

Preparation and fluorescence properties of novel alkaline earth silicate phosphors by reduction treatment of Eu^{3+} to Eu^{2+}

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The synthesis and emission spectrum control of novel Eu^{2+} -activated amorphous alkaline earth silicate phosphors from the reduction of Eu^{3+} -activated amorphous alkaline earth silicate phosphors is reported. The as-prepared Eu^{3+} -activated amorphous alkaline earth silicate phosphors emitted red. Reduction using Ni-metal powder in a H_2 (5%)/Ar (95%) atmosphere produced Eu^{2+} -activated amorphous barium silicate phosphor that emitted green. Eu^{2+} -activated amorphous calcium silicate was produced by reduction with ammonium chloride in air and emitted purple-blue. It was possible to control the emission spectrum by changing the reduction time. These results suggest the possibility to use three-band type phosphors for the fabrication of white light emitting diodes using one host crystal.

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1. Introduction

White light emitting diodes (LEDs) are produced by combining red, green and blue emitting tricolor LEDs, which was made possible by the development of the blue LED in 1993.¹⁾ White LEDs are expected to be used as a next generation light source for multiple applications, such as general illumination, traffic signals, display backlights, and as light sources for vegetable training.^{2)–4)} Moreover, LEDs have advantages over fluorescent lights, such as being mercury-free, having a longer operating life, and better energy efficiency.⁵⁾ However, to obtain white LED emission intensity with high efficiency by combining red, green and blue LEDs requires the independent control of the current value of each LED color.⁶⁾ In contrast, white LEDs are also fabricated by combining a blue LED with a yellow-emitting phosphor ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$).⁷⁾ Recently, white LEDs of this type have been widely used for general illumination lighting. However, the yellow-emission from $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ lacks red and blue-green emissions, so that the white light obtained has poor color rendering.^{8)–10)} One solution to this problem is to fabricate a white LED with high color rendering by combining red, green and blue emitting tricolor phosphors with near-UV irradiation or near-UV LEDs.¹¹⁾ These phosphors are prepared using different host crystals, such as nitrides, oxynitrides and sulfides, using solid phase synthetic methods that require high temperature and long reaction time.^{12)–14)} We have reported the preparation of phosphors by a soft process using a liquid phase reaction.^{15),16)}

We have also reported the preparation and fluorescence properties of Eu^{3+} -activated alkaline earth silicate phosphors which have the interlayer structure.^{16),17)} These phosphors were amorphous state, however remained the interlayer structure. The emission intensity was approximately 150% that of the commercially available red-emitting $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor. The fluorescence properties change by the reduction of Eu^{3+} to

Eu^{2+} . The Eu^{2+} ion has an electron in the 5d orbital, so that it is strongly influenced by the host crystal, according to, for example, the bonding strength of the host crystal, activator sites, and the coordination number.¹⁸⁾ Therefore, it is expected that an alkaline earth silicate would exhibit peculiar fluorescence properties by the reduction of red-emitting Eu^{3+} -activated alkaline earth silicate phosphors, although there has been no report of such. In this paper, we describe the preparation of green or blue phosphors with high emission intensities controlled with a broad excitation by the reduction of Eu^{3+} ion to Eu^{2+} ion in alkaline earth silicate phosphors.

2. Experimental procedure

Red-emitting Eu^{3+} -activated alkaline earth silicate phosphors were synthesized using $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (sodium silicate), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.95%) and CaCl_2 (96.0%), SrCl_2 (99.2%) or BaCl_2 (97.0%). NH_4Cl (99.0%) and metal Ni-metal powder (99.0%) were employed for reduction processing to produce Eu^{2+} -activated amorphous alkaline earth silicate phosphors.

2.1 Preparation of Eu^{3+} -activated amorphous alkaline earth silicate phosphors

The Eu^{3+} -activated alkaline earth silicate hydrate phosphors were synthesized by liquid phase reaction involving the addition of a $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ solution (0.125 mol/dm^3) to a mixed solution of CaCl_2 , SrCl_2 or BaCl_2 and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ to yield a $\text{Eu}/(\text{Eu} + \text{M})$ [$\text{M} = \text{Ca}, \text{Sr}, \text{or Ba}$] molar ratio of 0.10–0.25. Reaction was maintained at 50°C for 0.5 h with stirring of the suspension at 400 rpm. The suspension was filtered, dried, and then heated at 850°C for 0.5 h in air to enhance the emission intensity of the Eu^{3+} -activated amorphous alkaline earth silicate phosphors. This method serves as a low-temperature process compared with conventional solid phase synthesis.

2.2 Preparation of Eu^{2+} -activated amorphous alkaline earth silicate phosphors by reduction

Reduction of Eu^{3+} to Eu^{2+} for the production of Eu^{2+} -activated amorphous alkaline earth silicate phosphors was

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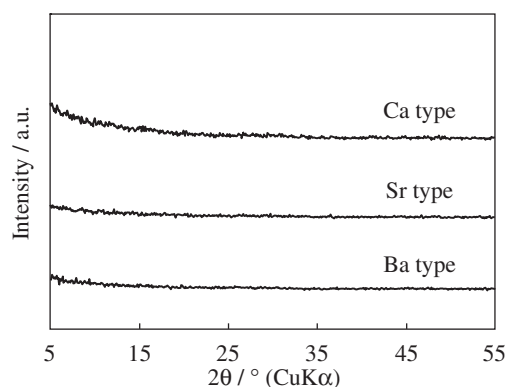


Fig. 1. XRD patterns of Eu^{3+} -activated alkaline earth silicate phosphors. Heating temperature: 850°C , Heating time: 0.5 h, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.25.

conducted at 800°C for 1–3 h in a reducing atmosphere H_2 (5%)/Ar (95%) using Eu^{3+} -activated amorphous alkaline earth silicate phosphors. Ni-metal powder (300 vol %) was also added to the samples and the same reduction processing was performed. Samples were obtained by magnetic separation. Reduction was also performed by the addition of ammonium chloride (300 vol %) and treatment at 350°C for 1–3 h.

Samples were characterized before and after the reduction treatment using X-ray diffraction (XRD). The fluorescence properties of the samples were measured using a fluorescence spectrophotometer (F-4500, Hitachi), a luminance meter (BM-5A, Topcon), and an emission spectrometer (MCPD7000, Otsuka Electronics Co., Ltd.). All measurements were carried out at room temperature.

3. Results and discussion

3.1 Fluorescence properties of Eu^{3+} -activated amorphous alkaline earth silicate phosphors

Figure 1 shows XRD patterns of Eu^{3+} -activated alkaline earth silicate hydrate phosphors obtained at 850°C . The heat treatment was performed at 850°C because calcium silicate hydrate is thermally decomposed at 854°C according to thermal gravimetric-differential thermal analysis (TG-DTA).¹⁷ Each Eu^{3+} -activated alkaline earth silicate phosphors was amorphous state, even for initial $\text{Eu}/(\text{Eu} + \text{M})$ molar ratios of 0.10–0.25 (data not shown). The emission intensities of the phosphors were decreased by crystallization, which occurred at different heating temperatures according to the alkaline earth metal present.

Figure 2 shows the excitation and emission spectra of Eu^{3+} -activated amorphous alkaline earth silicate phosphors obtained by excitation of the sample in the near-UV at 395 nm. Emission bands were observed at 589, 613, 651 and 700 nm, which were assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $\rightarrow ^7\text{F}_2$, $\rightarrow ^7\text{F}_3$ and $\rightarrow ^7\text{F}_4$ transitions of Eu^{3+} , respectively. The emission spectra of the Sr, Ba and Ca type phosphors were the same, which indicates that the fluorescence properties were not changed according to the ionic radius of the alkaline earth cation.

Table 1 shows the CIE chromaticity index and the internal quantum efficiency of the Eu^{3+} -activated amorphous alkaline earth silicate phosphors, of which the former showed no change in the Y values, but different X values. The $(^5\text{D}_0 \rightarrow ^7\text{F}_2)/(^5\text{D}_0 \rightarrow ^7\text{F}_4)$ intensity ratio ($=I$) of the Eu^{3+} ion was calculated for each of the Eu^{3+} -activated amorphous alkaline earth silicate phosphors. If I is high, then the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is high, i.e., the X values are lower, which confirms the correlativity of the X

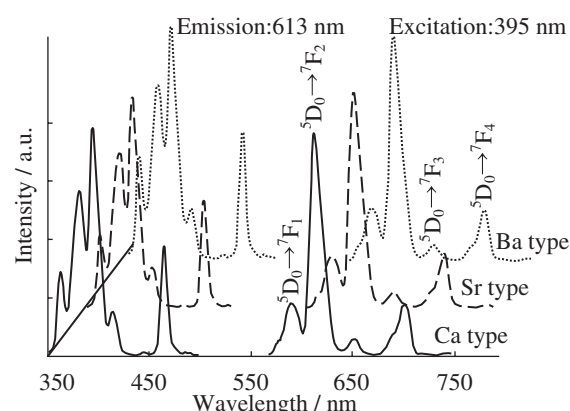


Fig. 2. Excitation and emission spectra of Eu^{3+} -activated amorphous alkaline earth silicate phosphors. Heating temperature: 850°C , Heating time: 0.5 h, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.25.

Table 1. CIE chromaticity index and quantum efficiency of Eu^{3+} -activated amorphous alkaline earth silicate phosphors

Host materials	X	Y	I	QE (%)
Ca type	0.633	0.330	3.61	63
Sr type	0.489	0.286	4.07	60
Ba type	0.443	0.273	4.41	56

I : the $(^5\text{D}_0 \rightarrow ^7\text{F}_2)/(^5\text{D}_0 \rightarrow ^7\text{F}_4)$ intensity ratio

and I values. The Eu^{3+} ion emits light by a $4f-4f$ transition; therefore, the crystal field should have little effect on the emission. However, in the Eu^{3+} -activated amorphous alkaline earth silicate phosphors, I and the chromaticity index are dependent on the constituent alkaline earth cation. The internal quantum efficiencies of all the Eu^{3+} -activated amorphous alkaline earth silicate phosphors were approximately 60%.

3.2 Fluorescence properties of Eu^{2+} -activated alkaline earth silicate phosphors obtained by reduction

Reduction processing of the phosphors was first performed under H_2 (5%)/Ar (95%) atmosphere at 800°C . The thermal decomposition of Eu^{3+} -activated amorphous alkaline earth silicate phosphors generates materials such as wollastonite at temperatures beyond 800°C , and the crystallinity have no the interlayer structures increased. Figure 3 shows XRD patterns of samples obtained by reduction under H_2 (5%)/Ar (95%), which confirms that the reduced phosphors remained amorphous state without the formation of new products. Figure 4 shows the emission spectra of reduced phosphors. Reduction under H_2 (5%)/Ar (95%) did not result in a new emission spectra due to Eu^{2+} ions in the Eu^{3+} -activated amorphous alkaline earth silicate phosphors, because the reduction temperature was too low. Therefore, Ni-metal powder was added under the same reduction atmosphere to catalyze the dissociation of hydrogen¹⁹ and allow reduction at low temperature, due to the presence of active hydrogen. Figure 5 shows XRD patterns of the phosphors obtained by reduction with Ni-metal powder under a H_2 (5%)/Ar (95%) atmosphere. The XRD patterns of the obtained alkaline earth silicate phosphors remained unchanged and no new phases were observed, i.e., no reaction with Ni occurred. Figure 6 shows emission spectra of the phosphors reduced with Ni-metal powder under a H_2 (5%)/Ar (95%) atmosphere. A new emission band was observed for the Eu^{3+} -activated amorphous barium

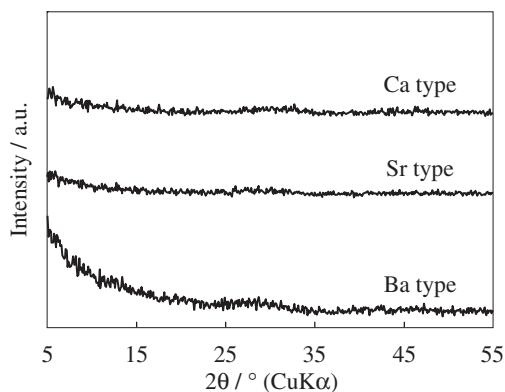


Fig. 3. XRD patterns of Eu^{3+} -activated amorphous silicate phosphors by reduction process using H_2 gas. Reduction temperature: 800°C , Reduction time: 1 h, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.25.

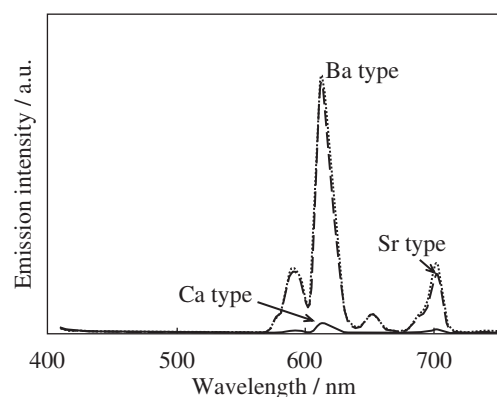


Fig. 4. Emission spectra of Eu^{3+} -activated amorphous alkaline earth silicate phosphors by reduction process using H_2 gas. Reduction temperature: 800°C , Reduction time: 1 h, Excitation wavelength: 395 nm, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.25.

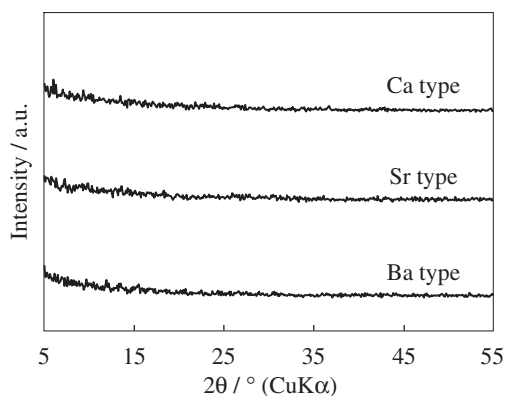


Fig. 5. XRD patterns of Eu^{3+} -activated amorphous silicate phosphors by reduction process using H_2 gas + Ni-metal powder. Reduction temperature: 800°C , Reduction time: 1 h, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.20.

silicate phosphor near 504 nm due to the formation of Eu^{2+} ions, which confirmed that active hydrogen was generated using Ni-metal powder and the phosphor was successfully reduced at low temperature. **Figure 7** shows the emission intensities of Eu^{3+} -activated amorphous barium silicate phosphor samples reduced for various times. The emission peak at 600 nm was gradually decreased with increase in the reduction time and was absent after reduction for 1 h. The peak at 504 nm gradually

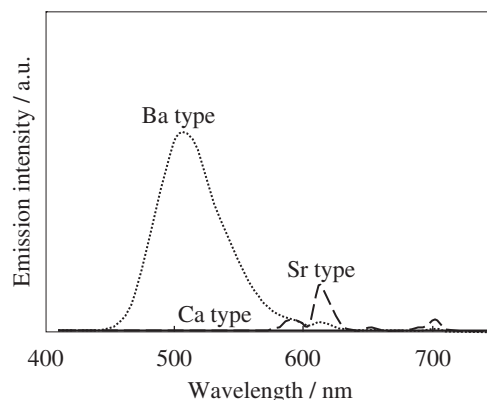


Fig. 6. Emission spectra of Eu^{3+} -activated amorphous alkaline earth silicate phosphors by reduction process using H_2 gas + Ni-metal powder. Reduction temperature: 800°C , Reduction time: 1 h, Excitation wavelength: 395 nm, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.20.

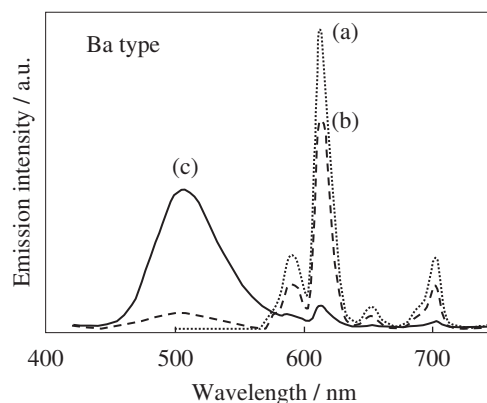


Fig. 7. Emission spectra of Ba type prepared at various restoration time. Reduction temperature: 800°C , $\text{Eu}/(\text{Eu} + \text{Ba})$ atomic ratio: 0.20, Reduction time/min, (a): 0, (b): 30, (c): 60, Excitation wavelength: 395 nm.

increased with extension of the reduction time. Therefore, the emission spectra of the red and green region could be controlled by changing the reduction time. The Ca and Sr based phosphors were not reduced, due to the ionic radius of Ba^{2+} is larger than those of Ca^{2+} and Sr^{2+} . Furthermore, ionic radii of divalent and trivalent europium differ. Thus, the phosphor expands after reduction, due to the formation of Eu^{2+} (0.112 nm) from Eu^{3+} (0.095 nm). It was considered that concentration quenching occurred due to distortion and collapse of the interlayer structure. Therefore, synthesis of the reduced phosphors was performed with a higher $\text{Eu}/(\text{Eu} + \text{M})$ molar ratio for the Eu^{3+} -activated amorphous alkaline earth silicate phosphor starting materials.

Ammonium chloride sublimes at 338°C , so that the reduction reaction temperature is expected to be further lowered under an ammonia atmosphere generated by the sublimation of ammonium chloride. **Figure 8** shows XRD patterns of phosphors obtained by reduction with ammonium chloride at 350°C . The phosphors remained amorphous state, although the crystallinity of the Ca based phosphor was slightly increased. Only the Ca based phosphor was reduced by reaction with ammonium chloride. **Figure 9** shows the emission spectra of phosphor samples obtained by reduction with ammonium chloride at various times. The emission peak near 420 nm was increased with increased reduction time. Therefore, the emission spectra of the red and blue region could be controlled by reduction using

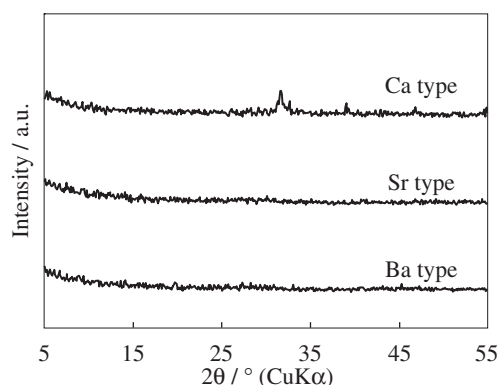


Fig. 8. XRD patterns of Eu^{3+} -activated amorphous silicate phosphors by reduction process using ammonium chloride. Reduction temperature: 350°C , Reduction time: 1 h, $\text{Eu}/(\text{Eu} + \text{M})$ atomic ratio: 0.20.

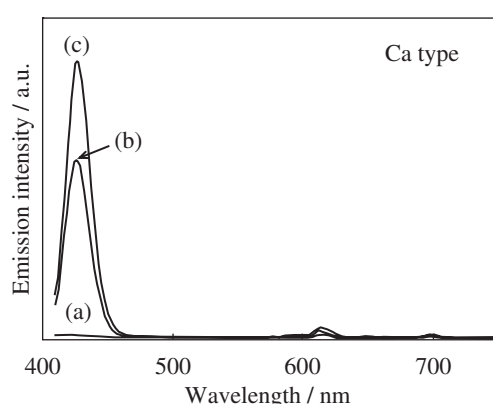
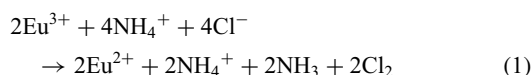


Fig. 9. Emission spectra of Eu^{3+} -activated amorphous calcium silicate phosphors by reduction process using ammonium chloride. Reduction temperature: 350°C , $\text{Eu}/(\text{Eu} + \text{Ca})$ atomic ratio: 0.20, Reduction time/h, (a): 1, (b): 2, (c): 3, Excitation wavelength: 395 nm.

ammonium chloride. It is thought that only the Ca based phosphor was reduced, because the coordination number for Ca^{2+} (6) is less than that for Sr^{2+} and Ba^{2+} (8/9). Therefore, it is considered that a lower coordination number alkali earth reacts more readily during reduction with ammonium chloride. There have been reports of $\text{Ca}_{0.98}\text{Eu}_{0.02}\text{Cl}_2$ and $(\text{CaCl}_2/\text{SiO}_2):\text{Eu}^{2+}$ phosphors prepared using calcium chloride as a starting material that emitted violet-blue at around 427 nm.^{20,21)} However, no diffraction peak due to calcium chloride was observed in the XRD patterns. Moreover, the emission color of the Ca based phosphor was returned from blue to red over time. It is thought that reduction with ammonium chloride occurs by the following reaction.



It is thought NH_4^+ ion is in the interlayer of Ca based phosphor. Thereafter, NH_4^+ ions are released from the interlayer and the charge compensation is affected by the oxidation of Eu^{2+} to Eu^{3+} , which results in the emission color reverting to red.

4. Conclusions

Novel alkaline earth silicate phosphors with controlled emission spectra were synthesized by the reduction of Eu^{3+} to Eu^{2+} . The reduced phosphors emitted after excitation with the same near-UV irradiation (395 nm) as that for the red emission of the unreduced phosphors. All phosphors obtained after reduction remained amorphous state. The Ba based phosphor could be reduced at low temperature (800°C) by the generation of active hydrogen with a Ni-metal powder catalyst in a H_2 (5%)/Ar (95%) atmosphere, resulting in a phosphor with green emission. The Ca based phosphor, reduced using ammonium chloride, emitted blue. The reduction of the phosphors could be controllable by changing the reduction time. That is, it is thought alkaline earth silicate phosphors with red, green and blue emission could be produced with one host crystal. Therefore, such amorphous alkaline earth silicate phosphors could be applied as three-band type phosphors for the fabrication of white LEDs.

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