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Generalized wet-chemical processing of phosphor monospheres and the effects of composition on photoluminescence

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Abstract. Basic carbonate monospheres of various lanthanide combinations are successfully synthesized by the urea-based homogeneous precipitation technique, which are then converted into well dispersed phosphor particles that emit diverse colours. Sequential precipitation is commonly observed for these mixed cation systems, calling for adequate annealing of the basic carbonate precursors to attain cation homogenization in the final oxide particles and thus better luminescence, through eliminating localized concentration quenching of luminescence. It is shown that, owing to their excellent dispersion and uniform size, the phosphor spheres are readily assembled into close-packed luminescent films, allowing their wide applications in white LEDs, plasma display panels (PDPs), and field emission displays (FEDs).

1. Introduction

Current advances in display technologies need phosphor particles of smaller size, narrower size distribution and a spherical shape to improve the resolution by decreasing pixel size, to attain better luminescence through close packing of the phosphor particles, and to achieve a more uniform luminescence with the uniform particle morphologies. Traditional synthetic techniques for phosphors, such as solid state reaction followed by crushing and spray pyrolysis, find difficulties to meet these requirements, as the final products either have high populations of defects, which quench luminescence, or other undesired characteristics such as hollow particle interior.

The urea-based homogeneous precipitation technique, which utilizes the slow hydrolysis of urea at elevated temperatures (>83°C) to supply precipitating ligands (mainly OH− and CO32−), is known to generate monospheres for a wide range of materials systems. Excellent examples can be found in the literature by Sordelet and Akinc for basic carbonate particles of yttrium [1] and by Matijević et al. for basic carbonates of heavy lanthanides [2]. It is noteworthy that these previous work largely dealt with single lanthanide systems, while research on multi-cation systems has been rather limited. We very recently demonstrated that this “boiling under proper condition” technique is applicable to Y/Eu binary and even Y/Gd/Eu ternary systems, and uniform phosphor particles can be converted from their
basic carbonate precursors by proper calcination [3,4]. In the present work, we extended this synthetic route to other mixed systems, and well-defined phosphor spheres that emit diverse colors are obtained.

2. Experimental procedure
Precursor synthesis was performed under magnetic stirring on a hot plate. An aqueous solution containing lanthanide nitrate (0.015mol/L) and urea (0.5mol/L) was first homogenized at room temperature for 1h before being heated to 90°C within 1h, where it was held for 2h to effect precipitation. All the starting materials are high purity chemicals supplied by Kanto Chemical Co. Ltd (Tokyo, Japan). After a natural cooling to ~50°C, the resultant precursor particles were collected via centrifugation, washed repeatedly with distilled water and ethanol, and were then dried in an air oven at ~60°C. Phosphor oxide was obtained by calcining the precursor at 1000°C for 4h, under flowing O₂ gas (200mL/L). Characterizations were achieved by elemental analysis, X-ray diffractometry (XRD, RINT-2200 V/PC, Rigaku, Tokyo), field-emission scanning electron microscopy (FE-SEM, S-5000, Hitachi, Tokyo), and photoluminescence spectroscopy (FP-6500, JASCO, Tokyo).

3. Results and discussion
Elemental analysis confirmed that the precursor particles are of basic carbonate type possessing a general composition of M(OH)CO₃•nH₂O (n≈1.5) and in each case precipitation is complete. Figure 1(a) shows FE-SEM morphologies of the precursor, with the Ho/Y mixed system as an example, where a highly uniform particle morphology and an average diameter of ~430nm were clearly observed. Our previous work [3,4] on Gd/Y, Eu/Y, and Eu/Gd/Y mixed systems confirmed that the growth of these basic carbonate spheres follows the cubic root law, suggesting a surface-diffusion controlled growth mechanism. Another important finding therein is that precipitation is not instantaneously stoichiometric for Eu, Gd, and Y, and the sequential precipitation leads to non-uniform cation distributions in each of the precursor sphere. Through tracking composition evolution with elemental analysis, it was confirmed that the (Y,Gd,Eu)(OH)CO₃ particles have more Y while less Eu and Gd (particularly Eu) going from the particle core to the surface. This differential precipitation phenomenon results in a clear cation-ratio dependent average size of the final particles.

Figure 1. (a) FE-SEM micrograph showing morphologies of the precursor spheres for the Ho/Y system, and (b) normalized cation content of the supernatant, as a function of the reaction time.

For the Ho/Y system, we analyzed the concentrations of cations left behind in the solution, as a function of the reaction time, and the results are presented in Figure 1(b). This system is chosen because Ho³⁺ and Y³⁺ possess similar (yet different) physicochemical properties arising from their very close ionic radii (0.0901nm for Ho³⁺ and 0.0900nm for Y³⁺, for 6-fold coordination). Clearly differential precipitation still happened, though much less pronounced than that observed from the Eu/Gd/Y system. It is thus concluded that differential precipitation is a common phenomenon for mixed lanthanide systems, and as a result adequate annealing (several hours at 1000°C, for example) of the basic carbonate precursor is called for to produce better phosphors [4], through cation homogenization via inter-diffusion and hence the elimination of localized concentration quenching of luminescence. Sequential precipitation and its extent are believed to be a result of interplay of two
factors: (1) increasing solubility product of the basic carbonate with decreasing ionic radius of Ln$^{3+}$, which retards nucleation, and (2) enhanced hydrolysis of Ln$^{3+}$ at a decreased ionic radius to yield $[\text{Ln(OH)}_x\text{(H}_2\text{O)}_y]^3-x$ $(x+y=6)$, which facilitates nucleation. Figure 1(b) also suggests that the inner part of the particle has more Ho than Y and that stoichiometric precipitation is achieved after 80min.

Figure 2. FE-SEM micrographs showing morphologies of the $[(\text{Y}_{1-x}\text{Gd}_x)_{0.95}\text{Eu}_{0.05}]_2\text{O}_3$ red phosphors converted from their basic carbonate precursors by annealing at 1000ºC for 4h, with (a) $x=0$, (b) $x=0.25$, and (c) $x=0.5$. The insets are the FE-SEM morphologies of their respective precursors.

Figure 3. Optical properties of the phosphor spheres shown in Figure 2. The left and right parts are the photoluminescence excitation (PLE) and photoluminescence (PL) spectra, respectively. The inset in the right part is the influence of Gd$^{3+}$ doping on luminous intensity.

Figure 2 shows morphologies of the $[(\text{Y}_{1-x}\text{Gd}_x)_{0.95}\text{Eu}_{0.05}]_2\text{O}_3$ red phosphors obtained by calcining their respective precursors in flowing O$_2$ at 1000ºC for 4h. It can be seen that the original spherical shape and the excellent dispersion of the precursor monospheres (the insets) are well preserved to the oxides. Under 256-nm UV excitation, the phosphor powders exhibit a sharp red emission, as seen from the digital picture shown in the upper-right corner of Figure 2(c).

Figure 3 shows photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the $[(\text{Y}_{1-x}\text{Gd}_x)_{0.95}\text{Eu}_{0.05}]_2\text{O}_3$ spheres. The broad yet strong band with a maximum at ~256 nm observed from the PLE spectra is ascribed to the transition by charge transfer (CT), that is, electronic transition from the $2p$ orbital of O$^{2-}$ to the $4f$ orbital of Eu$^{3+}$ activators. The three groups of excitation peaks found in the ranges 290-350nm, 350-450nm, and 450-500nm are assignable to the $^7\text{F}_{0,1} \rightarrow ^5\text{H}_6/\text{H}_5$, $^7\text{F}_{0,1} \rightarrow ^5\text{L}_6$, and $^7\text{F}_{0,1} \rightarrow ^5\text{D}_2$ electronic transitions of Eu$^{3+}$, respectively. For the Gd-containing samples, the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{J=9}$ intra $f/f$ transition of Gd$^{3+}$ is clearly observed on the PLE spectra at ~276nm, providing direct evidence for an energy transfer from Gd$^{3+}$ to Eu$^{3+}$. Partially replacing Y$^{3+}$ with Gd$^{3+}$ up to 50at% does not alter appreciably the position of the CT band but considerably red-shifts the band edge and significantly improves the band intensity. These are primarily due to the increased covalency by Gd$^{3+}$ addition, and might be understood by considering the bond structure of Eu$^{3+}$-O$^{2-}$-Ln$^{3+}$ (Ln=Y$^{3+}$ and Gd$^{3+}$). Since the electronegativities of Y$^{3+}$ and Gd$^{3+}$ are 1.22 and 1.20, respectively, these ions tend to attract electrons in the order Y$^{3+}$>Gd$^{3+}$. Replacing Y$^{3+}$ with Gd$^{3+}$ thus allows an easier charge transfer, leading to the enhanced intensity of the CT band and the red-shifted band edge. Upon UV excitation at 256nm, the phosphor spheres exhibit sharp lines ranging from 550nm to 650nm, which are associated
with the transitions from the excited $^4\text{D}_0$ state to the $^7\text{F}_J$ ($J=0, 1, 2$) emission states of Eu$^{3+}$. It is the $^5\text{D}_0\rightarrow^7\text{F}_2$ electric dipole transition that gives a red emission at 610nm, as typically observed. The peak has a full width at half maximum (FWHM) of 4nm, indicating that the emission is sharp and that the phosphor particles have excellent crystallinity and few defects. The incorporation of Gd$^{3+}$ does not alter peak position of the $^5\text{D}_0\rightarrow^7\text{F}_2$ transition but greatly improves the emission intensity, indicating that Gd$^{3+}$ ions effectively sensitize the red emission, as also expected from the energy transfer observed from the PLE spectra. Intensity of the 610nm emission increases linearly with increased Gd$^{3+}$ addition, and the [(Y$_{0.5}$Gd$_{0.5}$)$_{0.95}$Eu$_{0.05}$]$_3$O$_3$ sample exhibits an emission-intensity roughly 1.4 times that of the sample has no Gd$^{3+}$.

Figure 4. Phosphor monospheres that emit diverse colours. The scale bar in (a) represent 1.5μm and is applicable to (b)-(g). (h) is a close packed phosphor film constructed from the particles shown in Figure 2(a). The inset in (h) is the appearance of luminescence under 254nm excitation

Precursor synthesis via homogeneous precipitation followed by proper calcination is a versatile route that yields phosphor spheres of diverse lanthanide combinations, as shown in Figure 4. The excitation/emission (the strongest peak) wavelength (in nanometer) and the type of emission transition are as follows: 383/564 and $^4\text{S}_2\rightarrow^4\text{I}_{15/2}$ for Er$^{3+}$; 410/608 and $^4\text{G}_{5/2}\rightarrow^4\text{I}_{15/2}$ for Sm$^{3+}$; 275/543 and $^5\text{D}_1\rightarrow^7\text{F}_5$ for Tb$^{3+}$; 227/574 and $^7\text{F}_2\rightarrow^5\text{H}_{13/2}$ for Dy$^{3+}$; 450/552 and $^5\text{S}_2\rightarrow^5\text{I}_8$ for Ho$^{3+}$; 211/454 and $^1\text{D}_2\rightarrow^3\text{F}_4$ for Tm$^{3+}$; 254/610 and $^5\text{D}_0\rightarrow^7\text{F}_2$ for Eu$^{3+}$. Owing to the excellent dispersion and the high morphological uniformity, the monospheres readily undergo self-assembly to form close packed phosphor films, as is shown in Figure 4(h), where the film was made via slow drying an alcoholic suspension (solid loading: 1vol%) of the spheres shown in Figure 2(a) on a quartz substrate. This property allows the monospheres to be used in a wide range of display technologies of current interest.

4. Conclusions
Homogeneous precipitation of precursor particles, followed by proper calcination, was shown to be versatile for the synthesis of phosphor monospheres of a wide range of compositions. Adequate annealing of the basic carbonate precursor is needed to alleviate the composition gradients arising from sequential precipitation. The phosphor monospheres show high tendency of self-assembly and thus hold great potential for applications in various display technologies of current interest.

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