Effect of Tb^{3+} and Gd^{3+} on Photoluminescence behavior of Eu^{3+} doped La $_{0.6}$ Y $_{0.4}$ PO4 Phosphor

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Abstract -The present paper reports, synthesis and photoluminescence (PL) studies of Eu^{3+} (0.5%) doped La $_{0.6}$ $Y_{0.4}$ PO4 phosphor codoped with Tb^{3+} (0.5%) and Gd^{3+}(0.5%) respectively. The phosphors (La $_{0.6}$ $Y_{0.4}$ PO4 : Eu^{3+} (0.5%) : Tb^{3+} (0.5%) and La $_{0.6}$ $Y_{0.4}$ PO4 : Eu^{3+} (0.5%) : Gd^{3+} (0.5%)) were prepared by solid state diffusion reaction method, which is the suitable method for large-scale production. The received phosphor samples were characterized using XRD, SEM, PL, &CIE techniques. With dopent ($Eu^{3+)}$ and with codopents (Tb^{3+}& Gd^{3+}) the PL emission was observed in the range of 530-630 nm under 254 nm excitation. The ion radius distinction between La^{3+} and Y^{3+} is so large therefore, they show the pure monoclinic phase. From the XRD data, using the Scherer's formula, the calculated average crystallite size of La $_{0.6}$ $Y_{0.4}$ PO4: Eu^{3+} (0.5%) , La $_{0.6}$ $Y_{0.4}$ PO4 : Eu^{3+} (0.5%) : Tb^{3+} (0.5%) and La $_{0.6}$ $Y_{0.4}$ PO4: Eu^{3+} (0.5%) : Gd^{3+} (0.5%) is around 45.6nm, 41nm,and39nm respectively.The present phosphor can act as a single host for Red light emission which is used in display devices,lamps and bio-medical imaging applications.

Keywords: Photoluminescence (PL), Eu^{3+} doped phosphor, codopents, CIE coordinates

INTRODUCTION:

Red light emission from (600-630nm) Eu^{3+} doped phosphors are extensively used in lamp and display applications and many Eu^{3+} doped materials are being examined for use in new flat panel display technologies. Among them phosphate phosphors have proved to be potential candidates for such applications. [1]. The luminescence of the rare earth ions in inorganic hosts has been extensively investigated during the last few decades. In particular, rare earth ortho phosphates [REPO4] are a very interesting class of host lattices for activator ion due to their physical-chemical inercy (High insolubility, stability against high temperature or against high energy excitations), thus providing durable phosphor [2]. Moreover, these materials can present high excitabilities in the ultraviolet region, which enables them, applicability in plasma display panels (PDPS) and in new generation fluorescent lamps (mercury free) [3,4]. 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 colors in multi phosphor devices [5 – 7]. Mixed orthophosphates composed of two rare earth elements have also been investigated, indicating that these phosphates can be used as host lattices for spectroscopic investigations [8-14].

For REPO4 Phosphor small RE^{3+} with larger ion radius, the monoclinic crystal phase structure is preferred. For REPO4 phosphor of middle RE^{3+} with intermediate radius, a partly formation of hydrated hexagonal structure is favorable. For REPO4 phosphor of heavy RE^{3+} with a small radius, a tetragonal crystal phase is adopted. Therefore, it is very interesting that what will happen when rare earth ion with different radii are introduced into one REPO4 systems with PO_4^{3-} . In this paper, we have investigated a new crystal phase, structures, microstructures of the mixed ortho phosphates REPO4 (RE=La, Y) prepared by solid state diffusion reaction method. Because of the difference in ionic radii between these rare earth ions, the crystal phase microstructures of the products show obvious differences. At the same time Eu^{3+} ions and some codopents (Tb^{3+}, Gd^{3+}) have been doped in the mixed rare earth phosphates. In order to examine the influence of the codopents on the luminescence of Eu^{3+}, whose Photoluminescent behaviors are studied in detail.

SYNTHESIS OF MIXED PHOSPHATES

The starting materials Lanthanum oxide (La_2O_3), yttrium oxide (Y_2O_3), (NH_4) H_2PO_4 , Europium

oxide(Eu_2O_3),Gd_2O_3 and Terbium oxide (Tb_4O_7) of high purity (99.9%) chemicals were used as starting materials to prepare La $_{0.6}$Y $_{0.4}PO_4$ and Eu,Gd, Tb doped phosphor. Lanthanum oxide (La $_2O_3$), Yttrium oxide in stoichiometric proportions is weighed and ground into a fine powder using agate mortar and pestle. The grounded sample was placed in an alumina crucible and fired at 1200°C for 3 hours in a muffle furnace with a heating rate of 5°C /min. The sample is allowed to cool to room temperature in the same furnace for about 30 hours. Rare earth ions Eu,Gd, Tb were doped 0.5 molar percentages. The samples were found out to be white in color and studied photoluminescence behavior.

PHYSICAL CHARTERIZATION

The X-ray powder diffraction (XRD) pattern of samples is performed on a Rigaku-D/max 2500 using Cu Kα radiation. The surface morphology of the samples was studied using scanning electron microscopy (SEM) (XL 30 CP Philips). The particle size distribution histogram recorded and particle size was measured using laser based system Malvern instrument U.K. Spectrofluorophotometer (SHIMADZU, RF-5301 PC) was used for PL studies. All the PL spectra were recorded at room temperature.

RESULTS AND DISCUSSIONS

4.1 Crystal phase and microstructure of mixed rare earth phosphate:

The present study focuses on the XRD pattern of La^{3+} to Y^{3+} of 3:2 molar ratio, i.e. La$_{0.6}$Y$_{0.4}PO_4$ doped with Eu^{3+} and with codopents is shown in figure 1. From the XRD pattern, it was found that the prominent phase formed in La $_{0.6}$Y $_{0.4}PO_4$, after diffraction peaks were well indexed based on JCPDS no. 96-900-1648 indicating the monoclinic phase of monozite structure. The main peaks were founded around 29.218°,29.290°&29.343° corresponding to a d-value of about 3.10A° followed by other less intense peaks corresponds to the monoclinic system of crystal

4.2. SEM STUDY:

Characterization of particles, surface morphology and size of nano crystals is done routinely using scanning electron microscope. The main advantage of SEM is that they can be used to study the morphology of prepared nano particles and nano composites. Direct size measurements obtained from images are often used in conjunction with other measurements such as powder, X-ray diffraction (XRD). Figure 2shows the SEM

structures of Lanthanum Yttrium phosphate. All diffraction patterns were obtained using Cu Kα radiation (λ= 1.54060 A°). Measurements were made from 2θ=0° to 60° with steps of 0.008356°. Li et.al, have studied the crystal phase structure of the mixed rare earth phosphates indicating the pure LaPO $_4$ and YPO_4 crystallize in monoclinic phase and tetragonal phase respectively, while the mixed phosphate $La_{0.5}Y_{0.5}$ PO_4 belong to the hexagonal phase [15]. Bing Yan et.al studied with La^{3+} to Y^{3+} of 9:1 molar ratio, the product shows the pure monoclinic phase, just like pure LaPO$_4$ [15].

The crystallite size was calculated using the Scherrer equation D=k λ/β cos θ. Where the constant k= (0.9), λ the wavelength of X-rays (1.54060 A°), β the full-width at half maxima (FWHM) and θ the Bragg angle of the XRD peak. The calculated average crystallite size of La $_{0.6}$Y $_{0.4}PO_4$:Eu $^{3+}$ (0.5%) is ~ 45.6, La $_{0.6}$Y $_{0.4}PO_4$:Eu $^{3+}$ (0.5%) codoped with Tb^{3+} is~ 41nm and when codoped with Gd average crystallite size is ~39 nm. Fig. 1 is the. XRD pattern of La $_{0.6}$Y $_{0.4}PO_4$: Eu (0.5%.) along with codopents.
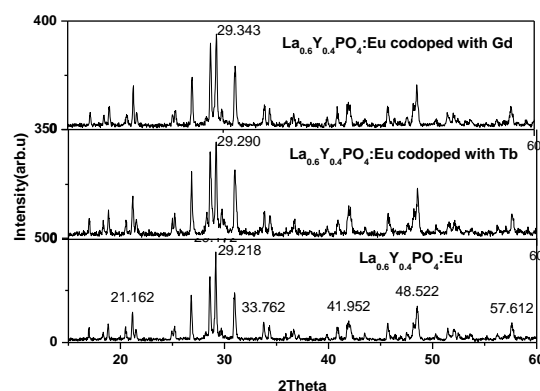
Figure :1 XRD Pattern of La $_{0.6}$Y $_{0.4}PO_4$: Eu(0.5%) phosphor

micrographs of La$_{0.6}$Y $_{0.4}PO_4$:Eu (0.5%), La $_{0.6}$Y $_{0.4}PO_4$:Eu (0.5%): Tb (0.5%) and La $_{0.6}$Y $_{0.4}PO_4$:Eu (0.5%): Gd (0.5%) phosphors. Direct size measurements obtained from images and the average particle diameter is observed. From the Scanning Electron Micrographs of La $_{0.6}$Y $_{0.4}PO_4$: Eu (0.5%) phosphors, it is found the particles are irregular in shape with various sizes from of submicron to few micros and also clusters are found.
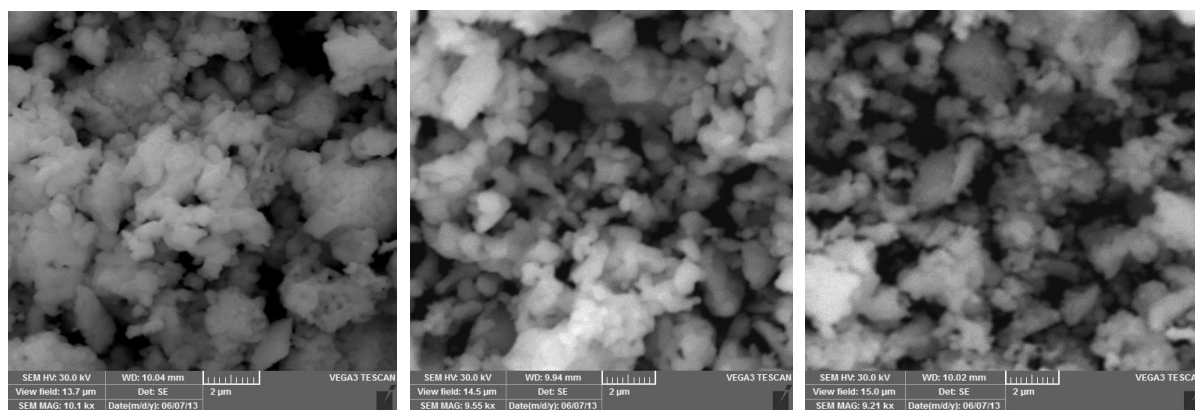
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Fig 2. SEM images of La $_{0.6}$Y $_{0.4}$PO$_4$: Eu (0.5%), La $_{0.6}$Y $_{0.4}$PO$_4$: Eu (0.5%):Tb(0.5%)& La $_{0.6}$Y $_{0.4}$PO$_4$: Eu (0.5%):Gd(0.5%)

4.3 Photoluminescence Study (PL)

The Photoluminescence Properties under 254 nm excitation of obtained mixed ortho phosphates are presented in figure 3. The excitation spectrum La $_{0.6}$ Y$_{0.4}$ PO$_4$:Eu^{3+} [figure 3a] presents a broad, intense band maximum at ~ 254 nm related to a ligand-metal charge transfer between PO$_4^{3-}$ groups and RE^{3+} ions. The strong Eu^{3+} intra-configurational f-f transitions are also observed in the excitation spectrum.
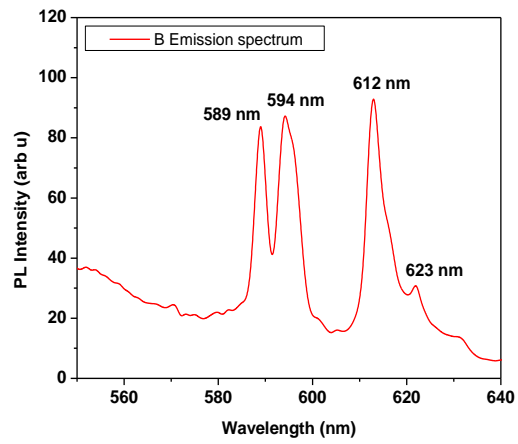
The emission spectrum of La $_{0.6}$ Y$_{0.4}$ PO$_4$: Eu^{3+} (figure 3b) display the characteristic $^5D_0 \rightarrow {}^7F_j$ (j=1, 2,3,4) transition of Eu$^{3+.}$ In general, when the Eu^{3+} ion is located at crystallographic site without inversion symmetry, its hypersensitive forced electric – dipole transition $^5D_0 \rightarrow {}^7F_2$ red emission dominates in the emission spectrum. If the Eu^{3+} site possesses an inversion center $^5D_0 \rightarrow {}^7F_1$ orange emission is dominant [16]. Emission spectrum consists of emission peaks in the range 530 – 630 nm which results from $^5D_j \rightarrow {}^7F_j$ (J= 1,2,3) transition of Eu^{3+} ion under 254 nm excitation. The Emission spectrum of La $_{0.6}$ Y$_{0.4}$ PO$_4$: Eu^{3+} codoped with Tb^{3+} consist of sharp emission peaks at 544 nm, 589 nm, 594 nm and 612 nm. The transition at 544 nm originates from the allowed transition $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+} which is having less intensity. The maximum intensity peak observed at 612 nm . The intensity of the 612 nm peak in Eu:Tb doped phosphor increased by two times when compared with the intensity of the 612 nm peak of La $_{0.6}$ Y$_{0.4}$ PO$_4$: Eu^{3+} (0.5%). The distinct emission line lying between 580 and 630 nm are observed due to transition from excited $^5D_0 \rightarrow {}^7F_J$ (J=0,1,2,3) levels of Eu^{3+} ions. The origin of these transitions (electric dipole and magnetic dipole) from emitting levels to transition levels depending upon of the location of Eu^{3+} ions in La $_{0.6}$ Y$_{0.4}$ PO$_4$: Eu^{3+} lattice and type of transition is determined by selection rule [17]. The most intense peak at 612 and hump at 623 nm correspond to the hypersensitive transition between $^5D_0 \rightarrow {}^7F_2$ levels due to the forced electric dipole transition mechanism. The less intense peak in the vicinity of 594 nm is ascribed to the magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ levels. The increase of intensity in La $_{0.6}$ Y$_{0.4}$

PO$_4$: Eu^{3+} codoped with Tb^{3+} is due to cross relaxation energy transfer (CRET). To develop an efficient quantum cutting phosphor is to utilize a pair of ions that can share the initial excitation energy [18]. CRET can occur by multiple – multiple interactions or by exchange interactions. [19].The Emission spectrum of La $_{0.6}$ Y$_{0.4}$ PO$_4$: Eu^{3+} codoped with Gd^{3+} consist of sharp emission peaks at 535 nm, 589 nm, 594 nm and 612 nm The emission at 535 nm originates from allowing transition $^5D_1 \rightarrow {}^7F_1$ of Gd^{3+} which having less intensity. In this case also maximum intensity peak observed at 612 nm. The intensity of 612 nm peak increased by two and half times when compared with La $_{0.6}$ Y$_{0.4}$ PO4:Eu^{3+}. The specific case of CRET process for the Gd^{3+}, Eu^{3+} pair [20] is shown in figure3(f). The excited Eu^{3+} is responsible for the first visible photon. Resonant energy migration among excited Gd^{3+} ion occurs from within the ^6P state until the energy resides nearby another Eu^{3+} ion to which it can transfer its energy. The curved arrow, labeled 2, indicates this. The second excited Eu^{3+} ion produces the second visible photon, achieving quantum splitting. The results indicate that La $_{0.6}$ Y$_{0.4}$ PO$_4$: Eu$^{3+:}$ Gd^{3+} can select as a potential candidate for FL (fluorescent lamp) and compact fluorescent lamps (CFL) (Ex 254 nm)

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3(a)
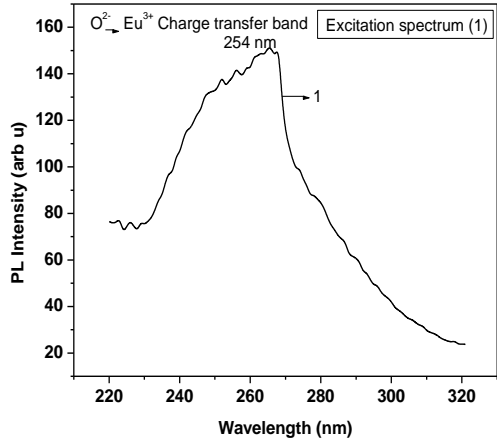
Fig:3(a):Excitation spectrum of La$_{0.6}$Y$_{0.4}$PO$_4$:Eu^{3+}(0.5%) ;   Fig:3(b): Emission spectrum of   La$_{0.6}$Y$_{0.4}$PO$_4$: Eu^{3+}(0.5%)

Fig:3(c):Excitation spectrum monitoring at 611 nm and Emission spectum of LaYPO$_4$:Tb(0.5%)&Eu(0.5%)under 254 nm Ex.
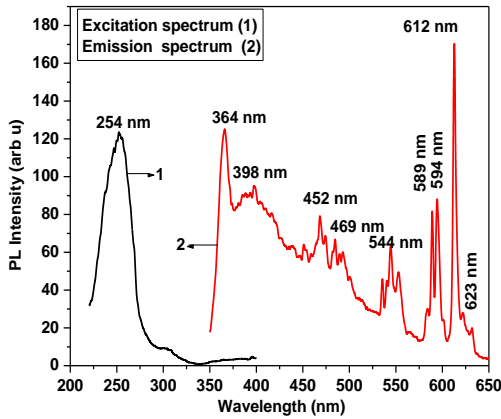
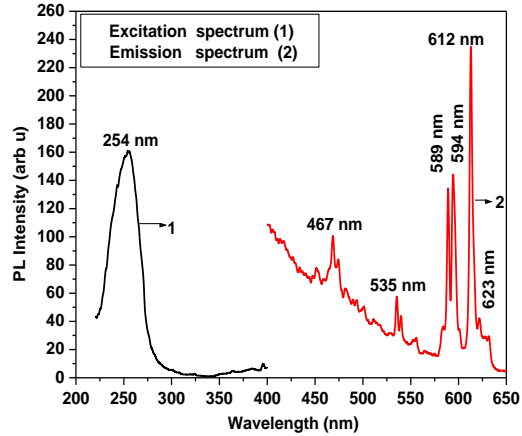Fig:3(d):Excitation spectrum monitoring at 611 nm and Emission spectum of LaYPO$_4$:Gd(0.5%)&Eu(0.5%)under 254 nm Ex.

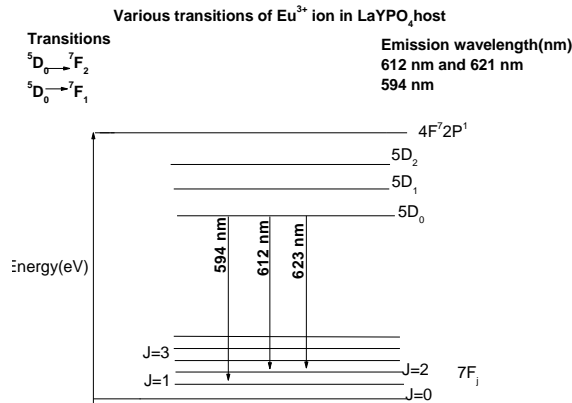3(c)   3(d)

Fig 3(e): Energy level diagrams for all possible transitions of Eu^{3+}ion

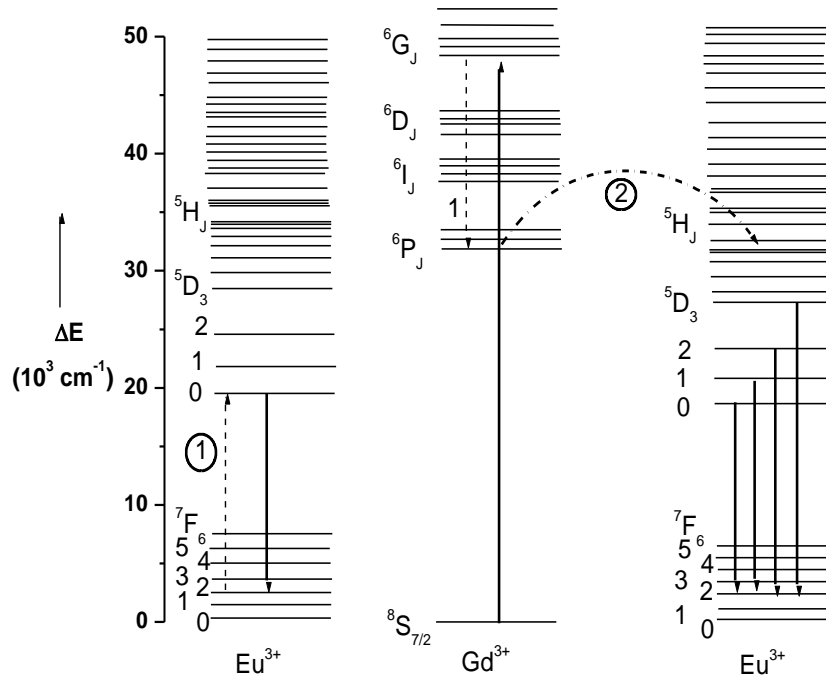Fig 3(e):Energy level diagram for all possible transitions of Eu^{3+}ion

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Fig:3(f):Energy level diagrams of Eu^{3+} and Gd^{3+} showing the cross-relaxation energy transfer process that leads to quantum splitting. The dotted arrows labeled 1 identify the resonant CRET which leave the first Eu^{3+} ion in its $^5D_0$ state from which the first photon is produced. The curved arrow labeled 2 describes the subsequent energy transfer from Gd^{3+} to a second Eu^{3+},which produces the second photon.

4.4 CIE Co-ordinates

The CIE co-ordinates calculated by the Spectrophotometric method using the spectral energy distribution of the $La_{0.6}Y_{0.4}PO_4$:Eu(0.5%) sample is shown in figure 4.The color co-ordinates for the $La_{0.6}Y_{0.4}PO_4$:Eu(0.5%) sample is x=0.667 and y=0.322 (these co-ordinates are very near to standard values of Red). Hence this phosphor having excellent color tunability to Red.
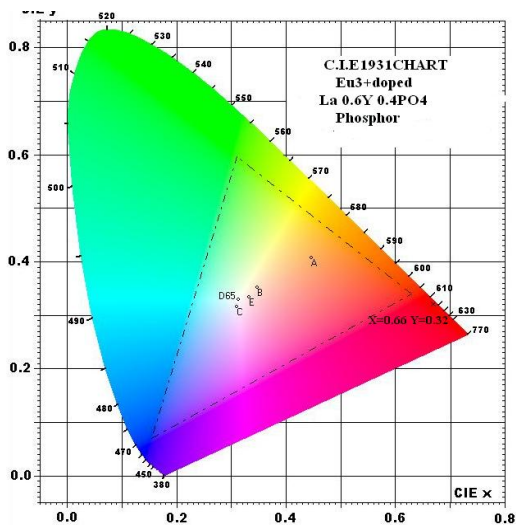

Fig. 4: C.I.E 1931 chart of Eu^{3+}doped $La_{0.6}Y_{0.4}PO_4$

CONCLUSIONS:

$La_{0.6}Y_{0.4}PO_4$ phosphor doped with the Eu and with co dopents (Tb, Gd) were synthesized via high temperature solid state diffusion reaction method. The crystal phases and microstructures of the products can be favorable for the formation of phosphors in pure phase $La_{0.6}Y_{0.4}PO_4$ presents the pure monoclinic phase and nano size crystalline material. The $La_{0.6}Y_{0.4}PO_4$: Eu (0.5%) and with codepents phosphor materials present very attractive luminescent property for the generation of the red color. Cross relaxation energy transfer process (CRET) observed when $La_{0.6}Y_{0.4}PO_4$: Eu(0.5%) codoped with Gd^{3+} as well as co doped with Tb^{3+}. The maximum PL intensity observed when $La_{0.6}Y_{0.4}PO_4$:Eu codoped with Gd^{3+}. From the PL studies, it is concluded that Eu(0.5%) : Gd (0.5%) doped $La_{0.6}Y_{0.4}PO_4$ phosphor under 254 nm excitation can act as a single host for producing Red light with good intensity for all practical display devices in particular compact fluorescent lamps.

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