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Synthesis, Characterization and Photoluminescence study of $LaPO_4$:EuTbCe phosphor

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Abstract

Synthesis, Characterization and Photoluminescence (PL) studies of the LaPO4 phosphor doped with Eu (0.5), Tb (1.0) and Ce varies with 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 mole percentages respectively are recorded at room temperature as well as the energy transfer process with concentration of rare earth doped ions. The phosphor was synthesized using the standard solid state diffusion reaction technique. The mixture was fired at 1200oC for 3 hours with heating rate of 5oC/min in a muffle furnace. The powder phosphors were characterized by X-ray diffraction, Particle size analysis, FTIR and scanning electron microscopy. The Photoluminescence (PL) excitation spectra were recorded for excitation wavelengths at 254 nm monitoring at 614. The PL emission of doped LaPO4 phosphor was recorded for 254nm excitation wavelengths. The PL emission peaks are found at 364, 381, 415, 438, 470, 488, 545, 589, 594, 614 and 622nm with good intensity.
Keywords: Photoluminescence [PL], Rare Earth ions [RE ions], XRD, Solid State Reaction [SSR].

1. Introduction

Recently various phosphors like $LaPO_4$: Ce,Tb has been good commercial green phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators. As a new green luminescent material, $LaPO_4$ Ce,Tb phosphor has been widely studied since it was found by different preparation methods.

These phosphors are widely used in displays and lighting devices. The useful applications of rare earth element compounds, especially lanthanide phosphate doped inorganic materials, have been touched upon broadly. Over the past a few years, they have been applied in many fields, such as optical display panels, cathode ray tubes, optoelectronic, sensitive device, electronic and plasma display panels due to their special chemical and physical properties. Various solution-phase routes, including solid state reaction, sol-gel, precipitation, water oil micro emulsion, polyol-mediated process, ultrasonification, hydrothermal, and mechanochemical method, have been tried to lower the reaction temperature and obtain high-quality $LaPO_4$ based nanoparticles. However, the simple and mass fabrication of $LaPO_4$ nanocrystals with narrow grain size distribution and uniform morphology still remains a challenge. It appears that the best solution both 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 $LaPO_4$ with good morphologies and fine crystal structures, and its emission intensity of luminescence was also studied. The present paper reports the Photoluminescence (PL) of the $LaPO_4$ phosphor doped with Eu, Tb and Ce rare-earth ions with different emission and excitation wavelengths, the doping concentration of Eu(0.5%), Tb(1.0%) and Ce are 0.5, 1, 2, 3, 4 and 5 molar percentages respectively.

2. Experimental Details

2.1 Sample preparation

All the chemical reagents were analytically pure and used without further purification. $LaPO_4$ phosphor doped with Eu, Tb and varying concentrations of Ce (0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 mol %) rare-earth ions prepared using solid state diffusion reaction method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La_2O_3), Diammonium Hydrogen Phosphate [$(NH_4)_2$ H PO_4), Cerium Oxide (CeO_2), Europium Oxide (Eu_2O_3) and Terbium Oxide (Tb_4O_7) of assay 99.9% were used as starting materials and grinded in an agate motor and pestle,

mixed and compressed into a alumina crucible and heated at 1200^{o}C for 3 hours with heating rate of 5^{o}C/min in the muffle furnace. The prepared samples were again grounded in to powder for taking the characteristic measurements.

2.2 Physical Characterization

All the phosphor samples were characterized by X-ray diffraction (Synchrotron Beam Indus -II) to identify the crystallinity and phase purity of the phosphor. The Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using 150 watts Xenon lamp as excitation source. The emission and excitation slit were kept at 1.5 nm, and recorded at room temperature. The Infrared spectra for the prepared solid nano powders were recorded in the range between 400 and 4000 cm^{-1} on a Fourier transform spectrometer. The particle morphology of the phosphor was characterized by SEM.

3 Results and Discussion

3.1 X-ray Diffractometry (XRD)

The crystallinity and phase purity of the product were firstly examined by XRD analysis. Fig.1 Show the typical X-ray diffraction (XRD) patterns of synthesized samples of $LaPO_4$ doped with Eu(0.5%), Tb(0.5%) and Ce(2.0%). The XRD patterns of doped $LaPO_4$ nanocrystals are in good agreement with the values from ICCD no.35-0731of $LaPO_4$, which shows that all the products are monazite $LaPO_4$ with monoclinic structure and primitive lattice, the lattice parameters are a=6.84, b=7.07, c=6.45 and $\alpha=\beta=90^0$, $\gamma=103.85^0$. From XRD patron the main peak was found around $2\theta=28.6^0$ corresponding to miller indices (1 2 0) and d value of about 3.1186A^0. All diffraction patterns were obtained using CuKα radiation (λ = 1.540598 A^0) at 40 kv and 30 mA, and divergence slit fixed at 1.52 mm. Measurements were made from $2\theta = 10^0$ to 80^0 with steps of 0.008356^0. The crystallite size 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 (0.112), λ = Wavelength of the X-rays.(0.154 nm in the present case), θ = Braggs angle of the XRD peak. The average crystallite size of $LaPO_4$ phosphors doped with Eu, Tb and Ce is 73.14 nm.

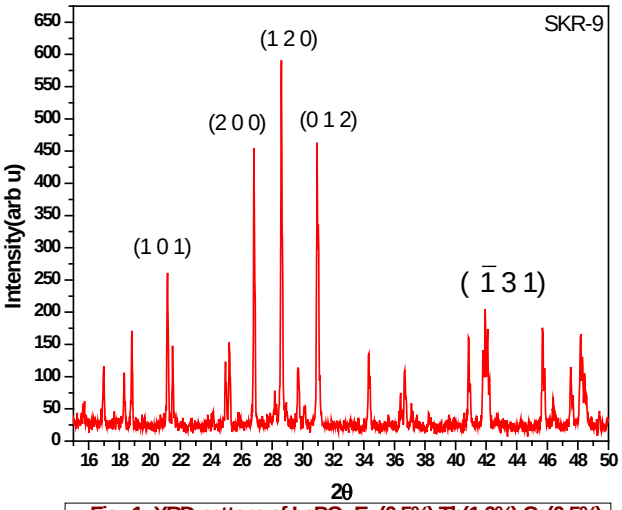


Fig:-1: XRD pattern of $LaPO_4$:Eu(0.5%),Tb(1.0%),Ce(0.5%)

3.2 SEM Analysis

Surface morphology and size of nano crystals is done routinely using scanning electron microscope. Fig:-2 and 3 shows SEM image of LaPO4: Eu, Tb, Ce. This appears to the particles looks irregular and agglomerated having size of 1 micron to 5 micron are observed from the SEM graphs.

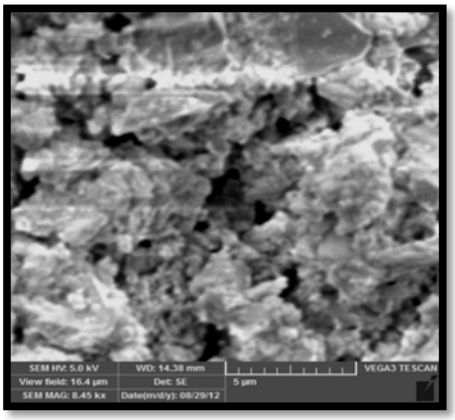


Fig.2. SEM Image of $LaPO_4$: Eu, Tb, Ce.(8.45 KX)

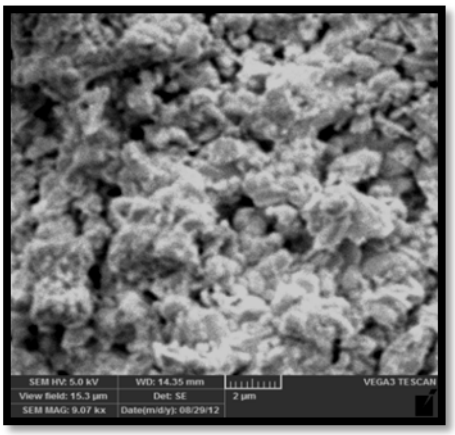
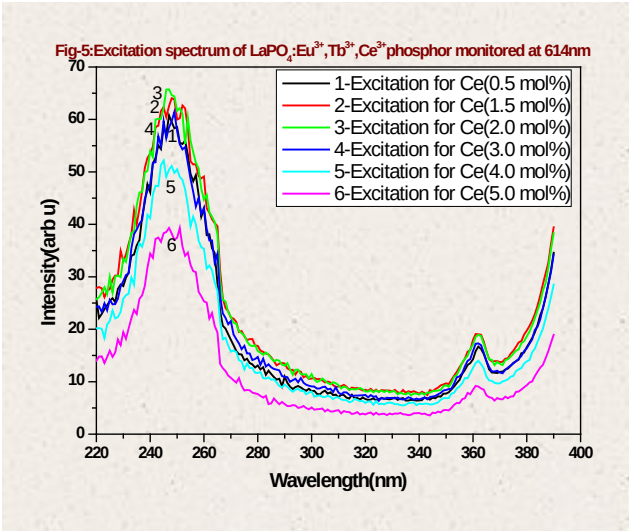


Fig.3. SEM Image of $LaPO_4$: Eu, Tb, Ce.(9.07 KX)

3.3 Photoluminescence Study

Figure-5 shows the excitation spectra of doped $LaPO_4$ with Eu,Tb concentrations are fixed with 0.5 mol % and Ce concentration vary 0.5.1.0,1.5,2.0,3.0,4.0 and 5.0 mol% respectively when monitored at 614nm . The excitation spectra of $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor recorded by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 614nm is shown in Fig. 5, the excitation spectra shows broad absorption peak in the range 220-270nm and followed by a emission around 360nm. From the graph it is found the Ce concentration is 0.5 mol % in the phosphor $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %), the excitation peak intensity of 254nm is 60 arb units, as Ce concentration increases in $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor the excitation intensity of 254nm peak increases up to 2.0 mol% in the phosphor, then after as Ce concentration increases in $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor the 254nm excitation peak intensity gradually decreases, table-1 is the variation of intensity of excitation spectrum when monitored 614nm on variation of Ce concentration in $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor for better comparison. The prominent excitation band observed at 254nm due to the transition of Eu^{3+} and this clearly indicates that in $LaPO_4$: Eu, Tb, Ce phosphor where in Eu stabilized as Eu^{3+} ion.



S.No	Concentration of Ce ion (mol %)	Intensities of the excitation peak(arb.u)
1	0.5	**60**
2	1.5	**64**
3	2.0	**66**
4	3.0	**62**
5	4.0	**52**
6	**5.0**	**40**

Table-1: Variation of intensity of excitation spectrum with Ce concentration of $LaPO_4$:Eu^{3+}, Tb^{3+},Ce^{3+} phosphor monitored at 614nm

Fig-6 is the PL emission of $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor, when Ce is varied from 0.5 to 5.0 mol % on excitation with 254nm. The phosphor $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) exhibits the following peaks 364,381,415,438,470,488,545,589,594,614 and 622nm with different intensities, for better comparison the emission of 545nm peak which is of Tb^{3+} and emission at 589 and 594nm followed by 614,622 are shown in figure-7. Both the figures are emission of $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor when excited with 254nm.

From the figures-6 and 7, it is found as Ce concentration increases in $LaPO_4$:Eu(0.5), Tb(1.0),Ce (0.5-5 mol %) phosphor, all observed peaks 360-545nm intensities are increases, the peak at 589, 594, 614 and 622nm intensities are gradually decreases as Ce concentration in $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) phosphor varied from 0.5 to 5.0 mol % . It is also to be noted the major peaks found at 488, 545, 589 and 594nm are well resolved with good intensity.

The 545nm peak which is the basic emission of Tb^{3+} increases its intensity as Ce concentration increased from 0.5 to 2.0 mol % for 254, 264 and 275nm(not shown) by nearly four times. As Ce concentration increases in phosphor $LaPO_4$:Eu(0.5), Tb(1.0) and Ce(0.5-5 mol %) the emission peak intensity of 589 and 594nm peaks gradually decreases for the excitations 254, as Ce concentration

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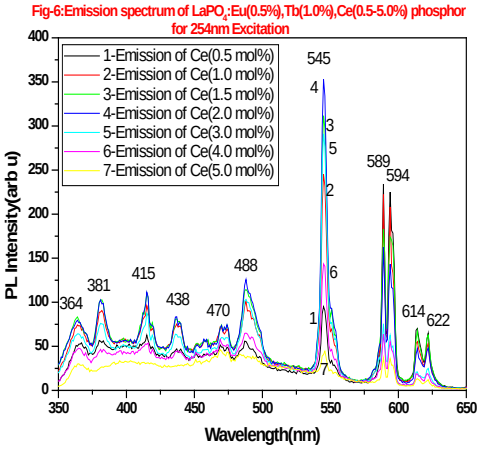
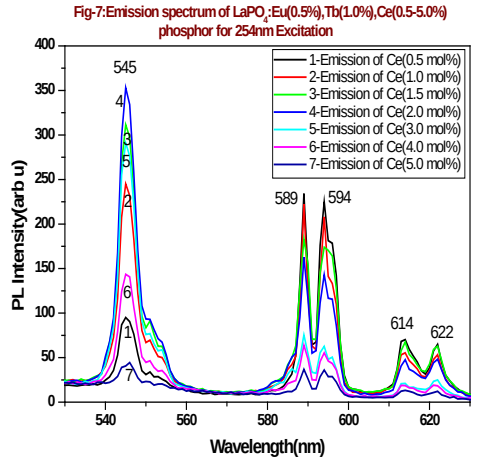
varied from 0.5 to 5.0 mol %. The intensity decreases from maximum to minimum approximately by seven times.





S No	Peak wavelength(nm)	Intensities of emission peaks for different Ce concentrations under 254nm Excitation						
		0.5 %	1.0%	1.5%	2.0%	3.0%	4.0%	5.0%
1	364	54	75	84	85	66	48	31
2	381	58	91	103	106	77	47	25
3	415	64	96	113	115	88	54	32
4	438	48	75	82	85	65	45	30
5	470	51	70	74	77	60	57	46
6	488	56	101	115	126	103	65	39
7	545	96	246	312	354	293	143	45
8	589	234	222	182	163	75	64	37
9	594	225	208	173	143	63	55	36
10	614	70	55	68	48	21	18	14
11	622	65	53	63	48	25	19	12

Table-2: Emission intensity for different peaks of $LaPO_4$:Eu(0.5),Tb(1.0) and Ce(0.5,1.0,1.5,2.0,3. 0 , 4.0,5.0 mol%) phosphor under 254nm Excitation.

Figure-8 is the variation of Photoluminescence intensity of different emission peaks with the variation of Ce concentrations, from figure it observed that Tb^{3+} emission peaks 381,415,488 and 545nm intensity is increases up to 2.0% of Ce concentration and farther decreases, the Eu^{3+} emission peaks like 589,594nm intensity gradually decrease as increase Ce concentration. Figure-9 is the Energy level diagrams for all possible transitions of Ce^{3+}, Eu^{3+} and Tb^{3+} ions for Excitation and Emissions, and energy transfer mechanism, in the prescience of Ce ion the Eu^{3+} transition are resolved along with Tb^{3+} transitions, as Ce concentration increases energy transfer fromCe^{3+} and Eu^{3+} to Tb^{3+}, so the Tb^{3+} peaks intensity increases and Eu^{3+} peaks intensity decreases.

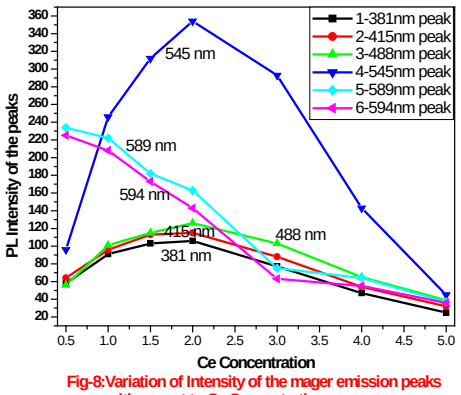


Fig-8:Variation of Intensity of the mager emission peaks withrespect to Ce Concentrations

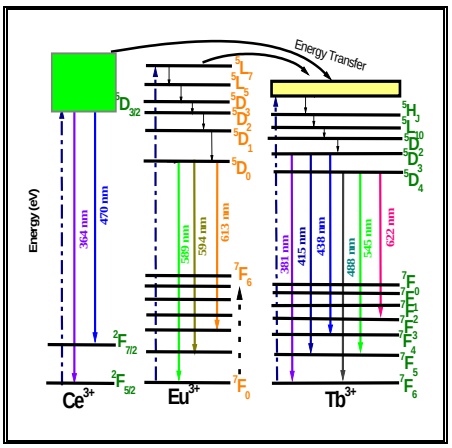


Fig-9:Energy level diagrams for all possible transitions of Ce^{3+}, Eu^{3+} and Tb^{3+} ions for Excitation and Emissions, and energy transfer mechanism.

3.4 Particle size analysis

The particle size distribution histogram of Eu, Tb and Ce doped $LaPO_4$ shows in fig-10. The prepared phosphor specimen particle size was measured by using laser based system Malvern Instrument U.K. The mean diameter of the particle size of Eu, Tb and Ce doped $LaPO_4$ is 70µm. As such many molecular particles agglomerate and from as a crystallite and many crystallites together become a particle. In the present case approximately 2000

crystallites together forms a particle of diameter is 70µm in Eu, Tb and Ce doped $LaPO_4$.

Superfine Eu, Tb and Ce doped $LaPO_4$ phosphor was successfully prepared by solid state reaction method and the preparation temperature was lowered from at least 1500 to 1200°C and got single phase phosphor. The calculated average crystallite size using Scherer's formula is ~73.14 nm. This method is easy for the preparation of Eu, Tb and Ce doped $LaPO_4$ phosphors and can be potentially applied to the synthesis of other high quality rare earth ions doped phosphate phosphor materials with nano structure. This phosphor can be useful in many lamps and display devices.

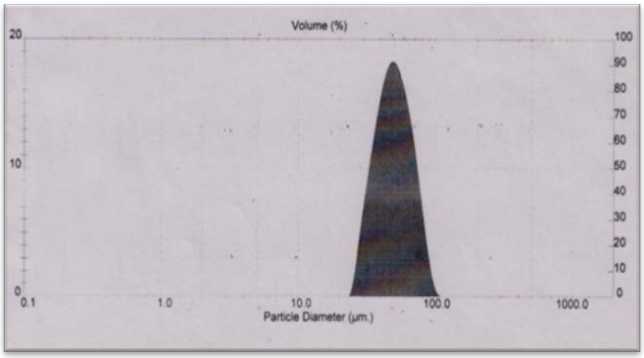
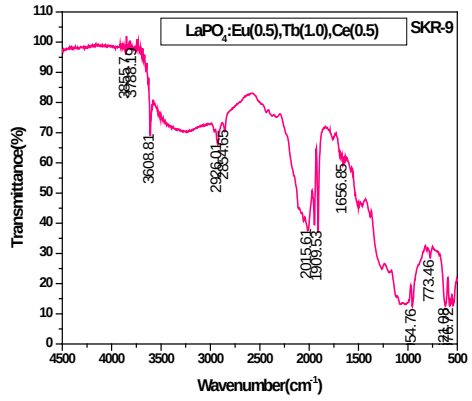


Fig:-10: Particle size image of $LaPO_4$: EuTb Ce.

3.5 FTIR study of LaPO4:Eu, Tb, Ce.

In order to determine the chemical bonds in a molecule FTIR analysis was carried out. Fig-11 is the FTIR of the Eu, Tb and Ce doped $LaPO_4$ phosphor, the main absorption around 3600 are assumed H-O-H stretching followed by other bonds of P-H bending, N-O stretching and CO-OH stretching. CO-OH and H-O-H stretching are due to absorbed CO_2 and H_2O molecules from atmosphere.

Fig:-11:FTIR Spectrum of $LaPO_4$:Eu, Tb, Ce.



CONCLUSION

1) LaPO4: EuTbCe phosphor were prepared using solid state synthesis method are successfully synthesized.
2) The excitation spectrum monitored at 614 shows the broad absorption peak in the range 220-270nm and followed by a emission around 360nm.
3) The prominent excitation band observed at 254nm due to the transition of Eu^{3+} and this clearly indicates that in $LaPO_4$: EuTbCe phosphor where in Eu stabilized as Eu^{3+} ion.
4) The phosphor shows the PL emission peaks at 364, 381, 415, 438, 470, 488, 545, 589, 594, 614 and 622 nm with good intensity.
5) The emission at 589nm and 594 nm originates from the allowed magnetic dipole (MD) transition $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$. The peak observed at 614 due to the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition has the less emission intensity.
6) From the emission spectrum it is clearly observed that the emission intensity of magnetic dipole was higher than that of electric dipole transition, due to this Eu^{3+} ions occupy a low symmetry site in $LaPO_4$: EuTbCe host. Both magnetic dipole transition and electric dipole transitions are shown in the emission spectra. If the magnetic dipole transition $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ having the highest intensity then Eu^{3+} ions in host lattice occupies an inversion centre. If the emission intensity of magnetic dipole transition was lower than that of electric dipole transition, which indicates that Eu^{3+} ions occupied without an inversion symmetric centers in the host.
7) The emission between 380–450 nm is due to transitions from the $^5D_3$ excited state. Above 480-630nm, the emission peaks are originated from $^5D_4$ excited states of Tb^{3+}. The emission peaks at 488,545 and 622 are $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4) characteristic emissions of Tb^{3+}, the emission peaks at 381,415 and 438nm correspond to the transitions of $^5D_3$ to $^7F_6$, $^7F_5$ and $^7F_4$ respectively.
8) The green-emission transition $^5D_4 \rightarrow {}^7F_5$ at 545 nm has been more intense in nature due to the nature of the dopant Tb^{3+} ion in the host matrix. Emission intensities from $^5D_3$ excited state decrease with increase of the cerium concentration.
9) When the concentration of Ce^{3+} increases more than 2 mol%, the emission intensity decreases. The decrease in the intensity with an increase in concentration was presumably due to the well-established theory of concentration quenching.
10) The two peaks at 364 and 470nm are due to transitions of Ce, $^2D_{3/2}(5d) \rightarrow {}^2F_{5/2}(4f)$ (364nn) and $^2D_{3/2}(5d) \rightarrow {}^2F_{7/2}(4f)$ (470nn).
11) The presence of Eu (0.5%) in LaPO4: Tb(1%)Ce(2%) sensitizes the basic emissions of Tb^{3+} as well as emits its own emissions in Eu^{3+} state.
12) The main peak in XRD pattern was found around 28.6^0 corresponding to a d- value of about $3.15A^0$,

followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate, which is also supported by particle size histogram. From XRD studies it is suggested the formation of single phase and also the phosphor is in nano crystallite form. From X-ray diffraction (XRD) patterns of synthesized sample of $LaPO_4$ dopped with Eu, Tb, Ce,. From XRD pattern it looks majority of the phosphor is in single phase of nanocrystals, which is in good agreement with the values from JCPDS no.35-731of $LaPO_4$, which shows that all the products are monazite $LaPO_4$ with monoclinic structure and primitive lattice. The full width at half maximum (FWHM) of XRD lines is 0.112. The average crystallite size of $LaPO_4$ phosphors doped with Eu, Tb, Ce is 73.14nm.

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