Synthesis and photoluminescence properties of novel red-emitting KMg$_4$(PO$_4$)$_3$: Eu$^{3+}$ phosphors for UV-excited white-light emitting diodes

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Abstract. The trivalent Eu$^{3+}$ activated KMg$_4$(PO$_4$)$_3$ phosphor has been successfully prepared via solid state diffusion technique. The phase formation and structural morphological studies carried out by XRD pattern and SEM analysis. The photoluminescence excitation spectra centred at 395 nm attributed to $^5$D$_{0}→^7$F$_{6}$ energy transition levels. PL emission spectra centred at 593 nm and 613 nm corresponds to $^3$D$_{0}→^5$F$_{1}$ (J=1,2) transitions of Eu$^{3+}$ in the host respectively. The experimental results showed that Eu$^{3+}$ singly doped KMg$_4$(PO$_4$)$_3$ phosphor under UV excitation gives intense red emissions. The critical Eu$^{3+}$ quenching concentration (QC) was determined to be 1.0 mol% along with excellent CIE coordinates of (0.6326, 0.3670). All the above results exhibit the prepared phosphor is promising material as UV excitable red emitting phosphor for w-LED.

Keywords: Phosphor; Down conversion; Luminescence; Chromaticity coordinates; W-LEDs

1. Introduction

In the recent year trivalent rare-earth (RE$^{3+}$) ions doped inorganic based phosphor received more attention as luminescent materials owing to their wide application in the various field such as w-LEDs, medical applications, non-inversion thermometry, solar energy conversion, temperature sensors, field emission displays and solid state lighting (SSL), due to existence of emissions attributes to electronic transitions in the 4f$_n$ configurations [1–3]. In the present era energy saving is the prime issue and hence major inclination towards w-LEDs in display technology owing to its excellent performance, low power consumption, durability, high compatibility, energy saving, as well as are of highly economical [4,5].In order to realize the excellent luminescent materials, it must exhibits some important characteristics such as prominent emission efficiency under n-UV/blue excitation, good thermal and chemical stability as well as narrow band emission with good absorption. In general two approach are adopted to achieve pc-w-LEDs include (i) combination of yellow emitting (YAG:Ce$^{3+}$) phosphor with blue emitting (InGaN) chip but owing to lack of red emission it shows high CCT and poor CRI which hinder its commerce alization. (ii) This limitation can be overcome with the approach of combination of RGB phosphor with n-UV or blue excitation chip to improve the optical properties[6]. The poor thermal stabilities and aging rates of the different phosphors also restrict their applications in w-LEDs [7,8]. Moreover, various components of inorganic luminescent phosphor materials encompass with borates [9], Aluminate[10], vanadates [11], tungstates [12], silicates [13] and phosphates [14] have been studied for generation of.
luminescent host. In general, phosphate based phosphor exhibits vital emission in visible region (400 nm-700 nm) revealed various applications in photocatalysis, electrochemistry, biology materials, x-ray images and displays laser [15,16]. In the recent various rare earth doped phosphate based phosphor are extensively studied such as KMg₄(PO₄)₃:Eu²⁺[17], (K₁₋ₓNaₓ)Mg₄(PO₄)₃Eu²⁺[18], KMg₄(PO₄)₃:Eu²⁺[19], KMg₄(PO₄)₃:Ce³⁺, Tb³⁺[20] etc which describe multicolour emissions corresponds to single excitation wavelength and exhibit its applicability in solid-state lighting. The Eu³⁺ ion exhibits emission in red region corresponds to wavelength around 593 nm and 613 nm derived from the intra-4f transition within the ⁴f⁶ configuration which enhance the performance of the phosphors-converted w-LEDs [21,22].

In present work, the series of Eu³⁺ singly doped phosphate based phosphor were prepared with the analysis of structural, morphological as well as photoluminescence behaviour of prepared phosphor. The obtained results revealed that as-prepared KMg₄(PO₄)₃:Eu³⁺ is potential material as n-UV excitable red emitting phosphor for w-LEDs.

2. Materials and Experimental

2.1. Experimental study

The series of KMg₄(PO₄)₃:xEu³⁺ (0.05≤x≤1.5) phosphor was synthesized by SSR technique. All the starting precursor such as magnesium carbonate (MgCO₃) (99.99%), Potassium Carbonate (K₂CO₃) (99.99%), Ammonium phosphate (N₂H₉PO₄) (99.99%) and spectrographically pure Eu₂O₃ (99.99%) are of analytical grade and used as received without purification. These materials were weighted by appropriate stoichiometric ratio. The concentration of Eu³⁺ varied from 0.05, 0.2, 0.5, 0.7, 1.0, 1.5 mol% and allowed to calcination followed by sintering via heat treatment of 800°C for 24hr in furnace results to achieve the crystalline structure of prepared materials. Finally, the resultant KMg₄(PO₄)₃:Eu³⁺phosphor grounded again into powder form and used for further studies. The Basic chemical reaction for pure KMg₄(PO₄)₃ along with schematic of block diagram was as follows:

4MgCO₃ + K₂CO₃ + 3N₂H₉PO₄ → KMg₄(PO₄)₃ + 6NH₃ + 4½H₂O + 4CO₂

2.2 Characterization

The prepared phosphor material was analysed by XRD, SEM and PL techniques. The XRD pattern analysis was carries out by PW3071XPERT-PRO X-Ray Diffractometer over the angular range of 10°-60° with the continuous scanning mode of 0.02° step size. The morphological analysis for prepared material was done by scanning electron microscope (JEOL JSM-58). The Photoluminescence
characteristics was studied using SHIMADZU RF-5301 PC spectrofluorophotometer equipped with Xenon flash lamp of 150 W at room temperature. The CIE chromaticity color coordinates was calculated using OSRAM SYLVANIA Color calculator with high accuracy.

3. Results and Characterization

3.1. XRD analysis

The crystal structure of as-synthesize undoped KMg₄(PO₄)₃ phosphor was analysed by XRD diffraction pattern exhibits all peaks were exactly coincide to the standard JCPDS data file no. 98-015-4111 and can indexed to be structure of orthorhombic with space group Pnmm (no. 58). The lattice parameters of host phosphor were evaluated revealed the formation of uniform and crystalline structure of synthesize phosphor materials [19,20].

3.2. SEM Study

The analysis of surface morphology of prepared phosphor was carried out by scanning electron microscope technique. The SEM analysis clear that the prepared materials shows irregular morphology with agglomerated particle size shown in figure 1. The particle with agglomeration revealed a porous structure with the particle is ranging from nanometre revealed its suitability for various lighting applications [23].

![Figure 1. SEM images of the KMg₄(PO₄)₃ phosphor.](image)

3.3. Photoluminescence properties

The photoluminescence excitation characteristics of KMg₄(PO₄)₃: Eu³⁺ phosphor recorded in emission wavelength of 613 nm as shown in figure 2. It exhibits that PLE spectrum is in the range of 350nm to 450nm with excitation peak centred at 395 nm ascribe to ⁷F₀→⁵L₆ transition of Eu³⁺ ions in the host [24]. The emission spectra for KMg₄(PO₄)₃: xeEu³⁺(0.05 ≤ x ≤ 1.5 mol%) phosphor at 395 nm is depicted in figure 3. It shows PL spectrum in the range of 550nm-650nm with two sharp peak cantered at 593nm and 613nm attributes to⁵D₀ → ⁷F₉(J = 1, 2) transition of Eu³⁺ ions in the host. The emission at 593nm with ⁵D₀ → ⁷F₁ transition corresponds to magnetic dipole (MD) transition, however the emission at the wavelength of 613nm corresponds to transition at ⁵D₀ → ⁷F₂ represent electric dipole transition[25]. The intense peak at 613nm represent the dominance of electric dipole transition, demonstrating that Eu³⁺ions is situated at the non-inversion site symmetry.
Figure 2. PLE spectrum of KMg₄(PO₄)₃:Eu³⁺ phosphor at 613 nm.

Figure 3. PL spectrum of KMg₄(PO₄)₃:xEu³⁺ phosphor (0.05≤ x ≤ 1.0 mol%) at λₑₓ=395nm.

The variation of PL intensity of KMg₄(PO₄)₃:xEu³⁺ with doped Eu³⁺ ions mol% is depicted in figure 4. It clears the gradual enhancement of PL intensity with dopant concentration revealed the maximum peak at 1.0 mol%. However, with further in ions concentration exhibits decrease in emission intensity owing to concentration quenching mechanism.
Figure 4. The luminescent intensity as a function Eu$^{3+}$ ions (mol %) in KMg$_4$(PO$_4$)$_3$:Eu$^{3+}$phosphor

3.4. CIE chromaticity coordinates

The phosphor performance of light emission can be studied by Commission International de L’Eclairage (CIE) co-ordinate. Figure 5 represent the CIE diagram of KMg$_4$(PO$_4$)$_3$:xEu$^{3+}$ phosphor at $\lambda_{ex}=395$nm. The CIE co-ordinates are obtain to be (0.6326, 0.3670) revealed that the prepared shows the emission in red region under UV excitation. It concludes that the prepared phosphor is the potential candidate for red emission in n-UV excitation may be useful white LEDs application.

Figure 5. CIE chromaticity coordinate of KMg$_4$(PO$_4$)$_3$:Eu$^{3+}$phosphor.

4. Conclusion

In summary the series of xEu$^{3+}$ (0.05 ≤ x ≤ 1.5) mol% doped phosphate based KMg$_4$(PO$_4$)$_3$ phosphor have been synthesized. The crystal structure, phase formation and morphological behaviour of the host materials was confirmed from XRD and SEM analysis. In luminescence studies the excitation spectra demonstrated that the phosphors shows suitability for UV excitation (395nm) exhibit emission in red region centred at 593nm and 613 nm ascribe to $^5$D$_0\rightarrow^7$F$_J$ (J=1,2) Eu$^{3+}$ ions transition in the host. The
optimized quenching concentration of prepared phosphor obtained at 1.0 mol %. The chromaticity coordinate of as synthesized KMg(PO₄)ₓ: 1.0 mol% Eu³⁺ phosphor was calculated to be (0.6326,0.3670). The obtained results, accomplished that prepared luminescent material is potential candidate as red color emission phosphor under UV excitation for economical w-LEDs.

5. References
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