The synthesis of green-emitting $GdPO_4$:Tb phosphor particles by the spray pyrolysis for PDP application

Kyo Kwang Lee, Yun Chan Kang*, Kyeong Youl Jung and Hee Dong Park
Advanced Materials Division, Korea Research Institute of Chemical Technology, Yusong-gu, Daejeon, Korea
yckang@krict.re.kr, 82-42-860-7378

Abstract

$GdPO_4$:Tb phosphor particles with spherical shape and high photoluminescence were prepared by spray pyrolysis. The brightness of prepared $GdPO_4$:Tb under the vacuum ultraviolet(VUV) illumination was comparable with that of the commercial Zn_2SiO_4:Mn phosphor particles. The photoluminescence spectra of $GdPO_4$:Tb phosphor particles had maximum peak at 547 nm, and the sharp peaks at 480 nm, 580 nm, and 620 nm. The spherical morphology of prepared $GdPO_4$:Tb particles was completely maintained even after the posttreatment up to 1100 °C. When the posttreatment temperature was over 1100 °C, the particles did not have the spherical shape anymore. The average particle size of $GdPO_4$:Tb phosphor particles prepared by using $(NH_4)_2HPO_4$ was changed from 0.5 to 1.9 μm and its effect on the PL intensity was investigated. It was found that the optimized $GdPO_4$:Tb particles have a good excitation spectrum comparable to that of the commercial Zn_2SiO_4:Mn phosphor particles under the VUV illumination from 140 to 220 nm. We concluded that the $GdPO_4$:Tb phosphor particles with spherical shape prepared by spray pyrolysis is a promising candidate for a green-emitting PDP phosphor.

1. Introduction

The high luminescence efficiency and appropriate decay time of phosphor materials are of importance to optimize the plasma display panels (PDPs). Also, the morphology of phosphor materials greatly affects the performance of PDPs. It has reported that the spherical morphology has many advantages in manufacturing PDP displays with high brightness and resolution. The spherical morphology is appropriate for obtaining a good phosphor layer within the barrier rib of SDR structure by the dot printing technique which is considered as more effective process than the screen printing one. Mn^{2+} doped Zn_2SiO_4 is well known as a good green-emitting phosphor for PDPs. However, this phosphor has a high discharge voltage and a relatively slow decay time. Therefore, it is necessary to search a new candidate replacing Zn_2SiO_4: Mn^{2+} phosphor.

$GdPO_4$:Tb particles have been studied as an alternative green-emitting phosphor[1,2]. Most commercialized phosphor particles have been prepared by the solid-state route which needs flux additives, high reaction temperature, long heating times, and post-milling process to obtain high-purity and small-sized particles[3,4]. As a result, the final obtained phosphor particles have irregular shape and high aggregated structure.

Spray pyrolysis is a promising technique to produce spherical phosphor particles, which have non-aggregated structure, fine size, and narrow size distribution[5]. In the spray pyrolysis, the particle structure and morphology are strongly affected by the preparation conditions such as preparation temperature, concentration of solute, and additives.

In this work, the effect of posttreatment temperature on the brightness of prepared $GdPO_4$:Tb particles was investigated. Also, the particle size of $GdPO_4$:Tb as one of important factors affecting the photoluminescence intensity was also controlled by changing the concentration of spray solution in order to optimize the photoluminescence efficiency of $GdPO_4$:Tb phosphor particles under the VUV excitation. The final goal of this work is to find the optimal condition and see if the $GdPO_4$:Tb particles with spherical morphology is good for PDP phosphor as a green-emitting phosphor.

2. Experimental

An ultrasonic spray generator with six vibrators was used to produce a large number of droplets which are carried into a hot furnace and followed by the drying and thermal decomposition to form particles. The length and inside diameter of cylindrical-shape quartz reactor used were 1200 and 50 mm, respectively. The flow rate of air used as carrier gas was 45 *l*/min, and the residence time of

droplets inside the reactor was 0.6 sec. The reactor temperature was maintained at 900 °C.

Gadolinium nitrate, terbium nitrate, ammonium phosphate ($(NH_4)_2HPO_4$) were used as the precursor of gadolinium, terbium, and phosphorous, respectively. Those precursors were dissolved in distilled water containing small amount of nitric acid to obtain a clear solution. The molar ratio of Tb activator with respect to Gd was kept as 0.17. The overall solution concentration was varied from 0.5M to 3M in order to control the average size of $GdPO_4$:Tb phosphor particles. The as-prepared particles were undergone by the posttreatment at the temperature ranging from 700 to 1200 ℃ for 3 h under air environment.

The crystallinity and morphology of particles were investigated with X-ray diffractometry (XRD) and scanning electron microscopy (SEM), respectively. The photoluminescence characteristics of the prepared particles were measured under vacuum ultraviolet(147nm) by Kr lamp. The average particle size of $GdPO_4$:Tb phosphor particles was measured by the laser particle size analyzer (MICROTRAC S3000).

3. Results and Discussions

Figure 1 shows the XRD patterns of $GdPO_4$:Tb particles prepared by the spray pyrolysis. In general, the as-prepared phosphor particles by spray pyrolysis had no brightness because they have amorphous phase and the high refractory characteristics of multicomponent materials. Therefore, a post calcination process at high temperature, which is lower than those of conventional process, is necessary for the crystallization of mother matrix and the activation of dopants. The as-prepared $GdPO_4$:Tb particles have amorphous phase and turned into the crystalline as the posttreatment temperature increases. The crystallinity of prepared $GdPO_4$:Tb particles was improved further more with increasing the posttreatment temperature up to 1050 °C as shown in Fig. 1. However, the peak intensity around $2\theta=30^\circ$ was reduced at 1200 °C, which indicates the loss of monoclinic phase of $GdPO_4$.

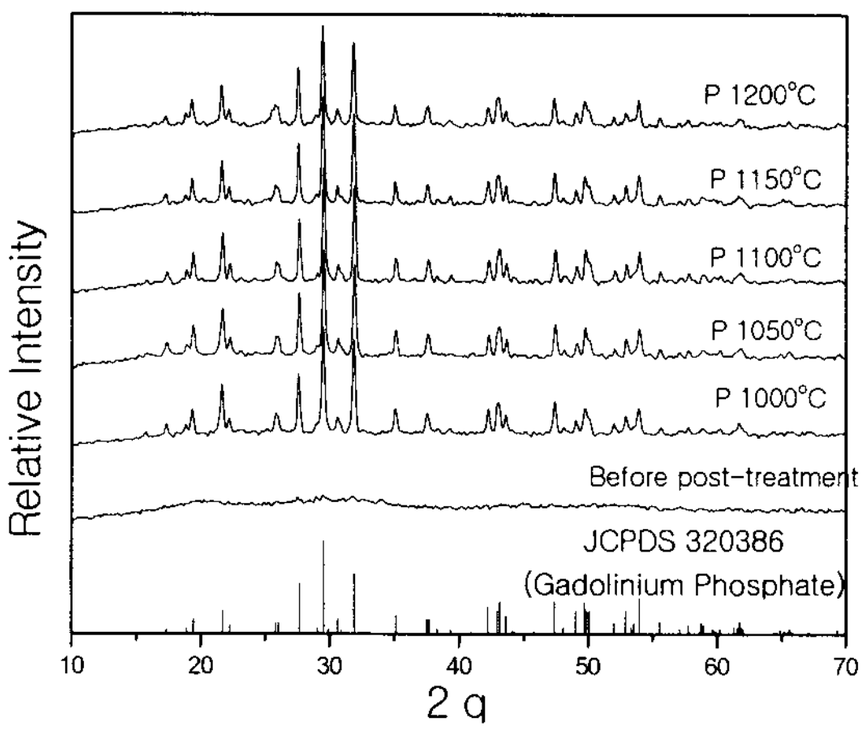


Figure 1. XRD patterns of the prepared $GdPO_4$:Tb particles at several posttreatmen temperatures.

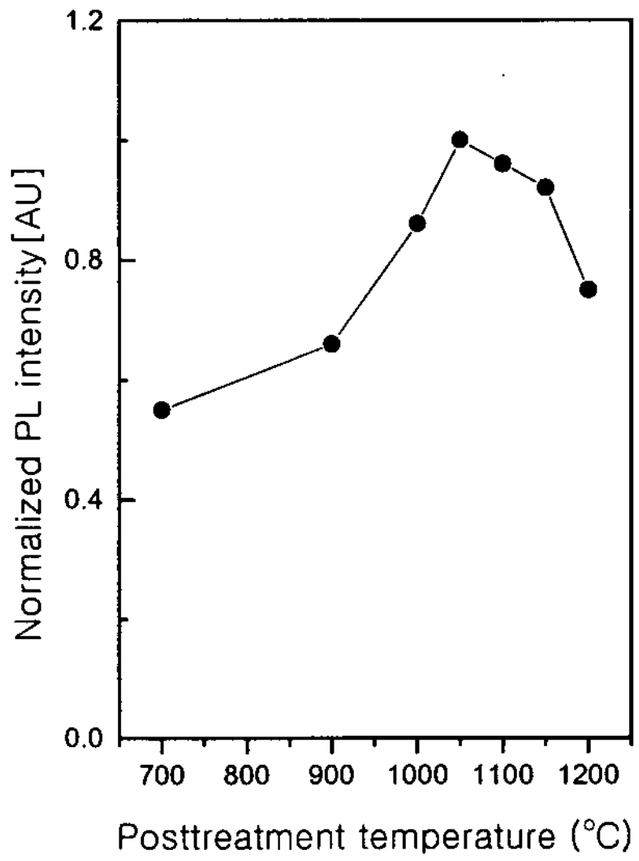


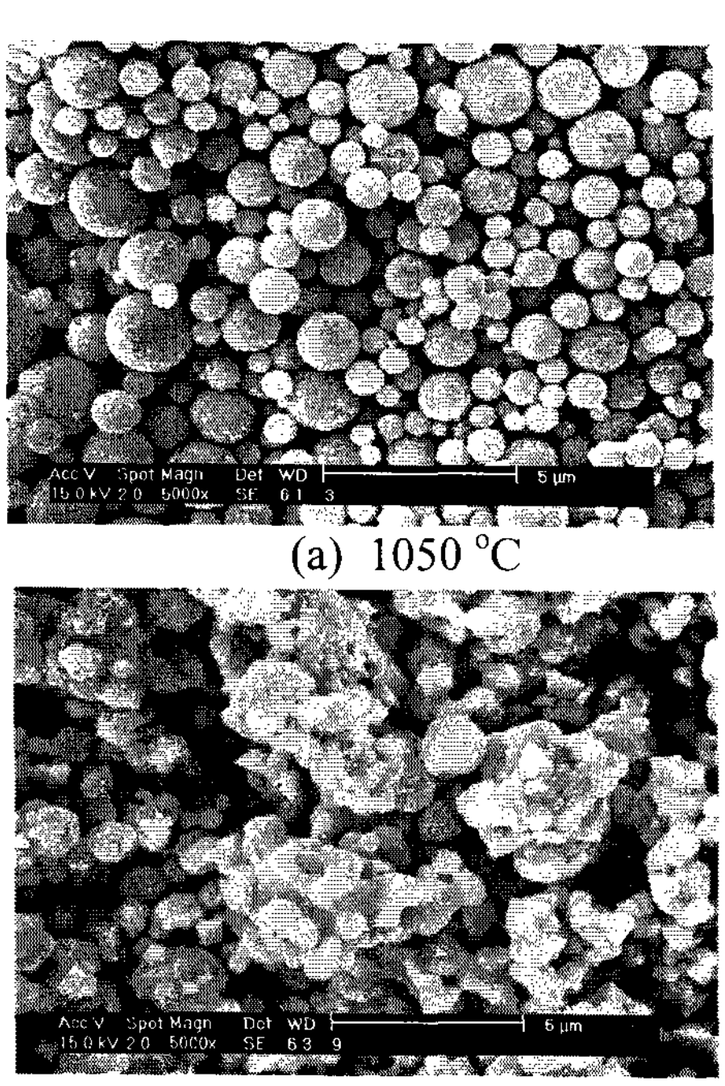
Figure 2. Photoluminescence (PL) intensities a a function of the posttreatment temperature.

Figure 2 shows the effect of the posttreatment temperature on the PL intensity of $GdPO_4$:Tb particles. The maximal PL intensity was obtained when the posttreatment temperarture was 1050 °C. The PL intensities of the $GdPO_4$:Tb phosphor particles prepared by spray pyrolysis were increased by elevating the posttreatment temperature up to 1050 °C because higher heat-treatment temperature produces higher crystallized phosphor particles. As a result, the higher posttreatment leads the reduction of bulk defects which act as a quenching site. When the posttreatment temperature was over 1050 °C, however, the PL intensities of the $GdPO_4$:Tb phosphor particles prepared by spray pyrolysis decreased due to the agglomeration.

Figure 3 shows the SEM photographs of $GdPO_4$:Tb particles posttreated at different temperatures. The particles posttreated at 1050 °C for 3 h had spherical morphology, dense structure, submicron size, narrow size distribution, and non-aggregation characteristics. When the temperature

was 1200 °C, however, a significant aggregation was observed. From this result, it is speculated that the dense structure with keeping a completely spherical shape is helpful for obtaining the high photoluminescence intensity and the high packing density of phosphor in PDP device.

The mean particle size and the size distribution are important factors affecting the brightness of phosphor materials coated as a film type in PDPs.



(a) 1050 °C

(b) 1200 °C

Fig. 3. SEM photographs of $GdPO_4$:Tb particles at different posttreatment temperatures.

Given that the high packing density of phosphor materials is good for the improvement of photoluminescence efficiency, the fine size and narrow size distribution of phosphor materials with spherical shape is necessary to optimize PDP performance. In terms of the high packing density, it seems that smaller particle is better for the improvement of PDP performance. However, the particles smaller than a limit size are not desirable in the view point of the photoluminescence intensity because smaller particles induces more light scattering which reduces the absorbance of phosphor particles for the incident VUV light. So, there exists an optimal particle size to give the best photoluminescence efficiency. Figure 4 shows the effect of the solution concentration on the emission spectra of $GdPO_4$:Tb particles under the illumination of 147 nm VUV. There are four absolute peaks resulted from the transition from $^5D_4$ to ^7F_j[2]. The peak around 536 – 540 nm due to $^5D_4$ $^7F_5$ transition is significantly dependent on the solution concentration. The average particle size of each sample measured by the laser particle size analyzer and PL intensity are shown in Table 1. The average particle size was increased monotonically from 0.5 to 1.9 μm as the overall solution concentration increases from 0.5 to 3.0M. The photoluminescence intensity of $GdPO_4$:Tb phosphor particles prepared by the spray pyrolysis was increased and saturated with increasing the average particle size up to about 1.5 μm. Therefore, it was concluded that the optimal particles size of $GdPO_4$:Tb phosphor particle is about 1.5 μm.

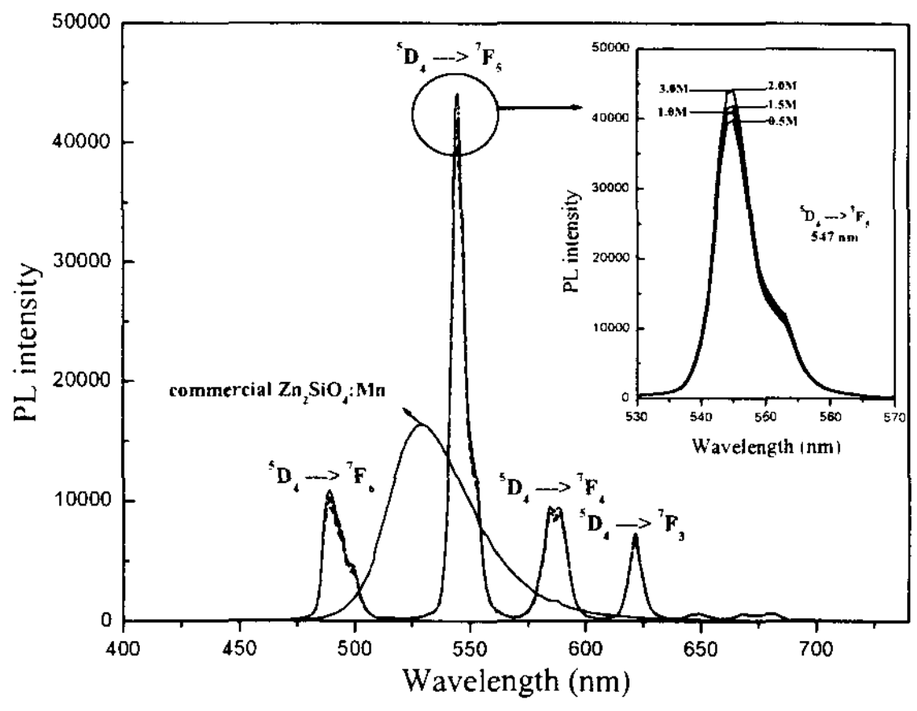


Fig. 4. Emission spectra of $GdPO_4$:Tb particles at different solution concentration.

Table 1. Average particle size size and relative intensity ($^5D_4 \rightarrow {}^7F_5$) for $GdPO_4$:Tb phosphors

Solution concentration	Average particle size	Relative intensity
0.5M	0.5μm	0.89
1.0M	0.8μm	0.91
1.5M	1.4μm	0.94
2.0M	1.5μm	1
3.0M	1.9μm	0.98

The discharge gas used in PDPs is Xe of which a resonance radiation line at 147 nm is used for the excitation of phosphor materials[6,7]. Also, the next most intensive radiation occurs at 173 nm. Therefore, the good PDP phosphor materials should have high photoluminescence efficiency under the VUV excitation of 147 or 173 nm. Figure 5 shows the excitation spectra of $GdPO_4$:Tb particles prepared by the spray pyrolysis and the commercial Zn_2SiO_4:Mn under the illumination of VUV light. The prepared $GdPO_4$:Tb particles with spherical shape have an excitation spectrum as good as the

commercial Zn_2SiO_4:Mn particles at the wavelength from 140 nm to 220 nm. Therefore, it was concluded that $GdPO_4$:Tb particles with spherical shape prepared by the spray pyrolysis is a promising green-emitting phosphor applicable to PDP displays.

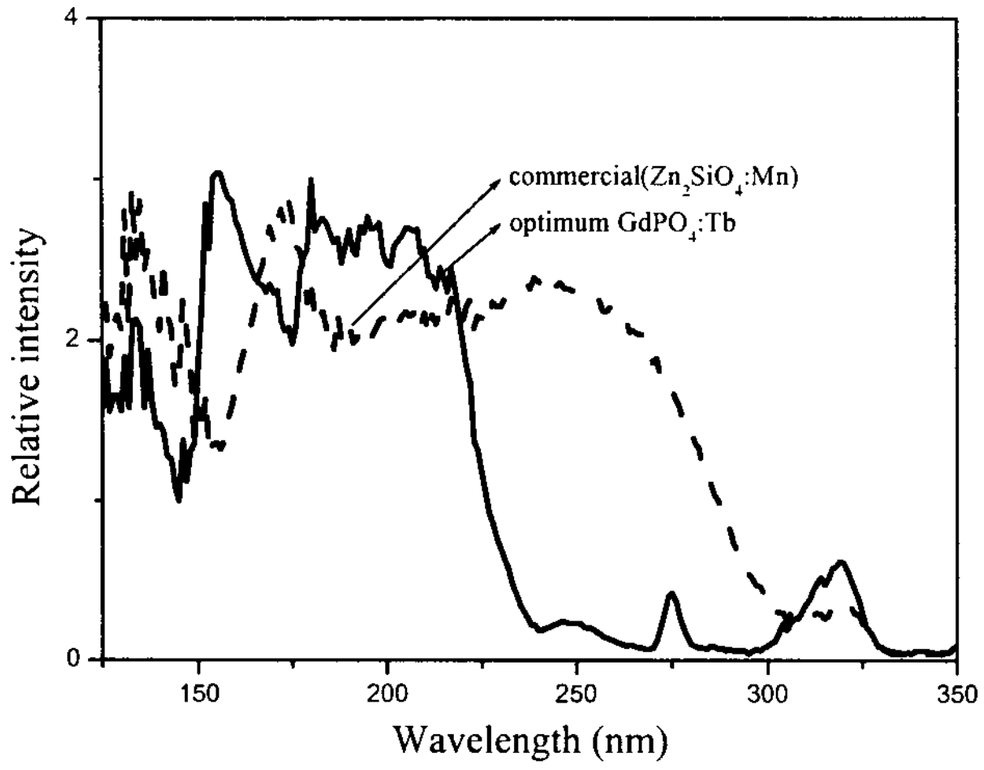


Figure 5. Excitation spectra of commercial Zn_2SiO_4:Mn(dot line) and $GdPO_4$:Tb particle prepared by spray pyrolysis(solid line).

4. Conclusions

Spray pyrolysis was applied to prepare a promising green-emitting $GdPO_4$:Tb particles with spherical shape. The $GdPO_4$:Tb particles prepared by spray pyrolysis had spherical shape, dense structure, and non-aggregation characteristics even after the posttreatment up to 1100 °C. The brightness of prepared $GdPO_4$:Tb particles after the posttreatment at 1050 °C for 3 h was 90 % when compared with that of Zn_2SiO_4:Mn. The highest PL intensity under the vacuum ultraviolet(VUV) excitation was obtained when the average particle size was about 1.5 μm. The optimized $GdPO_4$:Tb particles had good excitation spectrum comparable to that of the commercial Zn_2SiO_4:Mn phosphor particles under the illumination of VUV light at the wavelength between 140 to 220 nm. Therefore, the $GdPO_4$:Tb particles with spherical shape could be used as a green-emitting phosphor for PDP.

5. References

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