

Conclusions

The effect of trivalent RE ions Ce-Tb, Tb-Ce, Eu-Tb and Ce-Eu-Tb with various concentrations of Tb, Ce, Eu doped in lanthanum phosphate(LaPO₄).

- The PL emission of undoped LaPO₄ was observed at 469 nm which are at perfect blue region with less intensity.
- The PL emission of Ce³⁺ doped LaPO₄ phosphor generates a strong emission at 366 nm and at 469 nm. The intensity of peak at 366 nm is relatively high as compare to 469 peaks. . The two emission peak 366 nm and 469 nm are due to the two terminating levels, ²F_{5/2} and ²F_{7/2} of the 4f configuration of Ce³⁺ ions.
- The PL emission of Eu³⁺ doped LaPO₄ phosphor generates a strong emission nearly at 588 nm and at 595 nm. It is also observed the two additional peaks at 613 nm and 621 nm with less intensity. The photoluminescence emission at 588 nm and 595 nm is due to the magnetic dipole transition of ⁵D₀ → ⁷F₁ and the photoluminescence emission at 613 nm and 621 nm is due to the electric dipole transition of ⁵D₀ → ⁷F₂.The intensity of ⁵D₀ → ⁷F₁ (580-600 nm) band is more than intensity of ⁵D₀ → ⁷F₂ (610-630 nm) band due to localized energy transfer. The intensity of these emission transitions is usually used in order to gauge the quality of the luminescent material. Due to the little difference between ionic sizes of Eu³⁺ ion and La³⁺ ion, we assume that Eu³⁺ ions can occupy La³⁺ ion sites, which gives rise to a characteristic crystal splitting of the energy levels. The transitions are found to be split into components depending upon the host matrix composition.
- The PL emission of Tb³⁺ doped LaPO₄ phosphor generates a strong emission at 366 nm and at 469 nm. The intensity of peak at 366 nm is relatively high as compare to 469 peaks. It is also observed one additional peak at 545 nm with less intensity in the green region of the visible spectrum which is the allowed transition of Tb³⁺ ions. The emission transition ⁵D₄ → ⁷F₅ (545 nm) is responsible for green color observation as a single peak.

- PL emissions in LaPO_4 : Ce (0.5%), Tb (0.1 to 2.0 %) shows good results. When Tb concentration is 0.1 mole wt. % in LaPO_4 : Ce (0.5%), following emissions with less intensity are observed (when excited with 254 nm); emissions are 363, 380, 430, 437, 456, 473, 488, 545, 587, and 622 nm. The primary emissions in blue region (400 – 500 nm) and green emission around 535 nm, yellow emissions around 587 nm and red emission around 622 nm are observed. As the Tb concentration increased from 0.5 mole wt. % to 2.0 mole wt. %, all the peaks were observed to show more intensity marginally. It is interesting to note that the intensity of 380 nm peak grows linearly till the Tb concentration 1.5 mole wt. % in LaPO_4 : Ce (0.5%). Then the intensity reduces by 200 %, when Tb concentration is 2.0 % in LaPO_4 : Ce (0.5%). The same trend continued for 450, 437, 456, 473, 488 nm emissions. It is also interesting to note that 545 nm peak, which is primary emission of Tb^{3+} , grows its intensity linearly from 43 units to 800 units, when Tb concentration is 1.5 mole wt. %. When Tb concentration is 2.0 mole wt. % in LaPO_4 : Ce (0.5%), the 545 nm peak intensity is just reduced by 2 % as compared to Tb 1.5 % in the host phosphor. As it is known in LaPO_4 : Ce, Tb, Ce acts as sensitizer. The main peaks at 488, 545, 588, 622 nm are the 4f-4f emission peaks from Tb^{3+} when excited with 254 nm.
- In LaPO_4 : Ce, Tb, La acts as host, Ce acts as sensitizer, Tb^{3+} acts as activator and the four emission peaks in emission spectrum are produced by Tb^{3+} . 488 nm (${}^5\text{D}_4$ - ${}^7\text{F}_6$), 545 nm (${}^5\text{D}_4$ - ${}^7\text{F}_5$), 588 nm (${}^5\text{D}_4$ - ${}^7\text{F}_4$), 622 nm (${}^5\text{D}_4$ - ${}^7\text{F}_3$). The transition emission in ${}^5\text{D}_4$ - ${}^7\text{F}_5$ level is the strongest emission. The phosphor shows the peaks at 381, 415, 437, 457, 473, 488, 545, 588, 595, 614 and 622 nm with good intensity. In the trivalent rare earth ions, the luminescence arises mainly due to transitions within the 4 f shell. The efficiency of emission depends on the number of electrons in the 4f shell. Tb^{3+} ion has 8 electrons in the 4f shell, which can be excited in the 4f-5d excitation band. The electron in the excited $4f^7$ - 5d state remains at the surface of the ion and comes under the strong influence of the crystal field resulting in the splitting of the excitation band. The excitation Spectra thus has multiple peaks. The excited ion in the $4f^7$ - 5d state decays stepwise from this state to the luminescent levels ${}^5\text{D}_3$ or

5D_4 by giving up phonons to the lattice. Luminescence emission occurs from either of these states, with the ion returning to the ground state. The emission transition $^5D_4 \rightarrow ^7F_5$ (545 nm) is responsible for green color observation as a single peak. There are in fact multiple emission lines at each of these due to the crystal field splitting of the ground state of the emitting ions. As the Tb concentration increases, the PL intensity also increases. The optimum concentration of Tb^{3+} ions is 1.5 mol%, beyond which quenching effect is observed. The emission of 363 nm is due to crystal field.

- PL emissions in $LaPO_4: Tb$ (0.5%), Ce (0.1 to 2.0 %) shows good results. When excited with 254 nm; emissions are 363, 380, 415, 436, 469, 488, 545, 585, and 622 nm. The primary emissions in blue region (400 – 500 nm) and green emission around 535 nm, yellow emissions around 587 nm and red emission around 622 nm are observed. As the Ce concentration increased from 0.5 mole. wt. % to 2.0 mole wt. %, there is variation in PL intensity of all the peaks. It is interesting to note that 545 nm peak which is primary emission of Tb^{3+} grows its intensity maximum at 187 unit, when Ce concentration is 1.0 mole wt. %. When Ce concentration is 2.0 mole wt. % in $LaPO_4: Tb$ (0.5%), the 545 nm peak intensity is reduced by 40 % when compare to Ce 1.0 % in the host phosphor. The main peaks at 488, 545, 585, 622 nm are the f-f emissions from Tb^{3+} , when excited with 254 nm. In $LaPO_4: Ce, Tb$, La acts as host, Ce^{3+} acts as sensitizer, Tb^{3+} acts as activator, and the four emission peaks in emission spectrum are produced by Tb^{3+} .
- The strong luminescence of Tb^{3+} results from efficient energy transfer from Ce^{3+} to Tb^{3+} ions in the $LaPO_4: Tb^{3+}, Ce^{3+}$ phosphors. Two processes occur in the excited Ce^{3+} ions as: radiative transition to its ground state and non radiative transfer of the excitation energy to the Tb^{3+} . The Tb^{3+} ions act as the terminal of the energy transfer processes in the $LaPO_4: Tb^{3+}, Ce^{3+}$ phosphor. As the Ce concentration increases, the PL intensity also increases. Tb^{3+} practically cannot be directly excited in nanosized $LaPO_4: Ce, Tb$, but could be excited after energy transfer from Ce^{3+} only. Due to the small nanoparticle

size and a high impurity concentration, Tb^{3+} and Ce^{3+} ions are closely distributed, i.e. no isolated Tb^{3+} ions are present in the nanoparticles.

- The CIE co-ordinates of the undoped $LaPO_4$ sample are $x = 0.16$ and $y = 0.19$. The colour co-ordinates of the $LaPO_4: Ce, Tb$ sample are $x = 0.26$ and $y = 0.72$. The peak value of wave length is 545 nm, half-width 5 nm, coloration index $R = 25$, correlated color temperature 5330 K, and brightness value is 40.
- PL emission of Eu, Tb doped $LaPO_4$ phosphor shows peaks at 588, 595, 614 and 622 nm with good intensity. As the Tb concentration increases, the PL intensity also increases. The emission spectrum shows the emission transitions $^5D_0 \rightarrow ^7F_4, ^7F_3, ^7F_2, ^7F_1, ^7F_0$. The two emission bands corresponding to electronic transitions $^5D_0 \rightarrow ^7F_1$ (580-600 nm), $^5D_0 \rightarrow ^7F_2$ (610-630 nm) are observed. The emission bands are split in to two or more components due to crystal field effect of rare earth ions.
- The photoluminescence emission at 588 nm and 595 nm is due to the magnetic dipole transition of $^5D_0 \rightarrow ^7F_1$ and the photoluminescence emission at 614 nm and 621 nm is due to the electric dipole transition of $^5D_0 \rightarrow ^7F_2$. The intensity of $^5D_0 \rightarrow ^7F_1$ (580-600 nm) band is more than intensity of $^5D_0 \rightarrow ^7F_2$ (610-630 nm) band due to localized energy transfer.
- PL emission of Eu, Ce, Tb doped $LaPO_4$ phosphor shows peaks at 363, 380, 415, 437, 456, 473, 488, 545, 588, 595, 613 and 622 with good intensity.
- In $LaPO_4$ doped Ce^{3+}, Eu^{3+} and Tb^{3+} phosphor due to the little difference between ionic sizes of Eu^{3+} ion and La^{3+} ion, Eu^{3+} ions can occupy La^{3+} ion sites, which gives rise to a characteristic crystal splitting of the energy levels.
- Finally it is concluded that in doped $LaPO_4$ phosphor, the Ce^{3+} and Eu^{3+} ions sensitize the luminescence of Tb^{3+} ions and good PL intensity is obtained.
- When $LaPO_4: Ce, Eu, Tb$ powder is excited by 254 nm wave length UV light, its chromatic coordinates obtained are $x = 0.26$ and $y = 0.72$, the peak value of wave length is 545 nm, half-width is 5 nm, coloration index $Ra = 25$, Correlated color temperature 5330 K and brightness is 40. The color coordinate of the sample is very large and it decreases the level of red color.

Therefore LaPO_4 doped Ce^{3+} , Eu^{3+} and Tb^{3+} green phosphor has good luminescent properties and applications.

- The materials studied are very attractive luminescent properties for the generation of the three primary colors, due to the red, green and blue emissions of $\text{LaPO}_4:\text{Eu}^{3+}$, $\text{LaPO}_4:\text{Tb}^{3+}$ and $\text{LaPO}_4:\text{Ce}^{3+}$, respectively.

The effect of trivalent RE ions Tb-Eu, Gd-Eu, Tb-Gd-Eu with various concentrations of Tb, Gd, Eu doped in LanthanumYttrium Phosphate (LaYPO_4).

- The most important rare earth phosphors are Y, Eu, and Tb, which are used to emit light at the wavelengths (and therefore colors) to which our eyes are most sensitive. These three elements are used in different combinations of phosphors to emit blue, red, and green light. Tb is used for green light, while Eu and Y are used for blue and red. Very high levels of purity are necessary for these phosphors in lighting applications.
- The phosphors consisting of a rare earth phosphate (RE PO_4) ($\text{RE} = \text{La, Ce, Gd, or Y}$) matrix doped with RE cations find important applications, especially in optoelectronic and biomedicine. For most of these applications, particles with uniform shape and narrow size distribution are highly desirable. The availability of uniform phosphors with a different particle size and shape is also required for fundamental studies dealing with the effects of these morphological characteristics on the luminescence efficiency.
- The PL emission of un doped LaYPO_4 phosphor was observed at 469 nm in a perfect blue region with intensity 75 AU. The emission is due to magnetic dipole transition $^5\text{D}_2 \rightarrow ^7\text{F}_0$ with energy of 2.657 eV. The emission peak at 366 nm is due to the crystal field of the phosphor. Due to high crystal field the decrease of PL intensity is reported.
- The excitation of the $\text{LaYPO}_4:\text{Ce}$ (0.5%) phosphor with 254 nm wavelengths generates PL emission at 366, 398, and 451 and at 469 nm. The intensity of peak at 366 nm is relatively high as compare to other peaks. The PL intensity of 366 nm peak in the UV region increases but PL intensity of 469 nm peak in the blue region decreases. This may be due to strong crystal field and increase

in electro negativity of the phosphor due to concentration of Ce^{3+} in $LaYPO_4$ phosphor.

- The doping of Eu in $LaYPO_4$ shows all the allowed transitions of Eu in the red region [$^5D_0 \rightarrow ^7F_1$ at (587–594 nm), $^5D_0 \rightarrow ^7F_2$ at (611–620 nm)], which are well resolved but PL intensity is quenched by the characteristic blue emission of the $LaYPO_4$ phase. Therefore it is concluded that the crystal host which is a donor of energy, transfer less energy to the doped Eu^{3+} ion which is an acceptor of energy.
- The doping of Gd in $LaYPO_4$ did not show any change in PL properties of the phosphor. Effect of Gd^{3+} doping in $LaYPO_4$ is not seen on PL emission. Gd^{3+} ions emits in the ultraviolet region is not seen however it increases the intensity of $LaYPO_4$ emission by 10%. Gd^{3+} emission mainly occurs at 313 and 307 nm in UV region. The emission at 313 nm is due to the electric-dipole transition $^6P_{7/2} - ^8S_{7/2}$, while the emission at 307nm is due to the magnetic-dipole transition $^6P_{5/2} - ^8S_{7/2}$. Gd^{3+} is sufficiently excited via energy transfer from the host lattice and then Gd^{3+} can further transfer energy to Y^{3+} .
- The doping of Tb in $LaYPO_4$ phosphor shows that the PL intensity of 469 nm peaks in the blue region remains same but PL intensity of 366 and 398 nm wavelengths in UV region increases. The yttrium atoms may occupy the Tb atoms in the $LaYPO_4$ doped Tb compound which decreases the effect of Tb ions as a result the PL emission intensity of Tb^{3+} ions (545 nm) was quenched by the characteristic blue emission of the $LaYPO_4$ phase. PL intensity of characteristic blue emission (469 nm) of the $LaYPO_4$ phase in the blue region remains same but PL intensity of 366 and 398 nm wavelengths in UV region increases.
- Photoluminescence spectra of $LaYPO_4$ phosphor doped with Tb and Eu rare-earth ions, keeping Tb concentration constant at 0.5 mole wt. % and varying Eu concentration as 0.5, 1.0, 1.5, 2.0 mole wt. % at 254 nm shows peaks at 366, 397, 451, 469, 588, 595, 613 and 621 nm with good intensity. The effect of Eu doping generates 588, 595, 613, 622 nm peaks on overlapping of the $LaYPO_4$ due to site symmetry of the Eu^{3+} in $LaYPO_4$. The photoluminescence

emission at 588 nm and 595 nm is due to the magnetic dipole transition of ${}^5D_0 \rightarrow {}^7F_1$ and the photoluminescence emission at 613 nm and 621 nm is due to the electric dipole transition of ${}^5D_0 \rightarrow {}^7F_2$. The intensity of ${}^5D_0 \rightarrow {}^7F_1$ (580-600 nm) band is more than intensity of ${}^5D_0 \rightarrow {}^7F_2$ (610-630 nm) band due to localized energy transfer. As the Eu concentration increases when the Tb concentration remains at 0.5 mole wt. %, the 469 nm peak intensity decreases in sub linear way when excited with 254. However other PL emission of Eu in yellow red region increases their intensity. This may be due to increase in magnetic dipole of the phosphor on increasing concentration of Eu with fixed Tb concentration in LaYPO₄ phosphor as well as increase in electric dipole percentage. In Eu doped LaYPO₄: Tb (0.5%) phosphor, emission spectrum shows all the allowed transitions of Eu in the red region, which are well resolved but PL intensity is quenched by the characteristic blue emission of the LaYPO₄ phase because the crystal host which is a donor of energy, transfer less energy to the doped Eu³⁺ ion which is an acceptor of energy.

- The excitation of the Eu doped LaYPO₄: Gd (0.5%) phosphor with 254 nm wavelengths generates a broad emission from 350 nm to 650 nm. PL emission of doped LaYPO₄ phosphor shows peaks at 366, 397, 451, 469, 588, 595, 613 and 621 nm with good intensity. The peak at 613 nm corresponding to red color are generated from the forced electric transition [${}^5D_0 \rightarrow {}^7F_2$]. The Eu ions allow to occupy a site without inversion center. The intensities (588 nm) ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$ (595 nm) are highly suppressed as compared to the intensified ${}^5D_0 \rightarrow {}^7F_1 \rightarrow {}^5D_0 \rightarrow {}^7F_2$ (613 nm) due to symmetric site of Eu³⁺ ions in the host lattice. It is interesting to note that the effect of dopant Gd increases the PL intensity in the red region continuously with increase in Eu³⁺ concentration. Gd³⁺ (radius of 0.097 nm) can readily transfer energy to other rare earth ions because the energy difference between its ground and first excited state is the largest for all trivalent rare-earth ions, greater than 30,000 cm⁻¹ as shown in the energy level diagram of Gd³⁺.
- Photoluminescence spectra of LaYPO₄ phosphor doped with Tb, Gd and Eu rare-earth ions, keeping Tb and Gd concentration constant at 0.5 mole wt. %

and varying Eu concentration as 0.5, 1.0, 1.5, 2.0 mole wt. % at 254 nm excitation generates a broad emission from 350 nm to 650 nm. The PL intensity of 366 nm peak decreases with increase in Eu concentration. A small hump is appearing at 545 nm wavelength.

- It is concluded that addition of Gd^{3+} and Tb^{3+} ions in $LaYPO_4$: Eu phosphor enhances the 580-630 nm emission of Eu^{3+} .
- The TL glow curve of $LaYPO_4$ phosphor exhibit one peak at $257.98^\circ C$ temperature. But same phosphor doped with $Tb(0.5\%)$ constant and Eu with varying concentrations exhibits one emission peaks at $111^\circ C, 141^\circ C, 118^\circ C \& 115^\circ C$ temperatures and other hump like emission peaks are observed around $245^\circ C$.
- TL intensity peaks of doped phosphor also increases with increase in Eu concentration about nearby the same temps. i.e. $115^\circ C$ — $118^\circ C$ from 45 a.u. to 122 a.u. Similarly second hump like peak for Eu is observed around $245^\circ C$. Thus the kind and quantity of the ions that change phosphor characteristics differ from phosphor to phosphor.
- TL glow curve of $LaYPO_4$ phosphor doped with RE ions Tb, Gd and Eu exhibit well defined and well resolved one emission peaks around $114^\circ C$ & other emission peck around $229^\circ C$ temperatures with increasing intensity. This may be useful for TL dosimeter purpose.
- XRD pattern shows that all the products are in single phase with monoclinic structure.
- FTIR shows the bands of characteristic of the vibrations of the phosphate groups in monoclinic phase as well as absorbed water molecules.
- SEM image shows the particles with irregular shape having an average basal diameter of 500 nm and length of 1.5 μm .
- The particle size histogram shows the various sized particles having sizes in the range of 1 μm to 100 μm of various percentages. Therefore it was concluded that, more groundings of the phosphor material is required to get uniform particle size.

Future work

- The quantum efficiency of the phosphor is also plays an important role in selecting a phosphor for device application. Therefore the quantum efficiency studies can be undertaken.
- To find out exact emission center, EPR (Electron Paramagnetic Resonance) studies can under take.
- Thermoluminescence dosimeter [TLD] work also can be undertaken by considering the application potential and the decay of the phosphors (fading effect).
- To find out the trap depth, frequency factor and order of kinetics, the trapping parameters of TL peaks can be studied using different methods.
- Further study of effect of particle size, particle size distribution and particle shape on the luminescence properties of RE doped LaPO_4 and LaYPO_4 phosphors may be useful.
- The effect of different host materials and different synthesis methods on luminescence properties of rarer earth doped phosphor and their applications can also help the professionals to decide the required phosphor for their application.