

# Luminescence in Dy<sup>3+</sup> and Eu<sup>3+</sup> Activated K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

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**Abstract** The Dy<sup>3+</sup> and Eu<sup>3+</sup> activated K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> phosphors were prepared by a combustion synthesis. From a powder X-ray diffraction (XRD) analysis the formation of K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was confirmed. In the photoluminescence emission spectra, the K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>:Dy<sup>3+</sup> phosphor emits two distinctive colors: blue and yellow whereas K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>:Eu<sup>3+</sup> emits red color. Thus the combination of colors gives BYR (blue–yellow–red) emissions can produce white light. These phosphors exhibit a strong absorption between 340 and 400 nm which suggest that present phosphor is a promising candidate for producing white light-emitting diodes (LED).

**Keywords** Photoluminescence · Phosphors · Phosphate · X-ray diffraction · LED

## Introduction

The need for mercury-free fluorescent lamps for general lighting has become an important issue for light source manufacturers. LED technology has flourished for the past few decades. High efficiency, reliability, rugged construction, low power consumption and durability are among the key factors for the rapid development of the solid-state lighting based on high-brightness visible LEDs [1]. The phosphors based on phosphate host matrices have become

the topic of great interest for an extensive investigation due to their wide applications in lighting and displays. The phosphate system enjoys a range of compositional and structural possibilities that facilitate tailoring chemical and physical properties of interest for specific technological applications [2, 3]. Rare earth (RE) ions doped phosphates have excellent thermal stability and the tetrahedral rigid three-dimensional matrix of phosphate is thought to be ideal for charge stabilization [4]. White light LED is in high demand for the solid-state lighting technology because the most challenging application for white light LED is the replacement of conventional incandescent and fluorescent lamps [5]. Recently, Nagpure et.al. reported some phosphate based phosphors such as, Eu and Dy activated Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> [6], M<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F (M=Ba, Sr, Ca) [7] and Na<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>:RE (RE=Ce<sup>3+</sup>, Eu<sup>3+</sup> and Mn<sup>2+</sup>) phosphors via combustion synthesis [8] also Kim et.al.[9] studied the photoluminescence properties of Eu<sup>2+</sup> and Mn<sup>2+</sup> activated BaMgP<sub>2</sub>O<sub>7</sub> as a potential red phosphor for white emission. In phosphate based system; Dy<sup>3+</sup> ion activated phosphors have normally been used as high efficiency activators [10] and their photoluminescence spectra range from 450 to 700 nm. With respect to the phosphors presently used in white LED systems, most do not meet the optimum requirements. Accordingly, novel luminescent materials with improved properties are greatly in demand. In this paper, the phosphate K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>:Dy<sup>3+</sup> and Eu<sup>3+</sup> phosphors were synthesized by the combustion method and its luminescent properties were also investigated.

## Experimental

The Eu<sup>3+</sup> activated K<sub>3</sub>Al<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> phosphors were prepared via combustion synthesis. The starting AR grade materials (99.99% purity) were taken where potassium nitrate,

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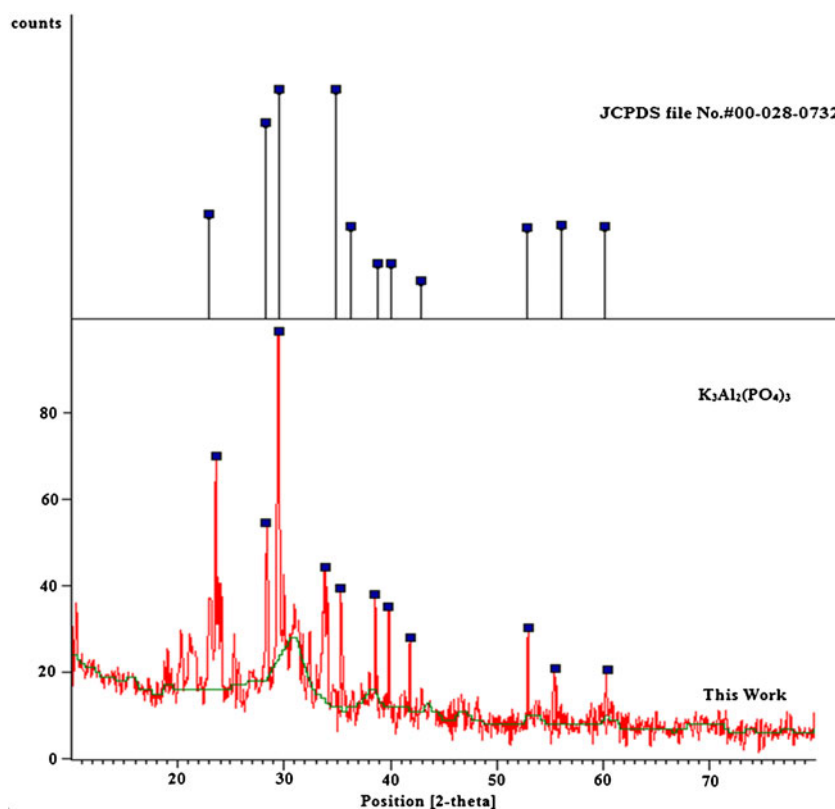
ammonium di-hydrogen phosphate, aluminum nitrate, europium oxide and urea used as fuel. In the present investigation, materials were prepared according to the chemical formula  $K_{3-x}Al_2(PO_4)_3:Eu_x$ .  $Eu^{3+}$  ions were introduced as  $Eu(NO_3)_3$  solutions by dissolving  $Eu_2O_3$  into dil.  $HNO_3$  solution for the preparation of  $K_{3-x}Al_2(PO_4)_3:Eu_x$  phosphor. After mixing all reagents for about 30 min, mixture was transferred to a furnace preheated at 550 C and the porous products were obtained. Same procedure followed for the  $K_{3-x}Al_2(PO_4)_3:Dy_x$  phosphor. The prepared host lattice was characterized for its phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-K $\alpha$  radiation) at a scanning step of 0.010, continue time 20s, in the 2 $\theta$  range from 10° to 60°. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

## Results and Discussion

### X-Ray Diffraction Study of Host Lattice

Figure 1 shows the XRD pattern of host  $K_3Al_2(PO_4)_3$  powder. The pattern of prepared compound was matched

**Fig. 1** XRD pattern of  $K_3Al_2(PO_4)_3$  host lattice compared with JCPDS file No. 00-028-0732

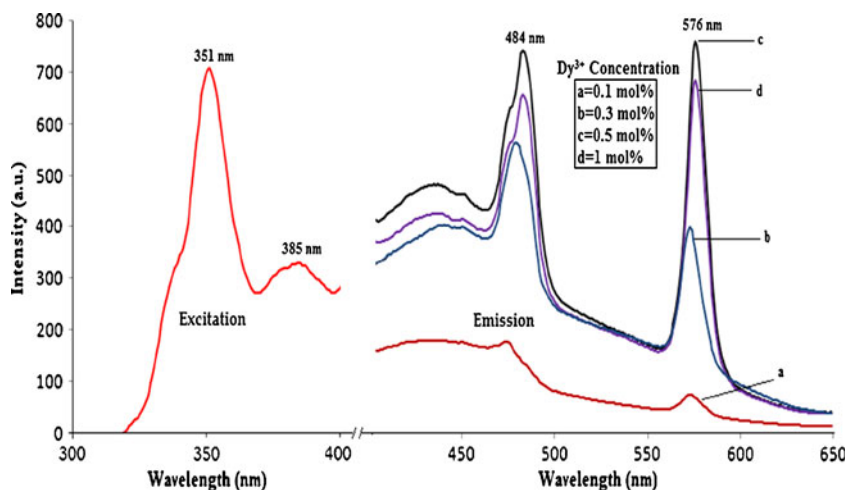


with JCPDS card No. 00-028-0732. This shows final product was formed in crystalline, homogeneous form and combustion reactions of the mixtures took place well.

### Photoluminescence Studies of $K_3Al_2(PO_4)_3:Dy^{3+}$

Figure 2 shows the excitation and emission spectrum of the  $K_3Al_2(PO_4)_3:Dy^{3+}$  phosphor. The excitation peak is observed at 351 nm and 385 nm due to the  ${}^6H_{15/2} \rightarrow {}^6F_{9/2}$  electronic transition of  $Dy^{3+}$  ion. Between these two excitation bands we choose 385 nm because it is suitable for solid state lighting. It is known that  $Dy^{3+}$  emission around 484 nm ( ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ ) due to magnetic dipole transition and 576 nm ( ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ ) due to electric dipole moment. The transition  ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$  is predominant only when  $Dy^{3+}$  ions are located at low-symmetry sites with no inversion centers [11]. A slight marginal shift in the peak position of  $Dy^{3+}$  ions with respect to Dy concentration is observed in all prepared phosphors. Such behavior is as expected for the emission involving  $f \rightarrow f$  transitions where ligand field changes with the host matrix. This excitation and emission of  $Dy^{3+}$  ion indicate that it is suitable for white light-emitting phosphor. As the ionic radii of  $Dy^{3+}$  (91.2 pm) is much larger than  $Al^{3+}$  (50 pm) and smaller to  $K^+$  (133 pm) so most of the  $Dy^{3+}$  ions are entering the lattice  $K_3Al_2(PO_4)_3$  phosphor and few of them are located at the surface. The charge compensating defects in the immediate vicinity is

**Fig. 2** PL emission spectra of  $K_3Al_2(PO_4)_3:Dy^{3+}$  under  $\lambda_{exc.}=385\text{ nm}$  and the excitation spectrum obtained while monitoring the emission wavelength at 576 nm



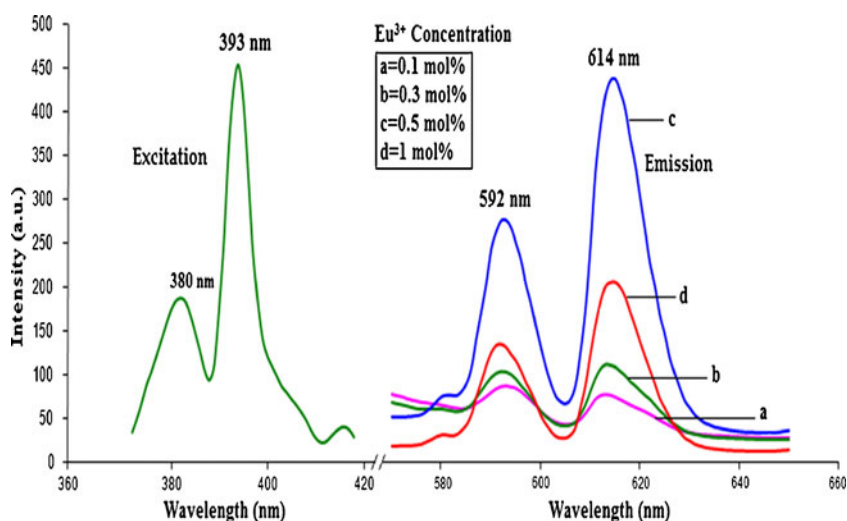
likely to influence the local site symmetry. This is reflected in the emission spectra, wherein asymmetry factor is higher in  $K_3Al_2(PO_4)_3$ . As  $Dy^{3+}$  ions progressively replace the  $Al^{3+}$  ions, an increase in PL emission intensity is observed and asymmetry factor progressively reduced. The low-symmetry location of  $Dy^{3+}$  results in emission of  ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$  transition. Hence,  $K_3Al_2(PO_4)_3$  phosphors shows strong PL emission intensity at 484 nm and 576 nm in Fig. 2. Usually, a low doping gives weak luminescence, but excess doping perhaps causes quenching of luminescence. The maximum intensity of  $Dy^{3+}$  is observed at 0.5 mol%

Photoluminescence Studies of  $K_3Al_2(PO_4)_3:Eu^{3+}$

Figure 3 presents the excitation and emission spectra of the  $K_3Al_2(PO_4)_3:Eu^{3+}$  phosphor. Under the excitation of 393 nm (i.e. excitation of the LED lighting), the phosphor

$K_3Al_2(PO_4)_3:Eu^{3+}$  has the orange and red emission bands at 592 nm and 614 nm. The main emission line is located at 614 nm, attributed to forced electric dipole transition  ${}^5D_0 \rightarrow {}^7F_2$  of  $Eu^{3+}$  ion, which is allowed as the  $Eu^{3+}$  does not occupy a center of symmetry site in the host lattice. Other transitions from the  ${}^5D_0$  excited levels to  ${}^7F_J$  ground states, such as  ${}^5D_0 \rightarrow {}^7F_1$  lines in the 570–600 nm range which is advantageous for obtaining a phosphor with good CIE chromaticity coordinates. The excitation band 393 nm which is caused by the f–f transitions from  ${}^7F_J$  of  $Eu^{3+}$  to excited levels, that is to say, the transition  ${}^7F_0 \rightarrow {}^5L_6$  of  $Eu^{3+}$  attribute to the 393 nm which is stronger excitation band. In the  $K_3Al_2(PO_4)_3:Eu^{3+}$  phosphor, one  $Eu^{3+}$  ion is expected to replace one  $Al^{3+}$  ion which will induces the lattice distortion and affect the luminescent intensity of  $Eu^{3+}$ . It is a good phenomenon that our phosphors can strongly absorb near ultraviolet light (393 nm), which is well in agreement with the near-UV or

**Fig. 3** PL emission spectra of  $K_3Al_2(PO_4)_3:Eu^{3+}$  under  $\lambda_{exc.}=393\text{ nm}$  and the excitation spectrum obtained while monitoring the emission wavelength at 614 nm



blue output wavelengths of GaN based LED chips. The linear emission peaks of  $\text{Eu}^{3+}$  can be observed in the range of 550–700 nm and ascribed to the transition  $^5\text{D}_0$  level to  $^7\text{F}_1$  and  $^7\text{F}_2$  levels of  $\text{Eu}^{3+}$ , respectively, such as  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  (589 nm, 593 nm) and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (610 nm, 623 nm). It is well known that the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition belongs to the magnetic dipole transition which scarcely changes the crystal field strength around the  $\text{Eu}^{3+}$  ions and this transition is independent of the symmetry and the site occupied by  $\text{Eu}^{3+}$  ions in the host. While the transition of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  belongs to a forced electric dipole transition and its intensity is very sensitive to the site symmetry of the  $\text{Eu}^{3+}$  ions. Thus, the ratio of  $R = ^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$  can measure the distortion from the inversion symmetry of the  $\text{Eu}^{3+}$  ion local environment [12–14]. In Fig. 3, the transition  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  is much stronger than the transition  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ , which suggests that the  $\text{Eu}^{3+}$  is located in a distorted (or asymmetric) cation environment. The variations of PL intensity ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of  $\text{Eu}^{3+}$ ) with different  $\text{Eu}^{3+}$  content are shown in Fig. 3. The intensity of the emission transitions was found to increase with an increase in the  $\text{Eu}^{3+}$  concentration up to 0.5 mol% and then it decreases because of concentration quenching.

## Conclusions

In the present work,  $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$  activated  $\text{K}_3\text{Al}_2(\text{PO}_4)_3$  phosphors were prepared by a combustion synthesis. Under the excitation of 385 nm, PL emission spectra of  $\text{K}_3\text{Al}_2(\text{PO}_4)_3:\text{Dy}^{3+}$  phosphor emits distinctive colors

specifically blue and yellow whereas under the excitation of 393 nm (i.e. excitation of the LED lighting) the PL emission spectra of the  $\text{K}_3\text{Al}_2(\text{PO}_4)_3:\text{Eu}^{3+}$  phosphor shows orange/red emission bands at 592 nm and 614 nm respectively.  $\text{Dy}^{3+}$  and  $\text{Eu}^{3+}$  activated  $\text{K}_3\text{Al}_2(\text{PO}_4)_3$  phosphors exhibit a strong absorption between 340 and 400 nm suggests that present phosphor is a promising candidate for producing white LEDs.

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