Novel Processing for Softly Agglomerated Luminescent Y₂O₃: Eu³⁺ Nanoparticles Using Polymeric Precursors

Mikrajuddin ABDULLAH,∗∗∗ I. Wuled LENGGORO,∗ Bin XIA∗∗∗ and Kikuo OKUYAMA∗

∗Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima-shi 739-8527
∗∗Department of Physics, Bandung Institute of Technology (ITB), Bandung 40132, Indonesia
∗∗∗Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

ポリマー溶液を用いた蛍光体 Y₂O₃: Eu³⁺ ナノ粒子の新規合成プロセス

Mikrajuddin Abdullah∗∗∗, I. Wuled Lenggoro∗, Bin Xia∗∗∗, 奥山喜久夫∗

∗広島大学工学研究科物質化学システム専攻, 739-8527 広島県東広島市鏡山 1-4-1
∗∗Department of Physics, Bandung Institute of Technology (ITB), Bandung 40132, Indonesia
∗∗∗Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

Synthesis of europium ion doped yttrium oxide (Y₂O₃:Eu³⁺) phosphor nanoparticles using a relatively high molecular weight polyethylene glycol is reported. Y₂O₃:Eu³⁺ materials could be prepared by simply heating in air provided that, water-soluble polymer be added into solutions containing metal nitrates. The polymer was expected to form carbonaceous materials around the produced primary particles to reduce the tendency of those particles to agglomerate. The carbonaceous materials could be removed by heating at higher temperatures, resulting in softly-agglomerated particles in the size range of 20–100 nm. The effect of synthesis parameters on particle morphology, crystallinity, and photoluminescence properties was investigated.

[Received September 14, 2004; Accepted November 26, 2004]

Key-words : Europium, Nanophosphors, Photoluminescence, Polyethylene glycol

1. Introduction

Although research on single nanometer size particles (below 10 nm) have attracted considerably attention, particles in the submicrometer size or sub-100 nm in size continue to be important for current applications. For instance, the pixel in a flat panel displays (FPD), which usually is several tens of micrometers in size can produce high quality pictures, and this pixel can be well developed using submicrometer size particles. In this technology, the most significant point to be explored is a rapid and simple method for producing softly-agglomerated particles in the sub micron down to sub-100 nm in size that give industrially sufficient optical luminescence properties.

Y₂O₃:Eu³⁺ is one of the most important luminescence/phosphor materials for displays and lightings.1,2 Conventionally, a few micrometer sized phosphor particles are prepared via a breakdown route, such as solid-state synthesis. There have been a number attempts to synthesis submicron order or sub-100 nm of Y₂O₃:Eu³⁺ phosphor particles by a variety of methods, including gas phase,3 spray pyrolysis,4,5 and wet-chemical routes.6–9 However, the challenge is to develop a fast method, where the produced fine (sub-micron and sub-100 nm) phosphor particles with highly crystallinity, and emitting a high luminescence intensity.

Another important issue is to develop a novel synthesis, which can produce softly-agglomerated nanometer-sized particles. It is well known that oxidation of organic polymer might form carbonaceous materials at a certain temperature, and this material can be removed by heating at higher temperatures in air. If we can produce nanoparticles which coated by carbonaceous materials, we could expect to obtain small particles because the suppression of agglomeration.

In previous reports, Y₂O₃:Eu³⁺ can be produced by heating their metal salts, typically chlorides or nitrate of yttrium and europium.10 In aqueous solution, metal ions appear as a Lewis acid. To produce carbonaceous material during heating the precursor, organic (polymer) can be added into the solution. There have been a few reports of Y₂O₃:Eu³⁺ preparation by using organic precursor as copolymer or chelating agent, such as N-isopropylacrylamide, 2-acylamido-2-methylpropane sulfonic acid11 ethylene diamine tetra acetic acid,9,11 and glycine.12 These authors proposed novel methodology using the polymerized solutions to control particle size with a diameter down to sub-100 nm. The use of a Pechini-type12 in-situ polymerizable complex method was also demonstrated for preparing sub-10 nm sized Y₂O₃:Eu³⁺.13 The Pechini type method are well known for the preparation of multi-component metal oxides.13 The method includes a combined process of metal complex formation and polymerization of organics. Citric acid14 or malic acid15 is used to form metal complexes, and their polyesterification with a polyhydroxy alcohol such as ethylene glycol forms a polymeric resin (polyester). Then, the post-firing of polymeric resin produces the desired metal oxides particles. However, the control of agglomeration of primary particles (nanoparticles) also became an issue through the polymeric precursor methods.

In order to overcome an agglomeration of the produced particles, these nanoparticles must be well separated each other, i.e., should be occur in a low concentration state, which can be achieved if the metal source and polymer do not undergo phase separation before reaction to occur. Phase separation can be hindered when using polymer that can form complex with metal ions. Since metal ion is a Lewis acid, some polymers can be added as Lewis base in the solution. The potential candidate for this polymer is polyethylene glycol (PEG), rather than the toxic ethylene glycol. We expect, a redox reaction between PEG and metal nitrate at elevated temperatures forms nanoparticles, and the exceed PEG form carbonaceous materials which eventually coat the produced
nanoparticles. The use of PEG with lower molecular weight (2000) for preparing nanocrystalline TiO₂ materials or thin films have been reported by a few groups. ¹⁵,¹⁶

In the present study, the production of a rare-earth ion doped oxide phosphor in a nanometer size will be investigated. The focus of this study was the production of Y₂O₃:Eu³⁺ which is known to emit a red luminescence. The effect of preparation conditions, such as PEG content and processing temperature on the morphology and luminescence of particles will be investigated.

2. Experimental

Y₂O₃:Eu³⁺ samples were produced by dissolving 1.915 g of Y(NO₃)₃, 6H₂O (Kanto Chemicals, purity > 99.99%) and various quantities of Eu(NO₃)₃, 6H₂O (Kanto Chemicals, purity > 99.95%), to produce specified values of Eu/Y mol/mol, in 10 mL of ultra pure water and stirred until a clear solution was obtained. Polyethylene glycol, H_2(EG)nOH, with n = 20000 and EG = OCH₂CH₂ (Wako Pure Chemicals) in various molar fractions: EG/Y = 0.0475 mol/mol, 0.095 mol/mol, and 0.142 mol/mol were added to the solution, followed by heating under stirring at 70°C for 20 min to produce clear viscous precursor solution. The precursor was then heated at 1000°C for 30 min in air, for obtaining the particles of Y₂O₃:Eu³⁺. It is worthy to note that there is no addition of hydroxycarboxylic acid such as citric acid or malic acid to form the metal complexes prior to the polyestification.

X-ray diffraction (XRD) patterns were obtained using a Rigaku Denki RINT2000, and excitation and photoluminescence spectra were obtained using a Shimadzu RF-5300PC spectrophotometer equipped with a Xe source. The phosphor powders were pressed on a cylindrical aluminum holder with a diameter of 4.5 mm and a height of 1.5 mm and formed a flat surface. All samples were pressed at the same pressure. Excitation light from the Xe source is directed to the surface of the sample and the excitation and luminescence spectra are observed in a reflection mode. We assume, only particles that located around the surface have been excited. Scanning electron micrograph (SEM) pictures were obtained using a FE-SEM Hitachi S-5000. Transmission electron micrograph (TEM) pictures were obtained using a TEM JEOL 2010.

3. Results and discussion

FE-SEM pictures, shown in Figs. 1(a)–(c), show the effect of the polymer fraction on particle size. When the polymer was absent, flakes particles above 2 micrometer in size were formed (Fig. 1(a)). A dramatic reduction in particle size occurred when the polymer was added to the precursor. The particle sizes, which were about 50 nm in size and nearly spherical in shape were observed in samples prepared using EG/Y = 0.0475 and 0.095 mol/mol. In addition, an appreciable effect of the polymer fraction on the particle size was observed, i.e., the particle size decreased with polymer content. The use of PEG with low molecular weight (200) or polyvinyl alcohol (PVA) with molecular weight of 10000 instead of PEG (20000) were also attempted. However, using these polymers, it was difficult to find the product particles with the condition of non- or soft-agglomerate.

The presence of large particles prepared without polymer can be explained briefly as following. When heating the precursor solution, water evaporates and solution becomes concentrated. When the concentration of the precursor, i.e., nitrate salt, exceeds its solubility in water at heating temperature, it precipitates out from the solution as a hydrated salt, (around 120°C for Y(NO₃)₃, 6H₂O, it melts and form liquid continuum that contain a high population density of the precursor molecules. Therefore, metal oxide particles are formed in close contact with each other when heating temperature is above the decomposition temperature of the precursor. The result is large agglomerates of particles, as shown in Fig. 1(a), and these nanoparticles inside the agglomerates are difficult to separate.

PEG is a Lewis base and can form complex ions with Y³⁺, a Lewis acid, in an aqueous solution. PEG can also be oxidized by strong oxidants such as metal nitrates. When mixing PEG in yttrium nitrate solution, PEG forms complex with Y³⁺ in the precursor solution. After heating at 70°C, the solution forms a viscous and clear solution. Further heating in the furnace causes chemical reaction between the nitrate precursor and PEG. The nitrate oxidizes the PEG, and the process is strongly isothermic with evolution of gases. This redox reaction leads to the formation of metal oxide nanocrystalline (Y₂O₃ and Eu₂O₃). The formation of the mixture of Y³⁺ and Eu³⁺ may also occur before the oxidation. Further calculations at higher temperatures gives rise to solid-state reactions between Y₂O₃ and Eu₂O₃ and forms Y₂O₃·Eu₂O₃ particles. Due to the formation of complex ions in the aqueous solution, the nitrate and PEG do not undergo phase separation before they start to react. A thermal investigation through the TG/DTA analysis of the starting precursors was also attempted, however only the behavior of PEG phase could be detected.

Depending on the amount of PEG, the redox reaction may form carbonaceous materials at certain temperature range coated on metal oxide particles and this can suppress particle agglomeration. These carbonaceous materials are ultimately oxidized and removed by heating at higher temperature in air. Therefore, a precursor containing PEG polymer is significantly different from the non-polymer synthesis process mentioned above, i.e., the particle size is dramatically reduced.

It can also be seen from Figs. 1(b) and (c) that changing the EG/Y slightly reduced the particle size. Adding more PEG in the precursor might intensify the coating of the oxide particles with carbonaceous materials. As a results, the size of oxide particles decreases when increasing PEG content.
Figure 1(d) shows a TEM picture of a sample prepared using EG/Y = 0.0475 mol/mol. The particle sizes are in the range between 20 nm to 100 nm. Facet surfaces are observed indicating that the particles are crystalline materials. This was also confirmed by the XRD data in Fig. 2. There is a trend for the crystallinity to decrease with increasing amounts of polymer. The products prepared using polymeric precursors showed improvement on the crystallinity rather than the product formed only from nitrate (without polymer). This comparison can be easily seen in the enlarged view of XRD peak at 2θ of around 29°. In Fig. 3, the XRD spectra ranging from 28 to 30.5° are depicted and fitted with the Lorentzian curves. The full width at half maximum (FWHM) for samples prepared without polymer is 2θ = 0.29°, while for samples prepared with polymer at EG/Y = 0.0475 mol/mol, 0.095 mol/mol, and 0.142 mol/mol are 0.22°, 0.27° and 0.24°, respectively. High crystalline materials will have small FWHM. This improvement on the crystallinity was caused by the presence of polymer during synthesis. Depending on the amount, the polymer may be burnt and cause high temperatures for a short period, which can assist crystallization of Y₂O₃:Eu.

The PL spectra of samples excited using a wavelength of 254 nm are displayed in Fig. 4, showing an intense 5D₀ → 7F₂ transition peak at 612 nm. The luminescence of the commercial powder (the best commercial Y₂O₃:Eu⁺⁺ of Kasei Optonix) is also shown as a comparison (spectrum (d)). The intensity of the 612 nm peak initially increased with increasing EG/Y (peaking at EG/Y = 0.0475 mol/mol) and then decreased with further increases in EG/Y. The luminescence intensity of the sample prepared using EG/Y = 0.0475 mol/mol was around 66% that of the commercial powder, as shown in Fig. 4(a). This value is considerably higher than that of submicron phosphor prepared by the spray pyrolysis of metal nitrate precursors, even though spray pyrolysis operated at higher temperatures (above 1400°C) and produced particles of larger sizes (in sub-micrometer). Most of the previous literatures on the synthesis of Y₂O₃:Eu⁺⁺ particles do not provide the comparison with the commercial phosphor.

The effect of dopant (Eu ion) concentration on the PL intensity was also investigated, as shown in the inset of Fig. 4. Initially, the PL intensity increased with increasing Eu/Y and then decreased. Fitting the data to a quadratic curve, one obtains the highest intensity when Eu/Y = 0.07 mol/mol. This value is close to the phosphor particles prepared by other methods, e.g. spray pyrolysis, which has the peak at Eu/Y = 0.06 mol/mol. A reduction in the intensity when Eu/Y > 0.07 mol/mol might be understood in terms of concentration quenching.⁴
The proposed synthesis method is promising for other phosphors. Using such a simple method (the total time used to produce final powder is around 1 h), it is possible to produce samples with properties that are comparable to the commercial phosphors. Continuous processing, which involves relatively few steps (batch for mixing polymer and metal nitrate precursors and a heating section) could readily realized. Further investigations of synthesis parameters suitable for the production of samples with properties equal to or even exceeding those of the commercial preparations are currently underway.

4. Conclusion

Nanometer-size Y$_2$O$_3$:Eu$^{3+}$ particles (in sub-100 nm), emitting a high luminescence intensity with good crystallinity were synthesized by adding a high molecular weigh polyethylene glycol to a solution of yttrium nitrate. The length of the entire process was as short as one hour or less, and scaling up for industrial application is readily feasible. The method can be used to produce various types of oxide based luminescent nanoparticles.

Acknowledgment We thank Mr. Takanori Nakayu for assistantship and Dr. Naoto Kijima for providing the commercial phosphor. Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship for M.A. is gratefully acknowledged. This work was supported by the NEDO's Nanotechnology Particle Project based on fund provided by the Ministry of Economy, Trade, and Industry, Japan, and the Ministry of Education, Culture, Sports, Science and Technology, through JSPS' Grant-in-Aid for Young Scientists (I. W. L.) and Grant-in-Aid for Scientific Research (K. O., I. W. L.).

References