

Preparation of $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$ White Luminescence Phosphor Particles and Thin Films by Using an Emulsion Liquid Membrane System

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Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$ phosphor particles and thin films were prepared by using an emulsion liquid membrane (ELM, water-in-oil-in-water (W/O/W) emulsion) system, containing VA-10 (2-methyl-2-ethylheptanoic acid) as extractant (cation carrier). A two-step extraction enabled efficient extraction for Sr^{3+} and rare earth ions, and the resulting precursor metal oxalate particles produced in the internal water phase of the ELM system were about 60 nm in diameter. Calcination of the oxalate particles in air gave submicrometer-sized Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$ particles, which showed blue and white luminescence, respectively, by UV excitation. Blue and white luminescence phosphor thin films were also prepared by soaking alumina substrates into the W/O emulsion containing precursor oxalate particles, followed by calcination in air.

Introduction

Oxide based luminescent materials have been widely used for displays, fluorescent lamps, X-ray phosphors, etc., due to their thermal and chemical stability. In 1998, Danielson et al. reported on a novel blue luminescent material, Sr_2CeO_4 , using a combinatorial technique.¹ This phosphor exhibits blue-white luminescence efficiently under excitation with UV light, cathode ray, or X-ray. Sr_2CeO_4 also acts as a sensitizer to transfer the absorbed energy to the dopants (activators), such as rare earth ions.^{2,3} In our previous study,⁴ Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Ln}^{3+}$ (rare earth-doped Sr_2CeO_4 , Ln = Eu, Ho, Tm, and Er) fine particles were prepared by using an emulsion liquid membrane (ELM, water-in-oil-in-water (W/O/W) emulsion) system containing D2EHPA (bis(2-ethylhexyl)phosphoric acid) as extractant (cation carrier), and photoluminescence properties of the resulting particles were investigated. In the D2EHPA system, Sr^{2+} and Ce^{3+} (and Ln^{3+}) ions were extracted simultaneously from the external water phase, and were stripped into the internal water phase, having restricted reaction area as “microreactor”, containing oxalic acid to form the submicrometer-sized oxalate particles. Calcination of the precursor oxalate particles obtained in the ELM system produced submicrometer-sized Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Ln}^{3+}$ particles. The Sr_2CeO_4 particles showed charge-transfer (CT) emission at 467 nm (blue) by UV excitation (λ_{ex} = 254 nm). The rare earth doped Sr_2CeO_4 particles showed characteristic emissions corresponding to doped rare earth ions, effected by energy transfer from the triplet excited state of the metal-to-ligand CT (MLCT) state for Sr_2CeO_4 to the rare earth ions. In particular, $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+}$ showed an uncommon emission in the blue region (around 467 nm) assigned to the $^5\text{D}_2-^7\text{F}_0$ transition in Eu^{3+} . In addition, the green and red emissions were also observed from $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+}$, and thus white luminescence was obtained at an appropriate Eu^{3+} content. The color rendering property of phosphor would be improved by adding

Dy^{3+} ions to $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+}$, since Dy^{3+} can emit yellow luminescence.⁵

Calcium halophosphate phosphor ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl})\text{:Sb}^{2+},\text{Mn}^{2+}$) is well-known as a white luminescence material.^{6,7} In this phosphor, Sb^{2+} emits blue luminescence (~ 475 nm) and Mn^{2+} emits orange luminescence (~ 570 nm) under UV irradiation. Selection of the proper Sb/Mn molar ratio leads to white luminescence. Another is a phosphor so-called three bands fluorescence phosphor that was obtained by mixing of phosphors for blue (450 nm, $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}^{2+}$), green (542 nm, $(\text{Ce},\text{Gd},\text{Tb}^{3+})\text{MgB}_5\text{O}_{10}$), and red (611 nm, $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$) luminescence.⁸ The feature of this phosphor is that the luminescence having a high color rendering and efficiency can be obtained by appropriate mixing of these three phosphors because of the narrow band emission. The rare earth-doped Sr_2CeO_4 phosphor can be a good candidate as a white luminescence phosphor, since this emits appropriate sharp emissions in the visible region in a single host lattice.

In the present work, Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$ phosphor particles were prepared in the ELM system containing 2-methyl-2-ethylheptanoic acid (VA-10) as an extractant. Ultrafine oxalate particles as precursor for the synthesis of Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$ could be prepared by the ELM system containing VA-10 as the cation carrier, comparing with the D2EHPA system previously used.⁴ The oxalate particles prepared in the ELM system were then calcined to obtain both blue luminescent material, Sr_2CeO_4 , and white luminescent material, $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$, and their size, morphology, and luminescence properties were investigated. The Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+},\text{Dy}^{3+}$ thin films were also prepared on alumina substrates by using the W/O emulsion containing the precursor oxalate particles as a soaking solution, according to the procedure previously employed for the preparation of Y_2O_3 nanoparticulate thin films.⁹

Experimental Section

Chemicals. 2-Methyl-2-ethylheptanoic acid (VA-10), supplied by Shell Chemical Co., was used as the extractant, and

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sorbitan sesquioleate (Span 83, supplied by Tokyo Kasei Kogyo Co., Ltd., Tokyo) was used as the surfactant. Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), europium nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), dysprosium nitrate hexahydrate ($\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), oxalic acid, ethylene glycol, and acetone were supplied by Wako Pure Chemical Industries, Ltd.

Preparation of Phosphor Particles. The oxalate particles were prepared as follows. The internal water phase (0.5 mol/L oxalic acid) and the organic membrane phase (kerosene containing 0.5 mol/L VA-10 and 5 wt % Span 83) were mixed at a volume ratio of 1:1, and were emulsified mechanically with a homogenizer (12 000 rpm). The resulting W/O emulsion (10 mL) was then added to the external water phase I, containing $\text{Sr}(\text{NO}_3)_2$ (2 mmol/L) and NH_3 (0.1 mol/L), and the solution was stirred vigorously with a magnetic stirrer (500 rpm), to form a W/O/W emulsion. After 1 h of stirring, the W/O emulsion was separated from the external water phase I, and then added to the external water phase II, containing $\text{Ce}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, and $\text{Dy}(\text{NO}_3)_3$ (total molar concentration of rare earths was 1 mmol/L) and CH_3COONa (20 mmol/L). After being stirred for 1 h, the W/O emulsion was separated from the external water phase II. This “two-step extraction” is needed since an appropriate pH region for Sr extraction is different from that for rare earth extraction, in the VA-10 system. The W/O emulsion was then demulsified by adding ca. 50 mL of ethylene glycol. The oxalate particles formed in the water droplets were separated by centrifuge and were washed with acetone three times and dried at room temperature. The oxalate particles were finally calcined in a furnace at 1273 K for 2 h in air to obtain Sr_2CeO_4 and $\text{Sr}_2\text{CeO}_4\text{:Eu}^{3+}, \text{Dy}^{3+}$ particles.

Preparation of Phosphor Thin Films. Alumina substrate (ca. 1 cm \times 1 cm) was pretreated by sonication in ethanol for 10 min, rinsed with deionized water, and then dried under vacuum. This substrate was soaked into the W/O emulsion containing the precursor oxalate particles in alumina boat, and then calcined in a furnace at 1173 K for 2 h in air, with a heating rate of 10 deg K/min. The obtained phosphor thin film was finally washed by sonication in ethanol for 10 min.

Analysis. The composite oxalate particles and oxide particles were characterized by means of scanning electron microscopy (SEM, Hitachi S-5000) and powder X-ray diffraction (XRD, Philips PW-3050). To determine the metal concentrations in each phase of the ELM system, the separated W/O emulsion was demulsified electrically and the organic phase was then stripped with 1 mol/L HCl. The metal concentrations both in the external water phase and in the resulting HCl solutions were measured by using an inductively coupled argon plasma atomic emission spectrometer (ICP-AES, Nippon Jarrell-Ash ICAP-575 Mark II). The metal concentrations in the internal water phase were calculated by mass balance. The photoluminescence spectra of the particles were measured with a spectrofluorometer (Hitachi F-4500, Xe lamp). The CIE chromaticity coordinates were determined with a spectroradiometer (USHIO, USR-40V/D).

Results and Discussion

Preparation and Characterization of Sr_2CeO_4 Particles. The VA-10 extractant is known as a “weak” extractant as compared to phosphoric acid extractants such as D2EHPA,¹⁰ and generally used for metal extraction from weakly acidic, neutral, and alkaline aqueous solutions.¹¹ The extraction of Sr^{2+} was therefore carried out from the ammoniacal solution (external water phase I). More than 90% of Sr^{2+} ions are successfully

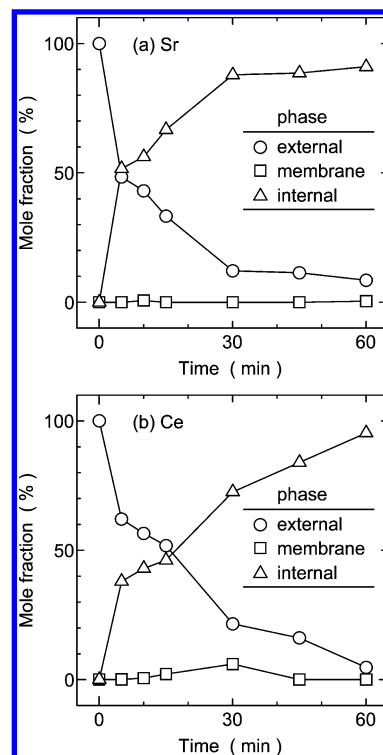


Figure 1. Time-course variations for the mole fraction composition of (a) Sr and (b) Ce ions in the external water phase, organic membrane phase, and internal water phase of the ELM system. The mole fraction in the initial external water phase is set as 100%.

transported into the internal water phase as shown in Figure 1a. The extraction of rare earth metals from alkaline solutions is, however, not feasible since precipitation of rare earth hydroxide occurs. The two-step extraction is therefore employed for the present VA-10 system, in place of the simultaneous extraction for Sr and rare earths employed in the D2EHPA system.⁴ As shown in Figure 1b, 95% of Ce^{3+} ions are transported successfully into the internal phase from the CH_3COONa solution.¹² No appreciable accumulation of metal ions (Sr^{3+} and Ce^{3+}) in the membrane phase is observed, indicating that the metal ions extracted are effectively stripped into the internal water phase by oxalic acid.

An SEM image of typical oxalate particles thus obtained by using the ELM system is shown in Figure 2a. The particles, ca. 60 nm in size and probably a mixture of Sr oxalate and Ce oxalate fine particles, are smaller than the oxalate particles obtained in the D2EHPA system (>100 nm).⁴ It is consistent with the results that the small rare earth oxalate particles (<100 nm) are mainly obtained in the VA-10 system.^{12–15} After being calcined in air at 1273 K for 2 h, the particles showed the characteristic XRD pattern of Sr_2CeO_4 , as shown in Figure 3a, which is similar to that for Sr_2CeO_4 prepared by the solid-state method (Figure 3b).⁴ In the VA-10 system, therefore, it is possible to prepare the Sr_2CeO_4 particles by feeding the metal ions at stoichiometric molar composition (molar ratio of Sr to Ce in the feed external water phase $(\text{Sr}/\text{Ce})_{\text{f}} = 2$), while $(\text{Sr}/\text{Ce})_{\text{f}} = 3$ or 4 is required in the D2EHPA system.⁴ A homogeneous mixture of the precursor oxalate particles smaller than 100 nm, prepared in the VA-10 system, may bring about the stoichiometric formation of Sr_2CeO_4 , under the moderate calcination condition compared to that employed in the solid-state method (1273 K for 72 h with two intermediate regrindings).⁴ Figure 2b shows the SEM image of the Sr_2CeO_4 particles prepared by using the VA-10 system. The Sr_2CeO_4 particles are somewhat sintered and the particle diameter increased up

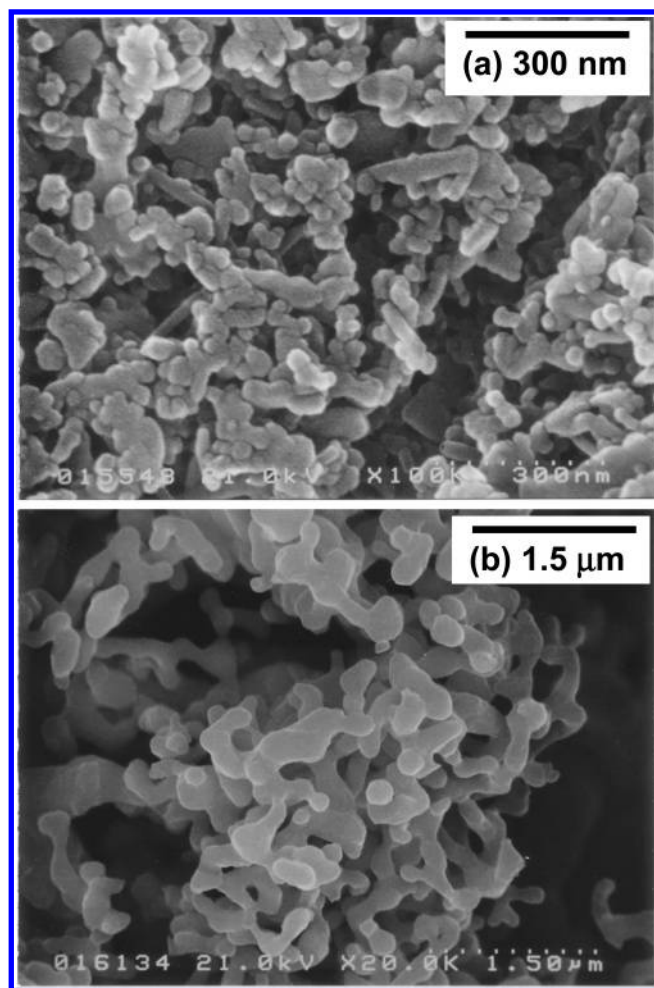


Figure 2. SEM images for (a) Sr–Ce oxalate particles prepared by using the ELM system and (b) Sr₂CeO₄ particles obtained by calcination of the oxalate particles.

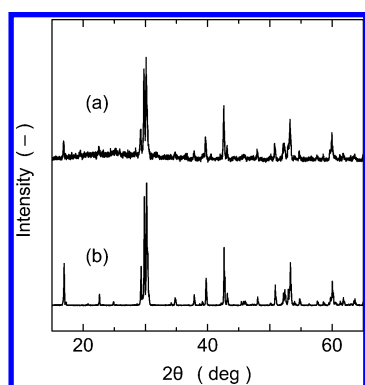


Figure 3. X-ray diffraction patterns for Sr₂CeO₄ particles (a) prepared by using the ELM system and (b) prepared by the solid-state method.⁴

to submicrometer size for the main component, as in the case for the particles prepared in the D2EHFA system.⁴ The sintering occurs because alkaline earth metals such as Ba, Sr, Ca, and Mg are relatively ductile metals.^{16,17} The Sr₂CeO₄:Eu³⁺,Dy³⁺ particles, prepared by feeding Eu(NO₃)₃ and Dy(NO₃)₃ in the external water phase II in addition to Ce(NO₃)₃, showed similar features for the SEM and XRD measurements.

Luminescent Properties of Sr₂CeO₄ and Sr₂CeO₄:Eu³⁺,Dy³⁺ Particles. Figure 4 shows the emission spectrum for the Sr₂CeO₄ particles prepared by using the VA-10 system when excited at 280 nm. A broad emission band is observed with a maximum at 467 nm (blue), and is attributable to the transition

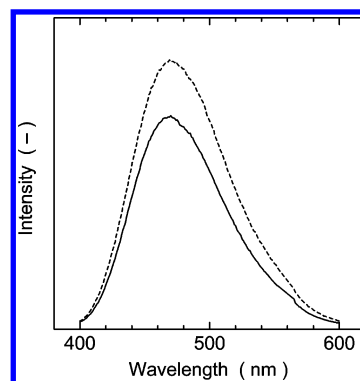


Figure 4. Photoluminescence spectra for Sr₂CeO₄ particles prepared by using the ELM system (solid line) and by the solid-state method (dotted line). $\lambda_{\text{ex}} = 280$ nm.

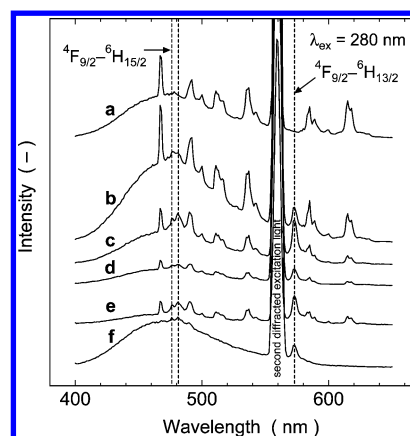


Figure 5. Photoluminescence spectra for Sr₂CeO₄:Eu³⁺,Dy³⁺ particles prepared by using the ELM system. $\lambda_{\text{ex}} = 280$ nm. Mole percent of Eu³⁺ and Dy³⁺ with respect to Ce³⁺ in the feed external water phase II was (a) 1 mol % of Eu³⁺ and 0 mol % of Dy³⁺, (b) 1 mol % of Eu³⁺ and 0.5 mol % of Dy³⁺, (c) 1 mol % of Eu³⁺ and 1 mol % of Dy³⁺, (d) 0.5 mol % of Eu³⁺ and 1 mol % of Dy³⁺, (e) 1 mol % of Eu³⁺ and 2 mol % of Dy³⁺, and (f) 0 mol % of Eu³⁺ and 1 mol % of Dy³⁺.

from the MLCT state to the ground state.² The emission intensity of the particles prepared in the ELM system was ca. 80% as high as that from the particles prepared by the solid-state method.⁴ This may be due to the decrease in the particle size, since the surface defects, which often suppress the emission intensity, increase with a decrease of the particle size and increase of the surface area.¹⁸ Calcination of the oxalate particles for longer than 2 h may possibly increase the emission intensity of the particles prepared in the VA-10 system, as in the case for the Sr₂CeO₄ particles prepared by using the D2EHFA system.⁴

As shown in the previous study,⁴ the Sr₂CeO₄:Eu³⁺ particles show white luminescence at appropriate Eu³⁺ content. However, the emission color of Sr₂CeO₄:Eu³⁺ is slightly reddish, because of the lack of emission in the green-yellow region. In the present work, therefore, Dy³⁺ was codoped, to achieve more natural white luminescence. Figure 5 shows the emission spectra for the Sr₂CeO₄:Eu³⁺,Dy³⁺ particles prepared by using the VA-10 system. The emission spectra changes significantly with the feed concentration of Eu³⁺ and Dy³⁺. In the spectra b–f, the new emission peaks around 480 and 574 nm appear as compared to spectra a, which are assigned to the ⁴F_{9/2}–⁶H_{15/2} and ⁴F_{9/2}–⁶H_{13/2} transitions in Dy³⁺, respectively,⁵ effected probably by the energy transfer from the triplet excited state of the MLCT state for Sr₂CeO₄ (sensitizer) to Dy³⁺ (activator), as is the case for other rare earth ions such as Eu³⁺, Ho³⁺, Tm³⁺, and Er³⁺.⁴ The particles a–c showed white luminescence, and the emission

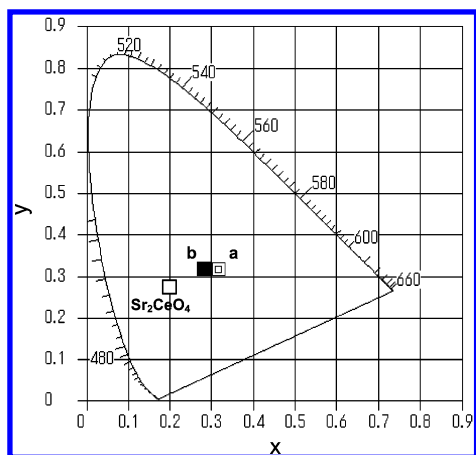


Figure 6. CIE chromaticity diagram for $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+},\text{Dy}^{3+}$ (a and b) and Sr_2CeO_4 particles prepared by using the ELM system. The preparation conditions for particles a and b are the same as in Figure 5.

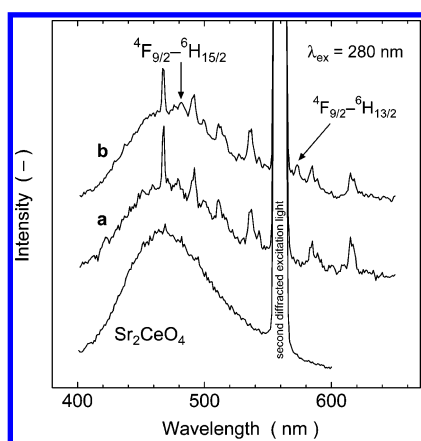


Figure 7. Photoluminescence spectra for $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+},\text{Dy}^{3+}$ (a and b) and Sr_2CeO_4 thin films prepared by using the ELM system. $\lambda_{\text{ex}} = 280$ nm. The preparation conditions for oxalate particles a and b are the same as in Figure 5.

from b seemed pure white, while the emission from a seemed slightly reddish and that from c seemed yellowish. CIE chromaticity diagram of the emission from $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+},\text{Dy}^{3+}$ particles a and b is shown in Figure 6, together with that from Sr_2CeO_4 particles. By doping Eu^{3+} and Dy^{3+} , the CIE chromaticity coordinate is changed to $x = 0.29$ and $y = 0.31$ for particle b, which is in the white region, from $x = 0.20$ and $y = 0.28$ for Sr_2CeO_4 , which is in the same region as that reported by Danielson et al.¹

Preparation of Phosphor Thin Films. Only two previous reports on the preparation and characterization of the Sr_2CeO_4 thin film, based on the pulsed laser deposition technique, have been published.^{19,20} The preparation of metal oxide particulate thin films with the ELM system, via casting the W/O emulsion containing precursor oxalate particles on the substrate followed by calcination, was achieved previously for Y_2O_3 nanoparticles.⁹ It was revealed that the carboxylic acid extractant such as VA-10 should be employed, since phosphorus was incorporated in the resulting metal oxide thin film when the phosphoric acid extractant such as D2EHPA was employed. In the present study, the W/O emulsion containing Sr and Ce oxalates was used as a soaking solution for the alumina substrate. The thin film obtained, via sintering of oxalate particles almost completely, was analyzed by means of XRD, and the film was found to contain Sr_2CeO_4 , $\text{Sr}_3\text{Al}_2\text{O}_6$, and CeO_2 phases. The reaction of alumina substrate and oxalate particles during the calcination

is thus found to be unavoidable. However, the obtained thin film showed blue luminescence similar to the Sr_2CeO_4 particles (Figure 7). This indicates that the thin film contains Sr_2CeO_4 acting as the blue phosphor together with some different oxides. When the W/O emulsion containing Sr–Ce–Eu or Sr–Ce–Eu–Dy oxalate particles was used as the soaking solution, the resulting thin film showed the luminescence spectrum corresponding to the doped rare earth ions and Sr_2CeO_4 itself, as shown by Figure 7 (a and b). The luminescence from the $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ thin film (a) was slightly reddish, as expected, while white luminescence was obtained from the $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+},\text{Dy}^{3+}$ thin film (b). Therefore, the blue and white phosphor thin films can be prepared based on the VA-10 system, though the films contain some impurities.

Conclusion

The present paper described the preparation of blue (Sr_2CeO_4) and white ($\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+},\text{Dy}^{3+}$) luminescence phosphor particles, by employing an emulsion liquid membrane system containing carboxylic acid extractant, VA-10. The Sr_2CeO_4 particles was obtained with a stoichiometric feeding molar ratio of $\text{Sr}/\text{Ce} = 2$, by employing the two-step extraction for Sr^{3+} and Ce^{3+} ions. White luminescence was achieved by codoping of Eu^{3+} and Dy^{3+} to the Sr_2CeO_4 particles. Blue and white luminescence phosphor films were also prepared on alumina substrates, by using the W/O emulsion containing precursor oxalate particles as a soaking solution followed by calcination.

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