Preparation and Characterization of Europium-doped Gadolinium Oxide Phosphors Using Oxalate Coprecipitation Method

In Yong Park¹ and Jongwon Lee
Department of Materials Engineering, Hanbat National University, Daejeon 305-719, Korea

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ABSTRACT

To synthesize \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \) phosphor, gadolinium-europium oxalate precursors were prepared from oxalic acid, \( \text{NaOH} \) or aqueous ammonia via coprecipitation method. The obtained precursors were heat-treated and then characterized by XRD, SEM and PL. The kinds and amounts of coprecipitant (\( \text{NaOH} \) or aqueous ammonia) were found to affect the powder morphology and properties of gadolinium-europium oxalate precursors. Two crystalline precursors and one amorphous precursor were synthesized. The nanometer-sized amorphous gadolinium-europium oxalate precursor was first prepared using the oxalate coprecipitation technique. The calcined powders obtained from the amorphous precursor were nearly spherical in shape, and a narrow size distribution was obtained. The \( \text{NaOH} \) coprecipitant was more effective in the preparation of nanometer-sized spherical powders. A thermal decomposition process was conducted for the three kinds of precursors. The photoluminescence property was also measured as a function of europium content, and concentration quenching occurred for samples with europium concentrations of over 10 mol%.

Key words: \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \), \text{Gd-Eu Oxalate}, \text{Phosphor}, \text{Nanoparticle}, \text{Photoluminescence}

1. Introduction

Recent developments in information technology have enabled a market shift in the display business from CRTs (cathode ray tubes) to flat panel displays (FPDs) such as LCDs (liquid crystal displays), PDPs (plasma display panels), FEDs (field emission displays) and ELs (electroluminescent displays).¹ Since these devices use different luminescent mechanisms, the properties and kinds of phosphor materials they use are also different. Accordingly, extensive research and development on those phosphors have been carried out.²⁻⁶

As the representative material for red phosphors, \( \text{Y}_2\text{O}_3: \text{Eu}^{3+} \) is widely used for three-band lamps, CRTs, PDPs, etc.²⁻⁵ \( \text{Gd}_2\text{O}_3 \) has the same cubic crystal structure as \( \text{Y}_2\text{O}_3 \), similar lattice parameters \( (a(\text{Gd}_2\text{O}_3)=1.0813 \text{ nm}, a(\text{Y}_2\text{O}_3)=1.0604 \text{ nm}) \), and a larger ionic radius \( (\text{Y}^{3+} (0.092 \text{ nm}), \text{Gd}^{3+} (0.097 \text{ nm}))) \), which enables easier production of solid solutions with \( \text{Eu}^{3+} (0.098 \text{ nm}) \) in a host phosphor matrix.³ Synthesis of \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \) phosphors showing higher PL intensity than that of commercially available \( \text{Y}_2\text{O}_3: \text{Eu}^{3+} \) was also reported.⁴⁻⁵

Selection of host materials and activators of phosphors for displays should be carried out using criteria based on their respective applications. Precise control over particle size, morphology, crystallinity and surface characteristics is needed for optoelectronic devices made of phosphor powders. Because the narrow size distribution and spherical shape of the powders result in higher packing density, these are the prerequisites for many display applications. Until now, the particle sizes of commercially available phosphor powders have been around a few microns, but smaller sizes, more spherical shapes and narrower particle size distributions are needed for use in high-definition (HD) displays.⁶

Among the many powder preparation methods available, chemical solution techniques have the merits of high purity, fine particle size, and homogeneity at the atomic level. In particular, the coprecipitation method using oxalic acid, which is one of those chemical solution techniques, can achieve higher particle homogeneity and lower firing temperature than solid-state reactions. However, the gadolinium oxalate powders obtained using this method were not spherical and nanometer-sized, but elongated and larger than 1 μm.⁷⁻⁹ Note that Hirai et al. ¹⁰ were able to obtain nano-sized \( \text{Gd}_2\text{O}_3 \) phosphors using the emulsion liquid membrane system with oxalic acid.

In order to synthesize nanometer-sized \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \) phosphor powders, this study evaluated the effects of the amounts and kinds of coprecipitant on the properties of precursors. As a result, three kinds of precursor powders were prepared. To achieve nanometer-sized \( \text{Gd}_2\text{O}_3: \text{Eu}^{3+} \) phosphor powders, the amount of \( \text{NaOH} \) should be controlled. The phase transition processes in the precursor powders were investigated by changing the calcination temperature, and by measuring the PL properties of the calcined powders.
2. Experimental

The starting materials were as follows: Gd(NO$_3$)$_3$·6H$_2$O (Aldrich Co., 99.9%), Eu(NO$_3$)$_3$·5H$_2$O (Aldrich Co., 99.9%) and HOOC-COOH·2H$_2$O (oxalic acid, Aldrich Co., 99%). NaOH and aqueous ammonia of GR grade were chosen as coprecipitants. All reagents were used without further purification.

A mixed aqueous solution of rare earth nitrates was added to either NaOH or aqueous ammonia and oxalic acid aqueous solution at ambient temperature. The effect of the NaOH and the aqueous ammonia addition on the precursor properties was evaluated. The experimental procedure for the coprecipitation technique was as follows. Gd and Eu nitrates were dissolved in distilled water. The total concentration of the cations, [Gd$^{3+}$]+[Eu$^{3+}$], was adjusted to 0.05 M, and the amount of Eu (Eu/[Gd+Eu]) was set to 5 mol%. Oxalic acid and NaOH were dissolved in distilled water in the other beaker. The amount of oxalic acid used was 1.5 times the number of moles of cations. Either NaOH or aqueous ammonia was used to neutralize the total cations and the oxalic acid, i.e., 3 times the number of moles of cations and 2 times the number of moles of oxalic acid. The concentration of alkali in this solution was 0.5 M, and that of the oxalic acid was 0.125 M. The alkali was used 100% in this case and denoted as 1.0NaOH. The mixed aqueous solution of oxalic acid and alkali was stirred using a magnetic stirrer. The other mixed solution of Gd and Eu nitrates was then added dropwise. After the addition of the cation solution, the total solution was stirred for 24 h. Precipitates were washed using water and ethanol to eliminate any remaining nitrates, sodium, etc. After drying at 100°C for 12 h, the oxalate precursor powders were calcined at 1000°C for 2 h.

The formation process of crystalline phases of powders calcined at high temperature was studied by XRD (Rigaku DMAX 2500H) using CuK$_\alpha$ radiation. The microstructure of the powders as a function of calcination temperature was examined by SEM (JEOL JSM-6300). The photoluminescence (PL) properties were investigated for the 300~850 nm range using a spectrometer (Spectron Laser Systems, SL 805G-10).

3. Results and Discussion

Three kinds of gadolinium-europium (denoted as Gd-Eu) oxalate precursors for red Gd$_2$O$_3$:Eu$^{3+}$ phosphor were prepared using a coprecipitation method with oxalic acid. Two compounds among these precursors showed crystalline phases, and the other was an amorphous one comprised of nanometer-sized particles. Physicochemical characterizations were conducted for the three precursor compounds.

In cases where aqueous ammonia was used as a coprecipitant, SEM and XRD results of the precursor are shown in Fig. 1. The supernatant pH was about 9.5. These precursor powders showed flower-like morphology, which corresponds to aggregates of flake-like particles. The diffraction pattern of the precursor powders was different from that of Gd$_2$(C$_2$O$_4$)$_3$·10H$_2$O (JCPDS Card No. 20-0411), and the crystal structure could not be identified.

Fig. 2 shows the SEM micrograph and XRD pattern of the precursor powders using NaOH as a coprecipitant. The used NaOH corresponds to the chemical equivalent of cations and oxalic acid, and the pH of the supernatant was about 12.2. The powder morphology of the Gd-Eu oxalate precursor powders was tens of nanometers of particles, and the XRD pattern showed an amorphous phase.

Hirai et al.\textsuperscript{6-8} have reported the synthesis of Gd-Eu oxalate composite powders from a homogeneous aqueous solution. This method is based on a preparation approach similar to the one used in this study. However, they obtained elongated Gd oxalate powders which were more than 1 µm in size, and neither spherical nor nanometer-sized. They were also able to synthesize spherical or nanometer-sized Gd oxalate using an emulsion liquid membrane system.\textsuperscript{50} After firing at high temperature, spherical and submicrometer-sized powders were fabricated, but showed a large particle...
Narrow particle size distribution and primary particles of about 20 nm can be achieved with a change in the reaction conditions of the emulsion method. From the literature review, an oxalate coprecipitation method from aqueous solutions may not be preferable for the synthesis of spherical nanometer-sized Gd-Eu oxalate precursor powders. However, this study represents that spherical and nanometer-sized particles were easily prepared using NaOH as a coprecipitant for the first time.

The effect of the NaOH amount on the morphology of precursor powders is shown in Fig. 3. As described above, the amount of NaOH used to neutralize all cations and oxalic acid is denoted as 1.0NaOH. Around 1 µm, irregular, tabular and elongated powders were prepared in the case of 0.5NaOH, which corresponded to half the equivalent NaOH (Fig. 3(a)). In the case of 0.6NaOH, (1) irregular, tabular and elongated shaped, (2) flake-like (similar to Fig. 1(a)), (3) plate-like, and (4) nanometer-sized particles were achieved (Fig. 3(b)). 0.7NaOH samples showed a mixture of mostly nanometer-sized fine particles and a small amount of plate-like ones (Fig. 3(c)). Most of the particles prepared with 0.8NaOH were around 20 nm as shown in Fig. 3(d).

Fig. 4 demonstrates XRD patterns of the as-prepared powders with varying NaOH content. The diffraction pattern of the 0.5NaOH sample matched that of Gd(C$_2$O$_4$)$_3$·10H$_2$O (Fig. 4(a)). However, 0.6NaOH powders showed Gd$_2$(C$_2$O$_4$)$_3$·10H$_2$O and unknown peaks around 15°-17°2θ. These unknown peaks were different from those shown in Fig. 1(b). The intensity of Gd$_2$(C$_2$O$_4$)$_3$·10H$_2$O and unknown peaks decreased with an increase in the added NaOH. The XRD pattern showed an almost amorphous phase in the case of...
When the amounts of NaOH were 0.5, 0.6, 0.7 and 0.8 equivalent, the supernatant pHs were 7.6, 8.4, 11.1 and 11.2, respectively. The change in pH between 0.6NaOH and 0.7NaOH was larger than the changes in the others. As shown in Figs. 3 and 4, the powder morphologies and XRD results might change greatly in this pH region. The formation of nanometer-sized particles in the 0.6NaOH sample was much less than those with higher NaOH contents as shown in Fig. 4. On the other hand, the pH change in the supernatant was not that large in over 0.7NaOH, and powder morphology showed mostly nanometer-sized particles. The content of nanometer-sized particles increased as NaOH increased. In order to achieve nanometer-sized particles from the oxalate coprecipitation method, therefore, the amount of NaOH should be used to the chemical equivalent of all cations and oxalic acid. When the supernatant pH was larger than 12, the nanometer-sized particles were easily prepared as can be seen in Fig. 2.

Fig. 5 shows SEM figures of the Gd$_2$O$_3$:Eu$^{3+}$ phosphor powders obtained by calcination of Gd-Eu oxalate particles prepared with (a) the chemical equivalent of aqueous ammonia, (b) the chemical equivalent of NaOH, and (c) half the chemical equivalent of NaOH at 1000°C for 2 h.

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Fig. 5 shows SEM figures of the Gd$_2$O$_3$:Eu$^{3+}$ phosphor powders obtained by calcination of Gd-Eu oxalate particles prepared with (a) the chemical equivalent of aqueous ammonia, 1.0NaOH and 0.5NaOH as the coprecipitants. The precursor powders were calcined at 1000°C for 2h. The XRD results of these oxide phosphors matched the Gd$_2$O$_3$ pattern (JCPDS Card No. 12-0797). When aqueous ammonia was used as a coprecipitant, the powder morphology showed irregular 100 nm-sized fine particles and their aggregates (Fig. 5(a)). In Fig. 5(b), the morphology of the phosphor powders obtained from the amorphous phase (1.0NaOH) showed a similar size of primary particles and pseudospherical shapes. On the other hand, the calcined phosphor powders from a Gd$_2$(C$_2$O$_4$)$_3$·10H$_2$O precursor retained the morphology of as-prepared powders as shown in Fig. 5(c), but hard agglomeration of nanometer-sized particles was found in microstructural analysis. In this experiment, NaOH as a coprecipitant was more effective than aqueous ammonia in synthesizing nanometer-sized Gd$_2$O$_3$:Eu$^{3+}$ red
phosphor powders.

With the use of the Scherrer equation,\(^\text{10}\) the average crystallite sizes calculated from 28.59° 2θ in (222) plane were 55 nm, 72 nm and 66 nm for Gd\(_2\)O\(_3\):Eu\(^{3+}\) phosphor powders in Figs. 5(a), (b) and (c), respectively (Fig. 6). In 500~650 °C, the crystallite sizes were about 20 nm for unknown oxalate and amorphous precursors. The crystallite size of the calcined powders from the Gd\(_2\)(C\(_2\)O\(_4\))\(_3\)·10H\(_2\)O precursor was about 30 nm, which was somewhat larger than the others. As the calcination temperature increased up to 1000 °C, the crystallite sizes increased over 2 times, but still remained at the nanometer scale.

The PL results of the calcined phosphor powders at 1000 °C for 2 h from the precursor using 1.0NaOH are shown in Fig. 7. After the photodetector of the spectrophotometer was set to 610 nm, whose position showed the strongest light emission for Gd\(_2\)O\(_3\):Eu\(^{3+}\) phosphor powders, the excitation spectrum was measured using a xenon lamp. PL excitation experiments were conducted to evaluate the band-to-band transition by the activator within the band gap of Gd\(_2\)O\(_3\). The excitation spectrum agreed well with the results found in the literature.\(^\text{11}\) The strong, large band at around 250 nm was elucidated as the electronic transition from the 2p orbital of O\(^2−\) to the 4f orbital of Eu\(^{3+}\), which was the charge transfer transition. Weak peaks at 330 nm were related to internal Gd\(^{3+}\)-f transitions. The weak peaks above 330 nm originated from the transitions of Eu\(^{3+}\)-f. PL emission was measured using 266 nm of the excitation source with an Nd-YAG laser, and emission wavelengths from the \(^{5}D\_0\rightarrow^{7}F\_n\) (n=0, 1, 2, 3) transition agreed well with the results in the literature.\(^\text{12,13}\)

PL emission results with changing Eu concentration in solution are shown in Fig. 9(b). PL intensities increased as Eu concentration increased up to 10 mol%. And then the PL intensity decreased above 10 mol% of Eu. This decrease in PL intensity is explained as concentration quenching.\(^\text{14}\) Activator Eu concentration in Gd\(_2\)O\(_3\):Eu for the maximum PL intensity was varied in the literature review. Pang et al.\(^\text{15}\) have reported that the maximum intensity obtains at 5 mol% in thin films, and Kim et al.\(^\text{16}\) show the maximum PL value at 14 mol% and 5 mol% for 254 nm and 147 nm excitation sources, respectively. These differences may originate from the preparation conditions of the samples and the measurement conditions of the optical properties.

4. Concluding Remarks

Using an oxalic acid coprecipitation method, three kinds of Gd-Eu oxalate precursors were prepared with varying coprecipitants and their concentrations. When equivalent NaOH was used as a coprecipitant, the pH of the final solution was over 12, and the precursor powders consisted of tens of nanometer-sized spherical particles. After calcination at 1000 °C for 2 h, the powder still remained spherical in shape with particles under 100 nm in size. When under-equivalent NaOH or aqueous ammonia were used as coprecipitants, the particles showed large and irregular shapes. After being calcined at high temperatures, the powders also showed hard agglomeration. For the nanometer-sized Gd\(_2\)O\(_3\):Eu\(^{3+}\) phosphor, the maximum emission intensity at 266 nm excitation was achieved for the 10 mol% of Eu concentration in initial solution. In this study, the nearly spherical and mono-dispersed Gd\(_2\)O\(_3\):Eu\(^{3+}\) phosphor powders were successfully synthesized via a coprecipitation method using oxalic acid and NaOH.

REFERENCES

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