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# $Ca_8MgY(PO_4)_7:Eu^{2+},Mn^{2+}$ for better angular chromatic harmony and high lumen for white diode

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**ABSTRACT**

The multifunctional phosphor $Ca_8MgY(PO_4)_7$ doping with $Eu^{2+}$ and $Mn^{2+}$ ions (CaMn) is utilized to stimulate the rate of light extraction and color harmony of the white light-emitting diode (WLED) package using remote phosphor design with two sheets of phosphor. The CaMn sheet helps to reduce the color variation and light scattering backward mainly caused by high concentration of yellow phosphor $YAG:Ce^{3+}$ film. The experimental results show a gradual increase of luminous flux and significant reduction of chromatic deviation in direct proportion to the increasing concentration of CaMn phosphor. Meanwhile, with more than 9% wt of CaMn concentration, the reduction of color rendering properties is presented because of the redundant green emission, leading to the lack of blue and yellow emission energies. Good color quality scale that peaks at 63 can be achieved with 2-4%wt. CaMn in the WLED packages. It is advisable to manage the concentration the green phosphor CaMn to attain desirable optical objectives.



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## 1. INTRODUCTION

The development in the lighting properties of white light-emitting diode (WLEDs) has been extensively researched. The WLED devices have been realized with high robustness, wide-range applications (backlighting, commercial lighting, landscape lighting), and high efficiency while offering low maintenance cost. The white light of a commercial light-emitting diode (LED) can be produced by mixing the emitted blue lights from a LED die with the converted yellow light from the yellow phosphor of $YAG:Ce^{3+}$ particles [1]. The luminescence of the package was reported to be adequately high, but the color rendering feature was below 90, and high temperature in the phosphor layer could reduce the lifespan and the conversion efficiency of the phosphor [2]. Also, a shortage of the red color emission in this type of phosphor-converted LED was observed, leading to inefficient color performance. Thus, the LED model using tri-color phosphor packaging was proposed for achieving superior color rendering index [3]. However, the lumen output of this package showed inferior results owing to the differences in the phosphor properties of absorption and aging process [4]. Studies demonstrated that the recommended phosphor materials for white LED should have single-phase feature, and dope with rare-earth or luminescent cations for the color tunability characteristic [5].

The Ca8MgY(PO4)7 is one of the multifunctional phosphors with excellent the electronic, optical and thermal features that are suitable for being applied in WLED production [6]. It was shown that the energy transfer from $Eu^{2+}$ sensitizer to $Mn^{2+}$ activator could successfully generate white light. This use of energy transfer between ions also can be well applied in many phosphor hosts owing to the outstanding chromatic reproducibility and low production cost [7], [8]. Thus, in this study, the single-phase phosphor $Ca_8MgY(PO_4)_7$ doping with $Eu^{2+}$ and $Mn^{2+}$ ions is prepared and applied to fabricate a WLED model with significant chromatic consistency as well as lumen. $Ca_8MgY(PO_4)_7$ can be produced with high temperature solid-state technique in a reducing atmosphere of 15% $H_2$ and 85% $N_2$. The crystal field strength and energy transfer analysis are conducted at the excitation wavelength 375 nm of near UV LED dies, with the change in $Eu^{2+}$ and $Mn^{2+}$ concentration to realize the color tunability and luminous property of the phosphor. Then, the effects of the phosphor $Ca_8MgY(PO_4)_7$:$Eu^{2+}$,$Mn^{2+}$ (shortened form: CaMn) on the WLED model are examined and discussed to obtain the improvement in lighting performances.

## 2. EXPERIMENTAL DETAILS

### 2.1. Phosphor characterization

Under the room temperature, the examination on the phosphor $Ca_8MgY(PO_4)_7$:$Eu^{2+}$,$Mn^{2+}$ phase purity is carried out with a X-ray diffractometer of Rigaku D-max 2200. The inputs of the diffractor are set at 1.5405 Å Cu $K\alpha$ radiation, 30 kV, and 30 mA. The photoluminescence-spectra measurement of the phosphor is provided with FPS 920 time resolved as well as steady state fluorescence spectrometers accompanied by excitation xenon and nF900 illumination sources of 450 W and 150 W, respectively [9], [10].

### 2.2. Simulation of a LED

The fabrication of white LED with CaMn phosphor layer, for assessing $Ca_8MgY(PO_4)_7$ influences imposed on the light features in dual-layer package, is performed at room temperature with the combination of near UV-LED dies having the excitation wavelength of 375 nm with a layer of yellow phosphor (YAG:$Ce^{3+}$) and the prepared CaMn green phosphor layer. The EVERFINE PMS-80 UV-VIS-IR spectrophotometer with 0.02 A direct current is utilized to provide the luminescence spectra of the produced LED package.

Blasse [11], [12] defined the critical transfer distance between $Eu^{2+}$ ions via the equation of:

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

with $R_c$ indicates the distance between the nearest $Eu^{2+}$ ions at $x_c$, $V$ presents the unit cell's volume, $N$ shows the available sites for the dopant in the unit cell, and $x_c$ means the critical concentration. Besides, $Eu^{2+}$ crystal field strength can be calculated by:

$$D_q = \frac{Ze^2r^4}{6R^5} \quad (2)$$

here, $Dq$ means the crystal field strength, $Z$ indicates the valence of the anion, $r$ is the mean of the radius of the $d$ wavefunction, while $e$ shows the electron charge, and $R$ presents the separation between the central ion and ligands.

When the concentration of $Y^{3+}$ increases, the rise in the integrated intensity of $Ca_8MgY(PO_4)_7$ lattice can be observed, meaning that this is a potential phosphor host for doping luminescent cations [13], [14]:

$$Ca8 - yMg1 - zY(PO4)7 :\ yEu2+, zMn2+ \quad (3)$$

the photoluminescence spectrum measurement of $Ca_{7.88}MgY(PO_4)_7$:$y$$Eu^{2+}$ displayed a broad spectral region from approximately 250 nm to around 450 nm. This might be demonstrated by the transition of the $Eu^{2+}$ from $4f^7$ ($^8S_{7/2}$) to $4f^65d^1$.

Thus, it can be assured that the phosphor can be excited under near-UV chips' emission. In addition to that, the luminescence of CaMn phosphor exhibits a continuous red-shift increasing with the higher concentration of $Eu^{2+}$ ions. This can be attributed to the smaller distance between $Eu^{2+}$ and $O^{2-}$ in the host due to the substitution of larger $Eu^{2+}$ for smaller $Ca^{2+}$.

## 3. RESULTS AND ANALYSIS

The influence of CaMn sheet imposed on the concentration of YAG:$Ce^{3+}$ is among the main forces that cause the change in total optical performances of the LED configuration. The decrease in yellow phosphor concentration can be observed when increasing the concentration of CaMn, illustrated in Figure. 1. It is reported that high concentration of YAG:$Ce^{3+}$ phosphor did not result in white light and increased lumen flux, but warm light and degraded luminescence owing to the backscattering phenomenon [15]. Therefore, this concentration reduction has many meanings to the lighting properties of a LED. It seems to be crucial for keeping the consistency in the determined average color coordinate of the package, limiting the temperature increase within the phosphor layer, and impacting the absorption and scattering ability of the two-layer phosphor packages, contributing to achieving desired white-light quality [16]-[18]. Thus, the effectiveness of using CaMn phosphor to reach the enhancement in color adequacy of double-layer remote phosphor WLED model could be implied. As can be seen, the concentration of the yellow phosphor significantly declines from 12% to 2% wt. when the weight percentage of the green phosphor CaMn grows from 2% to 30%.

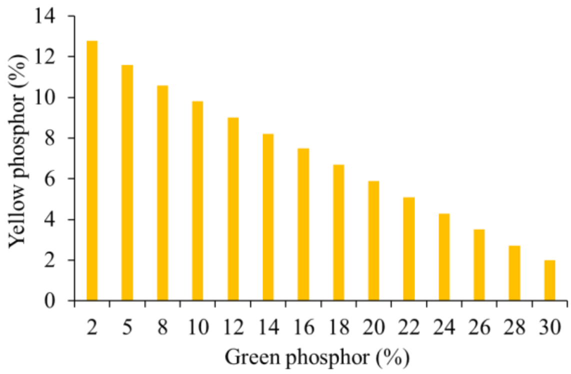


Figure 1. Keeping median CCT via altering content of phosphor

The addition of green phosphor CaMn also affects the emission intensity of the phosphor package, which is displayed in Figure 2. Specifically, the transmitting spectral intensity of the package showed improvement for the blue (between 450 and 485 nm) and green (between 500 and 565 nm) wavelength ranges, indicating that the total lumen output is enhanced. This also implied that the color elements needed for white-light generation, blue, yellow and green ones, are supplemented and balanced, and thus, might elevate the color uniformity of the LED. These findings on the advantages of using CaMn phosphor layer for the improvement of optical efficiency of the WLED package are further discussed and demonstrated via Figures 3–6, including the features of luminescence, color rendering and index and quality scale, and color deviation corresponding to the changes of the phosphor concentration [19]-[21].

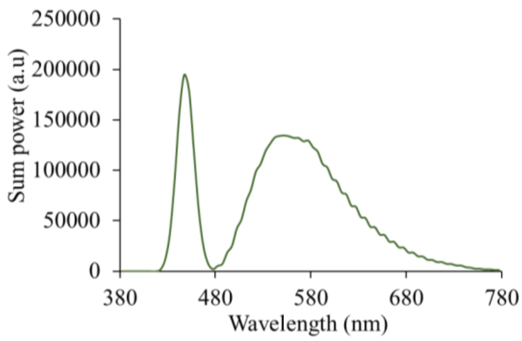


Figure 2. The emission spectra of 5,000 K WLEDs with the presence of CaMn layer

Figure 3 shows that there is a direct variation between the lumen output of WLED and the concentration of the green phosphor CaMn. In other words, higher concentration of the green phosphor helps increase the luminescence in WLED formation. The lumen in the packages gradually increases from-140 lm at 2% wt. CaMn to 160 lm at 30% wt. CaMn in the phosphor layer. This can be ascribed to the reduced backscattering and backward reflection of blue and yellow lights to enhance the conversion efficiency as well as the emission performance, owing to lower yellow phosphor concentration. Usually, high $YAG:Ce^{3+}$ concentration increases the rate of blue lights scattered back to the phosphor layer and unable to be re-emitted, leading to significant loss of light energy, and low yellow light conversion. Thus, the decrease in luminous output is likely to occur when the excessive concentration of yellow phosphor is presented. The addition of green phosphor layer CaMn probably stimulates the rate of blue lights being absorbed, converted and transmitted, and thus contributing to the stronger luminescent intensity of the two-layer remote phosphor package.

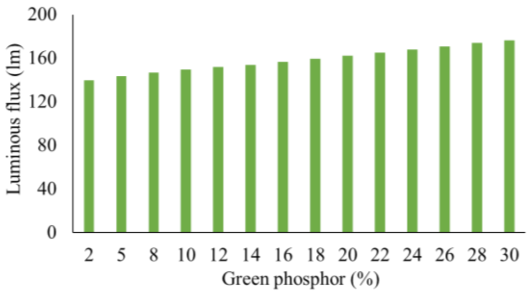


Figure 3. Luminous flux of WLED structure corresponding to CaMn concentration

Besides the luminous flux, the chromaticity of the double-layer remote phosphor configuration is another critical concern as it usually is inferior in this aspect. The color quality of the WLED phosphor package is investigated via three assessments of color rendering index (CRI), color deviation as well as color quality scale (CQS). The CRI is one of the most common measurements for evaluating the brightness and faithfulness of WLED lights [22], [23]. WLEDs that offer significant CRIs will have higher price than the others since it is better in revealing the true color of the illuminated objects [16]. Figure 4 shows the connection between the concentration of green CaMn phosphor and the CRI. As can be seen, the CRI declines with the growth of this phosphor concentration. The CRI reduces from above 60 to around 50 when 14% wt. CaMn is applied. The same trend is also observed when it comes to the CQS, illustrated in Figure 5. The CQS reaches its peak of nearly 64 at 2% wt. CaMn and then starts to decline and bottoms out at 56 with 14% wt. CaMn in the package. The decrease of these two-color parameters, CRI and CQS, can be demonstrated with the color imbalance caused by the excessive green-light proportion in the overall spectral energy. When the CaMn green phosphor is presented in the phosphor package, it obviously enhances the amount of green light element by absorbing the discharged blue as well as transmuted yellow light generated by the LED dies and the yellow phosphor layer, respectively, and then converting them into the green light. With an appropriate concentration, such as 2%-5% wt., CaMn phosphor layer could produce CRI and CQS above 60, while more than that, the color fidelity will be damage, because the green emission color places its dominance over the blue and yellow proportions. However, the CQS is more complex and has larger coverage over the color evaluation criteria than the CRI because this parameter accesses the LED-light color evaluation via the CRI, color coordinates and visual preference of the viewers. Thus, it could be said that reaching good CQS is more vital than having high CRI.

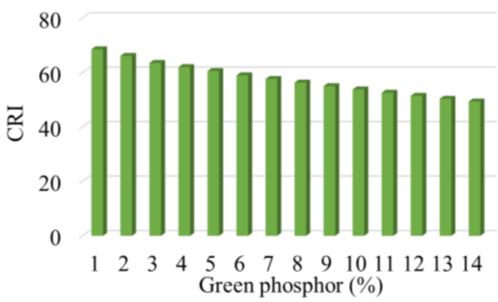


Figure 4. CRI in WLED structure and respective CaMn contents

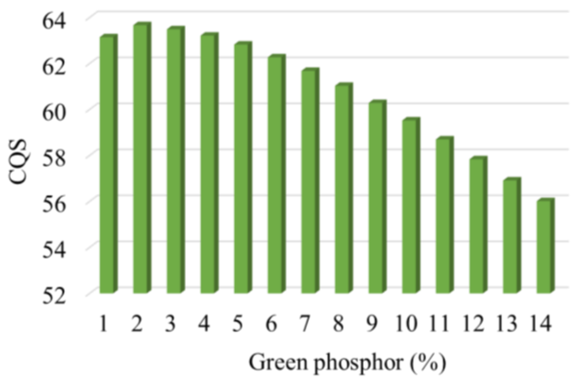


Figure 5. CQS in WLED structure and respective CaMn contents

In addition to the CRI and CQS, the angular chromatic homogeneity is another vital factor for identifying a high-color quality light source. In fact, the WLEDs with high CRIs also suffer the color inhomogeneity due to large color deviation (D-CCT). Hence, to achieve high color harmony, it is essential to attain the reduction in angular color variances. Figure 6 demonstrates the decrease of D-CCT when increasing the concentration of CaMn green phosphor layer. The green-light compensation and stimulated light scattering offered by the green phosphor layer lead to higher color uniformity. As can be seen, the D-CCT declines by about 250 K when there is 30% wt. concentration of CaMn. As mentioned above, the rise of CaMn concentration benefits not only the color uniformity but also the luminous flux, but somehow is an unfavorable factor to the CRI and CQS [17], [24], [25]. Thus, determining a suitable concentration of CaMn to use is crucial to the manufacturers. Here, after considering the optical factors of the LED model, the concentration of the green phosphor CaMn layer should remain below 9%wt. to achieve enhanced color uniformity and luminous flux while reaching good CQS above 60.

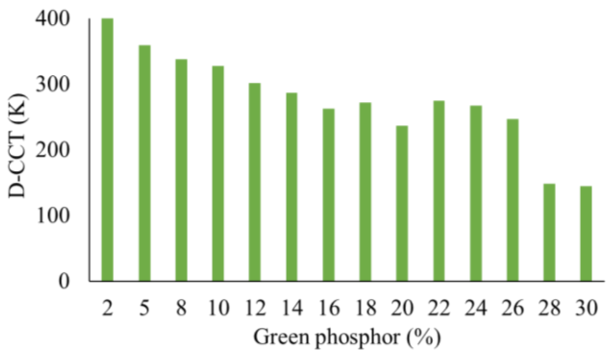


Figure 6. Color deviation of WLED structure corresponding to CaMn concentration

## 4. CONCLUSION

The green-emitting phosphor $Ca_8MgY(PO_4)_7:Eu^{2+},Mn^{2+}$ (CaMn) fabricated by solid-state method at high temperature is introduced to accomplish the enhancement of color fidelity and luminous efficiency for the double-layer remote phosphor WLED package. The proposed phosphor exhibits light red-shift from cyan emission color when adjusting the concentration of doped $Mn^{2+}$ ion. The benefits of using CaMn green phosphor is the reduction of backscattering for higher color uniformity and luminous output. The decrease CRI and CQS is also observed when increasing the content for CaMn layer, causing the dominance for green emission causing the color imbalance. The concentration CaMn must be lower than 9% wt. to achieve the enhancement in chromatic homogeneity and luminous flux while keeping the CRI and CQS above 60.

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