Gd_2O_3:Eu phosphor particles with spherical and filled morphology

Hyun Sook Roh[1,2], Yun Chan Kang[2], Hee Dong Park[2], and Seung Bin Park[1]*

[1]Dept. of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon, Korea, 305-701
[2]Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong-gu, Daejeon, Korea 305-600
yckang@krict.re.kr, +82-42-861-4245.

Abstract

Gd_2O_3:Eu phosphor particles were prepared by large-scale ultrasonic spray pyrolysis process. The morphological control of Gd_2O_3:Eu particles in spray pyrolysis was performed by adding polymeric precursors into spray solution containing nitrate salts. The effect of composition and amount of polymeric precursors on the morphology, crystallinity, and photoluminescence characteristics of Gd_2O_3:Eu particles was investigated. The influence of chain length of PEG on the morphology and photoluminescence intensity was investigated. Gd_2O_3:Eu particles prepared from aqueous solution containing no polymeric precursors had a hollow structure and rough surfaces after annealing process. The phosphor particles prepared from solution containing 0.1M CA and 0.1M PEG with high molecular weight as 1,500 had a spherical and filled morphology and the highest photoluminescence intensity, which was 48% higher than that of the Y_2O_3:Eu commercial product.

1. Introduction

Phosphors are required to have good luminescence properties like high luminescence efficiency, suitable emitting colors, and proper decay time. In addition to the luminescence properties, they should have good screening properties to produce phosphor layers with good uniformity, high packing density and proper adhesion strength to the substrate for practical application. The screening properties depend on many factors such as chemical stability, particle size, particle size distribution, surface properties and particle shape.

The characteristics of phosphor particles are strongly affected by synthetic process. The conventional solid-state reaction process has disadvantages in controlling the morphology and maintaining the uniformity in composition of phosphor particles. Therefore, many new processes to overcome these disadvantages are under investigation.

Spray pyrolysis is one of the promising processes for the preparation of the improved phosphor particles with spherical shape, fine size, narrow size distribution, and non-aggregation characteristics because of its particle formation mechanism. However, the hollowness of the particles has been obstacle, because the hollow phosphor particles have bad thermal and mechanical stability. The hollowness also causes the reduction in brightness and long-term stability. The morphology of particles prepared by spray pyrolysis is strongly affected by preparation conditions and type of precursors. The particles prepared under the severe conditions such as high precursors concentration, short residence time of particles within the reactor, and high temperature variation induced by large-size tubular reactor have more hollow and/or porous structure. Thus, a new technique is required to synthesis the spherical powders with solid structure by a large-scale spray pyrolysis.

Kang et al. showed the use of stable colloidal solution as a precursor solution was effective in controlling the morphology of the oxide phosphor particles in spray pyrolysis. Ahonen et al. attempted to control the morphology of particles by using metal alkoxide precursors hydrolyzing to form viscous inorganic polymers, which fill the internal part of the particle and make dense particles. However, alkoxide is rather expensive and hard to handle. Zhang et al. used the organic acid solution as a precursors solution for the preparation of $YBa_2Cu_3O_{7-x}$ superconductor powders and showed the particles prepared from the organic acid solution had a denser morphology than those prepared from nitrate and citrate precursor solutions. Che et al. showed that addition of ammonia into the spraying solution is effective in obtaining solid structure materials by forming ammine complex in the droplet.

Eu-doped Gd_2O_3 phosphor is well known as a good red phosphor for the applications in displays such as plasma display panel(PDP), field emission display (FED), and projection television and fluorescent lamps (FL). In the present work, Eu-doped gadollium oxide particles were prepared by a large-scale spray pyrolysis. The morphological control in spray pyrolysis was performed by adding various polymeric precursors into the spray solution.

2. Experimental

The general flow diagram of the large-scale spray pyrolysis process of the production of ceramic powders is given elsewhere. The solution (or suspension) of salts was atomized with 6 ultrasonic spray generators with a frequency of 1.7MHz. The prepared particles are collected with a bag filter. The spray solutions were obtained by adding nitrate precursors into distilled water. The overall solution concentration was 0.5M. The doping concentration of Eu was fixed at 10 at.% of Gd component. To investigate the effect of polymeric precursors on the morphology, crystallinity, and luminescence characteristics of the particles, polymeric precursors such as citric acid (CA) and ethylene glycol or polyethylene glycol (PEG) were added to spray solutions. PEG with molecular weight of 200, 400, 1500 was used as polymeric precursors.

The addition amounts of CA and EG or PEG were varied from 0.05M to 0.2M. The Gd_2O_3:Eu particles were directly prepared by spray pyrolysis at 900°C. The residence time of particles within a tubular reactor was 0.6 s, when the flow rate of carrier gas was 45L/min. The as-prepared particles were posttreated at 1150°C for 3h for further crystallization and activation of dopant.

The morphology and crystal structures of the particles were studied by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Photo-luminescence measurement was performed with spectrophotometer using a Xe lamp excitation source.

3. Results and Discussions

In the drying stage of spray pyrolysis, a droplet of the starting solution is carried into the reaction tube where it is heated and the solvent begins to vaporize. When the solution is supersaturated, depending on the solubility of salts and the degree of supersaturation, precipitation takes place on the surface of droplet (surface precipitation) or within the whole droplet (volume precipitation) to form a dense structure. In spray pyrolysis, hollow particles are formed when solute concentration gradient is created during evaporation. The solute precipitate first at the more highly supesaturated surface if sufficient time is not available for solute diffusion in the droplet. When the formed crust is impermeable to solvent, the pressure builds within the particles upon further heating and exploded particles fragments can result.

The Gd_2O_3:Eu particles prepared from aqueous solution with no polymeric precursors had a hollow and porous structure. The high drying and precipitation rates of nitrate salts at the surface of droplets caused the empty ball-like morphology. After post-treatment at high temperature, these hollow particles did not preserve their sphericity and were broken into non-spherical fragments due to their thermal instability.

The as-prepared phosphor particles from solution containing EG or PEG as a polymeric precursor had a clean surface and spherical morphology. However, the extent of hollowness of the particles was strongly affected by the chain length of PEG. The particles prepared from EG or PEG (M.W. 200 and 400) had a hollow structure and some were fractured after thermal treatment, while those prepared from solution with only PEG with M.W. 1,500 had a filled morphology. The existence of long chain polymer within the droplet and the increase of viscosity of spray solution by adding the polymer with high molecular weight, 1500 changed the drying and decomposition characteristics of precursor salts. Thus, the obtained particles showed relatively filled structure without fragments by the partial volume precipitation of nitrate salts. These relatively filled-structured particles became inwardly concave spherical structure during heat-treatment at high temperature.

Dissimilar to the particles synthesized from solution containing only an organic precursor with hydroxyl group, the particles prepared from aqueous solutions containing citric acid with carboxyl group (-COOH) and EG or PEG with hydroxyl (-OH) group had a completely spherical morphology, filled structure, and clean surfaces and conserved their sphericity after thermal treatment at high temperature irrespective of chain length of polymeric precursor with hydroxy group such as EG or PEG. The esterification reaction between carboxyl group in CA and hydroxyl group in EG or PEG within droplet forms highly viscous gel consisting of a three-dimensional network of polymer. The viscous gel promoted the volume precipitation by filling inside of the droplet and resulted in the formation of the particles with a spherical shape, filled morphology, and non-aggregation characteristics. Therefore, it can be concluded that the formation of three-dimensional network of polymer and gelation within the droplet are the key factors for the preparation of Gd_2O_3:Eu particles with filled and spherical morphologies.

The effect of addition of polymeric precursors on the crystal structure and crystallinity of Gd_2O_3:Eu particles was investigated. The particles had a pure cubic Gd_2O_3 phase and similar crystallinities irrespective of addition of organic precursors.

The photoluminescence (PL) intensities of particles prepared from solutions containing various polymeric precursors of different molecular weight (chain length) were characterized and compared with that of the Y_2O_3:Eu commercial product. All the phosphor particles were excited by UV light of 254 nm wavelength. The main emission peak of particles was 611 nm, which corresponds to the red emission. The photoluminescence intensity of phosphor particles under 254nm ultraviolet was strongly affected by the addition of polymeric precursor. In case of particles prepared from solution containing only EG or PEG, the longer chain length of added organic precursors (EG or PEG) is, the higher photoluminescence intensities the particles had. This result coincides with the morphological characteristics. The phosphor particles prepared by general spray pyrolysis have lots of defects, which reduce the brightness of phosphor particles, on the surface and/or inside particles because of their porosity and hollowness. The addition of organic precursors enabled the formation of particles with precise structure and improved the photoluminescence intensity of Gd_2O_3:Eu phosphor particles by eliminating defects.

The particles prepared from solution with 0.1M CA and 0.1M PEG (M.W. 1500) had the maximum photoluminescence intensity, which corresponds to 148% that of the Y_2O_3:Eu commercial product. This significant improvement in photoluminescence intensity was owing to the excellent morphological advantages such as spherical shape and filled morphology. The particles prepared by a general spray pyrolysis have lots of surface defects, which is one of causes of the poor brightness of phosphor particles prepared by spray pyrolysis. The introduction of the polymeric precursor highly improved the photoluminescence intensity of Gd_2O_3:Eu phosphor particles by decreasing the surface defect through forming the precise structure such as filled morphology.

4. Conclusions

The Eu-doped gadolinium oxide particles were prepared by a modified spray pyrolysis to improve the morphology and luminescence characteristics of the phosphor particles. The addition of polymeric precursors in spray pyrolysis was significantly effective in improving the morphological characteristics and brightness of Gd_2O_3:Eu phosphor particles. The particles prepared from solution containing proper amounts of polymeric precursors had a spherical and filled structure and sphericity of particles was preserved after thermal treatment. The viscous gel formed from the esterification reaction between CA and EG or PEG retarded the precipitation of nitrate salts and promoted the volume precipitation of droplets.

5. References

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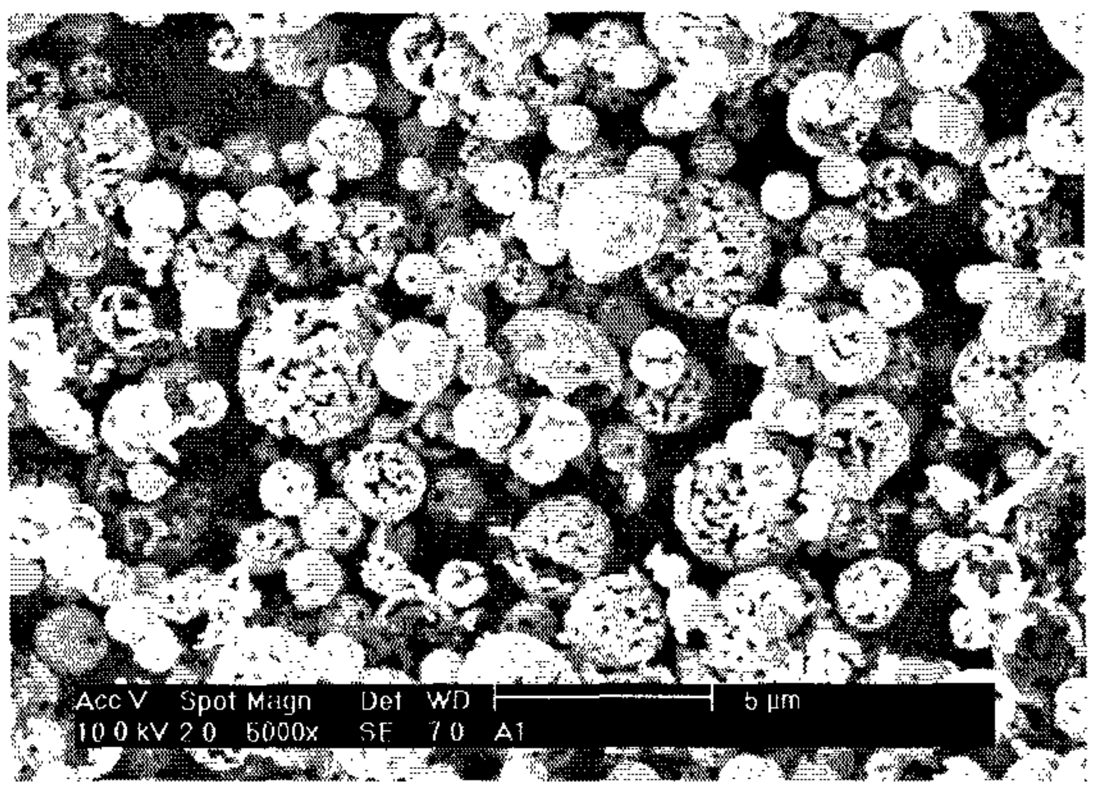
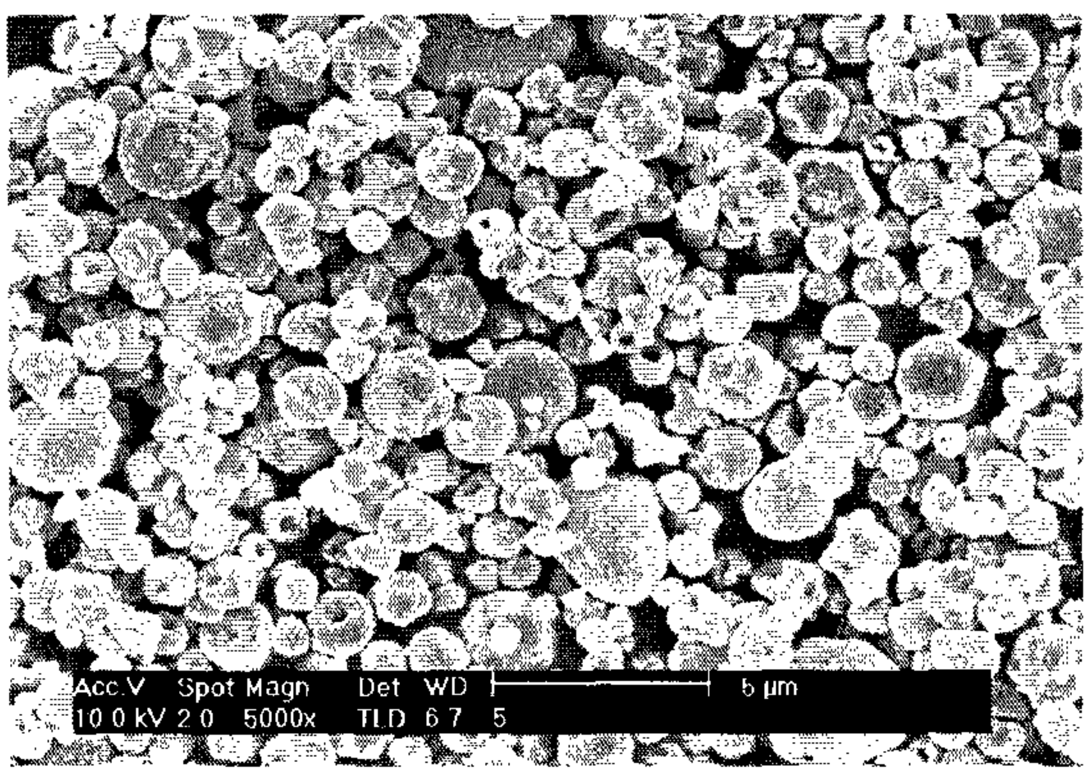
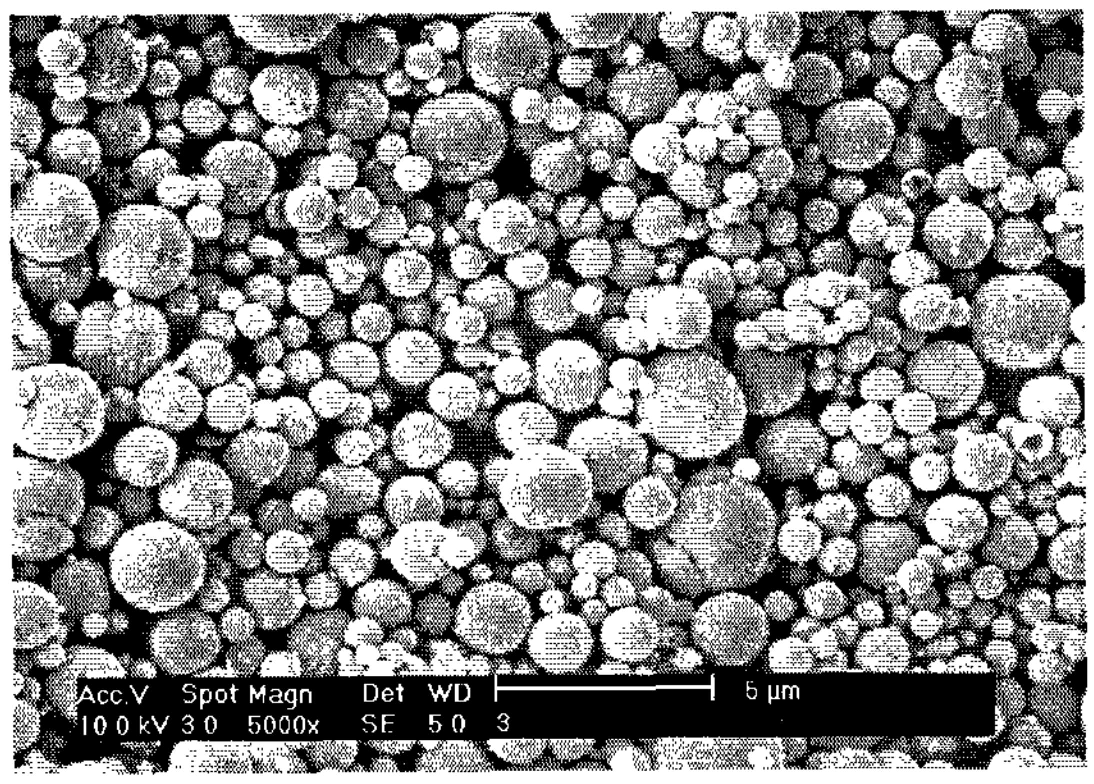


(b) No polymeric precursor



(b) PEG (M.W. 1500)



(c) 0.2M CA + 0.2M PEG (M.W. 200)

Fig. 1. SEM photographs of Gd_2O_3:Eu phosphor particles prepared from solutions containing various polymeric precursors.

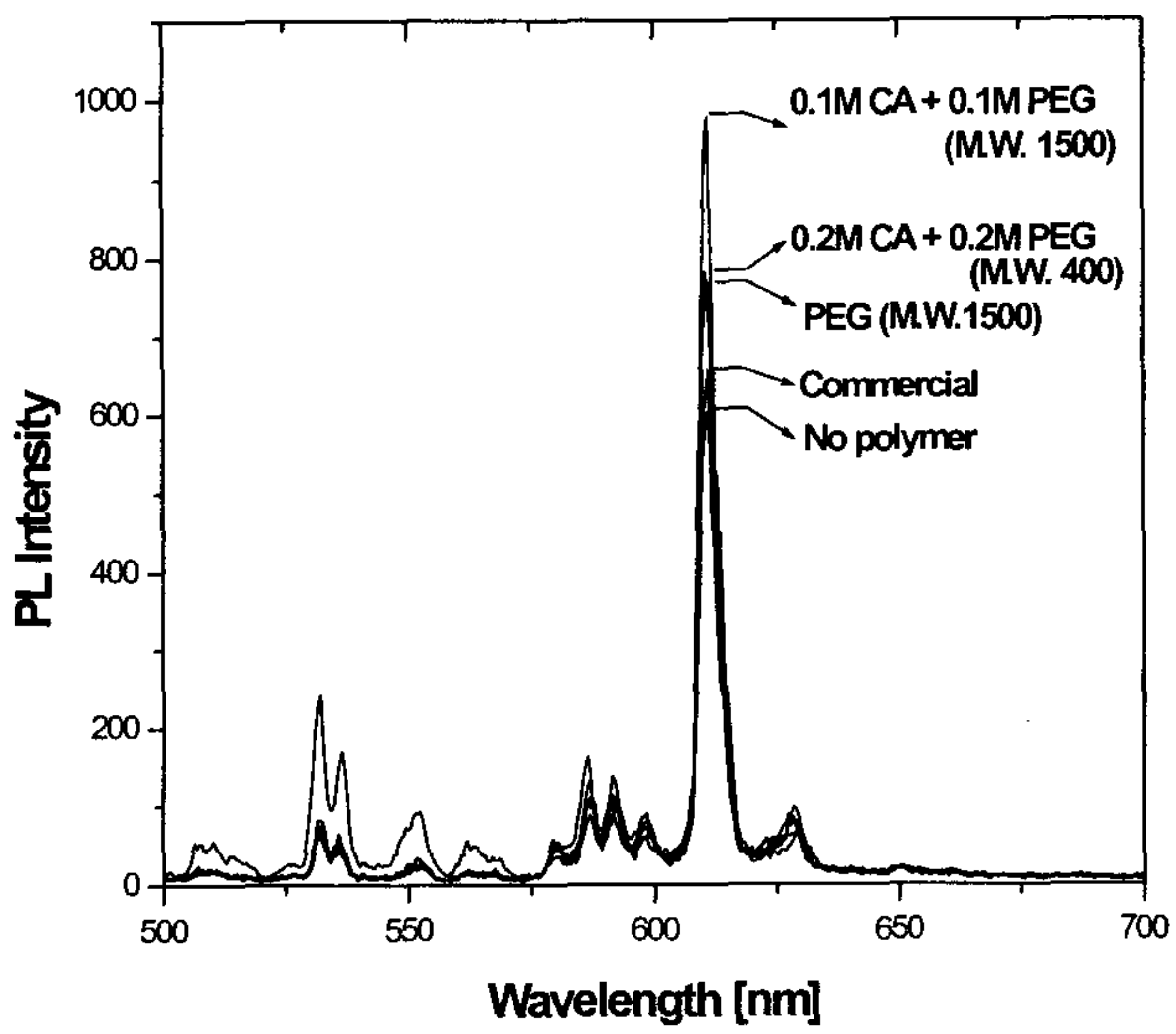


Fig. 2. PL spectra of Gd_2O_3:Eu phosphor particles prepared from solutions containing various polymeric precursors.