Alkali metal ion co-doped Eu³⁺ activated GdPO₄ phosphors:

Structure and photoluminescence properties

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Abstract

Series of alkali metal ion co-doped with Eu^{3+} activated GdPO_4 phosphors were synthesized by the conventional solid state method. Structural parameters were confirmed by the X-ray Rietveld refinement method. All the compounds are crystallized in the monazite phase with space group ($P12_1/n1$, No.14). Morphology and functional group analysis were performed on scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Room temperature photoluminescence (PL) spectroscopic results reveal that, on Eu^{3+} ion doping in the GdPO_4 host matrix, the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) at 581 nm responsible for orange light, dominates the red emission with respect to the electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) at 620 nm. It was found that the emission intensity increased up to 9 mol% of Eu^{3+} and then quenched due to multipolar interactions. Further, co-doping with Li^+ , Na^+ and K^+ ion in to Eu^{3+} activated GdPO_4 phosphor led to an enhancement in luminescence intensity by reducing the parity restriction of electric dipole transitions as a consequence of suitable local distortion of the crystal field surrounding the Eu^{3+} activator ion. The results of Judd–Ofelt theory and radiative parameters suggest that these phosphors have a short lifetime, good quantum efficiency, excellent color purity compared to other reported Eu^{3+} doped phosphors. These results illustrate the mechanistic effect of alkali metal ions doping on luminescent properties of rare earth ion doped GdPO_4 phosphors and help in optimization of their luminescent properties according to the practical requirements in optoelectronic and biomedical applications.

Keywords: GdPO_4 ; solid state method; Europium; Alkali metal ions; Phosphors; Judd-Ofelt analysis; Colour chromaticity.

1. Introduction

From past few decades, rare earth ions activated gadolinium orthophosphate (GdPO_4) phosphors generated great attention as multimodal agents mainly for optoelectronic and biomedical applications [1-5]. These interest because of their excellent ability of hosting activator ions in their lattice, higher quantum yields, lower photo-bleaching potential, high chemical and thermal stability, importantly low toxicity and bio-compatibility nature [6,7]. Meanwhile, high value of magnetic moment ($7.94 \mu\text{B}$) of Gd^{3+} arises due to the seven unpaired electrons in its electronic configuration and the resulting nanosecond paramagnetic relaxation properties made this moiety an efficient tool as a Magnetic Resonance Imaging (MRI) contrast agent for positive T1 images [8,9]. On doping with suitable rare earth ions, the GdPO_4 host lattice turned to be a bi-functional magnetic and luminescent material. Thus rare-earth ion activated gadolinium orthophosphate can be used as efficient multifunctional or multimodal solitary material with luminescent and magnetic properties [10,11]. Compared to other lanthanide ions, Eu^{3+} ion is the most attractive and an extensively used luminescent activator ion due to its broad excitation band, excellent red emission and high thermal stability [12]. As a consequence, Eu^{3+} activated GdPO_4 phosphors show both luminescent and paramagnetic properties [13, 14].

Lanthanide orthophosphates exist in five types structures namely, monazite (monoclinic structure), xenotime (tetragonal structure), rhabdophane (hexagonal structure), weinschenkite (monoclinic structure) and orthorhombic [15]. Likely, rare earth activated GdPO_4 also exists in two or more allotropic forms mainly based on their synthetic conditions such as pH, temperature, and reaction medium [16,17]. Europium activated GdPO_4 has been reported to crystallize in the

hexagonal structure at low temperature and at high temperature crystallizes in monoclinic structure [18-20]. Many previous reports discussed the energy transfer between Gd^{3+} and Eu^{3+} in GdPO_4 and it was clear that, the monoclinic phase of the $\text{GdPO}_4:\text{Eu}^{3+}$ phosphor exhibits enhanced luminescent properties as compared to the hexagonal structure. However, less attention has been paid for understanding the factors which like crystal structure and symmetry around the Eu^{3+} ion in the monoclinic phase, may correlate the variation of the phosphor luminescent properties with its crystal structure [18-20].

Efficiency of phosphor luminescence can be amplified by modifying the phosphor compositions by co-doping with suitable sensitizer ions. In fact, as mentioned in the literature, a very small quantity of co-doping of the sensitizers can play a huge role to improve the efficiency of the luminescent phosphor [21]. Alkali metal ions (Li^+ , Na^+ and K^+) are widely used sensitizers [22]. Because of their ionic radius and ionic charges which are different from those of the host (Gd^{3+}), the distortion of crystal lattice is introduced as well as a break of the local site symmetry which can lead to a better color purity [23]. Effects of sensitizers can be realized by several mechanisms; some of the co-dopants acting as direct sensitizers (i.e. with enhanced charge transfer) and others, (since alkali ions are having wide range of ionic radii) easily occupying both the Gd^{3+} substitutional sites and interstitial sites [23] or creating oxygen vacancies. As a consequence, an alteration of the local site symmetry of the crystal field around the rare-earth ions is observed and hence it is expected that co-doping with alkali metal ions will amplify the luminescent intensity [24-26].

To the best of our knowledge, till date there is no report on the structural and luminescent studies of alkali metal co-doped $\text{GdPO}_4:\text{Eu}^{3+}$ phosphors. And also, there is a lack of studies on the mechanistic effect of co-doping in these phosphors. It is very vital to evaluate the effect of

alkali metal co-doping on luminescent properties in multifunctional $\text{GdPO}_4:\text{Eu}^{3+}$ phosphors and further understand the overall mechanism of amplified luminescence. In the present work, alkali metal ions (Li^+ , Na^+ and K^+) co-doped with Eu^{3+} activated GdPO_4 phosphors were synthesized by the conventional solid state method and the comparative study was performed. The influence of co-dopants on the enhancement of photo-luminescent properties of Eu^{3+} activated GdPO_4 was investigated in detail.

2. Experimental

Series of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ ($0.0 \leq x \leq 0.11$) phosphors and monovalent alkali ion co-doped $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{A}_y\text{PO}_4$ ($\text{A}^+ = \text{Li}^+, \text{Na}^+ \text{ and } \text{K}^+$) phosphors were synthesized by the conventional solid state method. In the preparation of GdPO_4 host materials, analytical-grade gadolinium oxide (pre-heated at $800^\circ\text{C}/8 \text{ h}$. Gd_2O_3) and di-ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ were used as starting materials. While europium oxide (Eu_2O_3) was used as Eu^{3+} dopant source for preparing Eu^{3+} activated GdPO_4 phosphor. Further, Alkali carbonates, (Li_2CO_3 , Na_2CO_3 and K_2CO_3) were used as alkali metal ion sources, which act as a co-dopant in the preparation of $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{A}_y\text{PO}_4$ ($\text{A}^+ = \text{Li}^+, \text{Na}^+ \text{ and } \text{K}^+$) phosphors. In a typical synthesis of $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ phosphors, the requisite amounts of Gd_2O_3 (1.7219 g), Eu_2O_3 (0.0880 g) and $(\text{NH}_4)_2\text{HPO}_4$ (1.3206 g) were mixed and ground in agate mortar. The mixture was transferred into porcelain crucible and calcined at 950°C for 12 h. in a muffle furnace and cooled down to room temperature. The resulting white powder was used for further characterizations. Similarly, alkali ion co-doped Eu^{3+} ion activated GdPO_4 phosphors were synthesized. The phase purity of all the synthesized compounds were evaluated by the powder X-ray diffraction (XRD) measurements on PANalytical Empyrean powder diffractometer operated at 30 mA and 45 kV with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) source and a nickel filter. For Rietveld refinement analysis, data were

collected at a scan rate of $1^\circ/\text{minute}$ with a 0.026° step size for 2θ range from 10° to 90° [27]. The structural parameters were refined by using FullProf Suite programme. The morphologies of these phosphors were investigated using field emission scanning electron microscopy (FE-SEM, FEI Quanta 200) operated at an accelerating voltage of 10 kV. The Fourier transform infrared spectroscopy (FTIR) studies were performed on Perkin Elmer Spectrometer, Frontier using potassium bromide (KBr) as a reference sample. The excitation and emission spectra of these powder phosphors were recorded using a Jobin-Yvon Fluoro-Max spectro-fluorometer equipped with 450W Xenon lamp as excitation source. The room temperature luminescent decay measurements were recorded using Edinburgh Nano-second time resolved fluorescence spectrometer with excitation source 395 nm. All the above characterizations were performed at ambient conditions.

3. Results and Discussions

The powder X-ray diffraction patterns of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ ($0.0 \leq x \leq 0.11$) compounds were shown in Fig. 1. The sharp intense peaks revealed the crystalline nature of the samples and all the obtained diffracted peaks were matching very well with JCPDS card no. 84-0920 corresponding to the monoclinic space group $P12_1/n_1$ with monazite structure. We did not observe any additional peaks which might correspond to starting materials or any other secondary phase, suggesting that the synthesized compounds are in single phase.

The structural parameters for all the compounds were refined by the Rietveld method using powder XRD data. The refinement results confirmed that all the samples were crystallized in the monoclinic structure with space group $P12_1/n_1$ (no.14, $Z = 4$). In a typical, observed, calculated and the difference XRD patterns of $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ compound is shown in Fig. 2(a). There is a good agreement between the observed and calculated XRD patterns. All the refined

structural parameters were summarized in Table 1. In the monoclinic structure of GdPO_4 , the 9-coordinated Gd^{3+} ion is having ionic radii of 1.107 Å [7]. On substitution of 9-coordinated Eu^{3+} ion ($r_{\text{Eu}^{3+}} = 1.120 \text{ Å}$) with a comparable ionic radii to Gd^{3+} ion, we did not observe any appreciable change in the structural parameters (Table 1). The typical crystal structure of GdPO_4 (Fig. 3) was modeled by using Rietveld refined parameters through VESTA program. In the GdPO_4 monazite, the structure consists of alternating edge sharing of GdO_9 polyhedral and PO_4 distorted tetrahedra forming chains parallel to c -axis. The GdO_9 eight coordinated polyhedron has an irregular pentagon with two oxygen atoms above and two oxygen atoms below the plane of the pentagon. Rotation of the PO_4 tetrahedra caused by over-sized cation is the main reason for distortion in PO_4 tetrahedra and reduces the symmetry to monoclinic structure [28].

Powder X-ray diffraction patterns for $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{A}_y\text{PO}_4$ ($\text{A}^+ = \text{Li}^+, \text{Na}^+$ and K^+ , $x = 0.05$) phosphors were shown in Fig. 4. From Fig. 4, it is evident that Li^+ has the smaller ionic radii compared to Gd^{3+} and occupies the interstitial sites in host. In case of Na^+ ($r_{\text{Na}^+} = 1.24 \text{ Å}$) and K^+ ions ($r_{\text{K}^+} = 1.55 \text{ Å}$) have the larger ionic radii compared with Gd^{3+} ions, hence Li^+ , Na^+ and K^+ co-doped compounds are crystalized in single monoclinic phase, but 5 mol% K^+ ions co-doped compound diffractogram exhibits an extra line at two theta 24.54° , which might be corresponds to a secondary phase of gadolinium poly-phosphates ($\text{GdP}_5\text{O}_{14}$, JCPDS No. 36-0258). Figures S1 – S3 depicts the X ray diffraction patterns for Li^+ , Na^+ and K^+ ions (1, 3 and 5 mol%) co-doped Eu^{3+} activated GdPO_4 phosphors. Structural parameters were confirmed by the Rietveld refinement method for all the alkali co-doped Eu^{3+} activated GdPO_4 compounds. In Fig. 2(b-e)), shown the observed, calculated and the difference XRD patterns for $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$, $\text{Gd}_{0.92}\text{Eu}_{0.05}\text{K}_{0.03}\text{PO}_4$ and $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ compounds respectively. From Fig. 2 (b-e) it is evident that, observed, calculated and the

difference XRD patterns of $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ and $\text{Gd}_{0.92}\text{Eu}_{0.05}\text{K}_{0.03}\text{PO}_4$ showed the good agreement between the observed and calculated XRD patterns. But average match between the observed and calculated XRD patterns realized in $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ compound due to presence of small amount of impurity and the structural parameters of these co-doped compounds were listed in Table S1. It was noted that there was no considerable change in the lattice parameters or cell volume up to 5 mol% co-doping alkali metal ions with 5 mol% substitution of Eu^{3+} ion.

In order to confirm the phase purity and functional group analysis were performed by Fourier Transform Infrared (FT IR) spectroscopic method. FT IR spectra of GdPO_4 , Eu^{3+} and alkali metal ion co-doped with GdPO_4 phosphors are shown in Fig. 5. The major absorption band at 971 cm^{-1} can be assigned to the symmetric stretching mode of P-O bonds in PO_4^{3-} tetrahedra. The bunch of bands at 1064 to 1114 cm^{-1} was assigned to the asymmetric stretching modes originating from the P-O bond stretching vibration in PO_4^{3-} tetrahedra. The bands observed at 544 , 578 and 623 cm^{-1} can be assigned to the asymmetric bending vibrations and a weak band at 475 cm^{-1} arise from symmetric bending vibrations of P-O bonds in distorted PO_4^{3-} tetrahedra. Further, it is worth note that, the splitting of IR bands in the range of 1060 to 1120 cm^{-1} due to the reduction in the lattice symmetry from eight fold to nine fold symmetry within the monazite structure. No additional peaks were observed except above mentioned peaks in FTIR spectra which confirm the phase purity of the phosphors [29-33].

Field emission scanning electron micrographs (FE SEM) of Eu^{3+} and alkali metal ions co-doped GdPO_4 phosphors were recorded. Fig. 6(a-d) represents the FE SEM images of $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ and $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ respectively. The micrographs reveal that these phosphors are agglomerated and exhibit spherical

shape morphology. The particle diameter distribution ranges from 200 to 300 nm. To confirm the homogeneity of elements in the phosphors, the energy dispersive X-ray (EDX) elemental mapping was carried out. Fig. S4 and S5 show the elemental mapping of $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ and $\text{Gd}_{0.93}\text{Eu}_{0.07}\text{PO}_4$ compounds. These elemental mapping results confirmed that all the elements were evenly distributed over the entire area in both 5 mol% and 7 mol% Eu^{3+} ion doped GdPO_4 phosphors.

Fig. 7 represents an excitation spectrum of $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ phosphor recorded ($\lambda_{\text{em}} = 594$ nm) at room temperature. The local symmetry and occupancy of the Eu^{3+} are the key factors for the structurally induced enhancement of luminescence in these monoclinic phosphors. The excitation spectrum consists in a series of peaks in the range of 220 to 500 nm. The broad excitation band with the maximum intensity located at 238 nm corresponds to the charge-transfer (CT) ($\text{O}_2^- \rightarrow \text{Eu}^{3+}$) transition, which occurs due to the delocalization of electrons from the filled 2p shell of the O^{2-} ion to the partially filled 4f shell of the Eu^{3+} ion. The estimation of position of CTB due to Eu-O couple excitation energy was proposed by Jorgensen [34] as per the following equation:

$$\sigma = [\chi(x) - \chi(M)] \times (3 \times 10^4)(\text{cm}^{-1}) \quad (1)$$

Here σ signifies the position of the CTB (in cm^{-1}) while $\chi(x)$ and $\chi(M)$ denote the optical electro-negativity of the anion and the central metal ion, respectively which in the given case are $\chi(\text{O}) = 3.44$ and $\chi(\text{Eu}) = 1.2$. As per the given estimation, Eu-O CTB position equates to value of $42,000 \text{ cm}^{-1}$ (238 nm), thereby, perfectly matching with the observed emission spectra. It is evident that Eu^{3+} ions has similar co-ordination environment in the Gd^{3+} site in the host lattice. From literature it is well known that host lattices CT band mainly depends on the Eu-O bond length and local environment around the Eu^{3+} in the particular crystal field of host lattice. Hence

Eu-O and CT band of Eu^{3+} vary from one host lattice to another. A small shoulder peak on the CT band (275 nm) arises from $^8\text{S}_{7/2} \rightarrow ^9\text{I}_7$ transition and a sharp peak around 306 nm arises from $^8\text{S}_{7/2} \rightarrow ^6\text{P}_J$ transition of Gd^{3+} ions indicating the Gd^{3+} to Eu^{3+} energy transfer [35]. The value of the integrated area of the excitation peaks in the range 240-300 nm is much higher than that of the excitation peaks in the 360 to 415 nm range also supporting the Gd^{3+} to Eu^{3+} energy transfer mechanism [36]. There are multiple sharp excitation peaks arisen because of f-f transitions of Eu^{3+} and Gd^{3+} ions. Among these transitions electronic transitions of Eu^{3+} can be assigned as ($^7\text{F}_0 \rightarrow ^5\text{H}_J$) at 319 nm, ($^7\text{F}_0 \rightarrow ^5\text{D}_4$) at 361 nm, ($^7\text{F}_0 \rightarrow ^5\text{G}_J$) at 382 nm, ($^7\text{F}_0 \rightarrow ^5\text{L}_6$) at 394 nm, ($^7\text{F}_0 \rightarrow ^5\text{D}_3$) at 416 nm and ($^7\text{F}_0 \rightarrow ^5\text{D}_2$) at 465 nm [37]. The mechanism of excitation and charge transfer is shown in the energy level diagram (Fig. 8).

Fig. 9 shows the normalized emission spectra of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ ($x = 0.01, 0.03, 0.05, 0.07, 0.09$ and 0.11) phosphors were recorded at $\lambda_{\text{exi}} = 238$ nm. We observed sharp emission lines ranging from 580 to 720 nm, which corresponds to the electron transitions from the excited $^5\text{D}_0$ level to $^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) levels of the Eu^{3+} activator ion, respectively. A weak emission band observed at 582 nm can be assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition. The emissions which are attributed to an exhibition of intense orange-red colour are due to the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) at 594 nm and electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) at 620 and ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) at 684 and 698 nm, while another weak emission band from transition ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) is observed at 652 nm.

The magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) is independent of the co-ordination environment of the host lattice, which is not necessarily the case for the electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is sensitive to co-ordination environment of host lattice. Then the ratio of relative intensities for $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions known as asymmetric ratio can depict the

luminescent properties of the different compositions. It strongly depends upon the local symmetry of Eu^{3+} ions; in the present case, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is found to exhibit a relatively stronger emission with respect to emission due parity forbidden $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} ions showing that Eu^{3+} ions evidently occupy the inversion centre sites in the GdPO_4 host lattice [7]. This asymmetric ratio does not change much when varying in the concentrations of Eu^{3+} doping and values of asymmetric ratios for these phosphors are found to be in the range of 0.43-0.45 (Fig. S6a) and values are summarized in Table 2. When these phosphors are excited, respective intensities of magnetic and electric dipole transitions may vary due to different interaction. Indeed, in the Eu^{3+} activated GdPO_4 system with a monoclinic structure, Eu^{3+} ions is situated C_i (4e) inversion site and is co-ordinated with nine oxygen ions to form EuO_9 distorted or asymmetric polyhedron, with different Eu-O bond lengths [38]. From Fig. 9 (inset), the emission peak intensity initially increased up to 9 mol% of Eu^{3+} ion concentration to reach its maximum emission intensity at this value. Above 9 mol% doping, the emission intensity decreased notably due to the effect of concentration quenching [39]. Same results were expressed as the plot of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ peak emission intensity versus concentration of Eu^{3+} ion in mol% in Fig 10. Generally this concentration quenching phenomenon may take place in two ways, such as exchange interaction and electric multipolar interaction which can be determined by the critical distance (R_c) between Gd^{3+} ion (host) to Eu^{3+} (activator ion). Concentration quenching through exchange interaction is only possible when R_c value is less than 4 Å [40]. The average critical transfer distance (R_c) can be found using the following equation [41].

$$R_c \approx 2 \left[\frac{3V}{4\pi x_c N} \right]^{1/3} \quad (2)$$

Where x_c is the critical concentration of Eu^{3+} ions, V is the volume of the unit cell and N is the number of Eu^{3+} ions occupy per unit cell. In GdPO_4 case, $V = 280.01 \text{ \AA}^3$, $N = 4$ and $x_c = 0.09$ leading to a R_c for Eu^{3+} activated GdPO_4 phosphors of $11.41 \text{ \AA}$. This value of R_c higher than $4 \text{ \AA}$ ruled out the quenching by exchange interaction. Thus, it could be take place through electric multipolar interactions. There are many type of multipolar interaction such as dipole–quadrupole (d–q), dipole–dipole (d–d) and quadrupole–quadrupole (q–q) interactions are present [42]. And the type of interaction involved in the energy transfer can be determined by Van Uitert [43] equation:

$$\frac{I}{x} = \frac{k}{(1 + \beta(x)^{\theta/3})} \quad (5)$$

Where I/x denotes the emission intensity per activator (x), β and k are constants for a given host lattice, θ represents the interaction type between rare earth ions, here $\theta = 3, 6, 8, 10$ correspond to the energy transfer among the nearest-neighbor ions, dipole–dipole (d–d), dipole–quadrupole (d–q) and quadrupole–quadrupole (q–q) interaction, respectively. A plot of I/x versus x on a logarithmic scale of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ was shown in Fig. 11. The plot of $\log(I/x)$ on $\log(x)$ is found to be relatively linear, and the slope is determined to be -0.3342 and the value of θ is found to be approximately 1 and close to minimum θ value 3. Hence these results indicate that the energy transfer among the nearest-neighbor ions in the $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ phosphors reason for the concentration quenching [44].

To illustrate this effect, Fig. 12 compares the PL emission spectra of alkali metal ion ($\text{A}^+ = \text{Li}^+, \text{Na}^+ \text{ and } \text{K}^+, 5 \text{ mol. \%}$) co-doped $\text{GdPO}_4: \text{Eu}^{3+}$ phosphors. From these PL emission spectra it is evident that, there is no noticeable change in the shape and position of emission peaks except in the peak intensity. In the present work, all the three alkali metal ions enhance the

luminescence of the phosphor and compared to $\text{GdPO}_4:\text{Eu}^{3+}$ phosphors, the integral intensity of emission spectrum of 5 mol. % Li^+ , Na^+ and K^+ phosphors are enhanced by a factor of 3.91, 2.95 and 2.06 times respectively. Fig. S7 illustrates the alkali metal ion concentration dependent emission spectra of $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{Li}_y\text{PO}_4$, $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{Na}_y\text{PO}_4$ and $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{K}_y\text{PO}_4$ ($0.01 \leq y \leq 0.05$) phosphors under excitation at 238 nm. From Fig S7 it is evident that Emission intensity of the phosphor is increased, as the concentration of alkali metal increases in Eu^{3+} activated GdPO_4 from 1 mol% to 5 mol%. It should be noted that Li^+ is the most efficient one, and $\text{GdPO}_4:\text{Eu}^{3+}$ co-doped with Li^+ visualizes the highest orange-red emission intensity (Fig. 13). Enhancement in emission intensity with incorporation of alkali metal ions mainly takes place because the co-doping of these ions facilitates the charge transfer from the O^{2-} to Eu^{3+} , makes it more efficient, and acts as sensitizers for the transfer of excitation energy from host lattice to Eu^{3+} ion [45]. Furthermore, substitution of Li^+ , Na^+ , K^+ into the Gd^{3+} sites may result in the generation of a substantial number of oxygen vacancies at the surface of the phosphor. These oxygen vacancies might eventually act as sensitizer for the energy transfer from host lattice to Eu^{3+} ion due to the strong mixing of charge transfer states, resulting in overall enhancement of luminescence intensity [46, 47, 11].

Another noticeable effect of alkali metal ion co-doping is as illustrated in Fig. S6b. The increase in asymmetric ratio of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions which strongly depends on the co-ordination environment of Eu^{3+} ions. Generally addition of the co-doping ions in the GdPO_4 lattice create a stress of the nearest Gd^{3+} or of the Eu^{3+} ions at Gd^{3+} sites. Hence, the local symmetry surrounding the Eu^{3+} ions would be modified to offer a site with lower symmetry to activator ions. This lower symmetry is able to relax the parity selection rule and increase the

transition possibility of electron and also $^5D_0 \rightarrow ^7F_2$ transitions, and hence the enhancement in PL emission intensity [48].

Moreover, the local distribution enhances proportionately with the increase of the positive charge co-dopant and the host cation [49]. The co-dopant ions may either directly act as flux [50] or may otherwise get placed at the substitutional sites in the host lattice, thus, creating oxygen vacancies [23]. They hence, may act as an efficient sensitizer for promotion of the energy transfer [51]. The luminescence intensity varies extensively depending upon the size of co-dopant as well as activator with respect to that of host lattice ion. Thus, evident enhancement in the emission intensity could be observed which is attributed to the difference in the ionic radii of the alkali metal ions. The PLE intensity in as-prepared K^+ , Na^+ , and Li^+ co-doped $GdPO_4:Eu^{3+}$ monoclinic samples were found to be sequentially enhanced with respect to that of $GdPO_4:Eu^{3+}$, respectively. It owes to the fact that the ionic radius of Li^+ 0.92 Å is relatively shorter than that of Gd^{3+} (1.107 Å), while Na^+ and K^+ possess a relatively higher ionic radii 1.24 Å and 1.55 Å, respectively. With the ionic radii increasing; the difference of ionic radii gives rise to the diversity of the sub-lattice structures around the luminescent center ions, which in turn influences the spin orbit coupling and the crystal field of the Eu^{3+} ions, influencing the overall coordination conditions around Eu^{3+} ion. As a consequence, the Eu-O bond distance varies as a function of the ionic radius of the alkali metal ions in turn altering the peaks intensity and this fact is supported by XRD results in which unit cell volume increases with 5 mol% alkali metal ions content (Table S1).

The incorporation of alkali metal ions also creates some bound electron hole or oxygen vacancies due to the larger difference in radius and charge of A^+ ions compared to Gd^{3+} ions. It is evident that different co-dopants have different effect on PL intensity of $GdPO_4$ phosphor and

addition of co-doping ions in the GdPO₄ lattice is associated with the electro negativity and mismatches in size between co-dopant and host cation.

Fig. 14(a-d) illustrates the room temperature PL decay curves of a) Gd_{0.95}Eu_{0.05}PO₄, b) Gd_{0.90}Eu_{0.05}Li_{0.05}PO₄ c) Gd_{0.90}Eu_{0.05}Na_{0.05}PO₄ d) Gd_{0.90}Eu_{0.05}K_{0.05}PO₄. The decay experiments were performed at 395 nm excitation and emission wavelength was fixed at 594 nm. The lifetime decay curves are not well fitted by a mono-exponential equation ($I = I_0 \exp(-t/\tau)$). It can be observed that all decay curves can be well fitted to the double exponential function which can be written as:

$$I_t = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2) \quad (3)$$

Where I_1 and I_2 are the PL intensities at two different intervals of time and corresponding lifetimes of an excited state energy τ_1 and τ_2 respectively. The τ_{average} or τ_{exp} is calculated by using the following equation and Table 2 shows the experimental average lifetimes (τ_{exp}) for all Eu³⁺ and alkali metal ions ($A^+ = \text{Li}^+, \text{Na}^+ \text{ and } \text{K}^+$) co-doped GdPO₄ phosphors.

$$\tau_{\text{average}} = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2} \quad (4)$$

The term average lifetime denotes the average value of life times of Eu³⁺ ions present in various chemical and physical environments in the phosphor due to non-homogeneity or defect structure or in homogeneous energy transfer process within the Eu³⁺ energy levels. In this case Eu³⁺ ions present at the surface of the phosphor show a swift decay, meanwhile Eu³⁺ core ions exhibit slow decay comparatively to the earlier ions. This is the main reason for the bi-exponential nature of these Eu³⁺ GdPO₄ phosphors. From Table 2 it is evident that, decay life times have similar behavior with variation in luminescence intensity with respect to Eu³⁺ and

Alkali metal ions concentrations (Fig. 9 and S7). The doping of mono-valent alkali metal ions creates the oxygen vacancies. These oxygen vacancies, can act as sensitizers [36], and may facilitate the efficient energy transfer between the Gd–O and Eu–O, might be the reason for the longer life time values of the alkali metal ions co-doped phosphors compared to non-co-doped phosphors.

The emission spectra of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ ($0.01 < x < 0.11$), $\text{Gd}_{0.95-y}\text{Eu}_{0.05}\text{A}_y\text{PO}_4$ ($\text{A}^+ = \text{Li}^+$, Na^+ and K^+ , $0.01 < y < 0.05$) phosphors were used for the estimation of the Judd–Ofelt (J–O) intensity parameters for the Eu^{3+} ion. The Judd–Ofelt intensity parameters (Ω_λ) ($\lambda = 2, 4$) provide significant information about the local structure and bonding in the proximity of rare earth ions in a specific coordination environment [52, 53]. When the rare-earth ions enjoy a greatly symmetric environment, the value of Ω_2 comes out to be low. While on the other hand, Ω_4 is instead found to be more sensitive to macroscopic properties such as viscosity and rigidity of the matrix. The J–O parameters could be used to predict some informative radiative properties including the rate of parity-forbidden electric dipole radiative transition, radiative lifetime (τ_{rad}), branching ratios (β), stimulated emission cross-section (σ_e) and optical gain for the various transition possibilities (A_T) of the Eu^{3+} ions [52, 54]. The intensity of electric and magnetic dipole transitions is utilized to evaluate the electric and magnetic dipole line strengths of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ phosphors. By using calculated values of electric dipole line strengths, J–O intensity parameters Ω_λ ($\lambda = 2, 4$) can be determined by using equation:

$$S_{\text{calc}}^{\text{ed}}(J \rightarrow J') = \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle \varphi J \| U^\lambda \| \varphi' J' \rangle \right|^2 \quad (5)$$

Where $\langle\|U^\lambda\|\rangle$ denotes the doubly reduced matrix elements of unit tensor operator of rank λ , which were found out from the intermediate coupling approximation for $\varphi J \rightarrow \varphi' J'$ transition. The J–O intensity parameters are influenced by transition probabilities of the host, which consist in the crystal-field parameters, inter configurational radial integrals, and the interaction between the central ion and intermediate environment.

The measured line strengths ($S_{\text{meas}}^{\text{ed}}$) can be calculated from the excitation spectrum using the following expression:

$$S_{\text{meas}}^{\text{ed}}(J \rightarrow J') = \frac{3hc(2J+1)}{8\pi^3 \bar{\lambda} e^2 N_0} \frac{9n}{(n^2+2)^2} \Gamma_{\text{ex}} \quad (6)$$

Where J (J') denotes the angular momentum of the ground (excited) state, h is the Planck's constant, $(2J+1)$ indicates the degeneracy of the ground state, $\bar{\lambda}$ is the mean wavelength of the excitation band, e is the electron charge, n is the refractive index of GdPO_4 , N_0 is concentration of Eu^{3+} ion and Γ_{ex} is the integrated excitation intensity for each transition [55]. The Lorentz local field correction factor $[9n/(n^2+2)^2]$, depends on the refractive index of the host material. The measured line strengths were then used to evaluate the intensity parameters.

The magnetic dipole line strengths can be obtained from the corresponding values of oscillator strengths ($f_{\text{calc}}^{\text{md}}$) by:

$$S_{\text{calc}}^{\text{md}}(J \rightarrow J') = \frac{3h(2J+1)n^2}{8\pi^2 mc \nu} f_{\text{calc}}^{\text{md}} \quad (7)$$

The J–O parameters along with refractive index (n) were used to predict the radiative properties of Eu^{3+} and alkali metal ions co-doped phosphors. The radiative transition probability (A_R) for $J \rightarrow J'$ transition can be expressed as [56]:

$$A_R(J \rightarrow J') = \frac{64\pi^4 \nu^3 e^2}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} S_{\text{ed}} + n^3 S_{\text{md}} \right] \quad (8)$$

Where S_{ed} and S_{md} are the electric-dipole and magnetic-dipole line strengths. The radiative lifetime τ_R for an excited state J is calculated by [53]:

$$\tau_R(J) = \frac{1}{A_R(J \rightarrow J')} \quad (9)$$

The calculated Judd–Ofelt intensity parameters, radiative transition probability, non-radiative relaxation rate, radiative lifetime and quantum efficiency of Eu^{3+} and alkali metal ions co-doped phosphors are given in Table 2. The Ω_6 parameter is not calculated due to practical limitations in measurements in spectral range. Even though, $U^{(6)}$ matrix for Eu^{3+} ions which corresponds to $^5D_0 \rightarrow ^7F_6$ transition is generally weak and close to zero [57].

In addition out of other J-O parameters, Ω_2 is sensitive to the crystal field, the covalence and structural changes around Eu^{3+} ion and Ω_4 is independent of above factors. And hence a higher value Ω_2 indicates a distortion around the Eu^{3+} in GdPO_4 host lattice. As the concentration of Eu^{3+} doping increases, Ω_2 decreases due to the increase in the local symmetry around Eu^{3+} ion [58]. After alkali metal co-doping Ω_2 parameter increases drastically as a consequence of the distortion in the host lattice around Eu^{3+} ions. Another important fact is that the degree of covalence between ligands and activator ions is due to the high polarizability factor caused by P^{5+} and oxide ion.

The discrepancy between calculated radiative lifetime (τ_R) and experimental lifetime (τ_{exp}) was due to the manifestation of non-radiative relaxation rate (W_{NR}) and can be written as:

$$W_{\text{NR}} = \frac{1}{\tau_{\text{exp}}} - \frac{1}{\tau_{\text{rad}}} \quad (10)$$

The total transition probability (A_T) is given by [53]:

$$A_T = A_R + W_{\text{NR}} \quad (11)$$

From Table 2, it was found that the value of A_T increases as Eu^{3+} concentration increases up to 9 mol.% which was due to the increase in symmetry around Eu^{3+} ion. The luminescence quantum efficiency (η) is defined as the probability of emission of a photon per absorbed photon or the ratio of experimental lifetime to calculated radiative lifetime and can be expressed as:

$$\eta(\%) = \frac{\tau_{\text{exp}}}{\tau_{\text{rad}}} \times 100 \quad (12)$$

Table 2 lists the comparison of experimental lifetime and quantum efficiency for Eu^{3+} and alkali metal ions doped GdPO_4 phosphors. 5 mol% Li^+ doped GdPO_4 showed the highest quantum efficiency around of 85.7% and presents practical applicability towards solid state lightening and bio medical applications.

The Commission International de l'Eclairage (CIE) chromaticity coordinates of Eu^{3+} and alkali metal ions doped GdPO_4 phosphors were determined from the PL emission spectra at 238 nm excitation wavelength. Fig. 15(a and b) shows the CIE 1931 and CIE 1976 chromaticity diagram of 1) $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, 2) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$ 3) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ 4) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ excited at 238 nm. The color coordinates of Eu^{3+} and alkali metal ions doped GdPO_4 phosphors

were listed in Table 3. From Fig. 15(a and b) we can clearly see that the color coordinates lie in the orange-red region of the CIE chromaticity diagram.

Correlated color temperature (CCT) is another significant parameter to assess the phosphor efficiency which specifies the color appearance of light emitted by the light source. CCT is defined as the color temperature corresponding to the point on the Planckian locus which is nearest to the point representing the chromaticity of the illuminant considered on the (u', v') CIE 1976 chromaticity diagram (Figure 14b). CCT is calculated by transforming the (x, y) coordinates of the light source to (u', v') using the equations:

$$u' = \frac{4x}{-2x + 12y + 3} \quad (13)$$

$$v' = \frac{9y}{-2x + 12y + 3} \quad (14)$$

According to McCamy's approximation [59], the CCT value can be derived from CIE color coordinates using the expression:

$$T = -449 n^3 + 3525 n^2 - 6823.3 n + 5520.33 \quad (15)$$

Where $n = (x - 0.3320)/(y - 0.1858)$. The calculated CCT values for Eu^{3+} and alkali metal ions doped GdPO_4 phosphors were found to be in the range of 1620 to 2410 K (Table 3). Usually CCT values are less than 5000 K considered to be producing warm white light used for domestic applications [60]. Therefore these materials are suitable for red light production in domestic appliances.

The color purity of the phosphors is also important to realize better light source for LED applications. This concept is most useful for the narrow banded light sources. For broad banded

light sources (white light), CCT is more useful. So, there is a need to calculate the colour purity of emitted red light which can be calculated by using the following formula:

$$\text{Color purity} = \frac{\sqrt{(x - x_{ee})^2 + (y - y_{ee})^2}}{\sqrt{(x_d - x_{ee})^2 + (y_d - y_{ee})^2}} \times 100 \% \quad (16)$$

Where (x, y) , (x_{ee}, y_{ee}) and (x_d, y_d) are the chromaticity coordinates of the sample point, equal energy point (0.3101, 0.3162) (illuminant C) and the dominant wavelength point, respectively. The dominant wavelength point which is the wavelength of the spectrum locus where the line drawn from the chromaticity point of the illuminant, through the chromaticity point of the colour and then extended, intersects the locus [61]. The color purity of Eu^{3+} and alkali metal ions doped GdPO_4 phosphors were found to be in the range of 91- 97%, these values were very close to the standard red light source. The obtained color purity results are given in Table 3. They indicate that, the color purity increased with rare earth concentration up to 9 mol. % of Eu^{3+} doping. Furthermore, after co-doping with alkali metal ions, the color purity values are enhanced and improved to 97.4%. From the observed results, it is evident that 5 mo.% Li^+ co-doped Eu^{3+} activated GdPO_4 phosphor is the best compromise which shows maximum orange red emission brightness, excellent color chromaticity with better colour purity. Hence these phosphors are potential candidates for solid-state lighting, optoelectronic device and biomedical applications.

4. Conclusions

Series of Eu^{3+} and alkali metal ions ($\text{A}^+ = \text{Li}^+, \text{Na}^+$ and K^+) co-doped GdPO_4 monoclinic phosphors were prepared and their structural parameters were confirmed. The PL intensity of magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) is higher than the electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$)

signifying that Eu^{3+} ions are located at high symmetry local sites with an inversion center in GdPO_4 lattice. The incorporation of co-dopant ions in the host lattice is associated with the suitable local distortion of crystal field surrounding the Eu^{3+} activator. As a consequence of mismatches in size and electro-negativity between co-dopant and host cation an enhancement in PL emission intensity is observed. The luminescence intensity of the as-formed Li^+ co-doped samples was found to be higher than K^+ , Na^+ co-doped samples owing to the proportionate decrease in ionic radius of alkali metal ions. The mechanistic effect of alkali metal ions doping on magnetic dipole and electric dipole transitions was elaborated in terms of variation in asymmetric ratios. The alkali metal ions co-doped $\text{GdPO}_4:\text{Eu}^{3+}$ phosphors showed higher lifetime, better quantum efficiency, and excellent chromaticity with high color purity values promising their potential applications in optoelectronic and biomedical fields.

Supporting information

Figures S1 to S7 and Table S1 showing the Powder XRD patterns, EDS analysis PL emission, Variation of asymmetric ratio vs doping concentration and Rietveld refined structural parameters of alkali metal ions co-doped $\text{GdPO}_4:\text{Eu}^{3+}$ phosphors are in supplementary information.

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Figure captions

Fig.1. XRD patterns of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ phosphors ($x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.09, 0.11$) and the standard data for monoclinic GdPO_4 (JCPDS file no. 84-0920) as a reference.

Fig.2. Observed, calculated and the difference XRD patterns of a) $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, b) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, c) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ and d) $\text{Gd}_{0.92}\text{Eu}_{0.05}\text{K}_{0.03}\text{PO}_4$ phosphors.

Fig.3. Crystal structure of GdPO_4 compound.

Fig.4. XRD patterns of $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{A}_{0.05}\text{PO}_4$ phosphors and the standard data for monoclinic GdPO_4 (JCPDS file no. 84-0920) as a reference.

Fig.5. FTIR spectra of a) GdPO_4 , b) $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, c) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, d) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ and e) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ phosphors.

Fig.6. FE-SEM images of a) $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, b) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, c) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ and d) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ phosphors.

Fig.7. Excitation spectrum of $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ phosphor ($\lambda_{\text{em}} = 594 \text{ nm}$).

Fig.8. The schematic energy level diagram illustrating excitation, emission and charge transfer mechanism of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ phosphors.

Fig.9. Emission spectrum of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ ($0.01 \leq x \leq 0.11$) phosphors ($\lambda_{\text{ex}} = 238 \text{ nm}$).

Fig.10. Variation of the emission peak intensity with respect to Eu^{3+} ion concentration in $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ phosphors recorded at $\lambda_{\text{ex}} = 238 \text{ nm}$.

Fig. 11. Plot $\log(I/x)$ as a function of $\log(x)$ of $\text{Gd}_{1-x}\text{Eu}_x\text{PO}_4$ phosphors.

Fig.12. Emission spectrum of $\text{Gd}_{1-y}\text{Eu}_{0.05}\text{A}_y\text{PO}_4$ ($0.00 \leq y \leq 0.05$) phosphors ($\lambda_{\text{ex}} = 238 \text{ nm}$).

Fig. 13. Images of Eu^{3+} ion doped GdPO_4 and alkali ion co-doped GdPO_4 phosphors under UV light.

Fig.14. Photoluminescence decay curve of a) $\text{Gd}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, b) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Li}_{0.05}\text{PO}_4$, c) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{Na}_{0.05}\text{PO}_4$ and d) $\text{Gd}_{0.90}\text{Eu}_{0.05}\text{K}_{0.05}\text{PO}_4$ phosphors.

Fig.15. a) CIE 1931 chromaticity diagram b) CIE 1976 chromaticity diagram of $\text{Gd}_{1-y}\text{Eu}_{0.05}\text{A}_y\text{PO}_4$ phosphors excited at 238 nm.

Fig. 1.

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Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

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Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

Fig. 14.

Fig. 15.