

# The preparation of rare earth phosphate fine particles in an emulsion liquid membrane system†

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Phosphate particles of the selected rare earth metals have been prepared, using an emulsion liquid membrane [ELM, water-in-oil-in-water (W/O/W) emulsion] system, consisting of Span 83 (sorbitan sesquioleate) as surfactant and EHPNA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) as extractant (cation carrier). The rare earth ions are extracted from the external water phase of the ELM system and are stripped into the internal water phase, containing phosphoric acid solution, to form the corresponding rare earth phosphate particles. The morphology and size of the particles are well-controlled by using the ELM system, and submicrometer-sized spherical phosphate particles are obtained, while micron-sized and irregular-shaped phosphate particles are obtained in homogeneous aqueous solutions. The resulting submicrometer-sized spherical particles were characterized by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and thermal analysis (TG-DTA). The characterization of La-based particles revealed that the fine particles obtained were of hexagonal structure, but their crystalline structure was changed to a monoclinic structure by calcination at 1373 K. Composite  $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$  phosphor particles were then prepared by transporting  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ , and  $\text{Tb}^{3+}$  ions simultaneously, with the resulting particles showing good photoluminescence at 545 nm. In the ELM system, the size of the particles is able to be controlled in the range of 0.28 to 0.65  $\mu\text{m}$  by changing the concentration of Span 83, whereas that in the homogeneous system is about 0.7  $\mu\text{m}$ .

## 1 Introduction

An emulsion liquid membrane [ELM, water-in-oil-in-water (W/O/W) emulsion] system has been studied for the selective separation of metals, in which the metal ions, in the external water phase, are first extracted into the organic membrane phase and then stripped and concentrated into the internal water phase. Such internal water droplets obtained *via* the ELM system have been found recently to be capable of being used to prepare both size- and morphology-controlled fine particles, owing to the restricted reaction area of the micrometer-sized internal water droplet.<sup>1–5</sup> The internal water droplet is also remarkable with regard to its rather more hydrophobic property, as compared to homogeneous aqueous solutions, as this allows the formation of particles of lower hydration number and thus of a more characteristic morphology.<sup>3,5</sup> In addition, owing to the high selectivity of the ELM system, further purification and pre-concentration of the target metals are unnecessary.

Rare earth phosphate is useful for the production of phosphors, sensors, and heat-resistant materials, and several studies concerning the preparation of these materials have been reported.<sup>6–12</sup> In recent years, rare earth phosphate has become used especially for phosphor materials.<sup>7,10,13–16</sup> Phosphor particles, having spherical morphology, submicrometer size, and narrow particle size distribution, give rise to higher packing densities than prior commercial products, and are thus very effective in enhancing the luminescent efficiency.<sup>17–20</sup> The

control of morphology of the rare earth phosphate, however, is very important owing to the high reactivity of rare earth ions with phosphate ions. In previous studies,<sup>3,5</sup> the oxalate particles of the rare earth metals, as precursors of rare earth oxide particles, were prepared employing an ELM system.

The extension of the ELM methodology to the preparation of phosphate particles of the rare earth metals may be expected to produce both a controllable morphology and size of particle. In this work, the ELM system has therefore been applied to the case of rare earth phosphate particles. Firstly, the preparation of single-rare earth phosphates from La to Yb was investigated, and the characterization of the resultant particles carried out. Finally, composite  $\text{LaPO}_4\text{:Ce}^{3+}, \text{Tb}^{3+}$  phosphor particles, which exhibit a green luminescence emission, were then prepared *via* the ELM system by a simultaneous transport of all three metals, and the photoluminescence property also investigated, and compared to that of the particles obtained in the homogeneous aqueous solution.

## 2 Experimental

### 2.1 Reagents and procedures

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA, marketed as PC-88A by Daihachi Chemical Industry Co., Ltd.) was used as the extractant, and sorbitan sesquioleate (marketed as Span 83 by Tokyo Kasei Kogyo Co., Ltd.) was used as the surfactant. The rare earth chlorides, other than Ce, were prepared by the dissolution of the oxides in heated HCl followed by the removal of the excess acid by evaporation.  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ , ethylene glycol, and phosphoric acid materials were supplied by Wako Pure Chemical Industries, Ltd.

The internal water phase for the emulsion (0.3 or 1.5 mol l<sup>-1</sup>  $\text{H}_3\text{PO}_4$ ) and the organic membrane phase (kerosene containing

†Electronic supplementary information (ESI) available: SEM images of phosphate particles prepared in the homogeneous system, and SEM images of La phosphate particles prepared *via* the ELM system, following calcination for 2 h at 573 and 1373 K. See <http://www.rsc.org/suppdata/jm/b1/b105743j>

0.5 mol l<sup>-1</sup> EHPNA and 5 wt% Span 83 in most cases) were mixed at a volume ratio of 1 : 1 and were emulsified by the use of a mechanical homogenizer (12 000 rpm). The resulting W/O emulsion (10 ml) was added to an external water phase (50 ml of LnCl<sub>3</sub> solution, Ln = rare earth metal) and was stirred vigorously by a magnetic stirrer to form the W/O/W emulsion. The external water phase consisted of 0.01 mol l<sup>-1</sup> of LnCl<sub>3</sub> aqueous solution (light rare earth: La, Ce, Pr; middle rare earth: Eu, Tb; heavy rare earth: Er and Yb) in the case of the single metal systems, and was 0.006 mol l<sup>-1</sup> of LaCl<sub>3</sub>, 0.003 mol l<sup>-1</sup> of CeCl<sub>3</sub>, and 0.0015 mol l<sup>-1</sup> of TbCl<sub>3</sub> aqueous solution for the La/Ce/Tb ternary system. The pH value of the initial external water phase was 5.5–6. The size of the emulsion drops, when dispersed in the external water phase, was less than 2 μm. After stirring for 2 h, the W/O emulsion was separated from the external solution and was demulsified by the addition of about 50 mL of ethylene glycol. The particles, as formed in the water droplets, were separated by centrifugation and washed with acetone.

For studies involving the homogeneous system preparation of the rare earth metal particles, aqueous solutions of the rare earth metal (50 ml) and H<sub>3</sub>PO<sub>4</sub> (5 ml) were mixed and stirred for 1 h, and the precipitated particles separated by centrifugation and washed with acetone. The concentrations of the solutions were adjusted so that that of the aqueous rare earth metal solution was identical to that of the external water phase and that of the H<sub>3</sub>PO<sub>4</sub> identical to that of the internal water phase, as employed in the ELM system.

## 2.2 Analyses

The resultant phosphate particles were characterized by means of scanning electron microscopy (SEM, Hitachi S-5000), thermal analysis (TG-DTA, Shimadzu DTG-50), and powder X-ray diffraction (XRD, 40 kV and 30 mA, CuKα, Philips PW-3050). Prior to SEM examination, all the samples were sputter-coated with an approximately 10 nm thick platinum layer, in order to minimize possible surface charge effects. In order to determine rare earth metal concentrations in the organic membrane phase, the W/O emulsion was demulsified electrically and the organic phase was stripped with 3 mol l<sup>-1</sup> HCl solution. Metal concentrations in the resulting HCl and external aqueous solutions were measured using an inductively coupled argon plasma emission spectrometer (ICP-AES, Nippon Jarrell-Ash ICAP-575 MarkII). Metal concentrations in the internal water phase were then calculated by mass balance. H<sub>3</sub>PO<sub>4</sub> concentrations were determined by automatic titration with NaOH (Hiranuma Comtite-550). The measurement of particle photoluminescence spectra was carried out by spectrofluorometer (JASCO FP-6500, Xe lamp, excitation wavelength: 260 nm), following the dispersion of a fixed quantity (2 mg) of particles in 10 ml of ethanol by ultrasonic bath. A laser scattering particle-size distribution analyzer (Horiba LA-910W) was used to measure the size of both particles and internal water droplets.

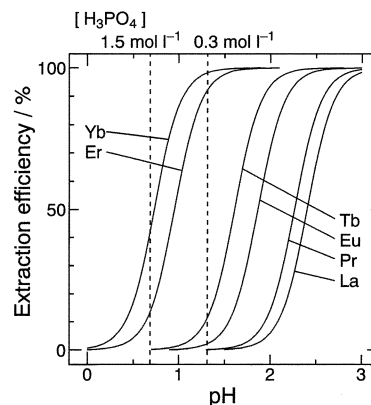
## 3 Results and discussion

### 3.1 Extraction behavior of rare earth metals

The conventional liquid–liquid extraction system, for the simple aqueous/organic two phase system, was studied first. Extraction equilibrium formulations for the rare earth metals from aqueous chloride media by EHPNA have been established as shown in eqn. (1), and the value of the corresponding extraction equilibrium constants,  $K_{ex}$ , determined.<sup>21</sup>



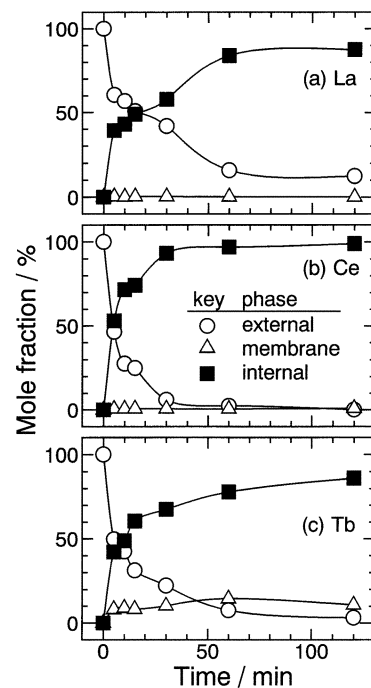
Fig. 1 shows the variation in the calculated equilibrium extraction efficiency for each rare earth metal as a function



**Fig. 1** Effect of equilibrium pH on the extraction efficiency for the rare earth metals.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$  and  $[\text{Ln}^{3+}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ .

of pH. At pH = 1.31 (corresponding to a H<sub>3</sub>PO<sub>4</sub> concentration of 0.3 mol l<sup>-1</sup>), the heavy metals Yb and Er are shown to be almost totally extracted, whereas the light and middle rare earths are extracted only slightly. At pH = 0.68 (H<sub>3</sub>PO<sub>4</sub> = 1.5 mol l<sup>-1</sup>), the extraction efficiencies for the heavy rare earths are reduced to about 40% for Yb and about 10% for Er. Since the stripping of the heavy rare earth metals from the organic membrane phase into the internal water phase does not occur at 0.3 mol l<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>, the precipitation of phosphate particles of the heavy rare earth metals, *via* the ELM system, must therefore, in these cases, be conducted using a concentration of 1.5 mol l<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> as the internal water phase.

Fig. 2 shows measured time course variations in the concentrations of the light and middle rare earth metals (La, Ce, and Tb) in the external water phase, the organic membrane phase, and in the internal water phase, for the ELM system with 0.3 mol l<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>, showing that a period of 2 h is needed for the transport of the rare earth metals from the external water phase to the internal water phase to be effected. In the La system, about 10% metal remains in the external water phase



**Fig. 2** Time course concentration variations for (a) La, (b) Ce, and (c) Tb ions in the external water phase, organic membrane phase, and internal water phase of the ELM system in single metal system.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$ ,  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$ ,  $[\text{Span 83}]_{\text{feed}} = 5 \text{ wt}\%$ , and  $[\text{Ln}^{3+}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ .

after 2 h, owing to the lower extractability of La as shown in Fig. 1. For the Tb system, however, 10% metal, after 2 h, remains in the organic membrane phase, owing to the higher extractability of Tb (lower stripping ability), as also shown in Fig. 1.

### 3.2 Preparation of single-metal phosphate particles

Following the extraction of the rare earth ions from the external water phase into the internal water phase, the following internal water phase reaction occurs and the rare earth phosphate particles are precipitated.

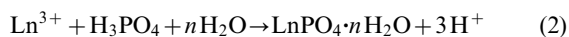
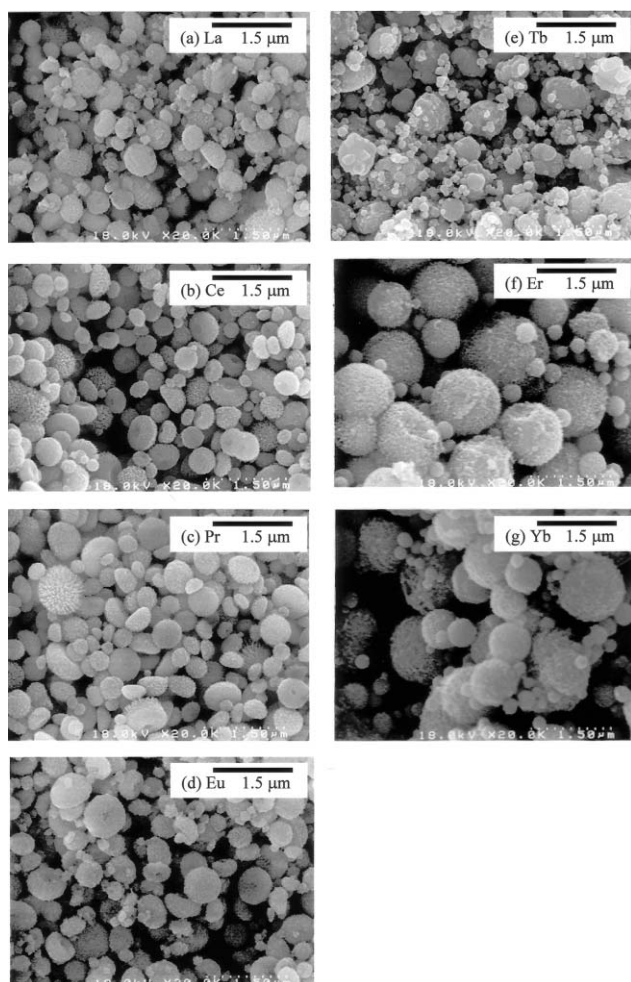
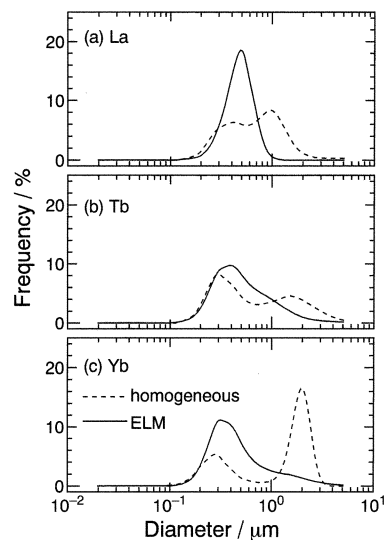


Fig. 3 shows SEM images for the single rare earth metal phosphate particles (La, Ce, Pr, Eu, Tb, Er, and Yb), which are as prepared in the ELM system. As explained earlier, for the heavy rare earth metals (Er and Yb), the particles were prepared using  $1.5 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$ . Well-defined spherical particles, with *ca.* 0.5–1.2  $\mu\text{m}$  diameter and fairly rough surface morphology, were obtained for these rare earth metals, with the morphology of these particles being very similar to those obtained in oxalate systems.<sup>3,5</sup> The present phosphate system, however, also has the advantage that the particles for the heavy rare earth metals can be obtained simply by changing the concentration of  $\text{H}_3\text{PO}_4$  in the internal water phase, whereas for the preparation of oxalate particles for heavy rare earth metals, the extractant must be changed from EHPNA to



**Fig. 3** Scanning electron micrographs of phosphate particles for (a) La, (b) Ce, (c) Pr, (d) Eu, (e) Tb, (f) Er, and (g) Yb prepared *via* the ELM system without calcination.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$ ,  $[\text{Ln}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ ,  $[\text{Span 83}]_{\text{feed}} = 5 \text{ wt}\%$ , and  $[\text{H}_3\text{PO}_4]_{\text{feed}} = (\text{a–e}) 0.3 \text{ mol l}^{-1}$  and (f and g)  $1.5 \text{ mol l}^{-1}$ .

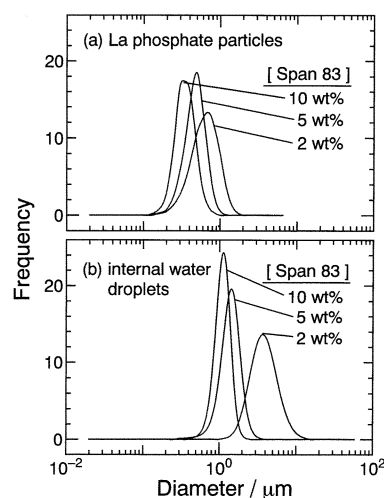


**Fig. 4** Size distributions for phosphate particles of (a) La, (b) Tb, and (c) Yb prepared in both ELM and homogeneous systems.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$ ,  $[\text{Ln}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ ,  $[\text{Span 83}]_{\text{feed}} = 5 \text{ wt}\%$ , and  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$  (a, b, and c – homogeneous) and  $1.5 \text{ mol l}^{-1}$  (c – ELM).

weaker VA-10 (2-ethyl-2-methylheptanoic acid) and DTMBPA [bis(1,1,3,3-tetramethylbutyl)phosphinic acid] extractants.<sup>3–5</sup>

Phosphate particles were also prepared in the homogeneous system. The case of La shows spherical particles with a particle size of about 1  $\mu\text{m}$ . Similar particles were also obtained for the other light rare earth systems (Ce and Pr). For both Tb and Yb, however, systems of randomly aggregated spherical particles of very rough surface morphology were obtained, and similar results to those for Yb were also obtained in the other middle and heavy rare earth metal systems (Eu and Er). The SEM images of the particles obtained in the homogeneous system are available as ESI (Fig. S1).<sup>†</sup>

Fig. 4 shows the size distribution of La, Tb, and Yb particles obtained with both ELM and homogeneous systems. These were measured using the laser scattering particle-size distribution analyzer, following the particle dispersion in ethanol. In all cases, submicrometer-sized particles are mainly prepared in ELM systems, while micrometer-sized particles also appear, in homogeneous system, together with the submicrometer-sized particles. Fig. 5 shows the effect of Span 83 concentration on



**Fig. 5** Size distributions for (a) La phosphate particles and (b) internal water droplets for differing Span 83 concentration, employed in the ELM systems containing EHPNA.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$ ,  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$ , and  $[\text{Ln}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ .

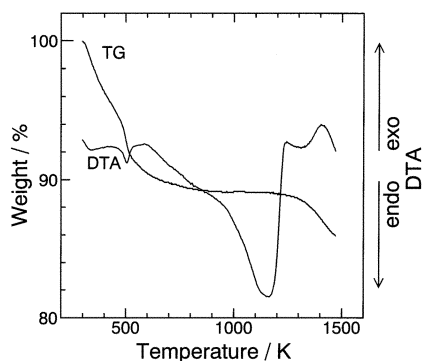


Fig. 6 TG–DTA curves for La phosphate fine particles prepared *via* the ELM system.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$ ,  $[\text{Ln}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ ,  $[\text{Span 83}]_{\text{feed}} = 5 \text{ wt}\%$ , and  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$ .

the size distribution obtained for the La phosphate particles and also the internal water droplet size in the ELM system. Thus, the water droplet size is seen to affect directly the resultant particle size and the particle size can thus be controlled directly. The ELM system is therefore effective in controlling both the particle size and the morphology of the phosphate particles, in the same manner as the oxalate particles reported previously.<sup>3–5</sup>

### 3.3 Thermal analyses of the particles

Calcination of the single rare earth phosphate particles, prepared in the ELM and homogeneous systems, was performed to study the thermal behavior of the particles. Fig. 6 shows the TG–DTA curves for La phosphate particles prepared in the ELM system. The TG curve indicates that significant weight losses occur in the temperature range 293–573 K, especially in the range 460–560 K. These weight loss steps are accompanied by the endothermic peak at 503 K in the DTA curve. This may correspond to the conversion of hydrated into anhydrous material. In addition, the much larger endothermic peak, shown at 1163 K, may correspond to a transition in the crystalline structure. Similar results were also obtained for particles prepared in the homogeneous system.

Particles prepared in the ELM system and also calcined at both 573 and 1373 K were characterized by XRD, as shown in

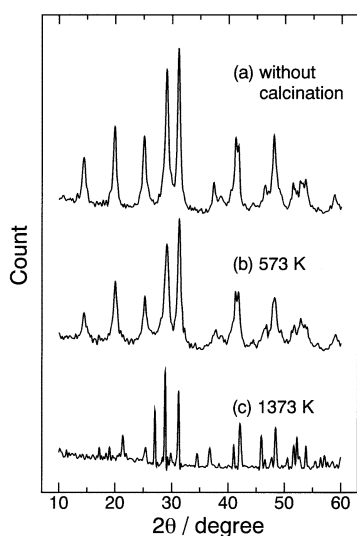


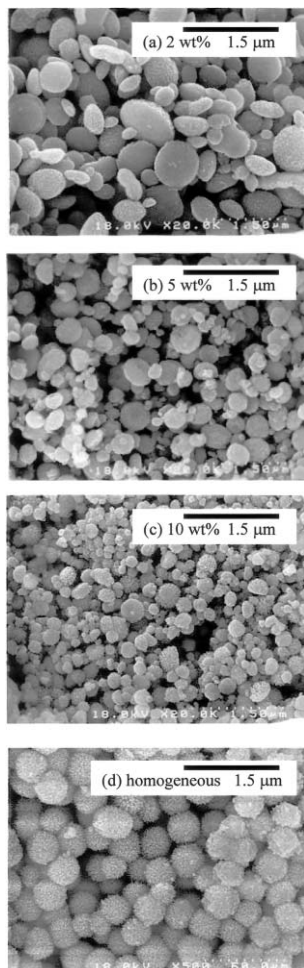
Fig. 7 X-Ray diffraction patterns for La phosphate particles prepared *via* the ELM system, before and following calcination for 2 h at the indicated temperature.  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$ ,  $[\text{Ln}]_{\text{feed}} = 0.01 \text{ mol l}^{-1}$ ,  $[\text{Span 83}]_{\text{feed}} = 5 \text{ wt}\%$ , and  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$ .

Fig. 7. The XRD pattern for particles without calcination shows that the particles obtained are of Brockite (hexagonal) structure.<sup>22</sup> Particles calcined at 573 K show no difference in the XRD pattern to that without calcination. This is expected from the results of TG–DTA analysis, which showed that only dehydration occurred by calcination at 573 K. For the phosphate particles calcined at 1373 K, significant differences are shown in the XRD pattern, thus indicating that the crystalline structure is changed by the calcination, with the particles following calcination at 1373 K consisting of a Monazite (monoclinic) structure.<sup>23</sup> In the case of size and morphology, no significant change is apparent for calcination at 573 K compared to the particles without calcination. Following calcination at 1373 K, however, the particles were sintered and aggregated. The SEM images of these calcined particles following prepared in the ELM system are also available as ESI (Fig. S2).<sup>†</sup> In previous research on oxalate particles,<sup>5</sup> particles obtained *via* the ELM system showed almost no characteristic peaks of the rare earth oxalate, while particles obtained in the homogeneous system showed the XRD peaks of a decahydrate structure. This may be because the restricted and hydrophobic internal water phase suppresses full hydration. In the case of phosphate, such suppression is not likely to occur since the hydration number here is only 0.5–1.

### 3.4 Application for the preparation of phosphor fine particles

Rare earth phosphate is known to be useful as a phosphor material, and  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  is used in luminescent lamps as a high efficient emitter of green light. In the first step, the  $\text{Ce}^{3+}$ , which is a sensitizer, is excited to the  $^2\text{D}(5\text{d})$  state by optical excitation, then the energy is transferred to the  $^5\text{D}_4$  state of  $\text{Tb}^{3+}$ , acting as an activator. The green luminescence is caused by transitions between the excited  $^5\text{D}_4$  state and the  $^7\text{F}_J$  ( $J = 0–6$ ) ground states of the Tb.<sup>12</sup> The  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  particles may be expected to be obtained *via* the ELM system, when transporting the three rare earth metals simultaneously. In the preparation of ternary composite particles, almost all the Ce was transported into the internal water phase. However, after stirring for 2 h, 15% of La remained in the external water phase and 24% of Tb remained in the organic membrane phase with  $0.3 \text{ mol l}^{-1} \text{ H}_3\text{PO}_4$  employed as the internal water phase. The SEM images obtained for the  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  particles, prepared *via* ELM and also particles obtained in the homogeneous system, without calcination, are shown in Fig. 8. The particles obtained in both the ELM and homogeneous systems are spherical, and are similar to those for single La phosphate, which acts as the host material. In addition, in the ELM system, the size of the particles is able to be controlled from 0.28 to  $0.65 \mu\text{m}$  by changing the concentration of Span 83, again reflecting the difference in the size of the water droplets, as shown in Fig. 5. The size of the particles obtained in the homogeneous system is *ca.*  $0.70 \mu\text{m}$ . The TG–DTA curve and XRD spectra for the ternary particles were also measured, and compared to the La phosphate. In these cases, no significant difference is also shown, except for the large endothermic DTA peak around 1163 K, which was shown in La particles, becoming broad. These results indicate that the crystalline structure of the ternary particles is also similar to those of La particles.

Typical photoluminescence spectra for  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  particles, prepared in both the ELM and homogeneous systems, are shown in Fig. 9. The particles obtained in both systems emit photoluminescence without calcination, and there is no significant difference in the photoluminescence spectra. It is one of the advantages that this phosphor material emits photoluminescence without calcination. The particles prepared in the ELM system are seen to possess equivalent luminescence intensity, although it may be difficult to quantify and compare the intensity from the dispersed particles of different particle

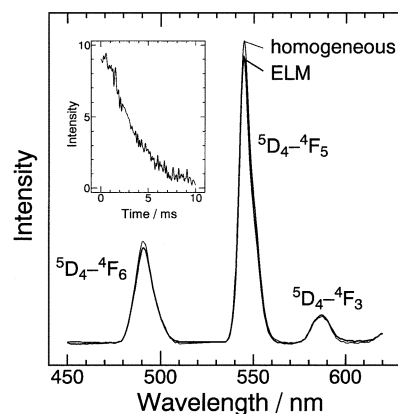


**Fig. 8** Scanning electron micrographs for  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  phosphor particles, prepared in the (a–c) ELM system and (d) homogeneous system, without calcination.  $[\text{La}]_{\text{feed}} = 0.006 \text{ mol l}^{-1}$ ,  $[\text{Ce}]_{\text{feed}} = 0.003 \text{ mol l}^{-1}$ ,  $[\text{Tb}]_{\text{feed}} = 0.0015 \text{ mol l}^{-1}$ , and  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$ . In the ELM system,  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$  and  $[\text{Span 83}]_{\text{feed}} =$  (a) 2 wt%, (b) 5 wt%, and (c) 10 wt%.

size. The ELM system is, therefore, useful for the preparation of the  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  particles, since both size and morphology can be controlled without changing the photoluminescence property.

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**Fig. 9** Photoluminescence spectra ( $\lambda_{\text{ex}} = 260 \text{ nm}$ ) for  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  particles prepared in both the ELM and homogeneous systems without calcination. Inset: luminescence decay curve ( $\lambda_{\text{ex}} = 260 \text{ nm}$  and  $\lambda_{\text{em}} = 545 \text{ nm}$ ) for particles prepared via the ELM system.  $[\text{La}]_{\text{feed}} = 0.006 \text{ mol l}^{-1}$ ,  $[\text{Ce}]_{\text{feed}} = 0.003 \text{ mol l}^{-1}$ ,  $[\text{Tb}]_{\text{feed}} = 0.0015 \text{ mol l}^{-1}$ , and  $[\text{H}_3\text{PO}_4]_{\text{feed}} = 0.3 \text{ mol l}^{-1}$ . In the ELM system,  $[\text{EHPNA}]_{\text{feed}} = 0.5 \text{ mol l}^{-1}$  and  $[\text{Span 83}]_{\text{feed}} = 5 \text{ wt}\%$ .

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