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Zn_2SiO_4 : Mn Phosphor Particles Prepared by Spray Pyrolysis Process

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Abstract

Green-emitting Zn_2SiO_4:Mn phosphor particles having a spherical shape and high luminescence intensities under VUV were prepared by spray pyrolysis process under severe preparation conditions. The type of precursor solutions affected the morphology and luminescence characteristics of the prepared particles. The particles prepared from the clear solution by laboratory-scale process had spherical shape and dense morphology, while the particles prepared from the severe preparation conditions had rough surface and collapsed structure. However, the particles prepared from the colloidal solution utilizing fumed silica were spherical in shape and filled morphology at the severe preparation conditions of high flow rate of carrier gas, high concentration of solution, and large reactor size. The prepared Zn_2SiO_4:Mn phosphor particles with complete spherical shape had higher photoluminescence intensity than that of the commercial product prepared by solid state reaction.

Keywords : phosphor, zinc Silicate, spray pyrolysis, plasma display Panel.

1. Introduction

Manganese-doped willemite, Zn_2SiO_4 is the main green phosphor in plasma display panels(PDP) because of high luminescence efficiency under vacuum ultraviolet(VUV) excitation[1,2]. Typically, Zn_2SiO_4:Mn phosphor particles have been prepared by solid-state reactions which require high reaction temperature, long heating time, and milling process. This mechanical process generates the phosphor particles with irregular morphology.

To overcome the disadvantages of conventional solid state reaction method, the various methods such as sol-gel[3], coprecipitation[4], and hydrothermal[5] have been developed. Moriomo and Matae[3] used a sol-gel method to prepare Zn_2SiO_4:Mn phosphors and compared it with that made by the solid state reaction. They found that emission intensity of the sol-gel derived material containing 2 mol% dopant was higher than that by the solid state reaction. Li et al.[5] investigated morphology of Zn_2SiO_4 particles with respect to the nature of anion, silica source, and the $NH_4OH:Zn^{2+}$ ratio in the hydrothermal processing.

Recently, gas phase reaction processes were applied to the preparation of multicomponent phosphor materials. Bihari et al.[6] prepared Y_2O_3:Eu nanocrystalline phosphors by gas-phase condensation by using CO_2 laser heating of ceramic pellets. It should be noted such gas-phase condensation method is currently confined to the preparation of phosphors with simple composition. Spray pyrolysis, which one of the gas phase reaction method was also applied to the preparation of multicomponent phosphor materials[7-9]. The phosphor particles prepared by spray pyrolysis have good characteristics such as spherical morphology, nonaggregation, fine

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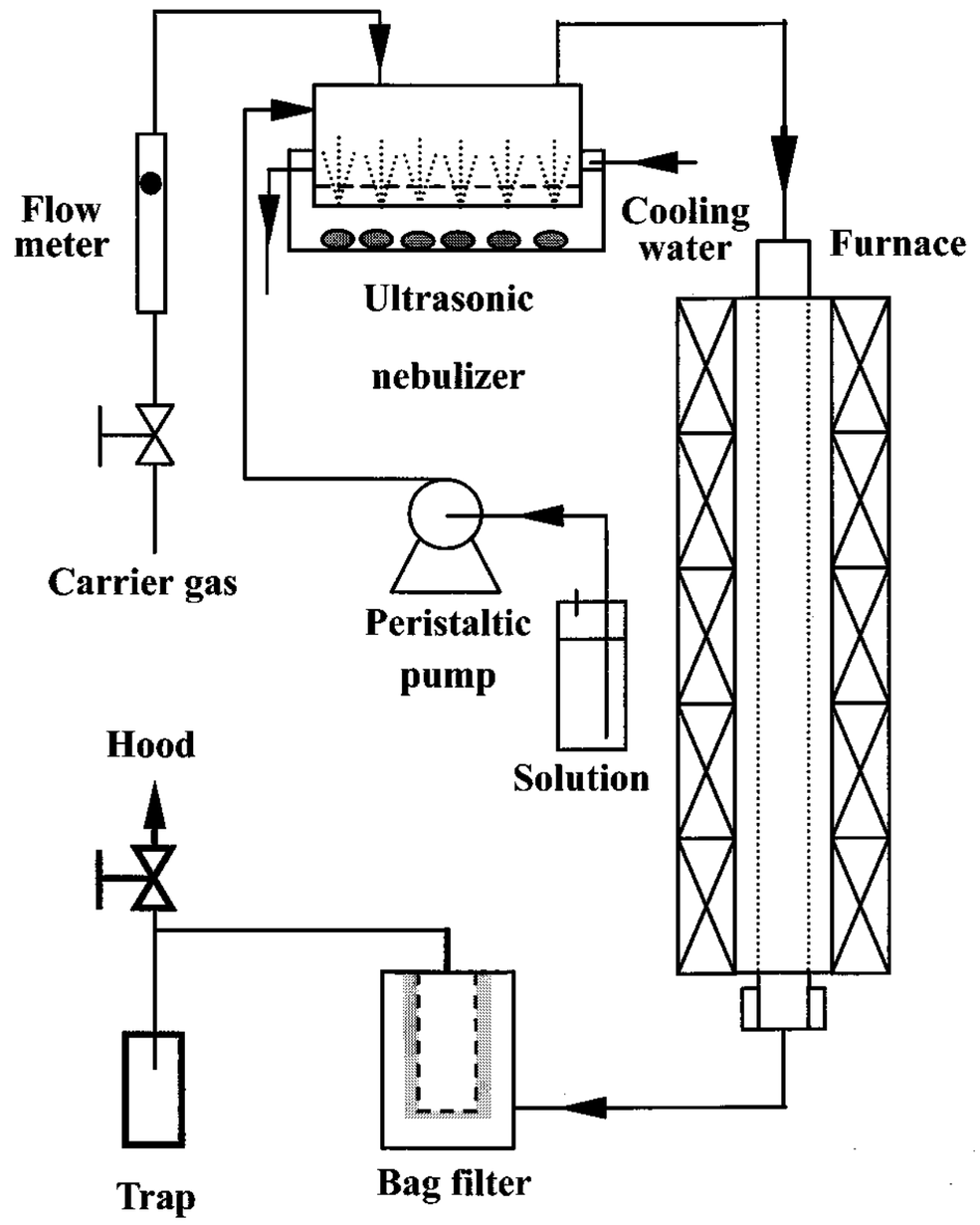


Fig. 1. The schematic diagram of the ultrasonic spray pyrolysis process.

size, and narrow size distribution for the application in displays. The use of spherical particles increase screen brightness and improves the resolution due to lower scattering of the evolved light and higher packing densities than irregular shaped particles[10,11]. Spray pyrolysis was also used in the preparation of Zn_2SiO_4: Mn phosphor particles having spherical shape and non-aggregated structure[12]. However, Zn_2SiO_4:Mn phosphor particles prepared from conditions for large-scale production of particles such as high flow rate of carrier gas, high concentration of solution, and large size of reactor had a hollow and collapsed structure. To solve the problem of Zn_2SiO_4:Mn phosphor particles in the pilot-scale apparatus, in this work, colloidal solution utilizing fumed silica was introduced by the spray pyrolysis method.

2. Experiments

Fig.1 shows the schematic diagram of the ultrasonic spray pyrolysis process. The apparatus used in this work was ultrasonic spray generator having six vibrators for large quantities of droplets. The length and internal diameter of quarts reactor was 1,200 mm and 50 mm, respectively. The flow rate of air used as the carrier gas was 45 L/min and the residence time of the particles inside the reactor was 0.65 sec. The colloidal solutions were prepared from zinc nitrate, fumed silica, and manganese precursors. The doping concentration of Mn was fixed at 10 mol% of Zn component. The as-prepared particles obtained by spray pyrolysis were post-treated above 1,000 °C for 3hrs and reduced at 775 °C for 1 hr under a reducing atmosphere for activation of Mn component. The morphology and crystallinity of the particles were investigated with scanning election microscopy(SEM) and X-ray diffractometry(XRD). Optical properties of the particles were measured under 147 nm by vacuum UV PL spectroscopy with Kr lamp.

3. Results and Discussion

Fig. 2 shows the SEM photograph of Zn_2SiO_4:Mn particles prepared from the clear solution utilizing tetraethyl orthosilicate(TEOS) as the silicon source by spray pyrolysis. The as-prepared particles with complete spherical shape and non-crystalline phase were post-

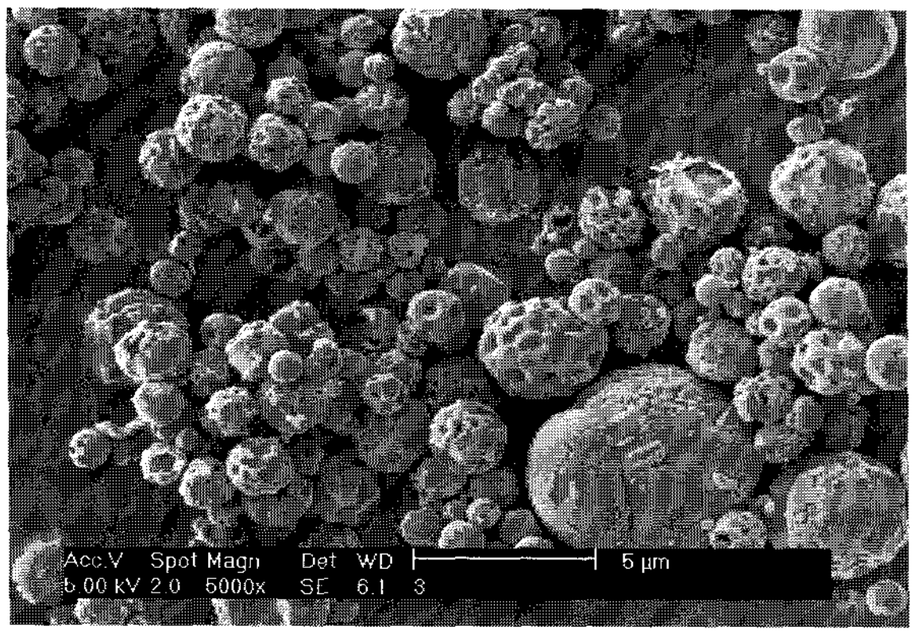


Fig. 2. SEM photograph of Zn_2SiO_4:Mn particles prepared from clear solution.

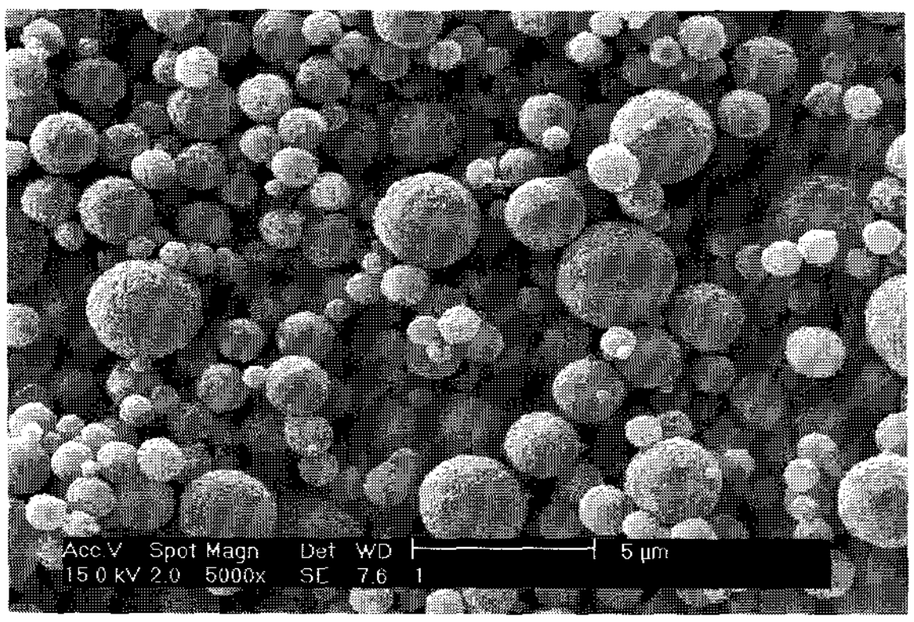


Fig. 3. SEM photograph of Zn_2SiO_4:Mn particles prepared from colloidal solution.

treated at 1,175 °C for 3 hrs. The post-treated particles had rough surface and collapsed structure. However, Zn_2SiO_4:Mn particles prepared from the colloidal solution utilizing fumed silica had spherical shape and filled morphology even after post-treatment as shown in Fig. 3. The morphology change of the particles prepared from the clear and colloidal solutions was due to the difference of drying stage of droplets. In the spray pyrolysis utilizing colloidal solution, precipitation of zinc and manganese precursors occurred onto the fumed silica particles in all positions of droplet. Thus, the particles prepared from the colloidal solution by spray pyrolysis had filled morphology. On the other hand, the as-prepared particles prepared from the clear solution had hollow morphology because of surface precipitation of precursors by high drying rate of droplet. The formation mechanisms of the Zn_2SiO_4:Mn particles from the clear and colloidal solutions are observed in Fig. 4.

Optical properties of the Zn_2SiO_4:Mn phosphor particles with spherical shape were optimized by changing the preparation and post-treatment conditions. Zn_2SiO_4: Mn phosphor particles were prepared from the colloidal solutions with different concentration of fumed silica. As the concentration of fumed silica increased from 100 % to 125 % of stoichiometric amount, the morphology of Zn_2SiO_4:Mn particles changed from irregular shape to spherical shape. The particles prepared from the solution with fumed silica of 14 % excess had complete spherical shape and filled morphology. In the XRD patterns of the Zn_2SiO_4:Mn particles prepared from the colloidal solution, the particles prepared from the solution with 100 % fumed silica had ZnO peaks were impurity phase. Single phase Zn_2SiO_4:Mn particles were obtained from the solution with fumed silica above 105% of stoichiometric amount. The PL emission spectra of Zn_2SiO_4:Mn phosphor particles prepared at different concentration of fumed silica were investigated. The photoluminescence intensity of the particles increased with increasing concentration of fumed silica. The optimum brightness of Zn_2SiO_4:Mn phosphor particles was obtained from the solution of 114 % fumed silica.

The characteristics such as morphology, crystallinity, and photoluminescence intensities of the Zn_2SiO_4:Mn particles prepared from the colloidal solution were also affected by post-treatment temperature. The as-prepared particles had spherical shape, submicron size, and narrow size distribution. Agglomeration between particles did not occur even after post-treatment below 1,175 °C, but the Zn_2SiO_4:Mn particles post-treated at 1,200 °C had agglomerated with rough surface. The brightness of the Zn_2SiO_4:Mn particles was increased increasing post-treatment temperature and the maximum brightness was obtained at 1,100 °C.

Fig. 5 shows SEM photographs of the Zn_2SiO_4: Mn particles prepared from the colloidal solution with different manganese precursors. The particles prepared from the solution with various manganese precursors were post-treated at 1,100 °C for 3 hrs and reduced at 775 °C for 1hr. Although Zn_2SiO_4:Mn particles were prepared from different manganese precursors, all the particles had spherical morphology and non-aggregation characteristics. The photolumine-scence intensities of the Zn_2SiO_4:Mn phosphor particles prepared from various manganese precursors are shown in Fig. 6. The particles prepared from the colloidal solution with manganese acetate had higher brightness than those prepared

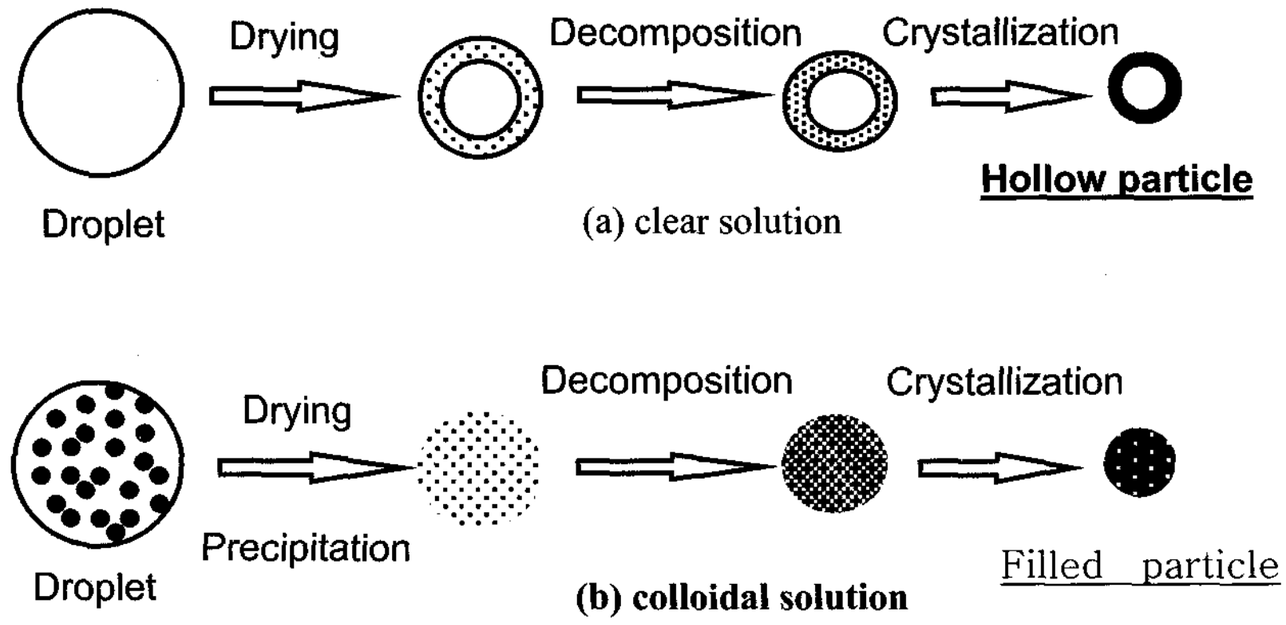
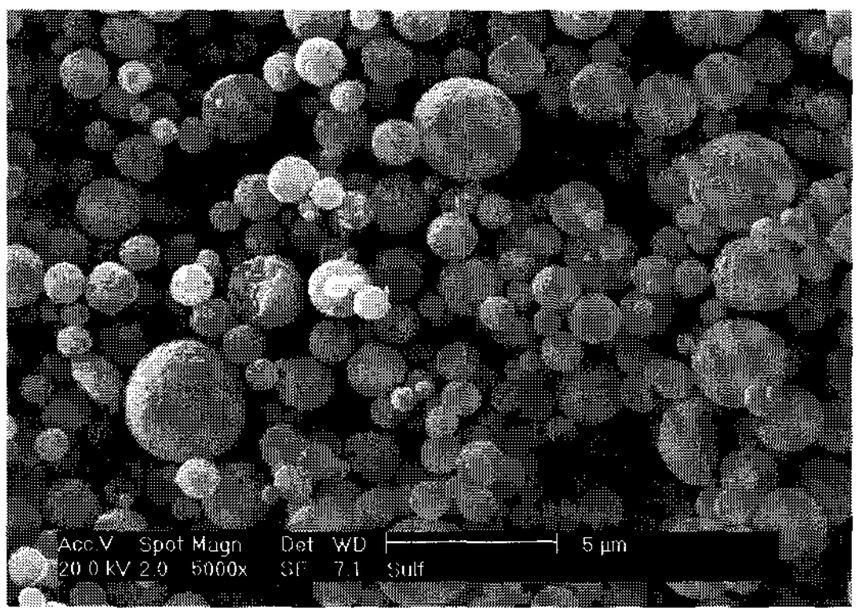
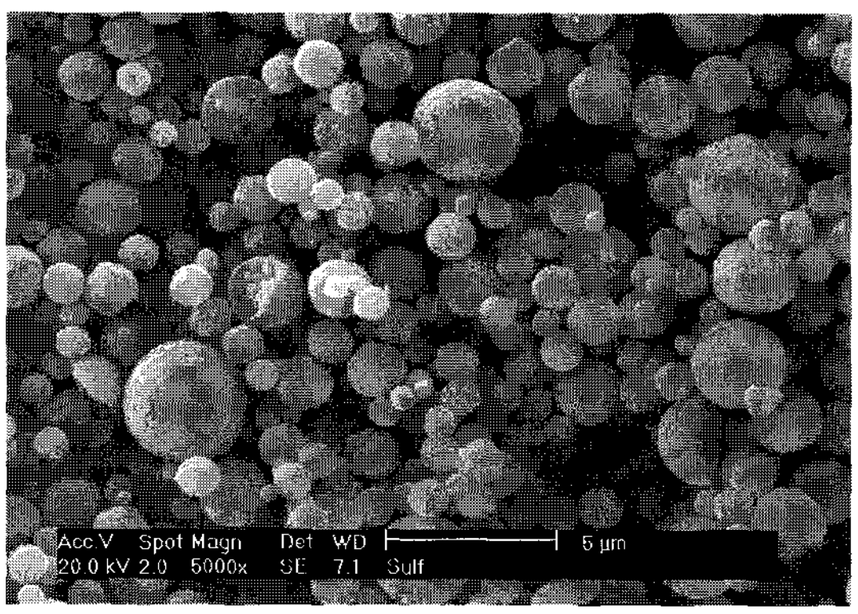


Fig. 4. Formation mechanisms of Zn_2SiO_4:Mn phosphor particles in spray pyrolysis.



(a)



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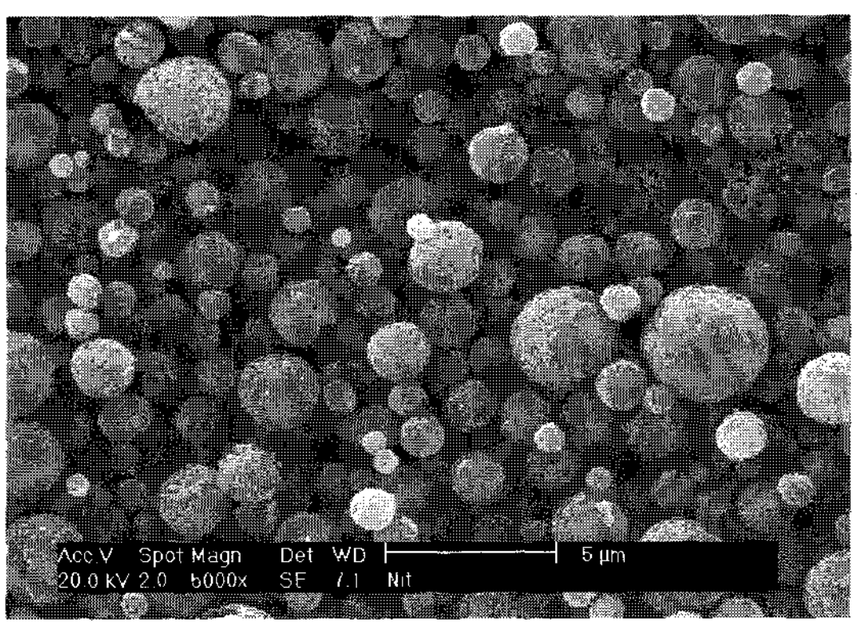

(c)

Fig. 5. SEM photographs of Zn_2SiO_4:Mn particles prepared from different Mn precursors, (a) Mn sulfate, (b) Mn chloride, (c) Mn nitrate.

from the other manganese precursor types. The photoluminescence intensities of the particles prepared from manganese acetate and manganese nitrate were higher than that of the commercial Zn_2SiO_4:Mn phosphor particles. Fig.7 shows the XRD patterns of the particles prepared from the different manganese components. All the particles had pure willemite structure and high crystallinity regardless of the type of manganese component. The type of manganese component did not affect the morphology and the crystatllinity of the Zn_2SiO_4:Mn phosphor particles. The difference in brightness of the Zn_2SiO_4:Mn particles

prepared from various manganese components was the result of the change of dispersion degree of manganese component.

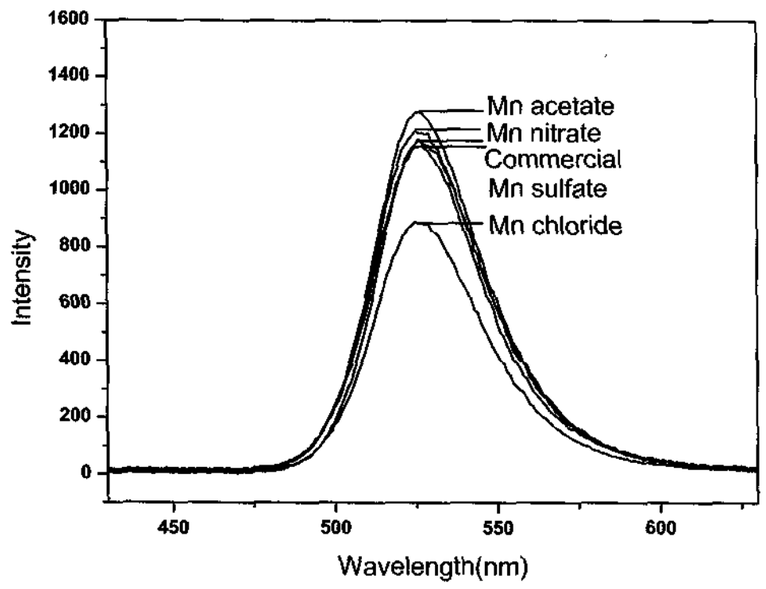

Fig. 6. The emission spectra of Zn_2SiO_4:Mn particles prepared from various Mn precursors.

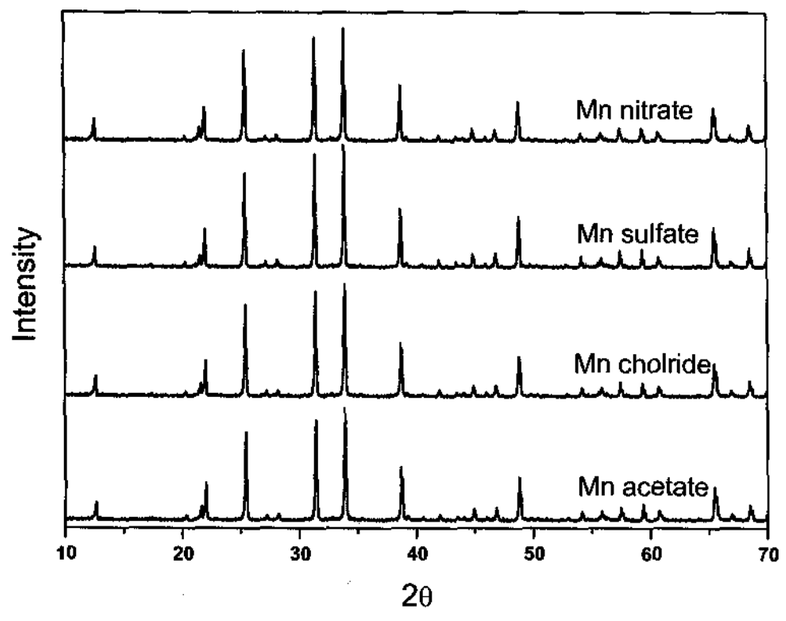

Fig. 7. XRD patterns of Zn_2SiO_4:Mn particles prepared from various Mn precursors.

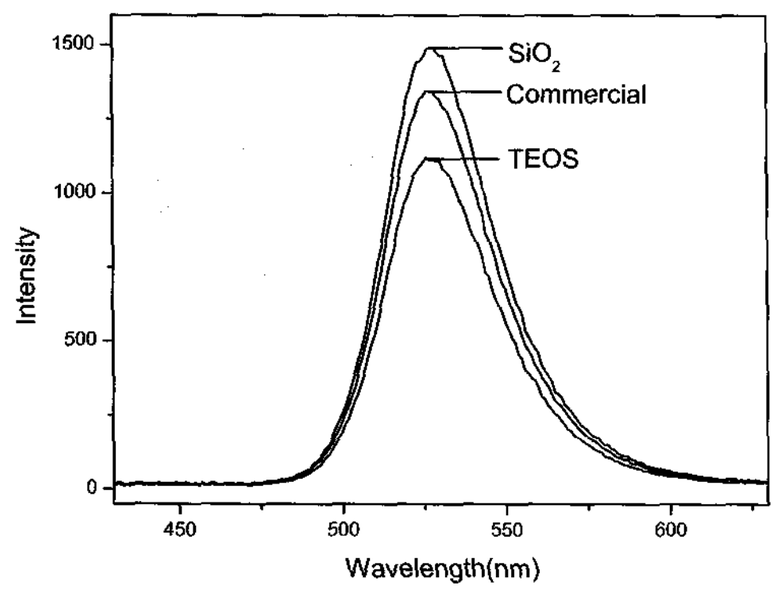

Fig. 8. Photoluminescence intensities of the prepared Zn_2SiO_4:Mn phosphor particles.

The photoluminescence intensities of the particles prepared by spray pyrolysis were compared with that of the commercial product prepared by solid state reaction method in Fig.8. The Zn_2SiO_4:Mn phosphor particles prepared by spray pyrolysis from the colloidal solution of fumed silica had higher photoluminescence intensity than that of the commercial product. The photoluminescence intensity of the particles prepared from the colloidal solution was 107 % of that of the commercial Zn_2SiO_4:Mn phosphor particles. However, the particles prepared from the clear solution utilizing tetraethyl orthosilicate(TEOS) have lower photoluminescence intensity than that of the commercial product. In Fig. 9, decay time of the Zn_2SiO_4:Mn phosphor particles prepared from the colloidal solution was compared with that of the commercial particles. Decay time(τ_{10}) of the prepared particles with doping concentration of Mn of 10 mol% was 7 ms, which is comparable with 6 ms of the commercial product.

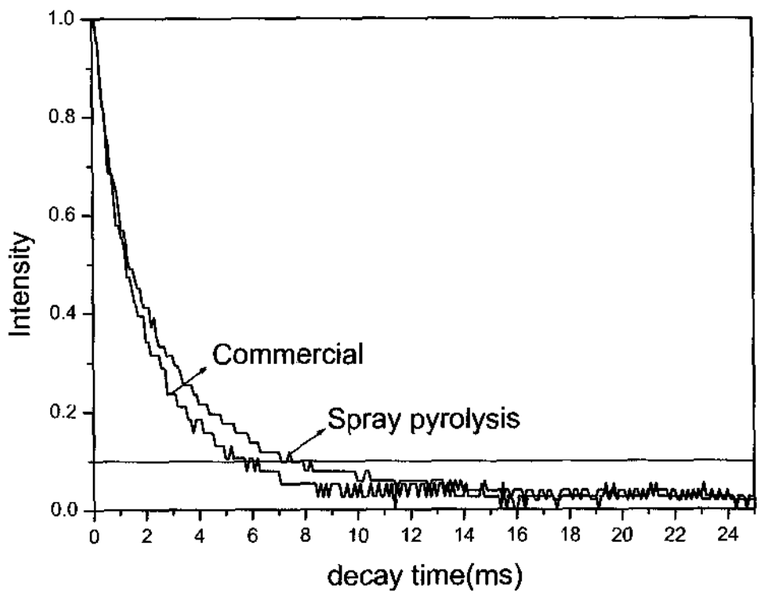

Fig. 9. Decay time of the prepared Zn_2SiO_4:Mn phosphor particles.

4. Conclusions

Zn_2SiO_4:Mn phosphor particles were prepared using the spray pyrolysis method at the severe preparation conditions. The as-prepared particles prepared from the severe preparation conditions had low thermal stability because of hollow structure. Thus, the morphology control of the Zn_2SiO_4:Mn particles were performed by introducing the colloidal solution. The morphology and luminescence properties of the Zn_2SiO_4:Mn particles were improved by introducing colloidal solution of fumed silica in spray pyrolysis method under severe preparation conditions. The change in morphology of the particles prepared from the clear and colloidal solutions was due to the difference of drying stage of droplet. The Zn_2SiO_4:Mn phosphor particles prepared from the

colloidal solution had higher brightness under vacuum ultraviolet than those prepared from the clear solution because of dense morphology.

References

[1] T. Miyata, T. Minami, K. Saikai and S. Takata, "Zn_2SiO_4 as a host material for phosphor-emitting layers of TFEL devices," J. Lumin., vol. 60, p. 926, 1994.

[2] C. Barthou, J. Benoit, P. Benalloul and A. Morell, "Mn^{2+} concentration effect on the optical properties of Zn_2SiO_4:Mn phosphors," J. Electrochem, Soc., vol. 141(2), p. 524, 1994.

[3] B. Y. Seong, C. H. Han, H. D. Park and D. S. Kim, "Preparation and luminescence properties of Zn_2SiO_4: Mn,Al green phosphors by sol-gel technique," J. Kor. Ceram. Soc., vol . 38[4], p. 337, 2001.

[4] I. F. Chang, J. W. Brownlow, T. I. Sun and J. S. Wilson, "Refinement of Zinc Silicate phosphor synthesis," J. Electrochem. Soc., vol. 136, p. 3532, 1989.

[5] Q. H. Li, S. Komarneni and R. Roy, "Control of morphology of Zn_2SiO_4 by hydrothermal preparation," J. Mater. Sci., vol. 30, p. 2358, 1996.

[6] B. Bihari, H. Eilers and B. M. Tissue, "Spectra and dynamics of monoclinic Eu_2O_3 and Eu^{3+} :Y_2O_3 nanocrystals," J. Lumin., vol. 75, p. 1, 1997.

[7] Y. C. Kang, S. B. Park, I. W. Lenggoro and K. Okuyama, "Gd_2O_3:Eu phosphor particles with sphericity, submicron size and non-aggregation characteristics," J. Phys. Chem. Solids, vol. 60(3), p. 379, 1999.

[8] Y. C. Kang, I. W. Lenggoro, K. Okuyama and S. B. Park, "Luminescence characteristics of Y_2SiO_5:Tb phosphor particles directly prepared by the spray pyrolysis method," J. Electrochem. Soc., vol. 146(3), p. 1227, 1999.

[9] Y. C. Kang, I. W. Lenggoro, S. B. Park and K. Okuyama, "Y_2SiO_5:Ce phosphor particles 0.5-1.4 μm in size with spherical morphology," J. Solids State Chem., vol. 146, p. 168, 1999.

[10] S. Oshio, K. Kitamura, T. Shigeta, S. Horii, T. Matsuoka, S. Tanaka and H. Kobayashi, "Firing technique for preparing a $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor with controlled particle shape and size," J. Electrochem. Soc., vol. 146(1), p. 392, 1999.

[11] S. Oshio, K. Kitamura, T. Shigeta, S. Horii, T. Matsuoka and T. Kanda, Processing of International Display Workshop, p. 621, 1997.

[12] Y. C. Kang and S. B. Park, "Zn_2SiO_4:Mn phosphor particles prepared by spray pyrolysis using a filter expansion aerosol generator," Mater. Res. Bull., vol. 35, p. 1143, 2000.