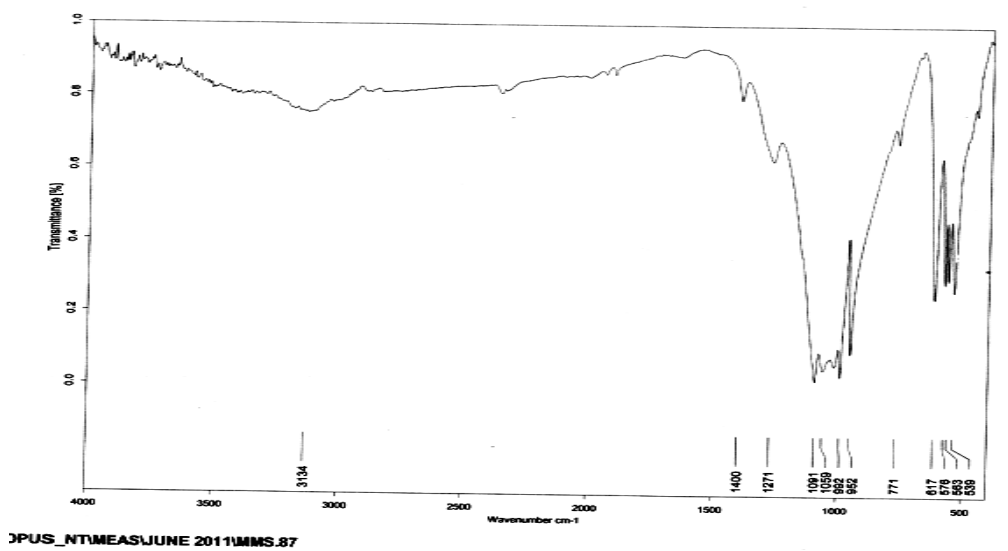


Fig.4.FT-IR spectra of LaPO₄

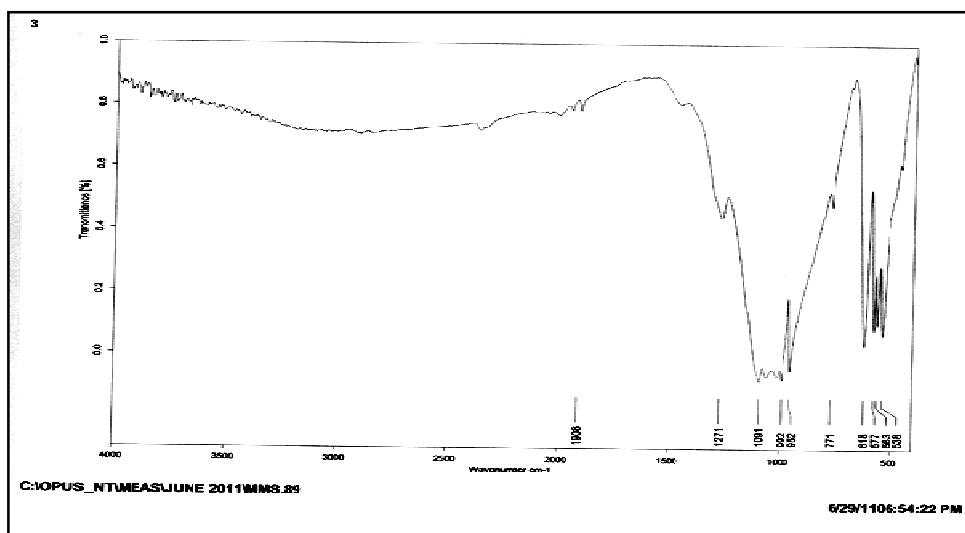


Fig.5.FT-IR spectra of LaPO₄:Eu

The data of infra red spectra of LaPO₄ in fig.4 presents the characteristic bands of the rare earth phosphate (assigned to the PO₄³⁻ group) in the 500-1100 cm⁻¹ wave number range. The wave numbers are:1091, 1059, 992, 952, 771,

617, 576,563,539 cm^{-1} . The bands observed at 1271,1400 ,3134 cm^{-1} can be attributed to the presence of water (stretching vibration of the O-H bond i.e. hydroxyl complexes)adsorbed by KBr during the pellet formation. The band observed at 3134 cm^{-1} may be due to the stretching vibration of O-H and N-H associated bonds. This band is not present in the sample LaPO_4 doped Eu. The bands located at 1271 and 1400 cm^{-1} is attributed to N-O bond in NO_3^- i.e. assigned to anti-symmetry stretching vibration of NO_3^- .

The data from fig.5 presents the characteristic bands of the rare earth phosphate (assigned to the PO_4^{3-} group) in the 500-1100 cm^{-1} wave number range. The wave numbers are:1096,1091,992,952,771,618,577,563,538 cm^{-1} . The peaks found in ν_3 region are: 952,992,1091 cm^{-1} and in ν_4 region are : 538,563,577,618 cm^{-1} in the pattern indicates that the specimen is $\text{LaPO}_4:\text{Eu}^{3+}$ with typical monoclinic structure.

Scanning Electron Microscope(SEM)

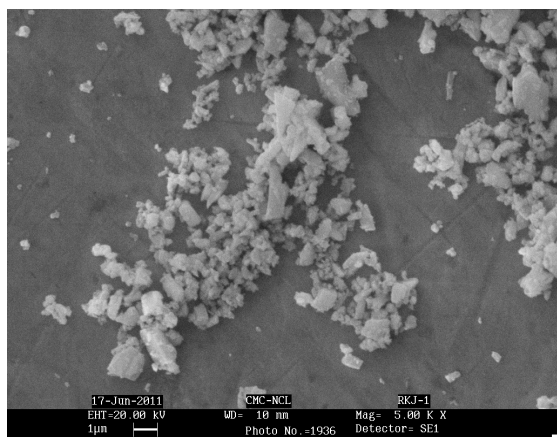


Fig.6.SEM image of LaPO_4

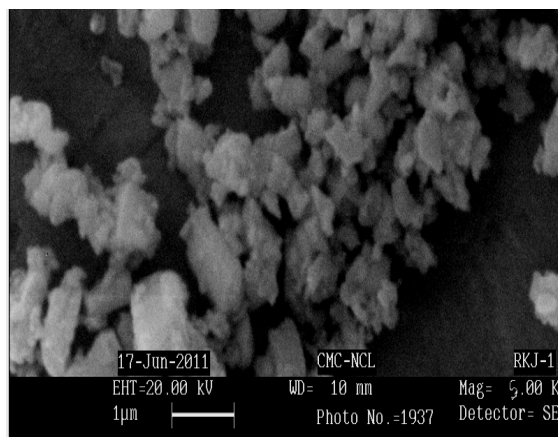


Fig.7.SEM image of LaP:Eu

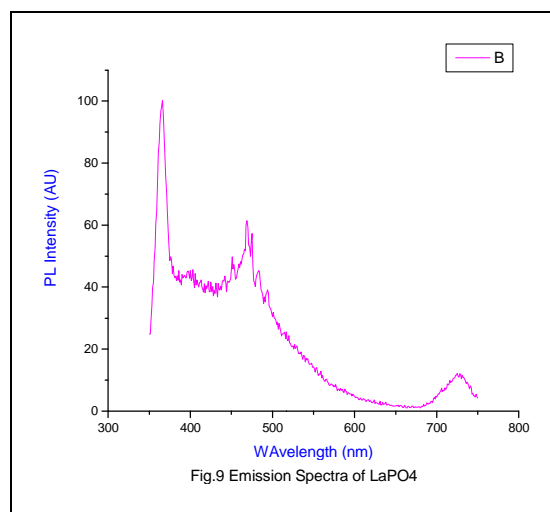
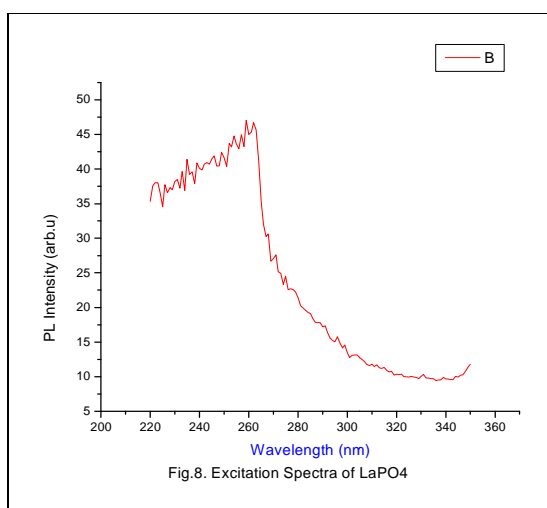


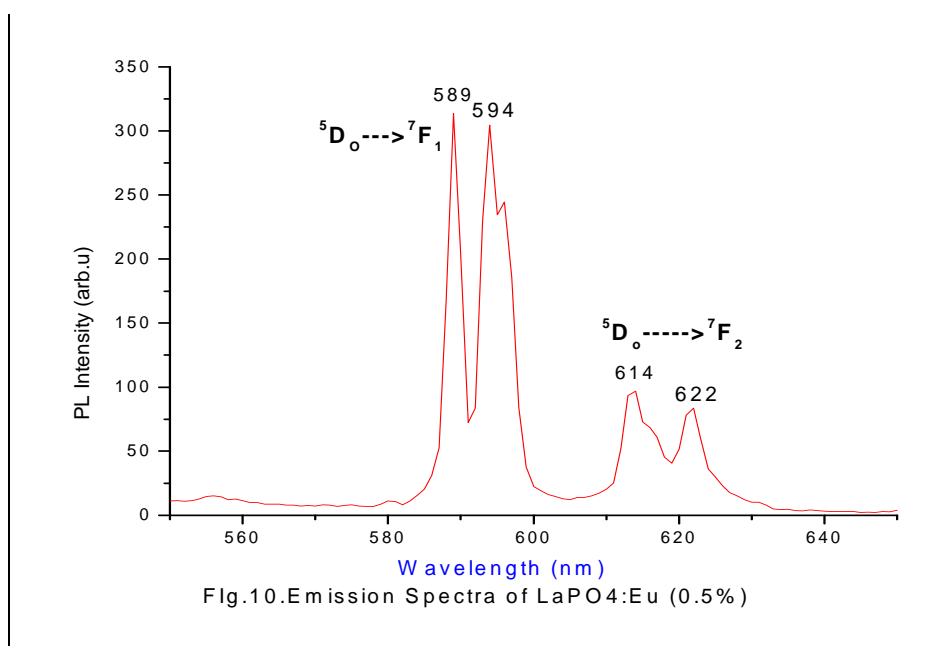
Fig 6 and fig.7 shows the SEM images of pure LaPO_4 and $\text{LaPO}_4:\text{Eu}$ sintered at 1200°C for 4 hours appears un-uniform may be due to the formation of fractal attribution to sort of self organization. The particles having irregular shapes of an average basal diameter of 300 nm and length of 1.5 μm .

Photoluminescence study:

The fig.8 and fig.9 gives the excitation and emission spectra of pure LaPO_4 .

The PL emission of undoped LaPO₄ phosphor was observed at 470 nm under the excitation of 254 nm wavelength a perfect blue region with very good intensity.

The emission spectra of LaPO₄: Eu (0.5%) is shown in fig.10 reveals the modification of the emission wavelength of pure phosphor. The peaks at 589 nm and 594 nm corresponding to orange red colour are derived from the allowed magnetic dipole moment transition [⁵D₀→⁷F₁], whose intensity is affected by the crystal environment surrounding Eu. The peaks at 614 and 622 nm corresponding to red colour are generated from the forced electric transition [⁵D₀→⁷F₂]. The Eu ions allow to occupy a site without inversion center. The intensities ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄ are highly suppressed as compared to the intensified ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂



CONCLUSION

The phase purity has been verified by XRD, SEM, EDAX and FTIR spectral analysis. The XRD data indicates that the peak position do not change with the substitution of La by Eu into monazite type LaPO₄ lattice. The PL intensity is very high therefore LaPO₄: Eu phosphors can be easily applied in various types of lamp and display.

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