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Synthesis of $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ phosphor via newly developed emulsion route

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$\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ phosphor was synthesized by what we have named *Emulsion–Evaporation (EE) method*, where W/O emulsions of metallic ions and precipitants were mixed and condensed in a rotary evaporator. The EE-derived precursor was amorphous below 600°C and directly crystallized to CSS above 800°C without passing any impurity phases. SEM/EDS and ²⁹Si-NMR analyses revealed that the EE process is superior in achieving homogeneity. $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ phosphor fired at 1350°C showed higher fluorescent emission than those prepared by a normal precipitation (PP) without EE route and by a solid state (SS) synthesis.

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1. Introduction

White LED (Light Emitting Diode) is globally expected as an energy-saving device aiming at a huge market. Currently, yellow phosphor excited by a blue LED is used to generate a white light. However, thus obtained white light sometimes appears “cold” or less natural since it is a mixture of only two colors of blue and yellow. In order to avoid it and to enhance the color rendition, the Red/Green/Blue-composed white lights are widely required.

A garnet-type $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ (CSS:Ce) phosphor is a candidate material for the white LED application since it emits strong and stable green light when excited by blue light.^{1,2)} A single phase of CSS:Ce can hardly be obtained by a conventional solid state (SS) synthesis.^{3–5)} Suzuki et al. employed such solution routes as a hydrothermal gelation (HTG) method⁶⁾ with an autoclave and a polymerizable complex (PC) method⁷⁾ for the synthesis of the CSS:Ce phosphor. It is reported that the HTG and PC methods provide much higher phase purity and fluorescent property than a normal SS method. On heating the PC-derived precursor, in addition, several impurity crystalline phases were found at 1000–1300°C before achieving a single phase of CSS at 1400°C.

In this article we introduce a simple, newly developed emulsion method to prepare the CSS:Ce precursor which directly crystallizes to the CSS:Ce phase without passing impurity crystalline phases.

2. Experimental

Reagent grade chemicals were used without further purification. Sc_2O_3 was dissolved in nitric acid at 80°C for 24 h. Then, $\text{Ca}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$ were dissolved in distilled water and added to the acidic solution at room temperature. Tetraethyl-orthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) was then added as a silicate source and partially hydrolyzed in the acid at 50°C for 90 min. Thus obtained starting solution will be denoted as “solution A”

or the metal-containing solution. Molar concentration was fixed at $[\text{Ca}(\text{NO}_3)_2]:[\text{Sc}_2\text{O}_3]:[\text{TEOS}]:[\text{Ce}(\text{NO}_3)_3] = 0.297:0.100:0.300:0.003$ mol/L, aiming at $(\text{Ca}_{2.97}\text{Ce}_{0.03})\text{Sc}_2\text{Si}_3\text{O}_{12}$. On the other hand, another starting aqueous solution named “solution B” containing precipitants was prepared by dissolving ammonium oxalate and ammonia water at $[(\text{NH}_4)_2\text{C}_2\text{O}_4] = 0.5$ mol/L and $[\text{NH}_3] = 1$ mol/L.

Each of the aqueous starting solution (5 mL) was ultrasonically emulsified in *iso*-octane (50 mL) with co-addition of two surfactants, 2.74 g of SPAN80 (sorbitan oleate, $\text{C}_{24}\text{H}_{44}\text{O}_6$, Kanto Chem., Japan) and 1.10 g of cetyltrimethylammonium chloride (C_{16}TAC , *ibid.*). The emulsified starting solutions were then mixed and reacted at 50–90°C for 3–24 h, after then it was centrifugally separated, washed several times, and finally dried in an oven at 100°C for 6 h. Chemical composition of the product after fired at 1000°C was found to be Ca:Sc:Si = 3.00:2.55:2.6 (assuming the Ca content is fixed at 3.00), which is far different from the nominal composition of Ca:Sc:Si = 3:2:3. As a consequence, such an ordinary emulsion processing was found to be unfavorable.

To improve it, we employed another operation after mixing the two emulsions. That is, the mixed emulsions were charged in a rotary evaporator and evacuated by an aspirator at 90°C for about 15 min. Here we name this simple process *Emulsion–Evaporation (EE) route* or method. Thus obtained material was black in color and gel-like. It was slowly calcined up to 600°C in air to diminish its volume by removing organic substances. The precursor was fired at 800–1350°C in air for 3 h to synthesize the final product of the CSS:Ce phosphor.

For comparison, the starting aqueous solutions A and B were simply mixed at 50°C without emulsifying to precipitate a precursor followed by a firing at the same temperatures as above. Also, commercial fine powders (CaCO_3 , ~5 μm; Sc_2O_3 , ~2 μm; SiO_2 , ~0.5 μm, CeO_2 , ~0.2 μm) were mixed with an agate mortar and a pestle, and then fired for solid-state synthesis of another comparison.

Products were characterized by XRD (X-ray Diffraction, Rigaku Miniflex, 30 kV-15 mA), TEM (Transmission Electron Microscopy, Hitachi H-7000 observed at $V_{\text{acc}} = 100$ kV), SEM

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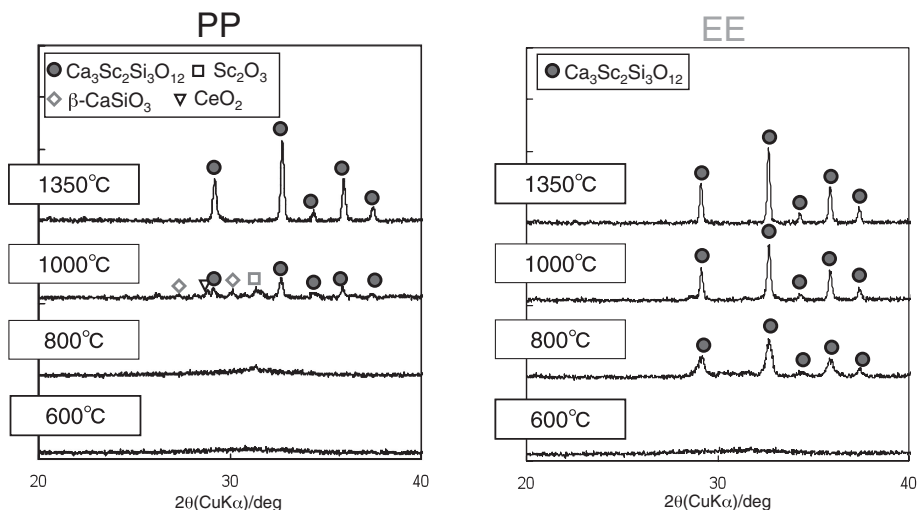


Fig. 1. XRD patterns of the samples PP and EE.

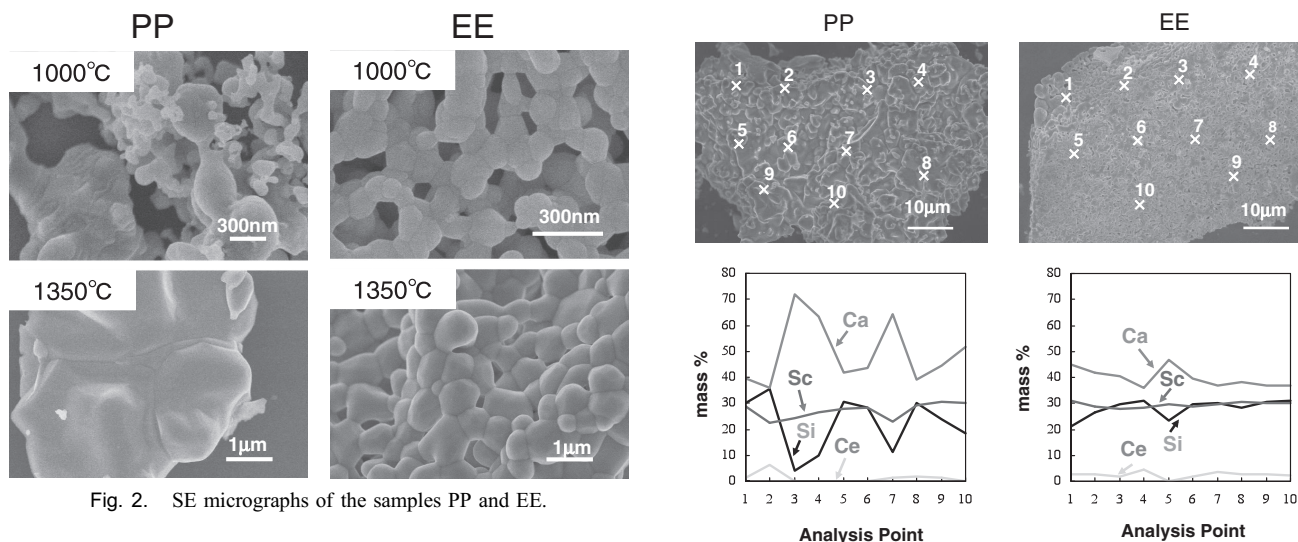


Fig. 2. SE micrographs of the samples PP and EE.

Fig. 3. SEM/EDS analyses of the samples PP and EE.

(Scanning Electron Microscope, Hitachi S-5200 observed at $V_{\text{acc}} = 1\text{--}5\text{ kV}$) attached with EDS analysis (Energy-Dispersive X-ray Spectroscopy, EDAX genesis XM4 accumulated at $V_{\text{acc}} = 5\text{ kV}$), and $^{29}\text{Si-NMR}$ (Nuclear Magnetic Resonance, JEOL JMX-CMX300). Fluorescence spectra were measured by using a spectrofluorophotometer (RF-5301SC, Shimadzu Coop.). Sample preparation procedure was as follows; well-dried phosphor powder was diluted in a quartz powder at 0.5 mass %. The diluted powder was packed in the area of $5 \times 5\text{ mm}^2$ in a hand-made glass cell. Repetitive errors ($n = 5$) in the mixing and the repacking steps in the measurement were found to be small enough to proceed the discussion in this study.

3. Results and discussion

Figure 1 shows the XRD patterns of two samples annealed at various temperatures, namely those prepared by the precipitation (PP) and the EE routes. Both of the samples were amorphous at 600°C. The sample EE started to crystallize at 800°C, where the sample PP was still amorphous. The sample PP was crystallized at about 1000°C accompanied with a considerable amount of such impurity phases as calcium silicate and scandium oxide. It is clear that the EE process is superior in obtaining a single phase of CSS from amorphous precursor. In the case of solid state (SS)

synthesis done here, no single phase of CSS was obtained even at 1350°C as will be shown in Fig. 5.

SE micrographs in **Fig. 2** show that the primary particle size in the EE sample is relatively uniform. The sample PP was not very uniform at 1000°C and tightly grew at 1350°C. **Figure 3** shows the SEM/EDS analysis results for PP and EE prepared at 1350°C. Deviation in the chemical compositions measured at several analysis points is obviously more homogeneous in EE than in PP, even if the XRD-apparent crystalline phase is similarly uniform as shown in Fig. 1. In order to further confirm the superior homogeneity of the EE process, solid $^{29}\text{Si-NMR}$ was adopted to the samples PP and EE fired at 600 and 1350°C. For references, a reagent chemical of fused silica and a previously prepared calcium silicate (Ca_2SiO_4) were subjected to the same measurement. As shown in **Fig. 4**, both samples at 1350°C showed similarly sharp spectrum at about -81 ppm , which locates in between the spectra of pure silica (ca. -110 ppm) and calcium silicate (ca. -69 ppm) and would be attributed to CSS of the garnet structure. At the lower temperature of 600°C, on the other hand, the difference was conspicuous. The sample EE at

600°C showed a broad and single peak at about -76 ppm, while that of PP showed two peaks at about -76 and -97 ppm. It is confirmed that the EE-derived precursor is homogeneous on atomic scale after calcination at 600°C and would gradually transform to a single phase of CSS on heating.

Why has the EE process been successful in achieving the homogeneous precursor? To be frank, the evaporation process after the emulsification was initially intended just to remove the solvents of water and *iso*-octane (boiling point $\sim 99^\circ\text{C}$). However, some chemical changes are possibly accompanied during the evaporation process. In order to examine the meaning of the EE process, the process without emulsification was attempted. That is, a separated mixture of the aqueous phase (solutions A and B, where the precipitation already occurred) and the oil phase (*iso*-octane) containing surfactants was processed in the rotary evaporator at 90°C . It was found that the amount of CSS fairly increased compared to the normal PP process at 1000°C as

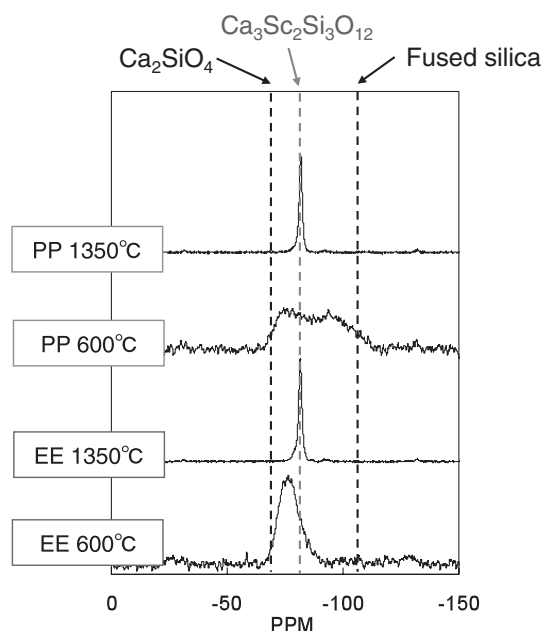


Fig. 4. ^{29}Si -NMR spectra for the samples EE and PP prepared at 600 and 1350°C .

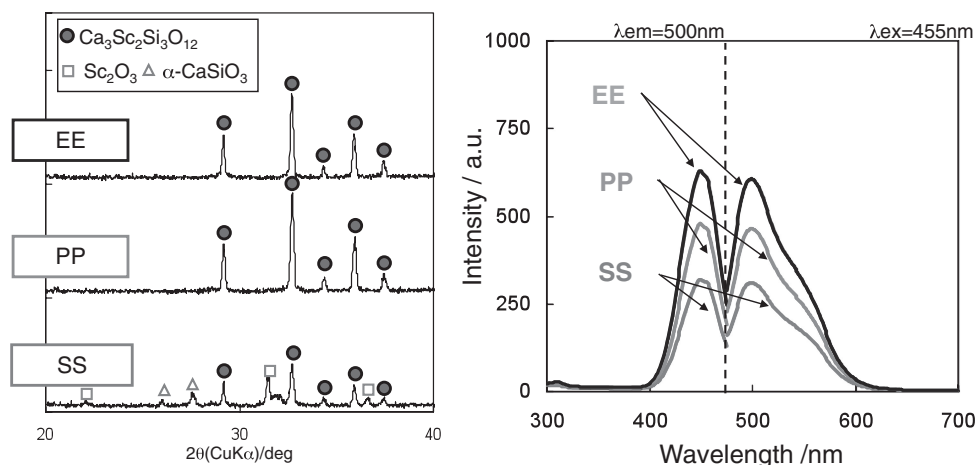


Fig. 5. Fluorescence spectra (right) for the samples EE, PP, and SS (solid state synthesis) prepared at 1350°C . XRD pattern of each sample is shown in the left part.

shown in Fig. 1. It implies that there would be a dissolution of the initial precipitates and a subsequent reprecipitation as well as an interaction with the surfactants and solvents. However, low temperature crystallization at 800°C and inhibition of impurity phase, which have been achieved in the EE process, were completely failed. It means that emulsification process is essentially important in the EE process. Further investigation is necessary to clarify what is really happening in the evaporation step.

Figure 5 shows the comparable XRD patterns as well as the fluorescence spectra (excited at $\lambda_{\text{ex}} = 455$ nm) and excitation spectra (emitted at $\lambda_{\text{em}} = 500$ nm) for three samples, namely PP, EE, and SS. As expressed in the formula $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$, the emission in this material is due to Ce^{3+} . It should be noted that the sample SS emits to a certain extent even though we started from CeO_2 and a heat treatment in air. It is inferred that cerium ion can be likely to enter the CSS matrix as Ce^{3+} .

Factors which enhance the fluorescence emission could be, (i) high crystallinity of the CSS matrix, (ii) phase homogeneity or being free from impurity phases that may interfere the emission, and (iii) microscopic homogeneity of Ce^{3+} which may suppress the concentration quenching. Judging from the XRD patterns in Fig. 5, the sample SS has an obvious impurity and its content of the phosphor is low. When we compare the samples PP and EE, either crystallinity or phase impurity is quite similar. The highest fluorescence property of the sample EE may be due to the microscopic homogeneity which might have been suggested in Figs. 2 and 3.

4. Conclusions

A simple method using W/O emulsion and rotary evaporator is successfully applied to the synthesis of the $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$ phosphor. This process does not require an autoclave with high pressure and high temperature above the boiling point of water and may be applicable to larger scale production of the CSS:Ce phosphor as well as the other phosphors or the other functional materials containing multiple cations. It was experimentally proved that both of the E's, emulsification and evaporation, are essentially necessary to achieve direct crystallization from amorphous at a low temperature of 800°C without passing impurity phases. In order to clarify what is really happening in the evaporation step, further investigation is expected as a future work.

References

- 1) Y. Shimomura and N. Kijima, U.S. Pat. Appl. 2004/0251809A1 (2004).
- 2) G. A. Novak and G. V. Gibbs, *Am. Mineral.*, **56**, 791–823 (1971).
- 3) Y. Shimomura, T. Kurushima, M. Shigeiwa and N. Kijima, *J. Electrochem. Soc.*, **155**, J45–J49 (2008).
- 4) Y. Shimomura, T. Honma, M. Shigeiwa, T. Akai, K. Okamoto and N. Kijima, *J. Electrochem. Soc.*, **154**, J35–J38 (2007).
- 5) Y. Shimomura, T. Honma, M. Shigeiwa, T. Akai, K. Okamoto and N. Kijima, *J. Electrochem. Soc.*, **154**, J234–J238 (2007).
- 6) Y. Suzuki, M. Kakihana, Y. Shimomura and N. Kijima, *J. Mater. Sci.*, **43**, 2213–2216 (2008).
- 7) Y. Suzuki, M. Kakihana, Y. Shimomura and N. Kijima, *Jpn. Soc. Powder Powder Metall.*, **54**, 44–47 (2007).