Hue dual-chromatic calcium chlorosilicate phosphor for lightemitting diode having yellow and white illumination

Huu Phuc Dang¹, Bui Van Hien², Nguyen Le Thai³

¹Institute of Applied Technology, Thu Dau Mot University, Binh Duong Province, Vietnam ²Faculty of Mechanical - Electrical and Computer Engineering, School of Engineering and Technology, Van Lang University, Ho Chi Minh City, Vietnam

³Faculty of Engineering and Technology, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

Article Info

Article history:

Received Nov 28, 2021 Revised Jul 11, 2022 Accepted Aug 19, 2022

Keywords:

Color quality scale Luminescence Mie theory White light-emitting diodes YAG:Ce

ABSTRACT

High-thermal solid phase reactions produced a series of bright green-yellow phosphors called Ca₃SiO₄Cl₂,Eu²⁺,Mn²⁺ (CaM). For example, powder dispersed reflection, photoluminescence excitation (PE), and along with emission spectra, were used to determine their luminous characteristics at between 10 K and 450 K of temperature. While the CaM exhibits wide absorption bands in the 250-450 nm range, which matches the near-uv of the InGaN-based chips, they also display two dominant absorptions, attributed to the 5d \rightarrow 4f Eu²⁺ transformation, as well as the ${}^{4}T_{1g}({}^{4}G) \rightarrow {}^{6}A_{1g}({}^{6}S)$ transfer of the two ions Eu2+ and Mn2+, respectively. Increasing the concentration of Mn²⁺ ion reduces the lifespan of the Eu²⁺ ion. This encourages an efficient energy exchange between these two ions. The UV light leakage issue in yellow LEDs was resolved by intergrating with n-UV InGaN chips and CaM. Powerful white LEDs were then created by mixing blue chlorophosphate with CaM. Its color coordinate was (0.3281,0.3071), and the associated color temperature (TC) was 6065 K, while the general hue rendering (Ra) and illuminating effectiveness (11 lm/W) were respectively 84.5 and 11 lm/W.

This is an open access article under the <u>CC BY-SA</u> license.



Corresponding Author:

Bui Van Hien

Faculty of Mechanical-Electrical and Computer Engineering, School of Engineering and Technology Van Lang University, Ho Chi Minh City, Vietnam Email: hien.bv@vlu.edu.vn

1. INTRODUCTION

A new revolution in lighting has occurred with the introduction of white light-emitting diodes (WLEDs), which have superior characteristics than conventional incandescent or fluorescent lights [1], [2]. It is possible to manufacture white LEDs in a variety of methods. Photoluminescence excitation (PC-wLED) which may be divided into two categories: blue (440-470 nm) and n-UV (390-410 nm) InGaN chips coupled with down-converting phosphors. YAG:Ce³⁺ (yellow) is a typical downconverting phosphor for InGaN chips in blue color [3]. Because red emission is rare with such white LEDs, the certainty of response index (CRI) (R_a 80) is poor. It's worth noting, as well, that white LEDs based on the blue InGaN semiconductor have a low color consistency when mass-produced. Since it has a greater output, the n-UV LED is believed to be more reliable and efficient. It is important to understand that the n-UV LED usually produces wavelengths less than 400 nm, which has minimal influence on PC-wLED chromaticity coordinate. Because of its high applicability, it's predicted that these LEDs will be widely used in solid-state lighting [4], [5]. A number of phosphors have been studied. The downside is that they have a poor down-converting effectiveness, weak chemical and thermal stability, or severe synthesis settings. As a result of their high

D 725

luminous efficacy, low synthesis heat, and physical chemistry durability, Eu^{2+} -activated chlorosilicates have recently received greater interest from researchers [6]-[8]. An orange-yellow phosphor made from Ca₃SiO₄Cl₂,Eu²⁺,Mn²⁺ (CaM) (green) was created by Liu and colleagues in 2005, however its CRI was poor due to a lack of blue or green component. There is a set of strong green/yellow dual-chromatic phosphors called CaM described in this study. Methodically, the very effective resource transmit among Eu^{2+} and Mn^{2+} ions was investigated in great detail. It was also possible to produce strong yellow LEDs with minimal UV leakage and high bottom efficiency along with optimal CRI and luminance efficiency WLEDs based on CaM, which is a breakthrough [9]-[11].

2. EXPERIMENTAL DETAILS

To make CaM powder, a solid-state process was at high temperatures was applied. CaCO₃, CaCl₂, SiO₂, and MnCO₃ (99.99%) were used as source materials. All raw ingredients were mixed and grounded in ratios 2:1:1.1 of CaCO₃, SiO₂, and CaCl₂ with the a small addition of Eu₂O₃ and MnCO₃ in an agate mortar and pestle. For 4 hours, they were maintained at 1123 K in 25% H₂/75% N₂ environment for 4 hours before being removed from the corundum crucible. Finally, samples were gently cooled to ambient temperature in a nitrogen environment within the tube furnace after they had been produced. Describes the solid-state process that produced Y₃Al₅O₁₂:0.06Ce [12], [13]. Powder scattering spectra, Eu²⁺ single doped specimens, and Eu²⁺-Mn²⁺-codoped ones. High reflection of phosphor is strong from 350 to 800 nm, and then drops drastically to 200nm owing to host absorption. On the basis of Figure 1, we may calculate that the low-energy side of the host absorption is about 5.4 eV. There are two wide bands that result from the 4f–5d electronic dipole that allow conversions of Eu²⁺ ions when it is doped singly into the host. There are two wide bands that result from the 4f–5d electronic dipole that allow conversions of Eu²⁺ ions (4f6-5d) when it is doped singly into the host. CaM has a similar spectrum, with the exception of the increased absorption. Metal–ligand charge carrier band of Mn²⁺–O₂ along with prohibited transitions of Mn²⁺ ion may also contribute to enhanced absorption intensity in the 250-550nm range.

A dual exponential equation gives a good match to all decay graphs [14].

$$I(t) = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2}$$
(1)

A and B represent the constants, while I_0 and I indicate the luminescence intensities at time zero. The duration of the exponential contents are written as τ_1 and τ_2 .

Following is a formula for calculating the power transmission efficiency (η_T) from Eu²⁺ to Mn²⁺ [15]:

$$\eta_T = 1 - I_d / I_{d0} \tag{2}$$

when the donor Eu^{2+} ion is absent from Mn^{2+} , I_{d0} and Id are the respective intensities of donor Eu^{2+} ions. At the same time, there is also an energy transfer efficacy, written as η_T . When the concentration of Mn^{2+} dopant increases, so does the energy transfer efficiency η_T until it reaches saturation [16], [17]. This is quite similar to the $Ce^{3+} \rightarrow Eu^{2+}$ of $BaZnS_3$.

3. RESULTS AND ANALYSIS

According to Figure 1, there is a reversal change in the ratio of green CaM to yellow YAG:Ce³⁺. Aside from maintaining the average CCTs, this modification also influences the absorption and scattering in WLEDs with double phosphors. This has a direct influence on the hue richness and lighting beam performance of WLEDs. As a consequence, the hue fidelity of WLEDs is specified by the phosphor's concentration. When the CaM was increased to 20%, YAG:Ce³⁺ concentration decreased for keeping average CCTs [18]-[20]. The same is true for WLED models having the CCT area of 5600-8500 K.

According to Figure 2, green CaM dosage affects the transmittance spectrum of white LEDs. A variety of options are available, depending on the requirements of the producers. A WLED aiming to acquire higher chromaticity is allowed to decrease its flux intensity slightly. Figure 2 also demonstrated that the white light consists of several spectral regions, primarily 420-480 nm and 500-640 nm. 5600 K, 6600 K, 7700 K, 7700 K and 8500 K spectra are shown in these five figures in the order listed. As can be seen, the intensity of light in two regions (420-480 nm and 500-640nm) tends to increase with the phosphor's dosage. As the two-band spectrum expands, the luminous flux rises. The blue-light dispersion in the phosphorous film and in WLEDs has risen, which means that color consistency will be preferred. When using CaM, this is a critical outcome. In particular, it is challenging to regulate the color homogeneity of the distant-phosphor arrangement at great values of WLED's CCT. From the presented finding in this study, CaM can boost the

hue standard of WLEDs, even at low color (5600 K) or elevated hue heats (8500 K) [21].

The efficacy of luminosity from the simulated two-film distant phosphor is displayed to affirm the benefit of using CaM phosphor. According to Figure 3, CaM-concentration increases (2-20% wt.) obviously result in the substantially increased luminous flux. When CaM concentrations were increased in all three median CCTs, hue divergence was considerably reduced, as seen in Figure 4. This can be explained by the red phosphor's absorption. It's the CaM that absorbs and turns the original blue color from the LED chip into green illumination. Additionally, the CaM also absorbs yellow light in extra to the blue coming from the LED chip. According to the absorbing characteristics of phosphor particles, the blue light is easier to be absorbed than the yellow light; in other words, the blue-radiation absorption is more significant than the other. In WLEDs with the existence of CaM, this leads to more green-light elements to be generated, promoting the uniform color distribution, which is regraded as a critical feature for high-fidelity WLEDs. Therefore, the white light that has great ability to re-create the object's colores faithfully probably adds more value to the WLED lamps and contributing to increasing these illuminating devices' prices. CaM phosphor utiluzation is beneficial to the production cost, meaning that CaM is broadly applicable.



Figure 1. Modifying the dosage of phosphor to preserve the mean CCT



Figure 3. The luminous flux of WLEDs as a function of CaM dosage



Figure 2. The emitting spectra of 7000 K WLEDs as a function of CaM dosage



Figure 4. The color deviation of WLEDs as a function of CaM dosage

Besides the hue uniformity, to get the better fidelity of white light for the WLED, the color rendition intent is also imperative. This means the WLED with good chromatic fidelity needs both adequate chromatic uniformity and great color rendition efficiency [22]-[24]. The color rendering index, shortened as CRI, one of the most used metrics for assessing an object's ability to disclose its actual color when illuminated by a tested light source. Besdies, as the CRI was reported to display a mismatch in the results, the color quality scale, abbreviated as cultural intelligence scale (CQS), was invented for overing coming such a drawback. This article examines both CRI and CQS for the color re-cration efficiency of the WLED's white light when using CaM green phosphor, as displayed in Figure 5 and Figure 6, respectively. If the green light proportion is excessive to dominate the distribution on the chroma scale, the other primary colors (blue, yellow, and orange-red) will be shortage, leading to the degraded color fidelity. In Figure 5, CRI shows a continuous decline as the concentration of CaM rises, due to the mentioned reason. In cases of the CQS, in Figure 6, we can observe an increase as the concentration of green-phosphor CaM is from 2-10% wt. The increase in CQS

can outweigh the effect of decreasing CRI because CQS covers the CRI, color coordination, and observer's preference. This means it is more significant and requires more effort to achive the adequate CQS [25]. These three essential elements make CQS a close approximation of a genuine color quality index. As seen in Figure 6, CQS is boosted in the presence of the distant CaM layer. The concentration has no effect on CQS, and the concentration is less than 10% wt has no effect on CQS. There is a severe color loss when green dominates when CaM concentrations are greater than 10% wt. If you want to use green phosphor CaM, the right concentration is necessary.





Figure 5. The color rendering index of WLEDs as a function of CaM dosage

Figure 6. The hue quality scale of WLEDs as a function of CaM dosage

4. CONCLUSION

A sequence of bright yellow phosphors, CaM, has been discovered and described. Because of their broad absorption band and adjustable emission, as well as their high efficiency energy transfer between the ions, they have good color stability with rising temperature. In contrast, the CaM yellow LED has considerably lower UV leakage than the yellow LED based on CaM. Its specifications: 0.3281, 0.3071; 6065 K; 84.5 lm/W; and 11 lumens per watt (lm/W).

ACKNOWLEDGEMENTS

This study was financially supported by Van Lang University, Vietnam.

REFERENCES

- J. Cheng *et al.*, "Luminescence and energy transfer properties of color-tunable Sr4La(PO4)30: Ce3+, Tb3+, Mn2+ phosphors for WLEDs," *Optical Materials Express*, vol. 8, no. 7, pp. 1850-1862, 2018, doi: 10.1364/OME.8.001850.
 J. Li, Y. Tang, Z. Li, L. Rao, X. Ding, and B. Yu, "High efficiency solid–liquid hybrid-state quantum dot light-emitting diodes,"
- [2] J. Li, Y. Tang, Z. Li, L. Rao, X. Ding, and B. Yu, "High efficiency solid–liquid hybrid-state quantum dot light-emitting diodes," *Photonics Research*, vol. 6, no. 12, pp. 1107-1115, 2018, doi: 10.1364/PRJ.6.001107.
- [3] Y. Peng, et al., "Flexible fabrication of a patterned red phosphor layer on a YAG:Ce3+ phosphor-in-glass for high-power WLEDs," Optical Materials Express, vol. 8, no. 3, pp. 605-614, 2018, doi: 10.1364/OME.8.000605.
- [4] K. Werfli *et al.*, "Experimental demonstration of high-speed 4 × 4 imaging multi-CAP MIMO visible light communications," *Journal of Lightwave Technology*, vol. 36, no. 10, pp. 1944-1951, 2018, doi: 10.1109/JLT.2018.2796503.
- [5] J. Cheng et al., "Luminescence and energy transfer properties of color-tunable Sr4La(PO4)3O:Ce3+,Tb3+,Mn2+ phosphors for WLEDs," Optical Materials Express, vol. 8, no. 7, pp. 1850-1862, 2018, doi: 10.1364/OME.8.001850.
- [6] C. Zhang, L. Xiao, P. Zhong, and G. He, "Photometric optimization and comparison of hybrid white LEDs for mesopic road lighting," *Applied Optics*, vol. 57, no. 16, pp. 4665-4671, 2018, doi: 10.1364/AO.57.004665.
- [7] Z. Zhao, H. Zhang, S. Liu, and X. Wang, "Effective freeform TIR lens designed for LEDs with high angular color uniformity," *Applied Optics*, vol. 57, no. 15, pp. 4216-4221, 2018, doi: 10.1364/AO.57.004216.
- [8] Z. Wen et al., "Fabrication and optical properties of Pr3+-doped Ba (Sn, Zr, Mg, Ta) O3 transparent ceramic phosphor," Optics Letters, vol. 43, no. 11, pp. 2438-2441, 2018, doi: 10.1364/OL.43.002438.
- [9] C. J. C. Smyth, S. Mirkhanov, A. H. Quarterman, and K. G. Wilcox, "27.5 W/m2 collection efficiency solar laser using a diffuse scattering cooling liquid," *Applied Optics*, vol. 57, no. 15, pp. 4008-4012, 2018, doi: 10.1364/AO.57.004008.
- [10] Z. Song, T. Guo, X. Fu, and X. Hu, "Residual vibration control based on a global search method in a high-speed white light scanning interferometer," *Applied Optics*, vol. 57, no. 13, pp. 3415-3422, 2018, doi: 10.1364/AO.57.003415.
- [11] C. McDonnell, E. Coyne, and G. M. O'Connor, "Grey-scale silicon diffractive optics for selective laser ablation of thin conductive films," *Applied Optics*, vol. 57, no. 24, pp. 6966-6970, 2018, doi: 10.1364/AO.57.006966.
- [12] S. R. Chung, C. B. Siao, and K. W. Wang, "Full color display fabricated by CdSe bi-color quantum dots-based white lightemitting diodes," *Optical Materials Express*, vol. 8, no. 9, pp. 2677-2686, 2018, doi: 10.1364/OME.8.002677.
- [13] Y. Wang, "Tunable white light emission of an anti-ultraviolet rare-earth polysiloxane phosphors based on near UV chips," *Optics Express*, vol. 29, no. 6, pp. 8997-9011, 2021, doi: 10.1364/OE.410154.

Hue dual-chromatic calcium chlorosilicate phosphor for LED having yellow and white ... (Huu Phuc Dang)

- [14] M. Gupta, A. K. Dubey, V. Kumar, and D. S. Mehta, "Indoor daylighting using fresnel lens solar-concentrator-based hybrid cylindrical luminaire for illumination and water heating," *Applied Optics*, vol. 59, no. 18, pp. 5358-5367, 2020, doi: 10.1364/AO.389044.
- [15] A. Ali *et al.*, "Blue-laser-diode-based high CRI lighting and high-speed visible light communication using narrowband green-/red-emitting composite phosphor film," *Applied Optics*, vol. 59, no. 17, pp. 5197-5204, 2020, doi: 10.1364/AO.392340.
- [16] X. Liu *et al.*, "Laser-based white-light source for high-speed underwater wireless optical communication and high-efficiency underwater solid-state lighting," *Optics Express*, vol. 26, no. 15, pp. 19259-19274, 2018, doi: 10.1364/OE.26.019259.
- [17] R. Fan, S. Fang, C. Liang, Z. Liang, and H. Zhong, "Controllable one-step doping synthesis for the white-light emission of cesium copper iodide perovskites," *Photonics Research*, vol. 9, no. 5, pp. 694-700, 2021, doi: 10.1364/PRJ.415015.
- [18] S. Donati, W. H. Cheng, C. N. Liu, H. K. Shih, and Z. Pei, "Embedding LiDAR and smart laser headlight in a compact module for autonomous driving," OSA Continuum, vol. 4, no. 5, pp. 1587-1597, 2021, doi: 10.1364/OSAC.424159.
- [19] Y. Chang, J.-K. Chang, H.-A. Chen, S.-H. Chang, C.-N. Liu, P. Han, and W.-H. Cheng "An advanced headlight module employing highly reliable glass phosphor," *Optics Express*, vol. 27, no. 3, pp. 1808-1815, 2019, doi: 10.1364/OE.27.001808.
- [20] Y. Sun, C. Zhang, Y. Yang, H. Ma, and Y. Sun, "Improving the color gamut of a liquid-crystal display by using a bandpass filter," *Current Optics and Photonics*, vol. 3, no. 6, pp. 590-596, 2019, doi: 10.1364/COPP.3.000590.
- [21] Y. Jen, X.-H. Lee, S.-K. Lin, C.-C. Sun, C.-S. Wu, Y.-W. Yu, and T.-H. Yang, "Design of an energy-efficient marine signal light based on white LEDs," OSA Continuum, vol. 2, no. 8, pp. 2460-2469, 2019, doi: 10.1364/OSAC.2.002460.
- [22] Y. Fang et al., "Giant enhancement of white light emission from Ca9Ln(PO4)7:Eu2+,Mn2+ (Ln=La, Lu, Gd) phosphors achieved by remote aluminum reduction," *Optical Materials Express*, vol. 10, no. 5, pp. 1306-1322, 2020, doi: 10.1364/OME.390069.
- [23] Q. Guo *et al.*, "Characterization of YAG:Ce phosphor dosimeter by the co-precipitation method for radiotherapy," *Applied Optics*, vol. 60, no. 11, pp. 3044-3048, 2021, doi: 10.1364/AO.419800.
- [24] H. Yuce, T. Guner, S. Balci, and M. M. Demir, "Phosphor-based white LED by various glassy particles: control over luminous efficiency," *Optics Letters*, vol. 44, no. 3, pp. 479-482, 2019, doi: 10.1364/OL.44.000479.
- [25] Z. Zhang, W. Li, N. Ma, and X. Huang, "High-brightness red-emitting double-perovskite phosphor Sr2LaTaO6:Eu3+ with high color purity and thermal stability [Invited]," *Chinese Optics Letters*, vol. 19, no. 3, pp. 030003, 2021, doi: 10.3788/COL202119.030003.

BIOGRAPHIES OF AUTHORS



Huu Phuc Dang D received a Physics Ph.D. degree from the University of Science, Ho Chi Minh City, in 2018. Currently, He is Research Institute of Applied Technology, Thu Dau Mot University, Binh Duong Province, Vietnam. His research interests include simulation LEDs material, renewable energy. He can be contacted at email: danghuuphuc@tdmu.edu.vn.



Bui Van Hien (D) 🛃 🖾 (P) is a lecturer at the Faculty of Mechanical - Electrical and Computer Engineering, School of Engineering and Technology, Van Lang University, Ho Chi Minh City, Viet Nam. His research interests are Optoelectronics (LED), Power transmission and Automation equipment. He can be contacted at email: hien.bv@vlu.edu.vn.



Nguyen Le Thai D E E C P received his BS in Electronic engineering from Danang University of Science and Technology, Vietnam, in 2003, MS in Electronic Engineering from Posts and Telecommunications Institute of Technology, Ho Chi Minh, Vietnam, in 2011 and PhD degree of Mechatronics Engineering from Kunming University of Science and Technology, China, in 2016. He is a currently with the Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam. His research interests include the renewable energy, optimisation techniques, robust adaptive control and signal processing. He can be contacted at email: nlthai@nttu.edu.vn.