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Dual preparation of hydrophobic and hydrophilic $BaWO_4$:Eu phosphors

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ABSTRACT

$BaWO_4$:Eu phosphors were prepared by performing a solvothermal reaction in a water–hexane bilayer system. A barium oleate (and europium oleate) complex was obtained in hexane *via* a phase transfer reaction involving Ba^{2+} (and Eu^{3+}) ions in an aqueous solution of sodium oleate. The outer surfaces of the nanometer-sized $BaWO_4$:Eu phosphors were capped by the long alkyl chain of oleate; therefore, the hydrophobic nanometer-sized $BaWO_4$:Eu phosphors preferentially dissolved in the hexane layer. The micrometer-sized $BaWO_4$:Eu phosphors were obtained in the water layer. The $BaWO_4$:Eu phosphors prepared in hexane and water yielded sharp strong absorption and emission peaks at 464 and 615 nm, respectively, due to the $^7F_0 \rightarrow {}^5D_2$ and the $^5D_0 \rightarrow {}^7F_2$ transitions of the Eu^{3+} ions. The $BaWO_4$:Eu phosphors are good candidate red-emitting phosphors for use in InGaN blue-emitting diodes, which have an emission wavelength of 465 nm.

1. Introduction

White light-emitting diodes (white LEDs) with eco-friendly, energy-saving, and long lifetimes have been used as a lighting source due to its advantage over fluorescence lamp [1–3]. Commercial white LEDs have been fabricated by coating $Y_3Al_5O_{12}$:Ce phosphors onto a InGaN blue LED chips [4–6]. White light is obtained by additive color mixing of the blue emission from blue LEDs and the yellow emission from $Y_3Al_5O_{12}$:Ce phosphors. To improve color rendering of white LED with natural color production, the phosphor-converting three-band white LEDs fabricated by coating blends of green- and red-emitting phosphor onto a blue LED chips must be developed [7–9].

Earth metal tungstates (or molybdates) doped with the trivalent europium ion (MXO_4:Eu, M = Ca, Ba, or Sr, X = W, or Mo) have been widely used as red-emitting phosphors in the display industry [10–13]. Recently, MXO_4:Eu phosphors have attracted attentions as red-emitting sources for the phosphor-converting three-band white LEDs. The characteristic atomic absorption due to its $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} ions in MXO_4:Eu appears at 464 nm [14,15]. As the emission wavelength of commercial blue LED is 465 nm, MXO_4:Eu can be a promise candidate for the red-emitting phosphor excited by blue LED.

In general, most MXO_4:Eu phosphors are synthesized using solid-state reactions at high temperatures over the range 800–1200 °C to obtain micrometer-sized MXO_4:Eu phosphors [16–18]. Recently, nanometer-sized MXO_4:Eu phosphors have attracted attention for their potential applications in transparent displays. The Mie scattering theory predicts that stable scattering-free MXO_4:Eu phosphors smaller than 50 nm should be useful in transparent displays [19,20]. The transparent displays can be available when nanometer-sized MXO_4:Eu phosphors used in the electronic matrix. Moreover, the scattering-free nanometer-sized phosphors have advantage over micrometer-sized phosphor prepared by solid-state reaction for fabricating the brighter white LED. When micrometer-sized phosphors are coated onto the blue LED chips, large portion of the blue emission is lost in back-scattering process. To eliminate this back-scattering process, the scattering-free nanometer-sized phosphors must be used for the brighter white LED. Therefore, the preparation method for the stable nanometer-sized phosphors must be developed.

Hydrothermal and solvothermal methods using a single solvent system are widely used to prepare nanometer-sized MXO_4:Eu phosphors [21–26]; however, water–nonpolar solvent bilayer systems are not extensively used to prepare nanometer-sized MXO_4:Eu phosphors. As the reaction occurs at the interfaces between water and the nonpolar solvent, water-nonpolar solvent bilayer systems are useful for forming nanometer-sized particles in the nonpolar solvent. Micrometer-sized particles may be obtained in the water layer. This work describes the preparation and photoluminescence properties of nanometer-sized hydrophobic

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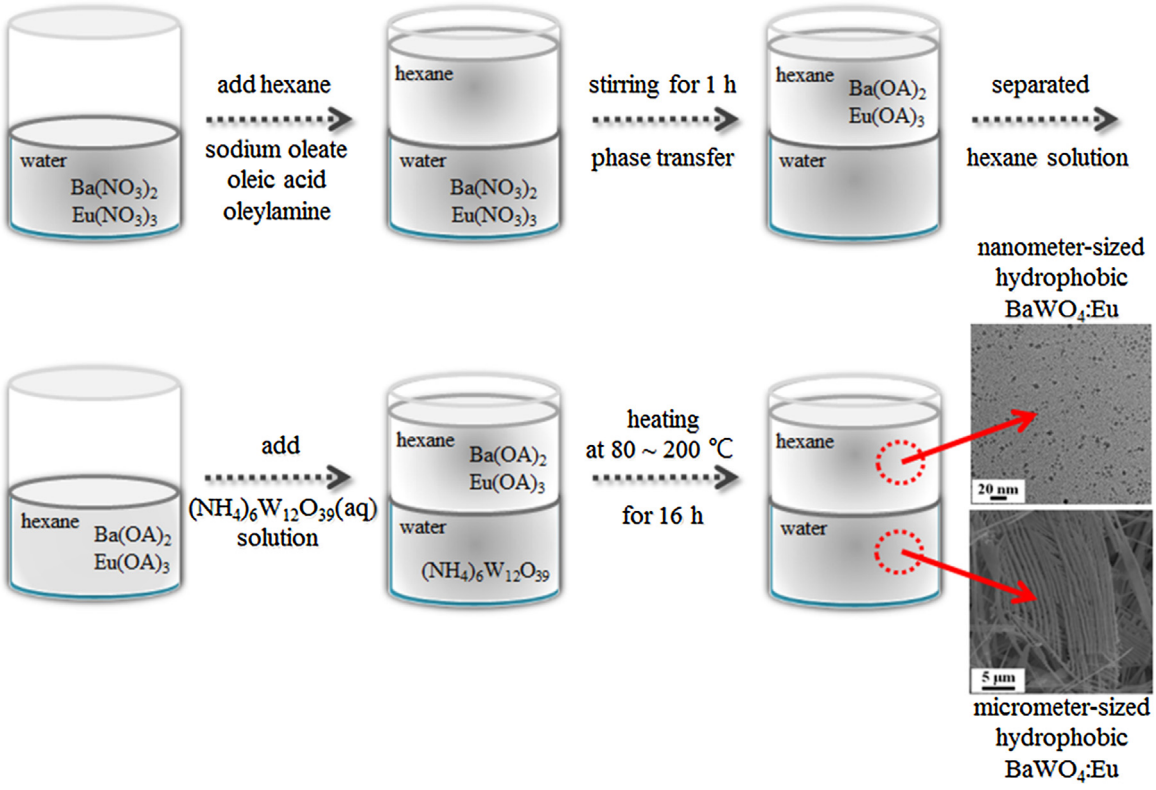
$BaWO_4$:Eu phosphors and micrometer-sized hydrophilic $BaWO_4$:Eu phosphors prepared in water–hexane bilayer systems.

2. Experimental

$Ba(NO_3)_2$ (Aldrich, 99%), $(NH_4)_6W_{12}O_{39}$ (Alfa Aesar), $Eu(NO_3)_3{\cdot}5H_2O$ (Aldrich, 99.9%), $NaNO_3$ (Aldrich, 99%), sodium oleate (TCI, 97%), oleic acid (Aldrich, 90%), and oleylamine (Aldrich, 98%) were used without further purification. In the synthesis of the $Ba_{0.8}WO_4$:0.1Eu^{3+},0.1Na^+ ($BaWO_4$:Eu was used here) phosphor, 0.160 M $Ba(NO_3)_2$, 0.020 M $Eu(NO_3)_3{\cdot}5H_2O$, and 0.020 M $NaNO_3$ were placed in 10 mL water. To this solution 1.218 g sodium oleate, 5.0 mL oleic acid, 5.0 mL oleylamine, and 40 mL hexane were added. The water–hexane bilayered mixture was vigorously stirred at room temperature for 1 h to allow the phase transfer of Ba^{2+} (Eu^{3+} and Na^+) ions with coordination of oleate anions from the aqueous solution to the hexane phase. The transparent hexane solution was used to deliver the precursors of Ba^{2+} (Eu^{3+} and Na^+) ions. $(NH_4)_6W_{12}O_{39}$ was dissolved in 10 mL of water to reach a total concentration of 0.0167 M. The hexane solution of Ba^{2+} (Eu^{3+} and Na^+) ions and the $(NH_4)_6W_{12}O_{39}$ aqueous solutions were mixed and transferred to a 100 mL Teflon-lined autoclave. The mixed solutions were heated to temperatures ranging from 80 °C to 200 °C for 16 h to prepare the $BaWO_4$:Eu phosphor. The $BaWO_4$:Eu product in the hexane layer was separated from the bottom aqueous layer solution using a separating funnel. The hexane solution was centrifuged at 4000 rpm for 10 min, and the clear top solution was separated from the lower non-transparent solution. The nanometer-sized $BaWO_4$:Eu phosphors were obtained by precipitating the products through the addition of 100 mL ethanol to the clear solutions. The nanometer-sized $BaWO_4$:Eu phosphors were then redispersed in hexane. Precipitation and redispersion were repeated several times to purify the nanometer-sized $BaWO_4$:Eu. $BaWO_4$:Eu phosphors were obtained using a centrifuge at 4000 rpm for 10 min. The nanometer-sized $BaWO_4$:Eu phosphors were dried in an oven at 60 °C for 12 h. Micrometer-sized $BaWO_4$:Eu phosphors in the aqueous layered solution were centrifuged, washed several times with ethanol, and dried at 60 °C for 24 h. Schematic diagram describing the experimental procedure for the preparing both nanometer-sized hydrophobic and micrometer-sized hydrophilic $BaWO_4$:Eu phosphors is presented in Scheme 1. A transparent suspension of nanometer-sized $BaWO_4$:Eu phosphors was prepared by dispersing 0.03 g nanometer-sized phosphors in 3 mL hexane in a 10 mL vial for 10 min. A less transparent suspension of the micrometer-sized $BaWO_4$:Eu phosphors was prepared by dispersing 0.03 g micrometer-sized phosphors in 3 mL water in a 10 mL vial for 10 min.

The crystal structures of the $BaWO_4$:Eu phosphors were confirmed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using Cu Kα radiation. The $BaWO_4$:Eu phosphors were examined using a Raman microscope (RamanRxn Microprobe; Kaiser). The shapes and fine structures of the $BaWO_4$:Eu phosphors were investigated using scanning electron microscopy (SEM, Hitachi S-4300), transmission electron microscopy (TEM, JEOL JEM-3010), and high resolution transmission electron microscopy (HRTEM, FEI Titan Themis^3 300). The photoluminescence properties of the $BaWO_4$:Eu phosphors were examined using a spectrum analyzer (DARSA, PSI). A SMD (surface mount device) type blue LED (NC LED, λ_{max} = 465 nm) with home-made pinhole



Scheme 1. Schematic diagram describing the experimental procedure for the preparing both nanometer-sized hydrophobic and micrometer-sized hydrophilic $BaWO_4$:Eu phosphors.