Synthesis of Mn-doped Zn$_2$SiO$_4$ phosphor particles by solid-state method at relatively low temperature and their photoluminescence characteristics

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Abstract Mn-doped Zn$_2$SiO$_4$ phosphor particles having submicrometer sizes were synthesized by a solid-state reaction method using methyl hydrogen polysiloxane-treated ZnO, fumed SiO$_2$ and various Mn sources. The crystallization and photoluminescent properties of the phosphor particles were investigated by X-ray diffraction(XRD), scanning electron microscope(SEM), and by their photoluminescence(PL) spectra. Due to the effect of the dispersion and coherence of the methyl hydrogen polysiloxane-treated ZnO, the Mn-doped Zn$_2$SiO$_4$ particles were successfully obtained by a solid state method at 1000$^\circ$C, and the maximum PL intensity of the prepared particles under vacuum ultra violet(VUV) excitation occurred at a Mn concentration of 0.02mol and a sintering temperature of 1000$^\circ$C.

Key Words : Solid-State Reaction, Phosphor, Photoluminescence, Zn$_2$SiO$_4$

1. Introduction

Inorganic phosphor materials have been widely used in modern lighting and display parts, such as fluorescent lamps, cathode-ray tubes, field emission displays and plasma display panels[1]. In particular, the luminescent properties of inorganic phosphors have been widely investigated for commercial use in flat panel displays(FPDs) in the recent years[2,3]. It is highly desirable to develop novel low-voltage phosphors for next generation field emission displays(FEDs), that have a high efficiency and good chemical stability under electron-beam bombardment in a high vacuum system[4,5]. Phosphor particles must have a small
diameter and narrow size distribution. Moreover, they must be non-aggregated, and have a spherical morphology for good luminescent characteristics. Mn-doped Zn$_2$SiO$_4$ is mainly used as a green-emitting phosphor material in plasma display panels because of its good luminescence characteristics and chemical stability under vacuum ultraviolet (VUV) excitation[6]. Green-emitting Mn-doped Zn$_2$SiO$_4$ is a well-known phosphor for its high luminescent efficiency and chemical stability. The emission of Zn$_2$SiO$_4$:Mn at 524nm is attributed to a d-level spin-forbidden transition for Mn$^{2+}$.

Up to the present time, the commercial Mn-doped Zn$_2$SiO$_4$ green phosphors have been synthesized mainly with a solid-state reaction method[7]. In the solid-state reaction method, a high reaction temperature, a long heating time, and a milling process are required. Due to this combination of requirements, new synthesis methods such as r. f. magnetron sputtering[8], sol-gel[9-12], hydrothermal[13,14], and an ultrasonic spray pyrolysis method[6] have been studied.

The objectives of the present study are to synthesize green-light-emitting phosphor particles with a submicron size at relatively low temperature using a solid-state reaction method, and to characterize their photoluminescent(PL) properties. The effect of different Mn sources and sintering temperatures on the PL characteristics of Mn-doped Zn$_2$SiO$_4$ phosphor particles is also investigated.

### 2. Experimental

Mn-doped Zn$_2$SiO$_4$ green phosphors were synthesized with a solid-state method. Fumed SiO$_2$ and methyl hydrogen polysiloxane-treated ZnO powders were mixed in a ball mill and sintered at 900°C for 5h in an air atmosphere to prepare Zn$_2$SiO$_4$ particles as a host material. After being reground, a respective Mn source(MnCO$_3$, MnO$_2$) was added and mixed homogeneously in the ball mill to prepare Mn-doped Zn$_2$SiO$_4$ phosphor[15]. This mixture were sintered at 1000°C, 1100°C, 1200°C, and 1300°C for 5h in an air atmosphere. The preparation procedure with the solid-state reaction method is shown in Fig. 1.

In all cases, the phase and crystallinity of the prepared phosphor particles were characterized using X-ray diffractometer(XRD, Sintag Model XDS 2000) with CuK $\alpha$ radiation. The particle morphology was determined in accordance with a scanning electron microscopy(SEM, Hitachi S-2500C). The photoluminescence characteristics of prepared particles were measured by a vacuum ultraviolet photoluminescence spectro-meter(VUV PL, Milton Roy 3000 Array) using a Kr lamp.

![Fig. 1] Synthesis procedure of the Mn-doped Zn$_2$SiO$_4$ phosphor particles using the solid-state reaction method.

### 3. Results and discussion

Fig. 2 shows the XRD patterns of Zn$_2$SiO$_4$ annealed at 900°C with pure ZnO and methyl hydrogen polysiloxane-treated ZnO. When the pure ZnO was used as a Zn source, the peak of the ZnO was detected, but when the methyl hydrogen polysiloxane-treated ZnO was used as a Zn source, only the pure Zn$_2$SiO$_4$'s peak was detected. Due to the effect of the dispersion and coherence of the methyl hydrogen polysiloxane-treated ZnO, only a relatively low sintering temperature was needed for the Zn$_2$SiO$_4$ crystal synthesis. Fig. 3 shows the XRD patterns of the Mn-doped Zn$_2$SiO$_4$ phosphor particles synthesized by the solid-state reaction method when sintered at 1000°C, 1100°C, 1200°C, and 1300°C using the Mn sources of MnCO$_3$ and MnO$_2$. All of the XRD analyses showed a typical Zn$_2$SiO$_4$ crystal structure.
with a 1000℃ sintering temperature. From the XRD analysis, the characteristic peaks of the dopants were not observed.

\[ \text{Fig. 2} \] XRD patterns of the Zn$_2$SiO$_2$ host material annealed at 900℃ (●:Zn$_2$SiO$_4$, ■:ZnO).
(a) pure ZnO, (b) methyl hydrogen polysiloxane-treated ZnO

\[ \text{Fig. 3} \] XRD patterns of the Zn$_2$SiO$_4$:Mn phosphor prepared with the solid-state reaction method at various sintering temperatures.
(a) MnCO$_3$ as the Mn source, (b) MnO$_2$ as the Mn source

Fig. 4 and 5 are the SEM micrographs of the Mn-doped Zn$_2$SiO$_4$ phosphor particles prepared with different MnCO$_3$ concentrations and different sintering temperatures. In Fig. 4, as the MnCO$_3$ concentration increased from 0.01 to 0.04mol, the particle size increased from 0.5 to 1.2μm. These as-prepared particles were sintered at 1000℃ for 5h. The results show that smaller particles were synthesized at a lower Mn concentration, and more agglomerated particles were synthesized at a higher Mn concentration. In Fig. 5, as the sintering temperature increased from 1000℃ to 1300℃, the particle size increased from 0.5 to 20μm.

\[ \text{Fig. 4} \] SEM micrographs of the Mn-doped Zn$_2$SiO$_4$ phosphor particles prepared using MnCO$_3$ as the Mn source at different Mn concentrations.
(a) 0.01mol, (b) 0.02mol, (c) 0.03mol, (d) 0.04mol

\[ \text{Fig. 5} \] SEM micrographs of the Mn-doped Zn$_2$SiO$_4$ phosphor particles prepared using MnCO$_3$ as the Mn source at different sintering temperatures.
(a) 1000℃, (b) 1100℃, (c) 1200℃, (d) 1300℃

Fig. 6 and 7 show the SEM micrographs of the Mn-doped Zn$_2$SiO$_4$ phosphors particle prepared with different MnO$_2$ concentrations and different sintering temperatures. In Fig. 6, as the MnO$_2$ concentration increased from 0.01 to 0.04mol, the particle size increased from 0.4 to 1.5μm. These as-prepared particles were
sintered at 1000℃ for 5h. The results show that smaller particles were synthesized at a lower Mn concentration, and more agglomerated particles were synthesized at a higher Mn concentration. In Fig. 7, as the sintering temperature increased from 1000℃ to 1300℃, the particle size increased from 0.4 to 15㎛.

Green light was emitted from these phosphor particles under VUV irradiation. Fig. 8 shows the dependence of Mn activator(MnCO₃, MnO₂) concentrations on the PL intensity for the Mn-doped Zn₂SiO₄ phosphor particles sintered at 1000℃. It was found that there were distinct differences in the PL intensity of the Mn-doped Zn₂SiO₄ phosphor particles at Mn concentrations ranging from 0.01mol to 0.03mol. The maximum PL intensity of a phosphor particle was shown at a Mn concentration of 0.02mol, and it decreased when the Mn concentration increased due to the concentration quenching effect[16].

![Fig. 7] SEM micrographs of the Mn-doped Zn₂SiO₄ phosphor particles prepared using MnO₂ as the Mn source at different sintering temperatures. (a)1000℃, (b)1100℃, (c)1200℃, (d)1300℃

![Fig. 8] PL spectra of the Mn-doped Zn₂SiO₄ particles prepared from different Mn concentrations. (a)MnCO₃ as the Mn source, (b)MnO₂ as the Mn source

![Fig. 9] PL spectra of the Mn-doped Zn₂SiO₄ particles prepared from different sintering temperatures. (a)MnCO₃ as the Mn source, (b)MnO₂ as the Mn source
The intensity of green luminescence depends highly on the sintering temperature in a range of 900℃-1300℃. With an increasing sintering temperature, the intensity of the green emission decreases and reaches a maximum at a 1000℃ sintering temperature. Fig. 9 shows these results. In addition, the PL intensity of using MnO2 as a Mn source was higher than that using MnCO3 as a Mn source. This result may be attributed to the effects of the particle size and shape of the phosphor particles.

4. Conclusion

Mn-doped Zn2SiO4 phosphor particles by a solid-state method were prepared at a relatively low temperature using methyl hydrogen polysiloxane-treated ZnO, fumed SiO2 and various Mn sources. The photoluminescent and crystalline properties of the particles were investigated as a function of the Mn source, sintering temperature and the Mn concentration. XRD results indicated that the Mn-doped Zn2SiO4 particles were successfully obtained by a solid-state method at a temperature of 1000℃, and that the phosphor particle sintered at 1200℃ for 5hr, had the highest crystallinity of Zn2SiO4. The phosphor particles prepared at 1000℃ were comparatively uniform in size at 0.5-1.0μm. With these, at a high temperature of 1300℃, large irregular particles were obtained. Due to the effect of the dispersion and coherence of the methyl hydrogen polysiloxane-treated ZnO, Mn-doped Zn2SiO4 phosphor particles were produced at lower temperatures compared to a conventional solid-state reaction method. The PL intensity decreased as the temperature increased with in the range of 1000℃ to 1300℃, and the optimal doping concentration of Mn was 0.02mol using MnCO3 and MnO2 as a Mn source. The optimal sintering temperature was 1000℃.

References


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<Research Interests>
Phosphor, Ultrasonic Spray Pyrolysis Method, Sol-gel method, Pearlescent Pigment

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