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Effect of Citric Acid As a Flux on EU 1.5% Doped Lapo$_4$: GD Phosphor

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Abstract: ***The present paper reports the effect of the citric acid as a flux on the photoluminescence (PL) properties of 1.5% of Europium dopedLaPO$_4$: Gd (1%) phosphor. The phosphors have been prepared under Standard Solid State Reaction method at 1200^o C for 3 hours. The main aim of the paper is to explore the effect of the citric acid as a flux on the emission intensities of LaPO$_4$: Gd, Eu System. Photoluminescence studies such as excitation and emission spectra of un-fluxed and the citric acid fluxed samples and their respective intensities are studied. Both the excitation spectra are monitored at 400 nm and the emission spectra are taken with 254 nm excitation wavelength. For all the practical display device purposes like fluorescent lamp and compact fluorescent lamp, the 254 nm, a mercury resonant radiation in low pressure discharge is used. Hence, by considering the device applications, the 254 nm excitation wavelength is selected for the measurements. The other characterizations like XRD, SEM and FTIR are done on the samples at room temperature. The XRD pattern was compared with JCPDS data and the crystal structure was also determined. The crystallite size was calculated using Scherrer's formula.***
Keywords: Phosphor, synthesis, photoluminescence, transition, solid state reaction, excitation and emission spectra

I. INTRODUCTION

The phosphors are widely used in lighting and display devices. The useful applications of rare earth element compounds, especially rare earth doped lanthanide phosphate inorganic materials, have touched upon broadly.

Over the past few years, they have been applied in many fields, such as optical display panels, cathode ray tubes (CRT), optoelectronic devices, sensitive devices, nano-scale electronic and plasma display panels (PDP) due to their significant chemical and physical properties. Various solution-phase routes - including solid state reaction, sol-gel, co-precipitation, water oil micro emulsion, polyol-mediated process, ultrasonification, hydrothermal and mechano chemical methods have been tried to lower the reaction temperature and obtain high quality $LaPO_4$ based nanoparticles.

However, the simple and mass fabrication of $LaPO_4$ Nano crystals with narrow grain size distribution and uniform morphology still remains a challenge. It appears that the best solution to control powder morphology and to produce low cost thin films is the use of soft chemistry routes. We adopted the standard solid state reaction technique to prepare $LaPO_4$ phosphor to obtain good morphologies and fine crystal structures and its excitation and emission intensities of luminescence are also studied.

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. Gd_2O_3 and Eu_2O_3 with fixed molecular weight of 1.0% and 1.5% were added respectively to it as dopants. They were weighed and taken into an agate mortar and pestle mixed ground thoroughly for 45 minutes to get fine powder. Acetone is added intermediately in grinding procedure to get small and uniform particle size. The obtained material was divided in to two parts. One of them was mixed with the Citric acid as 10% of its weight as a flux to observe the effect of citric acid as a flux in the photoluminescence emission characteristics of the$LaPO_4$: Eu,Gd system.Both the un-fluxed and the citric acid fluxed compounds were fired separately in a muffle furnace with a heating rate of 6^o C per minute, up to the temperature of 1200^{0}C for 3 hours in the open atmosphere.

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III. RESULTS AND DISCUSSIONS

A. PL Study

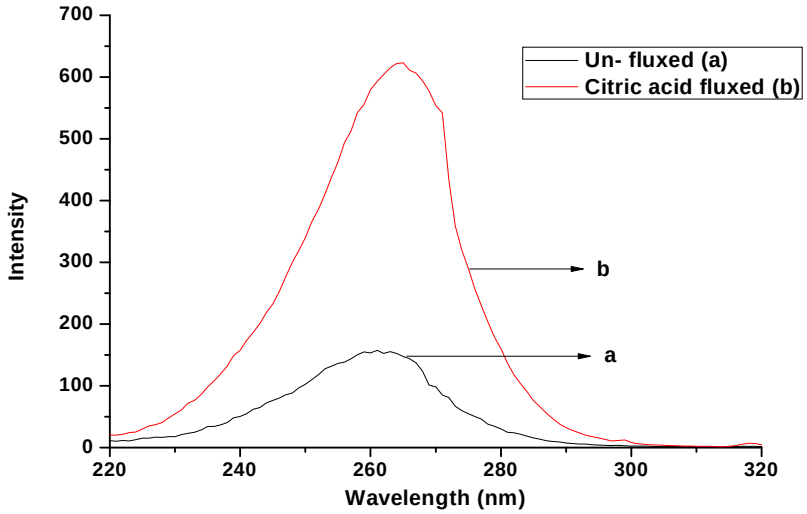


Fig. 1: Excitation spectra of $LaPO_4$: Gd (1%), Eu (1%) without and with citric acid as a flux

Fig.1 shows excitation spectra of $LaPO_4$: Eu1% andGd1% monitored at400nm for un-fluxed and the citric acid fluxed samples respectively. A broad Spectrum ranging from 220nm to 300nm, which peaks around 265 nm with good intensity is observed for the both samples. The citric acid doesn't alter the basic spectrum, but the intensity is increased around 5 times.

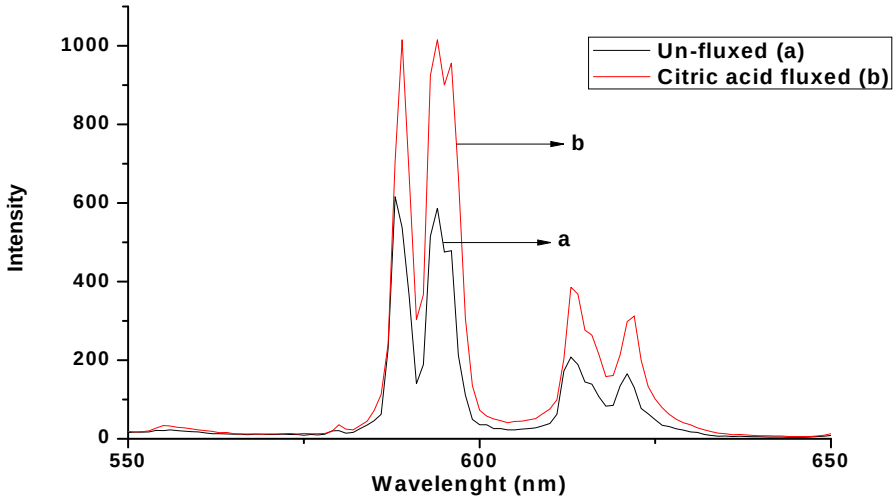


Fig. 2: Emission spectra of $LaPO_4$: Gd(1%), Eu(1%) without and with citric acid as a flux at 254 nm Ex.

Fig.2 is the emission spectra of $LaPO_4$: Eu1.5% andGd1% at an excitation wavelength of 254nm for un-fluxed and the citric acid fluxed samples. For all practical display device purposes like fluorescent lamp and compact fluorescent lamp, the 254 nm, a mercury resonant radiation in low pressure discharge is used. Therefore, by considering the application potential of this phosphor, the present set of Photoluminescent measurements was taken at the excitation of 254 nm, even though the maximum absorption band is around 265 nm. It should be noted that the 254 nm falls within the absorption band of $LaPO_4$: Eu (1.5%), Gd (1%). From the figure,the peaks found in yellow region are at 588 and 594nm wavelengths with good intensity, which are allowed transitions from magnetic dipole component from the crystal arises from Eu^{3+} ion. The emissions at 589 and 594nm are due to $^5D_0 \rightarrow {}^7F_1$ transition

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and the respective energies are 2.106 eV and 2.089 eV respectively and is attributed to magnetic dipole component from the crystal arises from Eu^{3+} ion. The emissions in the red region (613 and 621 nm) grow at the same phase. The emissions at 613 and 621 nm are due to $^5D_0 \rightarrow ^7F_2$ transition and the respective energies are 2.024 eV and 1.998 eV respectively and is attributed to sensitive electric dipole component from the crystal arises from Eu^{3+} ion.The emission intensities of all the peaks in yellow and red regions are almost $3\frac{3}{4}$ times when excited with 254 nm. The emission band in the red region attributes to hyper sensitive electric dipole component of the crystal arises from Eu^{3+} ion. The emission intensities of the yellow band and red band in the citric acid fluxed sample verywelly increased and the emissions in the yellow region goes out of the range of the machine ie. greater than 1016 units. From the figure, we can conclude that the role of the citric acid as a flux increases the photoluminiscent emissions to almost double.

B. XRD Study

Fig. 3 shows the XRD pattern of the $LaPO_4$: Gd (1%), Eu (1.5%)phosphor prepared without flux. From the figures it is clearly observed that the maximum peak obtained is at 28.49^o. 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 and for $LaPO_4$: Gd (1%), Eu (1%) 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 the figure is 28.9078 nm.

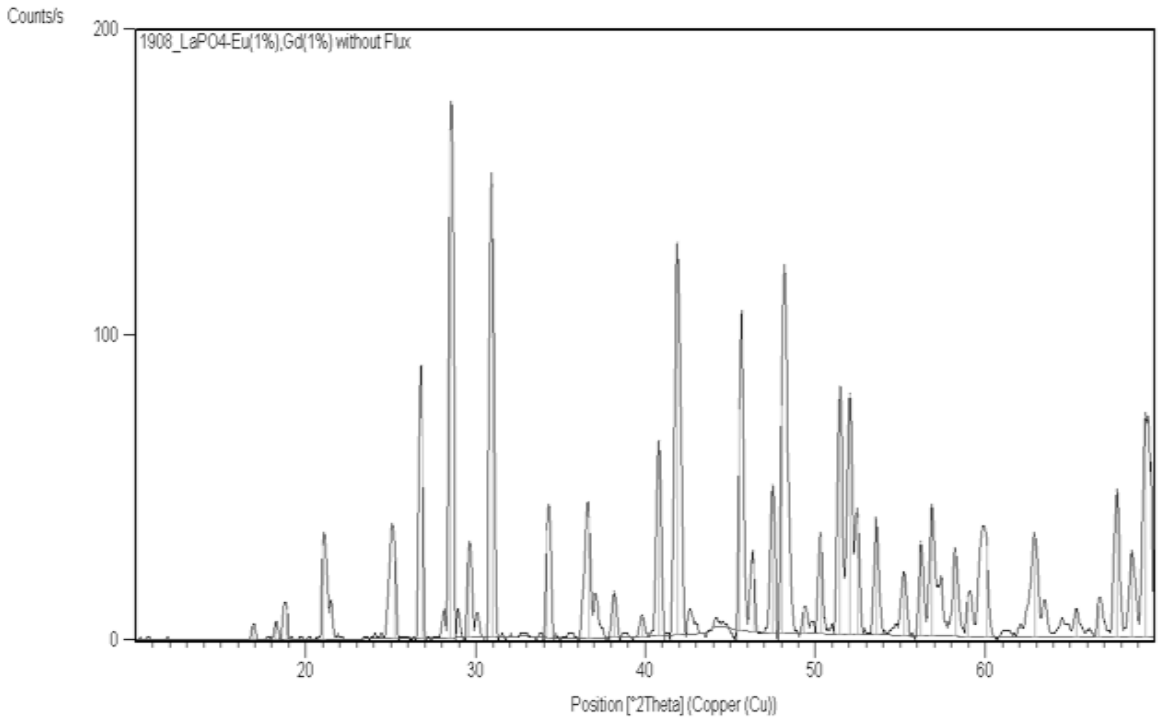


Fig. 3: XRD pattern of $LaPO_4$: Eu (1.5%), Gd (1.0%) phosphor without flux

C. FTIR Study

Fig. 4 shows the FTIR spectrum of $LaPO_4$: Eu (1.5%), Gd (1%), phosphor prepared without flux. From the figure, the most of the observed peaks are at 3625, 2375, 1425, 850, 650, 500 cm^{-1}. From FTIR it is observed that most of the bands are due to C-O, Gd-O, La-O, Eu-O and the O-H stretching band is observed at $3625cm^{-1}$. The band around $3625cm^{-1}$ is due to the H-OH stretching of absorbed water molecule from the atmosphere.

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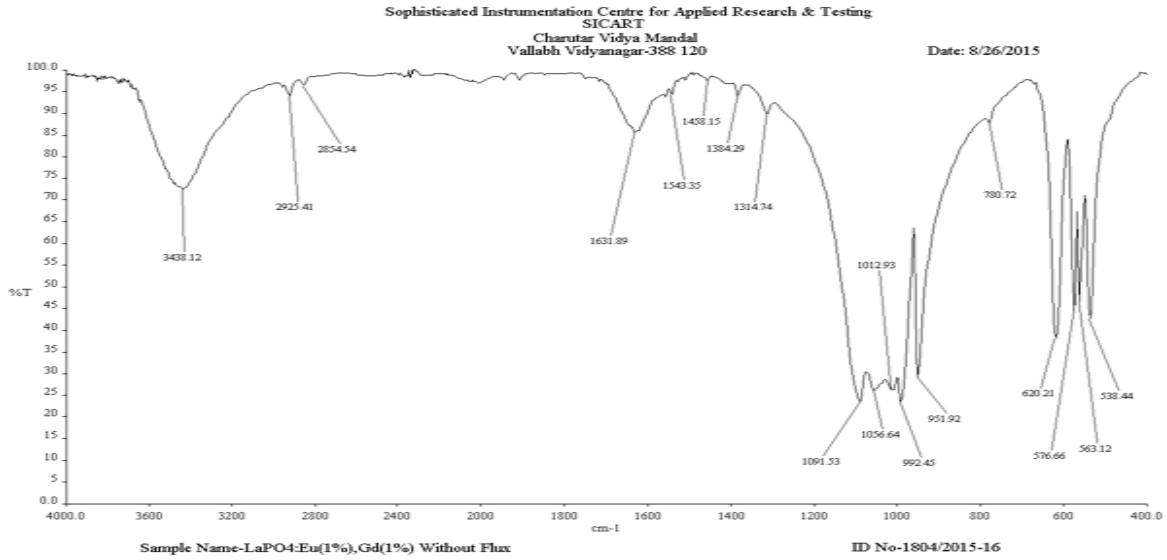


Fig.4: FTIR pattern of $LaPO_4$: Eu (1.5%), Gd (1.0%) phosphor without flux

D. SEM Study

Fig. 5 is the SEM of the $LaPO_4$: Eu (1.5%), Gd (1%)phosphor prepared without flux. From the Scanning Electron Micrograph of $LaPO_4$: Eu (1.5%), Gd (1%),with the measuring scale is 10 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 (1.7um). From SEM micrograph, good particles having mostly diffreent shapes of varying sizes mostly agglomarated together are found.

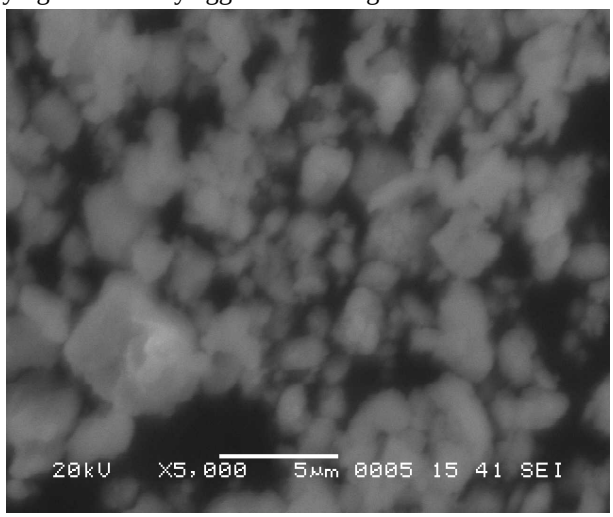


Fig. 5: SEM image of $LaPO_4$: Eu (1.5%), Gd (1%) phosphor without flux

E. XRD Study

Fig. 6 shows the XRD pattern of the $LaPO_4$: Eu (1.5%), Gd (1.5%)phosphor prepared with the citric acidas flux. From the figures it is clearly observed that the maximum peak obtained is at 31.9^o. 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 and for $LaPO_4$: Gd(1%), Eu (1%) 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 seen in the figure is **27.52 nm.**

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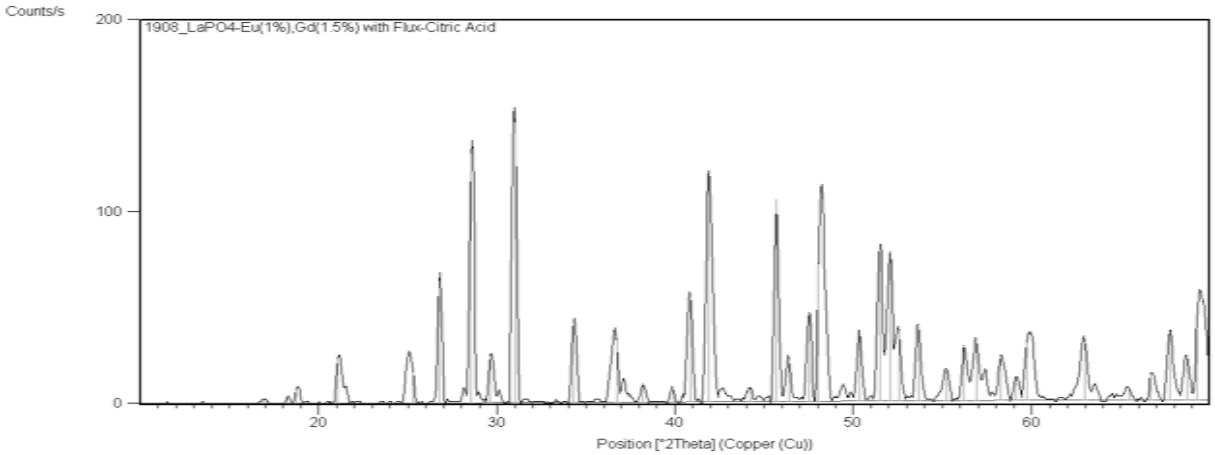


Fig. 6: XRD pattern of $LaPO_4$: Eu (1.5%), Gd (1%) phosphor with citric acid as flux

F. FTIR Study

Fig. 7 shows the FTIR spectrum of $LaPO_4$: Eu (1.5%), Gd (1.%) phosphor prepared with the citric acid as flux. From the figure the most of the observed peaks are at 3625, 2375, 1425, 850, 650, 500 cm^{-1}. From FTIR it is observed that most of the bands are due to C-O, Gd-O, La-O, Eu-O and the O-H stretching band is observed at 3625cm^{-1}. The band around 3625cm^{-1} is due to the H-OH stretching of absorbed water molecule from the atmosphere.

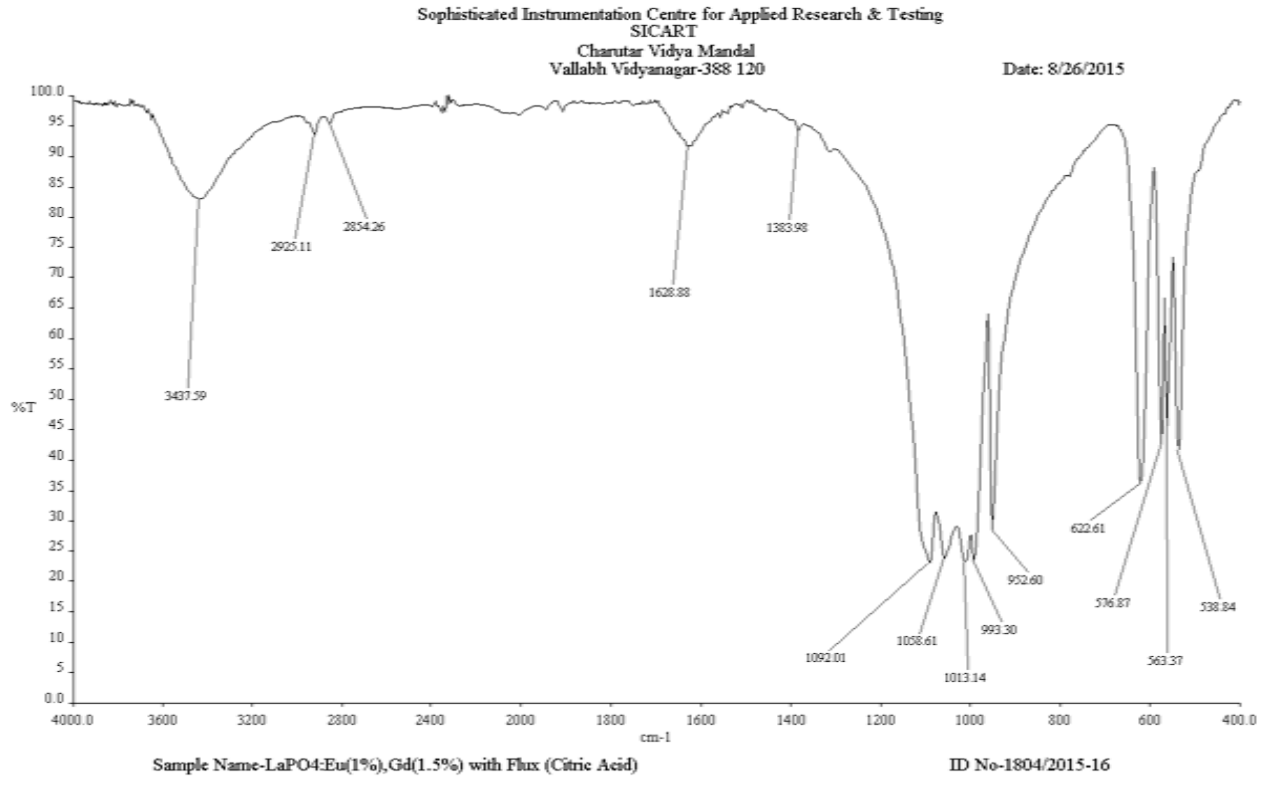


Fig.7: FTIR pattern of $LaPO_4$: Eu (1.5%), Gd (1.0%) phosphor with citric acid as flux

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G. SEM Study

Fig.8 is the SEM of the $LaPO_4$: Eu (1.5%), Gd(1%)phosphor prepared with the citric acid as flux. From the Scanning Electron Micrograph of $LaPO_4$: Eu (1.5%), Gd (1%)**,** 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, good particles having different shapes of varying sizes mostly agglomarated together are found.

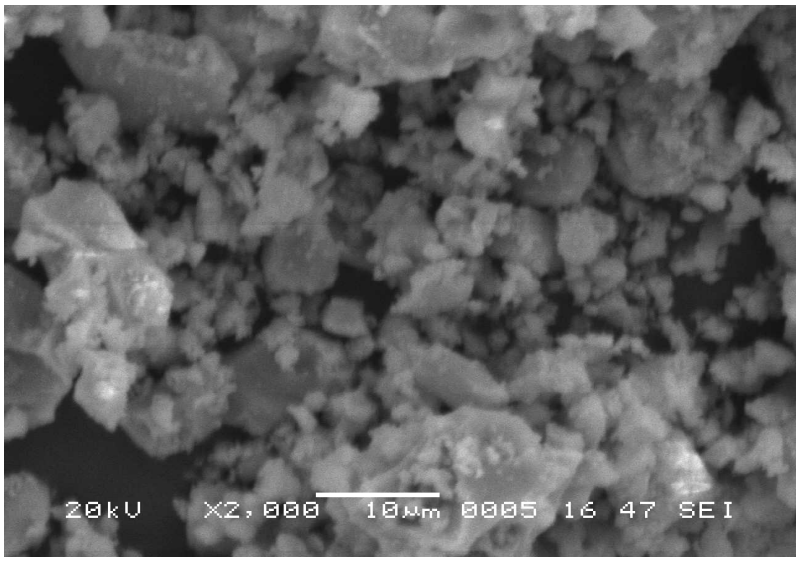


Fig. 8: SEM image of $LaPO_4$: Eu (1.5%), Gd (1%) phosphor with citric acid as flux

IV. CONCLUSIONS

A. $LaPO_4$ phosphor doped with Eu and Gd rare-earth ions is synthesized successfully using slid state reaction method.

B. Citric acid plays predominant role as a flux and enhances the emission intensities to almost double. This also allows us to conclude, the addition of the citric acid as flux leads to well formation of crystallites.

C. It is logically concluded that, the emissions in yellow band dominates by 4 times to the emissions in red band. 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 this phosphor. This may be due to the 7 unpaired electrons in Gd may be suppressing the electronic transitions of Eu^{3+} emissions in red band.

D. The emissions at 589 and 594nm are due to $^5D_0 \rightarrow ^7F_1$ transition and the respective energies are 2.106 eV and 2.089 eV respectively and is attributed to magnetic dipole component from the crystal arises from Eu^{3+} ion

E. emissions at 613 and 621 nm are due to $^5D_0 \rightarrow ^7F_2$ transition and the respective energies are 2.024 eV and 1.998 eV respectively and is attributed to sensitive electric dipole component from the crystal arises from Eu^{3+} ion.

F. The calculated crystallite size using Scherer's formula for the highest peak of un-fluxed $LaPO_4$: Gd (1%), Eu (1.5%) is around 24.86 nm. The average calculated crystallite size for all the observed peaks seen in the figure is 28.9078 nm.

G. The calculated crystallite size with the consideration of the highest intensity peak of the citric acid fluxed $LaPO_4$: Gd (1%), Eu (1.5%) phosphor is around 25.01 nm. The average calculated crystallite size by considering all the observed peaks presented in the figure is 27.52 nm.

H. The stretchings of the FTIR spectrum confirm the presence of the constituent elements that those are presented in the $LaPO_4$: Gd (1%), Eu (1.5%) phosphor.

I. From the SEM of un-fluxed $LaPO_4$: Eu (1.5%), Gd (1%), the average basal diameter of the particles is around 0.5 to 1.5 microns.

J. . From the SEM of the citric acid fluxed $LaPO_4$: Eu (1.5%), Gd (1%), the average basal diameter of the particles is around 1 to 3 microns.

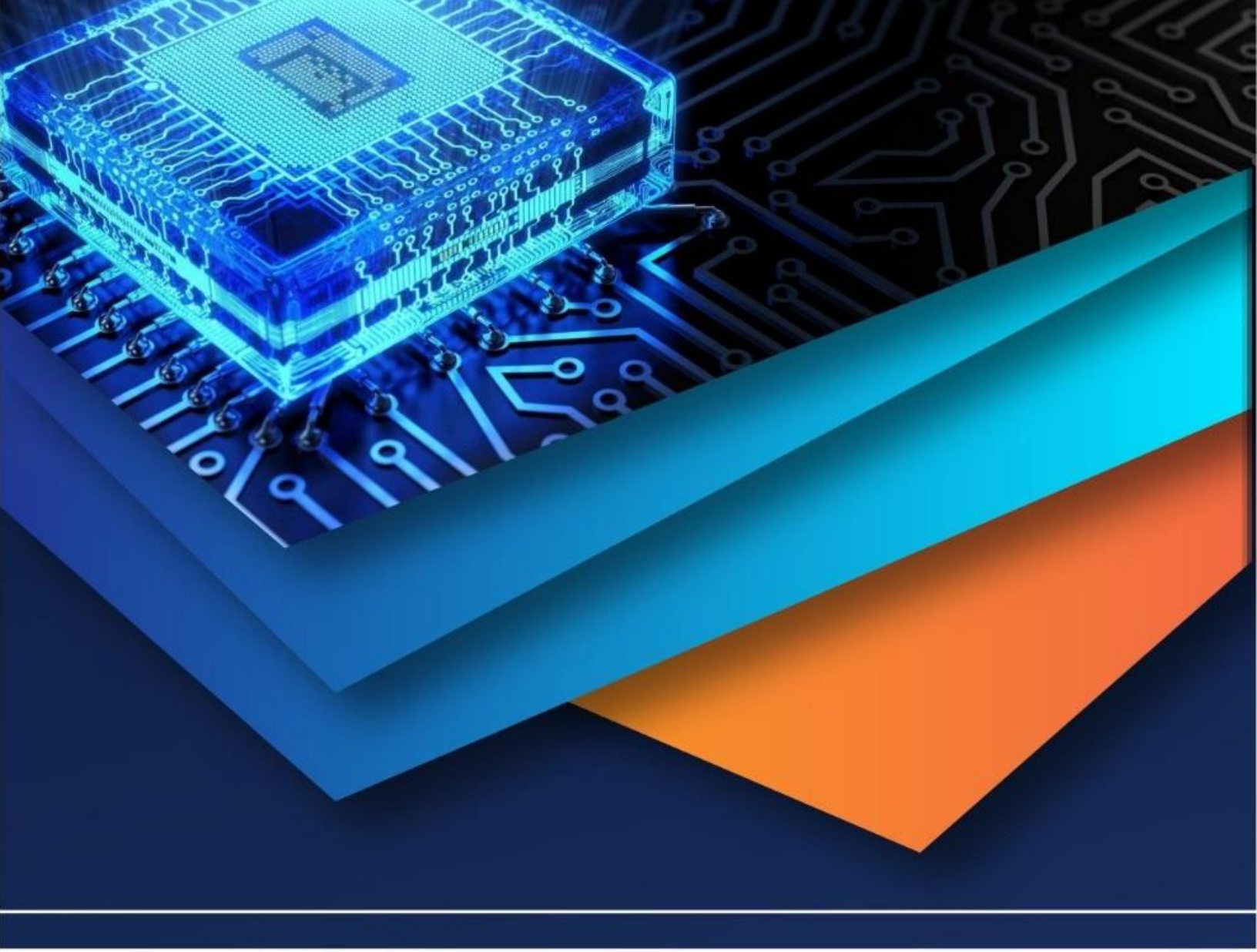
K. $LaPO_4$: Eu (1.5%), Gd (1%)can be a good candidate for device applications where in 254 nm is the excitation. For example, fluorescent lamp and compact fluorescent lamp.

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