

# Origin of blue emission of phosphors prepared by a solid-state reaction of $\text{Eu}^{3+}$ -doped $\text{LaCO}_3\text{OH}$ with $\text{Al}_2\text{O}_3$ in a hydrogen atmosphere



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## ABSTRACT

The phosphor powders prepared by calcining mixtures (1:1, 1:2, and 1:3 mol ratios) of  $\text{Eu}^{3+}$ -doped lanthanum(III) hydroxycarbonate ( $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$ ) and  $\delta$ -alumina ( $\delta\text{-Al}_2\text{O}_3$ ) powders under a mixed gas flow of  $\text{H}_2$  and  $\text{N}_2$  exhibited orange (593 and 617 nm) and blue (441 nm) emission peaks, which were associated with  $\text{Eu}^{3+}$ -doped lanthanum aluminate ( $\text{LaAlO}_3:\text{Eu}^{3+}$ ) and  $\text{Eu}^{2+}$ -doped lanthanum hexaaluminate ( $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}:\text{Eu}^{2+}$ ) phosphors, respectively. The relative amount of the latter phosphor increased with increasing reaction temperature and relative amount of  $\delta\text{-Al}_2\text{O}_3$  in the mixture. The conclusion that the blue emission is not associated with  $\text{LaAlO}_3:\text{Eu}^{2+}$  but  $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}:\text{Eu}^{2+}$  was supported by the following experimental results: the reduction of  $\text{LaAlO}_3:\text{Eu}^{3+}$  did not give a blue emission;  $\text{Eu}^{2+}$  ions occupied more than one site in the host; the line shape and position of the blue emission band were close to those of the single  $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}:\text{Eu}^{2+}$  phase. No formation of  $\text{LaAlO}_3:\text{Eu}^{2+}$  might be due to the increase in the ionic radius caused by the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ .

## 1. Introduction

Divalent europium ion ( $\text{Eu}^{2+}$ )-doped materials have been widely studied because of their luminescent properties. The luminescence of the  $\text{Eu}^{2+}$  ion is associated with the Laporte allowed  $4f^65d^1 \rightarrow 4f^7$  ( $5d \rightarrow 4f$ ) transition and its color can be tuned by changing the host lattice. Much effort has been made to realize white light emission by adjusting the relative amount of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ions coexisting in a single host [1–7]. One method of preparing  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  co-doped materials is to calcine  $\text{Eu}^{3+}$ -doped materials in a reducing atmosphere such as  $\text{H}_2$  and  $\text{CO}$ , but  $\text{Eu}^{3+}$  ions doped in some hosts are not reduced to  $\text{Eu}^{2+}$  ions, because  $\text{Eu}^{2+}$  has a larger ionic size than  $\text{Eu}^{3+}$ . To enable the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  in such a host, the crystal-site engineering approach, in which the coordination environment and crystal site size are modified, has been applied [4,6,7]. For example, Huang et al. enlarged the activator site in  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{F}_2:\text{Eu}^{3+}$  by replacing  $\text{Al}^{3+}\text{-F}^-$  by  $\text{Si}^{4+}\text{-O}^{2-}$ , leading to the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  [4].

Lanthanum aluminate ( $\text{LaAlO}_3$ ) with a perovskite-type structure has attracted much attention as a host material because of its reasonably large band gap ( $> 5$  eV) and high thermal stability ( $> 2100$  °C). Many studies have focused on trivalent rare earth ion ( $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Ho}^{3+}$ , or  $\text{Yb}^{3+}$ )-doped  $\text{LaAlO}_3$  owing to its great luminescent properties [8–12]. Mao et al. showed that the  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  co-doped phosphor powders prepared by a solid-state reaction among  $\text{La}_2\text{O}_3$ ,

$\text{Al}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$  powders in a mixed gas flow of  $\text{H}_2$  and  $\text{N}_2$  exhibited orange and blue (440 nm) emissions [1,2]. They assigned the blue emission to the  $5d \rightarrow 4f$  transition of  $\text{Eu}^{2+}$  in  $\text{LaAlO}_3:\text{Eu}^{2+}$ . Chen observed the intensity enhancement of the blue emission band at ca. 440 nm through the addition of  $\text{SiO}_2$  to the three-component ( $\text{La}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$ ) reaction system and explained the enhancement in terms of the charge compensation by the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , which was accompanied by the substitution of  $\text{Si}^{4+}$  ion for  $\text{Al}^{3+}$  ion in  $\text{LaAlO}_3:\text{Eu}^{3+}$  [5]. Considering that the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  in the  $\text{LaAlO}_3$  host may not occur because the ionic radius of  $\text{Eu}^{2+}$  is larger (by ca. 7 pm) than that (136 pm) of  $\text{La}^{3+}$  for a coordination number (CN) of 12 [13,14], the blue emission is not likely to be associated with  $\text{LaAlO}_3:\text{Eu}^{2+}$ . The origin of the blue emission at ca. 440 nm is therefore not clear yet.

In this study, we investigated the origin of the blue emission in phosphors obtained by calcining a mixture of  $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  and  $\text{Al}_2\text{O}_3$  powders under a mixed gas flow of  $\text{H}_2$  and  $\text{N}_2$ . The two-component ( $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  and  $\text{Al}_2\text{O}_3$ ) reaction system is preferable to the three-component ( $\text{La}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$ ) one in terms of the intensity of the blue emission band [15].

## 2. Experimental procedure

The starting materials,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

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(99.9%),  $\text{La}_2\text{O}_3$  (99.99%),  $\text{Eu}_2\text{O}_3$  (99.9%),  $\text{KNO}_3$  (>99.0%), and urea (99.0%) were purchased from Sigma-Aldrich Co. and used as-received without further purification.  $\delta\text{-Al}_2\text{O}_3$  (CR125, Baikalex International) was used as an Al source.

### 2.1. Synthesis of phosphors with blue emission from $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$ - $\text{Al}_2\text{O}_3$ reaction system

Orthorhombic (*o*-) $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  (2 mol%) powder was synthesized by refluxing an aqueous solution containing  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{KNO}_3$ , and urea, as described previously [16]. Mixtures (1:1, 1:2, and 1:3 mol ratios of  $\text{Ln}^{3+}$  ( $=\text{La}^{3+} + \text{Eu}^{3+}$ ) to  $\text{Al}^{3+}$  ions; hereafter, 1:1, 1:2, and 1:3 mixtures, respectively) of *o*- $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  and  $\delta\text{-Al}_2\text{O}_3$  were thoroughly ground in an agate mortar and then transferred into an alumina crucible. The crucible was heated to the reaction temperature (1100–1400 °C) under a mixed gas flow of  $\text{H}_2$  (10 vol%) and  $\text{N}_2$  (hereafter, 10 vol%  $\text{H}_2/\text{N}_2$ ). The gas flow rate was 100 mL/min and the duration was 3 h, unless stated otherwise.

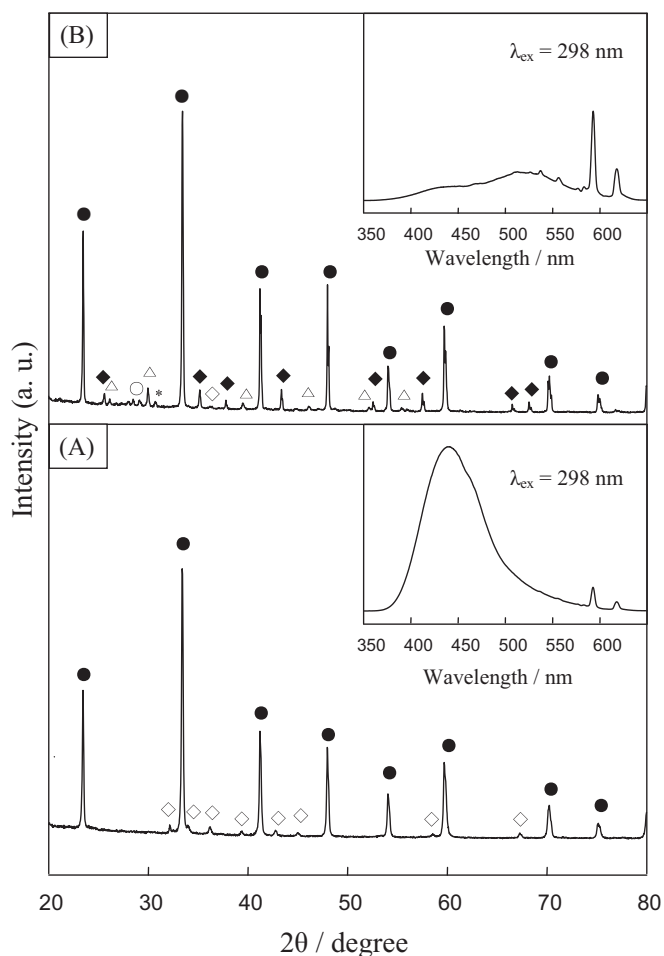
### 2.2. Product characterization

The product powders were characterized by powder X-ray diffraction (XRD) with a PANalytical X'Pert PRO MPD X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation operating at 40 kV and 30 mA. The excitation and emission spectra were measured on a JASCO FP-6500 spectrofluorometer using a 150 W xenon lamp.

## 3. Results and discussion

The reason why we selected the two-component ( $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  and  $\text{Al}_2\text{O}_3$ ) reaction system instead of the three-component ( $\text{La}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$ ) one is as follows. When these three components are not homogeneously mixed, the secondary  $\text{EuAl}_2\text{O}_4$  phase is susceptible to be formed. For example, Fig. 1 shows the difference in the XRD patterns and emission spectra between the homogeneous and inhomogeneous mixtures, which were prepared by grinding the three components in an agate mortar. As shown in Fig. 1(A), the product powder derived from the homogeneous mixture was a mixture of hexagonal (*h*-) $\text{LaAlO}_3$  (ICDD-PDF #98-005-7330) and  $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}$  (lanthanum hexaaluminate, ICDD-PDF # 98-001-8287) and had a blue emission band at 441 nm together with two weak peaks at 593 and 617 nm. The latter peaks were assigned to the magnetic dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and electric dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  ion, respectively [15]. On the other hand, the product powder obtained from the inhomogeneous mixture was a mixture of *h*- $\text{LaAlO}_3$ ,  $\text{EuAl}_2\text{O}_4$ , and unreacted hexagonal (*h*-) $\text{La}_2\text{O}_3$  (ICDD-PDF #98-001-0772) and  $\alpha\text{-Al}_2\text{O}_3$  (ICDD-PDF #01-088-0826). As shown in the inset in Fig. 1(B), the emission spectrum of the powder shows a green emission band at ca. 520 nm, which was associated with  $\text{EuAl}_2\text{O}_4$  [17]. As a result, the formation of  $\text{EuAl}_2\text{O}_4$  lowered the intensity of the blue emission band at 441 nm. The effect of the degree of homogeneity of the mixture on the product phase is much weaker for the two-component reaction system than for the three-component one. This is why we selected the two-component reaction system. The  $\text{EuAl}_2\text{O}_4$  phase was not formed in this work.

Mixtures of *o*- $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  (2 mol%) and  $\delta\text{-Al}_2\text{O}_3$  were calcined at 1200 °C and characterized by powder XRD and PL spectroscopy. As shown in Fig. 2(A, a), the XRD pattern of the sample obtained by calcining the 1:1 mixture exhibited peaks assigned to *h*- $\text{LaAlO}_3$  together with very weak peaks assigned to *h*- $\text{La}_2\text{O}_3$ . No peaks corresponding to unreacted  $\text{Al}_2\text{O}_3$  were observed because of their very low intensity [15]. For the samples obtained by calcining the 1:2 and 1:3 mixtures, however, weak peaks assigned to excess  $\alpha\text{-Al}_2\text{O}_3$  were detected (Fig. 2(A,b) and (A,c)). These three samples showed no distinct differences in their XRD patterns, except for the weak peaks



**Fig. 1.** XRD patterns of samples obtained by calcination of (A) homogeneous and (B) inhomogeneous mixtures of  $\text{La}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\delta\text{-Al}_2\text{O}_3$  powders (mole ratio of  $\text{La}^{3+}:\text{Eu}^{3+}:\text{Al}^{3+} = 0.95:0.05:2$ ) at 1300 °C for 3 h under a flow of 10 vol%  $\text{H}_2/\text{N}_2$ . ( $\diamond$ )  $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}$ , ( $\blacklozenge$ )  $\alpha\text{-Al}_2\text{O}_3$ , ( $\circ$ )  $\text{EuAl}_2\text{O}_4$ , ( $\triangle$ )  $\text{La}_2\text{O}_3$ , (\*) unidentified peak. The inset shows their emission spectra ( $\lambda_{\text{ex}} = 298$  nm).

assigned to *h*- $\text{La}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ ; however, as shown in Fig. 2(B), their emission spectra were quite different. The emission spectrum (Fig. 2(B, a)) of the sample obtained from the 1:1 mixture corresponded to  $\text{LaAlO}_3:\text{Eu}^{3+}$  [1,2,15,18]. As shown in the inset, the luminescence produced in response to irradiation from a 254 nm UV lamp appeared orange to the naked eye. On the other hand, for the samples obtained by calcining the 1:2 and 1:3 mixtures, a blue emission band at 441 nm, which was attributed to the  $5\text{d} \rightarrow 4\text{f}$  transition of  $\text{Eu}^{2+}$  ion, was observed together with orange emission peaks. For the 1:3 mixture, as shown in Fig. 2(B, c), the blue emission band was more intense than the orange emission peaks. As shown in the insets, the luminescence at 254 nm UV lamp irradiation changed from orange to violet with increasing amount of  $\delta\text{-Al}_2\text{O}_3$  in the mixture. These results show that the intensity ratio of the blue to orange emission peaks can be controlled by changing the molar ratio in the mixture of *o*- $\text{LaCO}_3\text{OH}:\text{Eu}^{3+}$  and  $\delta\text{-Al}_2\text{O}_3$ .

The effect of the calcination temperature on the emission spectrum was also investigated for the 1:2 mixture. As shown in Fig. 3(a), the XRD pattern of the sample obtained at 1100 °C exhibited the peaks assigned to *h*- $\text{LaAlO}_3$  and *h*- $\text{La}_2\text{O}_3$ . The XRD pattern (Fig. 3(b)) of the sample at 1200 °C is the same as that in Fig. 2(A,b). At temperatures  $\geq 1300$  °C, peaks assigned to  $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}$  with a distorted magnetoplumbite-type structure [19] were detected together with those for *h*- $\text{LaAlO}_3$ , and became more intense with increasing calcination temperature. For comparison, a single phase of  $\text{La}_{0.827}\text{Al}_{11.9}\text{O}_{19.09}:\text{Eu}^{2+}$  was obtained by calcining a mixture (1:14 in

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