Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ green phosphor for optic enhancement of the WLEDs dual-layer remote structure

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**ABSTRACT**

To enhance the dual-layer remote phosphorus configuration’s color standard help spread its application in the LED devices, the new green-emitting phosphor of Ca$_2$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ is proposed. The sol-gel method is used to dope the Eu$^{2+}$ ions with Ca$_2$Si$_2$P$_2$O$_{16}$. Increasing the ion Eu$^{2+}$ concentration can lead to high thermal stability, color-tunable ability, stronger green emission band, and higher photoluminescence extraction. The dual-layer structure’s color standards, as well as the luminous flux, are examined with different concentrations of Ca$_2$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ in the phosphor layer. Owing to the improved features, the green phosphor Ca$_2$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ has enhanced the emission intensity in the blue and green wavelengths, resulting in better color mixing and distribution. The luminescence shows the enhancement when increasing the concentration of Ca$_2$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$. However, the color rendering feature can present a reduction with more than 10% wt. green phosphor within the double-layer phosphor remote configuration, due to color balance’s loss.

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1. INTRODUCTION

Phosphors have been widely utilized in white lighting-emitting diodes (WLEDs) production. The Ca$_2$Si$_2$P$_2$O$_{16}$ is a natural silicate phosphor that is somehow superior to the conventional sulfide phosphors in terms of light conversion performance, excitation spectra, and chemical stability. In addition to that, it is cost-efficiency as the raw ingredient for fabrication is affordable [1], [2]. Thus, Ca$_2$Si$_2$P$_2$O$_{16}$ silicate phosphor is potential material for producing WLED with high efficiency. However, the application of this phosphor has not been thoroughly analyzed, and its performance was not excellent enough for the high-demand WLED market. Besides, analysis of Ca$_2$Si$_2$P$_2$O$_{16}$ on the optical application is barely reported. Its use in the biological field was first demonstrated in the research of Chen et al. in 2012 [3]. It was shown that Ca$_2$Si$_2$P$_2$O$_{16}$ is a potential biomaterial for the periodontal tissue regeneration aspect because it can help increase the periodontal ligament tissues as well as osteoblast/cementoblast-like tissue variation.

One of the favorite ion-doped phosphor materials in this lighting industry is the Eu$^{2+}$-doped one since it has an excellent ability to absorb the blue-emitting LED chips then emit visible lights [4]-[6]. Moreover, Eu$^{2+}$-doped phosphors possess efficient luminous performance and high stability thanks to the distorted coordination surrounding the Eu$^{2+}$ ions provided by the rigid frameworks with covalent Si–O bonds [7]-[9]. Thus, other studies mentioned other silicate phosphor doped with this Eu$^{2+}$ ion such as (Ba$_1$, xSr$_x$)$_2$SiO$_2$:Eu$^{2+}$ with high red emission at 598 nm [10]-[13] Ca$_3$SiO$_3$Cl$_2$:Eu$^{2+}$ with orange light emitted [14].

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and Sr₅(PO₄)₃(SiO₄):Eu²⁺ generating green lights [15]. Hence, we decided to dope Eu²⁺ ion with silicate Ca₃Si₂P₂O₁₀₆ phosphor host to enhance the efficiency of this phosphor. In addition to that, we will apply this Ca₃Si₂P₂O₁₀₆:Eu²⁺ to the double-layer remote phosphorus configuration with the aim of achieving better color uniformity as well as luminous efficacy of WLEDs. The preparation of doping Eu²⁺ ions into the Ca₃Si₂P₂O₁₀₆ phosphor host is carried out with the sol-gel technique. The WLEDs modeling featuring double-layer remote configuration is designed with LightTools software and the Monte Carlo method. The luminescence properties, including the heat consistency as well as luminous efficacy of this phosphor, are examined and reported. Plus, the calculations of transfer energy and activation energy of this green-emitting phosphor are demonstrated. The color quality factor of dual-layer WLED, which is among the most critical objectives of the study, is also investigated with the presence of various concentrations of Ca₃Si₂P₂O₁₀₆:Eu²⁺.

2. COMPUTATIONAL MODEL
2.1. The green-emitting phosphor Ca₃Si₂P₂O₁₀₆:Eu²⁺ composing

The green-emitting phosphor Ca₃Si₂P₂O₁₀₆:xEu²⁺ with x from 0.01 to 0.07 is fabricated utilizing the sol-gel method. The chemical composition of this phosphor includes the calcium nitrate Ca(NO₃)₂·4H₂O, tetraethyl silicate (Si(OC₂H₅)₄, TEOS), NH₄H₂PO₄, Eu₂O₃, and chelating material – citric acid. It is possible to prepare of Ca₃Si₂P₂O₁₀₆:xEu²⁺ with x=0.05 via creating three different solutions, then mixing and firing them under certain conditions [16].

The first solution (1) is prepared by slurrying 0.2053 g of Eu₂O₃ in diluted nitric acid HNO₃. It is then blended with Ca(NO₃)₂·4H₂O (5.234 g) in a 99.5% citric acid liquid. After that, a stirring process is performed constantly at 80°C until obtaining the clear solution (1). Next, solution (2) is attained via a process of mixing 0.767 g NH₄H₂PO₄ in deionized-water nitric acid. Specifically, the ratio of nitric acid to the ions is 2:1. In (3) solution is formed by blending 1.389 g TEOS, diluted HNO₃, and ethanol altogether, and finally hydrolyzing it using the stirring method in 20–40 minutes.

After obtaining the three solutions, the solutions will be mixed and stirred at room temperature for a few hours. Then to stimulate the metal citrates to polymerize, the ethylene glycol, with the ratio to the citric acid of 4:1, is added. After that, the mixture is gradually heated to 100 °C, and fired at this temperature in the next 2 hours. Then, the product is taken out and placed in an oven for the drying process under 100 °C–150 °C for about 5–15 hours. After this process finishes, the attained product is porous solid resins that are treated under 1000 °C lasting 8 hours in the air. Finally, the product is well-mixed and put into a covered carbon-integrated crucible for 10-hour firing at 1300 °C [17].

2.2. Characterization of phosphor and simulation of the dual-layer WLED model

The attained Ca₃Si₂P₂O₁₀₆:Eu²⁺ has a broad range of absorption wavelengths of 300 – 450 nm, which implies that this green phosphor can absorb the UV-light and blue-light from LED chips (360 – 400 nm). It exhibits two wavelengths that peak at 520 nm and 650 nm with high emission intensity. Also, as the concentration of Eu²⁺ in the phosphor host increased, the red-shift in the spectral band presented a switch to the region of near-white color, from the yellowish-green one. The Eu²⁺ particles’ conversion of energy is responsible for this color transition. The Eu²⁺ power conversion (from 4f⁻ ground position to 4f⁵5d⁻ excited position) is generally deducted from the transition energy of the free ion. The relation of this energy transfer can be demonstrated in P. Dorenbos’ research [18]:

\[ E_{em} = E_{free} - D - \Delta S \]  

in which \( E_{free}\) describes the constant value of every lanthanide particle relative to the fd-shift power of the free (gaseous) lanthanide particles. Meanwhile, \( D \) presents the red-shift deducted energy. The thermal-quenching activation energy \( \Delta E \) of the Eu²⁺ emission could be calculated using the modified formula of Arrheniус [19]-[22]:

\[ I_p = \frac{I_0}{1 + c \exp \left(- \frac{\Delta E}{kT} \right)} \]  

Here, \( I_p \) indicates the prime emitting ferocity, \( I_0 \) shows the severity at various temperature points, \( \Delta E \) describes the heat absorption’s activation power, and \( c \) is fixed for a specific host, while \( k \) denotes the Boltzmann absolute (8.617 x 10⁻⁵ eV K⁻¹). The calculated \( \Delta E \) was at about 0.222 eV, and the luminescent emission of this Ca₃Si₂P₂O₁₀₆:Eu²⁺ has high thermal stability. Thus, this phosphor is potentially used in the WLED package to attain tunable color and thermal steadiness features.

Phosphor layers used for the simulation of the WLED package are mainly comprised of the phosphor particles and silicone matrix. The flat phosphor-silicone layer is designed using the LightTools 9.0.
software and the Monte Carlo experiment [23]-[25]. To manage to simulate the LED model, the beginning task will be defining the essential parts and structure them, then, the concentration of the used phosphor, which is Ca₇Si₂P₂O₁₆:Eu²⁺, will be adjusted to examine its influences on the scattering, absorption, transmittance, and extraction of lights in the phosphor layers or the WLED package. The change in this green phosphor amount probably stimulates the fluctuation of yellow phosphor YAG:Ce³⁺ concentration, presented in more detail in the next section. The simulated WLEDs are investigated with the dual-layer structure featuring an 8500 K correlating color temperature (CCT). The actual WLED built with conformal phosphor coating method is demonstrated in Figure 1. The reflector of the WLED model is designed at 2.07 m, 8 mm, and 9.85 mm, in the height and the length of the bottom and top surfaces, respectively. The layer of yellow phosphor placed over LED chips is 0.08 mm thick. There are nine blue emitting LED chips attached to the reflectors cave. Each of them has a radiant flux of 1.16 W along with 453 nm optical wavelength, and 1.14 mm² x 0.15 mm in size (square base x height).

![Figure 1. Photograph of WLEDs](image)

3. RESULTS AND ANALYSIS

Ca₇Si₂P₂O₁₆:Eu²⁺ concentration becoming higher causes the yellow phosphor concentration to decrease, as displayed in Figure 2. This trend sustains the stable CCT of the WLED during its operating hours. In addition to that, the reduction of the yellow phosphor percentage in the phosphor compound has significant effects on both the scattering and absorbing ability of the packages, from which the color uniformity and the optical extraction efficacy get remarkable results. Also, from Figure 2, the influence from the particle size of green phosphor Ca₇Si₂P₂O₁₆:Eu²⁺ is observed. The increasing size of this green particle would be proportional to the yellow phosphor’s concentration. As can be seen, the highest YAG:Ce³⁺ concentration is at nearly 9% when 5%wt. and 20μm of Ca₇Si₂P₂O₁₆:Eu²⁺ are applied. Conversely, at the same particle size but higher concentration of green phosphor of 20%wt., the concentration of the yellow phosphor declines considerably to lower than 3%wt.

![Figure 2. Modifying the phosphor’s concentration to preserve the average CCT](image)

The Ca₇Si₂P₂O₁₆:Eu²⁺ addition to the dual-layer WLED remote phosphorus package improves the lighting performance, as observed in Figure 3. Particularly, the spectral regions at 420 nm - 480 nm and 500 nm - 640 nm in the wavelengths (when the maximum sum powers are ~1 and ~0.4, respectively) show enhancements with the green Ca₇Si₂P₂O₁₆:Eu²⁺ phosphor presence, compared with the reference spectrum (the spectral regions at 380 nm - 420 nm when there is no power). That leads to the improved luminous output of the WLED. Also, the enhancement in the spectral intensity of the blue wavelength implies that the
scattering of blue beams is boosted or the scattered lights in the phosphor structures are promoted. This probably results in more uniformity of WLED color distribution. Therefore, the green phosphor Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ is able to manage the color quality of WLEDs even at high CCT, such as the 8500 K WLED structure in this study. The addition of Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ benefits the luminous flux, which is displayed in Figure 4. As can be seen, when the amount of Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ in the phosphor compounding increases from 2%wt. to 20%wt., the luminescence flux becomes higher, regardless of the particle sizes (5% increase for particle sizes from 5μm, 10% increase for particle sizes from 8μm, 15% increase for particle sizes from 12μm and 20% increase for particle sizes from 17μm). The luminous flux is getting better when compared to the initial data (just tiny increase percentages for particle sizes smaller than 5μm).

Figure 3. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the 5000 K WLEDs emitting spectrum

![Figure 3. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the 5000 K WLEDs emitting spectrum](image)

Figure 4. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the WLEDs luminous flux

![Figure 4. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the WLEDs luminous flux](image)

Generally, the improvement in the luminous flux would be in reversed proportion to the color quality of the phosphor-converted WLED. Thus, if the procedure of LED fabrication focuses on the enhancement of color harmony of white light, a certain reduction in luminous flux can be acceptable. This also indicates that the selection of phosphor Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration is necessary for controlling both color adequacy and lumen efficiency at high levels. The change in concentration of Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ green phosphor does impact the chromatic properties of white lights, which is illustrated from Figure 5 to Figure 7.

Figure 5. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the WLEDs color deviation

![Figure 5. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the WLEDs color deviation](image)
Figure 6. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the WLEDs color rendering index

In Figure 5, the color deviation (D-CCT), one of the parameters to evaluate the chromatic homogeneity of the white light, decreases when the percentage of the green phosphor in the phosphorus layer increases. Compared to the D-CCT at 2%wt., when using 20%wt. of Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ this figure is reduced by approximately 500 K. The reduction in color variance results in better color uniformity. This benefit results from the enhanced scattering and absorption performance owing to the presence of the Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ phosphor layer. As mentioned above, the scattering of blue lights is enhanced not only benefits the luminance flux but also stimulates color blending, leading to higher uniformity. Additionally, the absorption characteristic of this green phosphor allows it to absorb the blue and yellow emitting lights from blue chips allowing the phosphor layer to convert these lights into the green-light elements. Notably, the blue-light absorption of this Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ is better than its yellow-light absorption. Therefore, the green emission becomes stronger, and more green beams are generated, which is beneficial to the color homogeneity metric of LED lights. Besides, the use of Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ can offer cost-efficiency fabrication since it has a lower price than many other phosphor materials. Hence, the manufacturers can apply this green phosphor in large-scale production.

Figure 7. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration functions as the WLEDs color quality scale

Besides color uniformity, two other important metrics should be analyzed when it comes to color-quality evaluation. The color rendering indices, which evaluate an item’s color faithfulness revealed under a lighting source in comparison with the natural light, slightly decrease when there is a higher amount of Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ in the phosphor film, demonstrated in Figure 6. This is probably attributed to the color imbalance caused by the green-light dominance. Particularly, the excessive rise of the Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration leads to the redundancy in the green color element, which is higher than the blue and yellow color ones and thus degrading the chromatic fidelity of the WLED light. However, this insignificant reduction in CRI would become accepted as CRI is somehow not an overall index of chromatic assessment. Recent studies have pointed out that CRI is a factor of another metric of color evaluation, the CQS. It includes two other factors, besides the CRI, the visual preference of the human, and the color coordinate. Thus, the CQS is considered the best parameter to examine the color quality of a light source. As in Figure 7, the CQS increases with the rise of the Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ concentration from 2% wt. to 10% wt. More than 10% wt. Ca$_7$Si$_2$P$_2$O$_{16}$:Eu$^{2+}$ will result in the reduction of both CRI and CQS due to the influence from the redundant green-color element. To obtain high and consistent CRI and CQS, the appropriate amount of green phosphor is suggested to be defined properly, for example, below 10% wt.
4. CONCLUSION
The paper proposes Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ as a new phosphor material for the dual-layer remote WLED structure to enhance its color quality and luminous efficacy. Ca$_2$Si$_3$P$_5$O$_{16}$ is doped with ion Eu$^{2+}$ using the chemical sol-gel technique. This phosphor has a broadband of absorption (300 – 450 nm), leading to the ability to be compatible with the near-UV-chip light emission. The Eu$^{2+}$-doped concentration dramatically affects the light features in this phosphor. Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ performs high luminescent thermal stability, and two peak wavelengths of 520 and 650 nm with high emission energy. After increasing the green phosphor Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ concentration to 20% wt., the green-emitting phosphor Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ would raise the luminous efficiency substantially when placed in the double-layer configuration. It is possible to improve the color uniformity via raising Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ amount since the higher the phosphor concentration is, the more the color deviation is reduced, and the higher the chromatic homogeneity becomes. As the green phosphor concentration is fewer than 10% wt., the double-layer configuration CRI and CQS show stability and enhancement. A higher concentration (> 10% wt.) of Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ probably reduces the color quality owing to the color imbalance caused by the excessive green light components in the package. Hence, identifying the proper Ca$_2$Si$_3$P$_5$O$_{16}$:Eu$^{2+}$ concentration is critical, based on the needs and objectives of the WLED producers.

REFERENCES
BIOGRAPHIES OF AUTHORS

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