Nano-sized Gd_2O_3:Eu phosphor particles of high brightness

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Abstract

To synthesize Gd_2O_3:Eu phosphor powder of nano size and high luminescence efficiency under UV (ultraviolet) and VUV (vacuum ultraviolet) light, organic additives such as citric acid and ethylene glycol and Na_2CO_3 flux were introduced in large-scale spray pyrolysis and critical conditions for forming nano-sized particles were investigated. The Gd_2O_3:Eu phosphor particles prepared from solutions with organic additives such as citric acid and ethylene glycol had micron size and spherical shape. However, the particles prepared from polymeric precursor solution with Na_2CO_3 flux had nano size and non-aggregation characteristics. The as-prepared spherical particles with micron size turned into nano-sized particles during post-treatment by re-crystallization process. The nano-sized Gd_2O_3:Eu phosphor particles showed higher brightness than the commercial Y_2O_3:Eu phosphor product under both UV light of 254nm and VUV light of 147 nm.

1. Introduction

For the high-resolution displays like plasma display panel (PDP) and field emission display (FED), phosphor dots (pixels) as small as 100 μm are commercialized. Such a fine dot naturally requires a small particle of less than 3 μm in diameter. Small particle phosphors are also useful in projection tubes because screen thickness directly determines the luminescence spot size and subsequent projected images. The luminescence performance of phosphors in plasma display panel (PDP) is governed by the absorption of the vacuum ultraviolet (VUV) light as well as the luminescence efficiency of phosphor material. It has been recently reported that the penetration depth of VUV radiation for phosphor material is in the range of the sub-micrometers. This suggests that small-sized phosphor materials are to be more effective for PDP applications. Moreover, a new phosphor printing technique such as ink-jet substituting for the screen printing technique must be applied to obtain the homogeneous phosphor screen inside the complicated cell structure, in which the use of phosphor particles with fine size and spherical shape is inevitable. It has been predicted that the optimum phosphor characteristics can be obtained with particle size on the order of sub-micrometer. However, contrary to this prediction, the small particles less than 1 μm have shown poor luminescence efficiency. This is due to the particle synthetic process. In the conventional solid-state reaction method, the repeating milling process for obtaining the small particles causes many surface defects, which is the main reason that the small particles prepared from the conventional method show inefficient photoluminescence (PL) properties. In the liquid phase reaction method, nano-sized phosphor particles can be obtained. However, annealing process for obtaining the highly efficient phosphor particles increases particle size and causes aggregation among particles. Therefore, it is necessary to develop a new synthetic method that allows one to prepare small size and efficient phosphor particles. In the present work, we introduced a modified spray pyrolysis using the solution of flux material and organic additives such as citric acid and ethylene glycol to produce the Gd_2O_3:Eu phosphor particles of nano size, non-aggregation, and high brightness under UV and VUV light and investigated the optimum preparation conditions for the formation of fine and highly efficient Gd_2O_3:Eu phosphor.

2. Experimental

Gd_2O_3:Eu phosphor particles are manufactured using large-scale ultrasonic spray pyrolysis process, details of which are described elsewhere. Large-scale spray pyrolysis equipment consists of 6 ultrasonic spray generators with 1.7MHz, a tubular quartz reactor with 1200 mm length and 50 mm ID, and a bag filter. The solution (or suspension) of salts was atomized with ultrasonic spray generators and introduced into a hot reaction column, where the droplets were dried,

decomposed, and/or crystallized in dispersed phase. The prepared particles are collected with a bag filter. The spraying solutions were obtained by adding gadolinium and europium nitrate salts into the double distilled water. The overall solution concentration was 1.0M. The europium doping concentration (x) of $Gd_{2-x}O_3:Eu_x$ was fixed at x=0.25. Organic additives such as citric acid (CA) and ethylene glycol (EG) were added into the spray solution to control the morphologies of phosphor particles in the large-scale spray pyrolysis. Sodium carbonate as a flux material was added to control the size and morphologies of Gd_2O_3:Eu phosphor particles and to improve the photoluminescence intensities. The content of sodium carbonate was varied from 0wt.% to 7wt.% of Gd_2O_3:Eu phosphor particles. The reactor temperature was maintained at 900°C. The corresponding residence time of particles within the tubular reactor was calculated as 0.6 s, when the flow rate of carrier gas was 45 L/min. The manufactured particles were annealed in the box furnace for 3 h to allow crystallization and activation of the europium dopant. The annealing temperature was varied from 1050 to 1200°C to investigate the influence of posttreatment temperature on the size, morphology, and luminescence characteristics of phosphor particles. The crystallinities and morphologies of the synthesized particles were characterized with X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Photoluminescence measurement was performed with spectrophotometer using a Xe lamp excitation source.

3. Results and Discussions

Fig. 1 exhibits the SEM photographs of the Gd_2O_3:Eu phosphor particles prepared from aqueous solutions containing various additives, in which all the samples were prepared at 900°C and post-treated at 1050°C for 3 h. The additive type in spray pyrolysis strongly affected the morphologies of the final particles.

The particles (Fig. 1 (a)) prepared from aqueous solution with nitrate precursors showed a fragmented structure. The hollow structure originated from the rapid drying and precipitation rates of salts on the surface of the droplet did not maintain its sphericity during annealing process for further crystallization and activation of dopant.

The addition of only Na_2CO_3 flux material did not change the morphological characteristics of Gd_2O_3:Eu particles but smoothening surface of the samples. However, the addition of polymeric precursors formed the spherical and filled structured particles with micron size even under the severe preparation conditions as shown in Fig. 1(b). When a droplet is passing a hot reactor, CA and EG dispersed in the droplet form the viscous gel (composed of three-dimensional polymeric network uniformly trapping metal nitrate salts within the droplet) by the esterification reaction. This viscous gel retards the precipitation rate of metal salts and leads to the volume precipitation of metal salts throughout the droplet. Thus, the as-prepared particles from solution containing only CA and EG had a micron size, completely spherical shape, and filled morphology even under the severe preparation conditions.

The addition of Na_2CO_3 flux material in the polymeric precursor-added solution totally changed the mean particle size and morphologies of Gd_2O_3:Eu phosphor particles. The particles (Fig. 1(c)) prepared from solution with polymeric precursors such as CA and EG and a flux material showed the nano size, spherical-like morphology, clean surface, and non-aggregation characteristics. The as-prepared particles with micron size and spherical shape turned into the nano-sized particles with non-aggregation characteristics during posttreatment by the recrystallization process. At the low annealing temperature, 500°C, the particles preserved their morphological characteristics similar to those prepared from solution with only CA and EG. At 700°C, the primary particles composing the spherical micron particles started to burst into the individual nano-sized particles. The obtained powders consist of micron-sized spherical particles conglomerated by the nano-sized primary particles and some of spherical-like nano particles. At high posttreatment temperature as 9000°C, the nano-sized particles with spherical-like shape characteristics were obtained. During the annealing process at high temperature, the micron-sized spherical particles turned into the nano-sized spherical-like particles by recrystallization process. At 1050°C, the particle showed a distinct nano-sized structure with clean surface and non-aggregation and the particle size was slightly increased in comparison with those posttreated at 1000°C. The mean particle size of the particles measured by laser particle size analyzer was 200 nm. The specific particle formation mechanism is under investigation.

The content of flux material is the critical factor determining the powder characteristics such as the mean particle size, morphology, and aggregated extent of particles. As the added Na_2CO_3 content was increased, the particle size and aggregated extent of particles increased. The particles with below 3wt.% Na_2CO_3 exhibited a non-aggregated and nano-sized structure, while those with above 3wt.% Na_2CO_3

showed a highly aggregated structure with micron size. The excess flux materials caused the growth of particles and aggregation by accelerating contacts among the particles.

The phosphor particles prepared by spray pyrolysis have many defects on the surface and inside of the particles because of their structural peculiarity such as high porosity, which is the main cause to reduce the luminescence characteristics of phosphor particles synthesized by spray pyrolysis. The general roles of flux material in spray pyrolysis are to promote the crystal growth and dopant activation and to eliminate the surface defects. This work demonstrates that the flux can play a role of synthesizing the nano-sized particles in large-scale spray pyrolysis using the solution containing the organic additives.

In Fig. 2, the influence of Na_2CO_3 content on the PL intensities of Gd_2O_3:Eu phosphor was investigated. The as-prepared particles were annealed at 1050°C for 3 h. The synthesized Gd_2O_3:Eu phosphor particles were excited by UV light of 254 nm wavelength. The main emission peak of particles was 611 nm, which corresponded to the red emission. The particles synthesized from the solution containing polymeric precursors exhibited the higher PL intensity than that of particles with no polymeric precursors. The addition of flux material was very effective in enhancing the luminescence characteristics of Gd_2O_3:Eu phosphor particles. As the Na_2CO_3 contents increase, PL intensities of Gd_2O_3:Eu phosphor particles increased. The particles prepared from solution with 7wt.% of Na_2CO_3 showed the significantly improved PL intensity, which corresponds to 133% that of particles with no flux material. This is due to the conventional roles of flux material in spray pyrolysis such as promoting the crystallite growth and eliminating the defects. The particles (Fig. 1(c)) with 1wt.% Na_2CO_3 showing nano size and non-aggregation characteristics exhibited similar PL intensity to that of particles (Fig. 1(b)) with micron size and spherical and filled morphology. The particles with 3wt.% Na_2CO_3 having nano size and non-aggregation characteristics exhibited high PL intensity, which was identical to 109% that of the commercial product. As a consequence, 3wt.% of Na_2CO_3 was chosen as an optimum flux content, at which the phosphor particles had nano size and good PL intensity. This demonstrates that the phosphor particles with nano size and high PL efficiency under UV light can be produced in large quantities by spray pyrolysis.

In conventional particle preparation process to form the nanometer size particles, severe milling process causing surface damage is inevitable. However, in this new process, nano-sized Gd_2O_3:Eu phosphor particles with non-aggregation characteristics were prepared at high post-treatment temperature without milling process.

The PL intensities of nano-sized Gd_2O_3:Eu phosphor particles were optimized by changing the doping concentration of europium, in which as-prepared particles from solutions containing CA, EG and Na_2CO_3 were posttreated at 1050°C for 3 h. The luminescence intensities of Gd_2O_3:Eu phosphor particles were strongly affected by the doping content of Eu. The optimum europium doping concentration (x) showing the maximum brightness of $Gd_{2-x}O_3$:Eu_x phosphor particles under VUV was 0.1, which was lower than that showing the maximum brightness under UV light of 254 nm.

The particle size and morphological characteristics of Gd_2O_3:Eu phosphor particles with 3wt.% of Na_2CO_3 were investigated in terms of the posttreatent temperature. Posttreatment temperature highly affected the powder characteristics of Gd_2O_3Eu phosphor particles as well as Na_2CO_3 content. The mean particle size and aggregation extent of particles increased with posttreatment temperature. At ≤ 1100°C, the nano-sized particles were obtained, while at 1200°C, the particles showed a highly aggregated micron-sized structure.

The effect of post-treatment temperature on the photoluminescence (PL) intensity of nano-sized $Gd_{2-x}O_3$:Eu_x (x=0.1) phosphor particles was investigated. The particles were excited by the vacuum ultraviolet light of 147 nm wavelength. The PL intensities of Gd_2O_3:Eu particles were increased with posttreatment temperature up to 1150°C. At 1050°C, the PL intensity of Gd_2O_3:Eu phosphor particles was significantly enhanced. The posttreated particles at ≥1050°C showed higher PL intensities under VUV light than the commercial Y_2O_3:Eu phosphor particles. The maximum PL intensity obtained at 1150°C was 115% that of the commercial product (Nichia co.), while they showed the aggregated characteristics. This is due to that high posttreatment temperature promoted the crystallite growth and decrease of surface defect during the annealing process. This is supported by XRD spectra.

A modified spray pyrolysis using the solution with polymeric precursors such as citric acid and ethylene glycol and Na_2CO_3 flux material was applied to the preparation of nano-sized Gd_2O_3:Eu phosphor particles with high crystallinity and luminescence efficiency under UV and VUV light. This new method enabled mass production of nano-sized phosphor particles of phase purity and high brightness. Nano-sized Gd_2O_3:Eu phosphor particles can be applied to the development of high efficient displays and lamps.

4. References

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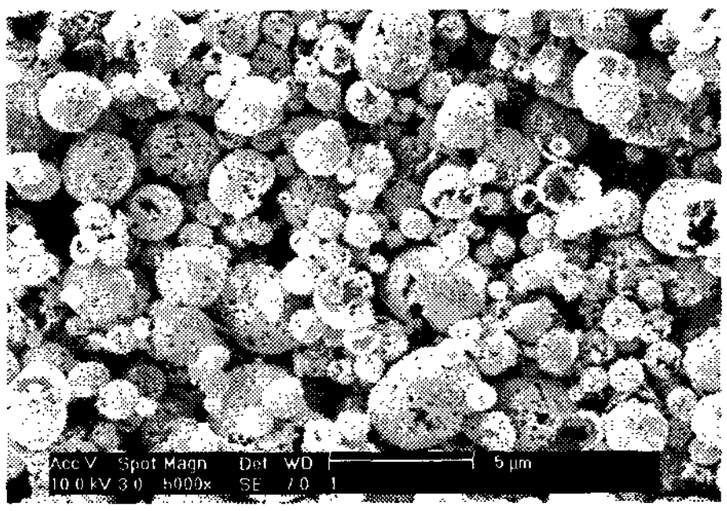
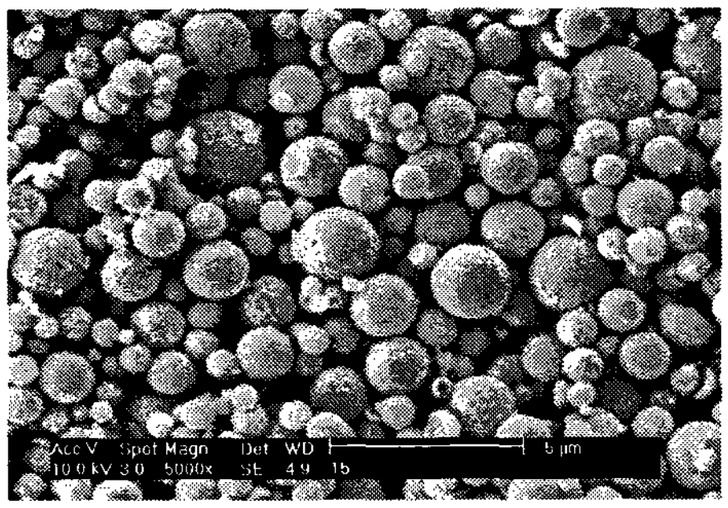
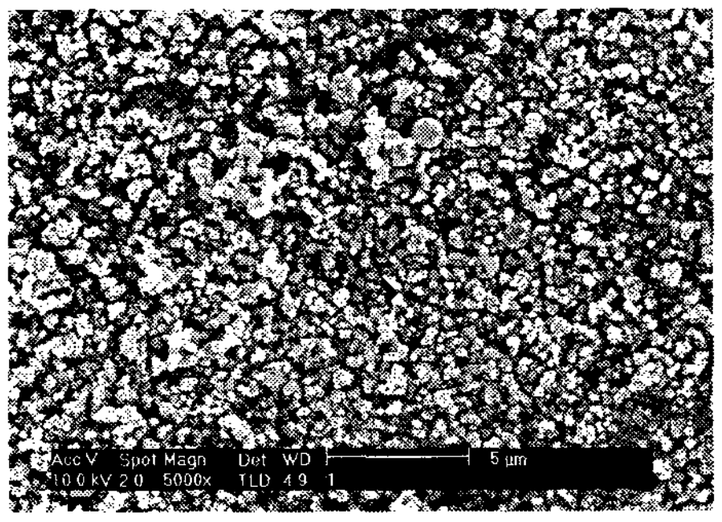


(a) No additives



(b) 0.2M CA + 0.2M EG



(c) 0.2M CA + 0.2M EG, 1wt.% Na_2CO_3

Fig. 1. SEM photographs of Gd_2O_3:Eu particles prepared from solutions with various additives.

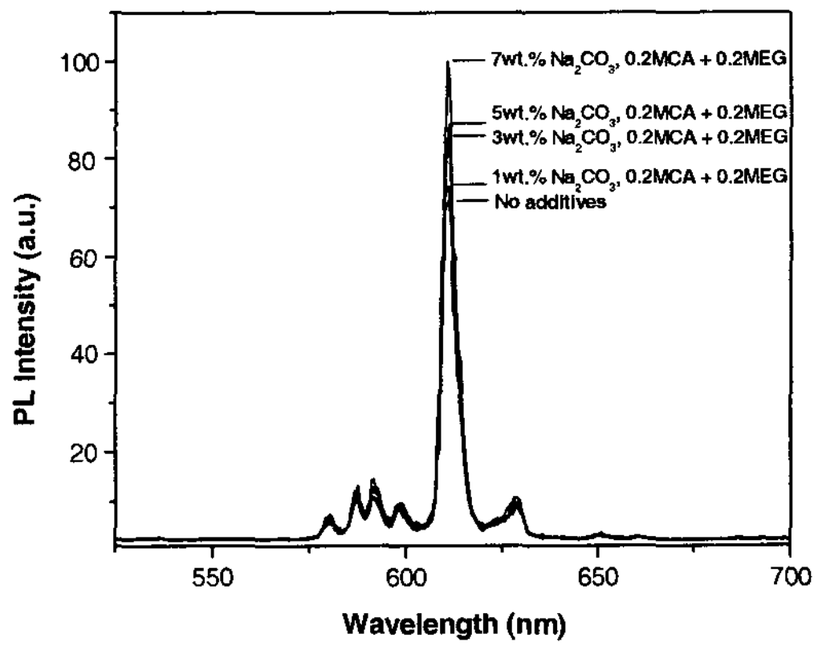


Fig. 2. Photoluminescence spectra of Gd_2O_3:Eu particles with different Na_2CO_3 contents.