Preparation and Luminescence Properties of PDP Green Phosphors using Polymer Matrix Technique

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The Zn_2SiO_4:Mn phosphors were prepared using polymer matrix technique in order to improve the performance of green emitting phosphors for plasma display panel(PDP). Zn_2SiO_4:Mn phosphor exhibits a strong green emission around 520-530 nm. The emission intensity and particle size of powders were controlled by sintering temperature and raw material composition. The zinc silicate Zn_2SiO_4:Mn single phase were obtained at lower temperature than prepared by solid-state reaction method. PL luminance of Zn_2SiO_4:Mn phosphor was similar to the commercial material.

Keywords : Green phosphor, Zn_2SiO_4:Mn, Nanoparticles, PDP

1. INTRODUCTION

The phosphors which are used for PDP requires an emission efficiency which is appropriate for the driving conditions of the display panel and also which has a fast response time, a short decay time, and superior color purity which is stable with heat[1-4].

Zn_2SiO_4 has a willemite structure, it is known that two Zn ions are arranged in different positions in a crystal lattice, also the Mn ion can be substituted in that position creating the synthesis Zn_2SiO_4:Mn. Emission of Zn_2SiO_4: Mn is made by the Mn ion which is an activator transit $3d^5$ electrons, and because it is transited from the lowest exited state $^4T_{1g}$(4G) to the ground state $^6A_{1g}$ (^6S), its color is green. When Mn ionic concentration increases, more Mn ion substitutes Zn's position and makes a pair, so it speeds up the decay process[5-7]. C. Barthou[8] found that there are two decay processes, because of the Mn single ion and pair ion, by minimizing and maximizing its concentration. However, it was determined that further study about the decay and emission process in the range of Mn concentration ($0.05 \leq x \leq 0.11$) was required in order to determine which has the best emission efficiency, which is the reason for this study.

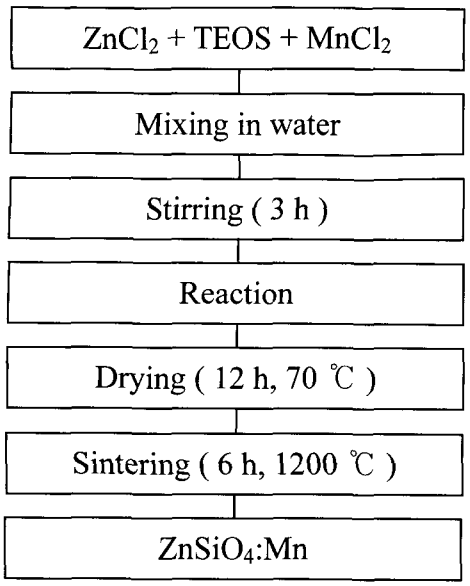
2. EXPERIMENTALS

2.1 Synthesis

It is a synthesis of three starting materials; zinc, silica, and manganese nitrates which are dissolved in water. After stirring this mixture for 6 hours with a magnetic stirrer, the solvent was impregnated with pulp. After drying this impregnated pulp in a drying oven for 6 hours, it was sintered at 1200 ℃ for 5 hours, then, put thru reduction treatment at 900 ℃ for one hour. At this time, to change all of the Mn ions to Mn^{2+}, 5 % H_2/N_2 (the gas mixture of nitrogen and a small amount of hydrogen 5 %) was used. After the reduction treatment, all the powders were white, so it was determined that when a Mn ion is in the state of oxidation, it exists as Mn^{2+}. Highly pure $Zn(NO_3)_2 \cdot 6H_2O$, Ludox HS-40, $Mn(NO_3)_2 \cdot 6H_2O$ were used as starting materials. Scheme 1 shows the general production process of Zn_2SiO_4: Mn phosphor using polymer matrix technique.

2.2 Measurements

To check the sample's crystallinity after the heat treatment, a Rigaku Company DMAX-33 X-ray diffractometer, was used to estimate the X-ray diffraction pattern. We used a PHILIPS XL 30S FEG scanning



Scheme 1. Preparation procedure of Zn_2SiO_4:Mn phosphor.

electron microscope, to see the particle size and morphology of the powder. VUV photoluminescence spectrometer with a D_2 lamp was used to see the emission characteristics of the synthesized phosphor. A SEM was used to estimate the particle size, morphology and particle size distribution of the synthesized phosphor.

3. RESULTS AND DISCUSSION

The activator of Zn_2SiO_4: Mn is the Mn, it is green in color, and the purity of the color is very superior. Zn_2SiO_4 is its host material and it has a willemite structure. The Zn and Si are surrounded by four O molecules, so it has a tetrahedral structure with Zn or Si inside[9].

Figure 1 shows an example of the X-ray diffraction analysis of the synthesized Zn_2SiO_4: Mn phosphor at various heat treatment temperatures. The ZnO peaks which did not reacted until 900 ℃ are visible. However, the non-reacted ZnO had totally disappeared at 1200 ℃ and only a single willemite phase was visible. Therefore, compared to the solid state reaction, which is heat treated at more than 1300 ℃, synthesized phosphor can be crystallized at a lower temperature, and it is also possible to see when the single phase is formed[10]. In addition, the phosphor was white, which means the Mn had reached a bivalent status.

Figure 2 comprises SEM of the Zn_2SiO_4:Mn particle prepared by polymer matrix technique at various concentrations. Generally, it is known that controlling the particle size and morphology of the phosphor has an effect on the brightness of the emission. This means that

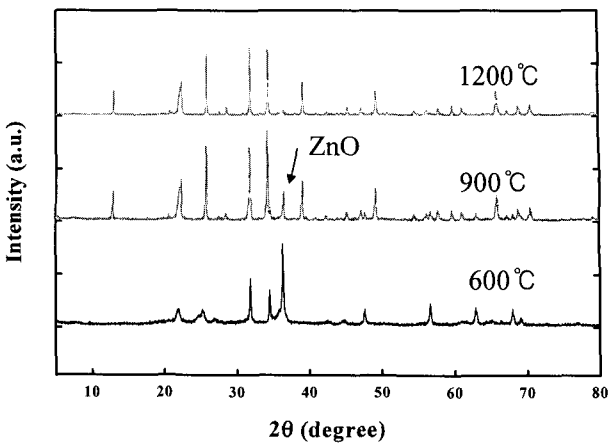


Fig. 1. XRD patterns of Zn_2SiO_4:Mn phosphors at various sintering temperatures.

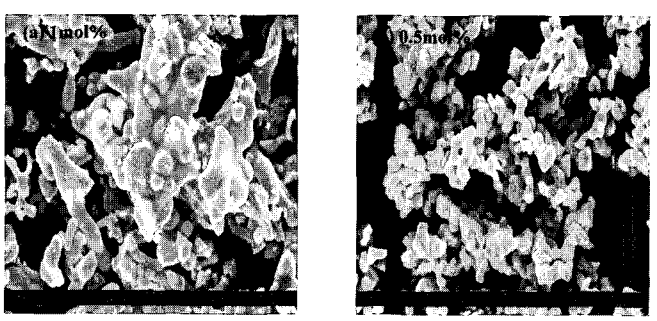


Fig. 2. SEM images of Zn_2SiO_4 doped with different Mn concentrations.

when the phosphor is in the best particle size condition, and when morphology is round, the efficiency in the quantum energy of the absorbed light energy can increase. The phosphor dopped with 0.5 mol% has a regular distribution with a regular shape. Whereas particles doped with 1 mol% Mn become aggregated and show an irregular shape.

Figure 3 shows the emission spectra according to the difference in Mn concentrations. The VUV PL characteristics were examined under the excitation of 147 nm. As a result, the phosphors emit very intensive green light with a narrow band in the wavelength range between 520 to 530 nm, and especially 0.5 mol% Mn doped Zn_2SiO_4 shows the best emission characteristics.

Figure 4 shows the emission characteristics (VUV PL characteristics) of the phosphor which was made, in Zn_2SiO_4: Mn by changing the Si concentration. As can be seen in figure, when the Si concentration is 0.3 mol, it has the best emission intensity.

Figure 5 shows the emission spectra of the green phosphor by changing the Zn concentration variously in the Zn_2SiO_4: Mn. When the Zn concentration is 1 mol, it shows the best emission intensity.

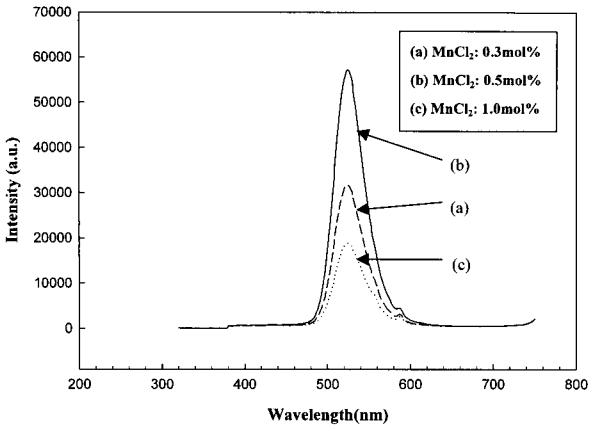


Fig. 3. PL emission spectra of Zn_2SiO_4 doped with various Mn concentrations.

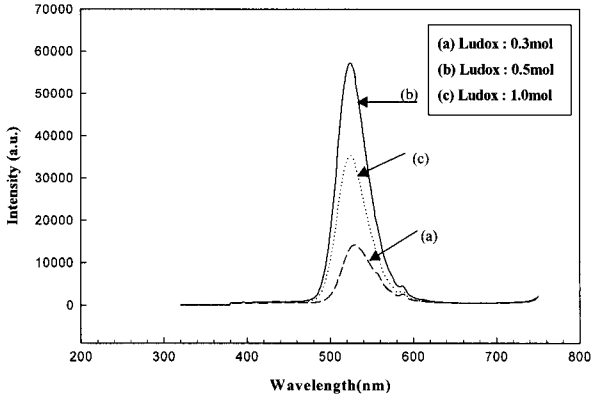


Fig. 4. PL emission spectra of Zn_2SiO_4: Mn phosphors with various Si contents.

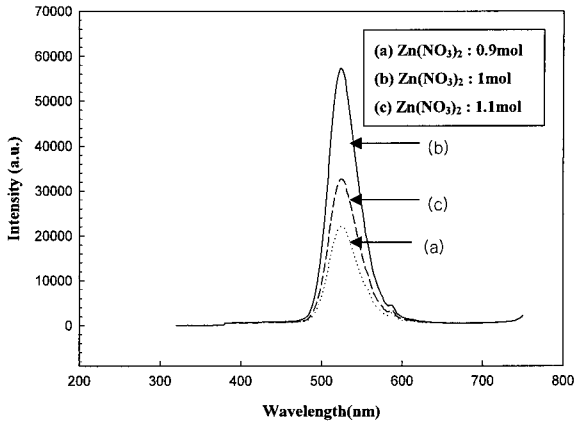


Fig. 5. PL emission spectra of Zn_2SiO_4: Mn phosphors with various Zn contents.

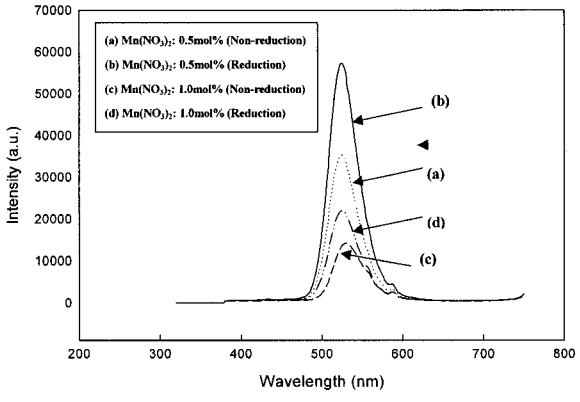


Fig. 6. PL emission spectra of Zn_2SiO_4:Mn phosphors with or without reduction.

In Fig. 6, a comparison was made to see the effect of reduction after heat treatment; two kind phosphors of Zn_2SiO_4: Mn with or without the reduction process. The differences between them were very clear. The reason is because before the reduction process, Mn is trivalent, so it is hard to substitute with Zn which is bivalent. If we perform a reduction, then because the trivalent Mn become bivalent, so it is easy to substitute with Zn.

Figure 7 shows the different emission intensities as a function of Mn concentrations. 0.5 mol% Mn doped phosphor showed the maximum emission intensity, when the concentration is higher, the emission intensity decreases.

The reason is, because of the concentration quenching effect, the emission intensity decreases. The emission of Zn_2SiO_4 phosphor is generally transited light energy without absorbing energy from the host material, so, the emission intensity is increased, usually by the best Mn concentration.

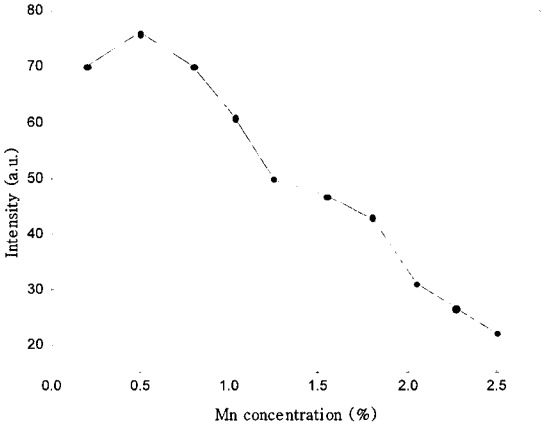


Fig. 7. PL emission intensities of Zn_2SiO_4:Mn phosphors as a function of Mn concentrations.

4. CONCLUSION

We synthesized Zn_2SiO_4:Mn green phosphor by using precursor to control the emission characteristics and particle size. Whereas the phosphors heat treated at temperatures higher than 1300 ℃ are proved to show pure willemite structure in the case of solid-state reaction

method, the polymer matrix technique the optimum phosphor powder of uniform shape with same structure when fired at lower temperature. The phosphors emit very intensive green light with a narrow band in the wavelength range between 520 to 530 nm, and especially 0.5 mol% Mn doped Zn_2SiO_4 shows the best emission characteristics. The emission intensity was maximized with Mn and Si concentrations of 0.5 mol% and 1 mol% Zn, respectively.

REFERENCES

[1] S. I. Moon, Y. Y. Shin, Y. D. Heo, Y. H. Kim, and M. S. Kong, "The phosphor for plasma display panels(in Kor.)", Chem. World, Vol. 37, No. 6, p. 26, 1997.

[2] S. Tanaka, I. Ozaki, T. Kunimoto, K. Ohmi, and H. kobayashi, "Blue emitting $CaAl_2O_4:Eu^{2+}$ phosphors for PDP application", J. Luminescence., Vol. 87-89, p. 1250, 2000.

[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. Cera. Soc., Vol. 38, No. 4, p. 337, 2001.

[4] J. I. Ahn, C. H. Han, and H. D. Park, "Luminescence properties of Zn_2SiO_4:Mn, M(M=Cr, Ti) Green phosphors prepared by sol-gel Method", J. Kor. Cera. Soc., Vol. 40, No. 7, p. 637, 2003.

[5] B. Y. Sung, C. H. Han, and H. D. Park, "Effect of pH and drying temperature on luminescent properties of Zn_2SiO_4:Mn,Al green phosphors by sol-gel technique", J. Kor. Cera. Soc., Vol. 42, No. 5, p. 333, 2005.

[6] A. Morell and N. E. Khiati, "Green phosphors for large plasma TV screens", J. Electrochem. Soc., Vol. 140, No. 7, p. 2019, 1993.

[7] Sohn, K.-S., Park, E. S., Kim, C. H., Park, H. D. J., "Photoluminescence behavior of $BaAl_{12}O_{19}$:Mn phosphor prepared by pseudocombinational chemistry method", Electrochem. Soc., Vol. 147, No. 11, p. 4368, 2000.

[8] Barthou, C., Benoit, J., Benalloul, P., Morell, A. J., "Mn^{2+} concentration effect on the optical properties of Zn_2SiO_4:Mn phosphors", Electrochem. Soc., Vol. 141, No. 2, p. 524, 1994.

[9] Stevels, A. L. N. and Vink, A. T., "Fine structure in the low temperature luminescence of $ZnSiO_4$:Mn and $Mg_4Ta_2O_9$:Mn," J. Lumin., Vol. 8, p. 443, 1974.

[10] Khistov, Tc. I., Popovich, N. V., Galaktionov, S. S., and Soshchin, N. P., "Preparation of zinc silicate luminophors by solution method", Inorg. mat., Vol. 32, No. 1, p. 80, 1996.