

Emission Color Shift From Yellow to Red in $\text{Ca}_6\text{BaP}_4\text{O}_{17}:\text{Eu}^{2+}$

Masato Iwaki¹, Kazuyoshi Uemastu¹, Mineo Sato², and Kenji Toda^{1,*}

* E-mail : ktoda@eng.niigata-u.ac.

¹ Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan.

² Department of Chemistry and Chemical Engineering, Niigata University, 8050 Ikarashi 2-nocho, Niigata 950-2181, Japan

Keywords: Eu^{2+} , $\text{Ca}_6\text{BaP}_4\text{O}_{17}$, emission color shift

ABSTRACT

We successfully obtained Eu^{2+} -activated $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ phosphors via the solid state reaction. With increasing the content of the Eu^{2+} ion, the emission peak shift from 550 nm to 610 nm. The Rietveld refinement shows that the Eu^{2+} ion preferentially occupies CaO_7 and CaO_8 sites in the host.

1 INTRODUCTION

The discovery of novel phosphors for white-light emitting diodes (wLEDs) have been conducted owing to its excellent features such as high luminescent efficiently, a long lifetime and environmentally friendly compared with a fluorescent lamp and a midget lamp [1]. Therefore, wLEDs are the attention for a next generation of lighting system. In general, the most commercial wLEDs are composed of a blue-LED (InGaN) and a yellow-emitting phosphors, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) [2]. Nevertheless, the system of this wLEDs have low color rendering index (CRI) due to the lack of the red emission region in the YAG: Ce^{3+} phosphor. Thus, another systems of wLEDs propose in order to solve this problem. For example, the white-LEDs combining with a blue LED and two different phosphors, green (or yellow) and red emission phosphors have been suggested. Moreover, near-ultraviolet LED (near-UV - LED) + blue/green/red emission phosphors can become the new system for white-LEDs [3] [4].

The typical red phosphors for wLEDs are nitride phosphors such as $\text{CaAlSiN}_3:\text{Eu}^{2+}$, $\text{SrLiAl}_3\text{N}_4:\text{Eu}^{2+}$ and $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ [5] [6] [7]. These nitride phosphors have sufficient luminescent efficiency excited the blue light and the excellent thermal stability. However, nitride phosphors are difficult to synthesize because nitride materials needs a special furnace, which can control the high temperature and pressure. Therefore, many researchers investigate novel oxide phosphor materials which can appear red emission under blue-light excitation. In the recent research, $\text{Sr}_6\text{Y}_2\text{Al}_4\text{O}_{15}$ with the large amount of the Ce^{3+} ion appeared the broad red emission under the blue light irradiation because the cerium ion could replace the Y^{3+} octahedral site with the strong crystal field, while the blue emission owing to the Ce^{3+} ion in Sr sites was also present [8]. Thus, an incorporation of the high concentration of activators with the 4f-5d allowed transition is the useful technique to develop the red emitting phosphor [9] [10].

We focus on the Eu^{2+} -activated $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ phosphors, which can appear the green-yellow emission excited blue light. This phosphor has been firstly reported by N. Komuro

et al [11]. Nevertheless, the emission color tuning by doping amount of Eu^{2+} has not been investigated. Furthermore, the host lattice of $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ have three different crystallographic alkali sites, CaO_7 , CaO_8 and BaO_{12} respectively (Fig. 1). Therefore, it indicates that the emission color of the Eu^{2+} -activated $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ phosphor can be tuned depending on the concentration of Eu^{2+} .

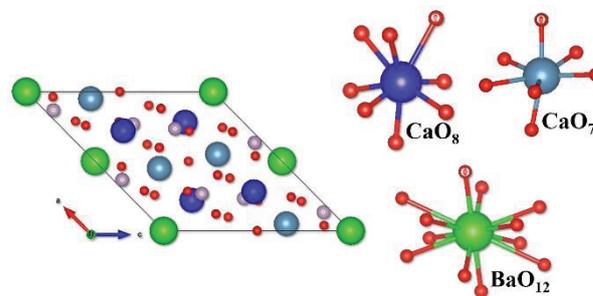


Fig. 1 Crystal structure of $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ and three crystallographic alkali sites.

In this study, $\text{Ca}_6\text{BaP}_4\text{O}_{17}:\text{Eu}^{2+}$ phosphors were synthesized by the conventional solid state reaction method. The crystal structure, lattice parameters and the site occupancies in Eu^{2+} -activated $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ were identified by the Rietveld refinement analysis from the X-ray powder diffraction. Moreover, their emission and excitation spectra, the quantum efficiency, the thermal stability, the lifetimes of Eu^{2+} and Commission Internationale de L'Eclairage (CIE) chromaticity coordinates are systematically investigated.

2 EXPERIMENT AND CHARACTERIZATION

$\text{Ca}_{6(1-x)}\text{Eu}_x\text{BaP}_4\text{O}_{17}$ (CBP: $x\text{Eu}^{2+}$) phosphors were synthesized by the solid state reaction. CaCO_3 (Kanto Chemical Co., Inc., 99.99%), BaCO_3 (Kanto Chemical Co., Inc., 99.99%), $(\text{NH}_4)_2\text{HPO}_4$ (Kanto Chemical Co., Inc., 99.0%) and Eu_2O_3 (Shin-etsu Chemical Co., Inc., 99.99%) are weighed in the stoichiometric ratio at Ca : Ba : P : Eu = $6(1-x)$: 1 : 4 : $6x$ ($0 \leq x \leq 0.20$). Then, sorted raw materials were mixed in acetone with an agate mortar. After drying, the mixtures were pelleted and heated at 1523 K for 6 h in a reducing atmosphere (95 vol.% Ar / 5 vol.% H_2) to reduce from Eu^{3+} to Eu^{2+} .

Powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (D2 PHASER; Bruker) with a monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm)

under 10 mA and 30 kV. The Rietveld refinement was carried out using the RIETAN-FP software [12]. Photoluminescence (PL), photoluminescence excitation (PLE) spectra were measured at room temperature using a spectrofluorometer (FP-6500 / FP-6600; Jasco Inc.) with 150 W Xenon lamp. Internal quantum efficiencies (IQE) are calculated via Quantaurus-QY (Hamamatsu Photonics Inc.). The decay curves of Eu^{2+} in $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ were measured by Quantaurus-Tau (Hamamatsu Photonics Inc.).

3 RESULT AND DISCUSSION

Fig. 2 shows the Rietveld refinement on X-ray powder diffraction data of the $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ host. R values, R_{wp} , R_p , R_e and S are converged to 8.973%, 6.174%, 5.106% and 1.757, respectively. It implies that the $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ is successfully synthesized without impurities. $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ has a monoclinic crystal structure with the space group of $C2/m$ (No. 12). Moreover, The refined cell parameters of $\text{Ca}_6\text{BaP}_4\text{O}_{17}$ is found to be $a = 1.2303(1)$ nm, $b =$

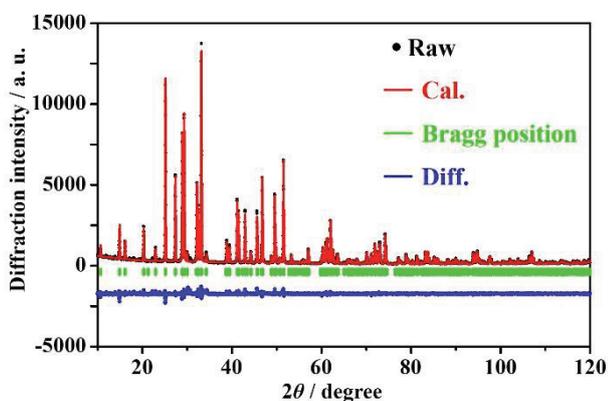


Fig. 2 Rietveld refinement on X-ray powder diffraction data of $\text{Ca}_6\text{BaP}_4\text{O}_{17}$.

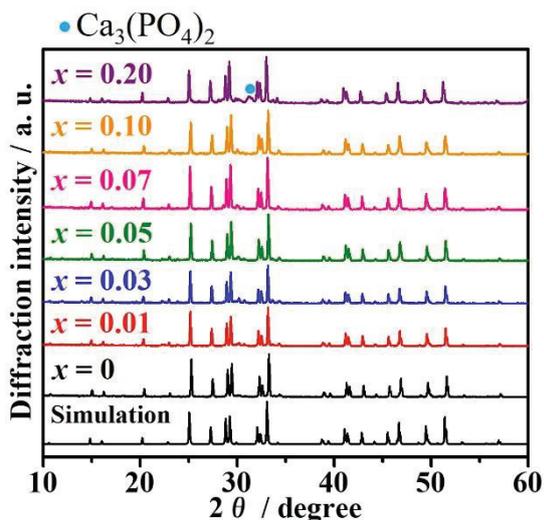


Fig. 3 X-ray diffraction patterns of CBP:xEu^{2+} ($0 \leq x \leq 0.20$).

$0.71044(2)$ nm, $c = 1.17160(8)$ nm and $V = 0.73109(10)\text{nm}^3$, respectively.

Fig. 3 shows the X-ray diffraction patterns of CBP:xEu^{2+} ($0 \leq x \leq 0.20$). All diffraction peaks are in agreement with the simulation pattern of $\text{Ca}_6\text{BaP}_4\text{O}_{17}$. Moreover, Until $x = 0.10$, impurity phases cannot be observed, while the diffraction peak of $\text{Ca}_3(\text{PO}_4)_2$ is appeared around 32° at $x = 0.20$.

The normalized emission spectra of CBP:xEu^{2+} ($x = 0.01, 0.05, 0.10, 0.20$) under the blue light excitation at 450 nm are shown in Fig. 4. The emission spectrum of CBP:0.01Eu^{2+} exhibits the broad green-yellow emission with the peak top of 550 nm and the full width half maximum (FWHM) of 131 nm. On the other hand, as the concentration of Eu^{2+} ion increases, the emission peak position are drastically shifted to the longer wavelength. Consequently, the emission band of CBP:0.20Eu^{2+} is located in the red emission region with the peak top of 611 nm and FWHM of 166 nm. It indicates that the location of the Eu^{2+} ion are varied depending on the content of activators. To determine the occupancy of the Eu^{2+} ion in the CBP host lattice, the Rietveld refinement of CBP:xEu^{2+} is also conducted. As a result, the lattice volumes of CBP:xEu^{2+} gradually increases as the concentration of the Eu^{2+} ion becomes higher, indicating that the larger Eu^{2+} ion are preferentially incorporated into smaller calcium sites rather than the barium site. Furthermore, from the Rietveld refinement, it seems that most of the Eu^{2+} ions are located in CaO_8 site, while a few amount of activators are substituted for CaO_7 sites.

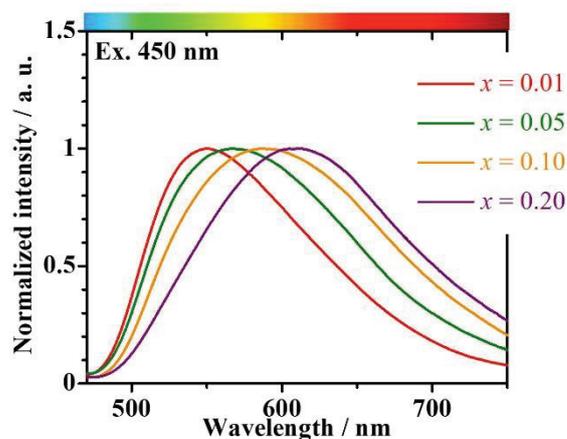


Fig. 4 Normalized emission spectra CBP:xEu^{2+} ($x = 0.01, 0.05, 0.10, 0.20$) excited at 450 nm.

4 CONCLUSION

We succeeded in synthesizing Eu^{2+} -activated CBP phosphors via the solid state reaction. From the Rietveld refinement, the Eu^{2+} ions are preferentially replaced to two calcium sites, CaO_7 and CaO_8 , respectively. As the concentration of the Eu^{2+} ion, the emission red shift from 550 nm to 610 nm is observed. The incorporation of the high concentration of activators with the 5d-4f transition is useful technique to develop the red emission phosphor materials.

5 REFERENCES

- [1] Z. Xia, Z. Xu, M. Chen, Q. Liu, Recent developments in the new inorganic solid-state LED phosphors, *Dalt. Trans.*, 45, pp. 11214–11232 (2016).
- [2] K. BANDO, K. SAKANO, Y. NOGUCHI, Y. SHIMIZU, Development of High-bright and Pure-white LED Lamps., *J. Light Vis. Environ.*, 22, pp. 2-5 (1998).
- [3] J.L. Leañó, M.-H. Fang, R.-S. Liu, Critical Review—Narrow-Band Emission of Nitride Phosphors for Light-Emitting Diodes: Perspectives and Opportunities, *ECS J. Solid State Sci. Technol.*, 7, pp. R3111–R3133 (2018).
- [4] L. Wang, R.-J. Xie, T. Suehiro, T. Takeda, N. Hirosaki, Down-Conversion Nitride Materials for Solid State Lighting: Recent Advances and Perspectives, *Chem. Rev.*, 118, pp. 1951–2009 (2018).
- [5] X. Piao, K. Machida, T. Horikawa, H. Hanzawa, Y. Shimomura, N. Kijima, Preparation of $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphors by the self-propagating high-temperature synthesis and their luminescent properties, *Chem. Mater.*, 19, pp. 4592–4599 (2007).
- [6] P. Pust, V. Weiler, C. Hecht, A. Tücks, A.S. Wochnik, A.K. Henß, D. Wiechert, C. Scheu, P.J. Schmidt, W. Schnick, Narrow-band red-emitting $\text{Sr}[\text{LiAl}_3\text{N}_4]:\text{Eu}^{2+}$ as a next-generation LED-phosphor material, *Nat. Mater.* 13, pp. 891–896 (2014).
- [7] R.-J. Xie, N. Hirosaki, T. Suehiro, F.-F. Xu, M. Mitomo, A Simple, Efficient Synthetic Route to $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ -Based Red Phosphors for White Light-Emitting Diodes, *Chem. Mater.*, 18, pp. 5578–5583 (2006).
- [8] Y. Kawano, S.W. Kim, T. Ishigaki, K. Uematsu, K. Toda, H. Takaba, M. Sato, Site engineering concept of Ce^{3+} -activated novel orange-red emission oxide phosphors, *Opt. Mater. Express.* 4, pp. 1770–1774 (2014).
- [9] G. Li, Y. Zhao, Y. Wei, Y. Tian, Z. Quan, J. Lin, Novel yellowish-green light-emitting $\text{Ca}_{10}(\text{PO}_4)_6\text{O}:\text{Ce}^{3+}$ phosphor: structural refinement, preferential site occupancy and color tuning, *Chem. Commun.* 52, pp. 3376–3379 (2016).
- [10] H. Nakamura, Massive red shift of Ce^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$ incorporating super-high content of Ce, *RSC Adv.* 10, pp. 12535–12546 (2020).
- [11] N. Komuro, M. Mikami, Y. Shimomura, E.G. Bithell, A.K. Cheetham, Synthesis, structure and optical properties of europium doped calcium barium phosphate—a novel phosphor for solid-state lighting, *J. Mater. Chem. C.* 2, pp. 6084–6089 (2014).
- [12] F. Izumi, *The Rietveld Method*, Ed. by R. A. Young, Oxford University Press, Oxford, Chap. 13 (1993).