Bulletin of Electrical Engineering and Informatics
Vol. 13, No. 1, February 2024, pp. 179~185
ISSN: 2302-9285, DOI: 10.11591/eei.v13i1.4753

$CaO:Tb^{3+}$ green-emitting phosphor for white light-emitted diode-phosphor applications: the improvement of light output intensity

Ha Thanh Tung[1], **Dieu An Nguyen Thi**[2]
[1]Faculty of Basic Sciences, Vinh Long University of Technology Education, Vinh Long Province, Vietnam
[2]Faculty of Electrical Engineering Technology, Industrial University of Ho Chi Minh City, Ho Chi Minh City, Vietnam

Article Info

Article history:

Received Nov 2, 2022
Revised Dec 16, 2022
Accepted Dec 21, 2022

Keywords:

$CaO:Tb^{3+}$
Color consistency
Luminous intensity
Mie-scattering theory
Scattering enhancement

ABSTRACT

The use of $CaO:Tb^{3+}$ with light green emission on for improvement of both luminescent output and chromatic fidelity of the white light emitted from a light-emitting diode (LED). The $CaO:Tb^{3+}$ is combined with the yellow-emitting phosphor of $YAG:Ce^{3+}$ to provide sufficient colored spectral proportion for the white light generation, enhancing the color performance. The phosphor combination is utilized for the three most applied LED structures: conformal, in-cup, and remote phosphor structures. The changes in optical properties of these three LEDs are monitored with adjustments in the proportion of $CaO:Tb^{3+}$. The higher proportion of the green phosphor results in higher scattering efficiency in all structures, offering better color coordination and stronger luminous flux. The color quality scale is somehow reduced when $CaO:Tb^{3+}$ concentration is more than a certain level. Therefore, depending on the phosphor configuration of the white light-emitting diode (WLED), the concentration of $CaO:Tb^{3+}$ should be modified to achieve a good color rendition with improved color consistency and luminous properties.

Corresponding Author:

Dieu An Nguyen Thi
Faculty of Electrical Engineering Technology, Industrial University of Ho Chi Minh City
Ho Chi Minh City, Vietnam
Email: nguyenthidieuan@iuh.edu.vn

1. INTRODUCTION

Solid-state lighting (SSL) has been immersed as an environmental-friendly and high-efficient illuminating solution that could replace coal-powered and gas-powered light bulbs [1], [2]. A diode emits white light-emitting diode (WLED), a typical semiconductor illuminating supply of SSL, has been recognized for excellent properties for example, outstanding shock resistance, low power consumption, and long-term operation that are suitable for wide-range lighting applications, from indoor to outdoor illumination. For the fabrication of the WLED, using phosphor to convert light emitted from a blue light-emitting diode (LED) chip for white light production is more favorable than using three chromatic LED chips of red, blue, and green due to its simplicity. The universal combination for phosphor-conversion LED is the yellow-emitting phosphor of $YAG:Ce^{3+}$ and GaN-blue chip [3]–[5]. The $YAG:Ce^{3+}$ has been reported to be the effective phosphor material for high-efficiency WLED owing to its excellent quantum efficiency and high chemical stability [6]. Other phosphor materials are proposed to combine with yellow-emitting phosphor to further enhance its advantages and improve its disadvantages in color adequacy by enhancing the scattering effectiveness of the phosphor layers [7], [8].

The phosphor with rare-earth ions, especially the lanthanide type, have been investigated and applied in several aspects such as SSL, sensors, imaging techniques, and lasers [9], [10]. Tb^{3+} is one of the most attractive lanthanide ions for doping in the phosphor composition owing to its efficient green emission provided by the 4f–5d transitions. Besides, the Tb^{3+} ion-doped glass matrix is reported to exhibit four emission regions of green, blue, yellow, and red [11], [12]. Thus, Tb^{3+} ion-doped phosphors can be potential for increasing the luminous output of a phosphor-converted WLED (pc-WLED). In this paper, the Tb^{3+}-doped CaO phosphor is applied to fabricate the pc-WLED package with high scattering efficiency [13]–[15]. The impacts of CaO:Tb^{3+} on the chromaticity and lumen performances of the WLEDs is investigated with various concentration of the green-phosphor concentration. The study performs the simulations of three phosphor packages, consisting of in-cup phosphor, conformal phosphor, and two-layered remote phosphor. The Mie-scattering theory is applied to validate the phosphor layers' diffusing [16]–[18]. The study demonstrates that this CaO:Tb^{3+} phosphor considerably promotes the illuminating beam and hue homogeneity of all three pc-WLEDs. Meanwhile, the color accuracy evaluated by the quality scale can be around 66 with appropriate control over the concentration of CaO:Tb^{3+}.

2. METHOD

2.1. Green-emitting CaO:Tb^{3+} phosphor composition and preparation

The composition of green-emitting phosphor CaO:Tb^{3+} includes three chemical ingredients of $CaCO_3$, CaF_2, and Tb_4O_7, as shown in Table 1. The preparation process of CaO:Tb^{3+} is performed through 5 steps, starting from making a chemical solution and ending with storing the product in a dry container [19], [20]. Initially, the required chemical components of CaO:Tb^{3+} composition are blended well in water or methanol for a complete solution. The combination is then dried in air and subsequently powdered. The powder is latterly heated up in a capped quartz tube with CO at 1200 °C and for 1 hour. As the firing time is over, the product is ground into powders and subsequently stored in a well-closed container. Note that, it is essential to keep the product dry to preserve its chemical characteristics. The product-CaO:Tb^{3+} phosphor-has a light green emission color with the highest intensities near 2.26-2.28 eV.

Table 1. Elements of CaO:Tb^{3+} phosphor

Materials	By mole (%)	By grams
$CaCO_3$	100	100
CaF_2	0.5	0.380
Tb_4O_7	1.5 (of Tb)	2.8

2.2. Structure of pc-WLEDs

The modeling process of three WLED models, including the conformal, in-cup, and remote phosphor packages, is performed with the LightTools simulation software and the Monte Carlo method [21]. The phosphor sheets covering the LED chip's surface are simulated with a flat silicon thin film. Two essential points that need to perform in the modeling process are the establishment of the structures and lighting features of each pc-WLED model, and the control over phosphor compounds' influences on the determined lighting features of the white illumination. Specifically, the performance of WLEDs' optical properties is monitored with the changing concentration of CaO:Tb^{3+} in the phosphor compound. Consequently, the green spectral proportion will be different, leading to significant changes in color uniformity and rendition, and luminescence intensity of the three pc-WLED packages. Additionally, the effects of CaO:Tb^{3+} on the chromatic and luminous features of the WLEDs are examined and demonstrated utilizing the light scattering by Mie-scattering theory.

The WLED models are simulated with a pre-set correlated color coordinate (CCT) of 8,500 K. Figure 1(a) shows the photograph of a real WLED using nine LED chips and the conformal phosphor coating approach. The illustrations of the conformal, the in-cup, and the remote phosphor structures are presented in Figures 1(b)-(d), respectively. Nine LED chips, with 1.14×0.15 mm in square base and altitude, respectively, is attached to the lead frame in three parallel columns. All the chips emit the radiant energy of 1.14 W with the maximum wavelength centered at 453 nm. The phosphor film with a 0.08 mm thickness is diffused on the LED chips' surface. The phosphor particles in spherical are 14.5 μm in their diameter. The reflector of the WLED model has the dimension of 8×2.07×9.85 mm (bottom×height×top). In the conformal (CPP) and in-cup (IPP) phosphor models, green-emitting phosphor CaO:Tb^{3+} is mixed with the yellow-emitting phosphor YAG:Ce^{3+} (Figures 1(b) and (c)). Meanwhile, in the two-layer remote (RPP) phosphor model, the CaO:Tb^{3+} phosphor and YAG:Ce^{3+} phosphor are separated into two layers with the green-emitting layer above the yellow-emitting film (Figure 1 (d)). In Figures 2 (a)-(c), there are various dosages of CaO:Tb^{3+} phosphor and spectral intensities of CPP-IPP-RPP.

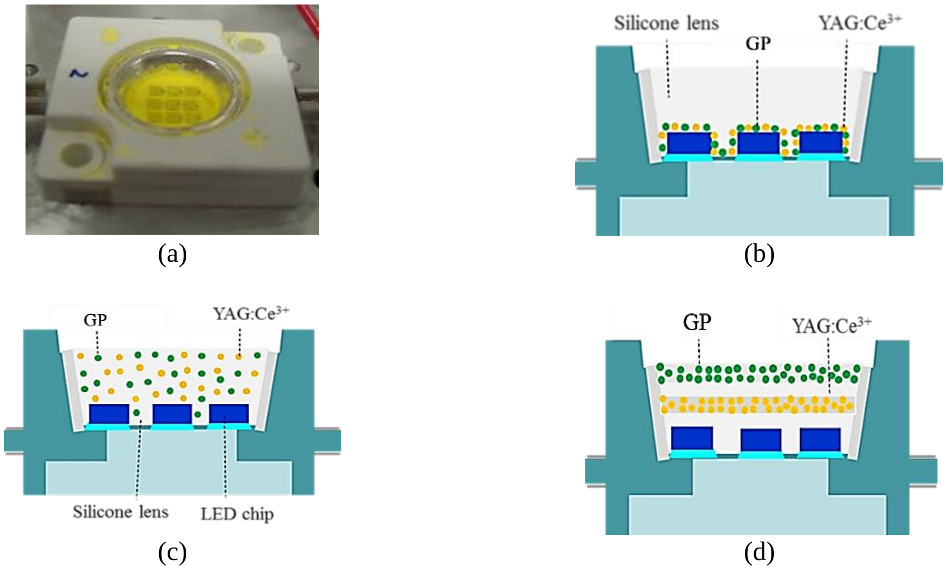


Figure 1. WLEDs utilizing down-conversion green-emitting phosphor CaO:Tb^{3+}: (a) the genuine WLED, (b) package CPP, (c) package IPP, and (d) package RPP

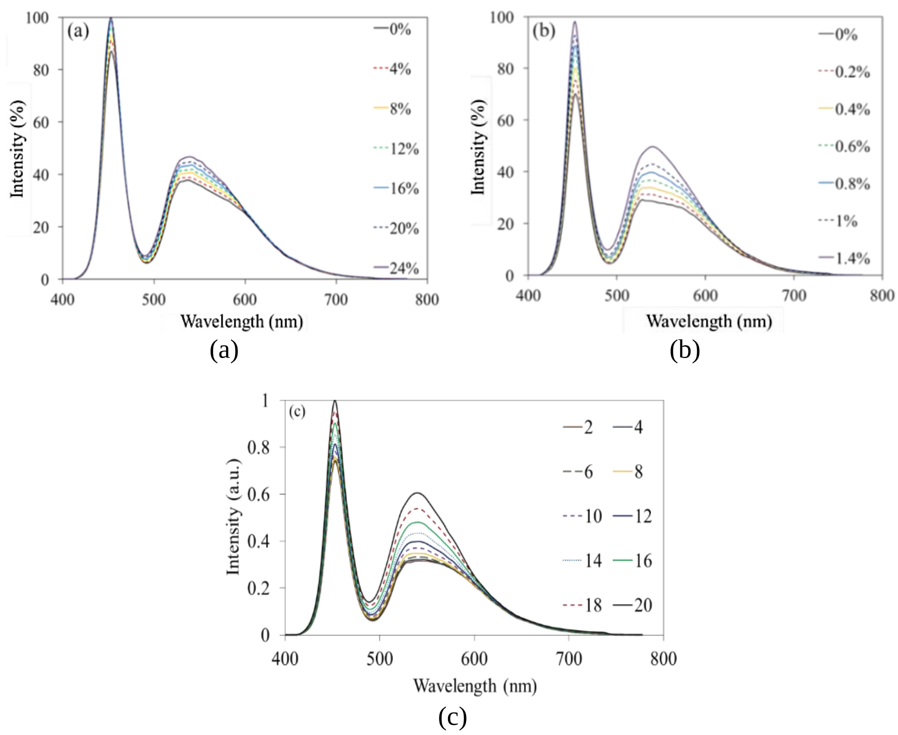


Figure 2. CaO:Tb^{3+} concentration and spectral intensities of: (a) CPP, (b) IPP, and (c) RPP

3. RESULTS AND DISCUSSION

Scattering computation for CaO:Tb^{3+} phosphor is performed applying the Mie-scattering theory [22]–[25]. By recognizing the scattering coefficient μ_{sca}, the effects of this green-emitting phosphor on the lighting efficiency can be validated. Particularly, μ_{sca}, depends on the diameter of the phosphor sphere and the wavelength, which can be expressed as (1)-(4):

$$\mu_{sca}(\lambda) = \frac{c}{\bar{m}} \bar{C}_{sca}(\lambda) \quad (1)$$

$$\bar{C}_{sca}(\lambda) = \frac{\int\int C_{sca,D}(\lambda) f(D) dD}{\int\int f(D) dD} \quad (2)$$

$$\bar{m} = \frac{\int\int m_i(D) f(D) dD}{\int\int f(D) dD} \quad (3)$$

$$C_{sca}(\lambda) = \frac{P_{sca}(\lambda)}{I_{inc}(\lambda)} \quad (4)$$

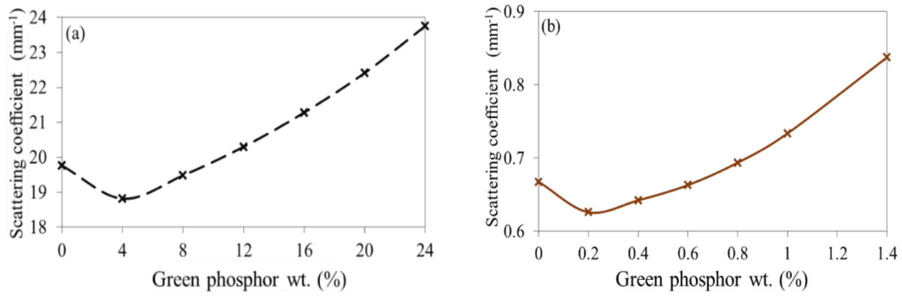
In (1)-(4), the wavelength and the phosphor's diameter are indicated by λ and D, respectively. In (1) c shows the concentration of the green-emitting phosphor (g/cm^3), $\bar{m}$ shows the mass of the phosphor, and $\bar{C}_{sca}(\lambda)$ shows the scattering cross-section of the phosphor sphere. In (2)-(4), $f(D)$ indicates the dimension dispersion, $C_{sca,D}$ indicates the diffusing cross-section connected with diameter D of the phosphor sphere, $P_{sca}(\lambda)$ presents the diffusing energy of the phosphorus photon, and $I_{inc}(\lambda)$ presents the degree of the phosphorus irradiation.

Besides, to ensure the stability of the WLED devices at the pre-set CCT value of 8,500 K, the change in yellow-phosphor concentration must be monitored under the adjustment of the green-phosphor concentration. The decrease in weight percentage of the yellow-emitting phosphor is required as that of the green-emitting phosphor CaO:Tb^{3+} increase, according to the following expression [26].

$$\sum W_{pl} = W_{yp} + W_s + W_{gp} = 100\% \quad (5)$$

W_{pl}, W_s, W_{yp} and W_{gp} present the weight percentages of the phosphor film package, the silicone, the yellow and green phosphor, respectively.

The values of μ_{sca} of CaO:Tb^{3+} are demonstrated in line charts in Figures 3(a) and (b) in CPP and IPP respectively. Three WLED structures show a similar trend of μ_{sca} with the increasing CaO:Tb^{3+} concentration. In particular, the μ_{sca}, at first, slightly decreases when the concentrations of CaO:Tb^{3+} increase to a certain number, 4 wt% in CPP and 0.2 wt% in IPP, and starts to increase significantly as the concentration of green phosphor continuous to rise. From this demonstration, the scattering enhancement can be obtained with the use of CaO:Tb^{3+}. The scattering stimulation helps to redirect the light path and reduce the light loss by internal reflection for significantly promoted light extraction [27]. Moreover, the scattering enhancement is reported to be an important feature for attaining better color performance of WLED devices. Hence, there is a high probability of achieving noticeable improvements in WLED performance in both luminous and color characteristics.



(a) (b)

Figure 3. CaO:Tb^{3+} concentration and scattering coefficients at 453 nm of: (a) CPP and (b) IPP

The luminous values of CPP, IPP, and RPP are illustrated in Figures 4(a)-(c), respectively. The luminous lines in all three WLEDs show a significant increase with larger proportions of CaO:Tb^{3+}. This enhancement of lumen efficiency in all WLEDs is probably the result of boosted light extracted by improved scattering and reduced reflection loss. This reinforces that CaO:Tb^{3+} is favorable for high-luminescence WLED devices.

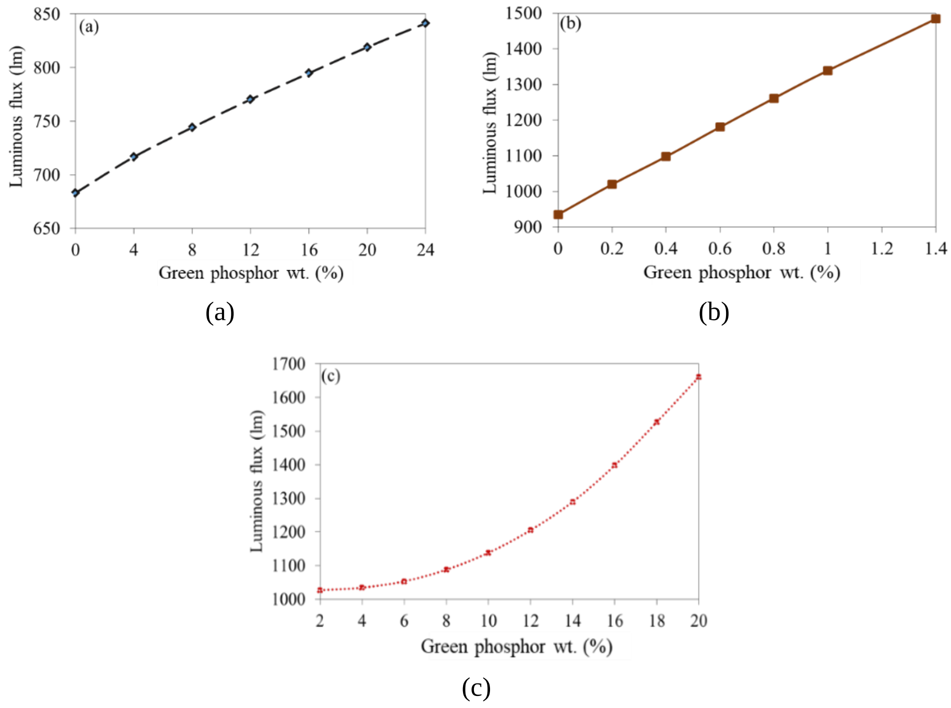


Figure 4. CaO:Tb^{3+} concentration and luminous intensities of: (a) CPP, (b) IPP, and (c) RPP

Via the demonstrated scattering coefficient by Mie theory, the effectiveness in enhancing the luminescence and the chromaticity of the WLED structures. To further examine the impacts of green-emitting phosphor CaO:Tb^{3+} with highly-efficient scattering properties, the paper presents specific results of each optical feature, including luminous fluxes (Figure 4), color deviation of CPP, IPP, RPP (Figures 5(a)-(c)) for the evaluation of color uniformity (CRI), and color quality scales (CQS) for the evaluation of color rendition and fidelity. In Figures 6(a)-(c), it illustrates CQS values of CPP-IPP-RPP according to various CaO:Tb^{3+} concentrations, in turn.

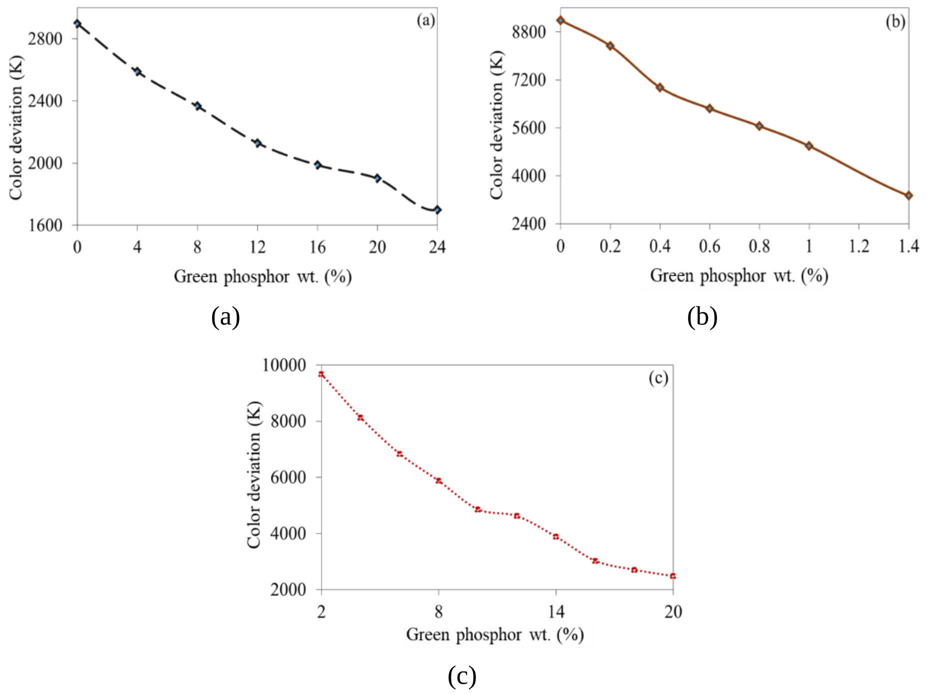


Figure 5. CaO:Tb^{3+} concentration and color deviation of: (a) CPP, (b) IPP, and (c) RPP

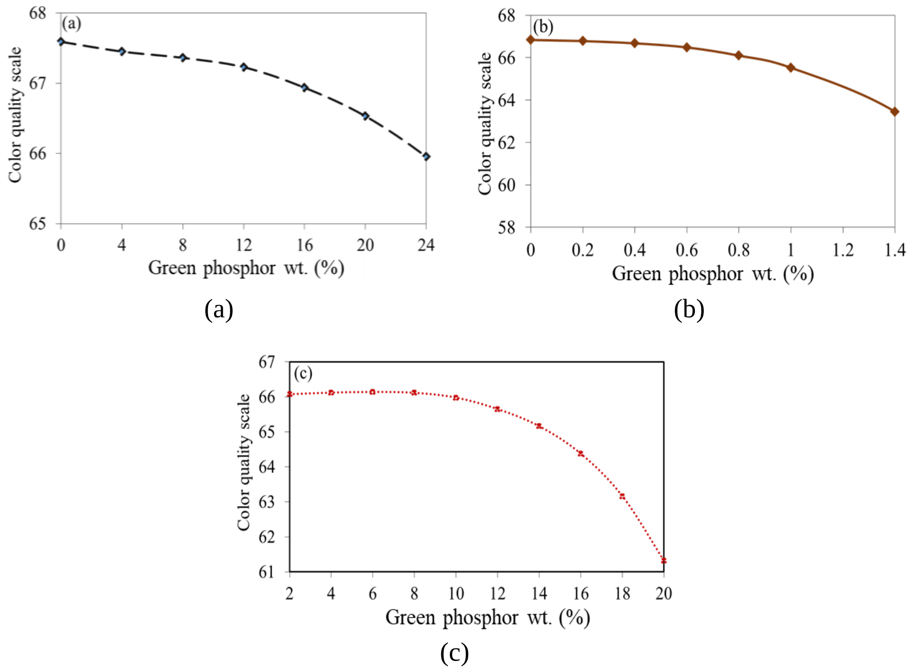


Figure 6. CaO:Tb^{3+} concentration and CQS values of: (a) CPP, (b) IPP, and (c) RPP

4. CONCLUSION

The study demonstrates the impacts of CaO:Tb^{3+} green-emitting phosphor on the color performance and luminous efficiency of three different WLED packages of CPP, IPP, and RPP. The scattering factor is analyzed to realize the changes in these optical features of WLEDs in connection with the modification of CaO:Tb^{3+} concentration. The scattering enhancement is obtained with the increasing concentration of this green phosphor, which encourages blue-light conversion and green-light generation. Moreover, the improved scattering boosts the light extraction efficiency for greater luminous intensity. The color consistency is also better since the color variation is reduced. Nevertheless, it is quite disadvantageous to the CQS as the increasing concentration of CaO:Tb^{3+} decreases the CQS values in all three WLED packages. Thus, if the IPP and RPP are applied for fabrication, it is advisable to keep the concentration of CaO:Tb^{3+} below specific levels (>0.4 wt% and ≥8 wt%, respectively) for good CQS while attaining lower color deviation and higher luminous flux. The findings of the study indicate that the CaO:Tb^{3+} is potential for high-efficiency WLED applications.

REFERENCES

[1] J.-S. Li, Y. Tang, Z.-T. Li, L.-S. Rao, X.-R. Ding, and B.-H. Yu, "High efficiency solid–liquid hybrid-state quantum dot light-emitting diodes," *Photonics Research*, vol. 6, no. 12, pp. 1107–1115, Dec. 2018, doi: 10.1364/PRJ.6.001107.

[2] P. P. Li *et al.*, "Very high external quantum efficiency and wall-plug efficiency 527 nm InGaN green LEDs by MOCVD," *Optics Express*, vol. 26, no. 25, pp. 33108–33115, Dec. 2018, doi: 10.1364/OE.26.033108.

[3] Y. J. Park *et al.*, "Development of high luminous efficacy red-emitting phosphor-in-glass for high-power LED lighting systems using our original low Tg and Ts glass," *Optics Letters*, vol. 44, no. 24, pp. 6057–6060, Dec. 2019, doi: 10.1364/OL.44.006057.

[4] Y. Liu *et al.*, "Preparation and reliability of flexible phosphor film for warm white LED," *Materials Technology*, vol. 33, no. 1, pp. 22–28, Jan. 2018, doi: 10.1080/10667857.2017.1376787.

[5] V. Subburaj, D. Jena, P. Perumal, and Y. Mahnashi, "High efficiency two-phase switched-capacitor converter with seven distinct negative voltage ratios for power saving applications," *International Journal of Electronics Letters*, vol. 8, no. 3, pp. 298–303, Jul. 2020, doi: 10.1080/21681724.2019.1600728.

[6] Y. Luo *et al.*, "White-light emitting diodes' spectrum effect on photosynthesis and nutrient use efficiency in Podocarpus macrophyllus seedlings," *Journal of Plant Nutrition*, vol. 43, no. 19, pp. 2876–2884, Nov. 2020, doi: 10.1080/01904167.2020.1798999.

[7] J. Hou *et al.*, "White-light-emitting from single-phased $(Ca,Eu,Mn)_9$ $Al(PO_4)_7$ phosphor with blue-white-yellow tunable luminescence properties for UV-based LEDs," *Materials Technology*, vol. 34, no. 3, pp. 135–142, Feb. 2019, doi: 10.1080/10667857.2018.1540331.

[8] M. Rajendran, K. Singh, and S. Vaidyanathan, "A novel Sm^{3+} -activated Li_3 $BaSrLn_3$ $(MO_4)_8$ [Ln=La, Gd, and Y; M = Mo and W] deep red-emitting phosphors for plant cultivation and white LEDs," *Journal of Information Display*, vol. 22, no. 2, pp. 63–81, Apr. 2021, doi: 10.1080/15980316.2020.1831630.

[9] S. Chen and M. Wei, "LED Illumination and Color Appearance of White-Balanced Images," *LEUKOS*, vol. 16, no. 3, pp. 203–215, Jul. 2020, doi: 10.1080/15502724.2018.1533409.

[10] G. S. Archer, "Effect of two different commercially available white light LED fixtures on broiler hatchability and chick quality,"

British Poultry Science, vol. 59, no. 3, pp. 251–255, May 2018, doi: 10.1080/00071668.2018.1436160.
[11] H. Zhang, Q. Su, and S. Chen, "Recent progress in the device architecture of white quantum-dot light-emitting diodes," *Journal of Information Display*, vol. 20, no. 4, pp. 169–180, Oct. 2019, doi: 10.1080/15980316.2019.1650129.
[12] D. Zhou, G. Yan, W. Zhang, J. Lin, and K. Qiu, "Synthesis and luminescence properties of $Zn_3B_2O_6$: Eu^{3+}, Li^+ red-emitting phosphor for white LEDs," *Ferroelectrics*, vol. 528, no. 1, pp. 114–121, May 2018, doi: 10.1080/00150193.2018.1448654.
[13] F. Rahman and A. F. George, "Temporal Luminescence of Broadband Light-Emitting Diodes and Their Use for Generating Customizable White Light," *LEUKOS*, vol. 16, no. 4, pp. 303–314, Oct. 2020, doi: 10.1080/15502724.2019.1707684.
[14] Z. Liu, Y. Liu, C. Pan, Y. Fang, and J. Hou, "K_2MnF_6/KHF_2 red phosphor synthesis by a low temperature way for high color rendering index white light emitting diodes," *Ferroelectrics*, vol. 565, no. 1, pp. 66–76, Sep. 2020, doi: 10.1080/00150193.2020.1761719.
[15] E. M. Gutzeit, V. V. Linde, V. E. Maslov and I. P. Shestopalova, "Effect of adaptation's taking into account for determination of color rendering index of white LED's," *2013 23rd International Crimean Conference "Microwave & Telecommunication Technology*", Sevastopol, Ukraine, 2013, pp. 766-767.
[16] K. J. Francis, Y. E. Boink, M. Dantuma, M. K. A. Singh, S. Manohar, and W. Steenbergen, "Tomographic imaging with an ultrasound and LED-based photoacoustic system," *Biomedical Optics Express*, vol. 11, no. 4, pp. 2152–2165, Apr. 2020, doi: 10.1364/BOE.384548.
[17] S.-H. Lin *et al.*, "Enhanced external quantum efficiencies of AlGaN-based deep-UV LEDs using reflective passivation layer," *Optics Express*, vol. 29, no. 23, pp. 37835–37844, Nov. 2021, doi: 10.1364/OE.441389.
[18] W. Pawlikowski, A. Barmaki, M. Narimani and S. Hranilovic, "Light-Emitting Commutating Diodes for Optical Wireless Communications Within LED Drivers," in *IEEE Photonics Journal*, vol. 12, no. 5, pp. 1-11, Oct. 2020, doi: 10.1109/JPHOT.2020.3020749.
[19] J. Li *et al.*, "On-Chip Integration of III-Nitride Flip-Chip Light-Emitting Diodes With Photodetectors," *Journal of Lightwave Technology*, vol. 39, no. 8, pp. 2603–2608, Apr. 2021, doi: 10.1109/JLT.2020.3048986.
[20] C.-M. Tsai, C.-S. Chang, Z. Xu, W.-P. Huang, W.-C. Lai, and J.-S. Bow, "Efficiency enhancement of III-nitride light-emitting diodes with strain-compensated thin-barrier InGaN/AlN/GaN multiple quantum wells," *OSA Continuum*, vol. 2, no. 4, pp. 1207–1214, Apr. 2019, doi: 10.1364/OSAC.2.001207.
[21] C. -H. Chiang, S. -J. Gong, T. -S. Zhan, K. -C. Cheng and S. -Y. Chu, "White Light-Emitting Diodes With High Color Rendering Index and Tunable Color Temperature Fabricated Using Separated Phosphor Layer Structure," in *IEEE Electron Device Letters*, vol. 37, no. 7, pp. 898-901, Jul. 2016, doi: 10.1109/LED.2016.2576498.
[22] A. Zhang *et al.*, "Enhanced amplified spontaneous emission from conjugated light-emitting polymer integrated with silicon nitride grating structures," *OSA Continuum*, vol. 2, no. 10, pp. 2875–2882, Oct. 2019, doi: 10.1364/OSAC.2.002875.
[23] T. Hiraoka, H. Nonaka and K. Urahama, "Generation of striped color images by using inverse line convergence index filter," *2014 International Conference of Advanced Informatics: Concept, Theory and Application (ICAICTA),* Bandung, Indonesia, 2014, pp. 69-74, doi: 10.1109/ICAICTA.2014.7005917.
[24] M. Vik and M. Viková, "Color Rendition of Artificial Light Sources: Past and Future," *2018 VII. Lighting Conference of the Visegrad Countries (Lumen V4)*, Trebic, Czech Republic, 2018, pp. 1-4, doi: 10.1109/LUMENV.2018.8520968.
[25] N. Doan Quoc Anh, N. Thi Phuong Thao and M. Voznak, "A novel application of green (La, Ce, Tb)PO4:Ce:Tb phosphor on the luminous efficacy and color quality of white LEDs," *2017 6th International Symposium on Next Generation Electronics (ISNE)*, Keelung, Taiwan, 2017, pp. 1-2, doi: 10.1109/ISNE.2017.7968737.
[26] T. Takebe, "ZnSe-based white LED," *CLEO/Pacific Rim 2003. The 5th Pacific Rim Conference on Lasers and Electro-Optics (IEEE Cat. No.03TH8671)*, Taipei, Taiwan, 2003, vol. 1, pp. 22, doi: 10.1109/CLEOPR.2003.1274502.
[27] R. Sinnadurai, M. K. A. A. Khan, M. Azri and Vikneswaran, "Development of white LED down light for indoor lighting," *2012 IEEE Conference on Sustainable Utilization and Development in Engineering and Technology (STUDENT)*, Kuala Lumpur, Malaysia, 2012, pp. 242-247, doi: 10.1109/STUDENT.2012.6408412.

BIOGRAPHIES OF AUTHORS

Ha Thanh Tung received the Ph.D degree in physics from University of Science, Vietnam National University Ho Chi Minh City, Vietnam, he is working as a lecturer at the Faculty of Basic Sciences, Vinh Long University of Technology Education, Vietnam. His research interests focus on developing the patterned substrate with micro-scale and nano-scale to apply for physical and chemical devices such as solar cells, OLED, and photoanode. He can be contacted at email: tunght@vlute.edu.vn.

Dieu An Nguyen Thi received a master of Electrical Engineering, HCMC University of Technology and Education, Vietnam. Currently, she is a lecturer at the Faculty of Electrical Engineering Technology, Industrial University of Ho Chi Minh City, Vietnam. Her research interests are theoretical physics and mathematical physics. She can be contacted at email: nguyenthidieuan@iuh.edu.vn.