ELSEVIER

Ceramics International 32 (2006) 865–870

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The characteristics of X1 type Y_2SiO_5:Tb phosphor particles prepared by high temperature spray pyrolysis

H.J. Lee, S.K. Hong, D.S. Jung, S.H. Ju, H.Y. Koo, Y.C. Kang *

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea

Received 4 April 2005; received in revised form 29 May 2005; accepted 5 July 2005
Available online 8 September 2005

Abstract

The X1 type Y_2SiO_5:Tb phosphor particles with high brightness were prepared by spray pyrolysis from spray solution with NH_4F flux material. The phosphor particles prepared by spray pyrolysis at high preparation temperature had spherical shape, fine size and dense morphology. The mean sizes of the phosphor particles prepared at 900 and 1650 °C were 1.3 and 0.9 μm. The emission spectrum of the phosphor particles prepared by spray pyrolysis at 1650°C had the characteristics of X1 type Y_2SiO_5:Tb phosphor. The photoluminescence intensity of the phosphor particles directly prepared by spray pyrolysis from spray solution with 20 wt.% NH_4F flux of the product at temperature of 1650 °C was 127 and 184% of the X1 and X2 type Y_2SiO_5:Tb phosphor particles post-treated at 1100 and 1300 °C, respectively. The Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis at 1650 °C had X1 type crystal structure because of short residence time of particles inside hot wall reactor of 0.4 s.

Keywords: A. Powders: gas phase reaction; C. Optical properties

1. Introduction

Spherical phosphor has many advantages such as high packing density, good slurry property, and smoother light intensity distribution. Thus spherical phosphor particle can optimize the optical and geometrical structure of phosphor layer. The particle size of a phosphor affects the amount of phosphor particles needed to produce an optimal coating for a particular application. Phosphors having smaller particle size can provide equivalent coverage densities at lower powder weights than larger sized particles. However, a reduction in the size of a phosphor usually results in lower emission brightness because of the higher intrinsic reflection coefficient associated with the smaller particles. Additionally, because of the difficulty in controlling the phosphor particle size during synthesis, the general practice of making a smaller size phosphor includes milling process after synthesis. The milling process results in a further loss in brightness of phosphor particles [1–3].

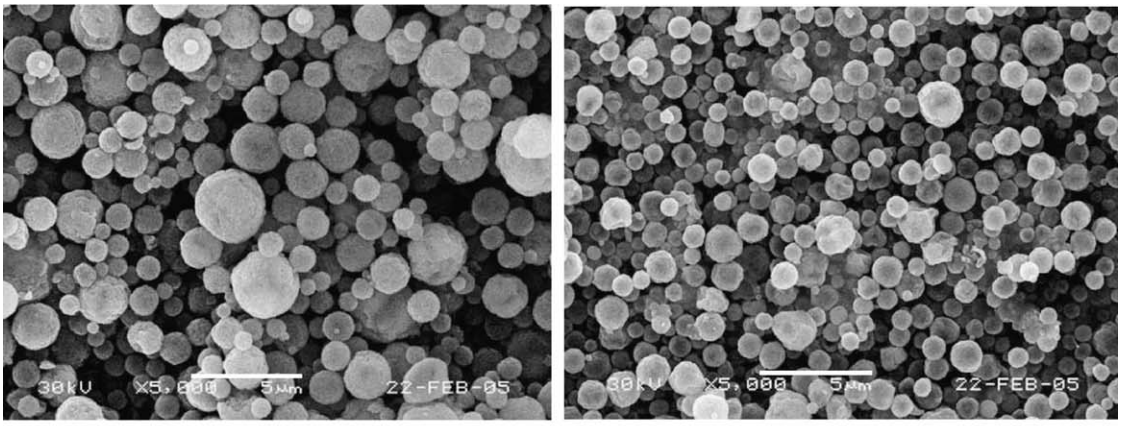
Spray pyrolysis is applied to the preparation of multi-component oxide phosphor particles [4–13]. The morphology and luminescence characteristics of phosphor particles were affected by the preparation conditions in the spray pyrolysis. Direct preparation of high brightness phosphor particles in the spray pyrolysis was introduced in several literatures [9–12]. Shimomura and Kijima prepared high luminance $Y_2O_3:Eu^{3+}$ red phosphor by spray pyrolysis method without post-heating [9–11]. The effect of ammonium chloride flux on the luminescence intensity of the $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor directly synthesized by spray pyrolysis without post-heating was also investigated by Shimomura and Kijima [12].

Tb-doped yttrium silicate (Y_2SiO_5:Tb) has been widely studied as green-emitting phosphor because of their high luminescence efficiency under electron beam and ultraviolet light [14,15]. It is known that Y_2SiO_5:Tb is polymorphic and crystallizes in the monoclinic X1 or X2 type, which is determined by the synthesis temperature. X1 and X2 types

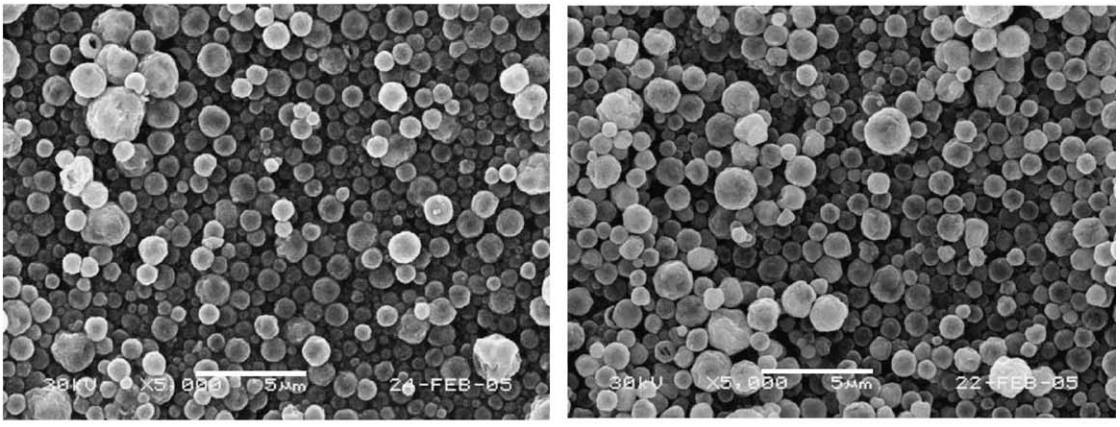
* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

0272-8842/$30.00
doi:10.1016/j.ceramint.2005.07.001

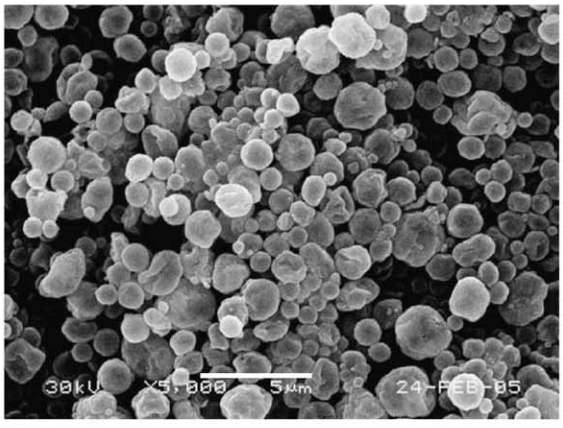
Y_2SiO_5:Tb phosphor particles were prepared by spray pyrolysis after post-treatment at different temperatures [15]. The Y_2SiO_5:Tb phosphor particles post-treated at 1100 °C had phase-pure crystal structure of X1 type. The crystal structure of X2 type appeared after post-treatment at 1200 °C, and the Y_2SiO_5:Tb phosphor particles with complete X2 type structure was obtained above 1300 °C. In the spray pyrolysis, the Y_2SiO_5:Tb phosphor particles with complete X2 type crystal structure had higher photolunminescence intensities than those with X1 type crystal structure. In this work, X1 type Y_2SiO_5:Tb phosphor particles were prepared by high temperature spray pyrolysis without post-treatment. The effect of preparation temperature on the morphology, crystal structure and photoluminescence characteristics of the Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis were investigated.



(a) No flux, P900 °C (b) No flux, P1650 °C



(c) 10 wt.% NH_4F, P1650 °C (d) 20 wt.% NH_4F, P 1650 °C



(e) 30 wt.% NH_4F, P 1650 °C

Fig. 1. SEM photographs of Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis without post-treatment.

2. Experimental

Tb-doped yttrium silicate phosphor particles with the composition of $Y_{1.8}SiO_5$:$Tb_{0.2}$ were prepared by spray pyrolysis at various preparation temperatures. Spray generator with six vibrators that has frequency of 1.7 MHz was used to produce large amount of droplets. The general flow diagram of the spray pyrolysis process is given elsewhere [6]. The solution of salts was atomized with ultrasonic spray generators and introduced into a hot reaction column, where the droplets were dried, decomposed and/or crystallized. The total concentration of metal components was 0.5 M. The content of ammonium fluoride used as flux material was varied from 0 to 30 wt.% of Y_2SiO_5:Tb phosphor particles. The flow rate of 10% H_2/N_2 mixture gas used as a carrier gas was 7 L/min.

The crystal structures of the particles were studied by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418). The morphology of particles was investigated using scanning electron microscopy (SEM, JEOL, JSM 6060). Photoluminescence measurement was performed with spectrofluorophotometer (SHIMADZU, RF-5301PC) using a Xe lamp excitation source.

3. Results and discussion

The morphology of the Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis from spray solution with and without NH_4F flux material at different preparation temperatures was shown in Fig. 1. The Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis without post-treatment had spherical shape and non-aggregation characteristics. The phosphor particles prepared at low preparation temperature had larger size than those prepared at high preparation temperature. The mean sizes, which were measured from the SEM photographs, of the particles prepared at temperature of 900 and 1650 °C were 1.3 and 0.9 μm, respectively. Densification of the Y_2SiO_5:Tb phosphor particles occurred at high preparation temperature in the spray pyrolysis. The phosphor particles prepared from spray solution with different additional amount of NH_4F had spherical shape and fine size.

The photoluminescence characteristics of the Y_2SiO_5:Tb phosphor particles before and after post-treatment were

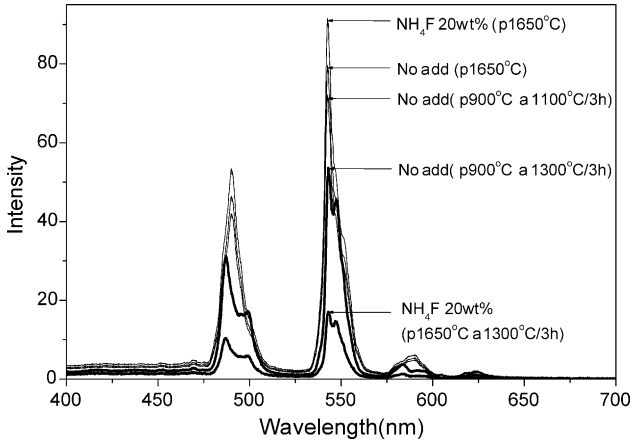


Fig. 2. Photoluminescence spectra of Y_2SiO_5:Tb phosphor particles before and after post-treatment. (p: preparation temperature, a: post-treatment temperature)

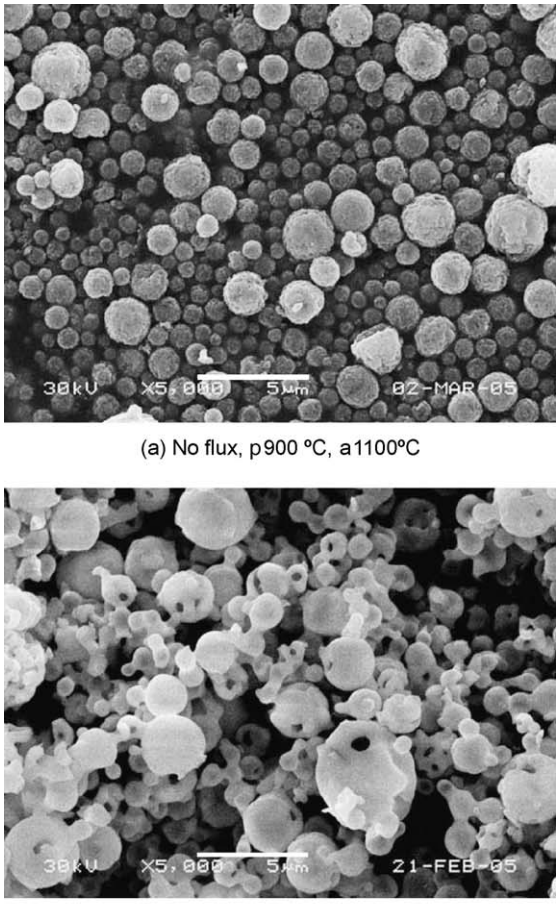


Fig. 3. SEM photographs of Y_2SiO_5:Tb phosphor particles after post-treatment.

shown in Fig. 2. The photoluminescence spectra of the Y_2SiO_5:Tb phosphor particles were measured under excitation wavelength of 241 nm. The emission spectra of the particles prepared by spray pyrolysis from spray solution with and without NH_4F flux at 1650 °C had the characteristics of X1 type Y_2SiO_5:Tb phosphor. Peak split of the emission spectrum between the wavelength of 542 and 547 nm did not occur. The particles prepared by spray pyrolysis at 900 °C had no light emission under ultraviolet excitation. The as-prepared particles obtained by spray pyrolysis at 900 °C were post-treated at 1100 and 1300 °C to improve the crystallinity and photoluminescence intensity of the Y_2SiO_5:Tb phosphor particles. The phosphor particles post-treated at 1100 °C had also emission spectrum of the X1 type Y_2SiO_5:Tb phosphor. On the other hand, peak split of the emission spectrum observed in the phosphor particles post-treated at 1300 °C. The phosphor particles prepared from spray solution with NH_4F flux at 1650 °C had higher photoluminescence intensity than that of the phosphor particles prepared from spray solution without flux material. The optimum additional amount of NH_4F flux was 20 wt.% of the product in improving the photoluminescence intensity of the Y_2SiO_5:Tb phosphor particles in the high temperature spray pyrolysis. The photoluminescence intensity of the phosphor particles prepared from spray solution with 20 wt.% NH_4F flux of the product at 1650 °C was 127 and 184% of the X1 and X2 type Y_2SiO_5:Tb phosphor particles post-treated at 1100 and 1300 °C, respectively. On the other hand, the X2 type Y_2SiO_5:Tb phosphor particles

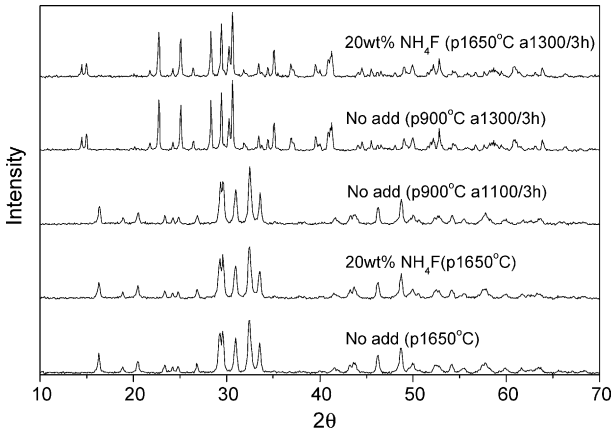


Fig. 4. X-ray diffraction spectra of Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis before and after post-treatment.

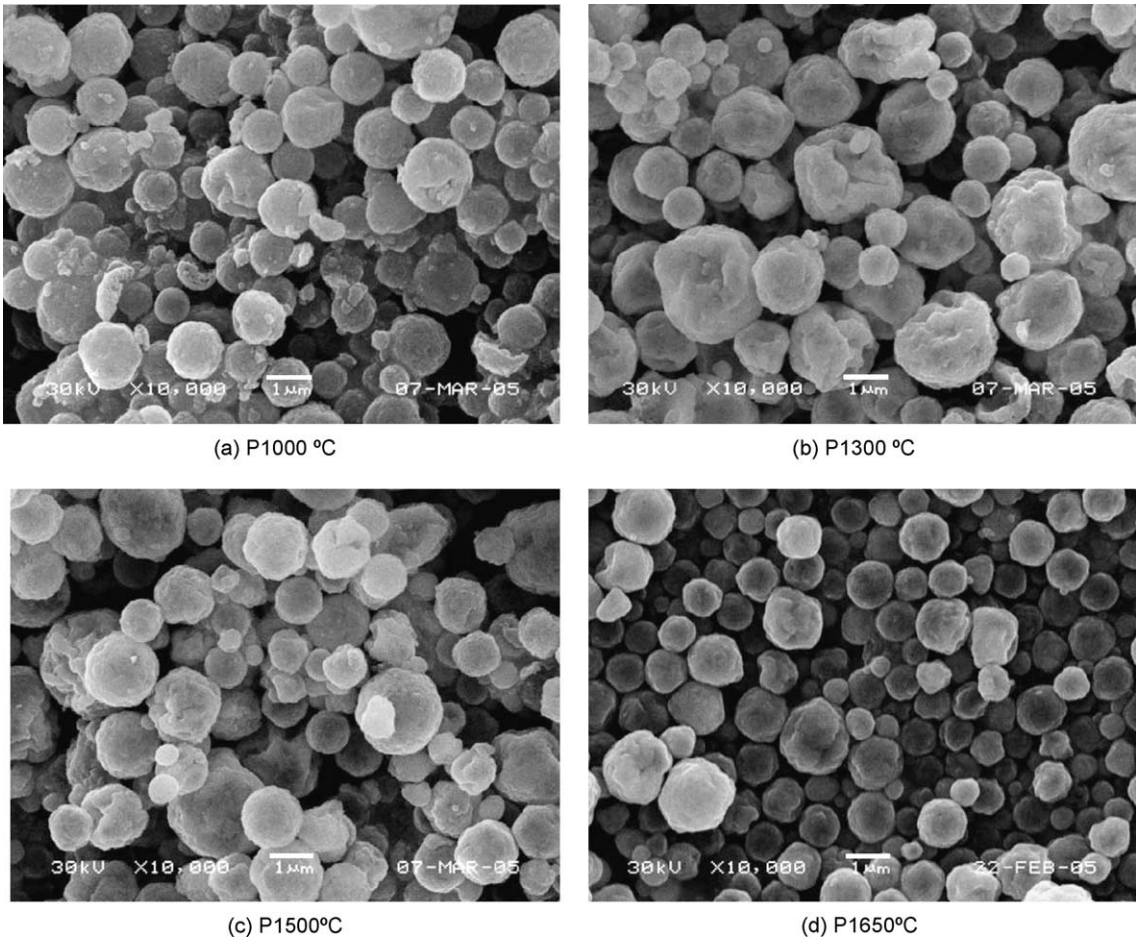


Fig. 5. SEM photographs of Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis at different preparation temperatures.

prepared from spray solution with NH_4F flux had low photoluminescence intensity after post-treatment at 1300 °C.

The morphology of the post-treated Y_2SiO_5:Tb phosphor particles is shown in Fig. 3. The as-prepared particles obtained by spray pyrolysis from spray solution with and without flux material were post-treated at 1100 and 1300 °C for 3 h under reducing atmosphere. The Y_2SiO_5:Tb phosphor particles prepared from spray solution without flux material had spherical shape and non-aggregation characteristics after post-treatment at 1100 °C. On the other hand, the Y_2SiO_5:Tb phosphor particles post-treated at 1300 °C had non-spherical shape and aggregation characteristics. The spherical shape of the Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis from spray solution with NH_4F flux at 1650 °C was also destroyed after post-treatment at 1300 °C. The crystal structure of the as-prepared and post-treated Y_2SiO_5:Tb phosphor particles was shown in Fig. 4. The particles prepared by spray pyrolysis from spray solution with and without NH_4F flux at 1650 °C without post-treatment had crystal structure of phase-pure X1 type Y_2SiO_5:Tb phosphor. The Y_2SiO_5:Tb phosphor particles post-treated at 1100 °C, in which the as-prepared particles were obtained from spray solution without flux material at 900 °C, had also phase-pure X1 crystal structure. The Y_2SiO_5:Tb phosphor particles directly prepared by spray pyrolysis at 1650°C had X1 type crystal structure because of short residence time of particles inside hot wall reactor as 0.4 s. Phase transition from X1 to X2 type crystal structure of the Y_2SiO_5:Tb phosphor particles did not occurred at preparation temperature of 1650 °C in the spray pyrolysis. However the Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis at 1650 °C had high crystallinity of X1 type crystal structure comparable with that of the particles post-treated at 1100 °C for 3 h. The particles prepared from spray solution with and without NH_4F flux had X2 type crystal structure after post-treatment at 1300 °C.

The effect of the preparation temperature in the spray pyrolysis on the morphology and photoluminescence intensity of the Y_2SiO_5:Tb phosphor particles was shown

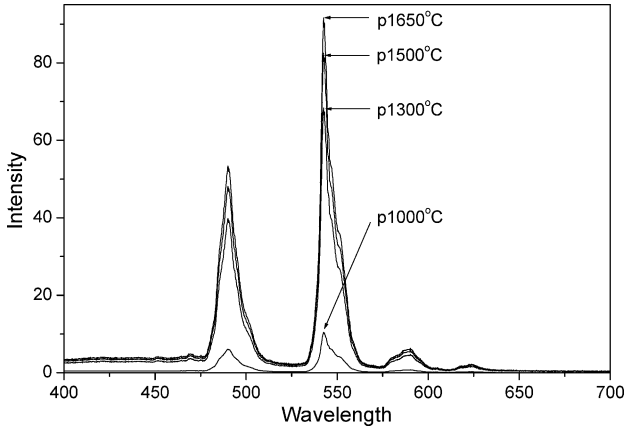


Fig. 6. Photoluminescence spectra of Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis at different preparation temperatures.

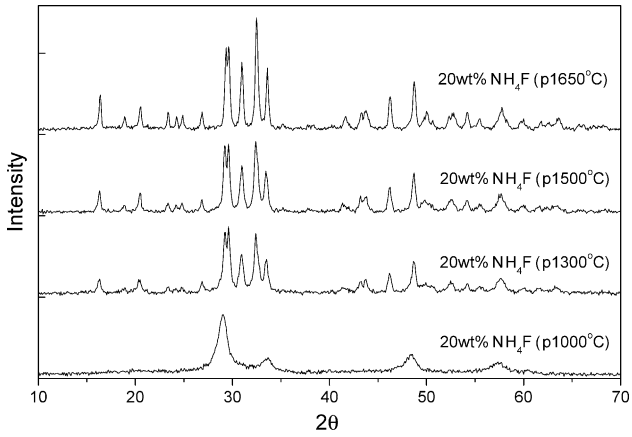


Fig. 7. X-ray diffraction spectra of Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis at different preparation temperatures.

in Figs. 5 and 6. The morphology of the Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis from spray solution with NH_4F flux was slightly affected by the preparation temperatures. The sphericity of the particles improved with increasing the preparation temperatures in the spray pyrolysis. The photoluminescence intensity of the Y_2SiO_5:Tb phosphor particles is strongly affected by the preparation temperatures. The photoluminescence intensity of the Y_2SiO_5:Tb phosphor particles increased with increasing the preparation temperature in the spray pyrolysis. However, the phosphor particles directly prepared by spray pyrolysis had the characteristic of emission spectrum of the X1 type Y_2SiO_5:Tb phosphor irrespective of the preparation temperatures. Fig. 7 shows the XRD spectra of the Y_2SiO_5:Tb phosphor particles directly prepared by spray pyrolysis at different preparation temperatures. The particles obtained at preparation temperature of 1000 °C had the crystal structure of yttrium oxide. Therefore, in Fig. 6, the emission spectrum of the particles obtained at preparation temperature of 1000 °C was that of the Y_2O_3:Tb phosphor particles. On the other hand, the particles directly prepared by spray pyrolysis above 1300 °C had main peak lines corresponding to X1 type Y_2SiO_5:Tb phosphor. The crystallinity of the X1 type Y_2SiO_5:Tb phosphor increased with increasing the preparation temperature in the spray pyrolysis.

4. Conclusions

The X1 and X2 types Y_2SiO_5:Tb phosphor particles were prepared by spray pyrolysis. The particles directly prepared by spray pyrolysis at high preparation temperatures had the crystal structure and photoluminescence characteristics of the X1 type Y_2SiO_5:Tb phosphor. The X1 type Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis from spray solution with NH_4F flux without post-treatment had spherical shape and non-aggregation characteristics. On the other hand, the X2 type Y_2SiO_5:Tb phosphor particles

prepared from spray solution without flux material after post-treatment at 1300 °C had non-spherical shape and aggregation characteristics. The X1 type Y_2SiO_5:Tb phosphor particles prepared by spray pyrolysis at high preparation temperature had high photoluminescence intensity because of phase purity and high crystallinity even at short residence time of the particles inside hot wall reactor.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation (KOSEF, R08-2004-000-10160-0).

References

[1] Y. Kimura, S. Sakai, N. Yoshida, U.S. patent 5,352,426 (1994).
[2] C.N. Chau, A.F. Kasenga, C.F. Chenot, L.F. Gray, U.S. patent 5,132,042 (1992).
[3] S. Erdei, F.W. Ainger, D. Ravichandran, W.B. White, L.E. Cross, Mater. Lett. 30 (1997) 389.
[4] M.J. Hampden-Smith, T.T. Kodas, J. Caruso, U.S. patent 6,180,029 B1 (2001).
[5] K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, J. Caruso, M.J. Hampden-Smith, T.T. Kodas, J. Lumin. 75 (1997) 11.
[6] J.R. Sohn, Y.C. Kang, H.D. Park, Jpn. J. Appl. Phys. 41 (2002) 3006.
[7] Y.C. Kang, H.S. Roh, S.B. Park, Adv. Mater. 12 (2000) 451.
[8] H.S. Roh, Y.C. Kang, H.D. Park, S.B. Park, Jpn. J. Appl. Phys. 42 (2003) 3429.
[9] Y. Shimomura, N. Kijima, J. Electrochem. Soc. 151 (4) (2004) H86.
[10] Y. Shimomura, N. Kijima, Electrochem. Solid-State Lett. 7 (2) (2004) H1.
[11] Y. Shimomura, N. Kijima, Electrochem. Solid-State Lett. 7 (5) (2004) H18.
[12] Y. Shimomura, N. Kijima, J. Electrochem. Soc. 151 (8) (2004) H192.
[13] I.W. Lenggoro, B. Xia, H. Mizushima, K. Okuyama, N. Kijima, Mater. Lett. 50 (2001) 92.
[14] Q. Su, J. Lin, H. Zhang, S. Wang, Mater. Res. Bull. 319 (1996) 189.
[15] H.S. Kang, Y.C. Kang, H.D. Park, Y.G. Shul, Appl. Phys. A 80 (2) (2003) 347.