



PHOTOLUMINESCENCE STUDY OF LaPO₄ PHOSPHOR

P.Kamala¹, SenthilKannan.K^{2*}, T. Malathi Rekha³ and K.V.R. Murthy⁴

¹The Hindu College, Machilipatnam-5210002, A.P., India.

²R&D Laboratory, Edayathangudy G.S Pillay Arts and Science College,
Nagapattinam 611002 TN, India.

³SPHM Kalasala Machilipatnam-5210002, A.P., India

⁴Display Materials Laboratory, Applied Physics Dept., Faculty of Technology and Engineering,
M. S. University of Baroda, Vadodara, Gujarat, India.

***Corresponding Author:** Dr SenthilKannan.K Dean-Research & Vice Principal, Research Scientist, Edayathangudy G.S Pillay Arts and Science College, Nagapattinam 611002 TN, India

ABSTRACT

A phosphor, most commonly, is a substance that put on views the phenomenon of luminescence. Somewhat perplexingly, this includes both phosphorescent materials, which show a slow crumble in brightness (> 1 ms), and fluorescent materials, where the emission decay takes place over tens of nanoseconds. Phosphorescent materials are known for their use in radar screens and glow-in-the-dark materials, whereas fluorescent materials are common in cathode ray tube (CRT) and plasma video display screens, fluorescent lights, sensors, and white LEDs. Phosphors are often transition-metal compounds or rare-earth compounds of various types. The most familiar uses of phosphors are in CRT displays and fluorescent lights [1-4]. CRT phosphors were regimented beginning around world war II and designated by the letter "P" followed by a number. Phosphorus, the chemical element named for its light-emitting behavior, emits light due to chemiluminescence, not phosphorescence [1, 5-7].

1. Introduction

A material can emit light either through incandescence, where all atoms radiate, or by luminescence, where only a small fraction of atoms, called emission centers or luminescence centers, emit light, the wavelength emitted by the emission center is dependent on the atom itself and on the surrounding crystal structure [7-10]. The scintillation process in inorganic materials is due to the electronic band structure found in the crystals. An incoming particle can excite an electron from the valence band to either the conduction band or the excitons band (located just below the conduction band and separated from the valence band by an energy gap). This leaves an associated hole behind, in the valence band. Impurities create electronic levels in the forbidden gap. The delayed de-excitation of those metastable impurity states [11-14], slowed down by reliance on the low-probability forbidden mechanism, again results in light emission (slow component).

2. Experimental

The sample is prepared using solid state reaction (SSR) technique. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La_2O_3), Diammonium Hydrogen Phosphate $[(\text{NH}_4)_2\text{HPO}_4]$, Rare Earth Oxides were grinded in an agate motor and mixed and compressed into a crucible and heated at 1200°C for four hours in a muffle furnace. The samples were kept at the set temperature for three hours then cooled down naturally. The sample is heated at 1200°C for 3 hours using muffle furnace with a heating rate of $4^\circ\text{C}/\text{min}$ and the samples were allowed to cool in the furnace and taken out when the muffle temperature is 100°C [15-17]. The formation of a phosphor host and doping process is critical and is highly dependent on the reaction temperature and conditions. Since the purity of starting chemicals is very important to the synthesis of phosphors, the starting chemicals are typically 99.9-99.999% in purity. It is important to minimize the concentration of specific contaminants such as Fe, Co, and Ni, which can seriously degrade phosphor performance. Required amounts of starting ingredients are mixed in the presence of an appropriate flux and fired at high temperatures (900 - 1500°C) in air or in a controlled atmosphere (N_2 , C, CO, or N_2 with 2-5% of H_2). The calcinations conditions such as firing temperatures, duration of firing, firing atmosphere, and rate of heating and cooling for a particular phosphor are optimized empirically [18-21]. The phosphor particle size and shape are also related to the morphology of starting chemicals and flux. The presence of flux materials of low melting compounds such as alkali halides helps to complete the doping process at lower temperatures. Most of the phosphors are prepared by a solid-state reaction. The general preparation procedure of solid-state reaction is well described in the literature and mostly used by the industry.

3. Characterizations:

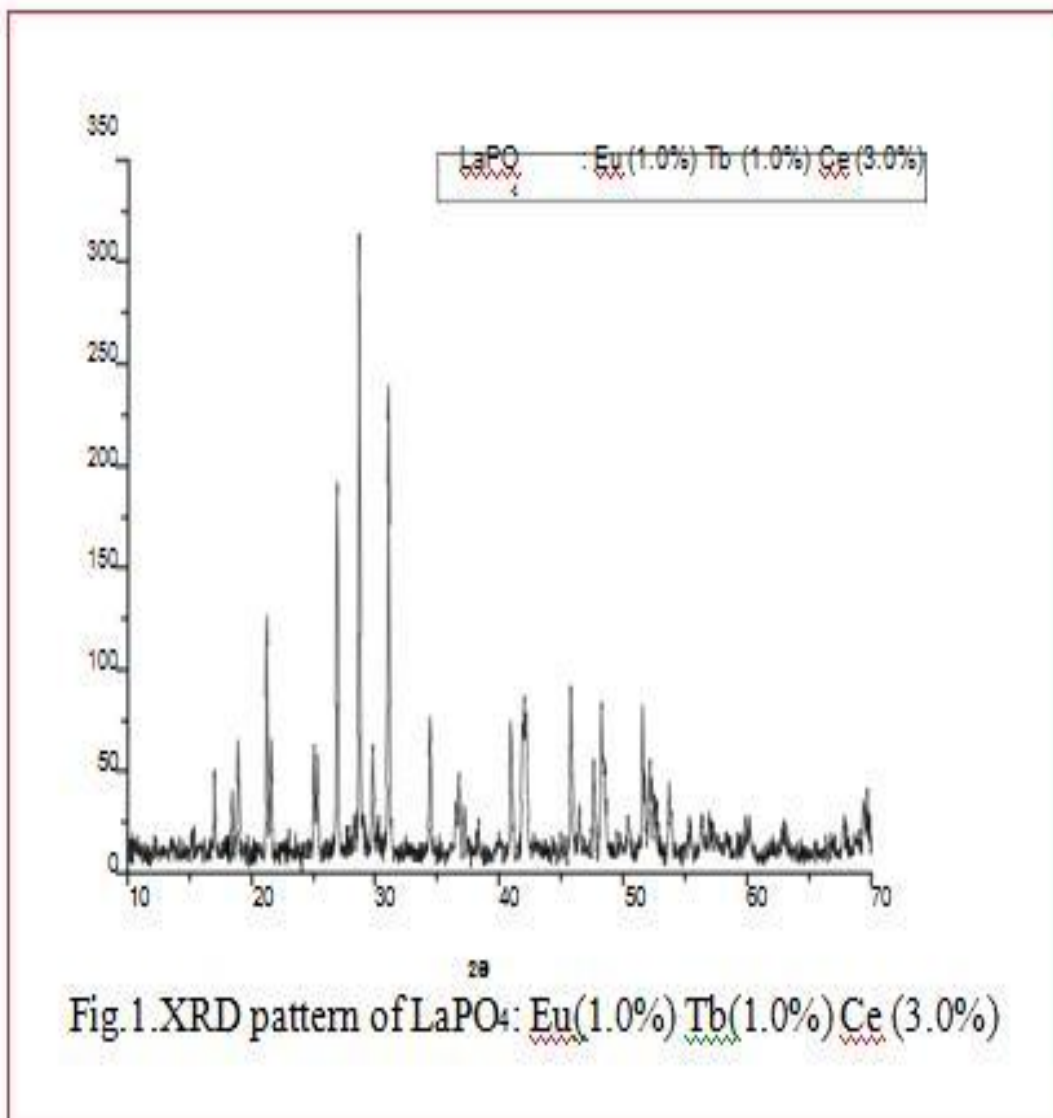
1. XRD
2. FTIR
3. PL
4. SEM

1. XRD

The crystallinity and phase purity of the product were firstly examined by XRD analysis. Fig 1 shows the typical X-ray diffraction (XRD) patterns of synthesized samples of pure LaPO₄:Eu,Ce. As shown XRD patterns of nano crystals are in good agreement with the values from JCPDS no.(35-731) of LaPO₄, Eu,Ce which shows that all the products are monazite LaPO₄ Eu,Ce with monoclinic structure. The crystalline phases were identified with the International Centre for Diffraction Data (ICDD) database. The main peak was found around 28.5° corresponding to a d- value of about 3.11 Å⁰, followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate. All diffraction patterns were obtained using CuKα radiation (λ = 1.540598 Å⁰) at 40 kv and 30 mA, and divergence slit fixed at 1.52 mm. Measurements were made from 2θ = 10° 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 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 = Braggs angle of the XRD

peak. D spacing = 3.12451

FWHM = 0.50184

2Theta = 28.869 deg

The average crystallite size of LaPO₄:Eu,Ce phosphors is 163.5326 Å i.e. 16.35 nm. The crystal growth of monoclinic LaPO₄:Eu,Ce is taking place around 1000°C. The XRD pattern of the LaPO₄:Eu,Ce powder heat treated at 1200 °C is similar to that of the powder heat treated at 1000 °C, which confirm that highly crystallized LaPO₄:Eu,Ce is already obtained at 1000 °C. Thus, 1000 °C is the required temperature to overcome the kinetic barrier and form the thermodynamically stable monoclinic structure the monoclinic structure (**JCPDS file 32-0493**)

2.FTIR

In order to determine the chemical bonds of the present studied phosphor FTIR analysis was carried out. Here is the FTIR of the Eu, Tb and Ce doped LaPO₄ phosphor, the main absorption are assumed H-O-H stretching followed by other bonds of C-H bending, C-O stretching and CO -OH stretching. CO-OH and H-O-H stretching are due to absorbed CO₂ and H₂O molecules from atmosphere and also 1033 is P-O or PO₄³⁻ 956 is P-O-P and 586 is P-O vibrations.

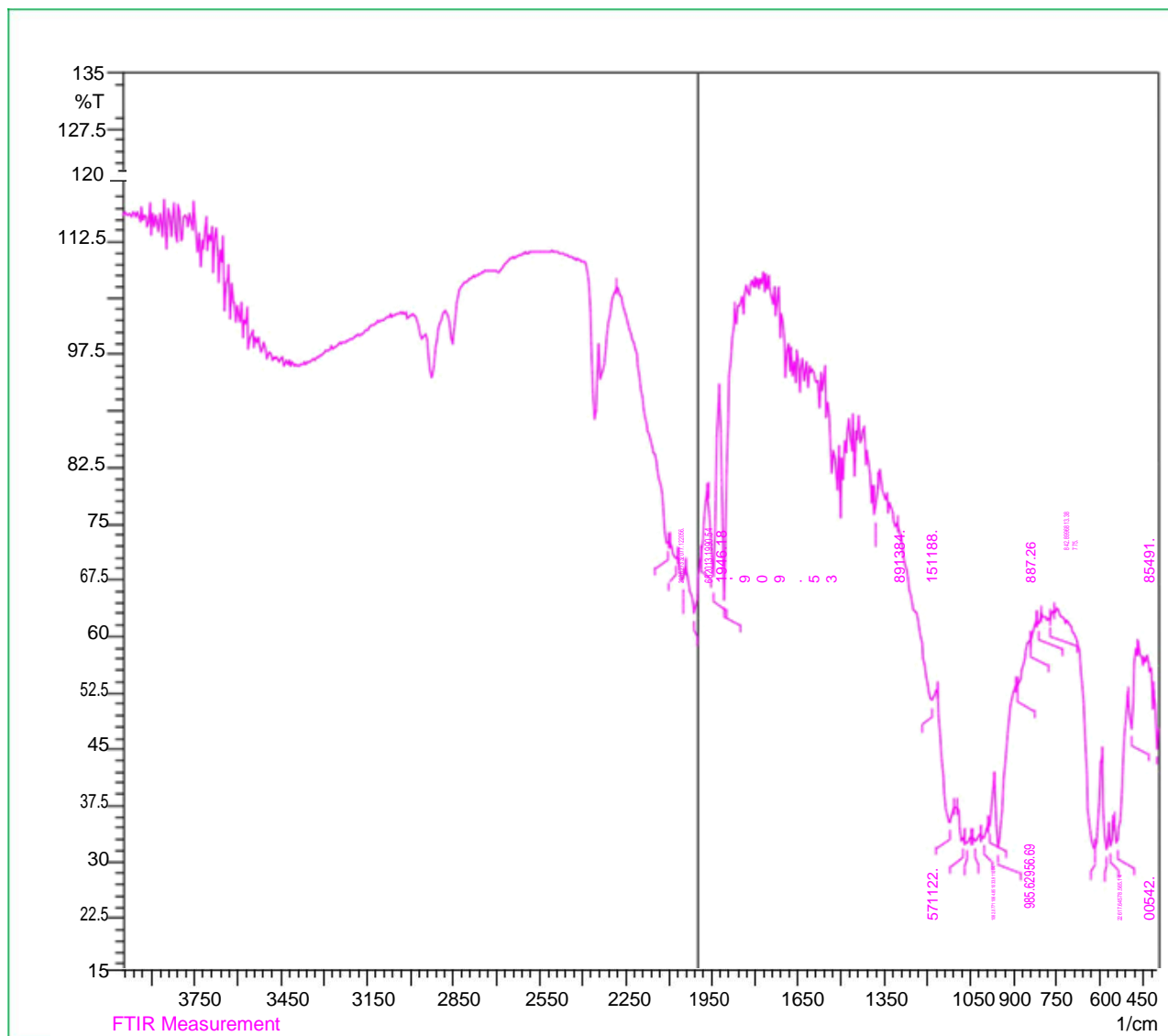


Fig.2. FTIR Spectrum

3 PL

The photoluminescence behavior of LaPO_4 at different perceptions such as LaPO_4 and are given in Table.1. The corresponding PL emission for the excitations are given in Fig.3A to 3O and the proportionate doping agents with are specified as a,b,c in the main figures.

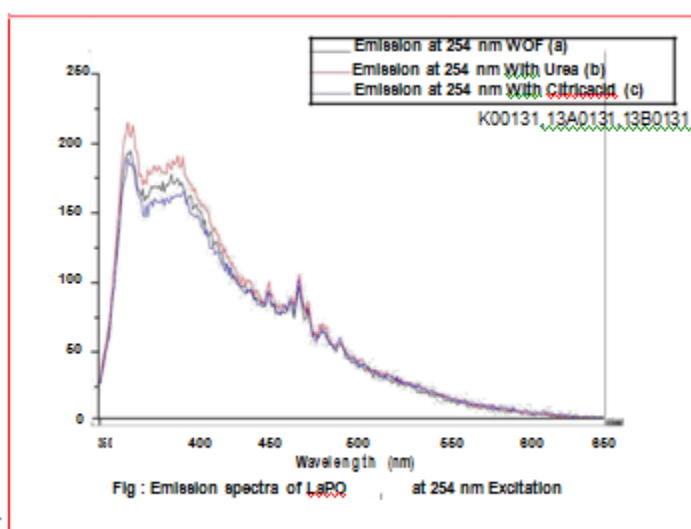
Table: 1. Details of emission wavelengths for excitations for pure and doped LaPO_4

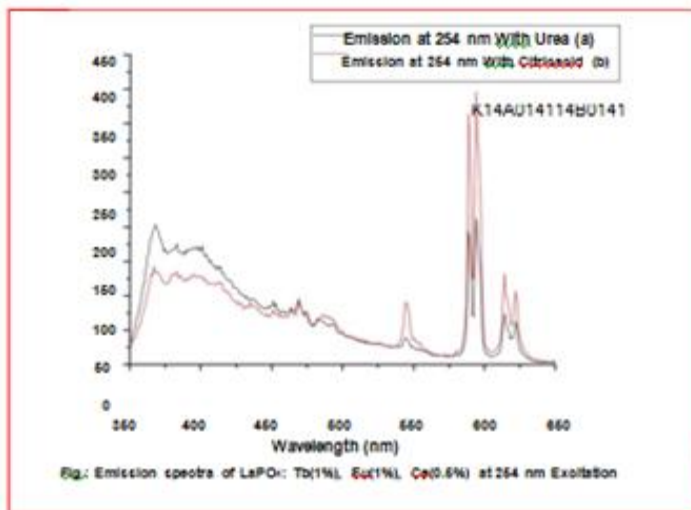
| S.No | Name of the Compound | Emission wavelength (nm) | Emission intensities under 254nm excitation | | |
|------|--|--------------------------|---|--------------|---------------------|
| | | | Without flux | Urea as flux | Citric acid as flux |
| 1 | LaPO ₄ Base | 369 | 195 | 215 | 190 |
| | | 393 | 178 | 191 | 165 |
| | | 469 | 97 | 105 | 102 |
| 2 | LaPO ₄ :Tb 1% Eu 1% Ce 0.5% | 545 | 203 | 39 | 91 |
| | | 590 | 215 | 193 | 364 |
| | | 595 | 238 | 212 | 395 |
| | | 614 | 76 | 74 | 132 |
| 3 | LaPO ₄ :Tb 1% Eu 1% Ce 1% | 622 | 65 | 62 | 106 |
| | | 545 | 172 | 37 | 78 |
| | | 590 | 217 | 236 | 360 |
| | | 595 | 229 | 262 | 399 |
| 4 | LaPO ₄ :Tb 1% Eu 1% Ce 1.5% | 614 | 78 | 91 | 136 |
| | | 622 | 66 | 75 | 105 |
| | | 545 | 65 | 61 | 73 |
| | | 590 | 370 | 215 | 329 |
| 5 | LaPO ₄ :Tb 1% Eu 1% Ce 2% | 595 | 512 | 228 | 350 |
| | | 614 | 134 | 83 | 115 |
| | | 622 | 109 | 70 | 92 |
| | | 545 | 146 | | 119 |
| 6 | LaPO ₄ :Tb 1% Eu 1% Ce 3% | 590 | 285 | | 315 |
| | | 595 | 305 | | 337 |
| | | 614 | 100 | | 112 |
| | | 622 | 83 | | 82 |
| | | 545 | 104 | | 223 |
| 7 | LaPO ₄ :Tb 1% Eu 1% Ce 4% | 590 | 214 | | 304 |
| | | 595 | 222 | | 335 |
| | | 614 | 83 | | 107 |
| | | 622 | 66 | | 87 |
| | | 545 | 135 | | 122 |
| 8 | LaPO ₄ :Tb 1% Eu 1% Ce 5% | 590 | 187 | | 221 |
| | | 595 | 198 | | 223 |
| | | 614 | 67 | | 80 |
| | | 622 | 59 | | 68 |
| 8 | LaPO ₄ :Tb 1% Eu 1% Ce 5% | 545 | 109 | 48 | 174 |
| | | 590 | 176 | 94 | 250 |
| | | 590 | 176 | 94 | 250 |
| | | 595 | 187 | 97 | 266 |
| | | 614 | 63 | 35 | 90 |
| | | 622 | 55 | 31 | 73 |

Table: 1A. Details of emission wavelengths for excitations doped LaPO₄

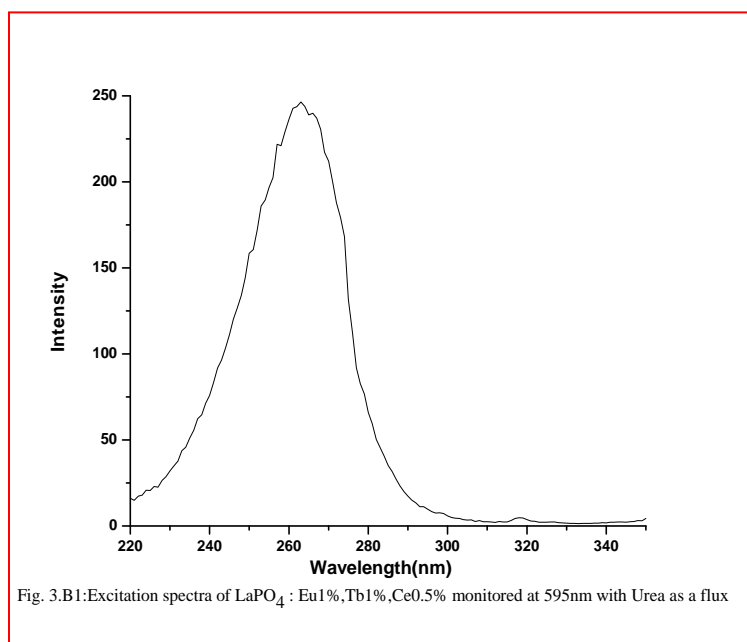
| S.No | Name of the Compound | Emission wavelength (nm) | Emission intensities under 275nm excitation | |
|------|--|--------------------------|---|---------------------|
| | | | Without flux | Citric acid as flux |
| 1 | LaPO ₄ :Tb 1% Eu 1% Ce 0.5% | 365 | 132 | 110 |
| | | 380 | 125 | 105 |
| | | 414 | 103 | 91 |
| | | 487 | 98 | 108 |
| | | 545 | 203 | 251 |
| | | 590 | 215 | 232 |
| | | 595 | 238 | 235 |
| | | 614 | 76 | 82 |
| | | 622 | 65 | 68 |
| 2 | LaPO ₄ :Tb 1% Eu 1% Ce 1% | 365 | 147 | 144 |
| | | 380 | 133 | 129 |
| | | 414 | 101 | 100 |
| | | 487 | 87 | 97 |
| | | 545 | 172 | 197 |
| | | 590 | 217 | 233 |
| | | 595 | 229 | 241 |
| | | 614 | 78 | 80 |
| | | 622 | 66 | 65 |
| 3 | LaPO ₄ :Tb 1% Eu 1% Ce 1.5% | 365 | 120 | 143 |
| | | 380 | 111 | 130 |
| | | 414 | 87 | 106 |
| | | 487 | 83 | 92 |
| | | 545 | 171 | 191 |
| | | 590 | 225 | 199 |
| | | 595 | 251 | 215 |
| | | 614 | 81 | 71 |
| | | 622 | 70 | 58 |
| 4 | LaPO ₄ :Tb 1% Eu 1% Ce 2% | 365 | 190 | 105 |
| | | 380 | 290 | 114 |
| | | 414 | 167 | 103 |
| | | 487 | 169 | 130 |
| | | 545 | 441 | 342 |
| | | 590 | 191 | 175 |
| | | 595 | 175 | 179 |
| | | 614 | 57 | 61 |
| | | 622 | 55 | 52 |
| | LaPO ₄ :Tb 1% Eu 1% Ce 3% | 365 | 131 | 150 |
| | | 380 | 136 | 219 |
| 5 | | 414 | 114 | 191 |
| | | 487 | 119 | 236 |
| | | 545 | 293 | 695 |
| | | 590 | 129 | 200 |
| | | 595 | 126 | 117 |
| | | 614 | 44 | 60 |
| | | 622 | 40 | 63 |
| 6 | LaPO ₄ :Tb 1% Eu 1% Ce 4% | 365 | 198 | 151 |
| | | 380 | 218 | 163 |
| | | 414 | 166 | 133 |
| | | 487 | 154 | 139 |
| | | 545 | 391 | 354 |

| | | | | |
|---|--------------------------------------|-----|-----|-----|
| | | 590 | 119 | 131 |
| | | 595 | 101 | 125 |
| | | 614 | 37 | 42 |
| | | 622 | 40 | 43 |
| 7 | LaPO ₄ :Tb 1% Eu 1% Ce 5% | 365 | 160 | 140 |
| | | 380 | 165 | 187 |
| | | 414 | 132 | 161 |
| | | 487 | 103 | 182 |
| | | 545 | 207 | 512 |
| | | 590 | 218 | 151 |
| | | 595 | 232 | 137 |
| | | 614 | 82 | 47 |
| | | 622 | 68 | 51 |

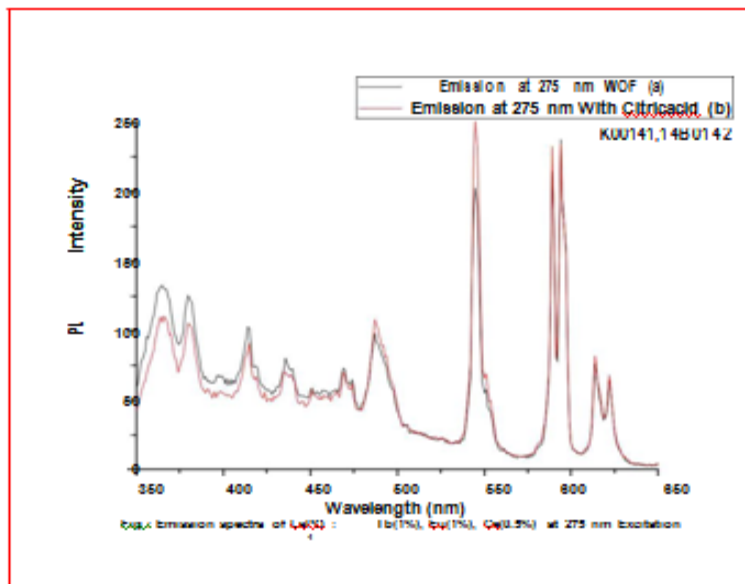




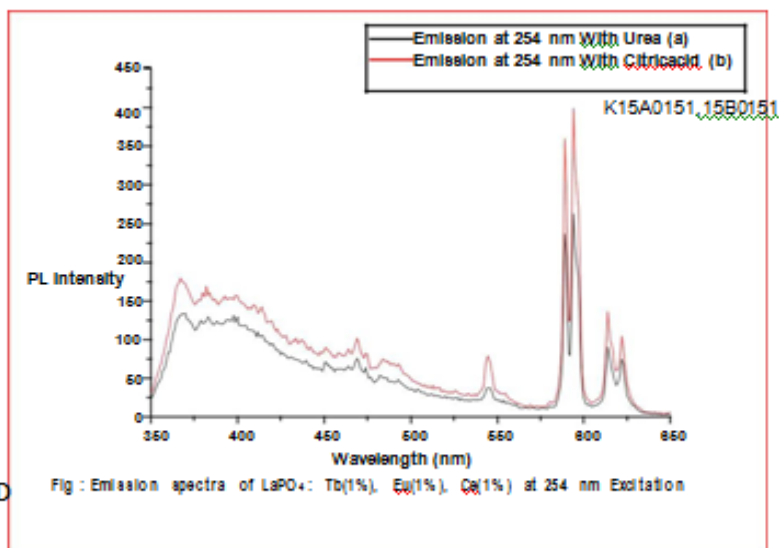
3B

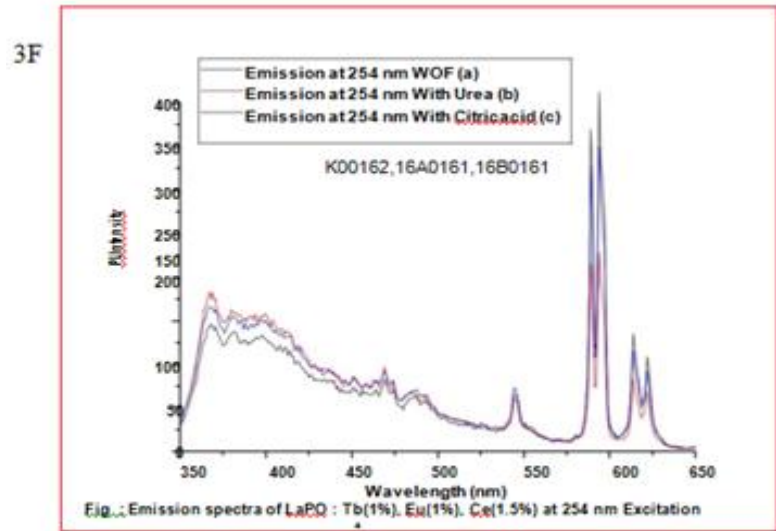
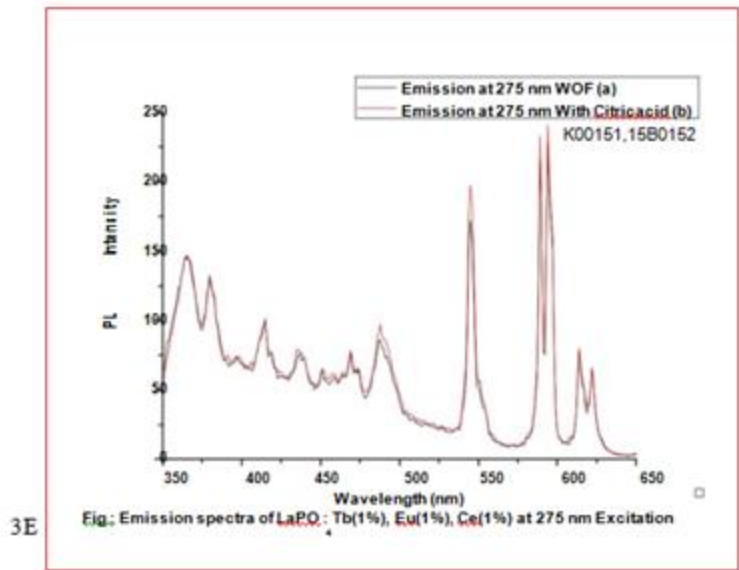


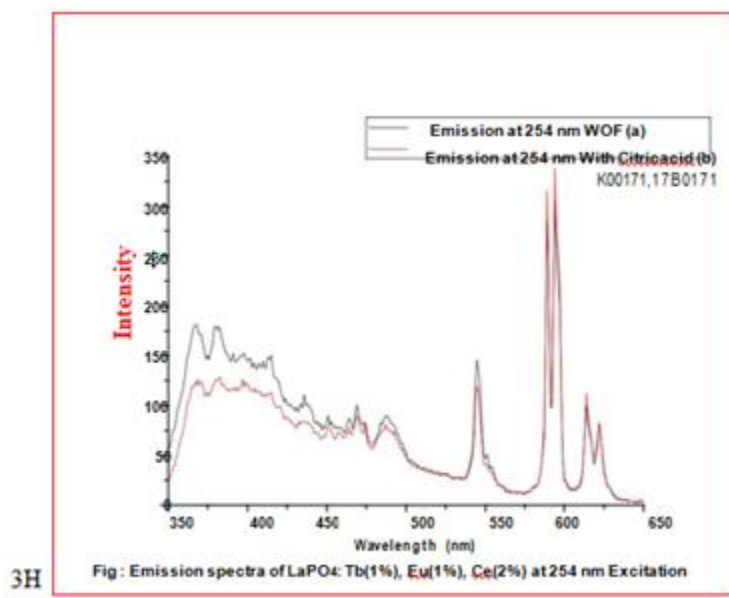
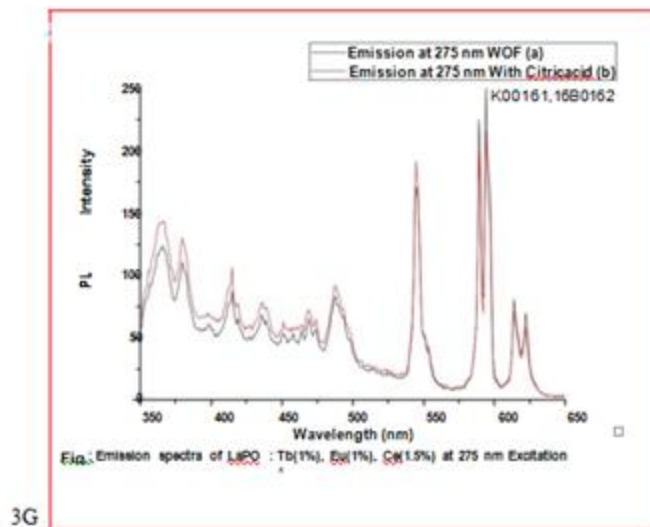
3C

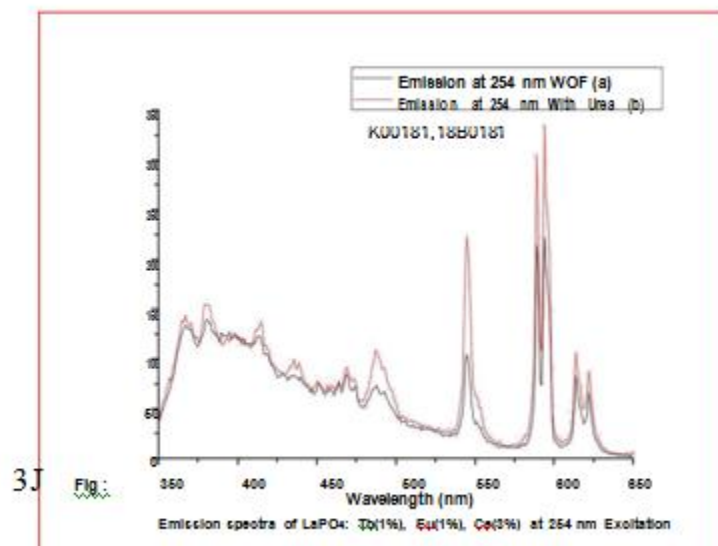
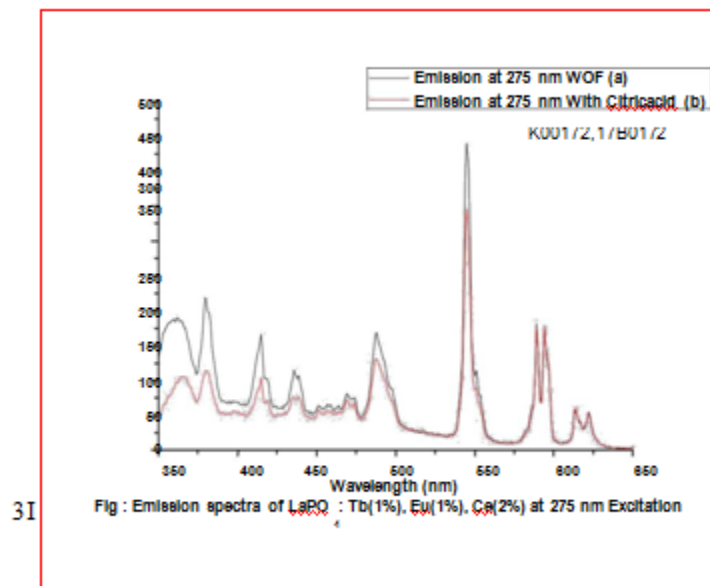


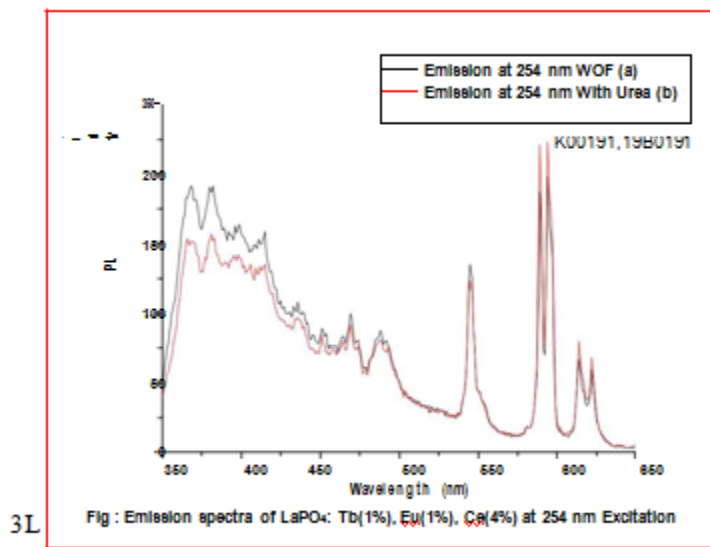
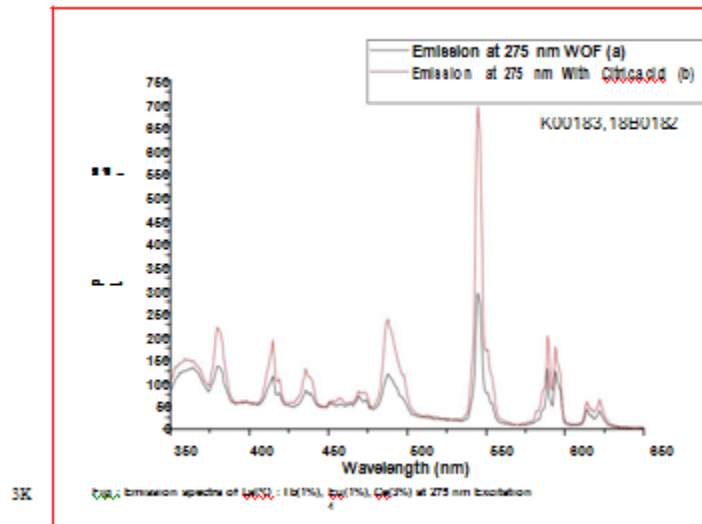
3D



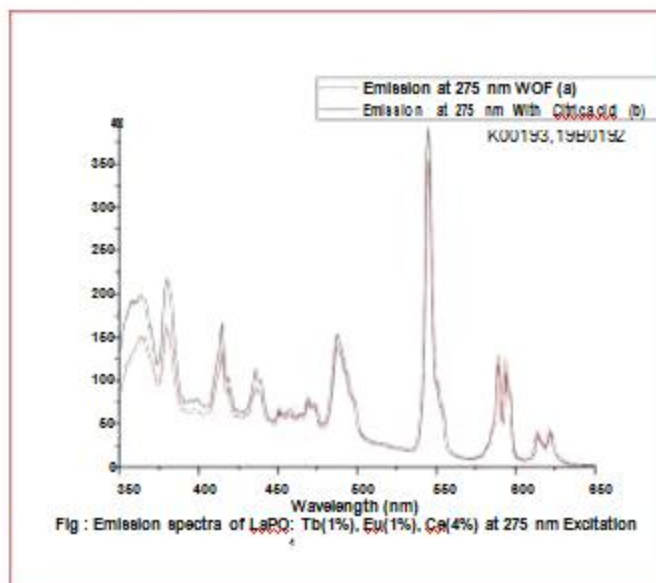




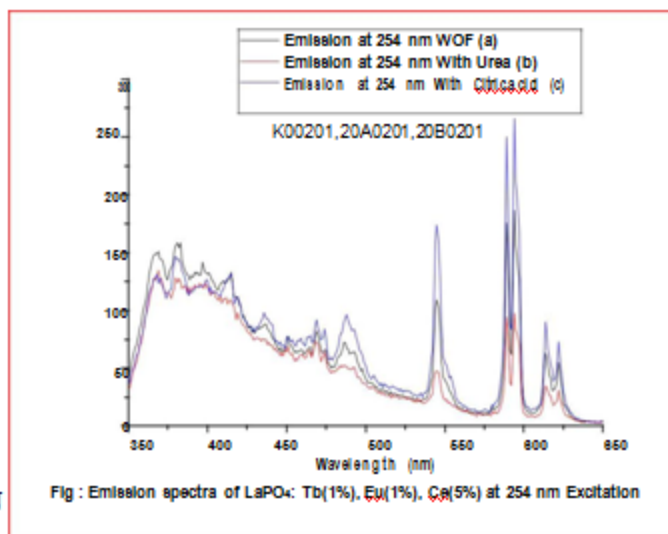


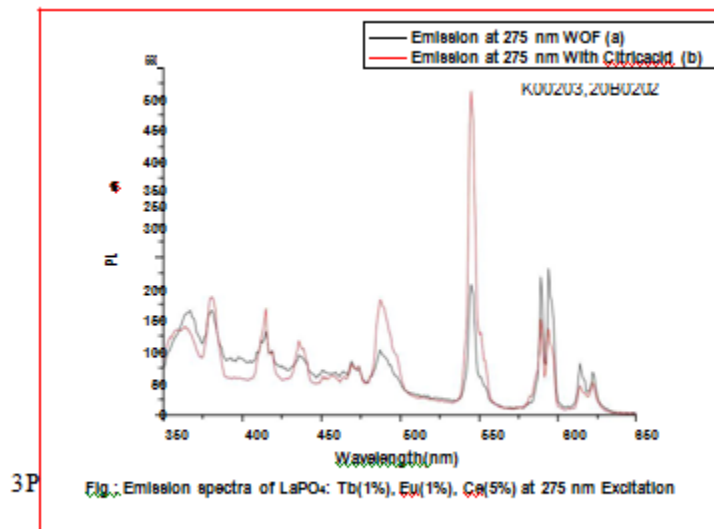
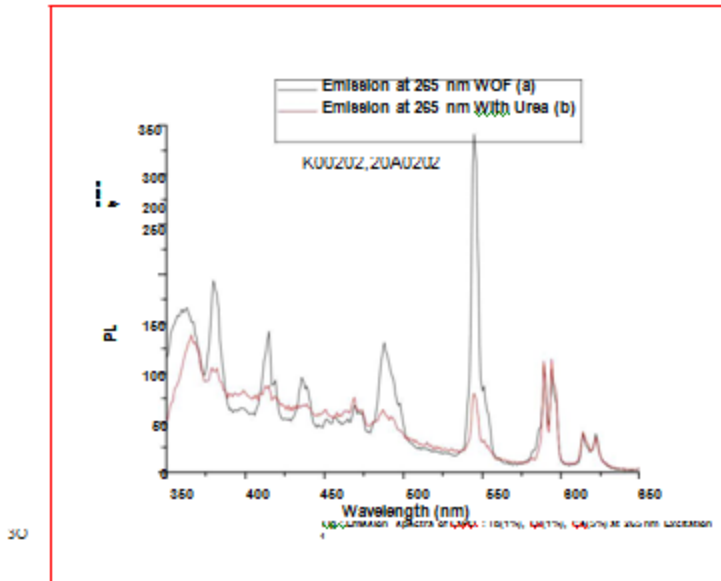


3M



3N





Results and Discussions:

The present section reports PL studies of LaPO₄: Tb(1%),Eu(1%), Ce(x) [x=0.5%, 1%, 1.5%, 2% 3%, 4% and 5%]. Total eight sets of LaPO₄: Tb, Eu, Ce are prepared.

Fig 3A is the PL emission when excited with 254nm. LaPO₄: Tb, Eu, Ce(x) were prepared without flux as well as 10% weight citric acid as flux. There are two excitation bands present. One is at 254nm and another is at 275nm.Total 15 figures are presented for 254 and 275nm excitations which are noted as fig3A to Fig3'O'. Fig 1A&B is the PL excitation and emission

intensities. There is no considerable PL seen in undoped phosphor. However on addition of Tb, Eu(1%) constant and varying Ce there are emissions at 545, 583 and 590nm. Fig 3B-1 is the excitation spectra for LaPO₄: Tb, Eu, Ce(0.5%) monitored at 595nm, 614 and 622nm with different intensities. The same phosphor is prepared with citric acid as flux and presented in Fig3B, curve B is formed. The intensities at 545, 590, 595, 614 and 622nm increases by 100%. Same phosphor is excited to 275nm and presented in fig3C. It is interesting to note that many emissions with different intensities at 365, 384, 420, 480, 545, 590, 595, 614 and 622nm are seen. However, the emission intensity at 545nm is highest followed by 590 and 595nm. Effect of citric acid as flux played a marginal increase in intensity. Fig 3D,3F, 3H, 3J, 3L and 3N are the PL of 254nm excited various Ce concentrations in LaPO₄: Tb, Eu(1%). From the figures, it is observed when the Ce is 1.5%, the emission intensities at 590, 595nm are maximum thereafter. These emission intensities started reducing as the Ce concentration increases. Effect of citric acid as flux has seen as increase in intensity marginally. Fig 3E, 3G, 3I, 3K, 3M and 3'O' are the PL emissions of 275nm excited LaPO₄: Tb, Eu(1%) by varying Ce(1%, 1.5%, 2%, 3%, 4% and 5%). From the figures, it is observed many emissions are present with reasonably good intensities at 365, 366, 380, 414, 487, 545, 590, 595, 614 and 622nm with different intensities. It is interesting to note as the Ce concentration increases, the peak at 545nm grows its intensity maximum for Ce3%. As the flux citric acid plays a major role in Ce3% LaPO₄: Tb, Eu(1%) varying intensity is maximum for 545nm and other emissions are predominant. From fig3K, it is understood the green emission at 545nm which is the characteristic emission of Tb³⁺ is 3 times more in intensity when compared to other Eu³⁺ emissions in LaPO₄: Tb, Eu. Ce(3%). From fig 3K, what we can conclude is Ce(3%) concentration plays a sensitizer role in LaPO₄: Tb, Eu. All the emissions are allowed transitions of Eu³⁺ as well as Tb³⁺. As the Ce concentration increases the emissions observed at 365, 366, 380, 414, 487, 545, 590, 595, 614 and 622nm intensities reduces. However the citric acid plays a major role for the emissions at 384, 414, 487 and 545nm. It is interesting to note that why only the Tb emissions are sensitizing for citric acid prepared LaPO₄: Tb, Eu phosphor when excited to 275nm.

4. SEM

SEM high voltage potential is 30.0 kV and width is 11.08 mm identified the crystalline size as 5micrometer with field of 28.5 micrometer and magnified for 4860 times by VEGA3TESCAN instrument. From which we can identify no gaps and no isolated islands and all the atoms in the material are closed pack and without any deviation and defect. SEM high voltage potential is 30.0 kV and width is 10.98 mm identified the crystalline size as 5micrometer with field of 17.1 micrometer and magnified for 4860 times by VEGA3TESCAN instrument. From which we can identify no void space but some isolated islands are there , without any **major flaws**.

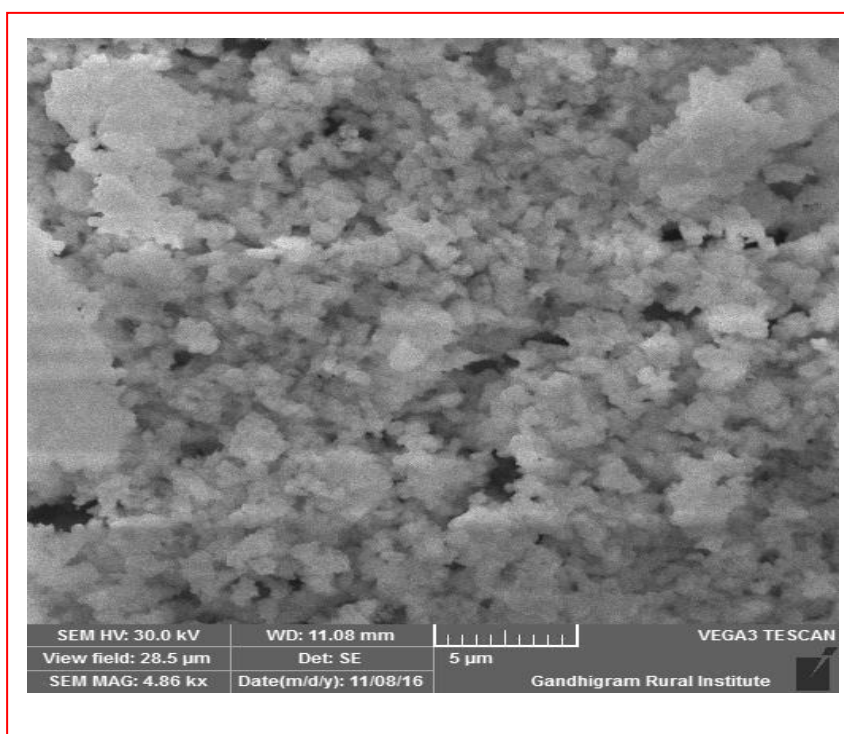


Fig 4 A SEM micrograph of LaPO₄ :Tb 1% Ce 1% Eu 1%

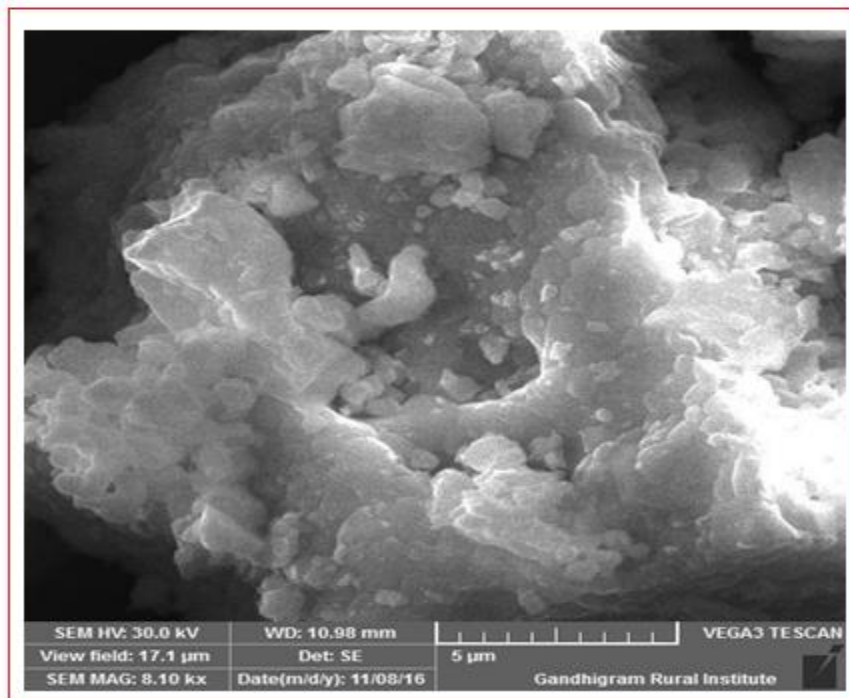


Fig 4 B SEM micrograph of LaPO₄:Tb 1% Ce 2% Eu 1%

4. Conclusion

The LaPO₄ has been grown and characterized by XRD, FTIR, PL, SEM studies and from XRD we can identify that the crystallite size of the particles and FTIR confirms the presence of functional groups and SEM confirms the morphology behavior of the material in various magnifications.

The PL study of LaPO₄: Tb, Eu with varying Ce concentrations brings the following conclusions.

1. Lower Ce concentrations when excited with 254 and 275nm gives rise 590 and 595 peak intensities more high.
2. For 275nm excitations gives rise 545nm intensity more in 3%Ce phosphor. Here, Ce is acting as a sensitizer and it sensitizes 545nm peak of Tb³⁺ emission.
3. Citric acid as a flux plays a major role to sensitize Tb³⁺ emissions at 487 and 545nm when compared to Eu³⁺ emissions.

All the PL emissions when excited with 254 or 275nm in with and without flux phosphors on varying Ce concentrations are the allowed PL emissions from Tb³⁺, Eu³⁺ and Ce³⁺. However Ce is playing a sensitizer role in LaPO₄: Tb, Eu phosphor.

By considering the above observations the phosphor LaPO₄: Tb, Eu, Ce(1.5%) prepared with citric acid is a very good device phosphor when excited with 254nm for 590-595nm emissions.

When the phosphor is doped with Ce and excited to 275nm prepared using citric acid as flux is a good phosphor for green emission at 545nm for Tb³⁺. Therefore, these two phosphors are very good for 590-595nm emissions when excited with 254nm and when excited with 275nm, the emission as 545nm. So, citric acid as flux plays a major role for enhancing the intensities of observed emissions.

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