Synthesis and luminescence properties of Dy\(^{3+}\) ions doped KMgPO\(_4\) phosphor for eco-friendly solid-state lighting

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Abstract. Dy\(^{3+}\) ions doped KMgPO\(_4\) phosphor was synthesized using a simple wet chemical method and reported the photoluminescence (PL) properties. The prepared XRD pattern matches well with the standard JCPDS file. Under 350 nm excitation, the KMgPO\(_4\):Dy\(^{3+}\) phosphor exhibits two emission peaks at wavelengths 470 and 577 nm, corresponding to the characteristic energy transitions \(^{4}\text{F}_{9/2}\rightarrow^{6}\text{H}_{15/2}\) and \(^{4}\text{F}_{9/2}\rightarrow^{6}\text{H}_{13/2}\), respectively. The PL intensity was found maximum at a Dy\(^{3+}\) ions concentration of 0.5 mol%. The findings are considered to be potential candidates for KMgPO\(_4\):Dy\(^{3+}\) phosphor for eco-friendly solid-state illumination.

Keywords. Wet chemical method; XRD; photoluminescence; phosphate phosphor; SSL.

1. Introduction

Among the different solid-state lighting (SSL) technologies, phosphor-converted white light-emitting diodes (pc-w-LEDs) are currently replacing traditional light sources, such as incandescent and fluorescent bulbs due to their energy efficiency and ease of maintenance. Phosphor-converted white light-emitting diodes (pc-w-LEDs) have evolved over the years to remain as the dominant leader in the lighting industry. The w-LEDs have perceived a lot of interest in recent decades due to their long life, small size, high efficiency, energy savings, eco-friendliness and other benefits [1, 2]. The orthophosphate is discovered to be a prominent host owing to its low sintering temperature, high physical chemistry stability and thermal stability. As a result, orthophosphate is a good host for photoluminescence (PL) compounds [3, 4]. The proposed research work will be focused on the preparation of Dy\(^{3+}\) rare-earth-doped orthophosphate phosphors. In particular, rare-earth phosphates have proved to be very useful host lattices for luminescence. Orthophosphate PO\(_4^{3-}\) has a tetrahedral structure of the phosphate family, with a phosphorus atom in the centre surrounded by four oxygen atoms. Commercial w-LEDs may now be made using a blue LED chip and the Y\(_3\)Al\(_2\)O\(_12\):Ce\(^{3+}\) yellow colour emitting phosphor. Some primary drawbacks of these YAG-based w-LEDs are due to their low CRI (\(R_\text{a} < 75\)) and CCT (> 6000 K), which are due to the lack of a red-emitting component [5].

Researchers worked hard to create an efficient and stable phosphor material that could be activated by n-UV and emitted in the visible range. So, after reviewing the literature on phosphates, we are drawn to the phosphate family of materials because of their simple synthesis technique [6], strong thermal stability [7], large bandgap [8] and chemical stability [9]. Rare-earth ions have played a significant role in the creation of many commercial phosphors and are currently being investigated for improving the optical properties of materials [10].

With respect to the other rare-earth dopants, Dy\(^{3+}\) ions are widely used as activators in different inorganic materials like borate and phosphate to produce novel phosphors for w-LEDs [11, 12]. The synthesized phosphor is constituted of two primary emission peaks of Dy\(^{3+}\) ions: first at 470 nm from the transition \(^{4}\text{F}_{9/2}\rightarrow^{6}\text{H}_{15/2}\) and the second at 577 nm from the transition \(^{4}\text{F}_{9/2}\rightarrow^{6}\text{H}_{13/2}\) [13]. Several rare-earth ion-doped phosphor component possible candidates for use in n-UV excited SSL has previously been reported: Ca\(_3\)B\(_2\)O\(_6\):Dy\(^{3+}\), Eu\(^{3+}\) [14], MgCaAl\(_{10}\)O\(_{17}\):Dy\(^{3+}\), Sm\(^{3+}\) [15] and Ca\(_2\)Al\(_2\)O\(_5\):Dy\(^{3+}\), Eu\(^{3+}\) and Tb\(^{3+}\) [16]. Nandanwar et al. [17] reported wet chemical synthesis technique of Ba\(_3\)(PO\(_4\))\(_2\):RE \((\text{RE} = \text{Dy}^{3+}, \text{Sm}^{3+}\) and Eu\(^{3+}\) phosphor. As a result of its importance in traditional SSL, the PL performance of rare-earth ions doped phosphate phosphors has been thoroughly studied. Ramteke et al. [18] investigated the PL performance of KMgPO\(_4\):Eu\(^{3+}\) phosphor phosphate samples for n-UV based solid-state illumination. This study shows that powder samples of KMgPO\(_4\):Dy\(^{3+}\) phosphors were first time
synthesized using a wet chemical technique. The wet chemical method is simple to prepare, has a low sintering temperature, low-cost procedures and is eco-friendly. The structural feature of the KMgPO4:Dy3+ phosphor was studied using XRD Rietveld structure refinement. The PL characteristics and CIE coordinates are also investigated. The findings suggest that KMgPO4:Dy3+ phosphors may be suitable for fabricating n-UV excited SSL.

2. Experimental

The powder samples studied were synthesized using a simple wet chemical method involving Dy2O3, K(NO3)2, Mg(NO3)6·H2O and NH4H2PO4 (Analytical Reagent, AR). The prerequisite materials were weighted by using the stoichiometric ratio using a nominal chemical formula of KMgPO4:Dy3+ phosphor. Initially, the mixtures were thoroughly mixed in a beaker with distilled water and agitated so that it looks transparent. As weighted Dy2O3 ions were taken in a test tube and dissolved in dil. HNO3 to convert it into suitable nitrates. Afterwards, dysprosium nitrates were added to the as-prepared transparent solution and agitated until it again became transparent. This transparent solution in a beaker was then kept on a magnetic stirrer at a temperature of 80°C for around 10 h. Pesticle and mortar were employed to produce a fine powder from this crystalline powder. The fine powder was then heated in a furnace at 800°C for 3 h and naturally allowed to cool at room temperature. The white colour powder synthesized produced by grinding was used for different characterizations. The Shimadzu RFPC5301 Spectrofluorophotometer was used to measure the PL of excitation and emission. A 1.5 nm spectral slit width was used to record emission and excitation spectra.

3. Results and discussion

3.1 XRD of KMgPO4 phosphor

The XRD pattern of KMgPO4 phosphor is depicted in figure 1, which matches with the standard XRD data of KMgPO4 phosphor in reference to Joint Committee on Powder Diffraction Pattern (JCPDS) PDF file number 500146. The KMgPO4 phosphor has orthorhombic crystal structure. All the peaks are due to the KMgPO4 phosphor single phase and no impurity peaks were observed. The XRD pattern for the undoped KMgPO4 phosphor has the crystalline phase shown by an intense peak. The formation of crystalline phase occurred due to the annealing of the compound [19].

The Rietveld refinement of the experimental data of as-prepared KMgPO4:Dy3+ phosphor was studied by the FullProf software using the standard structural model of the KMgPO4 phosphor (orthorhombic, space group Pm/n21), which is based on the particular similarity between the XRD pattern of sample and the standard JCPDS data. The peak profile function of Pseudo-Voigt was used, and then using linear interpolation the background was approximated. Figure 2 shows the graphical XRD profiles for the Rietveld refinement of the as-prepared KMgPO4:Dy3+ phosphor that was a difference (bottom), calculated (solid line), and observed (crosses). Short vertical lines represent the estimated pattern’s Bragg reflections. Table 1 shows the experimental crystallographic data for the KMgPO4:Dy3+ phosphors after Rietveld refinement. The calculated findings agree well with the experimental data showing refinement factor of $R_{wp} = 16.34$, $R_p = 8.68$, $R_{exp} = 11.41$ and $\chi^2 = 2.31$ indicating good fitting [20].
Table 1. Crystallographic data for the KMgPO₄:Dy³⁺ phosphor.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>KMgPO₄ phosphor</th>
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<tr>
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3.2 Photoluminescence properties of KMgPO₄ phosphor

The excitation spectra of Dy³⁺ ions doped KMgPO₄ phosphor is shown in figure 3. The strongest excitation peak is located at 350 nm wavelength in the region of 320–420 nm excitation wavelengths. In the excitation spectrum, numerous peaks are visible owing to the 4f–4f transition of the Dy³⁺ ion. The excitation peaks at 328, 350 and 387 nm relate to the f–f transitions of the Dy³⁺ ions, i.e., ⁶H₁₅/₂ → ⁶P₃/₂, ⁶H₁₅/₂ → ⁶P₇/₂ and ⁶H₁₅/₂ → ⁴I₁₃/₂, respectively [21].

Figure 4 depicts the PL emission spectra of KMgPO₄:xDy³⁺ (x = 0.1, 0.3, 0.5 and 1 mol%) phosphors with a monitored excitation peak at 350 nm. This emission peaks at 470 and 577 nm, which corresponds to the transitions of the Dy³⁺ ions, i.e., ⁴F₉/₂ → ⁶H₁₅/₂ and ⁴F₉/₂ → ⁶H₁₃/₂ [22, 23]. The emissions colours are blue (MD transition) and yellow (ED transition). The ⁴F₉/₂ → ⁶H₁₃/₂ transition, hypersensitive electric dipole transition with ΔJ = 2 is strongly affected by the surrounding environment. However, the ⁴F₉/₂ → ⁶H₁₅/₂ transition belonging to the magnetic dipole transition is hardly influenced by the crystal field around the Dy³⁺ ions. In the emission spectrum, mainly blue emission means Dy³⁺ ions is in a high-symmetry site, whereas mainly yellow emission indicates that Dy³⁺ ions is in a low-symmetry site [24, 25]. In our case, the blue emission intensity is the strongest, which means that Dy³⁺ ions occupy high symmetry sites [26, 27]. The only consequence of changing the doping concentration of Dy³⁺ ion is a change in the intensity of emission peaks in the host matrix. As a result, this phosphor shows its candidature for possible use in n-UV LED conversion phosphors in SSL applications.

Figure 5 depicts the emission spectra of KMgPO₄:Dy³⁺ phosphors (λₑₓ = 350 nm) with the variation in the percentage concentration of doped Dy³⁺ ions on relative luminescent intensity of luminescence at 470 nm for KMgPO₄ phosphor.
concentrations of Dy$^{3+}$ ions. The intensity of the PL emission is proportional to the doping concentration of Dy$^{3+}$ ions; however, the doping concentration has no subsequent effect on the location and form of the emission peak. The emission intensity reaches its maximum at 0.5 mol% of Dy$^{3+}$ ions [28]. The intensity of the emission then decreases owing to concentration quenching effect.

Figure 6 depicts the exact energy level diagram of Dy$^{3+}$ dopants doped in KMgPO$_4$ phosphor showing the excitation and emission process. The higher energy level excitation peaks at 328 nm, 350 nm, and 387 nm correspond to the f–f transitions of Dy$^{3+}$ ions ($^6P_{3/2}$, $^6P_{7/2}$ and $^4I_{13/2}$) and are populated at varying excitation wavelengths (328 nm, 350 nm and 387 nm). The excited Dy$^{3+}$ ions in the $^6P_{7/2}$ state jumped to the $^4F_{9/2}$ state after non-radiative relaxation. The Dy$^{3+}$ ions at the $^4F_{9/2}$ state radiatively relaxed to the $^6H_{15/2}$ and $^6H_{13/2}$ states, resulting in improved blue and yellow emissions [29].

3.3 CIE coordinates of KMgPO$_4$ Dy$^{3+}$ phosphors

As shown in figure 7, the chromaticity coordinates of KMgPO$_4$:Dy$^{3+}$ phosphors are measured relative to the emission spectrum utilizing 1931 CIE calculated software. The calculated CIE coordinates of KMgPO$_4$:Dy$^{3+}$ phosphor for blue colour is $x = 0.124$, $y = 0.057$, whereas the yellow colour is $x = 0.492$, $y = 0.506$) [30]. These findings demonstrate that the KMgPO$_4$:Dy$^{3+}$ phosphor system may generate blue-yellow light upon n-UV excitation. As a consequence, the KMgPO$_4$:Dy$^{3+}$ phosphor might be a promising candidate for SSL applications.

4. Conclusions

The KMgPO$_4$:Dy$^{3+}$ phosphor was successfully synthesized utilizing a wet chemical technique, and confirmed by the XRD measurement. PL excitation and emission characteristics were investigated. The XRD analysis confirmed that the materials crystallized into an orthorhombic structure. The KMgPO$_4$:Dy$^{3+}$ phosphor has a blue-yellow emission spectrum with two strong peaks at 470 and 577 nm under an excitation peak at 350 nm. As per the results of concentration quenching, the ideal concentration of KMgPO$_4$:Dy$^{3+}$ phosphor is 0.5 mol%. Studying the PL characteristics suggests that KMgPO$_4$:Dy$^{3+}$ phosphor might be a potential candidate for SSL applications.

References

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