The influences of LaVO$_4$:Eu$^{3+}$,Cr$^{3+}$ red phosphors on white light-emitting diode applications

Nguyen Hung Khanh$^1$, Nguyen Le Thai$^2$, Thuc Minh Bui$^3$, Huu Phuc Dang$^4$, Huynh Thanh Thien$^5$

$^1$Faculty of Engineering, Dong Nai Technology University, Bien Hoa City, Vietnam
$^2$Faculty of Engineering and Technology, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam
$^3$Faculty of Electrical and Electronics Engineering, Nha Trang University, Nha Trang City, Vietnam
$^4$Faculty of Fundamental Science, Industrial University of Ho Chi Minh City, Ho Chi Minh City, Vietnam
$^5$Faculty of Electrical and Electronics Engineering, Ton Duc Thang University, Ho Chi Minh City, Vietnam

ABSTRACT

In this present paper, the LaVO$_4$:Eu$^{3+}$,Cr$^{3+}$ (LV:Eu,Cr) red-orange phosphors are introduced in WLED fabrication. The LV:Eu,Cr phosphor is synthesized with high-temperature solid-phase reaction. The luminescence properties of the phosphor are monitored with ultraviolet-visible and near-infrared (UV-vis-NIR) measurements. The heat generating in the phosphor sample is also investigated with different power densities of the 980 nm laser. The phosphor exhibits absorption bands at 254 nm and 316 nm, suitable for UV light-emitting diodes (UV LED) applications. The Cr$^{3+}$ concentrations have noticeable effects on the luminescence of the phosphor. The increasing Cr$^{3+}$ dosage initiates reduction in Eu$^{3+}$ emission intensity and luminescence lifetime average. The heat-activated amount in the phosphor is also significant with the higher concentration of Cr$^{3+}$ ions. When using the LV:Eu,Cr phosphor in white light-emitting model (WLED), the dominant red-orange emission centered at 595 nm is observed, in addition to the blue peak at 453 nm. The luminosity, color rendition, and color uniformity of the WLED light are also discussed. The findings indicate that the phosphor can be combined with other high-efficiency blue and green phosphors to obtain the improved color rendition and luminous performances and used in heat-creating optical applications.

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Corresponding Author:

Huynh Thanh Thien
Faculty of Electrical and Electronics Engineering, Ton Duc Thang University
Ho Chi Minh City, Vietnam
Email: huynhthanthien@tdtu.edu.vn

1. INTRODUCTION

Rare earth-doped phosphors have a variety of uses in modern technology, including in the production of magnets, lasers, optical fibers, and medical applications such as in imaging and cancer treatment [1], [2]. Moreover, such luminescent materials are commonly utilized in various lighting applications, including fluorescent lamps, light-emitting diodes (LEDs), and cathode-ray tubes. Particularly, these rare-earth-doped phosphors offers sharp and strong emission when excited in the ultraviolet-visible (UV-Vis) and near-infrared (NIR) wavelengths [3], [4]. For example, in the NIR area, the Nd:YAG laser gives intense and broad emission band, sufficient for various applications [5]. Besides, they are used to fabricate biosensors by combining with biomolecules [6]. Additionally, when using in white LED production, as excited by an external energy source, such as a UV or blue light, these materials absorb energy and then release it as visible light. The color of the emitted light depends on the specific rare earth ion used and the
properties of the host matrix. Furthermore, it is possible to enhance the luminescence strength of rare-earth dopants in host substances by integrating other rare-earth classes to act as sensitizers [7]–[9]. One of the most investigated rare-earth dopants is the trivalent europium Eu3+. This rare-earth ion gives the bright red emission suitable for display applications and strong far-infrared lasing emission. It is also doped in various host materials including glass matrix, micro phosphors, nanoposphors, and bio mediums. Owing to its multiple energy levels, it can yield sharp 610 nm–615 nm red band when being doped in most of these host lattices. Besides, the bright red emission, their emission includes the orange (590 nm) and deep red regions (~650 nm and 700 nm). Moreover, previous studies reported that Eu3+-doped luminescent material could give stronger emission in red regions and greater luminescent performance than many other phosphor materials, owing to its narrow-band emission and long optical-active lifetime [10]–[12]. With such emission properties, Eu3+-doped phosphors are often utilized in LEDs in combination with blue- and green-emission materials for achieving high-color-rendition white light. In most of the host materials, however, the Eu3+ is often self-activated, and the emission in orange and deep red in neutral red (NR) region are relatively weak [13], [14].

In this study, we use the LaVO4 (LV) phosphor as the host material for doping the Eu3+ ions. The LV phosphor is self-activated and has high UV-light absorption efficiency. It also gives blue emission of 350–450 nm that can be well-absorbed by the Eu3+ ion dopants. After taking in such lights, the Eu3+ ion emits them in the region from 240 nm to 750 nm. Then, for the sensitizer, the Cr3+ ion is chosen as it can give wide emission range from blue to red, long lifetime phosphorescence due to its long-lived 2E state, and laser emission in either NIR or infrared areas. Besides, when being in the same host matrix, the Eu3+ is likely to transfer its energy by a small amount to the Cr3+, as the 4T1(4F) energy level of the CR3+ ion stays below the energy level 5D0 of Eu3+ [15]–[17]. This can initiate the decrease of Eu3+ luminescence-intensity lifespan. The phosphor Eu3+–Cr3+-doped LV (LV:Eu,Cr) phosphor is synthesized via the solid-phase reaction at high temperatures. Then, its luminescence and heat production are investigated. The phosphor is also used to build the conventional WLED model with blue LED and YAG:Ce3+ phosphor. The LV:Eu,Cr added dosage is varied for monitoring its influences on the light performances of the as-prepared white LED (WLED). The findings indicating the phosphor could be used for heat-generate application and solid-state LED lighting devices [18], [19].

2. METHOD

The synthesizing method for the LV:Eu,Cr luminescent phosphor is the high-temperature solid-phase reaction with the fixed Eu3+ doping concentration of 1.0 mol%. The initial ingredients of the phosphor composition are listed in Table 1. The stages of phosphor producing process can be described as follows. All the components are evenly weighed and blended with acetone in an agate mortar. Next, the mixture undergoes a calcinating process in a furnace at ~1200°C for 5 hours after being transferred into alumina crucibles. When the calcinating time is over, the product is cooled down to room temperature and followed by grinding into fine powders [20]. The WLED model built with LV:Eu,Cr phosphor, blue LED chips, and YAG:Ce phosphor is shown in Figure 1. The phosphor film for placing above the LED chip has a thickness of 0.08 mm. The LED chip bonded LED WLED package, in which the arrangement of components is clearly depicted. Figure 1(d) presents the 3D model of WLED simulation obtained with LightTools software.

The X-ray diffraction data of the LV:Eu,Cr phosphor is obtained using an X-ray diffractometer from Rigaku, Japan (MiniFlex 600) and refined with Rietveld refinement by FullProf Suite. The morphology and the energy dispersive X-ray spectroscopy of the phosphor are investigated with a scanning electron microscope unit (Zeiss EVO 18 research). Absorption spectral data of the phosphor is collected in the wavelength region from 200 nm to 800 nm with an UV-vis-NIR spectrophotometer (Lambda-750 PerkinElmer). The emission and excitation spectra of LV:Eu,Cr phosphors are measured with the Horiba Fluorolog-3 coupled with a 450-W xenon lamp and photomultiplier tube. The heat generation of the phosphor is examined with a thermo-couple setup excited with various power densities of a lasing diode of 980 nm for 5 minutes [21], [22].

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Purity (%)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>La2O3</td>
<td>&gt;99%</td>
<td>Himeida</td>
</tr>
<tr>
<td>V2O5</td>
<td>&gt;99%</td>
<td>Alpha Aesar</td>
</tr>
<tr>
<td>Eu2O3</td>
<td>&gt;99%</td>
<td>Merck</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>&gt;99%</td>
<td>Alpha Aesar</td>
</tr>
</tbody>
</table>

Table 1. The ingredients of LV:Eu,Cr composition

3. RESULTS AND DISCUSSION

3.1. Computational analysis of the phosphor luminescence

The phosphor samples of LV:Eu,Cr give different bands of absorption owing to the discrepancies in the Eu³⁺ and Cr³⁺ charge distribution. The phosphor’s absorption spectra, recorded in the range from 200 nm to 400 nm, exhibit two significantly intense bands centered at wavelengths of 254 nm and 316 nm. When the doping dosage of the ion Cr³⁺ varies, the absorption intensities change while the position of absorption centers stays the same. To determine the optical energy gap (E_{gp}) of the phosphor with the absorption spectra, the Kubelka–Munk function (F(R)) and Tauc equation are utilized, as expressed in (1) and (2), respectively [23].

\[ F(R) = \frac{(1 - R_\infty)^2}{2R_\infty} \]  
(1)

\[ F(R) = C \times \left( \frac{hv - E_{gp}}{h} \right)^a \]  
(2)

where \( R_\infty \) indicates the diffuse reflectance, \( hv \) represents the incident-photon energy, and \( C \) is the band tailoring parameter. Here, \( a \) indicates the transition type, which is determined to be ½ for the direct optical gap in this case. In the presence of increasing doping dosage of Cr³⁺ ions, there is a decrease in the \( E_{gp} \) of the phosphor, owing to the material’s metallic nature.

The excitation spectra of the LV:Eu,Cr phosphor are examined with the emission wavelengths of 614 nm and 700 nm as the intense red emission is observed at these wavelengths for Eu³⁺ and Cr³⁺, respectively. The data show that the excitation spectra of the phosphor show the multiple peaks from 316 nm to 464 nm with the most eminent peak at 316 nm, in all cases. Besides, under the 700 nm emission, the excitation spectrum has an additional weak peak near 386 nm owing to the presence of Cr³⁺. As the Cr³⁺ concentration rises, the excitation peaks' positions are unchanged but their intensity.

The emission spectra of the LV:Eu,Cr phosphor are examined under excitation wavelengths of 393 nm and 386 nm. The emission trend at 393 nm displays sharp bands within 420–750 nm regions, with the noticeable broad emission band in the deep red region (700–750 nm) assigned to the Cr³⁺ addition. The emission intensity of the phosphor shows reduction as the doping concentration of Cr³⁺ increases. This can be attributed to the energy transfer from the Eu³⁺ ions to Cr³⁺ ions. When being excited, the Eu³⁺ gives a small energy amount to the Cr³⁺, leading to the decrease in emission strength. This can be further determined with the luminescence lifetime of Eu³⁺ in the presence of Cr³⁺ in the phosphor host. Specifically, the lifetime of Eu³⁺ decreases with the increasing doping content of Cr³⁺. The decay curves of the luminescence under 393 nm excitation can be well fitted with the double exponential relation using (3):

\[ F(R) = \frac{(1 - R_\infty)^2}{2R_\infty} \]  
(1)

\[ F(R) = C \times \left( \frac{hv - E_{gp}}{h} \right)^a \]  
(2)
\[ I = A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2} \]  

(3)

where \( I \) represents the luminescent intensity at the time \( t \); \( \tau_1 \) and \( \tau_2 \) represent the lifetime of Eu\(^{3+}\) \(^{5}\!D_0\) levels \([24]\). Then, the luminescence lifetime average can be computed by (4).

\[ I = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \]  

(4)

In the thermal setup for the heat generation test, the LV:Eu,Cr phosphor produces great amount of heat when doping Cr\(^{3+}\) and this increases on the increase of Cr\(^{3+}\) content. The heat generation of the phosphor sample is also linked with the absorption of NIR radiation. Since both ions Cr\(^{3+}\) and Eu\(^{3+}\) absorb NIR light, they may potentially induce the heat creation in the phosphor. Additionally, the brown hue of the LV:Eu,Cr phosphors contributes generating heat in the samples owing to the thermal-phonon stimulation \([25]\).

3.2. Phosphor influences on the WLED model’s performance

The presence of LV:Eu,Cr phosphor has certain effects on the lighting properties of the WLED. Initially, the dosage of the YAG:Ce in the package should decrease to maintain the correlated color temperature (CCT) and induce the scattering activity. This can be seen in Figure 2, in which the increasing concentration of LV:Eu,Cr phosphor is followed by the gradual decrease of YAG:Ce amount. The scattering productivity of the phosphor package in the WLED is subsequently demonstrated in Figure 3. The data show that with the heightened doping amount of the LV:Eu,Cr phosphors, the scattering coefficient parameter increases, regardless of the light wavelengths. Such an improvement in light scattering can help stimulate the conversion efficiency for more red-emission color in and higher color uniformity.

![Figure 2](image2.png)

Figure 2. The concentration of YAG:Ce phosphor in the presence of increasing LV:Eu,Cr amount

![Figure 3](image3.png)

Figure 3. The scattering coefficients of the WLED phosphor package in the presence of LV:Eu,Cr phosphor

The angular CCT values and CCT variation tendency of the phosphor are presented in Figures 4 and 5, respectively. The angular CCT values of the WLED show significant variations as the concentration of the LV:Eu,Cr increases. The CCT line at 5 wt% LV:Eu,Cr nearly coincides with that at 0 wt% phosphor, indicating the influence of LV:Eu,Cr is not significant. On the increasing concentration of the LV:Eu,Cr phosphor, the CCT lines tend to decrease but with a very small amount. However, the CCT variation between different angles is large, which can be further discussed in Figure 5. As the CCT lines of 0-5 wt% of LV:Eu,Cr is nearly coincided, the CCT difference is not obvious. Continuously increasing the LV:Eu,Cr phosphor concentration leads to notably variations. The highest CCT difference is observed with 20 wt% while the lowest value is obtained at 40 wt% LV:Eu,Cr. So, it can achieve the highest color uniformity for the WLED with LV:Eu,Cr at 40 wt%.

The color fidelity of the WLED light can be further examined using the parameters of color rendering index (CRI) and color quality scale (CQS). Figures 6 and 7 depict the influence of increasing LV:Eu,Cr phosphor dosage on the CRI and CQS of the WLED, respectively. Particularly, both figures
The influences of LaVO₄:Eu³⁺,Cr³⁺ red phosphors on white light-emitting... (Nguyen Hung Khanh)
4. CONCLUSION

The present study demonstrates the LV:Eu,Cr phosphor synthesized with high-temperature solid-phase reaction method. The phosphor shows absorption bands at 254 nm and 316 nm, suitable for UV LED applications. With the increasing dosage of Cr3+, the phosphor emission intensity decreases slightly owing to the energy transfer from the Eu3+ to Cr3+ ions. The addition of Cr3+ also induces the emission band in deep red region of around 700–750 nm. Moreover, the increase of Cr3+ stimulate the heat generation in the phosphor materials, suggesting that the phosphor can be used in heat-creating optical devices. In applying to fabricate the WLED package, the presence of LV:Eu,Cr give the eminent orange-red emission band with the peak at 595 nm. The weaker emission peak at 453 nm is also noticed, indicating that the phosphor can be excited by the blue LED chips. With the increasing LV:Eu,Cr concentration, the scattering efficiency is improved, and the lowest CCT deviation is obtained at 40 wt%. However, the CRI and CQS slightly decrease due to the imbalance in color proportions. The lumen output shows small increase with 5 wt% of LV:Eu,Cr but gradual decrease as the concentration of the phosphor further increases. Thus, the phosphor can be used in combination with other high-efficiency blue and green phosphor to obtain the higher color rendition and luminous performances.

REFERENCES


Figure 8. The sum power of the WLED phosphor package in the presence of LV:Eu,Cr phosphor

Figure 9. The lumen output of the WLED phosphor package in the presence of LV:Eu,Cr phosphor
BIOGRAPHIES OF AUTHORS

Nguyen Hung Khanh received his B.S. in Mechatronics Engineering from Lachon University, Vietnam, in 2008, MS in Precision Mold and Die from National Kaohsiung University of Applied Sciences, Kaohsiung City, Taiwan, in 2011. Currently, he is a member of Dong Nai Technology University, Bien Hoa City, Vietnam. His research interests focus on heat transfer engineering, mechanical engineering, and electrical and electronic engineering. He can be contacted at email: nguyenhungkhanh@cdnu.edu.vn.

Nguyen Le Thai received his B.S. 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 Ph.D. 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 focus on the renewable energy, optimisation techniques, robust adaptive control, and signal processing. He can be contacted at email: nilthai@ntu.edu.vn.
Thuc Minh Bui got his B.S. and M.S. degrees in Electrical Engineering from Ho Chi Minh City University of Technology and Education in 2005 and 2008, respectively, and his Ph.D. degree in Electrical Engineering at from Yeungnam University in Gyeongsan, Korea, in 2018. He is currently a lecturer at the Faculty of Electrical and Electronics Engineering at Nha Trang University in Nha Trang City, Vietnam. His scientific interests include control theory, power converter, automation, and optical science with applications to industry and the environment. He can be contacted at email: minhbt@ntu.edu.vn.

Huu Phuc Dang received a Physics Ph.D. degree from the University of Science, Ho Chi Minh City, in 2018. Currently, he is a lecturer at the Faculty of Fundamental Science, Industrial University of Ho Chi Minh City, Ho Chi Minh City, Vietnam. His research interests include simulation LEDs material, and renewable energy. He can be contacted at email: danghuuphuc@iuh.edu.vn.

Huynh Thanh Thien received the Ph.D. degree in Electrical and Computer Engineering from the University of Ulsan, Ulsan, South Korea. He is working as a lecturer at the Faculty of Electrical and Electronics Engineering, Ton Duc Thang University, Ho Chi Minh City, Vietnam. His research interests include cognitive radio and next-generation wireless communications systems, game theory, deep learning, reinforcement learning, and semiconductor device. He can be contacted at email: huynhthanhthien@tdtu.edu.vn.