Impacts of Eu$^{2+}$-doped K$_3$LuSi$_2$O$_7$ phosphor and a scattering particle on conventional white light emitting diodes

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ABSTRACT

The K$_3$LuSi$_2$O$_7$ phosphor doping Eu$^{2+}$ rare-earth ions (KLS:Eu) was reported to possess broad emission band from near-ultraviolet to near-infrared. Additionally, this phosphor showed a wide absorption band of 250-600 nm, allowing it to be excited by blue-light chip of 460 nm, making it one of the suitable phosphor materials for a light emitting diode (LED). Besides, the scattering particle material CaCO$_3$ is incorporated into the yellow phosphor layer to serve the scattering-enhancement purpose. The combination of both materials aims at accomplishing improvements in performance of commercial LED package. The concentration of KLS:Eu is constant while that of CaCO$_3$ is modified. As a result, the scattering factor is regulated and become the key factor influencing the optical outputs of the simulated LED. The increasing CaCO$_3$ concentration enhances the phosphor scattering efficiency of light, helping to improve the lumen output and color-temperature consistency of the LED. However, the color rendering performance declines as a function of the CaCO$_3$ growing amount, despite the presence of a KLS:Eu phosphor layer. Further works should be done to optimize the application of KLS:Eu in cooperation with scattering particles for a higher-quality LED device.

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1. INTRODUCTION

The light emitting diodes (LEDs) of solid-state lighting sources which broad emission bands have been utilized in many fields such as commercial and industrial lighting, display, transportation, medical and biological solutions [1], [2]. The reasons making LEDs popular can include compactness, mercury-free production, long-time services, and low heat dissipation, compared to the conventional halogen light. To fabricate a package of LED, it commonly uses the cooperation of single or multiple phosphor materials and a blue, near-ultraviolet, or near-infrared chip cluster, depending on the application requirements [3]–[5]. This type of LED is also known as phosphor-converted LEDs. The conventional commercial LED utilized the YAG:Ce$^{3+}$ yellow phosphor and blue-pumped chip to generate white light. The high luminescence of this package was recognized but the color uniformity and rendition were noticeably low as the red spectrum was not presented in the visible wavelength band of the white light. Besides, the phosphor is often degraded due to humidity and heat exposure, leading to shorter service life and decreasing efficiency [6]–[8]. Therefore, investigations on developing phosphors with broadband emissions for high-quality LED modules have been extensively carried out.
Researches have interested in the rare-earth or metal ions, such as Pr$^{3+}$, Nd$^{3+}$, and Tm$^{3+}$ or Ni$^{2+}$, as dopants for inorganic hosts. Nevertheless, the 4f-4f transitions of these rare-earth ions result in sharp but narrow emission while presenting weak absorbance, which does not satisfy the various applications in sensing technology field. Besides, the Ni$^{2+}$ metal ion can achieve broadband emission in the near the near-infrared area, however, its efficiency is inferior. Unlike the rare-earth ions with 4f-4f transition, it is possible to obtain high efficacy, broad, and tunable emission with the Eu$^{2+}$ owing to its 4f-5d transition. Generally, the crystalline environment of the host material primarily influences the emission energy distribution of the Eu$^{2+}$ ions, including the bond lengths, the number of coordination, and the cation symmetries [9]. To get the broader emission band for Eu$^{2+}$-doped phosphors, especially in the near-infrared region for high-efficiency sensing devices, it is essential to strengthen the crystal field splitting and enhance the Eu$^{2+}$-originated centroid shift. A previous study showed that in the red-emission Rb$_{2}$YSi$_{2}$O$_{7}$:Eu$^{2+}$, the Eu$^{2+}$ tended to occupy the cation site having small coordination number, leading to large redshift and higher probability of stronger crystal field splitting to achieve the near-infrared emission for the phosphor [10]. Accordingly, when replacing ions Y$^{3+}$ and Rb$^{3+}$ with smaller ions Lu$^{3+}$ and K$^{+}$, it is possible to further induce the crystal-field-splitting strength [11], [12].

Besides, the commercial LED device confront the low light distribution uniformity as the light concentrated at the center of the LED. This drawback can be attributed to the inferior scattering of incident and converted light, leading to high color temperature of the generated white light, limiting the utilization of the LED device in general lighting aspects. The scattering factor plays a critical role in the angular uniformity of light distribution, which is a desirable property to diminish the yellow-ring phenomenon [13]. Among various methods of enhancing scattering of the phosphor layer, using the scattering particles caught significant attention from researchers. Articles presented that the CaCO$_{3}$ particle is the one inducing the greatest luminous flux of the phosphor-converted LED compared to other scattering particles such as TiO$_{2}$ or CaF$_{2}$ [14], [15]. Henceforth, this paper utilizes the Eu$^{2+}$-doped K$_{2}$Lu$_{2}$Si$_{2}$O$_{7}$ (KLS:Eu) for the commercial LED fabrication and CaCO$_{3}$ particle for scattering regulation. The effects of KLS:Eu phosphor and CaCO$_{3}$ material on the transmission power, scattering events, luminous and chromatic properties of the prepared LED are investigated and demonstrated. It indicates that the KLS:Eu phosphor can contribute to enhancing the yellow-to-orange emission band of the LED and high dosage of CaCO$_{3}$ can improve the conversion of blue light from yellow-red light of the phosphor layers. The luminous strength of the LED and the color-temperature consistency of the LED show improvements, but the chromatic rendition is lowered when the concentration of CaCO$_{3}$ increases and of KLS:Eu phosphor is constant. The phosphor and scattering particle are promising for LED model require improved luminous efficiency and color uniformity.

2. METHOD

The phosphor KLS:Eu was synthesized via the solid-state reaction route consisting a high-temperature (1,350 degrees Celsius) sintering phase in 80%N$_{2}$/20%H$_{2}$ atmosphere. The materials for the synthesis include K$_{2}$CO$_{3}$, Lu$_{2}$O$_{3}$, SiO$_{2}$, and Eu$_{2}$O$_{3}$, all of which are grounded and mixed stoichiometrically. The sintering phase was conducted with the mixture in an alumina crucible for 6 hours. The obtained product was cooled down to room temperature for the next investigations. The LED structure using KLS:Eu phosphor is shown in Figure 1. The real model of the prepared LED is presented in Figure 1(a). The remote phosphor structure was applied for incorporating the red phosphor and CaCO$_{3}$ particles to optimize the luminous output of the LED, as depicted in Figure 1(b). The CaCO$_{3}$ particles were incorporated into the yellow phosphor layer with the concentration ranging from 0 wt% to 50 wt%. The KLS:Eu phosphor concentration was fixed, and the layer did not include CaCO$_{3$} particle. Figure 1(c) is the 3D simulation obtained using the LightTools software version 9.0. Figure 1(d) depicts the LED chip cluster in which the utilized chips have radiant flux of 1.6 W and blue emission centering at around 460 nm [16]. The photoluminescence spectra of the LED device with CaCO$_{3}$ and KLS:Eu phosphor were collected using the NOVA fiber fiber spectrophotometer with 460 nm blue-chip excitation source. The stability and robustness of the phosphor when using in the LED is crucial as the internal temperature of the LED can reach 100 °C. The phosphor was tested under 80 °C and exhibited good chemical stability as the Eu$^{2+}$ was barely changed to the Eu$^{3+}$ after a long exposure. Besides, when the heat was increased from room temperature to more than 100 °C, the luminescence intensity of the phosphor decrease, by about 41% when temperature arrived to 150 °C. The thermal quenching effect may be attributed to this phenomenon, which can be examined using the thermal activating energy ($E_u$) based on Dorenbos work [17]:

$$E_u = \frac{T_w}{680} \text{ eV}$$

(1)
Where $T_q$ represents the thermo-quenching temperature. The thermo-quenching temperature is the temperature when emission intensity is about 50% of the room-temperature intensity. On the increasing of temperature, the blue shift in the emission peaks of the KLS:Eu phosphor was observed. This can be ascribed to the larger crystal field splitting of Eu$^{2+}$ in K$^+$ and Lu sites causing the smaller $E_a$ values. Thus, as the heat increases, the phosphor emission intensity at shorter wavelengths is stronger. The KLS:Eu phosphor can be well excited by the blue-chip excitation (460 nm) as its absorption band was obtained in a wide region of 250-600 nm owing to the 4f-5d transition of Eu$^{2+}$ ions occupied K and Lu sites in the K$_3$LuSi$_2$O$_7$ host. Additionally, with this wide-band absorption, the phosphor can exhibit deep red color when observing under natural light. This implies that the phosphor can provide the red spectra for the white light [18].

![Image](image.png)

Figure 1. Commercial LED model: (a) photo of a prepared LED package, (b) cross-section of the LED package, (c) simulation model by LightTools software, and (d) the chip cluster in the LED

3. RESULTS AND DISCUSSION

The transmission spectra of LED in the presence of the KLS:Eu phosphor can be seen in Figure 2, in which the concentration of CaCO$_3$ varies in a range of 0-50 wt%. All the sub figures show two eminent emission peaks centering at ~460 nm and ~560 nm and a minor peak at around 740 nm. These peaks could be emerged from the blue chips, the YAG:Ce phosphors, and the KLS:Eu phosphor, respectively. The insignificant peak at 740 nm in the emission range indicates that the KLS:Eu is somehow activated by the blue radiation from the LED chips but does not contribute much to the formation of white light. This can be attributed to the arrangement of phosphor layer in the simulation, in which the KLS:Eu is above the YAG:Ce/CaCO$_3$ phosphor layer. Such an arrangement could limit the LED-chip blue light interacting directly with the second phosphor layer, leading to the weaker emission.

On the increase of CaCO$_3$, there is no shift noticed in the emission band but the intensity. As the added amount of CaCO$_3$ increases, the intensity of the 460-nm peaks declines while that of the 560-nm peak increases. With CaCO$_3$ concentration of 10 wt%, the peak intensity does not change much, featuring that the 460-nm peak is greater than the 560-nm one. When the dosage of CaCO$_3$ reaches 30-35 wt%, two peaks are relatively equivalent. However, as CaCO$_3$ amount is beyond 35 wt%, the 460-nm peak starts to decline while the 560-nm noticeably increases, indicating the more effective blue-light utilization in the LED package. In other words, the observed increase in the yellow-orange region (520-590 nm) can be attributed to the efficient light conversion of the yellow phosphor YAG:Ce phosphor with higher CaCO$_3$ concentrations. On the other hand, with the addition of CaCO$_3$ particles, the concentration of YAG:Ce phosphor must be adjusted to support the stability of color temperature. Figure 3 shows the decline in YAG:Ce phosphor amount in response to the increase in showing the potential of CaCO$_3$ dosage. This decrease also attributed to the luminescence peak (560 nm) observed in green region [19].
The change in the emission peaks’ intensities when adding KLS:Eu phosphor with different amounts can be induced by the change in scattering performance of the light in LED package. We determined the scattering coefficients (SCs) and reduced scattering coefficients (RSCs) of the LED to see the effect of CaCO₃ amount on the scattering efficiency, as shown in Figures 4 and 5, respectively. In Figure 4, the SCs increases gradually when the CaCO₃ concentration increases gradually by a small of 5 wt% in each case (from 5-25 wt%, as shown in Figure 4(a)). However, as the CaCO₃ amount significantly surges to 50 wt%, the SCs value also grows noticeable, showing about 12.5 times greater than that with CaCO₃ amount at 5 wt% as shown in Figure 4(b). In terms of the RSCs, the increase between 5-15 wt% CaCO₃ is not much, just about 0.12 mm⁻¹ in each case as shown in Figure 5(a). However, the difference in RSCs becomes larger as the CaCO₃ amount increases further, especially at 380 nm wavelength, reaching 3 times and 6 times larger with CaCO₃ amount of 30 wt% as shown in Figure 5(a) and 50 wt% Figure 5(b) respectively. The introduction of CaCO₃ particle generally increase the scattering performance as all values go upward as the phosphor concentration increases [20]–[22]. Such phenomena help promote the forward scattering and conversion effectiveness of blue light. However, when the CaCO₃ increases, more blue light will be observed and converted into yellow light, so the intensity of the blue (460 nm) peak tends to decrease while that of the yellow (560 nm) peak is supplemented.

The luminous performance of the blue-pumped LED when using different amounts of CaCO₃ is demonstrated in Figure 6. Interestingly, the luminous flux intensity becomes stronger as the concentration of CaCO₃ increases, showing the potential of CaCO₃ in achieving better light extraction efficiency for the remote phosphor structure. Meanwhile, the color rendering index (CRI) decreases with the increasing dosage of CaCO₃ scattering particle, as shown in Figure 7. Referring to Figure 2, the presence of KLS:Eu phosphor does not contribute much to enhancing the visible red spectrum as it exhibits the emission peak at 740 nm in the near-infrared range. The high visible red-light energy is the key to significantly improved CRI value of the white LED. As a result, though the CaCO₃ at higher amount increase the scattering of blue light and better light conversion by the phosphors, the lack of visible red spectrum is not addressed to get higher CRI for the as-prepared LED.
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To verify the decline of color rendition in the presence of CaCO₃, we calculate the color quality scale (CQS), which is a newer color-evaluation parameter for LED light. The CQS can assess critical categories to give a more accurate result. Those categories include CRI, color coordination, and visual preferences of subjects. When the CaCO₃ is introduced and its concentration increases, the CQS values in Figure 8 gradually drop, which further confirm the insufficient red component in the visible white-light emission. The dominant yellow-light amount could be the cause for the CRI and CQS decreases as well as lumen-output increase. The high-intensity luminosity favors the monochromatic light as well as high blue-light emission. On the other hand, the high color-rendering performance requires broad band emission with sufficient red-light energy to give the optimal chromatic fidelity [23], [24]. Therefore, the KLS:Eu addition at high concentrations leads to the enhancement in the LED’s lumen output and the decline in CQS and CRI. Such findings also imply the improvement in color-temperature uniformity of the LED when using CaCO₃ with high amount in combination with KLS:Eu phosphor layer. The angular color temperature (A-CCT) and color deviation (D-CCT) as a function of increasing KLS:Eu concentration can be observed in Figures 9 and 10, respectively [25]. Overall, at 0° viewing angle, the A-CCT gradually declines when the concentration of KLS:Eu increases. Additionally, the D-CCT in cases of high KLS:Eu concentration is generally lower compared to that when KLS:Eu concentration is at 0 wt%. The lowest D-CCT is recorded with 35 wt% KLS:Eu. These results demonstrate the ability to enhance the luminous performance and reduce the D-CCT to get better color-temperature uniformity. It also indicates the need to modify the KLS:Eu compound to achieve stronger red-emission energy for the LED package require excellent color rendering efficiency.

Figure 5. Reduced scattering coefficients as a function of increasing CaCO₃ amount (a) CaCO₃ by 30% and (b) CaCO₃ by 50%

Figure 6. The LED lumen output as a function of increasing CaCO₃ amount

Figure 7. The CRI as a function of increasing CaCO₃ amount in the presence of KLS:Eu phosphor layer
4. CONCLUSION

The paper used Eu$^{2+}$-doped K$_3$LuSi$_2$O$_7$ phosphor and CaCO$_3$ scattering particles in commercial LED package to get improvements in the performance. The concentration of KLS:Eu is constant while that of CaCO$_3$ is modified as a mean to regulate the scattering factor of the as-prepared LED’s remote phosphor structure. On the increasing CaCO$_3$ concentration, the scattering efficiency of light enhances, allowing to achieve better blue-light utilization by the phosphor layer. As a result, the lumen output and color-temperature consistency of the LED improve with higher CaCO$_3$ amounts. However, the CRI and CQS performances decrease in response to the higher amount of CaCO$_3$, despite the presence of a KLS:Eu phosphor layer. For a higher-quality LED device and a wider application range of the phosphor-converted LED, further works should be done to optimize the application of KLS:Eu in cooperation with scattering particles, such as structure re-arrangement or phosphor compound modification.

REFERENCES

BIOGRAPHIES

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