

Green-emitting Yttrium Silicate Phosphor Particles Prepared by Large Scale Ultrasonic Spray Pyrolysis

Hee-Sang Kang^{***}, Yun-Chan Kang^{*†}, Hee-Dong Park^{*} and Yong-Gun Shul^{**}

^{*}Advanced Materials Division, Korea Research Institute of Chemical Technology,
P.O. Box 107, Yusong-gu, Daejeon 305-600, Korea

^{**}Department of Chemical Engineering, Yonsei University, 134, Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea

(Received 19 July 2002 • accepted 11 April 2003)

Abstract—Tb doped Y_2SiO_5 phosphor particles with spherical morphology, fine size, high crystallinity and good photoluminescence intensity were prepared by spray pyrolysis. The colloidal solution obtained by adding the fumed silica particles was introduced to control the characteristics of Y_2SiO_5 : Tb phosphor particles. The particles prepared from the colloidal solution had a spherical and filled morphology even after post-treatment. The particles post-treated below 1,200 °C had X1 type crystal structure but the crystal structure changed from X1 to X2 after post-treatment above 1,300 °C. When crystal structure was changed from X1 to X2, the PL intensity greatly increased. The maximum PL intensity of particles, which were prepared from the solution with 120% excess of stoichiometric fumed silica, was about 4 times higher than that of the particles prepared from the stoichiometric solution. The particles prepared from the stoichiometric solution of yttrium nitrate and fumed silica had mixed phases of X1 and X2 type and had impurity as Y_2O_3 . On the other hand, the particles prepared from the solution with 120% excess of stoichiometric fumed silica had high crystallinity of X2 type.

Key words: Phosphor, Spray Pyrolysis, Ceramic, Display

INTRODUCTION

Various types of multicomponent oxide particles have been widely studied for application in displays such as high definition (HD), projection television (PTVs), and flat panel displays (FPDs). These phosphor materials must have narrow size distribution, fine size, non-agglomeration, and spherical morphology for good luminescent characteristics. Therefore, the characteristics of phosphor materials are strongly affected by the synthetic method.

In general, phosphor materials have been mainly prepared by solid-state reactions [Ohno and Abe, 1994; Ravichandran et al., 1997; Chang et al., 1989]. The conventional solid-state reaction method requires a high-temperature process with long processing time, repeated milling processes, adding flux, and washing with chemicals. These mechanical and chemical processes tend to degrade the luminescence properties and produce the irregular shaped particles [Sohn et al., 1999; Lenggoro et al., 2000].

Recently, spray pyrolysis has been recommended as a promising method for producing the phosphor particles of the controlled characteristics of fine size, spherical shape, high purity, and aggregation-free particles. However, the problem of spray pyrolysis is the potential of forming hollow and/or porous particles [Hampden-Smith et al., 2001; Vanheusden et al., 1997; Kang et al., 2000]. The hollowness of phosphor particles causes the reduction of thermal and mechanical stability. Furthermore, it reduces the luminescence intensity of phosphor materials by acting as defects. The morphology of phosphor particles synthesized by spray pyrolysis is highly influenced by the operating conditions such as reactor temperature,

flow rate of carrier gas, precursor type, and precursor solution concentration [Jung and Park, 2001]. The particles prepared by large-scale spray pyrolysis tend to have a further hollow and/or porous structure than that prepared by laboratory-scale spray pyrolysis. Severe conditions such as short residence time, high temperature gradient within the reactor, and high solution concentration promote the formation of hollow-structured particles [Kang et al., 1999; Lim et al., 2002]. To overcome these problems in large-scale spray pyrolysis, a modified spray pyrolysis using the artificial colloidal solution was proposed [Kang and Park, 1999]. The colloidal particles dispersed in the droplet promote the volume precipitation by acting as a nucleation seed for the precipitation.

Yttrium silicate has been known to be good host material for cathodoluminescent phosphors [Kang et al., 1999; Yin et al., 1996; Meiss and Kemmler-Sack, 1991; Shen and Kachru, 1994]. In this work, terbium-doped yttrium silicate phosphors, one of the green phosphor materials, were prepared by large-scale spray pyrolysis. We attempted to control the characteristics of Y_2SiO_5 : Tb phosphor particles by using the artificial colloidal solution as a silicon source in large-scale spray pyrolysis.

EXPERIMENTAL

The general schematic diagram of spray pyrolysis system is given elsewhere [Sohn et al., 2002]. The system has a droplet generator, quartz reactor and particle collector. The apparatus used in this work was an ultrasonic spray generator having six vibrators with 1.7 MHz. The length and inside diameter of the quartz reactor were 1,200 and 50 mm, respectively. The flow rate of air used as a carrier gas was 45 L/min, and the residence time of the particles inside the reactor was 0.6 sec. The colloidal solution was obtained by adding fumed

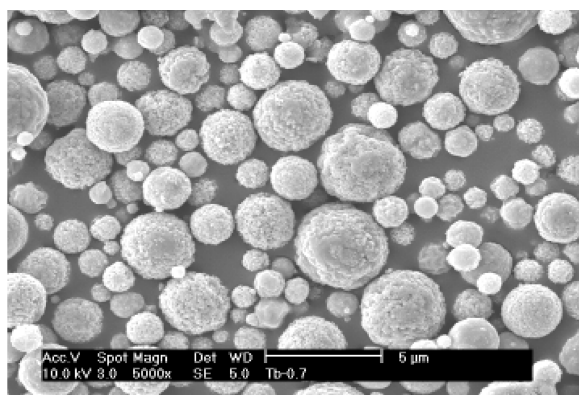
[†]To whom correspondence should be addressed.

E-mail: yckang@kricr.re.kr

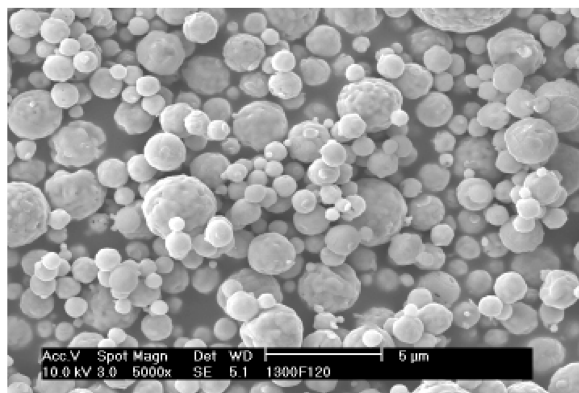
silica particles with size of 14 nm into the aqueous solution dissolved with nitrate salts of other components. The total concentration was 1 M and the doping concentration of terbium was fixed at 35 mol% of yttrium component. The particles were as-prepared at 900 °C by spray pyrolysis. The post-treatment temperature was changed from 1,000 °C to 1,400 °C. The photoluminescence characteristics of prepared particles were measured under ultraviolet (254 nm) by spectrofluorometer (Perkin Elmer LS50). The crystallinity and morphology of particles were investigated with X-ray diffractometry (XRD, RIGAKU DMAX-33 X-ray) and scanning electron microscopy (SEM, PHILIPS XL 30S FEG), respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the morphologies of as-prepared and post-treated $Y_2SiO_5 : Tb$ phosphor particles synthesized by a modified large-scale spray pyrolysis using fumed silica particles as a silicon source. The as-prepared particles had completely spherical shape, fine particle size, and non-hollow morphology even at severe preparation conditions. This is due to the particle formation mechanism of particles prepared from the colloidal solution. The fumed silica colloidal particles dispersed in the droplet induced volume precipitation by acting as a nucleation seed for the precipitation. Thus the as-prepared particles had filled and porous morphology. These filled particles prepared from the colloidal solution maintained their sphericity and non-aggregation characteristics even after post-treatment at



(a) $Y_2SiO_5 : Tb$ particles prepared from fumed silica before post-treatment.



(b) Post-treated $Y_2SiO_5 : Tb$ particles prepared from fumed silica.

Fig. 1. SEM photographs of $Y_2SiO_5 : Tb$ particles before and after treatment.

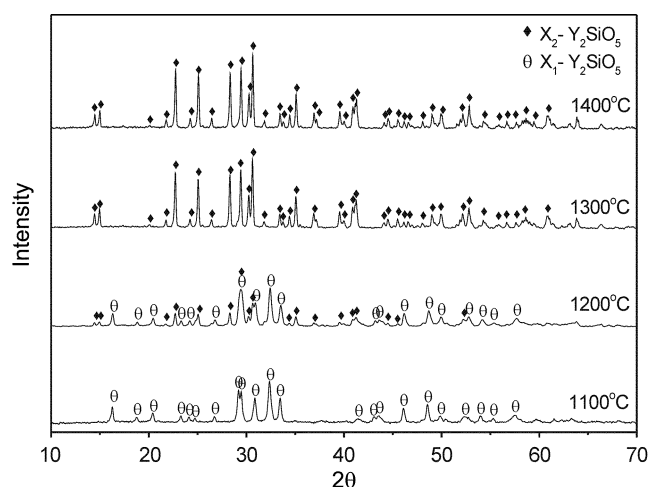


Fig. 2. XRD spectra of $Y_2SiO_5 : Tb$ particles annealed at different temperatures.

1,300 °C as shown in Fig. 1(b). The porous morphology of as-prepared particles turned into dense structure after post-treatment.

The luminescence characteristics of phosphor are strongly affected by the phase purity and crystallinity of particles. The effect of post-treatment temperature on the crystal structure of prepared particles is shown in Fig. 2. In this case, the $Y_2SiO_5 : Tb$ phosphor particles were prepared from the solution with 110% excess of stoichiometric fumed silica. $Y_2SiO_5 : Tb$ is polymorphic and crystallizes in the monoclinic X1 or X2 type determined by the synthetic temperature. The $Y_2SiO_5 : Tb$ phosphor particles post-treated at 1,100 °C had phase-pure crystal structure of X1 type. The crystal structure of X2 type appeared after post-treatment at 1,200 °C, and the $Y_2SiO_5 : Tb$ phosphor particles with complete X2 type structure was obtained above 1,300 °C. In the spray pyrolysis, the high mixing degree of each component inside particle reduced the formation temperature of phase-pure and high crystallinity $Y_2SiO_5 : Tb$ phosphor particles.

The emission spectra of $Y_2SiO_5 : Tb$ phosphor particles prepared from colloidal solutions at different post-treatment temperatures were shown in Fig. 3. The luminescence characteristics of prepared phos-

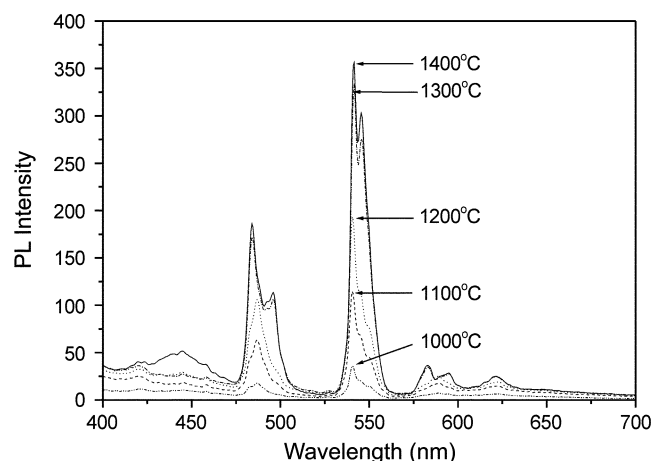


Fig. 3. Emission spectra of $Y_2SiO_5 : Tb$ particles annealed at different temperatures.

phor particles were affected by the post-treatment temperatures. The PL intensity of phosphor particles increased with increasing post-treatment temperatures because of high crystallinity and phase purity of phosphor particles post-treated at high temperatures. In Fig. 2

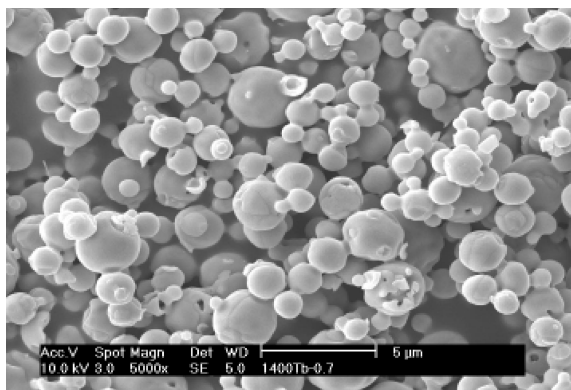


Fig. 4. SEM photograph of Y_2SiO_5 :Tb particles prepared from fumed silica annealed at 1,400 °C for 3 h.

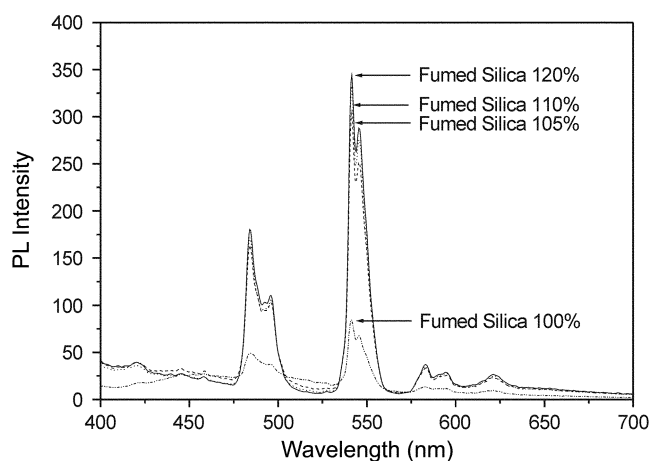


Fig. 5. Emission spectra of Y_2SiO_5 :Tb particles prepared from different ratios of yttrium nitrate and fumed silica.

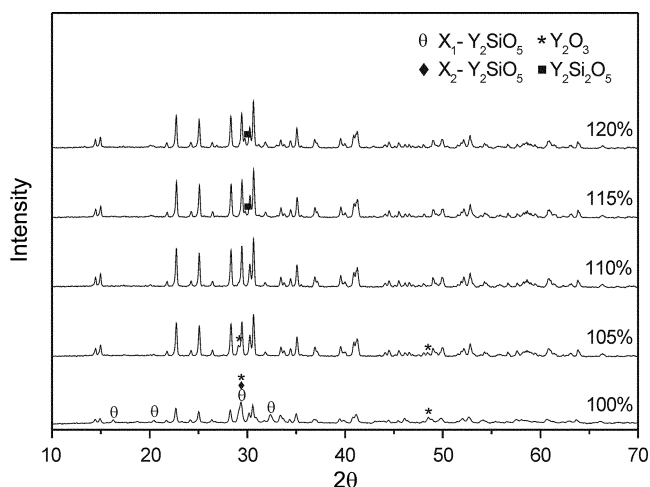
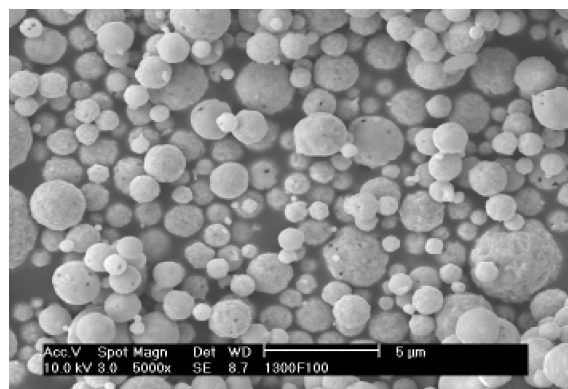


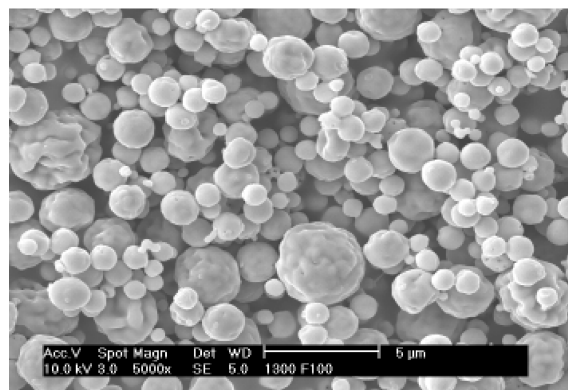
Fig. 6. XRD spectra of Y_2SiO_5 :Tb particles prepared from different ratios of yttrium nitrate and fumed silica.

and Fig. 3, the Y_2SiO_5 :Tb phosphor particles with complete X2 type crystal structure had higher PL intensities than those with X1 type crystal structure. The Y_2SiO_5 :Tb phosphor particles obtained at 1,400 °C had a maximum brightness. However, aggregation between particles occurred at 1,400 °C as shown in Fig. 4. The PL intensity of spherical shape Y_2SiO_5 :Tb phosphor particles post-treated at 1,300 °C was 93% of that of phosphor particles post-treated at 1,400 °C.

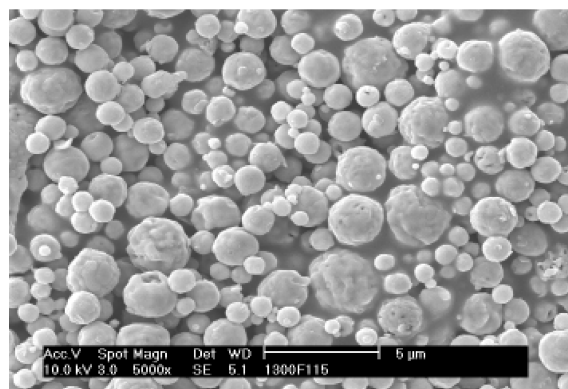
The added amount of fumed silica used as silicon source affected the crystal structure and PL intensity of prepared Y_2SiO_5 :Tb phosphor particles. Fig. 5 shows the emission spectra of Y_2SiO_5 :Tb phosphor particles prepared from solutions with different ratios of yttri-



(a) Fumed silica 100%



(b) Fumed silica 110%



(c) Fumed silica 115%

Fig. 7. SEM photographs of Y_2SiO_5 :Tb particles prepared from different ratios of yttrium nitrate and fumed silica.

um nitrate and fumed silica. The as-prepared particles by spray pyrolysis were post-treated at 1,300 °C for 3 h. The maximum PL intensity of particles, which were prepared from the solution with 20% excess fumed silica, was about 4 times higher than that of the particles prepared from the stoichiometric solution. From the results of XRD spectra as shown in Fig. 6, phase-pure X2 type Y_2SiO_5 : Tb phosphor particles were obtained from the solution with 110% excess of stoichiometric fumed silica. The particles prepared from the stoichiometric solution of yttrium nitrate and fumed silica had mixture phases of X1 and X2 type and had impurity as Y_2O_3 . The particles prepared from the solution with 105% excess of stoichiometric fumed silica had high crystallinity of X2 type with small impurity peaks of Y_2O_3 . On the other hand, the particles prepared from the solution with 115-120% excess of stoichiometric fumed silica had impurity phase as $Y_2Si_2O_5$. However, the Y_2SiO_5 : Tb phosphor particles prepared from the solution with 120% excess of stoichiometric fumed silica had maximum brightness in spite of small impurity phase as $Y_2Si_2O_5$. Fig. 7 shows the SEM photographs of Y_2SiO_5 : Tb phosphor particles with different ratios of yttrium nitrate and fumed silica. All Y_2SiO_5 : Tb phosphor particles post-treated at 1,300 °C had spherical morphology and non-agglomeration characteristics. The mean particle size of phosphor particles measured from the SEM photograph [Fig. 7a] was 1.4 μm .

CONCLUSIONS

Green-emitting Y_2SiO_5 : Tb phosphor particles were synthesized under severe preparation conditions by large-scale spray pyrolysis. The particles prepared from the colloidal solution containing the fumed silica particles with the size of 14 nm had a spherical and filled structure even after the post-treatment. The effect of post-treatment temperatures and different ratios of yttrium nitrate and fumed silica on crystallinity and photoluminescence intensity of Y_2SiO_5 : Tb phosphor particles was investigated. The Y_2SiO_5 : Tb phosphor particles prepared from the solution with 120% excess of stoichiometric fumed silica had high crystallinity of X2 type and high photoluminescence intensity.

REFERENCES

- Chang, L. F., Brownlow, J. W., Sun, T. I. and Wilson, J. S., "Refinement of Zinc Silicate Phosphor Synthesis," *J. Electrochem. Soc.*, **136**(11), 3532 (1989).
- Hampden-Smith, M. J., Kodas, T. T. and Caruso, J., "Oxygen-Containing Phosphor Powders, Methods for Making Phosphor Powders and Devices Incorporating Same," US. Patent 6, 180029 B1 (2001).
- Jung, K. Y. and Park, S. B., "Effect of Calcination Temperature and Addition of Silica, Zirconia, Alumina on the Photocatalytic Activity of Titania," *Korean J. Chem. Eng.*, **18**(6), 879 (2001).
- Kang, Y. C. and Park, S. B., "Preparation of Zinc Oxide-Dispersed Silver Particles by Spray Pyrolysis of Colloidal Solution," *Mater. Lett.*, **40**(3), 129 (1999).
- Kang, Y. C., Lenggono, I. W., Okuyama, K. and Park, S. B., "Luminescence Characteristics of Y_2SiO_5 : Tb Phosphor Particles Directly Prepared by the Spray Pyrolysis Method," *J. Electrochem. Soc.*, **146**(3), 1227 (1999).
- Kang, Y. C., Roh, H. S. and Park, S. B., "Preparation of Y_2O_3 : Eu Phosphor Particles of Filled Morphology at High Precursor Concentrations by Spray Pyrolysis," *Adv. Mater.*, **12**(6), 451 (2000).
- Lenggono, I. W., Iskandar, F., Mizushima, H., Xia, B., Okuyama, K. and Kijima, N., "One-Step Synthesis for Zn_2SiO_4 : Mn Particles 0.3-1.3 μm in Size with Spherical Morphology and Non-Aggregation," *Jpn. J. Appl. Phys.*, **39**, L1051 (2000).
- Lim, M. A., Kang, Y. C. and Park, H. D., " Gd_2O_3 : Eu Phosphor Particles Prepared from the Polymeric Precursors in Spray Pyrolysis," *J. Electrochem. Soc.*, **148**(12), H171 (2002).
- Meiss, D. and Kemmler-Sack, S., "Energy Transfer Terbium(3+) \rightarrow Europium(3+) in Cathodoluminescence for Oxyorthosilicates of X1 and X2 Type: System Europium(3+), Terbium(3+)-Doped Yttrium Oxyorthosilicate (Y_2SiO_5)," *Phys. Status Solidi*, **A124**(1), 371 (1991).
- Ohno, K. and Abe, T., "The Synthesis and Particle Growth Mechanism of Bright Green Phosphor YAG: Tb," *J. Electrochem. Soc.*, **141**(5), 1252 (1994).
- Ravichandran, D., Roy, R., Chakhovskoi, A. G., Hunt, C. E., White, W. B. and Erdei, S., "Fabrication of $Y_3Al_5O_{12}$: Eu Thin Films and Powders for Field Emission Display Applications," *J. Lumin.*, **71**, 291 (1997).
- Shen, X. A. and Kachru, R., " $7F_0-5D_1$ Transition in Eu^{3+} : Y_2SiO_5 ," *J. Opt. Soc. Am.*, **B11**, 591 (1994).
- Sohn, J. R., Kang, Y. C. and Park, H. D., "Morphological Control of Y_2O_3 : Eu Phosphor Particles by Adding Polymeric Precursors in Spray Pyrolysis," *Jpn. J. Appl. Phys.*, **41**, 3006 (2002).
- Sohn, K. S., Cho, B. H. and Park, H. D., "Photoluminescence Behavior of Manganese-Doped Zinc Silicate Phosphors," *J. Am. Ceram. Soc.*, **82**(10), 2779 (1999).
- Vanheusden, K., Seager, C. H., Warren, W. L., Tallant, D. R., Caruso, J., Hampden-Smith, M. J. and Kodas, T. T., "Green Photoluminescence Efficiency and Free-Carrier Density in ZnO Phosphor Powders Prepared by Spray Pyrolysis," *J. Lumin.*, **75**(1), 11 (1997).
- Yin, M., Zhang, W., Xia, S. and Krupa, J. C., "Luminescence of Nanometric Scale Y_2SiO_5 : Eu^{3+} ," *J. Lumin.*, **68**, 335 (1996).