Effect of Eu$^{2+}$ concentration on the photoluminescence properties of red-emitting CaSrSiO$_4$:Eu$^{2+}$ phosphors

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1. Introduction

White light-emitting diodes (LEDs) are gaining attention as a next-generation solid-state lighting source because they consume less power and last longer than incandescent bulbs and fluorescent lamps and do not contain hazardous materials such as mercury. White LEDs are typically a combination of a blue LED and yellow phosphors, such as Y$_2$Al$_5$O$_{12}$:Ce$^{3+}$ and (Sr, Ba)$_2$SiO$_4$:Eu$^{2+}$. With this type of white LED, high-efficiency phosphors excited by a blue or near-ultraviolet/violet LED with blue, green, and red phosphors have been proposed and employed in practical applications.

With this type of white LED, high-efficiency phosphors excited by a blue or near-ultraviolet/violet LED are needed. There are many reports about oxide- and nitride-based green phosphors; however, red phosphors for practical use are limited to nitrides such as (Ca,Sr)Al$_5$O$_{12}$:Eu$^{2+}$ and Sr$_2$Si$_5$N$_8$:Eu$^{2+}$. Red phosphors are hindered by high production costs because high temperature and pressure are necessary for the syntheses of nitride-based phosphors. In contrast, the syntheses of oxide-based phosphors are more convenient because they do not require high temperature or pressure; however, there have been few reports on the topic of oxide-based red phosphors. Therefore, finding new oxide-based red phosphors is one of the most important issues related to white LEDs.

Recently, we reported the fabrication of new silicate phosphors using a solution parallel synthesis method with propylene glycol-modified silane (PGMS). Among the new phosphors, orthorhombic Ca$_3$SiO$_4$:Eu$^{2+}$ (10 mol%) exhibited a particularly strong orange-red emission peaking at 615 nm under blue light excitation. In addition, we reported deep-red emitting Eu$^{2+}$ activated Ca$_3$SiO$_4$ phosphors with high Eu$^{2+}$ concentrations (40 mol%) for which the wavelength of the maximum emission peak was 650 nm. The origin of the deep-red emission from Ca$_3$SiO$_4$:Eu$^{2+}$ is strongly related to the peculiar coordination environments of Eu$^{2+}$ at two kinds of Ca$^{2+}$ sites. These results indicate that red emission appears in association with increasing Eu concentration on Ca$_3$SiO$_4$:Eu$^{2+}$.

In this study, we report the effect of Eu$^{2+}$ concentration on the photoluminescence properties of CaSrSiO$_4$:Eu$^{2+}$. The relationships between their emission properties and the coordination environments of Eu$^{2+}$ in two kinds of Sr/Ca sites are discussed.

2. Experimental procedure

Figure 1 shows a flowchart of phosphor powder preparation using PGMS. Details on the preparation of PGMS solution are described in our previous works. The compositions were set to Ca$_{1-x}$Sr$_x$SiO$_4$:Eu$^{2+}$ with $x = 0.1–0.9$. CaCO$_3$, SrCO$_3$, and Eu$_2$O$_3$ were dispersed into distilled water followed by the addition of PGMS solution (2 M Si). In order to achieve a uniform dispersion of Ca, Sr, Eu, and Si in the sample, the paste-like mixture was washed well in various stoichiometric ratios and then dried at 120°C. The dried substance was crushed into a powder using a mortar and pestle. The powder was heat treated in air at 1000°C for 3 h to remove the organic constituents derived from PGMS. The obtained precursors were then mixed with BaCl$_2$ (20 wt%) as flux and heat treated at 1200°C for 4 h under a flow of an Ar$–$H$_2$ gas. The residual BaCl$_2$ and the byproducts, such as Ca, Sr, and Ba carbones, were removed from the sintered powder with washing with water and ethanol and drying. The obtained samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Rietveld refinement was performed using the RIETAN-FP program to refine the lattice constants and site occupancies of Eu$^{2+}$, Ca$^{2+}$, and Sr$^{2+}$ in Ca$_{1-x}$Sr$_x$SiO$_4$:Eu$^{2+}$ ($x = 0.1–0.9$). In the Rietveld refinement of these samples, we selected the crystal structure of Ca$_3$SiO$_4$ (ICSD#20544) as a starting model structure. The
quality of the refinements was judged using $R_{wp}$ (R-weighted pattern), $R_e$ (R-expected pattern), and the “goodness of fit” indicator, $S$ ($R_{wp}/R_e$). All the values were defined in Ref. 17. A crystal structure model was drawn using the VESTA program. The excitation and emission spectra were obtained with a fluorescence spectrophotometer (Jasco-FP6500). For all the samples, the emission spectra were measured using a 455-nm excitation, and the excitation spectra were monitored at the wavelength of the maximum emission intensity. The emission and excitation spectra were normalized by the maximum emission and excitation intensities of a commercial YAG:Ce3+ sample (P46, Kasei Optonix).

### 3. Results and discussion

**Figure 2** shows the XRD patterns of Ca$_{1-x}$/Sr$_{1-x}$/SiO$_4$:xEu ($x = 0.1-0.9$). All samples were identified as having the orthorhombic $\alpha'$-CaSrSiO$_4$ structure with space group $Pna2_1$. The XRD peaks shifted slightly to the lower-angle side with increasing Eu concentration. The lattice constants of these samples were estimated by Rietveld refinement. Table 1 shows the lattice constants of Ca$_{1-x}$/Sr$_{1-x}$/SiO$_4$:xEu with $x = 0.1-0.9$. These results indicate that lattice constants with three directions increase with increasing Eu concentration. Considering the ionic radii of Ca$^{2+}$ (1.23 Å, CN = 10), Eu$^{2+}$ (1.35 Å, CN = 10), Sr$^{2+}$ (1.36 Å, CN = 10), such a lattice expansion should be caused by the substitution of Ca$^{2+}$ by Eu$^{2+}$ in the CaSrSiO$_4$ lattice. On the other hand, unknown peaks were also observed in the samples with $x = 0.8$ and 0.9. Thus, both samples might contain impurities.

**Figure 3** shows SEM images of the precursor and final powders of Ca$_{1-x}$/Sr$_{1-x}$/SiO$_4$:xEu ($x = 0.1, 0.7$, and 0.9). Well-grown grains with habit planes (10-30 μm) were observed in the final powders [Figs. 3(b) and 3(c)], whereas agglomerated secondary particles consisting of primary particles (~1 μm) were observed in the precursor powders [Fig. 3(a)]. Although we cannot provide an ultimate explanation of this phenomenon at this stage, we assume that the precursor powders were slightly dissolved into molten BaCl$_2$ (m.p. = 962°C), and that liquid-phase crystal growth occurred during heat treatment at 1200°C.

We also recognized that Sr$^{2+}$, Ca$^{2+}$, and Eu$^{2+}$ ions were substituted by Ba$^{2+}$ derived from the BaCl$_2$ flux. The compositional analysis of the samples using ICP measurements revealed that the atomic ratio of Ba$^{2+}$ to total divalent cations was approximately 3–5 mol%. This could be attributed to the migration and rearrangement of these cations during heat treatment at 1200°C. Although these well-grown particles were observed in the samples with $x = 0.1$ and 0.7, fine particles were observed for the sample with $x = 0.9$. This implies that the crystal growth was suppressed due to insufficient reduction from Eu$^{3+}$ to Eu$^{2+}$ in the samples with $x = 0.9$ during heat treatment.

**Figure 4** shows the emission and excitation spectra of Ca$_{1-x}$/Sr$_{1-x}$/SiO$_4$:xEu ($x = 0.1-0.9$). The left side of this figure shows increasing Eu concentration. The table constants of these samples were estimated by Rietveld refinement. Table 1 shows the lattice constants of Ca$_{1-x}$/Sr$_{1-x}$/SiO$_4$:xEu with $x = 0.1-0.9$. These results indicate that lattice constants with three directions increase with increasing Eu concentration. Considering the ionic radii of Ca$^{2+}$ (1.23 Å, CN = 10), Eu$^{2+}$ (1.35 Å, CN = 10), Sr$^{2+}$ (1.36 Å, CN = 10), such a lattice expansion should be caused by the substitution of Ca$^{2+}$ by Eu$^{2+}$ in the CaSrSiO$_4$ lattice. On the other hand, unknown peaks were also observed in the samples with $x = 0.8$ and 0.9. Thus, both samples might contain impurities.

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the excitation spectrum monitored at the maximum emission wavelength for each sample, and the right side of the figure shows the emission spectra excited at 455 nm. The vertical axis represents the relative emission intensity normalized by commercial YAG:Ce\(^{3+}\) powder. Each sample showed a broad orange-red or red emission, which can be ascribed to the 4f\(^{7}\)d\(^{1}\) electronic transition of Eu\(^{2+}\) ions. As Eu concentration increased, the maximum emission wavelength shifted from 610 nm for the samples with \(x = 0.1\) to 639 nm for the samples with \(x = 0.7\). In addition, the full width at half maximum (FWHM) of the emission was slightly broaden from 120 nm (\(x = 0.1\)) to 127 nm (\(x = 0.7\)), and the intensity of the emission was slightly reduced. The excitation band was located from 350 to 500 nm, indicating that they were efficiently excited by near-ultraviolet, violet, and blue LED light. The samples with \(x = 0.8\) and 0.9 were not red shifted, and the emission intensities significantly decreased for both samples. This could be attributed to the existence of impurity phases in both of the samples; these impurity phases were attributed to insufficient Eu reduction during heat treatment, as mentioned above.

From these results, it is worth noting that (1) a deep-red emission peaking at 639 nm was observed for Ca\(_{1—x/2}\)Sr\(_{1—x/2}\)SiO\(_4\):Eu, and (2) no significant concentration quenching was observed, even at high Eu concentration (up to \(x = 0.7\)).

In order to clarify the peculiar luminescence phenomena due to Eu\(^{2+}\), we discuss the crystallographic features of Ca\(_{1—x/2}\)Sr\(_{1—x/2}\)SiO\(_4\):Eu phosphors. Figure 5 shows the crystal structure of CaSrSiO\(_4\) drawn by the VESTA program. As mentioned above, the crystal structure of CaSrSiO\(_4\) was identified as orthorhombic \(\alpha\)-L-CaSrSiO\(_4\) with space group Pnma\(_{1}\). This crystal structure possesses six different alkaline earth sites (denoted as Ca1, Ca2, Ca3, Sr1, Sr2, and Sr3) at which Eu\(^{2+}\) ions can be substituted. Therefore, it should be important to consider the effects of Eu\(^{2+}\) substitution and the coordination environment of Eu\(^{2+}\) at the Sr (n) and Ca (n) sites (\(n = 1—3\)) of CaSrSiO\(_4\) on luminescence.

First, the site occupancies of Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), and Eu\(^{2+}\) were estimated for various Ca\(_{1—x/2}\)Sr\(_{1—x/2}\)SiO\(_4\):Eu samples by Rietveld refinement. In the refinements, the occupancy of Eu\(^{2+}\) at the Sr (n) or Ca (n) sites (\(n = 1—3\)) was fixed; thus, Eu\(^{2+}\) ions were assumed to be uniformly distributed among the Sr (n) and Ca (n) sites. We also estimated that the Ba\(^{2+}\) concentrations was 3.5 mol% for all samples because small amounts of Sr\(^{2+}\), Ca\(^{2+}\), and Eu\(^{2+}\) at Sr (n) sites were substituted by Ba\(^{2+}\) from the flux during heat treatment at 1200°C, as mentioned above.

Table 2 shows the site occupancies of Sr\(^{2+}\), Ca\(^{2+}\), Eu\(^{2+}\), and Ba\(^{2+}\) in Ca\(_{1—x/2}\)Sr\(_{1—x/2}\)SiO\(_4\):Eu samples with \(x = 0.1, 0.3, 0.5,\) and 0.7. These results indicate that Eu\(^{2+}\) preferentially occupied Sr (n) sites in all samples because the ionic radius of Eu\(^{2+}\) is close to that of Sr\(^{2+}\). In addition, as the Eu\(^{2+}\) concentration increased, a certain amount of Eu\(^{2+}\) occupied not only the Sr (n) sites, but also the Ca (n) sites. In the samples with \(x = 0.5\) and 0.7, the concentration of Eu\(^{2+}\) at the Ca (n) site was approximately 20 mol%. It is likely that the preferential substitution of Eu\(^{2+}\) for Sr (n) site kept the Eu concentration at the Ca (n) site relatively low, inhibiting the concentration quenching even at high Eu concentration.

Next, based on the crystallographic data of the \(\alpha\)-L-CaSrSiO\(_4\) structure, the average bond length of M—O (M = Ca, Sr) and the polyhedral volume of M—O were roughly estimated using the VESTA program. In these estimations, the M—O bond distances were limited to 3.6 Å. Table 3 shows the average M—O bond distances and M—O polyhedral volumes of CaSrSiO\(_4\). The average estimated bond lengths of Ca—O were shorter than those of Sr—O, and the polyhedral volumes of the Ca sites were smaller than those of the Sr sites.

As mentioned above, the emissions observed in the samples were attributed to the 4f\(^{7}\)d\(^{1}\) electronic transition of Eu\(^{2+}\) ions. The 4f orbital is well shielded from its surroundings by the rounding anions, resulting in the crystal field splitting of the 4f\(^{7}\)d\(^{1}\) energy level. Hence, the emission of Eu\(^{2+}\) is strongly influenced by the coordination environments of the Eu\(^{2+}\) ion. Dorenbos systematically investigated the red shift in the emission spectra of Eu\(^{2+}\) activated Ca- and Sr- based oxides, sulfides, and selenides. They concluded that redshift in the Ca-based compounds is always larger than in Sr-based compounds.

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**Table 2.** Site occupancies of Sr, Ca, Eu, and Ba at Sr (n) and Ca (n) sites for various Ca\(_{1—x/2}\)Sr\(_{1—x/2}\)SiO\(_4\):Eu samples

<table>
<thead>
<tr>
<th>Occupancy (mol%)</th>
<th>Sr (n) site</th>
<th>Ca (n) site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sr</td>
<td>Ba</td>
</tr>
<tr>
<td>Sr 0.1</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Sr 0.3</td>
<td>86</td>
<td>7</td>
</tr>
<tr>
<td>Sr 0.5</td>
<td>63</td>
<td>7</td>
</tr>
<tr>
<td>Sr 0.7</td>
<td>43</td>
<td>7</td>
</tr>
</tbody>
</table>

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![Fig. 4. Emission and excitation spectra of Ca\(_{1—x/2}\)Sr\(_{1—x/2}\)SiO\(_4\):Eu (x = 0.1—0.9).](image)

![Fig. 5. Crystal structure of CaSrSiO\(_4\) (ICSD#20544).](image)
This implies that the large crystal field splitting on the 5d band of Eu$^{2+}$ in Ca sites is due to the smaller ionic radius of Ca$^{2+}$ compared with that of Eu$^{2+}$ and the shorter bond lengths between Eu$^{2+}$ and the nearest anions.20 Therefore, the broad orange-red or red broad emission from CaSrSiO$_4$ samples originated from the combination of different orange-red or red emission from Eu$^{2+}$ ion substituted at smaller Ca (n) sites (n = 1–3) which have slightly different coordination environment.

Diaz et al. investigated the relationship between the coordination environment and the emission wavelength of Eu$^{2+}$ in Ba- and Sr-based borates.21 They concluded that the magnitude of the Stokes shift is strongly related to the distortion of the polyhedra of Ba and Sr sites in the compounds. This relationship was also suggested by Denault et al. for Sr$_2$Ba$\text{2+}$_2SiO$_{1+}$_4Eu solid solutions.22 To speculate the distortion of the M-O polyhedra in CaSrSiO$_4$, the distortion of CaSrSiO$_4$ lattice was estimated. Table 4 shows the relationship between the coordination environment and the emission wavelength of Eu$^{2+}$ in the compounds. Based on this behavior, we speculate that the distortion of the polyhedral at the Ca (n) sites occurs with increasing Eu concentration, and the red shift of CaSrSiO$_4$Eu samples may attributed to some changes in the crystal field around Eu$^{2+}$ ion with increasing Eu concentration. Several other factors should be taken into account when considering the redshift behavior of Eu$^{2+}$ doped inorganic phosphors, such as reabsorption of the emission, 5d-orbit hybridization of Eu$^{2+}$ with the host crystal and the energy transfer between Eu$^{2+}$ ion. Further work is needed to explore these effects.

4. Conclusion

Ca$_{1-x}$/Sr$_{1-x}$/Si$_{3-x}$/O$_{1+}$_4Eu (x = 0.1–0.9) phosphors were synthesized via an aqueous solution method using PGMS, and the effects of the Eu concentration on their photoluminescence properties were investigated. The resulting phosphor sample (x = 0.7) showed strong red emission peaking at 639 nm. The excitation spectra of the samples were observed in the range of 350–500 nm. This indicates that red emission is efficiently excited by near-ultraviolet, violet, and blue LED light. The red emission from Ca$_{1-x}$/Sr$_{1-x}$/Si$_{3-x}$/O$_{1+}$_4Eu phosphors with high Eu$^{2+}$ concentrations originated from the large crystal field splitting due to the substitution of Eu$^{2+}$ at smaller Ca (n) sites. The results imply that the photoluminescence properties of various oxide, nitride and sulfide phosphors can be controlled by the substitution of Eu$^{2+}$ or Ce$^{3+}$ activators at the specific crystal sites, such as small and distorted alkali earth sites.

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