


Cite this: *RSC Adv.*, 2023, 13, 26179

# Tailored efficient energy transfer Tb<sup>3+</sup>, Eu<sup>3+</sup> activated/co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphor by substitution of alkali metals: the effect of charge compensation

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Phosphites are the new emerging candidates in the field of luminescence in the modern era. In the present investigation, Tb<sup>3+</sup>/Eu<sup>3+</sup> activated/co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphor was prepared by a wet chemical method, and the effect of R<sup>+</sup> (Na<sup>+</sup>, K<sup>+</sup>) ions on photoluminescence (PL) properties of these phosphors are investigated. Phase identification and crystal structure of the prepared phosphor were determined using XRD and Rietveld refinement, respectively. Morphological study and elemental analysis of the proposed phosphor with elemental analysis of the sample were performed using SEM and EDS. The PL properties of the proposed phosphor showed three simultaneous emission peaks in the visible range, giving color-tunable emission. The charge compensation of Na<sup>+</sup> and K<sup>+</sup> ions make a significant impact on the PL intensity of Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors. The PL intensity of Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors was significantly enhanced by factors 1.2 and 1.4 when Na<sup>+</sup> and K<sup>+</sup> charge compensators, respectively, were introduced. To manifest the charge compensation effect of alkali metals the optimum intense sample in the co-doped sample was used. These results indicate the potential candidacy of the studied phosphor for further improvement in PL properties for application in solid-state lighting.

Received 10th May 2023  
Accepted 21st August 2023

DOI: 10.1039/d3ra03115b

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## 1. Introduction

The scientific world has been paying close attention to lanthanide-based phosphors because of their outstanding photophysical characteristics,<sup>1</sup> including narrow emission,<sup>2</sup> significant Stokes shift,<sup>3</sup> strong photostability,<sup>4,5</sup> photochromic luminescence,<sup>6,7</sup> and long lifespan.<sup>5,8,9</sup> They are employed in almost all areas of science and technology, including solid-state lighting,<sup>10–13</sup> scintillators,<sup>14,15</sup> photonics,<sup>16–18</sup> detectors,<sup>19,20</sup> catalytic processes,<sup>21,22</sup> vitality,<sup>23,24</sup> and environmentalism,<sup>25</sup> due to their exceptional photophysical properties. The lanthanides Dy<sup>3+</sup>, Tb<sup>3+</sup>, and Eu<sup>3+</sup> ions exhibit extremely different emission bands in the visible and NUV regions, making them a desirable contender for WLEDs and solar power.<sup>26–33</sup> Nevertheless, the performance of the doping and the kind of inorganic host in which it was successfully doped determine the luminescence performance, longevity, and quantum yield.<sup>34,35</sup> The inorganic oxides, phosphates, and fluoride phosphors have a number of advantageous characteristics that make them suitable

luminescence hosts. The simplicity of the synthesis, lack of toxicities, high level of structural, chemical, and mechanical integrity, diversity of structure, photochromic optical characteristics and endurance, and self-activated luminescence are a few of the characteristics.<sup>36–40</sup> The host-dopant energy transfer exerts considerable control over the luminescence lifespan and quantum efficiency of systems that are doped with lanthanides to produce luminous hosts.<sup>41,42</sup> The choice of dopant and host has been shown in multiple papers from all over the world on Ln<sup>3+</sup>-activated phosphates to have a very large impact on the host-to-dopant energy transfer efficiency. Overall, when the size of the dopant can be accommodated inside the host lattice, the host-to-dopant exchange of energy is enhanced. A number of additional difficulties in producing luminescence hosts with the best optical properties are the strain and defect development caused by the size and charge imbalance among rare earth ions such as lanthanides and the host matrices.

A monovalent alkali metal ion co-doped as a charge compensator is considered the most popular solution to this problem.<sup>43,44</sup> The generation of cationic vacancies, which could offer non-radiative pathways and lower the light output of such phosphors, is thought to result from trivalent doping at a divalent site.<sup>45–47</sup> Lithium, sodium, and potassium are the most commonly used alkali metals. To observe the impact of the charge compensation effect, many rare earth-activated

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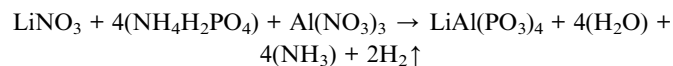
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luminous phosphors are currently being researched. Sobierajska *et al.*<sup>48</sup> examined the impact of substituting lithium as a charge compensator on the luminescence properties of  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2\text{:Eu}^{3+}$  phosphor. In order to look into the site occupancy choice for the charge compensation co-doping, the concentration of  $\text{Eu}^{3+}$  ions was 1 mol% and the concentration of  $\text{Li}^+$  ions was between 0.5 and 5 mol%. According to the luminescence characteristics of  $\text{Eu}^{3+}$  ions, the Ca1 site is predominantly substituted for Ca2 when the co-dopant ( $\text{Li}^+$  ions) concentration is below 2 mol%. The inclusion of  $\text{Eu}^{3+}$  ions at the Ca2 site was indicated by a red shift in the C-T band when the co-dopant level increased. Cao *et al.*<sup>49</sup> disclosed that the solid-state chemical technique was used to create the  $\text{CaZrO}_3\text{:Eu}^{3+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Li}^+$  phosphors. The  $\text{CaZrO}_3\text{:Eu}^{3+}$ ,  $\text{Bi}^{3+}$  phosphor's clearly luminescent qualities can be improved by 1.6 times by co-doping  $\text{Li}^+$  ions in their fluxing and charge-compensating roles. Yang *et al.*<sup>50</sup> used  $\text{Ba}_{0.92}\text{SiO}_3\text{:0.08Eu}$ ,  $\text{Ba}_{0.88}\text{SiO}_3\text{:0.08Eu}$ , and  $\text{Ba}_{0.84}\text{SiO}_3\text{:0.08Eu}$  to study the effect and mechanism of varied charge compensation on the luminous properties of Eu-doped  $\text{BaSiO}_3$ .  $0.08\text{R}^+$  ( $\text{R} = \text{Na}, \text{K}$ ) phosphors were prepared using the technique of co-precipitation, and the precursors used were calcined in air. It was discovered that the phosphor  $\text{Ba}_{0.84}\text{SiO}_3\text{:0.08Eu}$ ,  $0.08\text{Na}^+$  performed more effectively at high temperatures and had an extended lifespan than the phosphor  $\text{Ba}_{0.92}\text{SiO}_3\text{:0.08Eu}$ , indicating that the co-doping of  $\text{Na}^+$  ions was advantageous to this phosphor. Various kinds of hosts have nevertheless currently been studied. For instance, the charge compensation for phosphite-based phosphors has not been the subject of any known studies. Thus, in the present study, the effect of charge compensation of alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ) on the photoluminescence (PL) properties of  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$  activated/co-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphite phosphors was investigated.

## 2. Experimental

Pure and  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$  activated/co-activated samples of  $\text{LiAl}(\text{PO}_3)_4$  phosphors were synthesized by the wet chemical method.<sup>51</sup> In the proposed synthesis,  $\text{LiNO}_3$  99% extra pure,  $\text{Al}(\text{NO}_3)_3$  98% extra pure,  $\text{NH}_4\text{H}_2\text{PO}_4$  98% extra pure,  $\text{NaNO}_3$  99% extra pure,  $\text{KNO}_3$  99% extra pure,  $\text{Eu}_2\text{O}_3$  99.9% AR grade,  $\text{Tb}_4\text{O}_7$  99.9% AR grade were used. The typical chemical reaction for the synthesis of the host material is given as follows:



A predefined amount of all reagents was taken in a stoichiometric ratio for the preparation of the host material. These reagents were dissolved in a separate beaker containing around 50 ml of double distilled water using a magnetic stirrer, and all these mixtures were mixed together in one beaker. The final solution was continuously stirred for 45 min with constant heating for proper mixing and to evaporate the excess water. A white precipitate was obtained, which was kept in the hot air oven for 12 hours at 90 °C. After that samples were cooled at room temperature and the final product was obtained. For the

synthesis of  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$  activated/co-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphite phosphors, stoichiometric amounts of  $\text{Tb}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$  (aiming to replace  $\text{Li}^+$  ion) were dissolved in nitric acid and then added in the solution mixture and rest of the procedure was kept the same. A similar procedure was adopted to prepare alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ) metal ion-doped samples. In singly activated phosphor the concentrations of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions were varied from 0.3 to 1.5 mol%. In the co-activated phosphor, the concentration of  $\text{Tb}^{3+}$  ions was kept fixed at 1 mol% and the concentration of  $\text{Eu}^{3+}$  ion was varied from 0.3 to 1.5 mol%. While studying the charge compensation effect in co-activated phosphor the concentrations of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions were fixed at 1 mol% and 1.5 mol%, respectively, and the concentration of alkali ( $\text{Na}^+/\text{K}^+$ ) was varied from 0.2 to 1 mol%. The final products obtained were then used as is for further characterization.

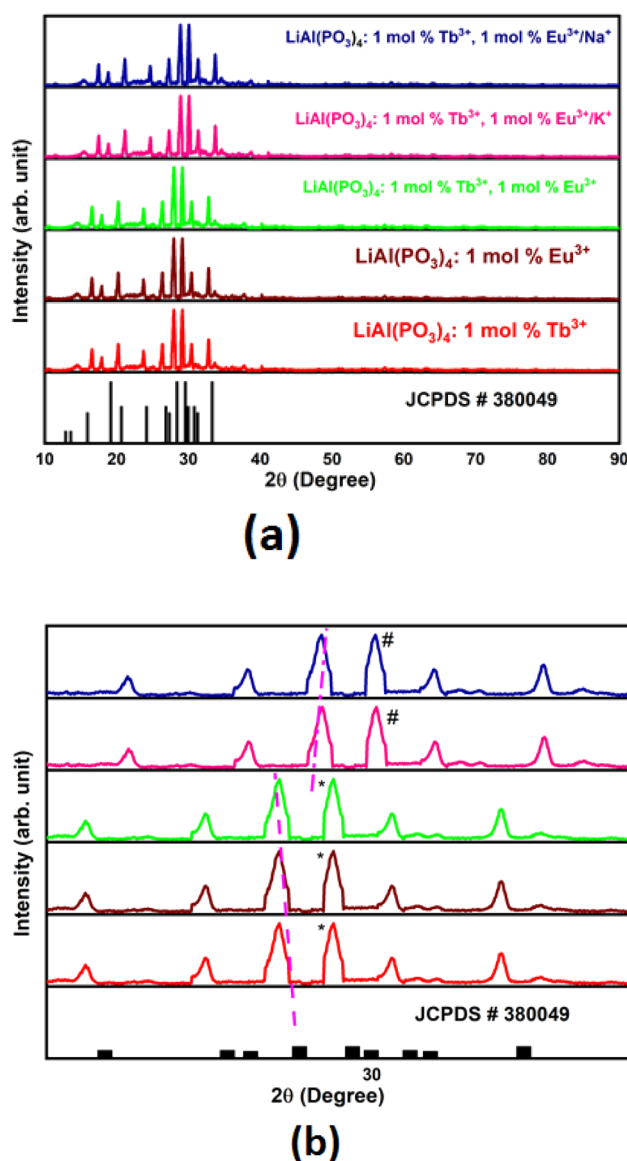


Fig. 1 (a) XRD patterns of  $\text{Tb}^{3+}/\text{Eu}^{3+}$  activated/co-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphors and  $\text{LiAl}(\text{PO}_3)_4$  phosphors doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}/\text{M}^{1+}$  ( $\text{M} = \text{Na}, \text{K}$ ) compared with the standard XRD. (b) Zoomed XRD patterns showing shifting of the diffraction peaks.



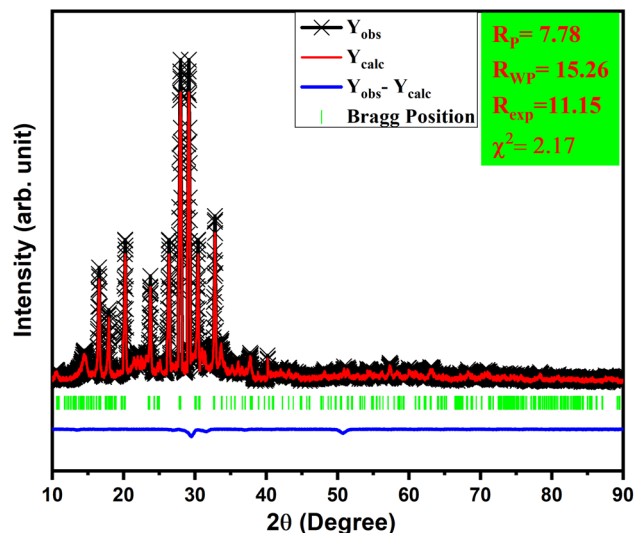


Fig. 2 Rietveld refinement of  $\text{LiAl}(\text{PO}_3)_4$  phosphor doped with  $\text{Tb}^{3+}$  (1 mol%).

X-ray diffraction (XRD) analysis of phosphors was carried out to clarify the phases and crystalline structure using Rigaku miniflex d 600 X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154059 \text{ nm}$ ) operated at 40 kV, 15 mA, and the patterns were recorded in the range of  $10\text{--}90^\circ$ . The infrared spectra were recorded on an alpha II Bruker Fourier transform infrared (FTIR) spectrometer. Morphological and elemental mapping analyses were performed using a scanning electron microscope (Carl Zeiss EVO-18) equipped with energy-dispersive X-ray spectroscopy (EDS). The PL excitation and emission spectra of phosphor samples were recorded using a SHIMADZU spectrofluorophotometer RF-5301 PC.

### 3. Results and discussion

#### 3.1 XRD analysis and crystal structure

Powder XRD patterns of  $\text{Tb}^{3+}/\text{Eu}^{3+}$ -activated/co-activated  $\text{LiAl}(\text{PO}_3)_4$  and  $\text{LiAl}(\text{PO}_3)_4$  phosphors doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}$

$\text{M}^{1+}$  ( $\text{M} = \text{Na}, \text{K}$ ) are depicted in Fig. 1(a). As observed in this figure, the XRDs of all prepared phosphors are in good agreement with the standard pattern, JCPDS PDF no. #380049. However, some peaks are shifting towards a lower angle [Fig. 1(b)]. The shift in the XRD peaks towards lower angles might be due to change in the ionic radii in host lattice and rare earth ions and alkali ions doped ( $\text{Tb}^{3+}$ ,  $r = 1.04 \text{ \AA}$  CN = 8;  $\text{Eu}^{3+}$ ,  $r = 1.066 \text{ \AA}$ , CN = 8), ( $\text{Li}^+$ ,  $r = 0.92 \text{ \AA}$  CN = 6,  $\text{Na}^+$ ,  $r = 1.18 \text{ \AA}$  CN = 8;  $\text{K}^+$ ,  $r = 1.51 \text{ \AA}$  CN = 8). Moreover, there were no extra impurity peaks, and hence, the samples were prepared in a very good manner.

To validate this statement, Rietveld refinement was performed on the XRD pattern, as shown in Fig. 2. Rietveld refinement was carried out together with their difference profile and Bragg locations utilizing the Fullprof Suite programme to verify this claim.<sup>52–54</sup> The visualization requirements were met by the reliability factors along with the parameters  $R_{\text{wp}} = 15.26$ ,  $R_p = 7.78$ ,  $R_{\text{exp}} = 11.15$ , and  $\chi^2 = 2.17$ . The volume of the unit cell obtained from the Rietveld refinement was  $916.439 \text{ \AA}^3$ .

Fig. 3 depicts the ball and stick and the polyhedral crystal structure orthorhombic with lattice data  $a = 12.43 \text{ \AA}$ ,  $b = 8.22 \text{ \AA}$ ,  $c = 8.91 \text{ \AA}$ , and  $\alpha = \beta = \gamma = 90.00^\circ$ . *Pbcn* space group is the crystallization space for  $\text{LiAl}(\text{PO}_3)_4$ .  $\text{Li}^+$  forms deformed  $\text{LiO}_4$  tetrahedra by bonding with four  $\text{O}^{2-}$  atoms, which share corners with four comparable  $\text{PO}_4$  tetrahedra and an edge-edge with an  $\text{AlO}_6$  octahedron. There are four Li–O bond lengths in total: two shorter ( $1.92 \text{ \AA}$ ) and two longer ( $2.07 \text{ \AA}$ ).  $\text{Al}^{3+}$  forms  $\text{AlO}_6$  octahedra by bonding with six  $\text{O}^{2-}$  atoms, which share corners with six  $\text{PO}_4$  tetrahedra and an edge-edge with one  $\text{LiO}_4$  tetrahedra. Al–O bond separations vary and range from  $1.89 \text{ \AA}$  to  $1.92 \text{ \AA}$ . Two different  $\text{P}^{5+}$  locations exist. In the first  $\text{P}^{5+}$  site,  $\text{P}^{5+}$  forms  $\text{PO}_4$  tetrahedra by bonding with four  $\text{O}^{2-}$  atoms. These tetrahedra share corners with one  $\text{AlO}_6$  octahedron, two equivalent  $\text{LiO}_4$  tetrahedra, and two equivalent  $\text{PO}_4$  tetrahedra. The octahedral corner-sharing tilt angles are  $42^\circ$ . The P–O bond separations vary and range from  $1.48 \text{ \AA}$  to  $1.62 \text{ \AA}$ . In the second  $\text{P}^{5+}$  site,  $\text{P}^{5+}$  forms  $\text{PO}_4$  tetrahedra that share corners with two equivalent  $\text{AlO}_6$  octahedra and corners with two equivalent  $\text{PO}_4$  tetrahedra *via* bonding with four  $\text{O}^{2-}$  atoms. The octahedral

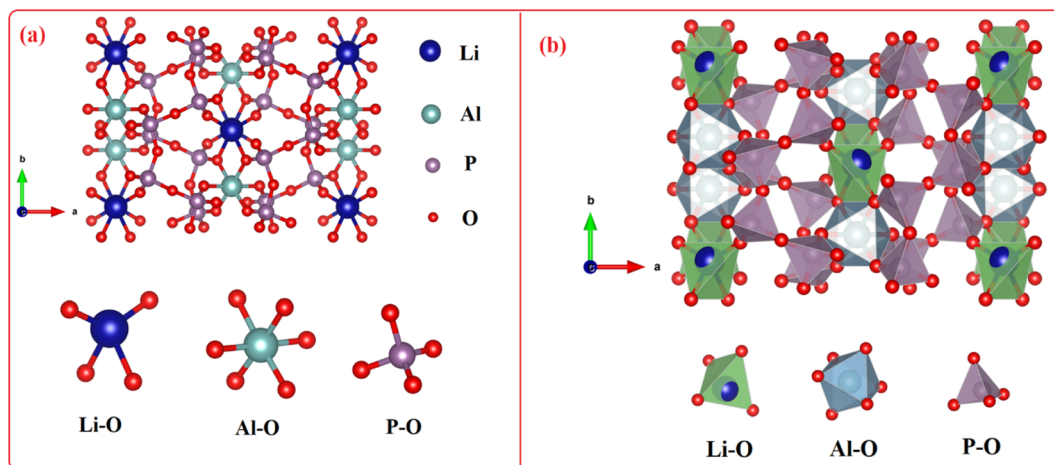


Fig. 3 The crystal structure of  $\text{LiAl}(\text{PO}_3)_4$  material obtained from Rietveld refinement.





**Table 1** Overview of the structural parameters of the  $\text{LiAl}(\text{PO}_3)_4$  material

		x	y	z	Occ.	U	Site	Sym.
1	O1	0.2442	0.1049	0.0804	1	0.006	8d	1
2	O2	0.3951	0.4079	0.3732	1	0.006	8d	1
3	O3	0.3199	0.1413	0.4604	1	0.006	8d	1
4	O4	0.1204	0.3658	0.3773	1	0.006	8d	1
5	O5	0.0623	0.1985	0.1353	1	0.006	8d	1
6	O6	0.4329	0.0286	0.1344	1	0.006	8d	1
7	P1	0.13919	0.18251	0.00584	1	0.006	8d	1
8	P2	0.35134	0.03648	0.01166	1	0.006	8d	1
9	Li1	0	0.0028	0.25	1	0.006	4c	2
10	Al1	0	0.3676	0.25	1	0.006	4c	2

corner-sharing tilt angles range from  $42^\circ$  to  $47^\circ$ . There is a range of P–O bond separations between 1.50 Å and 1.60 Å. There are six incompatible  $\text{O}^{2-}$  locations.  $\text{O}^{2-}$  is coupled to two  $\text{P}^{5+}$  atoms at the first  $\text{O}^{2-}$  site in a bent  $120^\circ$  geometry that is deformed.  $\text{O}^{2-}$  is bound to two  $\text{P}^{5+}$  atoms in the second  $\text{O}^{2-}$  site at an abnormal angle of  $120^\circ$ . One  $\text{Al}^{3+}$  and one  $\text{P}^{5+}$  atoms are connected by a  $150^\circ$  bent, twisted geometry to  $\text{O}^{2-}$  at the third  $\text{O}^{2-}$  site.  $\text{O}^{2-}$  is bound to one  $\text{Li}^+$  and one  $\text{P}^{5+}$  atom in a bent  $150^\circ$  geometry at the fourth  $\text{O}^{2-}$  location.  $\text{O}^{2-}$  is bound to one  $\text{Al}^{3+}$  and one  $\text{P}^{5+}$  atom in bent  $120^\circ$  distortion geometry at the fifth  $\text{O}^{2-}$  site. One  $\text{Li}^+$ , one  $\text{Al}^{3+}$ , and one  $\text{P}^{5+}$  atom are joined by  $\text{O}^{2-}$  in a deformed trigonal planar geometry at the sixth  $\text{O}^{2-}$  site. The structural parameters for  $\text{LiAl}(\text{PO}_3)_4$  phosphor are summarized in Table 1.

### 3.2 SEM and EDS analysis

In order to investigate the morphology and elemental mapping in the prepared phosphors, SEM and EDS analysis were performed. SEM micrographs of the prepared phosphors are shown in Fig. 4. As observed in Fig. 4, samples are in the micrometer range with irregular shapes and sizes. The microscopic size of the prepared phosphor makes it a potential phosphor candidate as per the point of view of WLED.<sup>53,55,56</sup>

EDS analysis was performed in order to investigate the presence of elements or any other impurities in the prepared phosphor. The EDS analysis of  $\text{LiAl}(\text{PO}_3)_4$  phosphors doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}/\text{M}^{1+}$  ( $\text{M} = \text{Na}, \text{K}$ ) is depicted in Fig. 5. EDS confirmed that all the raw materials used in the synthesis were present in the prepared phosphor, and no other impurities were observed. The insets of Fig. 5(a) and (b) show the wt% distribution of precursors used in the prepared phosphor.

### 3.3 Photoluminescence investigation

The PL excitation and emission spectra of  $\text{Tb}^{3+}$  (1 mol%) activated  $\text{LiAl}(\text{PO}_3)_4$  phosphor are depicted in Fig. 6. The excitation spectra of the 544 nm emission of phosphor exhibit a broad excitation band in the UV region centred at 262 nm and characteristic peaks in near UV and blue regions. These characteristic excitation peaks attributed to f–f transitions  $^7\text{F}_6 \rightarrow ^5\text{D}_2$ ,  $^7\text{F}_6 \rightarrow ^5\text{L}_{10}$ , and  $^7\text{F}_6 \rightarrow ^5\text{D}_3$  are positioned at 345 nm, 365 nm, and 378 nm, respectively.<sup>57–59</sup> The PL emission spectra of  $\text{Tb}^{3+}$ -activated  $\text{LiAl}(\text{PO}_3)_4$  triggered by excitation at 378 nm showed one

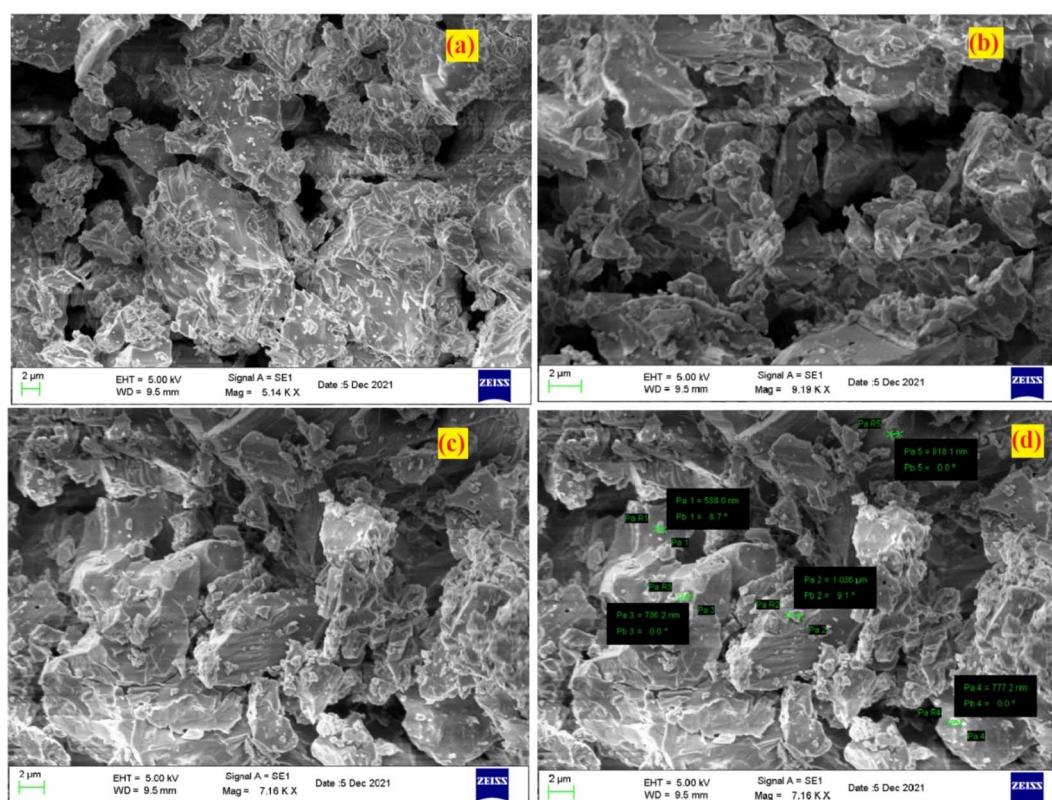


Fig. 4 SEM micrograph of  $\text{LiAl}(\text{PO}_3)_4$  phosphors doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}/\text{M}^{1+}$  ( $\text{M} = \text{Na}, \text{K}$ ).



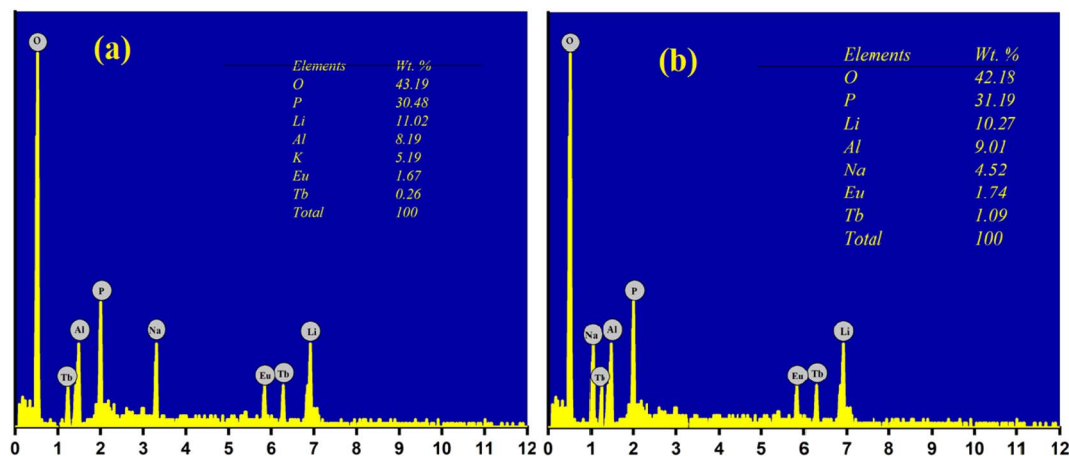


Fig. 5 EDS analysis of LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors doped with Tb<sup>3+</sup>/Eu<sup>3+</sup>/M<sup>1+</sup> [M = Na (a), K (b)].

dominant emission peak in the green region positioned at 544 nm. The peak attributed at 544 nm is due to the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition.<sup>60</sup> It was also observed that the emission intensity increased with Tb<sup>3+</sup> ion concentration up to 1 mol%, after which the concentration quenching was observed.

Similarly, Eu<sup>3+</sup> ion-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors were also investigated by PL spectroscopy. The PL excitation and emission spectra of the Eu<sup>3+</sup> activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors are displayed in Fig. 7. The PL excitation spectra monitored at 614 nm exhibited 4 characteristic excitation bands positioned at 261 nm, 395 nm, 465 nm, and 535 nm. The peak observed at 261 nm is due to the O<sup>2-</sup> → Eu<sup>3+</sup> charge transfer band. However, other bands observed in the NUV region (395 nm), blue region (465 nm), and green region (535 nm) are due to <sup>7</sup>F<sub>0</sub> → <sup>5</sup>L<sub>6</sub>, <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>3</sub> and <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>1</sub> transition, respectively.<sup>61,62</sup>

Eu<sup>3+</sup>-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors after further excitation at 395 nm gave two characteristic emission peaks positioned at

591 nm and 614 nm in the orange and red regions, which are ascribed to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> magnetic dipole transition and <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> electric dipole transition of Eu<sup>3+</sup> ions, respectively.<sup>32,63,64</sup> The peak due to the electric dipole transition is more intense than the magnetic dipole transition, which indicates that the location of the Eu<sup>3+</sup> ion is at the non-centrosymmetric site in the host lattice. The variation in the emission intensity of the Eu<sup>3+</sup>-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors showed a pattern similar to that of Tb<sup>3+</sup>-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors, which indicated that the doping of rare earth ion occurred at the same site in the host lattices.

The reason behind the concentration quenching effect observed in the PL emission intensity of the rare earth ion-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphor is the critical transfer distance (*R<sub>C</sub>*), which is the minimum distance between the nearest activator at a critical concentration *X<sub>C</sub>*. The critical transfer distance can be calculated using Blasse formula,<sup>65–67</sup>

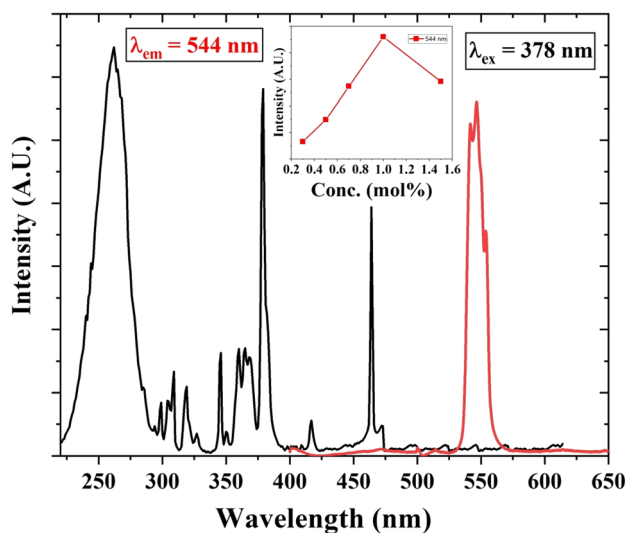


Fig. 6 PL excitation and emission spectra of Tb<sup>3+</sup> (1 mol%) activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors (inset: the variation of emission intensity of 544 nm peak with Tb<sup>3+</sup> ion concentration).

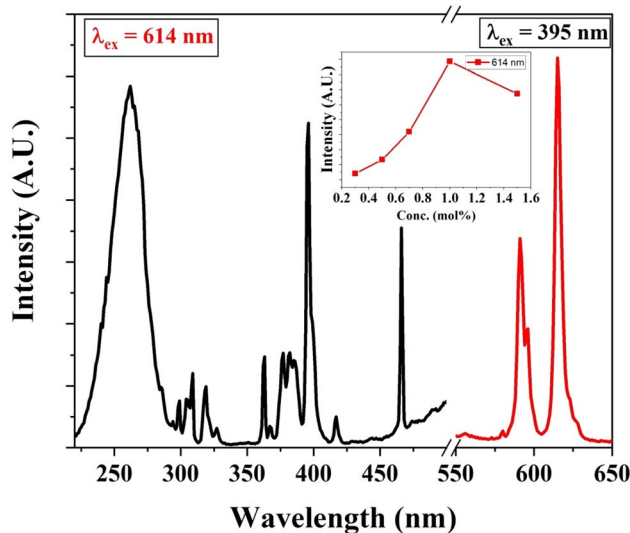


Fig. 7 PL excitation and emission spectra of Eu<sup>3+</sup> (1 mol%) activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors (inset: the variation of emission intensity of 614 nm peak with Eu<sup>3+</sup> ion concentration).

$$R_C = 2 \left( \frac{3V}{4\pi X_C N} \right)^{1/3} \quad (1)$$

where,  $V$  ( $=916.439 \text{ \AA}^3$ ) is the volume of the unit cell,  $X_C = 1 \text{ mol\%}$ , and  $N = 4$  number of cationic sites in the unit cell. The value of  $R_C$  for both rare earth ion-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphors was found to be 35.244. If the value of  $R_C$  is more than 5, the electric multipolar interaction will be the predominant mechanism causing the concentration quenching event, otherwise, an exchange interaction will be responsible. Because the calculated value of  $R_C$  is more than 5 it indicates that the electric multipolar interaction is responsible for the concentration quenching effect in rare earth ion-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphor.

The energy transfer criterion was satisfied by the spectral overlap shown in Fig. 8. The spectral overlapping occurred between the excitation–excitation of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ion-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphors. As per the criteria, the excitations of both rare earths overlapped, and it was observed that the excitation of  $\text{Eu}^{3+}$  is on the higher wavelength side as compared to the excitation of  $\text{Tb}^{3+}$  ions. Therefore, the energy can be transferred from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  ions.

To satisfy the energy transfer criteria,  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$  co-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphors were prepared by keeping the concentration of  $\text{Tb}^{3+}$  ions constant at 1 mol% and  $\text{Eu}^{3+}$  concentration varying from 0.3 mol% to 1.5 mol%. The PL emission spectra of this co-activated phosphor triggered at 378 nm excitation are displayed in Fig. 9 and have three characteristic emission peaks centred at 544 nm 591 nm and 614 nm. The peaks attributed in emission spectra are already known for  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions and their transitions are already mentioned in the above section.

The variation in the intensity of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  emission peaks is depicted in Fig. 10. As observed, the intensity of the peak centred at 544 nm ( $\text{Tb}^{3+}$  ions) was diminished and peaks centred at 591 nm and 614 nm ( $\text{Eu}^{3+}$  ions) increased with the concentration of  $\text{Eu}^{3+}$  ions. This shows the energy is transferred from  $\text{Tb}^{3+}$  ions to  $\text{Eu}^{3+}$  ions. The energy transfer efficiency ( $\eta_T$ )

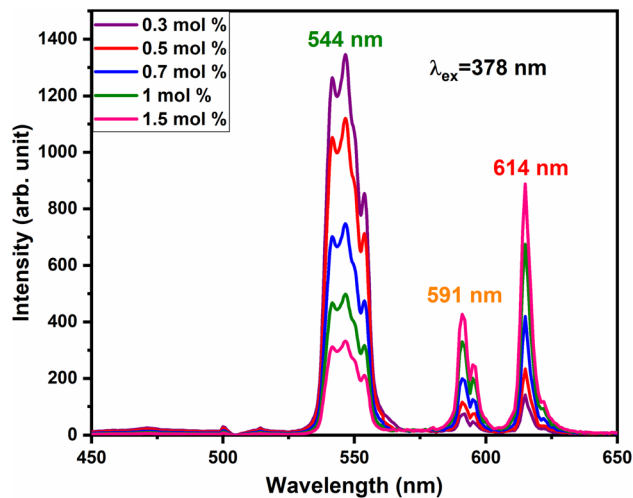


Fig. 9 PL emission spectra of  $\text{LiAl}(\text{PO}_3)_4:\text{Tb}^{3+}$  (1 mol%),  $y\text{Eu}^{3+}$  phosphors at an excitation of 378 nm.

from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  can be calculated using the following equation;<sup>68</sup>

$$\eta_T = 1 - \frac{I_s}{I_{SO}} \quad (2)$$

where  $I_s$  and  $I_{SO}$  are the luminescence intensities of  $\text{Tb}^{3+}$  with and without the presence of  $\text{Eu}^{3+}$ , respectively. The  $\eta_T$  from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  in  $\text{LiAl}(\text{PO}_3)_4$  phosphors was calculated as a function of the  $\text{Eu}^{3+}$  concentration, displayed in Fig. 10. The value of  $\eta_T$  was found to increase gradually with an increase in  $\text{Eu}^{3+}$  content. When the  $\text{Eu}^{3+}$  ion concentration increased to 1.5 mol%, the transfer efficiency increased to 42.13%, indicating an efficient energy transfer from  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$ . The energy-level diagram of  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  ions showing a possible scheme of energy transfer is displayed in Fig. 11.

To investigate the charge compensation effect on  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$  co-activated  $\text{LiAl}(\text{PO}_3)_4$  phosphors, alkali metal ions ( $\text{Na}^+$  and  $\text{K}^+$ ) were introduced as charge compensators. The charge

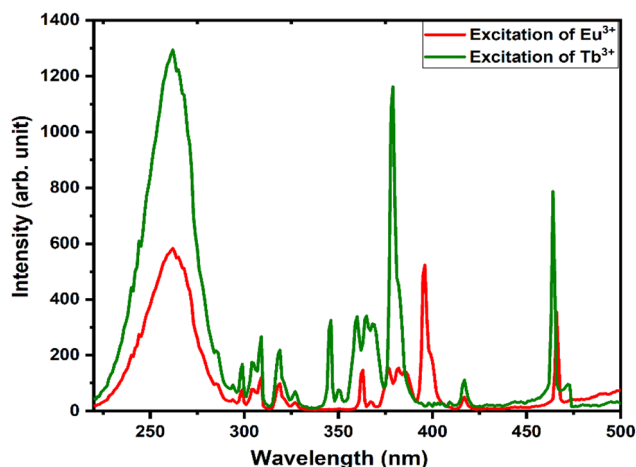


Fig. 8 Spectral overlap between the excitations of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  activated  $\text{LiAl}(\text{PO}_3)_4$  phosphors.

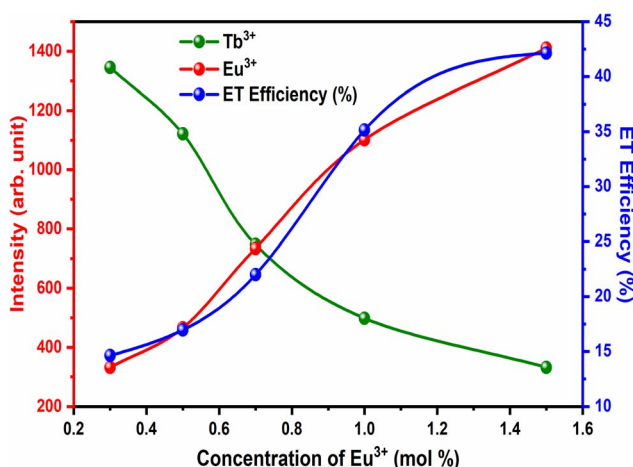
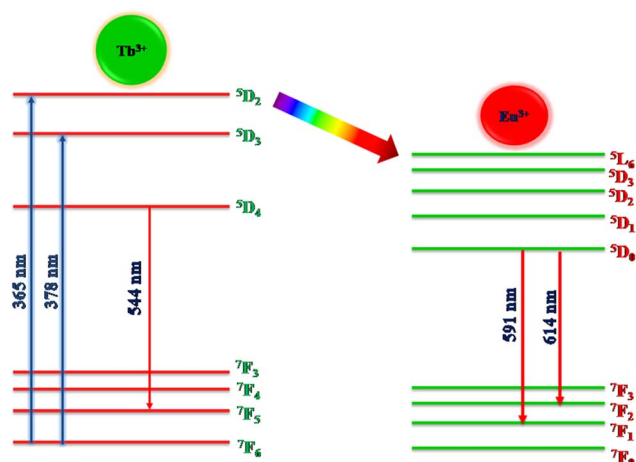


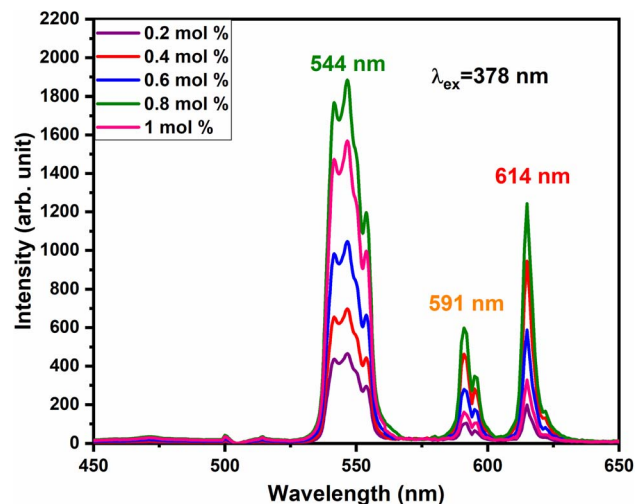
Fig. 10 ET efficiency and PL emission intensity of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  for different concentrations of  $\text{Eu}^{3+}$ .





Fig. 11 Energy-level diagram and energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup>.

compensation phenomena were observed in the LiAl(PO<sub>3</sub>)<sub>4</sub>:Tb<sup>3+</sup>–Eu<sup>3+</sup> host lattice as rare earth ions (Tb<sup>3+</sup>/Eu<sup>3+</sup>) doped into the LiAl(PO<sub>3</sub>)<sub>4</sub> phosphor. As per the Kröger–Vink notation,<sup>69</sup> the charge compensation is required for Tb – Eu<sup>3+</sup> sites. The proximity of charge compensating defects (almost certainly V<sub>K</sub> vacancies or O<sub>i</sub><sup>•</sup> interstitials) gives rise to local deformation of the EuO<sub>4</sub> tetragonal and lifts the inversion symmetry and the charge compensation phenomena that occurred here. The PL emission spectra of Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors doped with Na<sup>+</sup> and K<sup>+</sup> as charge compensators are shown in Fig. 12 and 13, respectively. The charge compensation of Na<sup>+</sup> and K<sup>+</sup> ions make a significant impact on the PL intensity of Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors. The PL intensity was significantly enhanced by 1.2 and 1.4 times that of the Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors when charge compensators Na<sup>+</sup> and K<sup>+</sup> were introduced. To manifest the charge compensation effect of alkali metals the optimum intense sample in the co-doped sample was used. The PL emission spectra of 1 mol% Tb<sup>3+</sup>, 1.5 mol% Eu<sup>3+</sup> co-activated

Fig. 13 PL emission spectra of LiAl(PO<sub>3</sub>)<sub>4</sub>:Tb<sup>3+</sup>(1 mol%), Eu<sup>3+</sup>(1.5 mol%), zK<sup>+</sup> phosphors at 378 nm excitation.

LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors displayed in Fig. 12 and 13 by charge compensating Na<sup>+</sup> and K<sup>+</sup> consisted of different mol% of Na<sup>+</sup> and K<sup>+</sup> ions, respectively. It was observed that the PL emission intensity enhanced by both the charge compensation and the optimum sample obtained in both charge compensations is 0.6 mol% for Na<sup>+</sup> and 0.8 mol% for K<sup>+</sup> ions.

However, the ionic radius of Na<sup>+</sup> ions is 1.18 Å and for K<sup>+</sup> is 1.51 Å. Comparatively, the ionic radius of the Na<sup>+</sup> ion is close to

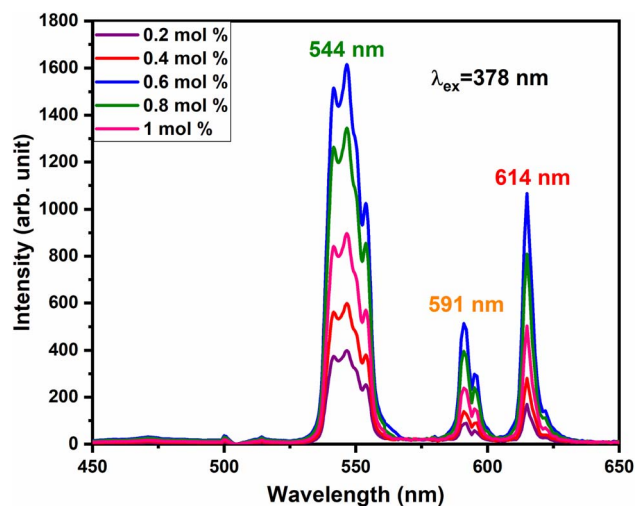
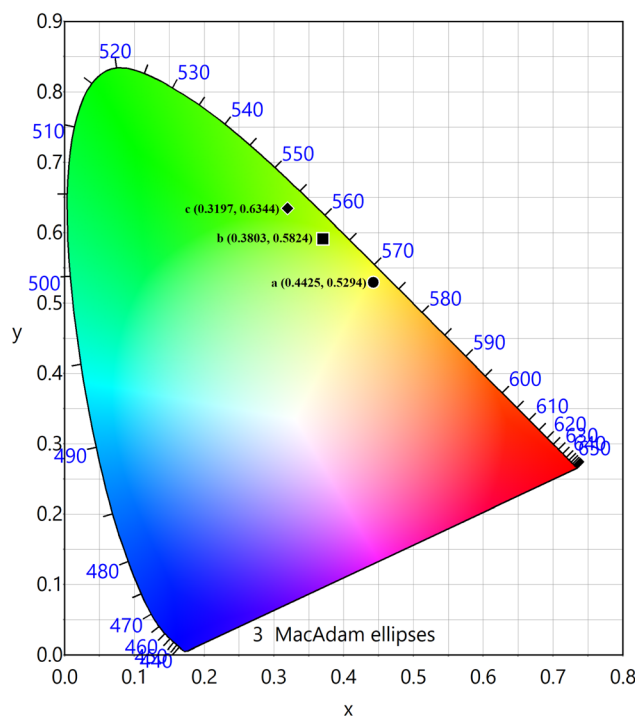
Fig. 12 PL emission spectra of LiAl(PO<sub>3</sub>)<sub>4</sub>:Tb<sup>3+</sup>(1 mol%), Eu<sup>3+</sup>(1.5 mol%), zNa<sup>+</sup> phosphors at 378 nm excitation.Fig. 14 CIE chromaticity diagram of (a) LiAl(PO<sub>3</sub>)<sub>4</sub>: 1 mol% Tb<sup>3+</sup>, 1 mol% Eu<sup>3+</sup>, (b) LiAl(PO<sub>3</sub>)<sub>4</sub>: 1 mol% Tb<sup>3+</sup>, 1 mol% Eu<sup>3+</sup>, 0.6 mol% Na<sup>+</sup> and (c) LiAl(PO<sub>3</sub>)<sub>4</sub>: 1 mol% Tb<sup>3+</sup>, 1 mol% Eu<sup>3+</sup>, and 0.8 mol% K<sup>+</sup> phosphors.

Table 2 Overview of the CIE chromaticity and color purity of LiAl(PO<sub>3</sub>)<sub>4</sub>-doped phosphors

Sr no.	Sample	X	Y	X <sub>d</sub>	Y <sub>d</sub>	Color purity (%)
a	LiAl(PO <sub>3</sub> ) <sub>4</sub> : 1 mol% Tb <sup>3+</sup> , 1 mol% Eu <sup>3+</sup>	0.4425	0.5294	0.3017	0.6884	54.36
b	LiAl(PO <sub>3</sub> ) <sub>4</sub> : 1 mol% Tb <sup>3+</sup> , 1 mol% Eu <sup>3+</sup> , 0.6 mol% Na <sup>+</sup>	0.3803	0.5824	0.3017	0.6884	69.47
c	LiAl(PO <sub>3</sub> ) <sub>4</sub> : 1 mol% Tb <sup>3+</sup> , 1 mol% Eu <sup>3+</sup> , 0.8 mol% K <sup>+</sup>	0.3197	0.6344	0.3017	0.6884	66.07

that of the Li<sup>+</sup> ion. Thus, the doping of Na<sup>+</sup> ion has a weaker strengthening effect on the crystal field and K<sup>+</sup> doping has a stronger strengthening effect on the crystal field. Therefore, PL intensity was comparatively enhanced in K<sup>+</sup> doping than in Na<sup>+</sup> doping.

### 3.4 Photometric characterization

The PL emission spectra of the produced Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors were examined using Commission de l'Eclairage (CIE) coordinates, as shown in Fig. 14. The useful criteria to gauge the caliber of the luminescence phosphor are the CIE chromaticity coordinates. Table 2 displays the CIE coordinates. The PL emission was shifted towards the red region on charge compensating alkali metal ions into Tb<sup>3+</sup>, Eu<sup>3+</sup> co-activated LiAl(PO<sub>3</sub>)<sub>4</sub> phosphors with efficiency enhancement. This shows the photochromic nature of the prepared phosphors. As shown in Table 2, the produced phosphors' colour purity varied. The provided formula determines colour purity of the phosphor;<sup>7,70,71</sup>

$$\text{Color purity} = \frac{\sqrt{(X - X_i)^2 + (Y - Y_i)^2}}{\sqrt{(X_d - X_i)^2 + (Y_d - Y_i)^2}} \times 100\% \quad (3)$$

where, (X, Y), (X<sub>i</sub>, Y<sub>i</sub>), and (X<sub>d</sub>, Y<sub>d</sub>) are color-coordinates of the sample point and CIE equal-energy illuminant, and dominant wavelength of the light source, respectively.

## 4. Conclusion

The charge compensation effect and photochromic properties of LiAl(PO<sub>3</sub>)<sub>4</sub>: x mol% Tb<sup>3+</sup>, y mol% Eu<sup>3+</sup>, z mol% R<sup>+</sup> (R = Na, K) doped materials were investigated in this work. LiAl(PO<sub>3</sub>)<sub>4</sub>: x mol% Tb<sup>3+</sup>, y mol% Eu<sup>3+</sup>, z mol% R<sup>+</sup> (R = Na, K) phosphors were prepared by the wet chemical method. The crystal structure of the prepared sample was in the orthorhombic crystal system. The surface morphological behavior and particle size of the prepared phosphor are in the sub-micrometer region, as confirmed by SEM analysis. In the green to red regions, the PL examination of this phosphor revealed four significant emission peaks. In this phosphor, the efficiency of the mechanism of energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup> ions was determined to be 42.13%. Moreover, the charge compensation of the alkali metals can help in improving the intensity of the prepared phosphors by a factor of approximately 1.3 and also shows the photochromic nature of the phosphor. Therefore, all of the indicated results support the studied phosphor material for

standing in the race for the development of efficient phosphors for use in color-tunable WLEDs and displays.

## Author contributions

Prashant N. Parale – investigation, formal analysis, writing – original draft. Abhijeet R. Kadam – visualization, methodology, investigation, validation, writing – original draft. S. J. Dhoble – supervision, visualization, conceptualization, project administration. K.V. Dabre – supervision, visualization, conceptualization, writing – original draft.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors. The authors are thankful to R. T. M. Nagpur University, Nagpur, for its research facilities and to the authorities at Taywade College, Mahadula-Koradi for constant encouragement.

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