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Luminescent Eu(III) and Tb(III) activator ions in $La(OH)_3$ and La_2O_3 nanowire matrices

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ABSTRACT

Understanding the role of the host oxide material is very important for developing phosphor materials. Here, Eu(III)- and Tb(III)-doped $La(OH)_3$ nanowires were prepared by a facial hydrothermal method, and Eu(III)- and Tb(III)-doped La_2O_3 nanostructures were obtained by a post-thermal treatment. Their physicochemical characteristics were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and ultraviolet-visible absorption spectroscopy. The photoluminescence (PL) counter mapping profiles were obtained to understand the photoluminescence mechanism. All the emission profiles were assigned based on the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of Eu(III) and the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of Tb(III) ions. The hygroscopic La_2O_3 host is unstable under ambient conditions and changed slowly to more stable $La(OH)_3$. PL decay lifetime was observed be longer for the annealed sample with lower doping concentration due to a higher crystallinity.

1. Introduction

The development of phosphor materials has been pursued actively for modern light display and biomedical applications [1–4]. Activator ions are commonly doped in an oxide host material to obtain enhanced light emitting efficiency. Eu(III) and Tb(III) activator ions are used most widely as red and green phosphor materials, respectively [5–11]. The red and green emissions are generally associated with $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$ transitions, respectively. In a luminescent mechanism, the role of the host material is very important. The host material adsorbs incident light energy and transfers its energy to a doped activator ion, which emits unique photons corresponding to the energy levels of the activator ion [5–11]. Lanthanum (La) hydroxide and oxide exhibit high luminescence efficiency and have been reported to be a good support host material [5–9]. Huang et al. synthesized Tb(III)-doped $La(OH)_3$ nanorods at various pH using a mixture of ammonia and hydrazine hydrate as the alkaline source by a hydrothermal method, and examined the green emission and cathodoluminescence properties [5]. Mendez et al. synthesized Eu(III)-doped La_2O_3 by the post thermal annealing of Eu(III)-doped $La(OH)_3$ and examined its cathodoluminescence. They reported that rapid and longer high temperature annealing was important for minimizing the rehydroxylation of La_2O_3 to form a less efficient $La(OH)_3$ support [6]. Zhang et al. showed that $La(OH)_3$:Ln^{3+} (Ln = Yb/Er, Yb/Tm, Yb/Ho) microrods exhibited efficient up-conversion photoluminescence properties [8]. Dordevic et al. examined the photoluminescence and decay life times as a function of temperature for Eu(III)-doped $La(OH)_3$ and La_2O_3 [9]. They reported that the photoluminescence intensity and lifetime of Eu(III)-doped La_2O_3 had no significant temperature effect compared to those of Eu(III)-doped $La(OH)_3$. La_2O_3 is commonly obtained by the post thermal annealing of $La(OH)_3$, which has been synthesized using hydrothermal and solvothermal methods. The most commonly reported morphologies for $La(OH)_3$ include nanorods, nanowires and nanotubes [12–21].

In this study, $La(OH)_3$ and La_2O_3 was chosen as a host material and Eu(III) and Tb(III) activator ions were used as dopants to investigate the role of the host material and obtain the resulting photoluminescence profiles using a 2D and 3D-photoluminesce contour mapping technique [22–31]. This is the first detailed report of the luminescence properties of Eu(III) and Tb(III) ions doped in $La(OH)_3$ and La_2O_3 matrices and the effects of a change in the crystal phase. A full understanding of the matrix effect to the photoluminescence of an activator ion is crucially important for the development of phosphor materials.

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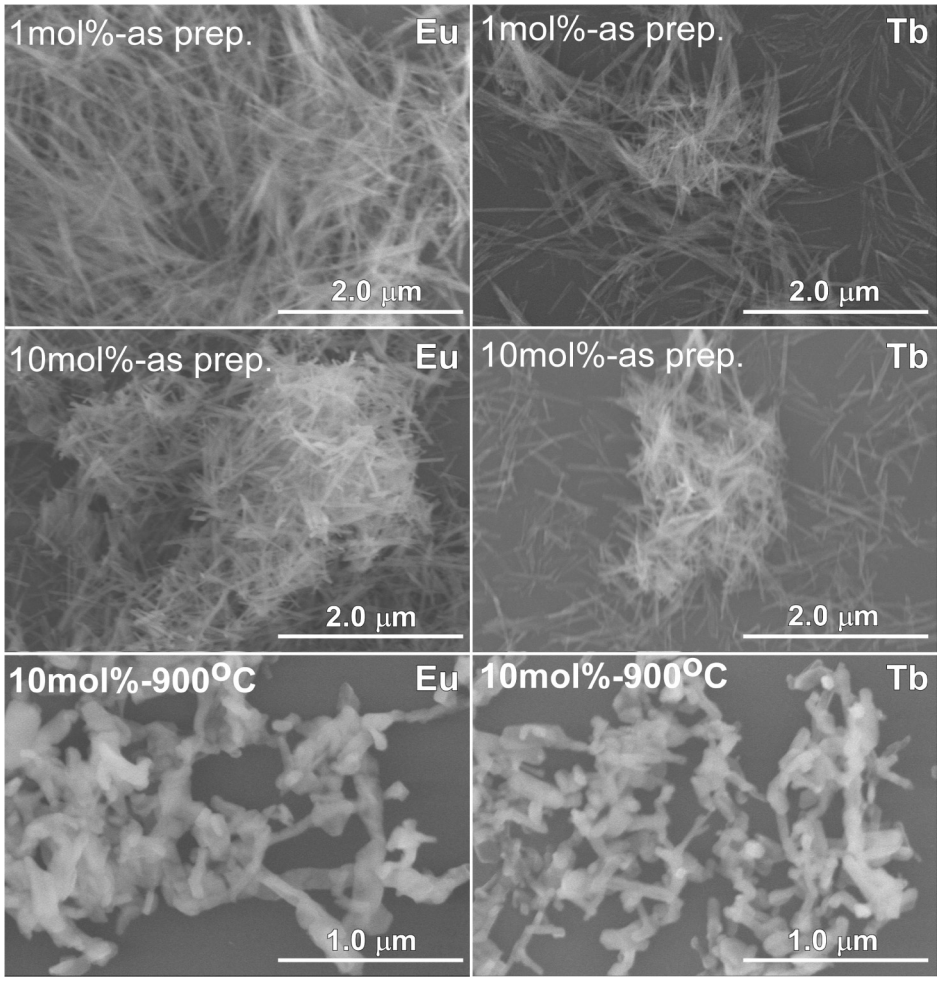

Fig. 1. SEM images of the as-prepared 1 and 10 mol% Eu(III)- and Tb(III)-doped samples and the corresponding 900 °C-annealed 10 mol% Eu(III)- and Tb(III)-doped samples.

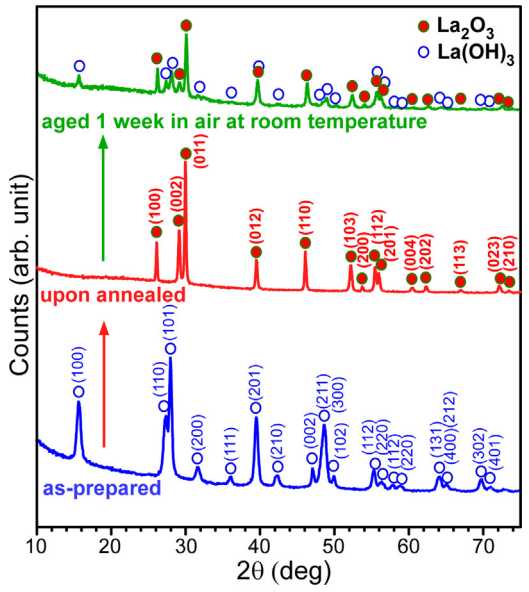

Fig. 2. Typical XRD patterns of the as-prepared, 900 °C-annealed (taken within 4 h upon cooling), and aged (1 week in air at room temperature) doped samples.

2. Experimental

To prepare Eu(III) and Tb(III)-doped $La(OH)_3$ nanowires, 0.1 M aqueous Eu(III), Tb(III), and La(III) solutions were first prepared by dissolving Eu(III) nitrate pentahydrate (Sigma–Aldrich, 99.9%), Tb(III) nitrate pentahydrate (Sigma–Aldrich, 99.9%) and La(III) nitrate hexahydrate (Sigma–Aldrich, 99.9%) in water, respectively. Subsequently, 10.0 mL 0.1 M La(III) nitrate hydrate and 20.0 mL deionized water were mixed, an appropriate amount (1 and 10 mol% ratios of Eu or Tb vs. La) of the 0.1 M Eu(III) or Tb(III) solution was added. After stirring the solution, 1.0 mL of an ammonia (~30%) solution was added to promote precipitation. The solution in a tightly capped Teflon bottle was placed at 120 °C for 12 h. The sample was cooled naturally to room temperature and washed repeatedly with deionized water and ethanol. The centrifuged white power product was dried in an oven (70 °C) for several days. To prepare the Eu(III)- and Tb(III)-doped La_2O_3 samples, the as-prepared samples were thermal-treated at 900 °C for 4 h under ambient air conditions. The surface morphologies of the as-prepared and annealed powder samples were examined by scanning electron microscopy (SEM, Hitachi SE-4800). The microstructure was examined by high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 S-TWIN) at an acceleration voltage of 200 kV. The crystal structure was determined by X-ray diffraction (XRD, PANalytical X'Pert Pro MPD) using Cu Kα radiation (40 kV and 30 mA) with a step size of 0.013°