Enhance Color Rendering Index via Full Spectrum Employing the Important Key of Cyan Phosphor

Mu-Huai Fang,† Chenchen Ni,† Xuejie Zhang,† Yi-Ting Tsai,† Sebastian Mahlik,‡ Agata Lazarowska,‡ Marek Grinberg,‡ Hwo-Shuenn Sheu,† Jyh-Fu Lee,§ Bing-Ming Cheng,§ and Ru-Shi Liu‡,⊥,†

†Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
‡Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk, 80-308 Gdańsk, Poland
§National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan
⊥Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 106, Taiwan

Supporting Information

ABSTRACT: A new concept called “full-spectrum lighting” has attracted considerable attention in recent years. Traditional devices are usually combined with ultraviolet–light-emitting diode (LED), red, green, and blue phosphors. However, a cyan cavity exists in the 480–520 nm region. Hence, cyan phosphors are needed to compensate for the cavity. (Sr,Ba)5(PO4)3Cl:Eu2+ phosphors feature an extremely unique and tunable photoluminescence spectrum. Nevertheless, the tuning mechanisms of these phosphors remain unclear. In this study, we elucidate the mechanism of the cation size-controlled activator uneven-occupation and reoxidation in (Sr,Ba)5(PO4)3Cl:Eu2+ phosphors. This mechanism could help tune the optical properties of related apatite families and structures with multiple cation sites and strongly uneven occupation of activators and cations. Finally, the package of the LED device is constructed to show that both color rendering index Ra and R9 are higher than 95. Thus, the device could be a potential candidate for full-spectrum lighting.

KEYWORDS: cyan phosphor, full spectrum, M5(PO4)3Cl, LED, activator redistribution

White light-emitting diodes (LEDs) have been employed in different illumination systems worldwide. An increasing number of traditional illumination devices are being replaced by LEDs because of their high brightness, low energy consumption, long lifetime, and eco-friendliness.1–6 LEDs are applied not only in lighting but also in extensive fields, such as agriculture lighting, automobile, and backlighting.7–9 UV–LED chips with red, green, and blue phosphors have attracted considerable attention as next-generation LED devices because of their high color rendering index.10 A new concept called “full-spectrum lighting” (FSL) has attracted much attention in recent years. However, the cyan cavity in the 480–520 nm region (Figure S1) decreases color vividness. Hence, a cyan phosphor is important to obtain real full-spectrum lighting. The M5(PO4)3Cl:Eu2+ (M = Ca, Sr, Ba) system has been selected as the candidate phosphor because of its high water resistance and high quantum efficiency. Norzol et al.11 first proposed that two Sr sites are available and that Ca prefers to occupy one of the Sr sites in (Ca,Sr)5(PO4)3Cl:Eu2+. In 2013, Shang et al.12 reported that Ca2Ba3(PO4)3Cl:Eu2+ phosphors could emit light with a peak maximum at 410 nm but are hardly excited by light over 400 nm. In 2015, Deressa et al.13 first reported Ba2+-doped Sr5(PO4)3Cl:Eu2+ phosphors. The emission wavelength of Sr5(PO4)3Cl:Eu2+ is approximately 450 nm. Ba2+ doping broadens the full width at half-maximum of Sr5(PO4)3Cl:Eu2+. However, the luminescent intensity and spectrum of this phosphor remain to be analyzed in detail. The luminescent properties of Sr4.7−xBa0.3(PO4)3Cl:Eu2+ with a high Ba2+ concentration are unique and tunable. Previous studies analyzed activator redistribution in some phosphor systems.14–18 To the best of our knowledge, a system featuring activator-preferred occupation, activator-uneven distribution, change of activator oxidation state, and squeezed-out behavior remains to be observed and analyzed. In the present study, we analyze the structure and luminescence properties of Sr4.7−xBa0.3(PO4)3Cl in detail. We also propose a mechanism for the unique behavior of the system. Finally, LED devices are constructed to show that both color rendering index Ra and R9 are higher than 95.

The X-ray diffraction (XRD) patterns of Sr4.7−xBa0.3(PO4)3Cl (0 ≤ x ≤ 2.5) are shown in Figure 1a. All patterns are pure phase except for some Eu2O3.

Received: August 15, 2016
Accepted: November 1, 2016
Published: November 1, 2016

DOI: 10.1021/acsami.6b10233
ACS Appl. Mater. Interfaces 2016, 8, 30677–30682
impurities when $x$ is higher than 2. Both Sr$_x$(PO$_4$)$_3$Cl and Ba$_x$(PO$_4$)$_3$Cl possess a hexagonal $P6_3/m$ structure, which allows them to form a solid solution. The XRD peaks slightly shift toward low scattering angles as $x$ increases because the ionic size of Ba$^{2+}$ is larger than that of Sr$^{2+}$. Two crystallographic coordination environments of Sr$^{2+}$ are present and denoted as Sr(I) and Sr(II). Sr(I) is coordinated by nine oxygen ions, whereas Sr(II) is coordinated by six oxygen and two chloride ions (Figure 1b). To further investigate the structure, we employed synchrotron XRD and Rietveld refinement (Figure S2). Lattice parameters $a$, $c$, and $V$ linearly increase because of the increased ionic size of Ba$^{2+}$. Interestingly, Ba$^{2+}$ is not equally distributed within the Sr$^{2+}$ site. The occupation value of Ba$^{2+}$ at the Sr(I) site is close to zero and slightly increases when $x$ is higher than 1.5 (Figure 1c). The result reveals that Ba$^{2+}$ has a strongly preferred occupation in different Sr$^{2+}$ sites.

To investigate the effect of Ba$^{2+}$-preferred occupation in the system, the room-temperature photoluminescence (PL) spectra

**Figure 1.** (a) XRD patterns with different $x$ values in Sr$_{4.7-x}$Ba$_x$Eu$_{0.3}$(PO$_4$)$_3$Cl ($0 \leq x \leq 2.5$). (b) Sr coordination environment of Sr(I) and Sr(II). (c) Ba occupation value at Sr(I) and Sr(II).
and photoluminescence excitation (PLE) spectra are determined (Figure 2a). The excitation spectra range from 300 to 430 nm. The excitation spectra consist of several overlapping broad bands that are independent of the Ba$^{2+}$ concentration in all considered samples. When excited by 330 nm UV light, the emission peak maximum shifts from 446 to 472 nm as $x$ increases (Figure 2b). The XRD patterns indicate that two crystallographic Sr$^{2+}$ sites exist. Therefore, the PL spectra of Sr$_{4.7-}$.Ba$_x$,Eu$_{0.3}(PO_4)_3$Cl are decomposed into two Gaussian bands. The higher energy emission band with peak maximum at 448 nm corresponds to Eu$^{2+}$ located at the Sr(II) site, whereas the lower energy emission band with peak maximum at 488 nm corresponds to Eu$^{2+}$ at the Sr(I) site, which are denoted as Eu(SrII) and Eu(SrI), respectively. Although the excitation spectra appear similar in Figure 2a, we expect to observe different excitation spectra for the two well-defined Eu(SrII) and Eu(SrI) emission bands. As a result, the low-temperature excitation spectra at 450 and 500 nm are determined. Although the excitation spectra overlap largely with each other, the 420-440 nm region is different. Under an excitation wavelength of 420 nm, both Eu(SrII) and Eu(SrI) are simultaneously excited, but the excitation is dominant for Eu(SrII). The emission spectrum shows the maximum peak at approximately 450 nm and a tail at approximately 500 nm. By contrast, Eu(SrI) could be independently excited under 440 nm, and the emission maximum wavelength is approximately 500 nm.

Interestingly, the emission spectrum of Sr$_{4.7-}$Eu$_{0.3}(PO_4)_3$Cl seems to be a symmetry band, although both Sr(I) and Sr(II) sites exist in the structure. This phenomenon conflicts with our expectation that the emission spectrum of Sr$_{4.7-}$Eu$_{0.3}(PO_4)_3$Cl is an asymmetry band consisting of Eu(SrII) and Eu(SrI). However, the emission spectra gradually change from a symmetry to an asymmetry band after Ba$^{2+}$ doping. In consequence, we boldly assume that Eu$^{2+}$ ions only occupy the Sr(II) site at the beginning. After Ba$^{2+}$ doping, Eu$^{2+}$ ions are partly squeezed from the Sr(II) to the Sr(I) site. To verify our assumption, the decay curve is used to investigate the behavior of the two Sr$^{2+}$ sites (Figure 2d). First, $\lambda_{abs} = 440$–460 nm is used to detect the luminescence overlap region of Eu(SrII) and Eu(SrI). The luminescence decay of Sr$_{4.7-}$Eu$_{0.3}(PO_4)_3$Cl is single exponential, which indicates that Eu$^{2+}$ occupies only one site. By contrast, the PL decays of Sr$_{4.7-}$Ba$_x$,Eu$_{0.3}(PO_4)_3$Cl (0.5 $\leq x \leq 1.5$) are nonexponential and considered as a superposition of two exponents. This finding indicates that Eu$^{2+}$ ions occupy both Sr(II) and Sr(I) sites. In addition, the luminescence decays of $\lambda_{abs} = 480$–520 nm are single exponential for Sr$_{4.7-}$Ba$_x$,Eu$_{0.3}(PO_4)_3$Cl (0.5 $\leq x \leq 1.5$) because of the Eu(SrI) single site luminescence. The lifetime calculated from the decay curve is shown in Figure S3b. The lifetime observed from 440 to 460 nm is short and gradually decreases, whereas the lifetime observed from 480 nm to 520 increases after Ba$^{2+}$ doping. This phenomenon may be attributed to the nonradiative energy transfer from Eu(SrII) to Eu(SrI) sites.

Some Eu$_2$O$_3$ impurities exist in the samples with high Ba concentrations (Figure S4c). This phenomenon is uncommon in solid state reaction. To investigate the underlying reasons, the oxidation state of Eu ions with high Ba$^{2+}$ concentrations is analyzed by Eu$^{3+}$ characteristic PL spectroscopy (Figure S4). Three characteristic narrow peaks appear at approximately 625 nm, and the intensity slightly increases with increasing Ba$^{2+}$ concentration. This condition means that Eu$^{2+}$ gradually oxidizes to Eu$^{3+}$ after Ba$^{2+}$ doping. Moreover, X-ray absorption near-edge structure (XANES) spectroscopy is applied to determine the charge variation of Eu (Figure 3). The L$_{3}$ edge of Eu shows two peaks at 6974 and 6984 eV, suggesting the 2p$_{1/2}$ $\rightarrow$ 5d transition of Eu$^{2+}$ and Eu$^{3+}$, respectively. Ba$^{2+}$ doping slightly increases the signal of Eu$^{3+}$ and decreases the signal of Eu$^{2+}$. However, the Eu$^{3+}$ signal in the sample with a high Ba$^{2+}$ concentration considerably increases, and most of the Eu$^{2+}$ ions are changed to Eu$^{3+}$ as $x = 2.5$. This phenomenon may be attributed to the size difference between Ba$^{2+}$ and Sr$^{2+}$. When $x = 1.5$, the Eu$^{3+}$ is mainly at the Sr(I) site. However, when large Ba$^{2+}$ is doped into Sr(I), Eu$^{2+}$ ions are forced to shrink the size and hence be oxidized to small Eu$^{3+}$ ions. The direct effect of Eu oxidization is the extremely low PL intensity when $x = 2.5$, and the results agree with the photoluminescence spectrum shown in Figure 2b.

Integrating the results above, we propose a mechanism of cation size control activator redistribution (Figure 4). Initially, Eu$^{2+}$ ions only occupy the Sr(II) site; hence, the decay curve is single exponential, and the PL spectrum is symmetrical ($x = 0$). After a small amount of Ba ions is doped into the crystal (0.5 $\leq x \leq 1.5$), Ba prefers to occupy the Sr(II) site because of the larger space of the Sr(II) site compared with that of the Sr(I) site. Eu$^{3+}$ ions partially transfer from the Sr(II) to the Sr(I) site because of the limited space in the Sr(II) site, causing the change in the decay curve and the PL spectrum. After further Ba doping (1.5 $\leq x \leq 2.5$), the space for Ba at the Sr(II) site reaches the limit, and Ba starts to dope in Sr(I), which is in accordance with the results shown in Figure 1c. In addition, the space of Eu$^{2+}$ in the Sr(I) site is decreased by the large Ba$^{2+}$ ions. This process forces Eu ions to change from large Eu$^{2+}$ ions...
to small Eu³⁺ ions or exist as Eu₃O₅ to save space, which could be observed in the XRD pattern and the PL spectrum.

Thermal stability is also an important property of phosphor materials. In this study, we use temperature-dependent photoluminescence (TDPL) spectroscopy to analyze the thermal stability of Sr₄.7−ₓBaₓEu₀.3(PO₄)₃Cl (Figure 5a). The thermal stability of the phosphor is obviously enhanced by the doping of Ba ions. For Sr₃.2Ba₁.5Eu₀.3(PO₄)₃Cl, the PL intensity at 150 °C retains 86% of the intensity at 25 °C. Normally, when heavy atoms are doped, the lattice vibration decreases and hence increases the thermal activation energy, which consequently increases the thermal stability. To study the thermal properties in depth, the decay times of different detected wavelengths and temperatures are measured as shown in Figure S5. To analyze the temperature shortening of the emission decay time τ, we should consider the following formula

$$
\tau = \frac{1 + \exp\left(\frac{E_v}{kT}\right)}{1 + \exp\left(\frac{E_a}{kT}\right)}
$$

(1)
where \( \tau \) is the PL radiative decay time, \( E_a \) is the activation energy, and \( P \) is the probability of the nonradiative depopulation. Fitting relation 1 to the experimental data, we estimate a single nonradiative pathway for Eu at the Sr(II) site in Sr4.7Eu0.3(PO4)3Cl, characterized by activation energy \( E_a = 609 \text{ cm}^{-1} \) and probability \( P = 14 \times 10^6 \text{ s}^{-1} \) (Figure 5b). For Eu at the Sr(II) centers in Sr3.2Ba1.5Eu0.3(PO4)3Cl, we obtain similar results of activation energy \( E_a = 776 \text{ cm}^{-1} \) and probability \( P = 98 \times 10^6 \text{ s}^{-1} \), indicating that we are dealing with the same band deactivation for Eu at the Sr(II) site. In Sr3.2Ba1.5Eu0.3(PO4)3Cl, the Eu at Sr(I) site luminescence quenching is characterized by activation energy \( E_a = 3273 \text{ cm}^{-1} \) and probability \( P = 5 \times 10^6 \text{ s}^{-1} \). This phenomenon can be related to the autoionization of Eu2+, considered as the transition from the excited state 4f75d1 to the conduction band. In addition, the charge transfer band and band absorption are indispensable information to construct the band structure and energy band diagram of Sr4.7Eu0.3(PO4)3Cl. In this study, Sr4.7(PO4)3Cl:Eu3+ is synthesized to obtain the more accurate energy, and \( P \) and probability \( \tau \). The energy gap (\( E_{\text{vac}} \)) is approximately equal to 1.08E\text{\text{as}}, that is, 8.02 eV for Sr4.7Eu0.3(PO4)3Cl. Furthermore, the emission energies of Eu from Sr(II) and Sr(I) are 2.78 and 2.45 eV, respectively. To verify the obtained values, we combined the charge transfer energy, PL energy, and \( E_a \) calculated from the decay curve as shown in Table S2. The band gaps calculated from Eu(SrII) and Eu(SrI) are 7.98 and 8.07 eV, respectively, which agree with the spectral value of 8.02 eV as shown in Figure 5d.

To demonstrate the potential of (Sr,Ba)4.7Eu0.3(PO4)3Cl in actual applications, LED packages are constructed. The devices are combined with UV–LED, red phosphor (Ca,Sr)-AlSiN3:Eu2+, green phosphor (Ba,Sr,Ca)2SiO4:Eu2+, and different blue phosphors. As the most well-known blue phosphor, BaMgAl10O17:Eu2+, is chosen to be the comparison group. To compare the three devices, the point in the CIE diagram should be the same and on the blackbody radiation line; a correlated color temperature of 3000 K is selected as shown in Figure 6a. The measured color rendering index (Table S4). When Sr4.7Eu0.3(PO4)3Cl is single exponential but becomes non-exponential after Ba2+ doping, which also proves the transfer of Eu from the Sr(II) to the Sr(I) site. As further compressed by Ba2+, Eu(SrI) is squeezed out as Eu2O3 because of the limited Sr(II) space. Moreover, Eu2+ oxidation is examined by XANES and Eu3+ characteristic PL spectroscopy. The mechanism scheme is then provided. In addition, the thermal stability and energy level diagram are examined by TDPL and decay curve.

The mechanism of the size-controlled behavior with activator uneven-occupation and reoxidation could help tune the PL spectrum in related apatite families, such as Ca2(PO4)3(F,Cl,OH), Ca2(PO4)3F, and their solid-solution compounds. The mechanism is also expected to be applied in structures with more than two cation sites and strong activator-preferred occupation. The tuning method and provided mechanism could help understand and explain the results. Real full-spectrum lighting can be achieved by Sr3.2Ba1.5Eu0.3(PO4)3Cl. The LED package device not only possesses high Ra and R9 values (>95) but also compensates for the 480–520 nm cyan gap, which widens the research on full-spectrum lighting.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b10233.

Experimental methods, X-ray Rietveld refinement, Eu3+ characteristic emission spectra, temperature-dependent decay, energy level, quantum efficiency, package result (PDF)

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: rsliu@ntu.edu.tw.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Ministry of Science and Technology of Taiwan (Contracts MOST 104-2113-M-002-012-MY3, MOST 104-2119-M-002-027-MY3, and MOST 104-2923-M-002-007-MY3) and National Center for Research and Development Poland Grant (PL-TW2/8/2015).

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