

Synthesis of Mn-doped Zn₂SiO₄ phosphor particles by solid-state method at relatively low temperature and their photoluminescence characteristics

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상대적으로 낮은 온도에서의 고상법에 의한 망간이 도핑된 Zn₂SiO₄ 형광체 입자의 제조 및 형광특성

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Abstract Mn-doped Zn₂SiO₄ phosphor particles having submicrometer sizes were synthesized by a solid-state reaction method using methyl hydrogen polysiloxane-treated ZnO, fumed SiO₂ 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 Zn₂SiO₄ particles were successfully obtained by a solid state method at 1000°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°C.

요 약 Methyl hydrogen polysiloxane으로 처리한 ZnO, fumed SiO₂와 다양한 망간 전구체를 이용하여 서브마이크로미터 크기를 갖는 망간이 도핑된 Zn₂SiO₄ 형광체 입자를 고상법으로 제조하였다. 결정화와 광발광 특성은 XRD, SEM, PL스펙트럼을 이용하여 분석하였다. 고상법으로 제조한 망간 도핑된 Zn₂SiO₄는 methyl hydrogen polysiloxane 처리한 ZnO의 분산과 응집 때문에 1000°C에서 성공적으로 얻어졌고, 진공자외선 여기하에서 제조된 입자의 최대 PL강도는 0.02mol Mn, 1000°C에서 확인되었다.

Key Words : Solid-State Reaction, Phosphor, Photoluminescence, Zn₂SiO₄

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

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diameter and narrow size distribution. Moreover, they must be non-aggregated, and have a spherical morphology for good luminescent characteristics. Mn-doped Zn₂SiO₄ 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 Zn₂SiO₄ is a well-known phosphor for its high luminescent efficiency and chemical stability. The emission of Zn₂SiO₄:Mn at 524nm is attributed to a d-level spin-forbidden transition for Mn²⁺.

Up to the present time, the commercial Mn-doped Zn₂SiO₄ 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.

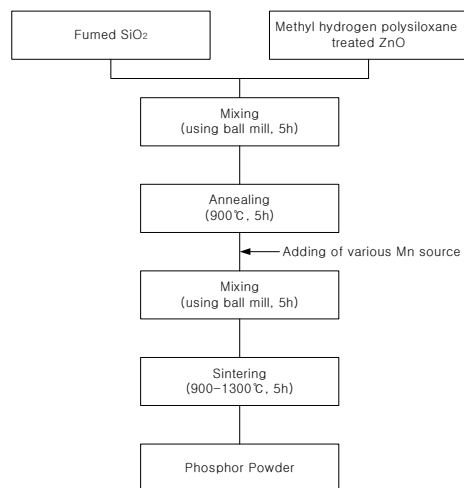
The objectives of the present study are to synthesize green-light-emitting phosphor particles with a submicron size at relatively low temperature using a solid-state reaction method, and to characterize their photoluminescent(PL) properties. The effect of different Mn sources and sintering temperatures on the PL characteristics of Mn-doped Zn₂SiO₄ phosphor particles is also investigated.

2. Experimental

Mn-doped Zn₂SiO₄ green phosphors were synthesized with a solid-state method. Fumed SiO₂ 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 Zn₂SiO₄ particles as a host material. After being reground, a respective Mn source(MnCO₃, MnO₂) was added and mixed homogeneously in the ball mill to prepare Mn-doped Zn₂SiO₄ 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 α 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.

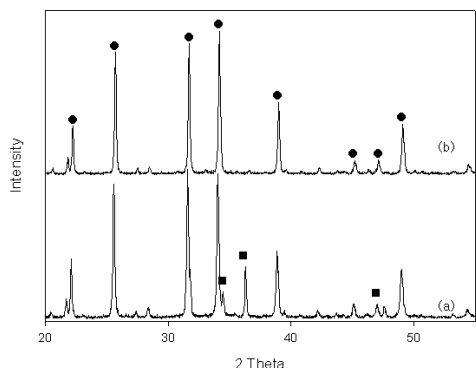


[Fig. 1] Synthesis procedure of the Mn-doped Zn₂SiO₄ phosphor particles using the solid-state reaction method.

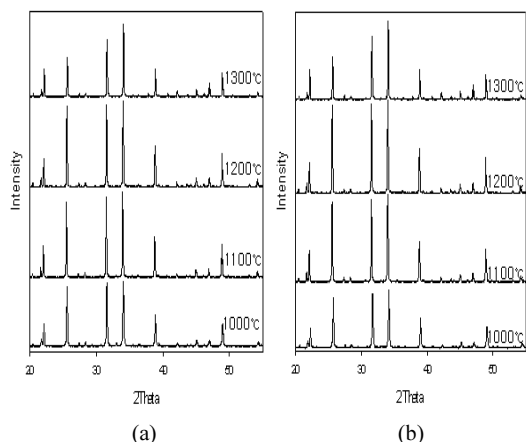
3. Results and discussion

Fig. 2 shows the XRD patterns of Zn₂SiO₄ 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 Zn₂SiO₄'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 Zn₂SiO₄ crystal synthesis. Fig. 3 shows the XRD patterns of the Mn-doped Zn₂SiO₄ 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 MnCO₃ and MnO₂. All of the XRD analyses showed a typical Zn₂SiO₄ crystal structure

with a 1000°C sintering temperature. From the XRD analysis, the characteristic peaks of the dopants were not observed.



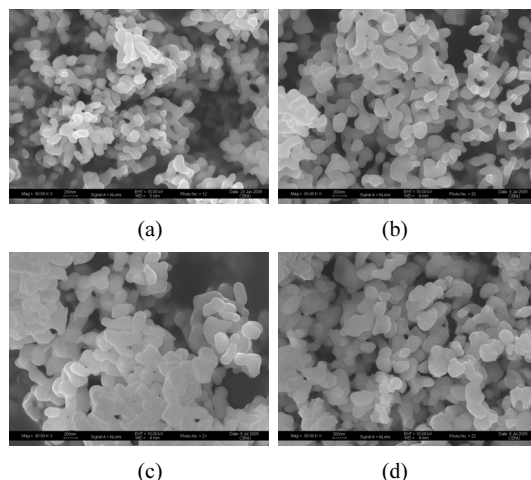
[Fig. 2] XRD patterns of the Zn_2SiO_4 host material annealed at 900°C (●: Zn_2SiO_4 , ■: ZnO). (a) pure ZnO, (b) methyl hydrogen polysiloxane-treated ZnO



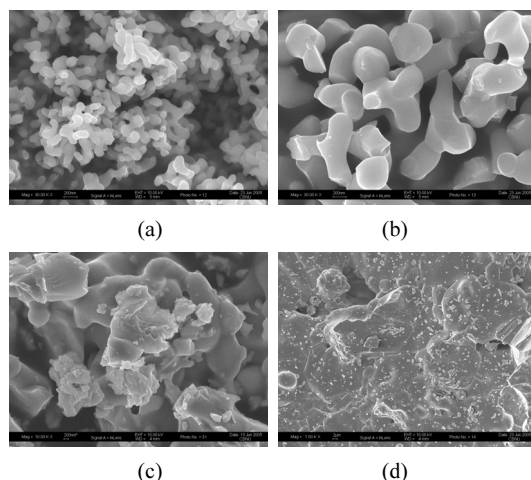
[Fig. 3] XRD patterns of the $Zn_2SiO_4:Mn$ phosphor prepared with the solid-state reaction method at various sintering temperatures. (a) $MnCO_3$ as the Mn source, (b) MnO_2 as the Mn source

Fig. 4 and 5 are the SEM micrographs of the Mn-doped Zn_2SiO_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 1.2 μm . These as-prepared particles were sintered at 1000°C 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°C to 1300°C, the particle size increased from 0.5 to 20 μm .



[Fig. 4] SEM micrographs of the Mn-doped Zn_2SiO_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

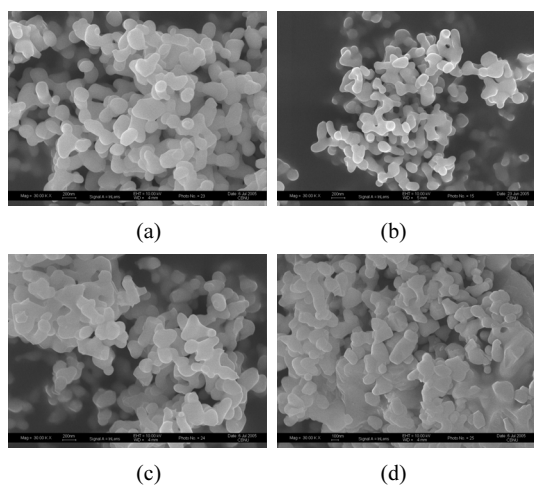


[Fig. 5] SEM micrographs of the Mn-doped Zn_2SiO_4 phosphor particles prepared using $MnCO_3$ as the Mn source at different sintering temperatures. (a) 1000°C, (b) 1100°C, (c) 1200°C, (d) 1300°C

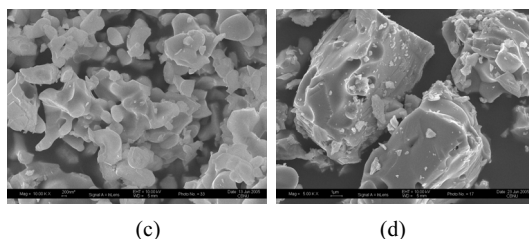
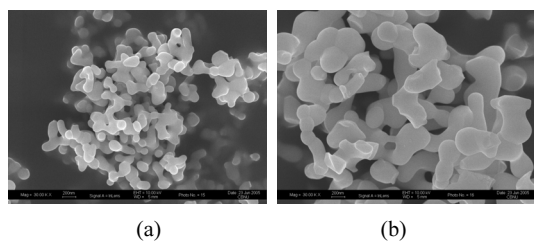
Fig. 6 and 7 show the SEM micrographs of the Mn-doped Zn_2SiO_4 phosphors particle prepared with different MnO_2 concentrations and different sintering temperatures. In Fig. 6, as the MnO_2 concentration increased from 0.01 to 0.04mol, the particle size increased from 0.4 to 1.5 μm . These as-prepared particles were

sintered at 1000°C 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°C to 1300°C , the particle size increased from 0.4 to $15\mu\text{m}$.

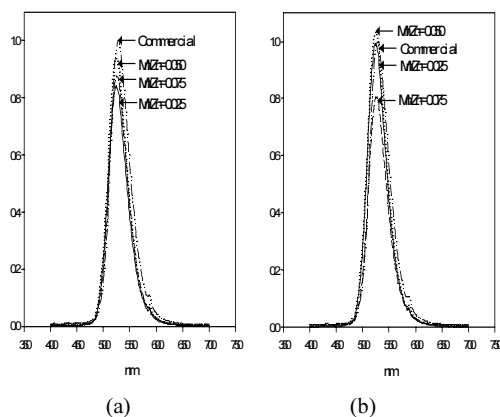
Green light was emitted from these phosphor particles under VUV irradiation. Fig. 8 shows the dependence of Mn activator ($MnCO_3$, MnO_2) concentrations on the PL intensity for the Mn-doped Zn_2SiO_4 phosphor particles sintered at 1000°C . It was found that there were distinct differences in the PL intensity of the Mn-doped Zn_2SiO_4 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].



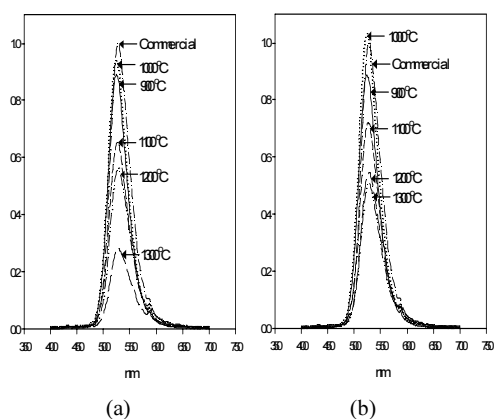
[Fig. 6] SEM micrographs of the Mn-doped Zn_2SiO_4 phosphor particles prepared using MnO_2 as the Mn source at different Mn concentrations. (a) 0.01mol , (b) 0.02mol , (c) 0.03mol , (d) 0.04mol



[Fig. 7] SEM micrographs of the Mn-doped Zn_2SiO_4 phosphor particles prepared using MnO_2 as the Mn source at different sintering temperatures. (a) 1000°C , (b) 1100°C , (c) 1200°C , (d) 1300°C



[Fig. 8] PL spectra of the Mn-doped Zn_2SiO_4 particles prepared from different Mn concentrations. (a) $MnCO_3$ as the Mn source, (b) MnO_2 as the Mn source



[Fig. 9] PL spectra of the Mn-doped Zn_2SiO_4 particles prepared from different sintering temperatures. (a) $MnCO_3$ as the Mn source, (b) MnO_2 as the Mn source

The intensity of green luminescence depends highly on the sintering temperature in a range of 900 °C-1300 °C. With an increasing sintering temperature, the intensity of the green emission decreases and reaches a maximum at a 1000 °C 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 °C, and that the phosphor particle sintered at 1200 °C for 5hr. had the highest crystallinity of Zn₂SiO₄. The phosphor particles prepared at 1000 °C were comparatively uniform in size at 0.5-1.0 μm. With these, at a high temperature of 1300 °C, 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 °C to 1300 °C, and the optimal doping concentration of Mn was 0.02mol using MnCO₃ and MnO₂ as a Mn source. The optimal sintering temperature was 1000 °C.

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