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# A correlation between a phase transition and luminescent properties of $Sr_2SiO_4$ : $Eu^{2+}$ prepared by a flux method

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Sr<sub>2-x</sub>Eu<sub>x</sub>SiO<sub>4</sub> powders were prepared by a flux method, and then a correlation between a phase transition and luminescent properties were investigated. The  $\beta \leftrightarrow \alpha$ ' transition depended on the synthesizing conditions such as firing temperature, duration time, and europium concentration, resulting in a change of luminescence. Eu<sup>2+</sup> ions contributed to the stabilization of the  $\alpha$ '-form even at room temperature, which led to a decrease of the  $\beta/\alpha$ ' phase ratio with an increase of the Eu<sup>2+</sup> concentration. The  $\beta$ -form exhibited a higher PL intensity and a blue-shift compared with the  $\alpha$ '-form.

Key words: Strontium silicate, Solid-state reaction, Phase transition, Luminescence.

#### Introduction

Orthosilicate powders have been focused on as phosphors for white LEDs (Light emitting diodes) due to their high durability against high power, high temperature, and the packaging resins. Since they can be efficiently excited by blue and ultraviolet (UV) lights, the luminescent properties of many silicate phosphors have been studied:  $Sr_2SiO_4:Eu^{2+}$  ( $\lambda_{em} = 490-580$  nm),  $Mg_2SiO_4:Mn^{2+}$  ( $\lambda_{em} = 680$  nm),  $Ba_2SiO_4:Eu^{2+}$  ( $\lambda_{em} = 500$  nm),  $Ca_2SiO_4:Eu^{2+}$  ( $\lambda_{em} = 490$  nm),  $Zn_2SiO_4:Mn^{2+}$  ( $\lambda_{em} = 524$  nm), and  $Zn_2SiO_4:Tb^{3+}$  ( $\lambda_{em} = 545$  nm) [1-6].

Among them,  $Sr_2SiO_4:Eu^{2+}$  strontium orthosilicate is one of the promising candidates that can replace  $Y_3Al_5O_{12}$ :Ce<sup>3+</sup> (YAG:Ce<sup>3+</sup>) that is the most popular and commercial yellow phosphor. Sr<sub>2</sub>SiO<sub>4</sub> has a polymorphism of the  $\beta$ - form (monoclinic) and the  $\alpha$ '-form (orthorhombic), whose transformation is displacive and can be simply accomplished by a rearrangement of atoms without breaking coordination bonds, showing very similar XRD patterns between the two forms. The  $\beta$ - and  $\alpha$ '-forms are isostructural with  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> and  $\alpha'_{H}$ -Ca<sub>2</sub>SiO<sub>4</sub> ( $\beta$ -K<sub>2</sub>SiO<sub>4</sub>), respectively [7]. Ca<sub>2</sub>SiO<sub>4</sub> has five structures depending on the temperatures:  $\gamma$ ,  $\beta$ ,  $\alpha'_L$ ,  $\alpha'_H$ , and [8]. The transition temperature of  $\beta \leftrightarrow \alpha'$  of  $Sr_2SiO_4$  is about 85 °C, which is relatively low for a silicate, while those of  $\beta \leftrightarrow \alpha'_{L}$  and  $\alpha'_{L} \alpha'_{H}$  in  $Ca_2SiO_4$  are 700 °C and 1160 °C, respectively. However, it is reported that  $\alpha'$ -Sr<sub>2</sub>SiO<sub>4</sub> can be stabilized even at room temperature by substituting a small amount of Ba<sup>2+</sup> or Ca<sup>2+</sup> ions for  $Sr^{2+}$ , even though the high temperature  $\alpha$ '-forms of pure Sr<sub>2</sub>SiO<sub>4</sub> and Ca<sub>2</sub>SiO<sub>4</sub> can not be quenched to room temperature [9-11]. There are two  $Sr^{2+}$  sites of 10cordinated Sr(I) and 9-cordinated Sr(II) for which  $Eu^{2+}$  ions can be easily substituted due to the similarity of ionic sizes, leading to two emission bands around 490 nm and 560 nm, respectively [12].

Most of the previous reports on the luminescent properties of europium doped  $Sr_2SiO_4$  have been related to the  $\alpha$ '-form, but rarely to the  $\beta$ -form. Accordingly, in this study, we focused on the  $\alpha' \leftrightarrow \beta$  phase transition and correlated luminescence with various firing conditions and europium concentrations.

## **Experimental Procedure**

Sr<sub>2-x</sub>Eu<sub>x</sub>SiO<sub>4</sub> powders were prepared by firing mixtures of SrCO<sub>3</sub> (Aldrich, 99.9<sup>+</sup>%), SiO<sub>2</sub> (High Purity Chemical, 99.9%), and Eu<sub>2</sub>O<sub>3</sub> (Aldrich, 99.99%). After ball-milling for 24 hours, they were fired at 800-1300 °C flowing 50sccm (5% H<sub>2</sub> + 95% N<sub>2</sub>) gas in an electric tube furnace. NH<sub>4</sub>Cl was added as a flux, which facilitated the solidstate reactions and enhanced the luminescent properties by accelerating the kinetics of the formation of the desired compounds by increasing diffusion coefficients [13-16]. The crystalline phases and photoluminescence (PL) of the powders prepared were determined by XRD (X-ray diffractometer, SIEMENS D5005) using CuK<sub>α</sub> radiation ( $\lambda = 1.5406$ Å) and a PL system (PSI Darsa 5000) with a xenon lamp as an excitation source, respectively.

#### **Results and discussions**

To investigate the phase formations and effects of  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> on PL properties, we intentionally tried to form the  $\beta$ -phase (monoclinic) as well as the  $\alpha$ '-form (orthorhombic). XRD patterns and PL spectra of 1.95SrCO<sub>3</sub>-SiO<sub>2</sub> - 0.025Eu<sub>2</sub>O<sub>3</sub> - 2 wt% NH<sub>4</sub>Cl powders as a function of firing temperatures are shown in Fig. 1 (a) - (d) and Fig. 2,

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Fig. 1. XRD patterns of  $1.95Sr_2SiO_4$ -SiO $_2$ -0.025Eu $_2O_3$  fired at various temperatures for 3 hours. (a) 800 °C, (b) 1000 °C, (c) 1200 °C, and (d) 1300 °C



Fig. 2. PL spectra of  $1.95Sr_2SiO_4$ -SiO $_2$ -0.025Eu $_2O_3$  fired at various temperatures for 3 hours. (a) 800 °C, (b) 1000 °C, (c) 1200 °C, and (d) 1300 °C

respectively. A single phase  $\alpha$ '-Sr<sub>2</sub>SiO<sub>4</sub> was synthesized at 800 °C, and with an increase in the temperature significant differences in phases were not observed but for the weak appearance (arrow marks) of  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub> at 1300 °C as shown in Fig. 1 (d). As shown in the PL spectra excited by 450 nm (Fig. 2), with a rise in the firing temperature, PL peaks in the yellow region continuously moved to shorter wavelengths (blue-shift) and also the PL intensity increased. This indicated that the crystal field surrounding the Eu<sup>2+</sup> ions changed due to the secondary  $\beta$ -phase formation in addition to the main  $\alpha$ '-form, resulting in these changes of the luminescent properties. Accordingly it could be speculated that, besides  $\alpha$ '-Sr<sub>2</sub>SiO<sub>4</sub> as the main phase, the  $\beta$ -form had been already created even at less than 1300 °C, of which the amount continuously increased with the temperature, even though it could not be detected by XRD due to the very small quantity. From these results we have to consider two points of view: a phase transition and luminescence. Even though  $\alpha$ '-Sr<sub>2</sub>SiO<sub>4</sub> is a stable phase at high temperature, with this experimental conditions, it was a dominant phase at room temperature rather than the  $\beta$ form of the low temperature phase. This phenomenon was mainly ascribed to the dopant europium ions, and details will be given later in this paper.

Regarding the luminescence, it was reported that the PL spectra of  $Sr_2SiO_4:Eu^{2+}$  exhibited two excitation peaks and two related emission bands around 495 nm and 560 nm originating from  $4f \rightarrow 5d$  energy transitions of two substitutional sites of Eu(I) and Eu(II) for Sr(I) and Sr(II), respectively [10, 17-19]. There are two cation sites for  $Sr^{2+}$  in  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub>: Sr(I) is ten-coordinated and Sr(II) is nine-coordinated by oxygen atoms [11]. For the application as white LEDs composed of blue LEDs  $(\lambda \sim 450 \text{ nm})$  and yellow phosphors, we focused only on yellow emissions around 560 nm with an excitation by 450 nm in this experiment. As described above, the increase of PL intensity and the blue-shift were thought to be attributed to the increase of the  $\beta$ -phase coexisting with the in dominant  $\alpha$ '-phase, because there are differences of the distance of ligands (Sr-O), the angle of the a- and c-axis, and crystallographic symmetry between these two forms. At this time the exact crystal structure of  $\alpha$ '- $Sr_{2-x}Eu_xSiO_4$  is not known, but similar studies have been carried out. For instance, Catti et al. [10] reported that in  $\alpha$ '-Sr<sub>1.9</sub>Ba<sub>0.1</sub>SiO<sub>4</sub> (orthorhombic), the SiO<sub>4</sub> tetrahedron was abnormally small and Sr(I)-O bond strength was weak due to the mirror symmetry compared with  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub> (monoclinic). On the other hand, in  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub>, the SiO<sub>4</sub> tetrahedron had a normal size and Sr(I)-O bond strength was enhanced due to the loss of the (100) symmetry plane.

To clarify the effects of the  $\beta$ -form, we synthesized  $Sr_2SiO_4$ :Eu<sup>2+</sup> powders by varying the duration times at 1300 °C to enable both  $\beta$ - and  $\alpha$ '-forms to coexist. XRD patterns of 1.95 SrCO<sub>3</sub> - SiO<sub>2</sub> - 0.025Eu<sub>2</sub>O<sub>3</sub> - 2 wt% NH<sub>4</sub>Cl powders fired at 1300 °C as a function of duration time are shown in Fig. 3. We could obviously observe the  $\beta$ -form as well as the  $\alpha$ '-form by XRD, and corresponding PL properties strongly depend on  $\beta/\alpha$ ' phase ratios,  $\{I_{\beta}/\alpha\}$  $(I_{\alpha'}+I_{\beta})$ , as shown in Fig. 4.  $I_{\alpha'}$  and  $I_{\beta}$  are integral peak intensities of (112) of the  $\alpha$ '-form and (301) of the  $\beta$ -form in XRD patterns, respectively. These two peaks were most suitable to discriminate  $\beta$ - and  $\alpha$ '-forms from each other. The  $\beta/\alpha$ ' phase ratio peaked at 5 hours, and accordingly the PL peak wavelength was shortest at the same condition. These results were in good agreement with those of Fig. 1 and 2, confirming that the  $\beta$ -form contributed to an increase of the PL intensity and the blue-shift.

To investigate the contribution of  $Eu^{2+}$  ions to the stabilization of the high-temperature  $\alpha$ '-form even at room temperature, the  $\beta/\alpha$ ' phase ratio of  $Sr_{2-x}Eu_xSiO_4$  powders, which were prepared at 1300 °C as a function



Fig. 3. XRD patterns of  $Sr_2SiO_4$ :Eu<sup>2+</sup> (0.05mol) fired at 1300 °C for (a) 1 hour, (b) 3 hours, (c) 5 hours, and (d) 10 hours.



**Fig. 4.** A correlation between  $I_{\beta}/(I_{\alpha} + I_{\beta})$  of XRD patterns of Fig. 3 and peak wavelengths.  $[I_{\alpha}: integral peak intensity of (112) of \alpha'-form, I_{\beta}: integral peak intensity of (301) of \beta-form]$ 

of  $Eu^{2+}$  concentration, were measured by XRD as shown in Fig. 5.

When Eu was not added, the  $\beta$ -form alone was formed, while the  $\alpha$ '-form began to be created by adding Eu. The  $\beta/\alpha'$  phase ratio slightly decreased up to  $\times = 0.03$ , and then drastically dropped up to  $\times = 0.07$  at which the  $\alpha'$ -form alone appeared. This evidently demonstrated that Eu<sup>2+</sup> ions in Sr<sub>2</sub>SiO<sub>4</sub> contributed to the stabilization of the  $\alpha'$ -form at room temperature. The  $\alpha'$ -Sr<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> formed at high temperature had to be turned into the  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> during the cooling process by a displacive transformation, but Eu<sup>2+</sup> ions prohibited the phase transition. Similar results were reported for  $\alpha'$ -(Sr, Ba)<sub>2</sub>SiO<sub>4</sub> [9, 10] and a'-(Sr, Ca)<sub>2</sub>SiO<sub>4</sub> [11].

Regardless of the size of the ions substituted, smaller  $(Ca^{2+})$  or larger  $(Ba^{2+})$  than  $Sr^{2+}$ , both ions caused the



**Fig. 5.**  $I_{\beta}/(I_{\alpha} + I_{\beta})$  of  $Sr_{2:x}Eu_{x}SiO_{4}$  as a function of x.  $[I_{\alpha}:$  integral peak intensity of (112) of  $\alpha$ '-form,  $I_{\beta}:$  integral peak intensity of (301) of  $\beta$ -form]

stabilization of the  $\alpha$ '-form at room temperature. According to Catti *et al.* [11], when the x value was very small or large in Sr<sub>2-x</sub>Ca<sub>x</sub>SiO<sub>4</sub>, a single phase  $\beta$ -form was synthesized, while the  $\alpha$ '-form together with the  $\beta$ -form was always observed at intermediate x values.

Conclusively, the sizes of substituted cations (Ca<sup>2+</sup>, Ba<sup>2+</sup>, and Eu<sup>2+</sup>) for Sr<sup>2+</sup> did not contribute to the stabilization of the  $\alpha$ '-form, but their replaced random positions in the host materials and related disorders mainly led to it. PL spectra as a function of x are shown in Fig. 6 With increasing x, both a red-shift (inset) and a decrease of PL intensity are seen, which is assigned to the decrease of the  $\beta/\alpha$ ' phase ratio as described above. Regarding the decrease of PL intensity, besides the  $\beta/\alpha$ ' phase ratio we have to consider the concentration quenching effect that led to the diminution of the PL. However, since a maximum PL intensity was not observed, the Eu<sup>2+</sup> concentration at which the concentration quenching effect arose could not be determined.



Fig. 6. PL spectra of  $Sr_{2,x}Eu_xSiO_4$  fired at 1300 °C as a function of Eu concentrations. (a) x = 0.005, (b) x = 0.01, (c) x = 0.03, (d) x = 0.05, and (e) x = 0.07.

In summary,  $\beta$ -Sr<sub>2</sub>SiO<sub>4</sub> is clearly superior to  $\alpha$ '-Sr<sub>2</sub>SiO<sub>4</sub> in PL intensity for application in white LEDs. However, it is thermodynamically impossible to obtain a single phase  $\beta$ -form by adding Eu<sup>2+</sup> ions, which led to the stabilization of the  $\alpha$ '-form even at room temperature.

## Conclusions

The  $\beta \leftrightarrow \alpha'$  phase transition was observed in Sr<sub>2-x</sub>Eu<sub>x</sub>SiO<sub>4</sub> powders by varying the Eu<sup>2+</sup> concentration, which affected the luminescent properties. When Eu<sup>2+</sup> ions were not added (x = 0), a single phase  $\beta$ -form was acquired. With increasing x, the  $\alpha'$ -form began to coexist with the  $\beta$ -form, and then the  $\beta/\alpha'$  phase ratio sharply decreased up to x = 0.07 at which almost a single  $\alpha'$ -form was obtained. This indicated that Eu<sup>2+</sup> ions contributed to the stabilization of the  $\alpha'$ -form at room temperature. The  $\beta$ -form was evidently superior to the  $\alpha'$ -form in luminescent properties, showing a higher PL intensity and the blue-shift.

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