Synthesis and Characterization of Eu (1%) and Gd (0.1% to 2%) Doped LaPO4 Phosphors

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Abstract - Cerium and Terbium doped $LaPO_4$ Phosphor is a good commercial green emitting phosphor which was mostly used in display devices. The present paper reports the synthesis, photoluminescence and other characterizations like XRD, SEM and FTIR for $LaPO_4$: Eu (1%), Gd (0.1 to 2.0%) phosphor. The photoluminescence studies of the phosphor with Citric acid as a flux was also reported. $LaPO_4$ phosphors doped with 1% of Europium and co-doped with Gadolinium with various concentrations from 0.1 to 2.0%, prepared under Standard Solid State Reaction [SSR] method at a calcinating temperature of 1200 º C for 3 hr was presented. Well indexed peaks at 589, 593, 613 and 621 nm are observed with very good intensity. The Orange Red wavelengths at 589 and 593 nm dominate the red emissions at 613 and 621nm. The peaks at orange region 589 and 593 nm are due to $^5d_0 \rightarrow {}^7f_1$ transition and are due to electronic dipole of the electron. The red peak at 613 nm is due to $^5d_0 \rightarrow {}^7f_2$ transition and the peak at 621 nm is due to $^5d_4 \rightarrow {}^7f_5$ transition and are due to magnetic dipole of electron. All the emissions are allowed transitions of Europium. It is obvious from the data that, Gd as co-dopant is not able to resolve any new emissions; however, the intensities are increased with the increase of concentration of Gd from 0.1% to 2%.

Keywords: Solid State Reaction [SSR], Photoluminescence [PL], XRD, SEM, FTIR and Transitions

I INTRODUCTION

Rare earth (RE) doped inorganic compounds has excellent luminescence properties and fascinated great research interest in the past years. The entire rare earth doped lanthanide ortho phosphates have many prospective applications in the field of lighting and display devices. They are also adopted in the fields such as sensors, proton conducters, ceramics, and thermal resistance materials. Rare earth ions are characterized by a partially filled ^{4}f shell, shielded by $^5s_2$ and $^5p_6$ orbitals in a host. Consequently, it gives sharp emission transition lines in the spectra. In the midst of all, the inorganic silicates are the most attractive phosphors due to their special properties like water and chemical resistance and visible transparency**.** Regarding white LEDs Eu^{2+} doped silicates have significant application, because it absorb UV radiation from LED chip and efficiently emit light in visible region. They are well identified for their excellent luminescent properties such as high efficiency, easy fabrication, high thermal stability and wide availability of inexpensive raw materials**.** At present, the researcher want to examine the photoluminescence properties on the formation of Eu doped and Gd co-doped $LaPO_4$ phosphor and also the effect of Citric acid as flux in this system.

II MATERIALS AND METHOD

Lanthanum oxide (La_2O_3), Ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) were taken as base materials in a molecular stoichiometry of 2:1 to prepare $LaPO_4$ Phosphor. It was doped with 1% of Eu_2O_3 and co-doped with Gd_2O_3 at various concentrations from 0.1% to 2%. They were mixed and grounded thoroughly in an agate mortar with pestle for 45 min. Acetone medium was used intermediately in the grinding procedure to get fine grain and uniform size. The obtained powder mixture was annealed in a muffle furnace at a heating rate of 6ºC per min, up to the temperature of 1200ºC and soaked for 3 hr and allowed to cool naturally to room temperature. They were synthesized using Solid State Reaction (SSR) method in open air atmosphere. Citric acid was added in the proportion of 10% of the total weight of the phosphor and the same process was followed to prepare the phosphor with flux. The obtained powders seem to be white in colour. They were taken in to agate mortar and ground with pestle to obtain fine grained powder. The obtained powders of different phosphors were studied for their characterizations like photoluminescence, XRD, SEM and FTIR.

III RESULTS AND DISCUSSIONS

Photoluminescence Study: Figure 1 is the excitation spectrum of $LaPO_4$: Eu1%, Gd1% monitored at 400 nm wavelength. A broad excitation band ranging from 220 to 300 nm is observed.

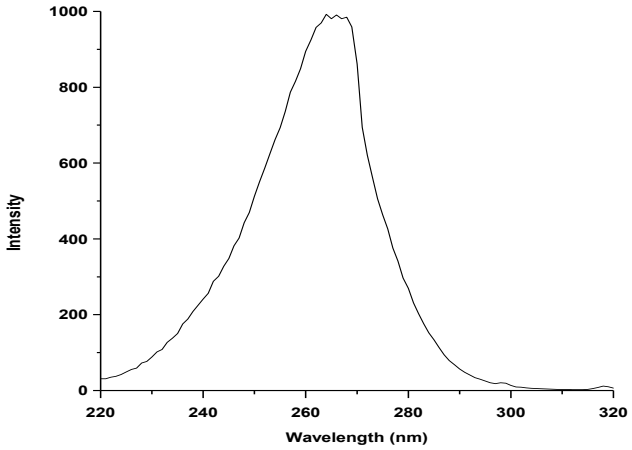

Fig. 1 : Excitation spctrum of $LaPO_4$:Eu1%, Gd1% monitored at 400 nm

Figure 2 is the emission spectrum of undoped $LaPO_4$ with 254 nm excitation. A broad spectrum from 350 to 650 nm with many spiky peaks with significant swell around 400 nm and 460 nm was observed. There is in fact multiple emission lines evolved and are due to the crystal field splitting of the ground state of the emitting ions.

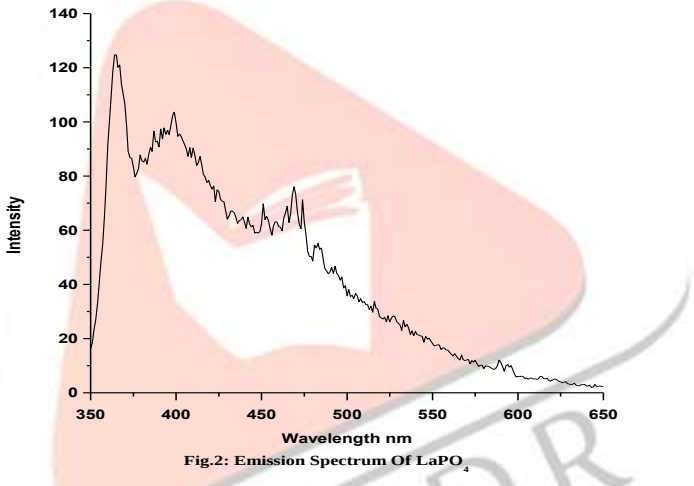

Fig.2: Emission Spectrum Of $LaPO_4$

Figure 3 is the PL emission spectra of $LaPO_4$: Gd (1%), Eu (0.1 to 2%) at 254 nm excitation. It is observed from Fig. 3 that well resolved PL emissions are found at 589, 594, 613 and 621 nm. However, 2 siblings are associated at 596 and 616nm along with main peaks are observed. All the emissions are allowed transitions of Europium. The luminescence arises mainly due to transitions from 7f shell. The efficiency of emission depends on the number of electrons in the 7f shell. The Eu^{3+} ion has 6 electrons in the 4f shell, which can be excited in the 7f - 5d excitation band. The electron in the excited 7f state remains at the surface of the ion and comes under the strong influence of the crystal field resulting in the splitting of the emission band. Gd as co-dopant may not able to resolve any new emissions; however, the intensities are increased with the increase of concentration of Gd from 0.1% to 2%. Finally, when Gd is 2%, highest emission intensity at 589 and 594 nm, the orange-red region are observed along with 613 and 621 nm emissions at red region.

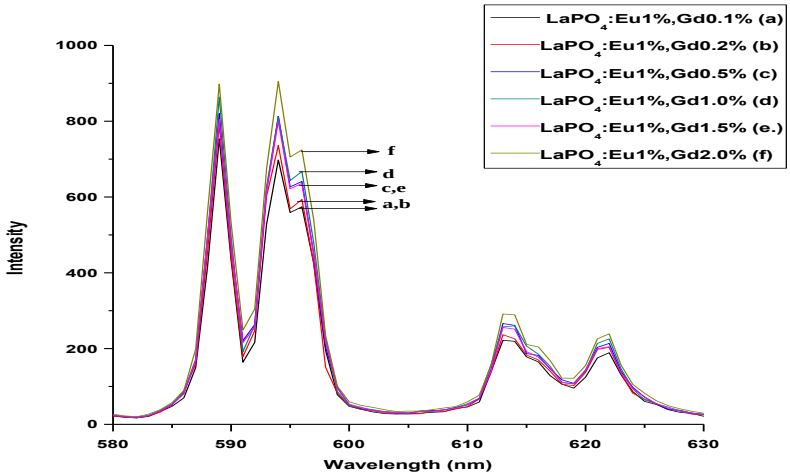

Fig.3 : Emission Spectra of $LaPO_4$:Eu, Gd at 254 nm Excitation

It is interesting to note that, as the concentration of Gd increases, the intensities of all the emissions are increases linearly from 0.1 to 2%, however, the phosphor with 1.5% of Gd deviates the linearity, all the emissions in this sample has lesser intensity than that of 0.5% and 1% doped samples. And also 594 nm and 613 nm emissions of 1% Gd doped phosphor records lesser intensity than that of 0.5%. All the emissions and their respective intensities are shown in Table 1 for the better understanding. From the tabular form it is obvious that, when the concentration of Gd increased from 0.1% to 2%, it enhances the intensity of 589 nm emission to 20%, and the other emissions to around 30%. The respective emission intensities were tabulated in Table 1 for better understanding.

Figure 4 is the PL emission spectra of $LaPO_4$: Eu (1%), Gd (0.1 to 2%) phosphors fluxed with citric acid, at 254 nm excitation. Citric acid as a flux show diversified change in the emission intensities of the phosphors among varying concentrations of Gd. Citric acid as a flux increases the emission intensity of 1.5% Gd doped sample around 10%, for samples of 1% and 0.1% slightly increased, for sample of 0.2% slightly decreased and for 0.5% and 2% samples intensity decreases by more than 10%. The respective emission intensities were tabulated in Table 2 for better understanding.

The peak at orange region 589 and 594 nm are due to $^5d_0 \rightarrow {}^7f_1$ transition and is due to magnetic dipole of the crystal. The PL emissions at red region 613 nm is due to $^5d_0 \rightarrow {}^7f_2$ transition and is due to electric dipole. The peak at 621 nm is due to $^5d_4 \rightarrow {}^7f_5$ transition and is due to magnetic dipole of electron. All the emissions at 589, 594, 613 and 621 nm and overlapped peaks at 596 and 616 nm along with main peaks are allowed transitions of Europium 3+ state.

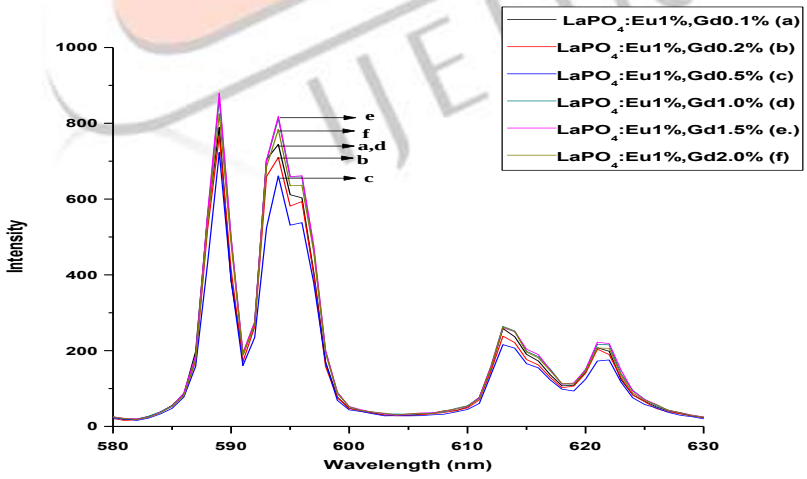

Fig. 4: Emission spectra of $LaPO_4$:Eu (1%), Gd (varying) at 254 nm ex. with citric acid as flux

λ_{em} nm	Emission Intensities of $LaPO_4$: Eu, Gd Phosphor Under 254 nm Excitation					
	Eu 1%, Gd 0.1%	Eu 1%, Gd 0.2%	Eu 1%, Gd 0.5%	Eu 1%, Gd 1.0%	Eu 1%, Gd 1.5%	Eu 1%, Gd 2.0%
589	753	791	820	864	804	898
594	698	736	813	811	800	906
613	222	236	266	258	256	292
622	189	203	214	226	205	239

Table 1: Emission wavelengths and their respective intensities of $LaPO_4$: Eu (1%), Gd (0.1 - 2%) phosphors at 254 nm excitation

λ_{em} nm	Emission Intensities of $LaPO_4$: Eu,Gd Phosphor with Citric acid as a flux under 254 nm Excitation					
	Eu 1%, Gd 0.1%	Eu 1%, Gd 0.2%	Eu 1%, Gd 0.5%	Eu 1%, Gd 1.0%	Eu 1%, Gd 1.5%	Eu 1%, Gd 2.0%
589	789	766	723	865	879	825
594	745	710	661	813	818	784
613	258	238	216	264	261	262
622	208	204	175	217	222	207

Table 2: Emission wavelengths and their respective intensities of $LaPO_4$: Eu (1%), Gd (0.1 - 2%) phosphors at 254 nm Ex. with citric acid as a flux.

XRD: Figure 5 shows the XRD pattern of the $LaPO_4$: Eu (1%), Gd (1%) phosphor prepared without flux. From the figures it is clearly observed that the maximum peak intensity is obtained at 28.49º. The calculated crystallite size using Scherer's formula $d = K.\lambda/\beta \cos\theta$, where 'K' is the Scherer's constant (0.94), 'λ' the wavelength of the X-ray (1.5418 Å), 'β' the full-width at half maxima (FWHM) (0.3444), 'θ' the Bragg angle of the highest peak is around **24.86 nm**. From XRD pattern it is found, the phosphor may not be in single phase. Many crystallites agglomerate together and form a particle. The average calculated crystallite size for all the observed peaks seen in Fig. 5 is **28.9078 nm.**

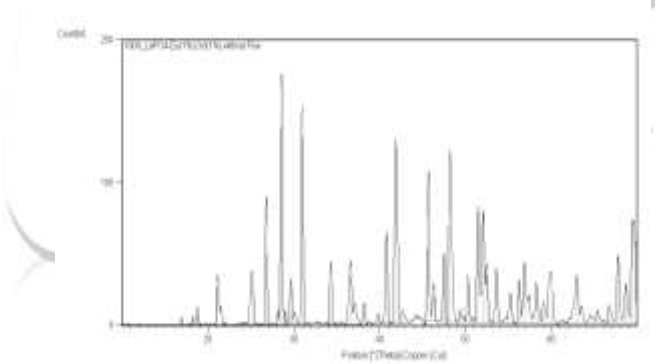

Fig. 5: XRD of $LaPO_4$: Eu (1%), Gd (1.0%) without flux

Figure 6 represents the XRD pattern of the $LaPO_4$: Eu (1%), Gd (1.5%) phosphor prepared with the citric acid as a flux. From the figure it is clearly observed that the maximum peak obtained is at 31.9º. The calculated crystallite size using Scherer's formula is around **25.01 nm**. From XRD pattern it is found the phosphor may not be in single phase. Many crystallites agglomerate together and form a particle. The average calculated crystallite size for all the observed peaks is **27.52 nm.**

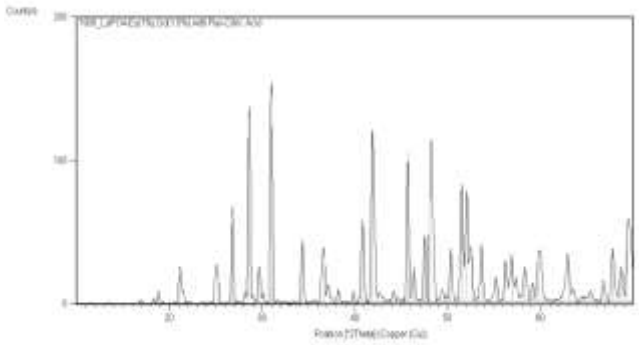

Fig. 6: $LaPO_4$: Eu (1%), Gd (1.5%) with citric acid as flux

SEM: Figure 7 is the SEM of $LaPO_4$: Eu (1%), Gd (1%) phosphor prepared without flux. From the Scanning Electron Micrograph with the measuring scale of 5 microns, it appears to be mostly irregular shape with smooth surface having an average basal diameter less than one (735 nm) micron to two microns (1.7 μm). From SEM it is observed, good particles having mostly different shapes of varying sizes and agglomarated together.

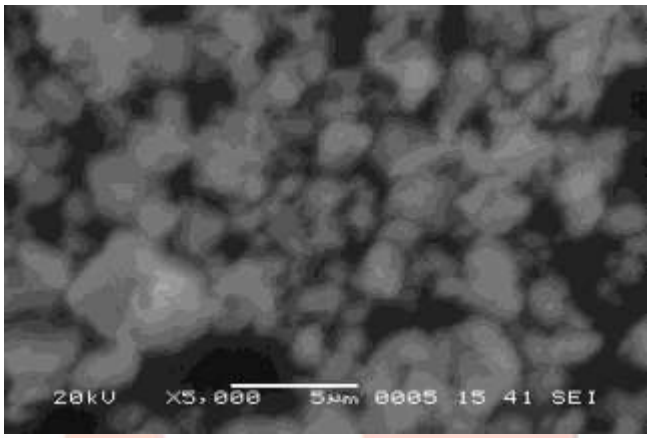

Fig. 7: SEM of $LaPO_4$: Eu (1%), Gd (1%) without flux

Figure 8 is the SEM of the $LaPO_4$: Eu (1%), Gd (1.5%) phosphor prepared with the citric acid as a flux. From the Scanning Electron Micrograph of $LaPO_4$: Eu (1%), Gd (1.5%)**,** with the measuring scale is 10 microns it appears to be mostly irregular shape with smooth surface having an average basal diameter more than one micron to three microns. From SEM micrograph it is observed that, good particles having mostly diffreent shapes of varying sizes and agglomarated together.

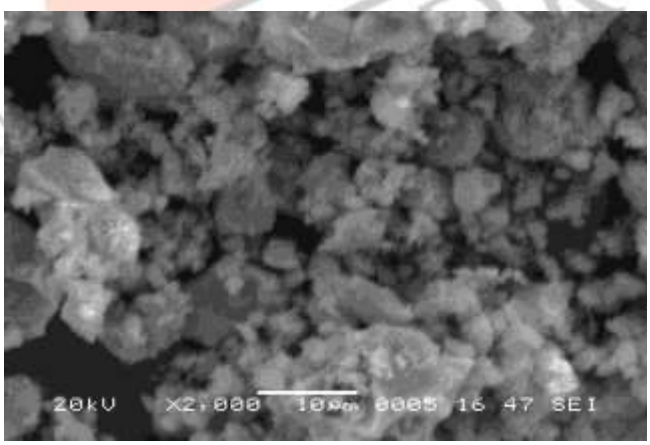

Fig. 8: $LaPO_4$: Eu (1%), Gd (1.5%) with citric acid as flux

FTIR: Figure 9 shows the FTIR spectrum of $LaPO_4$: Eu (1%), Gd (1%), phosphor prepared without flux. From the figure, the observed peaks are at 3625, 2375, 1425, 850, 650, 500 cm^{-1}. Most of the bands are due to C - O, Gd - O, La - O, Eu - O stretchings. The O - H stretching band is observed at 3625 cm^{-1}. The band around 3625 cm^{-1} is due to the H - OH stretching of absorbed water molecule from the atmosphere.

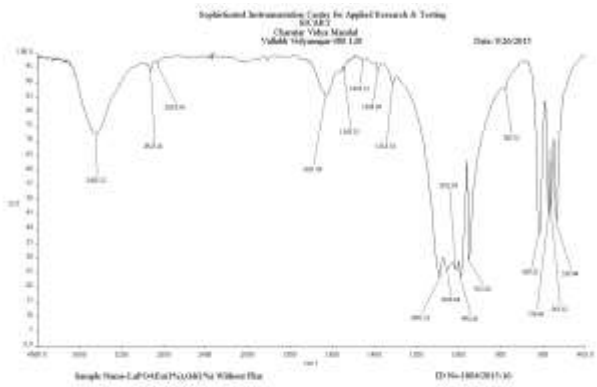

Fig. 9: FTIR of $LaPO_4$: Eu (1.0%), Gd (1.0%)

IV CONCLUSIONS

$LaPO_4$: Eu, Gd phosphor is successfully synthesized using SSR method. By observing the Table 1 and 2 with Eu (1%) column in Table 1, it is concluded that Gd did not change the primary emissions and intensities of Eu^{3+} in $LaPO_4$: Gd. Therefore, it is interesting to state that, apart from sensitizing the $LaPO_4$: Eu matrix by Gd co-dopant also enhanced the magnetic dipole component emissions of Eu^{3+} as Gd concentration increases in $LaPO_4$: Eu phosphor.

Therefore, it is concluded, the presence of Gd in $LaPO_4$: Eu matrix sensitizing the magnetic dipole emissions. Normally, the ratio of magnetic dipole to electric dipole emissions is 1 : 2 or 1 : 1. But, in the present case, magnetic dipole emissions are 4 and electric dipole emissions are 1. This is the highlight of the present work. This may be due to the 7 unpaired electrons in Gd may be suppressing the electronic transitions of Eu^{3+} emissions in red band. On comparison with Fig. 3 and 4, the emission intensities increase in Gd variated the Citric acid used flux prepared $LaPO_4$: Eu (1.5%) looks good and may be due to the formation of single phase $LaPO_4$: Gd (0.1% to 2.0%) in Eu (1%) constant.

From Fig. 4, it is concluded that the maximum intensity of 589 and 594 nm are found for 1.5% Gd concentration in $LaPO_4$: Eu (1.0%). Therefore, it is concluded that Eu (1%) $LaPO_4$: Gd (1.5%) may be a good phosphor in the Citric acid flux medium.

From XRD pattern of the unfluxed $LaPO_4$: Eu (1%), Gd (1%) phosphor, the calculated crystallite size of the highest peak is 24.86 nm. and the average value for all the observed peaks is 28.9078 nm.

From XRD pattern of the Citric acid fluxed $LaPO_4$: Eu (1%), Gd (1.5%) phosphor, the calculated crystallite size of the highest peak is 25.01 nm. and the average value for all the observed peaks is 27.52 nm.

From SEM of unfluxed $LaPO_4$: Eu (1%), Gd (1%) phosphor, the average basal diameter is less than one (735 nm) micron to two microns (1.7 μm).

From SEM of Citric acid fluxed $LaPO_4$: Eu (1%), Gd (1.5%) phosphor, the average basal diameter is more than 1 micron to 3 microns.

From both SEM pictures, good particles having mostly different shapes of varying sizes and agglomarated together are found.
From FTIR, the bands of C - O, Gd - O, La - O, Eu - O and O - H stretchings were observed.

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 multi phosphor devices. The luminescent properties of these compounds can be used for developing a tri-colour phosphor containing only the quite stable lanthanide- activated lanthanum phosphates for applications in PDPs and lamps without mercury. So, the red and yellow emissions of Eu^{3+} respectively can be used for the design of novel phosphors. Therefore, the $LaPO_4$: Gd, Eu phosphors can be easily applied in various types of lamp and display devices due to its good PL performance. In this regard, our target product is a very promising phosphor.

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