

## Novel green $\text{Sr}_4\text{ScAl}_3\text{O}_{10}:\text{Eu}^{2+}$ phosphor prepared by the melt quenching technique

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New green-emitting  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}:\text{Eu}^{2+}$  phosphor was prepared using a novel melt quenching synthesis method. The temperature of raw materials irradiated with the strong light of the Xe arc-lamp was rose up to about 2273 K, followed by a sharp drop in the temperature after turn off the lamp. This method is a useful tool for rapid screening of novel phosphor materials.

**Key words:** Melt synthesis, Phosphor, Rare earths, Scandium Aluminate, Morphology, Luminescence.

### Introduction

Present two colors white LEDs produce pseudo white light by the complementary color of blue LED and yellow phosphor. Blue light excitable yellow emitting  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  or  $(\text{Ba},\text{Sr})\text{SiO}_4:\text{Eu}^{2+}$  phosphors were used as the conventional LED phosphors [1]. The pseudo-white light consisting yellow photoluminescence of phosphor and blue emission of the LED is not true white light. To obtain high color rendering, the three primary colors (blue, green and red) of light were required.

This study was focused on perovskite-type  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  compound for new green-emitting phosphor. The  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  exhibits outstanding chemical stability because of the strong three-dimensional network structure [2]. The structural property of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  was characterized by M. Rath and Hk. Müller-Buschbaum. Fig. 1 shows the crystal structure of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$ . The structure is oxygen-defect B-site ordering ( $\text{AlO}_6$  and  $(\text{Sc},\text{Al})\text{O}_6$  octahedra) perovskite. Therefore,  $\text{Eu}^{2+}$  doped  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  can be an attractive candidate of new phosphors for true-white LEDs. However, synthesis of  $\text{Eu}^{2+}$  doped  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  phosphor is not easy by the conventional solid-state reaction because of poor reactivity of high melting point raw materials,  $\text{Sc}_2\text{O}_3$  (melting point 2823 K) [3] and  $\text{Al}_2\text{O}_3$  (2324 K) [4].

In this paper, we disclose a new synthesis technique, melt synthesis, for the phosphors with high melting

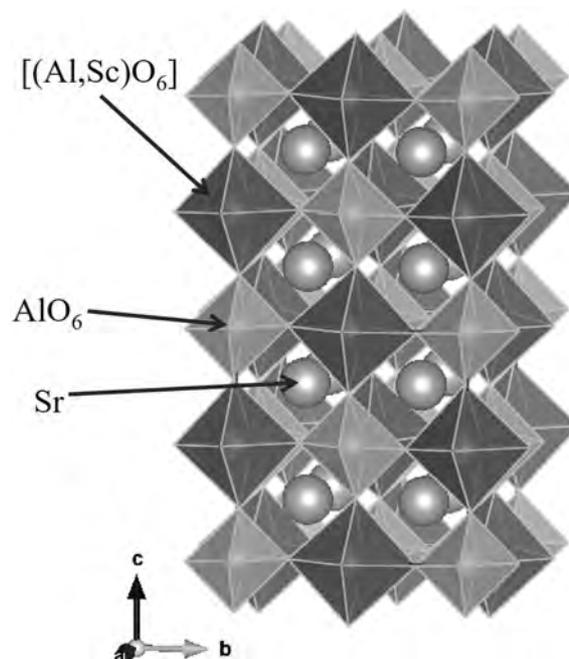


Fig. 1. Crystal structure of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$ .

temperature. The single phase  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}:\text{Eu}^{2+}$  sample prepared by the melt synthesis technique showed green emission under long wavelength UV and blue light excitation. Therefore, melt synthesis technique is suitable for preparing multi component homogeneous phosphor compounds.

### Experimental

$\text{Eu}^{2+}$  doped  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  phosphors were synthesized

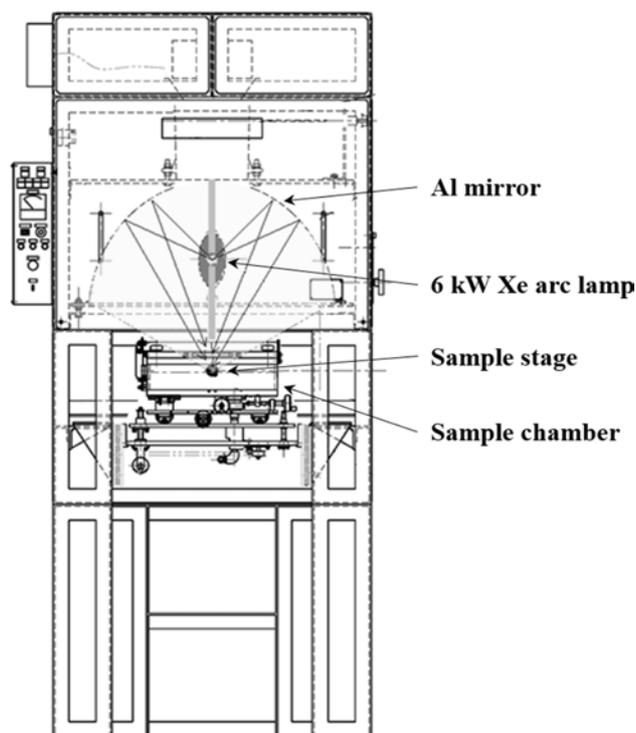
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using a combinatorial arc-imaging furnace. High purity carbonate and oxide reagents,  $\text{SrCO}_3$  (Kanto Chemical Co., Inc., 3N),  $\text{Sc}_2\text{O}_3$  (Shin-Etsu Chemical Co., Ltd., 4N),  $\text{Al}_2\text{O}_3$  (Kanto Chemical Co., Inc., 3N) and  $\text{Eu}_2\text{O}_3$  (Shin-Etsu Chemical Co., Ltd., 4N) were used as the starting raw materials.

As shown in Fig. 2, our combinatorial melt synthesis furnace is specially designed to heat small-size samples up to very high temperature (above 2273 K) [5]. The light emitted from a 6 kW xenon arc-lamp is collected by an ellipsoidal aluminum metal mirror and focused to the sample on the sample stage. Powders of mixed raw materials are placed on a water-cooled Cu hearth with 24 dimples for the samples in the chamber. The sample was heated in 95 vol% Ar - 5 vol%  $\text{H}_2$  atmosphere within a few seconds then rapidly cooled after closing the shutter of light. A spherical molten sample with multiple cations was mixed homogeneously and directly solidified on a Cu hearth. The cooling rate was estimated to be more than 100 K/s [6]. The crushed powder samples were annealed up to 1473 K for 12 h in 95 vol%  $\text{N}_2$  - 5 vol%  $\text{H}_2$  atmosphere.

The products were identified by powder X-ray diffraction measurement (MX-Labo; Mac Science Ltd.) and observed with scanning electron microscopy (JEOL Ltd. JMS-5310LV). The fluorescence properties of the crushed samples were measured using a spectrofluorometer with a Xe lamp light source (FP-6500/6600; Jasco, Inc.). All measurements were carried



**Fig. 2.** Optical system of the arc-imaging furnace. The light source is a 6 kW Xenon arc lamp. The light is reflected by a collection mirror to heat a sample on a sample stage.

out at room temperature. For comparison,  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}:\text{Eu}^{2+}$  phosphor samples were also synthesized by a solid-state reaction at 1473 K for 12 h in 95 vol%  $\text{N}_2$  - 5 vol%  $\text{H}_2$  atmosphere).

## Result and Discussion

Fig. 3 shows picture of the spherical molten  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  sample (phosphor ball) under the fluorescent lamp. The molten sample prepared using the arc image furnace showed green emission under the UV light excitation. Currently, most common white LEDs consist of the yellow phosphors sealed in an epoxy or silicone matrix and blue LED. The polymers were easily deteriorated by heat from the high power LED and LDs. To solve this problem, many researchers were committed to the development of Phosphor in Glass (PiG) systems [7, 8]. However, the glass system should be selected by considering refractive index and a reactivity between the glass and phosphor powder. Since the large difference of refractive index makes a large influence on the light scattering, the choice of glass is limited. In the view of practical application, it is preferable to use single composition  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  phosphor ball as an all-inorganic wavelength converter for high power LED and LDs. In addition, the phosphor balls show excellent mechanical and thermal stabilities because the as-prepared phosphor balls were strongly sintered.

Body colors of as-prepared samples synthesized using the melt technique were orange tinged with yellow. Fig. 4 shows the diffuse reflectance spectrum of the as-prepared  $(\text{Sr}_{0.90}\text{Eu}_{0.10})_4\text{ScAl}_3\text{O}_{10}$  phosphor. The intense reflection in the visible spectral range is in agreement with the observed orange-yellow body color. Fig. 5 shows the X-ray diffraction patterns of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  samples prepared using the conventional solid state reaction. Fig. 6 shows the X-ray diffraction patterns of



**Fig. 3.** Photograph of  $(\text{Sr}_{0.97}\text{Eu}_{0.03})_4\text{ScAl}_3\text{O}_{10}$  phosphor under the fluorescent lamp.

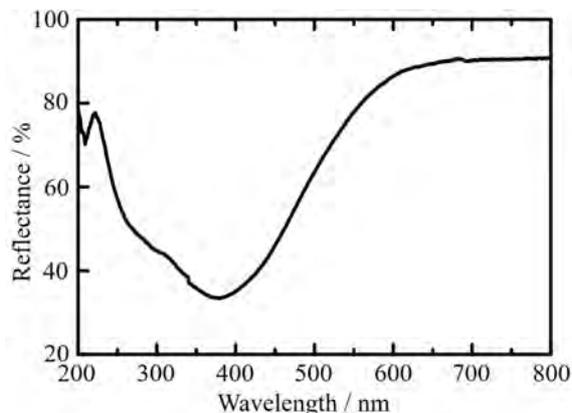


Fig. 4. Diffuse reflectance spectrum of the as-prepared  $(\text{Sr}_{0.90}\text{Eu}_{0.10})_4\text{ScAl}_3\text{O}_{10}$  phosphor.

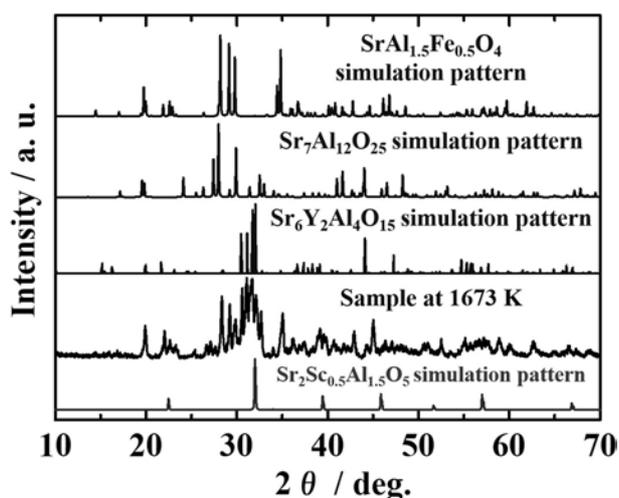


Fig. 5. X-ray diffraction patterns of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  samples prepared using the conventional solid state reaction.

$(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  phosphor obtained by the melt synthesis and simulation pattern calculated from The Inorganic Crystal Structure Database (FIZ Karlsruhe-NIST) (#72014). Single phase of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  sample could not be synthesized by the solid state reaction up to 1673 K and could be only succeeded by the melt synthesis technique. A peak of unknown phase is detected at the X-ray diffraction pattern of  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  ( $x = 0.10$ ). This is probably due to a solubility limit of  $\text{Eu}^{2+}$  ion for the  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}$  matrix.

Fig. 7 shows the excitation and emission spectra of the  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  ( $x = 0.01, 0.03, 0.05, 0.1$ ) phosphors synthesized by the melt technique. The  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}:\text{Eu}^{2+}$  sample produces broad green emission band extends from 450 - 650 nm with an emission peak of 526 nm owing to the 5d-4f transition of  $\text{Eu}^{2+}$  ion. The PLE spectrum shows a broad absorption band from 300 to 450 nm peaking at 350 nm. Therefore, this novel phosphor can be well excited by ultraviolet and visible light, in agreement with the widely applied near UV LED chip. Although no sharp linear emission

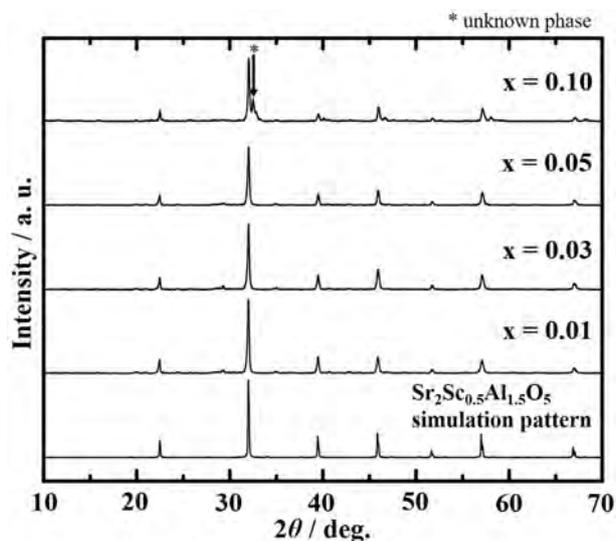


Fig. 6. X-ray diffraction patterns of  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  phosphors obtained at different  $\text{Eu}^{2+}$  concentrations and simulation pattern calculated from The Inorganic Crystal Structure Database (FIZ Karlsruhe-NIST) (#72014).

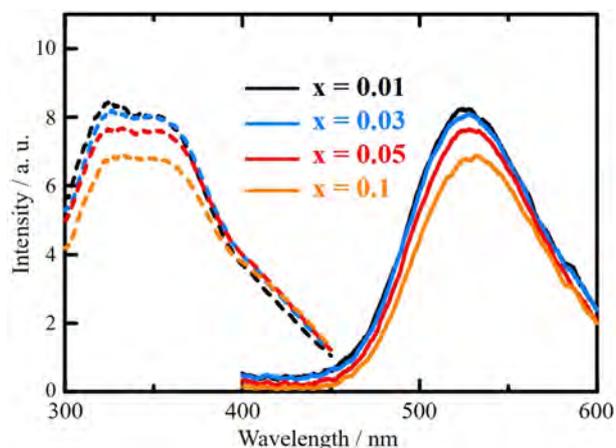
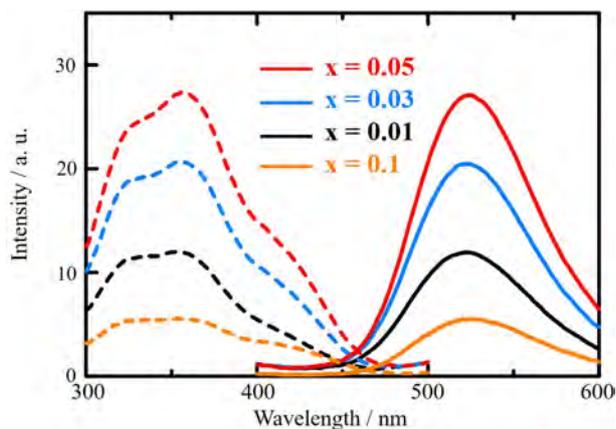
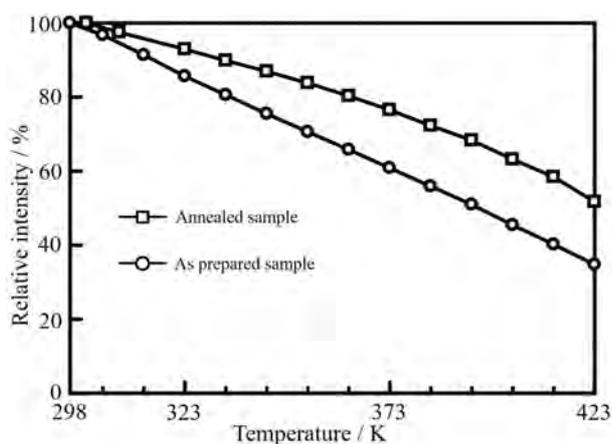


Fig. 7. Excitation and emission spectra of the  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  ( $x = 0.01, 0.03, 0.05, 0.1$ ) phosphors synthesized by the melt technique.

peaks from  $\text{Eu}^{3+}$  were observed in the red range, orange-yellow body color can be reasonably attributed to the absorption of some defects related to oxygen vacancies around the europium site. The emission intensity shows very weak concentration quenching behavior with the europium concentration because of incomplete reduction of the europium in the high viscosity melt under the above-mentioned melt synthesis condition [9, 10]. The gas diffusion in the viscous melt is too slow to permit significant reductive reaction with the outside atmosphere. The emission efficiency of  $\text{Sr}_4\text{ScAl}_3\text{O}_{10}:\text{Eu}^{2+}$  is improved by reducing the number of defect centers. After high temperature annealing at 1473 K for 12 h in 95 vol%  $\text{N}_2$  - 5 vol%  $\text{H}_2$  atmosphere, the orange-yellow body colors for the as-prepared



**Fig. 8.** Excitation and emission spectra of the  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  ( $x = 0.01, 0.03, 0.05, 0.1$ ) phosphors after high temperature annealing (1473K for 12 h in 95 vol%  $\text{N}_2 - 5$  vol%  $\text{H}_2$  atmosphere).



**Fig. 9.** Temperature dependence of the relative emission intensity for  $(\text{Sr}_{0.97}\text{Eu}_{0.03})_4\text{ScAl}_3\text{O}_{10}$  phosphor.

samples become light yellowish white. This color change is in agreement with the excitation spectra indicating small visible light absorption. The emission intensity of the annealed sample was more than four times higher than that of the as-prepared sample. As shown in Fig. 8, the concentration quenching phenomena of annealed phosphors were also studied. In contrast to the as-prepared samples, the emission intensity of annealed  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  phosphors increases until  $x = 0.05$  and shows clear concentration quenching behavior with the europium concentration. Fig. 9 shows the relative emission intensity for the  $(\text{Sr}_{0.97}\text{Eu}_{0.03})_4\text{ScAl}_3\text{O}_{10}$  sample at different temperatures. The thermal quenching of phosphors used in the white LEDs are important properties, which play a role in the luminous efficacy and color rendering of white LEDs. The emission

intensity of  $(\text{Sr}_{0.97}\text{Eu}_{0.03})_4\text{ScAl}_3\text{O}_{10}$  decreased with the increase of the temperature. About 52% of the emission intensity still remains when the phosphor is heated up to 423 K. This thermal quenching property is comparable to that of  $\text{SrBaSiO}_4:\text{Eu}^{2+}$  [11] and better than as-prepared sample.

## Summary

Well-crystallized and single phase  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  phosphors were synthesized by the melt synthesis technique.  $(\text{Sr}_{1-x}\text{Eu}_x)_4\text{ScAl}_3\text{O}_{10}$  phosphors had a broad excitation band extend from 300–450 nm and an appropriate green emission band. These phosphor balls were obtained in a quite short reaction time (within 1 min) for these reactions. In contrast, the samples synthesized by the conventional solid state reaction method were not single phase. The melt synthesis technique is a new useful and powerful method for rapid screening of new phosphor materials.

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