

Ce³⁺ sensitize RE³⁺ (RE=Dy, Tb, Eu, Sm) doped LaPO₄ nanophosphor with white emission tunability

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Abstract. Crystalline Ce³⁺ co-doped LaPO₄:RE (RE=Dy³⁺, Tb³⁺, Eu³⁺, Sm³⁺) and mix doped rare earth ions of Dy³⁺, Tb³⁺ and Eu³⁺ were prepared by the polyol method at 150°C. Strongly enhance luminescence intensity is obtained with the co-doping of Ce³⁺ with LaPO₄:Dy³⁺ and LaPO₄:Tb³⁺ due to charge transfer (CT) occurring from Ce³⁺ to Dy³⁺ and Ce³⁺ to Tb³⁺, where as there is no significant changes in luminescence intensity of Ce³⁺ co-doped Eu³⁺ and Sm³⁺ doped LaPO₄ samples. The luminescence color can be tuned from green to white by varying the excitation wavelength for the mix ions Ce³⁺, Dy³⁺, Tb³⁺ and Eu³⁺ doped with LaPO₄.

Keywords: white emission; nanoparticle; mix ions doping; luminescence

1. Introduction

Phosphors of inorganic host nanomaterials doped with lanthanide ion (Ln³⁺), REPO₄, REVO₄, RE₂O₃, (RE³⁺=Y, La, Gd, Lu) are of immense importance for different applications including phosphors lamps, display devices, biological labeling, etc (Fang *et al.* 2003, Goldys *et al.* 2003, Ningthoujam 2012, Riwotzki *et al.* 2001, Wang *et al.* 2008). The tunability of different emission colour and enhancement of luminescence intensity of these Ln³⁺ doped inorganic host has emerged as an area of interest among many researchers. The multicolor emission can be achieved by selecting different lanthanide activators or by maintaining the concentration of the activators (Li *et al.* 2009, Niu *et al.* 2012, Xu *et al.* 2010). Also, by tuning the intensity ratio of emissions from different activators multicolor emission can be achieved (Wang *et al.* 2008). Also, Gautama and Veggel (2011) have tune blue electroluminescence of surface-modified Eu²⁺-doped GaN@SiO₂ nanoparticles to industrial standards with a peak at 450 nm and Commission Internationale de l'Eclairage (CIE-1931) coordinates of X=0.15 and Y=0.15.

Recently, generation of inorganic nanophosphors emitting white light for flat panel display (FPD) technology has been a major challenge (Yu *et al.* 2011, Lin *et al.* 2010, Liu *et al.* 2008). However, these nanophosphors have their limitation, i.e., lower luminescence quantum yield and shorter decay due to the large surface defects. These surface defects can be minimized through various mechanism, such as forming core-shell structures or annealing etc. (Wang *et al.* 2010,

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Sahu *et al.* 2012, Vetrone *et al.* 2009). Another approaches involves co-doping of different rare earth ions in the Ce^{3+} sensitized phosphor to giving enhance luminescence and different color phosphor (Zheng *et al.* 2011). Ce^{3+} has strong energy absorption in the range 250-280 nm due to 4f-5d transition and emission in the range 330-400 nm due to 5d-4f transition (Li *et al.* 2009). Ce^{3+} acts as sensitizer if there is overlapping of electric dipole fields of the sensitizer (emission) and activator (absorption) (Dexter 1953). A few examples of white light emitting phosphor are Eu^{3+} and Dy^{3+} ions co-doped Sr_2CeO_4 , Ce^{3+} and Sm^{3+} ions co-doped yttrium aluminum garnet, and Ce^{3+} , Tb^{3+} , Mn^{2+} co-doped borosilicate glass (Yu *et al.* 2011, Lin *et al.* 2010, Liu *et al.* 2008).

In the present study LaPO_4 is doped with Ce^{3+} ion different rare earth ions in and further multi Ln^{3+} ions such as Dy^{3+} , Tb^{3+} and Eu^{3+} were co-doped with $\text{LaPO}_4\text{:Ce}^{3+}$ using ethylene glycol as solvent and reaction medium. The advantages of using ethylene glycol over other solvents may be summarizes as prevention of aggregation after nucleation, re-dispersible of the particles in aqueous/organic solvents, development of polymer/ sol-gel-based luminescent materials, etc. The incorporation of the various Ln^{3+} ions into the LaPO_4 host has been studied by X-ray diffractometer. The luminescence properties of all the prepared samples are studied.

2. Experimental details

2.1 Sample preparation

LaPO_4 : 5 at.% RE (RE= Dy^{3+} , Eu^{3+} , Sm^{3+} , Tb^{3+}) co-doped with 7at.% Ce^{3+} were synthesized in ethylene glycol. Lanthanum oxide, La_2O_3 (Aldrich), Europium oxide, Eu_2O_3 (Aldrich), dysprosium carbonate, $\text{Dy}_2(\text{CO}_3)_3$ (Alfa Aesar), samarium nitrate, $\text{Sm}(\text{NO}_3)_3$, (CDH) and ammonium dihydrogen phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich) were obtained from Sigma Aldrich used as precursor for La^{3+} , Dy^{3+} , Sm^{3+} and PO_4^{3-} respectively without further purification. In a typical synthesis, 500 mg of La_2O_3 and 47 mg of $\text{Sm}(\text{NO}_3)_3$ (5 at.% Sm^{3+} doped LaPO_4 nanoparticles) were dissolved in 1 mL of concentrated hydrochloric (HCl) acid in a 100 mL round bottom flask. Excess acid was removed by evaporating several times with double distilled water. The resulting transparent solution was mixed with 50 mL of Ethylene glycol (EG) and 360 mg of $\text{NH}_4\text{H}_2\text{PO}_4$ were added. The reflux was carried out at 150°C for 3 h. The resulting white precipitate was collected by centrifugation at 10 000 rpm after washing with acetone. The same procedure was followed for the preparation of all the other doped samples by taking stoichiometric amounts.

2.2 Characterization

The X-ray diffraction (XRD) patterns of samples were recorded using PANalytical powder diffractometer (X'Pert PRO) with CuK_α (1.5405 Å) radiation with Ni filter. TEM micrographs were recorded using JEOL-JEM2100F. Perkin Elmer, Spectrum 400 spectrometer is used for the FT-IR observation of solvent using ZnSe sample holder. All the luminescence spectra and lifetime of the prepared samples were recorded using Perkin Elmer (LS-55) at room temperature.

3. Results and discussion

3.1 XRD study

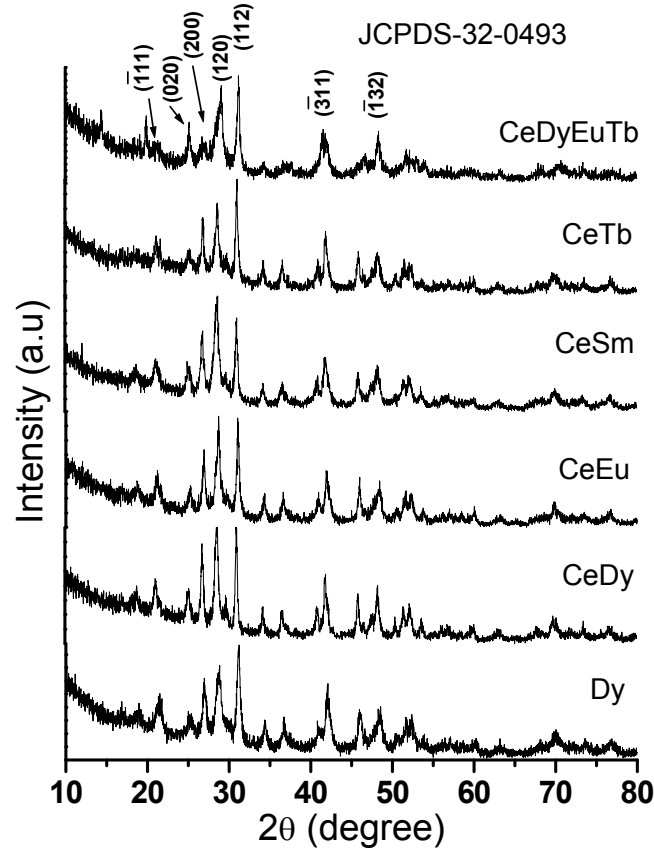


Fig. 1 XRD patterns of $LaPO_4$ doped with (a) Dy^{3+} , (b) $Ce^{3+}:Dy^{3+}$, (c) $Ce^{3+}:Eu^{3+}$, (d) $Ce^{3+}:Sm^{3+}$, (e) $Ce^{3+}:Tb^{3+}$, (f) $Ce^{3+}:Dy^{3+}:Tb^{3+}:Eu^{3+}$ asprepared nanoparticles

Table 1 Lattice parameter, unit cell volume and crystallite size of different as-prepared nanoparticles

Sample (Number indicates at. %)	Lattice parameters			Unit cell volume ($\text{\AA}^3$)	Size (nm)
	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)		
JCPDF 32-0493 (Monoclinic)	6.8366	7.0769	6.5095	306.58	-
5Dy: $LaPO_4$	6.805	7.060	6.435	301.84	14.06
7Ce:5Dy: $LaPO_4$	6.827	7.038	6.479	302.77	19.00
7Ce:5Tb: $LaPO_4$	6.840	7.059	6.457	302.34	19.24
5Ce:5Eu: $LaPO_4$	6.820	7.062	6.489	302.80	17.68
7Ce:5Sm: $LaPO_4$	6.805	7.073	6.490	303.92	15.58
7Ce:5Dy:5Tb:5Eu: $LaPO_4$	6.881	7.027	6.438	300.06	10.71

The X-ray diffraction (XRD) patterns of as-synthesized $LaPO_4$ doped with Dy^{3+} ; Ce^{3+}, Dy^{3+} ; Ce^{3+}, Eu^{3+} ; Ce^{3+}, Sm^{3+} ; Ce^{3+}, Tb^{3+} and $Ce^{3+}, Dy^{3+}, Eu^{3+}, Tb^{3+}$ are shown in Fig. 1. The XRD patterns of all the as-synthesized samples unambiguously match with monoclinic phase of $LaPO_4$, JCPDS-32-0493 having space group P21/n (14). Absence of any diffraction peaks from source compound indicated that the dopant ions are well incorporated into the host La^{3+} lattice in $LaPO_4$ matrix.

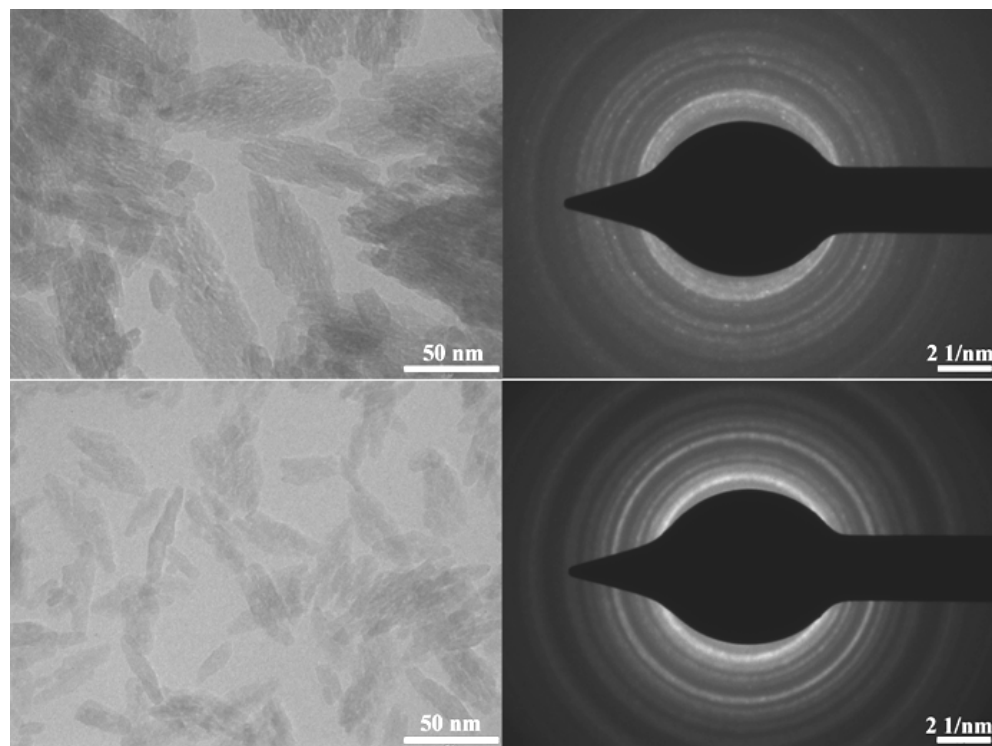


Fig. 2 TEM image of 3 at.% Ce^{3+} codoped (a) $\text{LaPO}_4:\text{Sm}^{3+}$ (5 at.%) and (b) $\text{LaPO}_4:\text{Tb}^{3+}$ along with their corresponding SAED patterns (b)

Table 1 summarized the lattice parameters of the prepared sample along with its unit cell volume. From the table it is clear that the unit cell volume decreases with the doping of smaller lanthanide ions to the larger host La^{3+} ion. This indicates that the dopant as well as the co-dopant successfully substituted La^{3+} ions in the LaPO_4 matrix. This behavior is understandable since, the ionic radius of Ce^{3+} (1.14 Å), Sm^{3+} (1.09 Å), Eu^{3+} 1.07, Tb^{3+} (1.04 Å) Dy^{3+} (1.02 Å) are less than La^{3+} (1.18 Å) on basis of 8 co-ordination numbers, (Shannon1976). The crystallite size of the prepared samples were calculated by using Scheerer equation and it is found to be in the range of 10-19 nm.

3.2 TEM and FTIR study

Fig. 2 shows the TEM images along with its selected area electron diffraction (SAED) pattern of (a) Ce^{3+} co-doped $\text{LaPO}_4:\text{Tb}^{3+}$ and (b) Ce^{3+} co-doped $\text{LaPO}_4:\text{Sm}^{3+}$. The crystallinity of samples is clearly seen from the SAED pattern. All the particles are rod shaped with a uniform size of with an average diameter of 20-40 nm and length of 70-150 nm.

The infra red (IR) spectrum of Ce^{3+} doped $\text{LaPO}_4:\text{Tb}$ nanoparticles is shown in Fig. 3. In the spectrum, bands present at 552, 571 and 627 cm^{-1} corresponds to the bending vibrations of $(\text{PO}_4)^{3-}$ (ν_4) while bands at 884, 947 and 1072 cm^{-1} are assigned to stretching vibrations of $(\text{PO}_4)^{3-}$ (ν_3), (Ferhi 2009, William 1975, Silverstein 2007, Nakamoto1986). Bands at 1661 cm^{-1} (bending) and 3311 cm^{-1} (stretching) correspond to O-H group of ethylene glycol molecule. The bands at 2858 and 2932 cm^{-1} correspond to the stretching vibrations of CH_2 group of ethylene glycol molecule

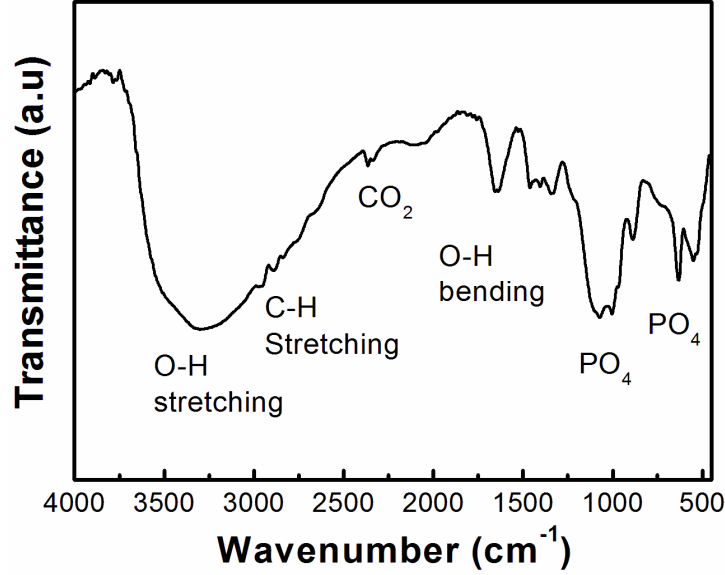


Fig. 3 FT-IR spectra of Ce^{3+} (7 at.%) co-doped $LaPO_4:Dy^{3+}$ (5 at. %) codoped asprepared nanoparticles

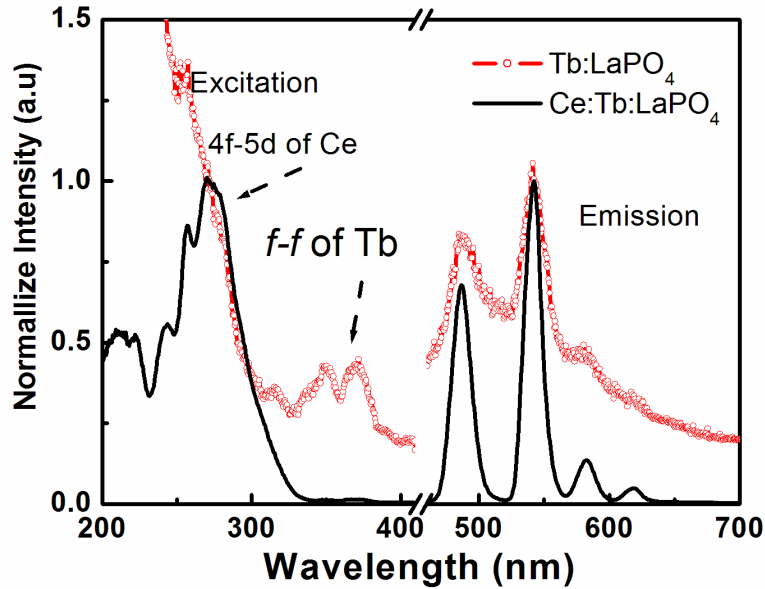


Fig. 4 Excitation and emission spectra of Tb^{3+} doped $LaPO_4$ with and without Ce^{3+} . Excitation is monitored at 545 nm and emission after 272 nm excitation

whereas, its bending vibration (scissoring) is observed at 1462 cm^{-1} . The peak at 2361 cm^{-1} is due to absorption of CO_2 gas from atmosphere on the surface of particles (Phaomei *et al.* 2011, Gallini *et al.* 2005, Ningthoujam *et al.* 2008). It has been reported that presence of ethylene glycol along with nanoparticles help in dispersion and incorporation of these nanoparticles in polar mediums (Yaiphaba *et al.* 2010).

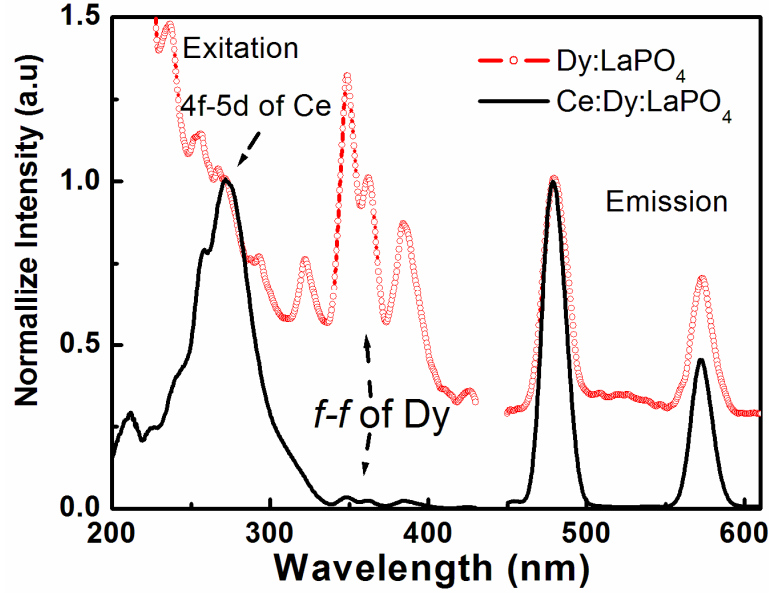


Fig. 5 Excitation and emission spectra of Dy^{3+} doped LaPO_4 with and without Ce^{3+} . Excitation is monitored at 480 nm and emission after 272 nm excitation

3.3 Photoluminescence studies

The excitation and emission spectra of Ce^{3+} co-doped with Tb^{3+} and Dy^{3+} in LaPO_4 host are shown in Figs. 4 and 5. Co-doping of Ce^{3+} with Tb^{3+} and Dy^{3+} in LaPO_4 host significantly enhances the luminescence intensity when excited at 272 nm corresponding to $4f-5d$ transition of Ce^{3+} due to the charge transfer from Ce^{3+} to Tb^{3+} and Ce^{3+} to Dy^{3+} (Riwotzki 2001). There are two dominant emission peaks at 480 nm (blue) and 572 nm (yellow) corresponding to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (magnetic dipole) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (electric dipole) transitions, respectively for $\text{LaPO}_4:\text{Dy}^{3+}:\text{Ce}^{3+}$ (Li *et al.* 2009, Liu *et al.* 2008). And for $\text{LaPO}_4:\text{Tb}^{3+}:\text{Ce}^{3+}$ two prominent emission peaks around 487 nm (blue) corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_6$ magnetic dipole transition and 543 nm (green) corresponds to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ electric dipole transition (Yaiphaba *et al.* 2010, Li *et al.* 2009). In the case of Ce^{3+} co-doped with Eu^{3+} and Sm^{3+} there is no charge transfer from Ce^{3+} to Eu^{3+} and Sm^{3+} . In the excitation spectra monitoring emission wavelength at 590 nm, (Supplementary Fig. 1) Eu-O charge transfer band (CTB) around 245 nm is higher than that of the peaks correspond to $^7\text{F}_{0,1} \rightarrow ^5\text{H}_{3,6}$, $^7\text{F}_{0,1} \rightarrow ^5\text{D}_0$, $^7\text{E}_{0,1} \rightarrow ^5\text{G}_1$, $^5\text{L}_7$ and $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transitions of Eu^{3+} around 325 to 400 nm (Goldys 2003). When excited at 245 nm the emission intensity of Ce^{3+} co-doped $\text{LaPO}_4:\text{Eu}^{3+}$ decrease to that of $\text{LaPO}_4:\text{Eu}^{3+}$. This indicates that co-doping of Ce^{3+} with Eu^{3+} shows no significant charge transfer between Ce^{3+} and Eu^{3+} . The emission spectra show prominent peaks at 590 (orange) and 617 nm (red) corresponds to the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) and electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), respectively (Goldys 2003). Similarly, Ce^{3+} co-doped $\text{LaPO}_4:\text{Sm}^{3+}$ (Supplementary Fig. 2) shows no significant changes in the luminescence intensity. The emission spectra consist of three main peaks at 561, 597 and 641 nm corresponding to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transitions, respectively. $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transitions are magnetic dipole allowed transitions with selection rule $\Delta J=0$ and ± 1 and the peak at 641 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition) is

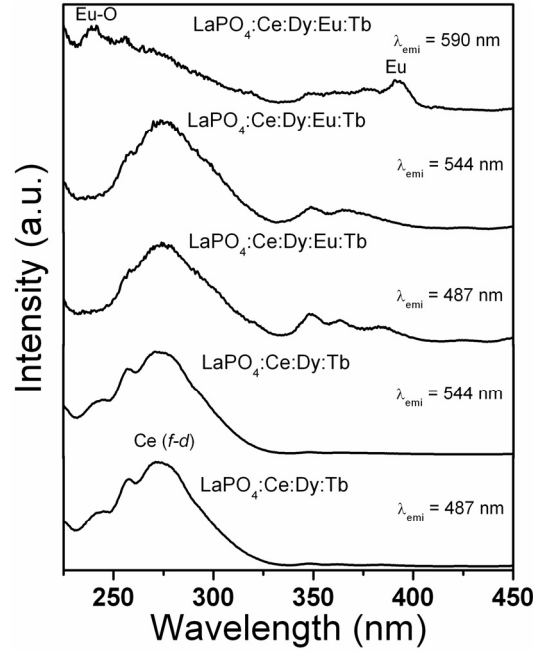


Fig. 6 Excitation spectra of $LaPO_4:Ce^{3+}$ (7 at.%): Dy^{3+} (5 at.%): Tb^{3+} (5 at.%) and $LaPO_4:Ce^{3+}$ (7 at.%): Dy^{3+} (5 at.%): Eu^{3+} (5 at.%): Tb^{3+} (5 at.%) monitoring at different emission wavelengths

electric dipole allowed transition which obeys the selection rule $\Delta J=2$ (Kodaira *et al.* 2007).

Fig. 6 shows the excitation spectra of multi ions co-doping, $LaPO_4:Ce^{3+}:Dy^{3+}:Tb^{3+}$ and $LaPO_4:Ce^{3+}:Dy^{3+}:Eu^{3+}:Tb^{3+}$ monitoring at different emission wavelength 544 nm (Tb^{3+} emission), 487 nm (Dy^{3+} emission) and 590 nm (Eu^{3+} emission). In the entire emission wavelength monitored an excitation peak around 230 to 330 nm is observed. The excitation peak at 240 nm when monitoring the emission wavelength at 590 nm arises due to the Eu-O charge transfer, the electrons in the valance band of O^{2-} absorbed this energy then it transferred to the incompletely filled $4f$ shell of Eu^{3+} . The excitation peak at 272 nm when monitoring the emission wavelength at 487 nm and 544 nm is arises due to the $4f-5d$ transitions of Ce^{3+} . This indicates that Dy^{3+} and Tb^{3+} can be excited at 272 nm due to the co-doping of Ce^{3+} . Without Ce^{3+} co-doping the maximum excitation wavelength of Dy^{3+} and Tb^{3+} is observed at 380 nm and 350 nm in $LaPO_4$ host respectively. Moreover, co-doping of Ce^{3+} bring the excitation wavelength of Eu^{3+} , Dy^{3+} and Tb^{3+} in the range of 230 to 330 nm indicating that at this excitation wavelength the entire three dopant ions will give its characteristic emission such as Red, Blue and Green respectively. Fig. 7(a) gives the emission spectra of Ce^{3+} co-doped $LaPO_4:Dy^{3+}:Tb^{3+}$ at 245 and 272 nm excitation. Thus, on excitation at 245 and 272 nm give emission peaks at 544, 618 nm for Tb^{3+} and at 487 nm due to the overlapping of Dy^{3+} emission peak at 480 nm and Tb^{3+} peak at 487 nm similarly a broad peak at 578 nm due to the overlapping of Dy^{3+} emission peak at 572 nm and Tb^{3+} peak at 585 nm. From Fig. 7(b), when Eu^{3+} is co-doped with $LaPO_4:Ce^{3+}:Dy^{3+}:Tb^{3+}$ and excited at 245 nm an extra peak at 590 nm for Eu^{3+} emission is observed. But when excited at 272 nm the emission peaks are remain the same as that of Ce^{3+} co-doped $LaPO_4:Dy^{3+}:Tb^{3+}$. It is also clearly indicates that there is no charge transfer process occur between Eu^{3+} and Ce^{3+} however due to the co-doping of Ce^{3+} all the doped ions (Eu^{3+} , Dy^{3+} and Tb^{3+}) can be excited at 245 nm. Thus, by tuning the excitation

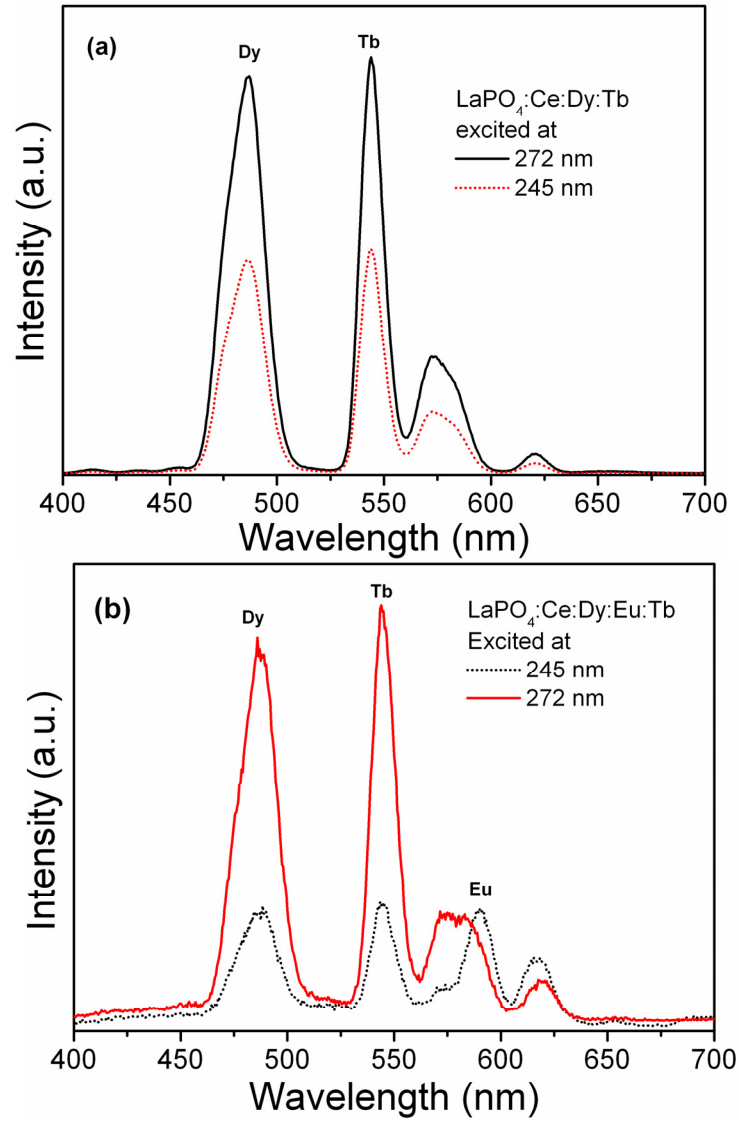


Fig. 7 Emission spectra of (a) $\text{LaPO}_4:\text{Ce}^{3+} (7 \text{ at.}\%):\text{Dy}^{3+} (5 \text{ at.}\%):\text{Tb}^{3+} (5 \text{ at.}\%)$, (b) $\text{LaPO}_4:\text{Ce}^{3+} (7 \text{ at.}\%):\text{Dy}^{3+} (5 \text{ at.}\%):\text{Eu}^{3+} (5 \text{ at.}\%):\text{Tb}^{3+} (5 \text{ at.}\%)$ monitoring excitation wavelength at 245 and 272 nm

wavelength, the intensity of Red, Blue and Green can be adjusted for different color. The CIE coordinate is calculated for all the samples and it is given in Table 2 and the corresponding CIE coordinate diagram is shown in Fig. 8. It is clearly seen that Eu^{3+} , Dy^{3+} , Sm^{3+} and Tb^{3+} give Red, Blue, Yellow, and Green color respectively. Upon mix doping of Dy^{3+} , Tb^{3+} and Ce^{3+} ($\text{LaPO}_4:\text{Dy}^{3+}:\text{Tb}^{3+}:\text{Ce}^{3+}$) a light green color with CIE coordinates $x=0.25$ and $y=0.44$ is observed irrespective to the monitoring excitation wavelength at 245 and 272 nm. Further Eu^{3+} ions is co-doped to this phosphor ($\text{LaPO}_4:\text{Dy}^{3+}:\text{Eu}^{3+}:\text{Tb}^{3+}:\text{Ce}^{3+}$) the phosphor color shifted to almost white with CIE coordinates $x=0.31$ and $y=0.40$ at excitation wavelength 272 nm finally gives white when excited at 245 nm with CIE coordinate $x=0.35$ and $y=0.37$.

Table 2 CIE chromaticity coordinates of different prepared sample at different excitation wavelength

Sl.No.	Sample (Number indicates the at.%)	Excitation wavelength	Co-ordinates	
			x	y
1	$LaPO_4:5Eu:7Ce$	240 nm	0.581	0.312
2	$LaPO_4:5Sm:7Ce$	400 nm	0.414	0.440
3	$LaPO_4:5Dy:7Ce$	272 nm	0.245	0.290
4	$LaPO_4:5Tb:7Ce$	272 nm	0.243	0.545
5	$LaPO_4:5Dy:5Tb:7Ce$	245 nm	0.254	0.447
6	$LaPO_4:5Dy:5Tb:7Ce$	272 nm	0.253	0.449
7	$LaPO_4:5Dy:5Tb:5Eu:7Ce$	245 nm	0.351	0.375
8	$LaPO_4:5Dy:5Tb:5Eu:7Ce$	272 nm	0.311	0.401

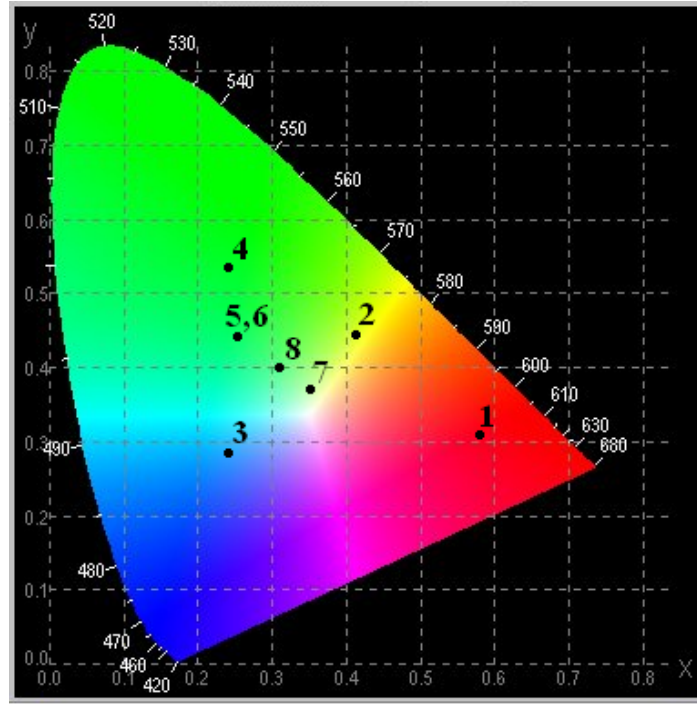


Fig. 8 CIE coordinates diagram for different samples at different excitation wavelength (1) $LaPO_4:5Eu:7Ce$ (240 nm), (2) $LaPO_4:5Sm:7Ce$ (400 nm), (3) $LaPO_4:5Dy:7Ce$ (272 nm), (4) $LaPO_4:5Tb:7Ce$ (272 nm), (5) $LaPO_4:5Dy:5Tb:7Ce$ (245 nm), (6) $LaPO_4:5Dy:5Tb:7Ce$ (272 nm), (7) $LaPO_4:5Dy:5Tb:5Eu:7Ce$ (245 nm), (8) $LaPO_4:5Dy:5Tb:5Eu:7Ce$ (272 nm)

4. Conclusions

Different phosphor, Ce^{3+} co-doped $LaPO_4:RE$ ($RE=Eu^{3+}, Dy^{3+}, Tb^{3+}, Sm^{3+}$), mix doping $LaPO_4:Dy^{3+}:Tb^{3+}$ and $LaPO_4:Dy^{3+}:Eu^{3+}:Tb^{3+}$ were prepared. It is observe that luminescence intensity significantly enhance due to strong energy transfer occur between Ce^{3+} to Dy^{3+} or Ce^{3+} to Tb^{3+} in $LaPO_4:Ce^{3+}:Dy^{3+}$ and $LaPO_4:Ce^{3+}:Tb^{3+}$ respectively. While, there is no enhancement

observed for $\text{LaPO}_4:\text{Ce}^{3+}:\text{Sm}^{3+}$ and $\text{LaPO}_4:\text{Ce}^{3+}:\text{Eu}^{3+}$. However, due to the co-doping of Ce^{3+} with mix doped rare earth ions such as Dy^{3+} , Eu^{3+} and Tb^{3+} in LaPO_4 host the excitation wavelength can be tuned in the region 230-330 nm and a green emission is observed for $\text{LaPO}_4:\text{Ce}^{3+}:\text{Dy}^{3+}:\text{Tb}^{3+}$ when excited at 245/272 nm and a white emission is observed for $\text{LaPO}_4:\text{Ce}^{3+}:\text{Dy}^{3+}:\text{Eu}^{3+}:\text{Tb}^{3+}$ when excited at 245 nm. These prepared samples could be potential green and white emitters.

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Supplementary Figures

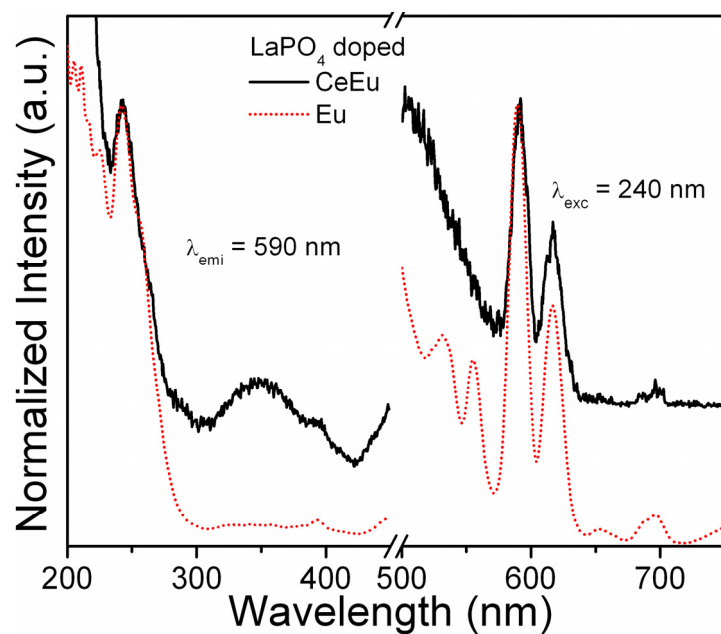


Fig. S1 Normalized excitation and emission spectra of $\text{LaPO}_4:\text{Eu}^{3+}$ (5 at.%) and $\text{LaPO}_4:\text{Ce}^{3+}$ (7 at.%) : Eu^{3+} (5 at.%)

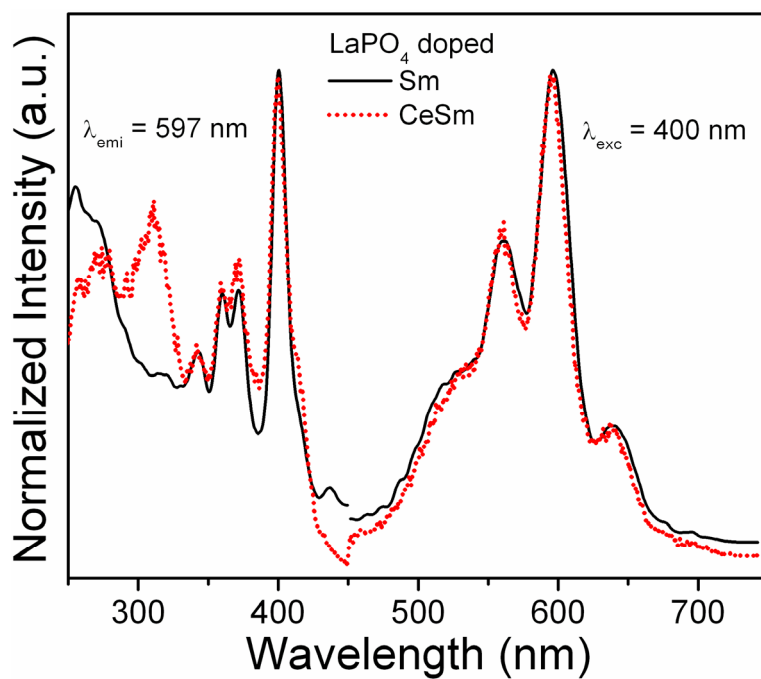


Fig. S2 Normalized excitation and emission spectra of $\text{LaPO}_4:\text{Sm}^{3+}$ (5 at.%) and $\text{LaPO}_4:\text{Ce}^{3+}$ (7 at.%) : Sm^{3+} (5 at.%)