

Effect of Erbium Doping on Structural and Photoluminescence Properties of LaPO₄: Eu Phosphor

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ABSTRACT

The present paper reports the Photoluminescence (PL) of the LaPO₄ phosphor doped with Er and Er:Eu rare-earth ions. The phosphors were synthesized using the standard solid state reaction technique and ground using mortar and pestle, fired at 1200°C for 4 hour in a muffle furnace. The X-Ray diffraction pattern reveals the grain size of the particle. The Infrared spectra for the prepared solid nanopowders were recorded in the range between 400 and 4000 cm⁻¹ on a Fourier transform spectrometer (Bruker Make, Vector-22 Model, OPUS_NT FT-IR). The PL emission of pure LaPO₄ phosphor was observed at 470 nm and effect of Er and ,Er:Eu doped with LaPO₄ also has been discussed.

Key words:- Rare-earth ions, photoluminescence, LaPO₄, XRD, FT-IR.

INTRODUCTION

Phosphors are widely used in displays and lighting devices. Morphology of phosphors i.e. shapes and size of the powder particles is one of the key parameters to use phosphors for various applications. The research for oxide-based phosphors has been increasing due to their applications in many field , such as cathode ray tube , light emitting diodes and field emission displays, nanoscale electronic and plasma display panels[1–4] due to their special chemical and physical properties. Oxide-based phosphors attract researcher's attention due to the advantages of their good stability upon excitation by electron beam. It is important to develop phosphors with high quantum efficiency, controlled morphology and small particle sizes. The broad emission band is suitable for the doping of RE ions in persuing new luminescent materials. The RE materials exhibit excellent sharp-emission luminescence properties with suitable sensitization

and effectively used in designing of white light emitting materials. Various solution-phase routes, including solid state reaction, sol-gel, precipitation, water oil micro emulsion, polyol-mediated process, ultrasonification, hydrothermal, and mechano chemical method[5-8], 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. 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. The present paper reports the Photoluminescence (PL) of the LaPO_4 phosphor doped with Er and Eu:Er rare-earth ions. These crystals could find applications as optical materials emitting in visible and near IR region and their behavior can provide a useful comparison for community working with the corresponding materials.

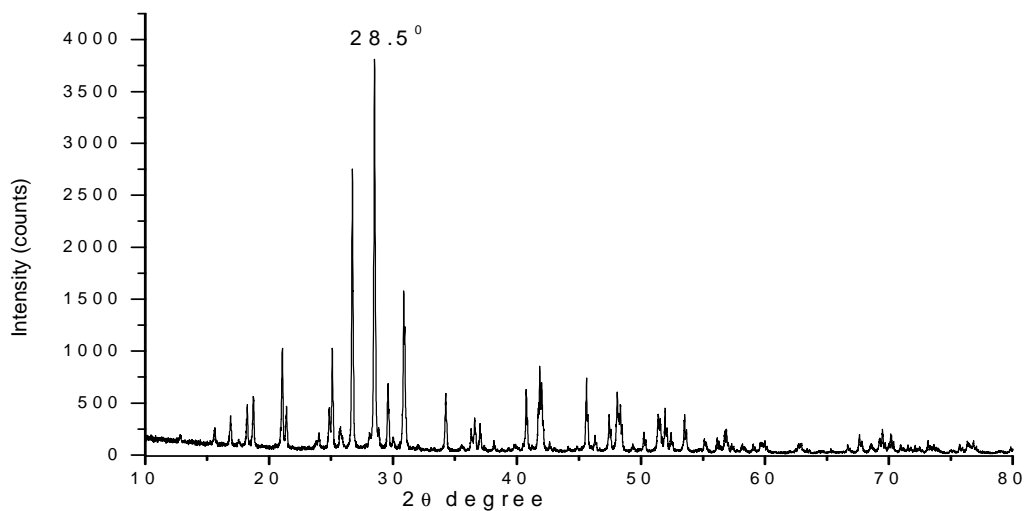
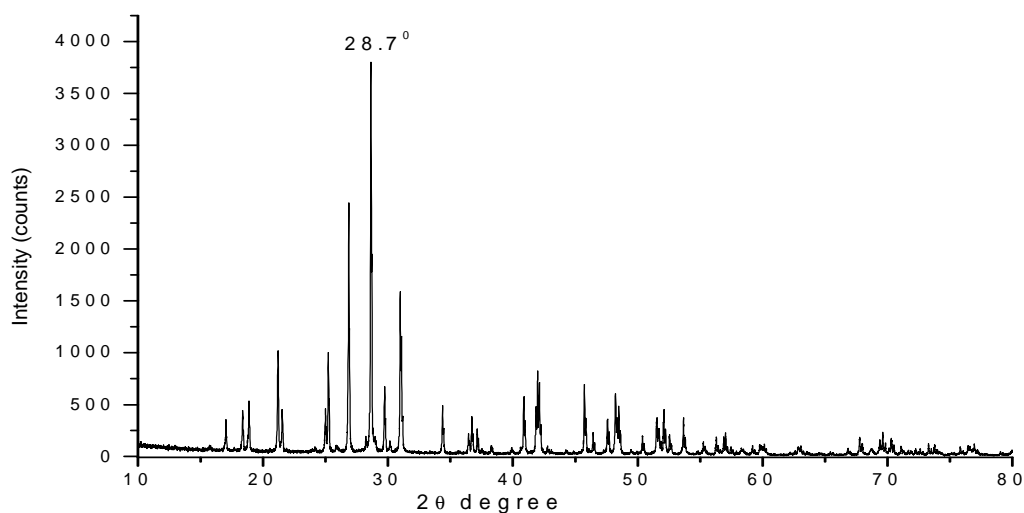
MATERIALS AND METHODS

The samples were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La_2O_3), Diammonium Hydrogen Phosphate [$(\text{NH}_4)_2 \text{HPO}_4$], Erbium Oxide (Er_2O_3) and Europium Oxide (Eu_2O_3) were grinded in an agate motor and mixed and compressed into a crucible and heated at 1200°C for 4 hour in a muffle furnace. The samples were kept at the set temperature for four hours then cooled down naturally. All samples were prepared with the same synthesis technique. 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. *The Infrared spectra for the prepared solid nanopowders were recorded in the range between 400 and 4000 cm^{-1} on a Fourier transform spectrometer (Bruker Make, Vector-22 Model, OPUS_NT FT-IR).*

RESULTS AND DISCUSSION

PHASE PURITY AND STRUCTURE:-

The crystallinity and phase purity of the product were firstly examined by XRD analysis. Fig 1 and 2 shows the typical X-ray diffraction (XRD) patterns of synthesized samples of pure LaPO_4 and LaPO_4 doped with Er. The XRD pattern of LaPO_4 :Er nano particle is similar to that of bulk powder except for the much broader peaks of nano particles[14]. This results from the very small size of LaPO_4 nanoparticles. The peaks in the diffraction pattern seems to match with those of LaPO_4 (JCPD no.- 32-0493) indicating monoclinic phase of monazite structure. These XRD pattern also agree with that of LaPO_4 doped Eu nanoparticles reported by Riwotzki [12-13] The main peak was found around 28.7° corresponding to a d- value of about 3.10\AA , followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate[5-7]. All diffraction patterns were obtained using $\text{CuK}\alpha$ 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° .

Fig.1 XRD Pattern of LaPO₄Fig.2 XRD Pattern of LaPO₄:Er

When crystallites are less than approximately 100 nm in size, appreciable broadening in X-ray diffraction lines occurs. The crystallite 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 (FWHM) of XRD lines

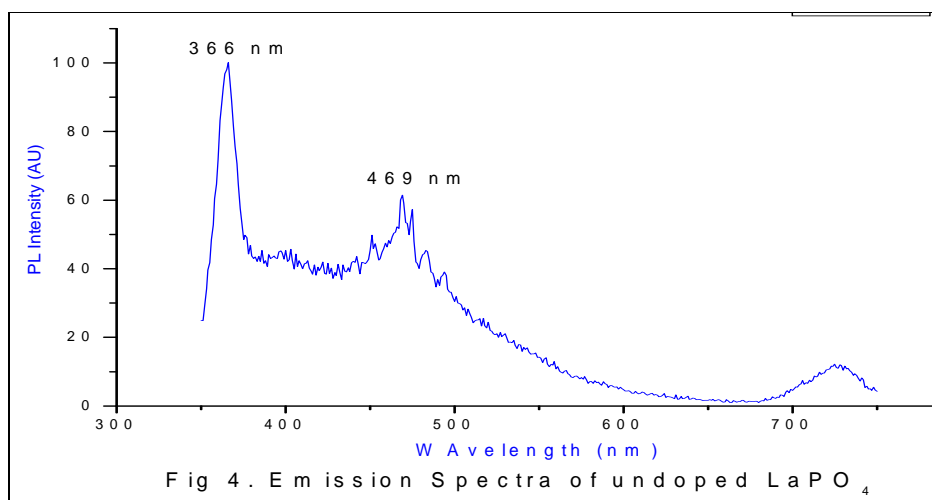
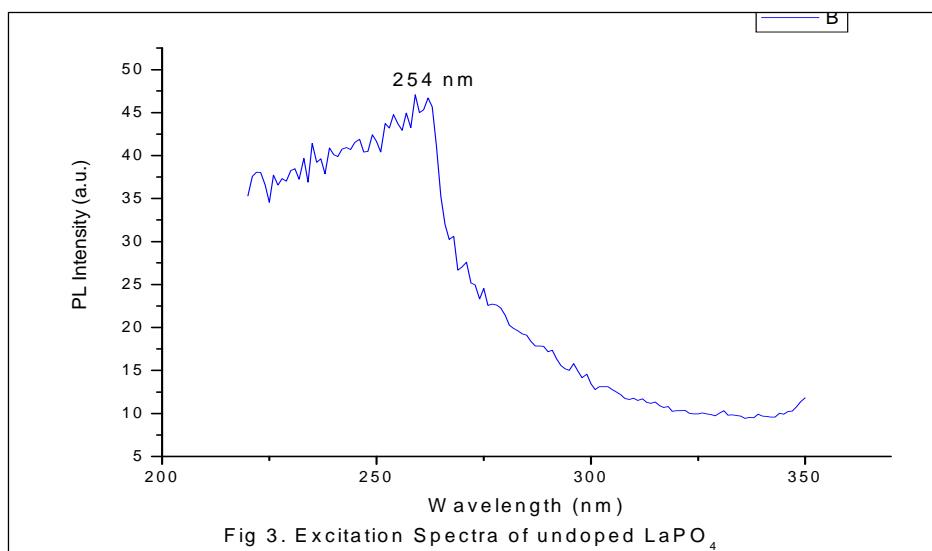
λ = Wavelength of the X-rays.(0.154 nm in the present case)

θ = Bragg's angle of the XRD peak.

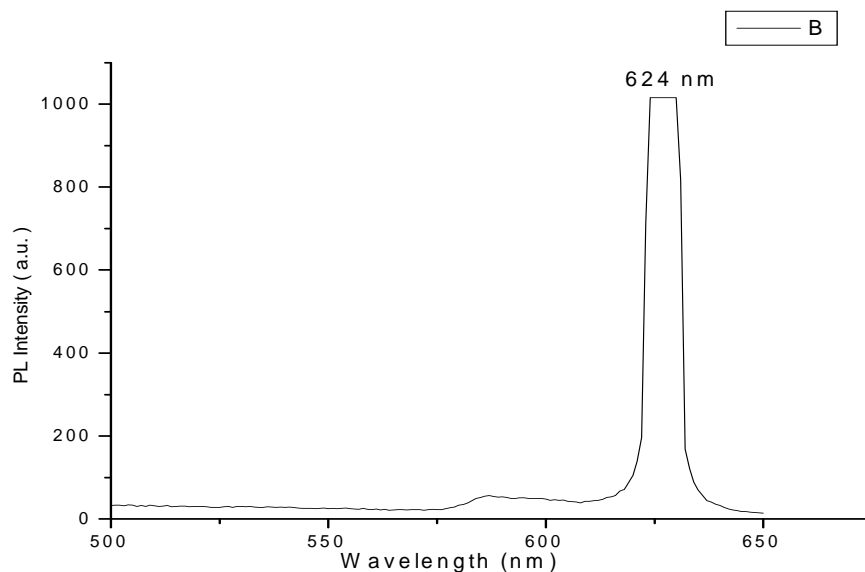
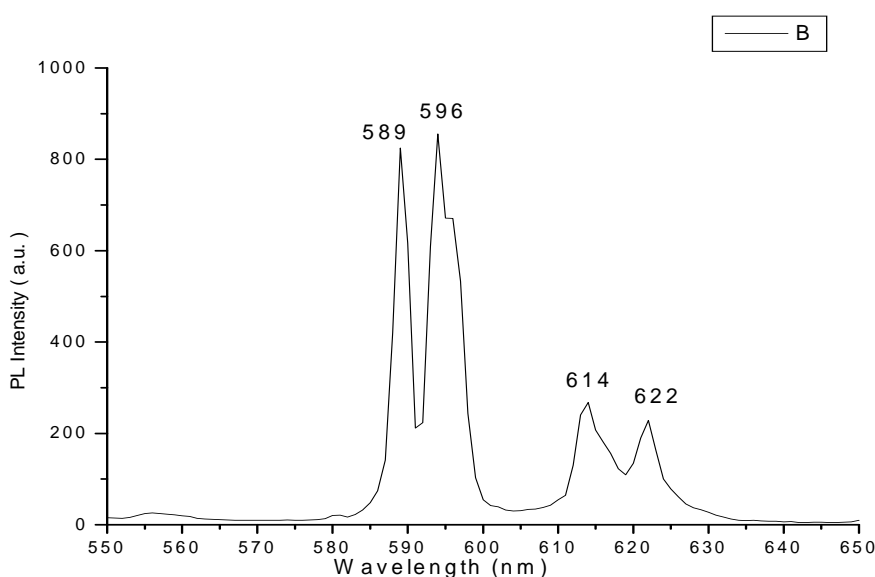
The average crystallite size of LaPO₄ phosphors is 59 nm and when doped with RE dopants Er (0.5%) and Eu (0.5%) , the crystallite size becomes 76 nm.

Photoluminescence Study:-

Figure-4 shows the PL emission of undoped LaPO_4 phosphor was observed at 470 nm a perfect blue region with very good intensity.



The emission spectra of $\text{LaPO}_4:\text{Er}$ (0.5%) is shown in fig.5 reveals the modification of the emission wavelength of pure phosphor. However the effect of Er,Eu dopant and co-dopant effectively modified the emission wavelength but the intensity slightly decreased as shown in fig.6. Under the excitation of 254nm wavelength, PL emission of doped LaPO_4 phosphor shows peaks at 589, 596, 614 and 622nm with good intensity.

Fig.5. Emission spectra of LaPO₄:Er(0.5%)Fig.6. Emission Spectra of LaPO₄:Er(0.5%):Eu(0.5%)**Fourier transforms infrared spectroscopy:-**

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 LaPO₄ doped Eu and LaPO₄ doped Eu, Er has been depicted in fig 7 and fig.8 respectively shows FTIR analysis. The most of the bands are characteristics of vibration of phosphate group. So the characteristics of monoclinic phase of four bands located at 537, 577, 618, 771 cm⁻¹ were clearly observed.

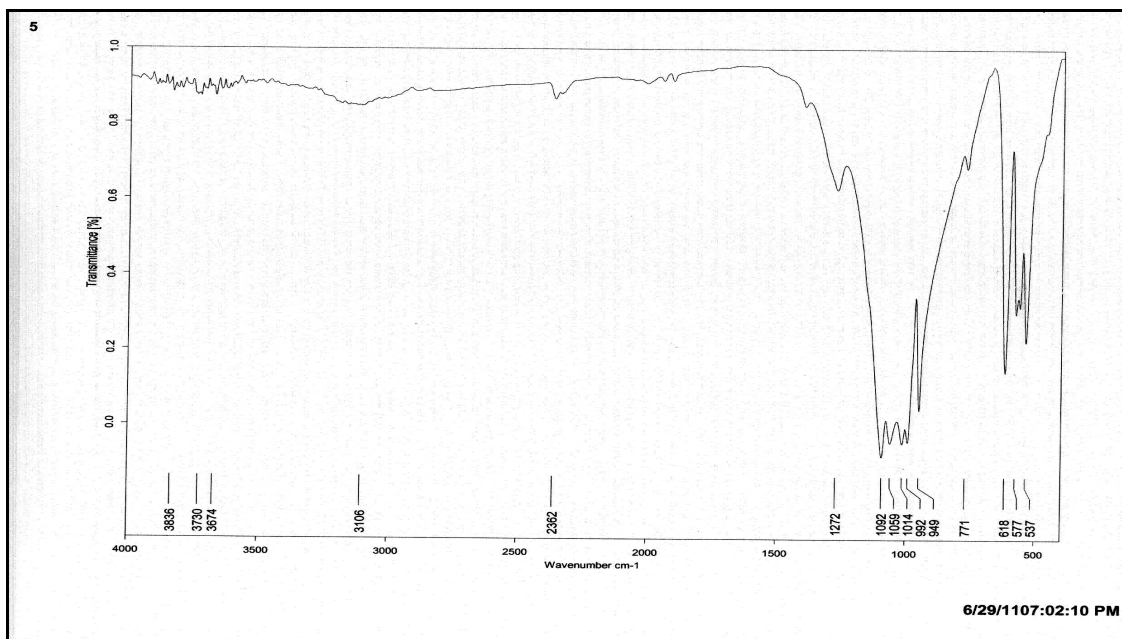


Figure 7. FTIR spectra of LaPO₄:Er(0.5%)

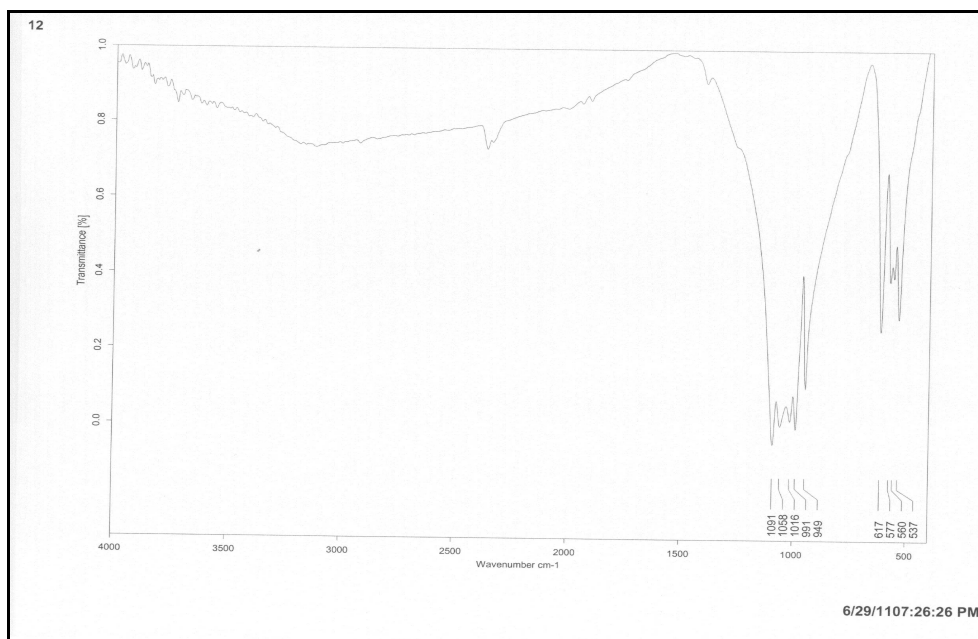


Fig.8. FTIR spectra OF LaPO₄: Eu (0.5%),Er (0.5%)

SR.No.	Material	FTIR Peaks(wave number cm ⁻¹)
01	LaPO ₄ :Er (0.5%)	537,577,618,771,949,992,1014,1059,1092,2362,3106,3674,3730,3836
02	LaPO ₄ :Er(0.5%),Eu (0.5%)	537, 560, 577, 617, 949, 991, 016, 1058, 1091

The data from the graph shows that, the presence of H₂O in the material is detected by the broad peaks 3674, 3730, 3836 in LaPO₄ doped Er. These bands may be due to the stretching vibration of hydroxyl (OH) complexes, which is due to the absorbed water molecules on the surface of the phosphor material. Whereas such peaks are not observed in sample LaPO₄ doped Er, Eu.

CONCLUSION

LaPO₄ phosphor doped with Er and Eu rare-earth ions, were prepared using solid state synthesis method are successfully synthesized. The main peak in XRD pattern was found around 28.7° corresponding to a d -value of about 3.10 Å, followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate. The PL intensity is very high therefore; the LaPO₄:Er:Eu phosphors can be easily applied in various types of lamp and display.

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REFERENCES

- [1] Letant S E, VAN Buuren T W, Terminello L *J.Nano Letters*, **2004**, 4(9): 1705–1707.
- [2] Wang Xun, Zhuang Jing, Peng Qing, LI Ya-dong. *Nature*, **2005**, 437(7055):121–124.
- [3] Gao Pu-xian, Ding Yong, Mai Wen-jie, Hughes W L, lao Chang-shi, WANG Zhong-lin. *Science*, **2005**, 309(5741) 1700–1704.
- [4] Buddhudu S, Kam C H, et.al. *Materials Science and Engineering B*, **2000**, 72(1): 27–30.
- [5] Colomer M T, Gallini S, Jurado J R. *Journal of the European Ceramic Society*, **2007**, 27(13/15): 4237–4240.
- [6] Nedelec J M, Mansuy C, Mahiou R. *Journal of Molecular Structure*, **2003**, 651: 165–170.
- [7] Rajesh K, Shajesh P, Seidel O, Mukundan P, Warriar K G K. *Advanced Functional Materials*, **2007**, 17(10):1682–1690.
- [8] Gallini S, Jurado J R, Colomer M T. *Journal of the European Ceramic Society*, **2005**, 25(12): 2003–2007.
- [9]. B. S. Chakrabarty, K. V. R. Murthy, T. R. Joshi, *Turk J Phys*, 26 (**2002**) , 193-197.
- [10]. M. Koedam and J. J. Opstelten, *Light Res. Tech.*, 3, **1971**, 205.
- [11] B.Schrader, VGH, Germany and Newyork, (**1995**)
- [12] K. Riwotzki, H. Meysamy, A. Kornowski, M. Haase, *J. Phys. Chem. B* 104 (**2000**) 2824.
- [13] K. Riwotzki, H. Meysamy, H. Schnablegger, A. Kornowski, M. Haase, *Angew. Chem. Int. Ed.* 40 (3) (**2001**) 573.
- [14] Ha-Kyun Junga, Jae-Suk Oha, Sang-Il Seoka, Tack-Hyuck Leeb *Luminescence journal* 114 (**2005**) 307-313