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Ceramics International 29 (2003) 611–618

CERAMICS INTERNATIONAL

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Preparation and characterizations of Zn_2SiO_4:Mn green phosphors

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Received 25 January 2002; received in revised form 2 September 2002; accepted 20 September 2002

Abstract

$Zn_{2-x}Mn_xSiO_4$ green phosphors were prepared with a new solution reaction method and compared with the ones prepared with the conventional solid-state reaction method. Photoluminescent and crystalline properties were examined as functions of the firing temperatures and the manganese (Mn) concentrations. The zinc silicate $Zn_{2-x}Mn_xSiO_4$ crystalline structures were obtained at 1400 °C and at 1100 °C for the samples prepared with the solid-state reaction and the solution reaction method, respectively. The maximum emission intensity of $Zn_{2-x}Mn_xSiO_4$ phosphors under vacuum ultra violet (VUV) excitation occurred at the Mn concentration of $x=0.02$. The solution-reacted phosphors were composed of small round-shaped grains which were about 0.5–1.0 μm in size, whereas, the solid-state reacted phosphors were composed of rectangular-shaped grains which were relatively large, 1–2 μm. The decay time was about 6–9 ms for both $Zn_{2-x}Mn_xSiO_4$ phosphor samples at $x=0.12$.

Keywords: Phosphors; Preparation; Photoluminescence; Solid-state reaction; Chemical preparation

1. Introduction

The manganese doped willemite $Zn_{2-x}Mn_xSiO_4$ is an efficient green phosphor widely used in plasma display panels (PDP), cathode ray tubes (CRT) and fluorescent lamps due to their high saturated color, strong luminescence and long life span. Intensive research has been carried out to improve their physical, chemical and photoluminescent properties through new synthetic processes and optimization of the host and activator species [1–5]. Phosphors with a high quantum efficiency, good color purity and proper decay time are required to achieve the high-definition color PDPs.

Up to now, the commercial Zn_2SiO_4:Mn green phosphors have been fabricated mainly with the solid-state reaction method [6]. However, the solid-state reaction method has some disadvantages such as high firing temperature and difficulties to control the particle sizes and shapes despite of simple processing. Therefore, in order to overcome these problems, new fabrication methods such as the hydrothermal [7], sol–gel [8,9] and fume pyrolysis methods [10] have been studied and produced good photoluminescence. However, there have been some difficulties to commercialize green phosphors due to the complexity of those new fabrication methods.

In this paper, we studied the optimum preparation conditions for $Zn_{2-x}Mn_xSiO_4$ phosphors prepared with the new solution reaction method and compared their properties with phosphors prepared with the conventional solid-state reaction method. The emission spectra, crystalline properties and decay time as functions of firing temperatures and activator concentrations were also investigated.

2. Experiments

$Zn_{2-x}Mn_xSiO_4$ green phosphors were prepared with two different methods. The first one is the conventional solid-state reaction method and the second one is the solution reaction method which has newly been developed in this experiment [11]. In the case of the solid-state reaction method, SiO_2 and ZnO powders were

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0272-8842/03/$30.00
doi:10.1016/S0272-8842(02)00208-0

mixed in the ball mill and fired at 800 for 4 h under an air atmosphere to prepare Zn_2SiO_4 powders as a host component. The prepared Zn_2SiO_4 powders and the $MnSO_4$ activator compound were mixed homogeneously in the ball mill to prepare $Zn_{2-x}Mn_xSiO_4$ phosphors with Mn concentrations ranging from $x=0.005$ to $x=0.20$. The mixed phosphor materials were then fired at temperatures between 1100 °C and 1400 °C for 4 h under an air atmosphere. Fig. 1 shows the flow chart of the green phosphors prepared with the solid-state reaction method.

In the case of the solution reaction method, $Zn_{2-x}Mn_xSiO_4$ precursor solution was prepared using $Zn(NO_3)_2{\cdot}6H_2O$, silicic acid and $MnSO_4$ as starting raw materials. The precursor solution was then stirred homogeneously in the flask. Subsequently, a mixture of ammonia and zinc components with the composition ratio of NH_4OH:Zn = 3:1 was added to it. After that, the prepared solution was stirred for 5 h and then the precipitated phosphors were filtered out using micro-filters. The filtered powders were dried at 50 °C in a dry oven and fired at temperatures ranging from 900 °C to 1200 °C for 4 h under an air atmosphere. The preparation procedure with the solution reaction method is shown in Fig. 2.

The crystal phases of the phosphors were identified by X-ray diffraction (XRD) analysis using CuK_α radiation and the surface morphologies were analyzed using scanning electron microscopy (SEM). The emission spectra and color coordinates were obtained using an optical spectra multichannel analyzer (OSMA) and a vacuum ultraviolet spectrometer (VM-504) under 254 nm and 147 nm excitation wavelength, respectively. The particle size distributions were analyzed by a particle size analyzer (PSA). The luminescent decay curves were also measured by a time correlated single photon counting apparatus (FL 900CD).

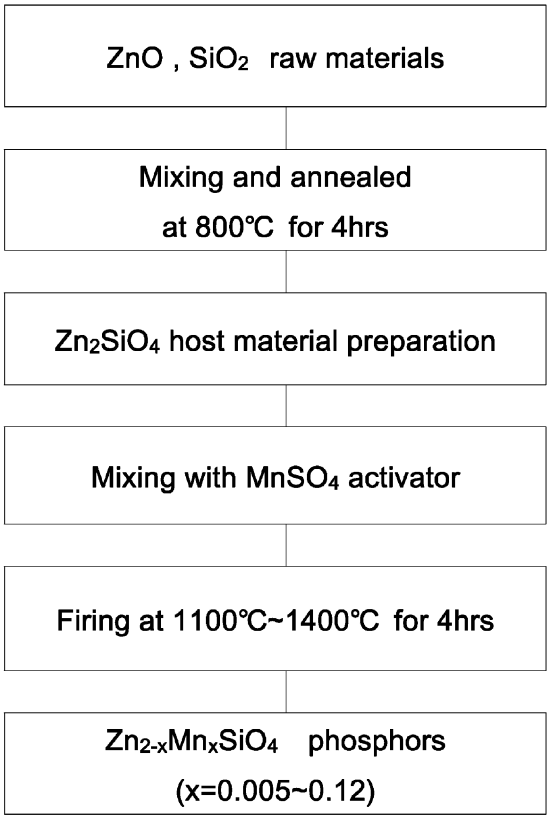

Fig. 1. Flow chart for the sample preparation of $Zn_{2-x}Mn_xSiO_4$ phosphors prepared with the solid-state reaction method.

3. Results and discussion

Fig. 3 shows the X-ray diffraction patterns for $Zn_{2-x}Mn_xSiO_4$ ($x=0.1$) phosphors prepared with the solid-state reaction method when fired at 1100 °C, 1200 °C, 1300 °C and 1400 °C. The XRD analysis showed that typical zinc silicate crystal structures appeared at a firing temperature of 1400 °C. Unreacted zincite and silica crystal phases were also detected at temperatures below 1300 °C. These unreacted phases had an effect on the emission intensities of the phosphor particles as described in Fig. 5.

Fig. 4 shows the X-ray diffraction patterns for $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors which were prepared with the solution reaction method when fired at 900 °C, 1000 °C, 1100 °C and 1200 °C. Typical zinc silicate crystal structures appeared at a firing temperature of 1200 °C, lower than the firing temperature of the solid-state reacted phosphors. Unreacted ZnO peaks were observed at around $2\theta=36°$ at temperatures below 1100 °C. The peak intensities increased with increasing firing temperatures. In order to investigate the crystallinity of the phosphors according to the firing temperatures, the FWHM (full width at half maximum) values of the main peaks were measured. The FWHM values decreased from 0.44° to 0.32° as the firing temperatures increased from 900° to 1200°. This result suggests that crystallinity can be improved with the increase of the firing temperature. XRD analyses of phosphor samples showed that good quality green phosphors can be synthesized at lower firing temperatures with the solution reaction method rather than the solid-state reaction method.

Fig. 5 shows emission intensities of $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors prepared with the solid-state and the solution reaction methods at various firing temperatures ranging from 900 °C to 1400 °C. For both samples, emission intensities increased sharply when the firing temperatures increased. Emission intensities of the solution reacted samples were increased about 9 times when increasing firing temperatures from 900 °C to 1200 °C. At lower temperatures, the decrease of emission intensities may be ascribed to the unreacted impurity phases as shown in the previous XRD analyses of Figs. 3 and 4.

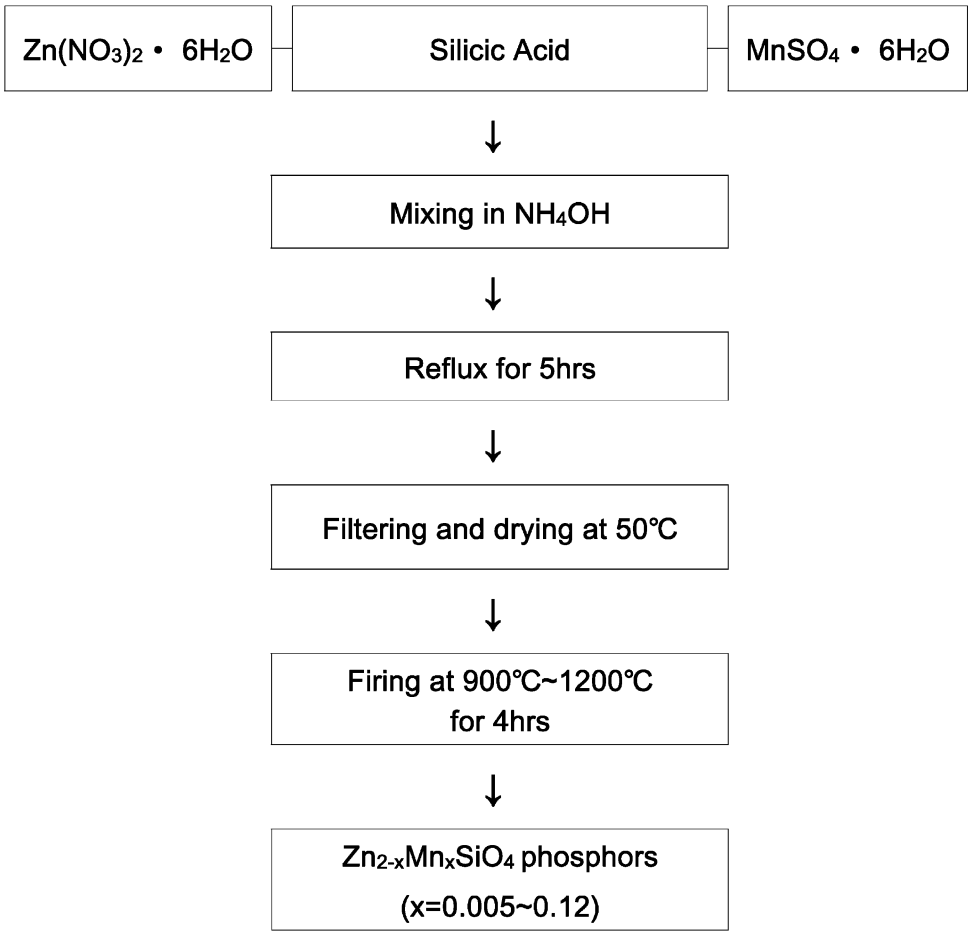

Fig. 2. Flow chart for the sample preparation of $Zn_{2-x}Mn_xSiO_4$ phosphors prepared with the solution reaction method.

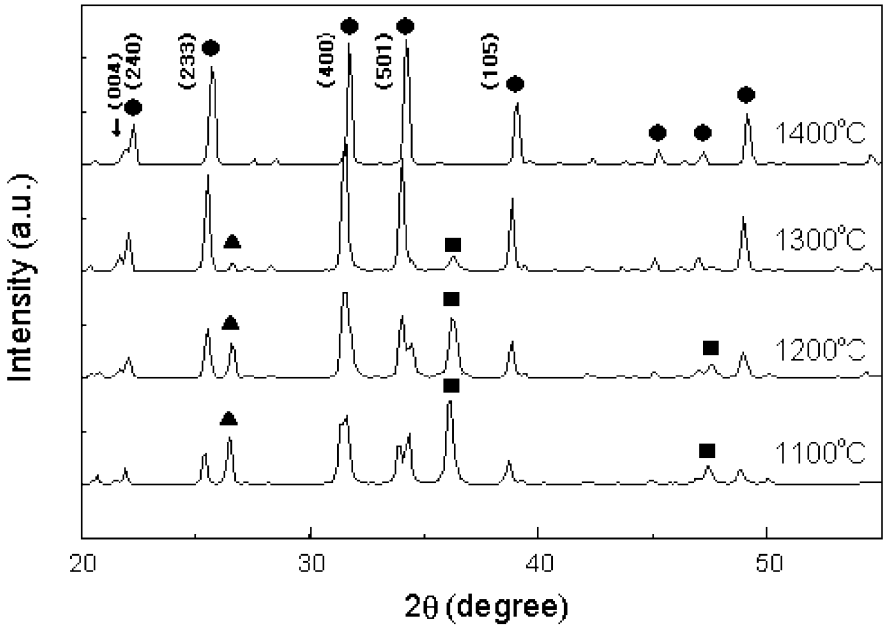

Fig. 3. X-ray diffraction patterns of $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors prepared with the solid-state reaction method as a function of the firing temperatures (●: Zn_2SiO_4, ▲: SiO_2, ■: ZnO).

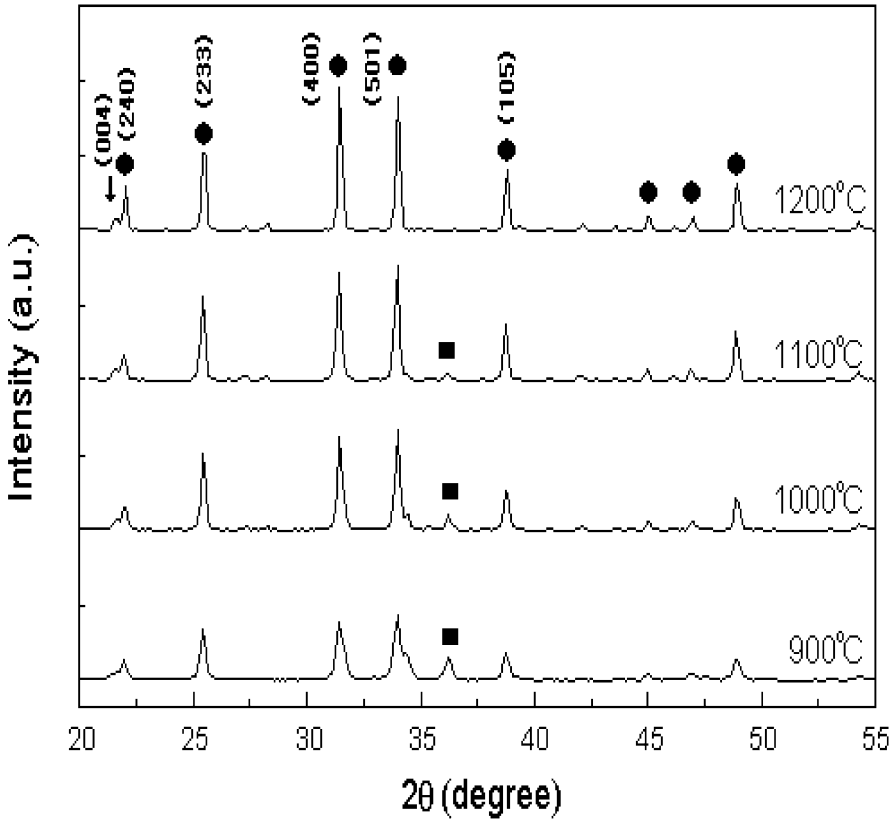

Fig. 4. X-ray diffraction patterns of $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors prepared with the solution reaction method as a function of the firing temperatures (●: Zn_2SiO_4, ■: ZnO).

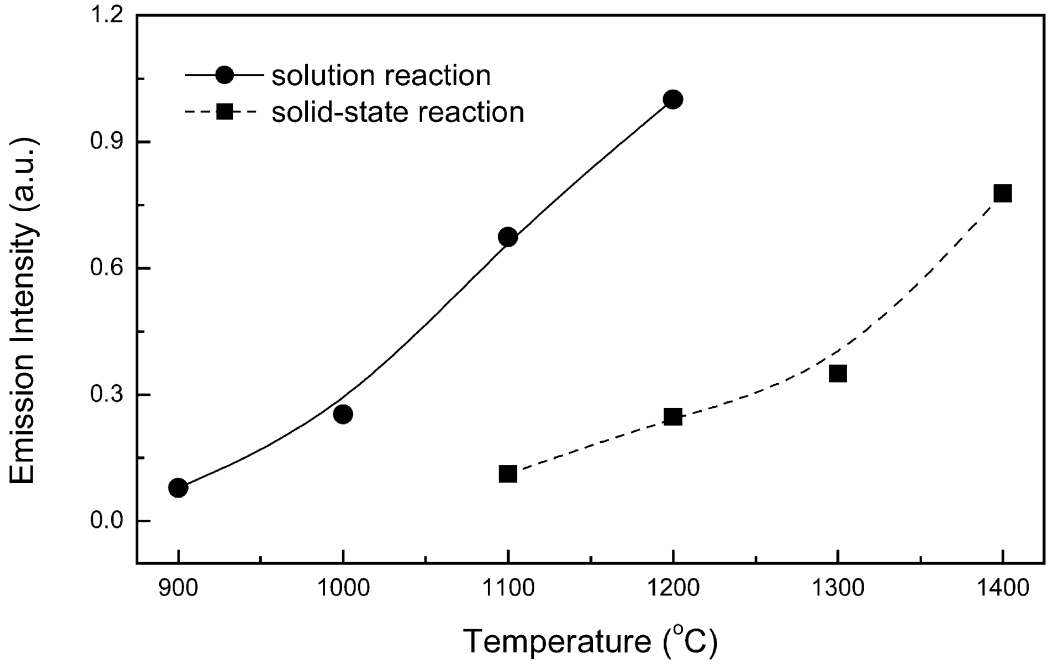

Fig. 5. Emission peak intensity of $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors prepared with the solid-state reaction and the solution reaction method as a function of the firing temperatures under 254 nm excitation.

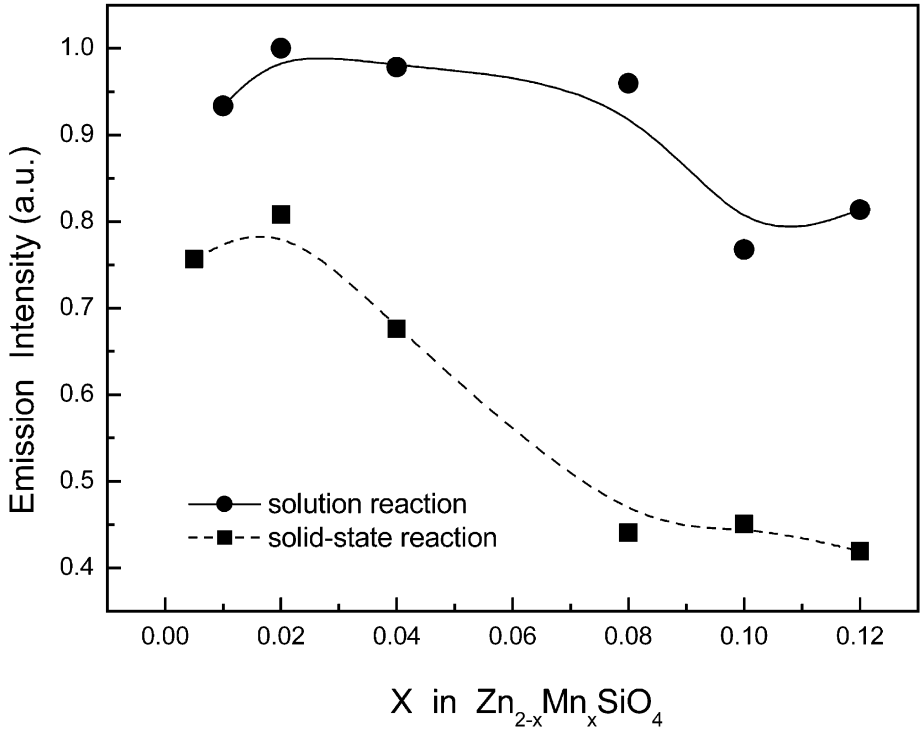

Fig. 6. Emission peak intensity of $Zn_{2-x}Mn_xSiO_4$ phosphors fired at 1400 °C with the solid-state reaction and fired at 1200 °C with the solution reaction method as a function of Mn concentrations under 147 nm excitation.

Fig. 6 shows the dependency of Mn activator concentrations on luminous intensity for $Zn_{2-x}Mn_xSiO_4$ ($x=0.005$–0.2) phosphors fired at 1200 °C in the solution reaction method and fired at 1400 °C in the solid-state reaction method. We found that there were no distinct changes in the emission intensity of $Zn_{2-x}Mn_xSiO_4$ phosphors prepared with the solution reaction method at Mn concentrations ranging from $x=0.02$ to $x=0.08$, but at the Mn concentration of $x=0.10$, emission intensity decreased slightly. It is generally believed that light energy excites the Zn_2SiO_4 phosphors luminous center, with no energy absorption from the host material (i.e. Zn_2SiO_4) [12]. Therefore, the increased emission intensity may originate mainly from optimum Mn concentrations, which play the role of luminous activator centers.

In contrast, the maximum emission intensity of phosphors prepared with the solid-state reaction was shown at a Mn concentration of $x=0.02$, and it decreased when increasing Mn concentrations at above $x=0.04$ due to the concentration quenching effect [12]. Similar behavior according to Mn concentration changes in Zn_2SiO_4:Mn phosphors under VUV were reported by Ropp [13]. The emission intensity of solution-reacted phosphors was higher than that of the solid-state reacted ones. This result may be attributed to the effects of particle size and shape in the phosphor samples.

In order to investigate these differences, SEM analysis was carried out for both samples.

Fig. 7 shows the SEM micrographs for the samples prepared at 1200 °C with the solution reaction method and at 1400 °C with the solid-state reaction method, respectively. SEM observation showed that the solution-reacted phosphors are composed of small, round shaped grains which are about 0.5–1.0 μm. Whereas, the solid-state reacted phosphors were composed of rectangular shaped grains with relatively large size of 1–2 μm.

It is generally recognized that photoluminescent properties of phosphors depend on their shape and size. Namely, the particle size and shape of the phosphors should be optimized to obtain the maximum quantum efficiency through energy absorption.

In this experiment, green phosphors prepared with the solution reaction method showed relatively better results concerning size and shape. The small, round shaped phosphor particles had higher emission intensity than the large, rectangular shaped ones as shown in Figs. 6 and 7. These results are attributed to higher quantum efficiency obtained through the suppression of incident light scattering and large bulk density in a small specific surface area of the round and small particle phosphors as reported by Matsuoka et al. [14]. In addition, the FWHM values of the phosphors synthesized by the solid-state reaction could be decreased by the larger particle size effect according to the Scherrer Formula [15], which might result in the improvement of crystallinity of phosphors. However, the emission

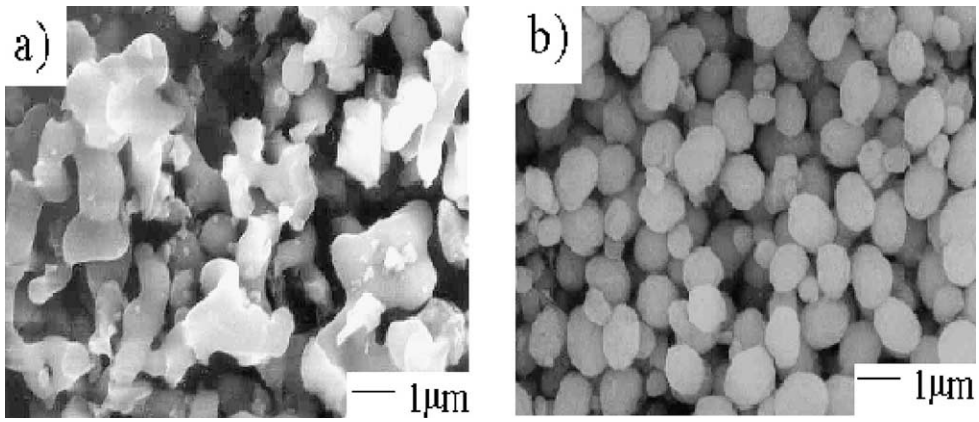

Fig. 7. SEM micrographs of $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors prepared with the (a) solid-state reaction method (1400 °C) and the (b) solution reaction method (1200 °C).

intensity of the solid-state reaction phosphors showed a low value compared with the phosphors prepared with the solution reaction method as shown in Fig. 5. At present, it is difficult to describe the reason why higher crystallinity phosphors prepared with the solid-state reaction (1400 °C) showed a low emission intensity. Perhaps, the emission intensity of the phosphors is greatly affected by the particle shape and size distribution rather than by the crystallinity determined by FWHM values in the XRD analyses.

Fig. 8 shows the particle size distributions for phosphor samples prepared at 1200 °C with the solution reaction method and at 1400 °C with the solid-state reaction method. The solution-reacted phosphors of an average 0.8 μm showed better uniformity than those prepared with the solid-state reaction. In the samples prepared with the solid-state reaction, there was a small amount of large size particles, above 2 μm.

The color purity of $Zn_{2-x}Mn_xSiO_4$ ($x=0.005$–0.2) phosphors as a function of Mn concentration is shown in Fig. 9. The color purity improved from 63% to 72% as the Mn concentrations increased from $x=0.01$ to $x=0.12$ for the samples prepared with the solution reaction method. The color purity increased drastically up to a Mn concentration of $x=0.04$ and saturated after that point. Similar result was also reported by

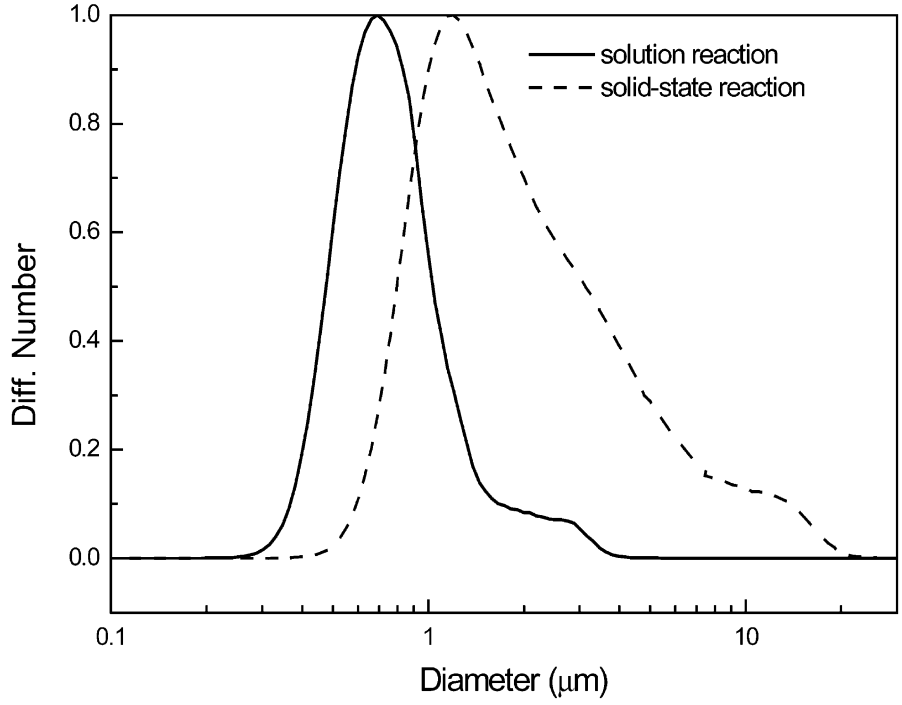

Fig. 8. Particle size distribution curves of $Zn_{2-x}Mn_xSiO_4$ ($x=0.08$) phosphors prepared with the solid-state reaction method fired at 1400 °C (dot line) and the solution reaction method fired at 1200 °C (solid line).

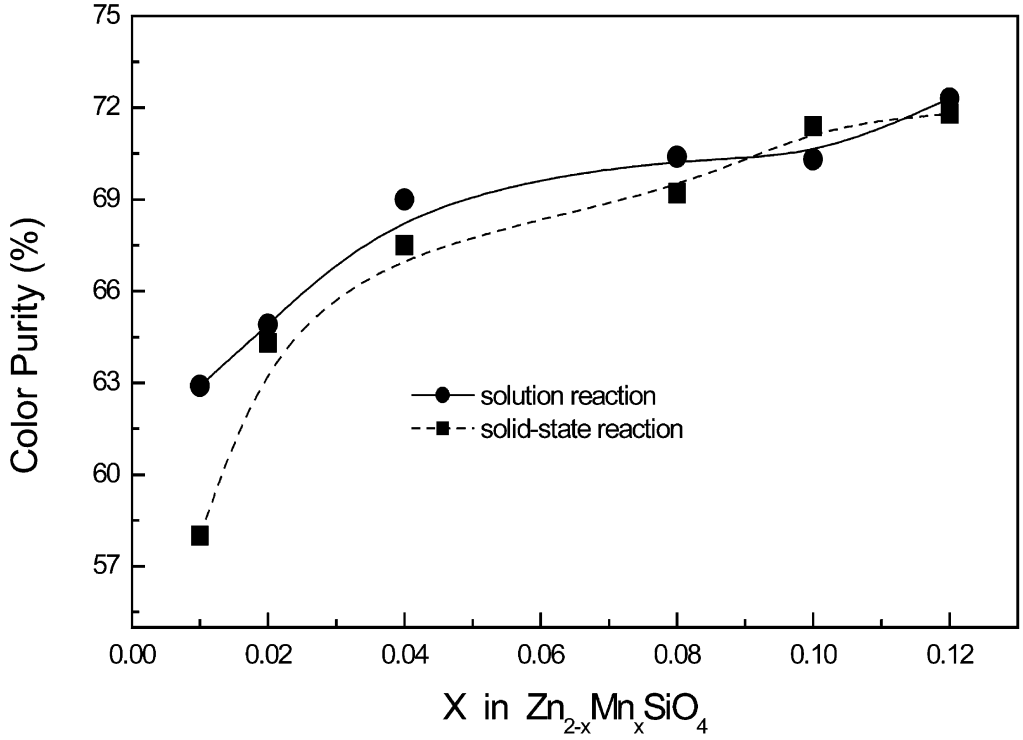

Fig. 9. Color purity of $Zn_{2-x}Mn_xSiO_4$ phosphors prepared with the solid-state reaction (1400 °C) and with the solution reaction method (1200 °C) as a function of Mn concentrations.

Morell et al. [1], in which the color purity of $Zn_{2-x}Mn_xSiO_4$ green phosphors was improved by increasing Mn concentrations up to $x=0.05$. That phosphors doped with the Mn concentrations ranging from $x=0.001$ to $x=0.12$ were highly saturated in the color coordinators. As a result of this experiment, it was shown that color purity was improved by increasing Mn concentration, although the emission intensity decreased at the Mn concentration of above $x=0.02$. Consequently, this suggests that there is no direct

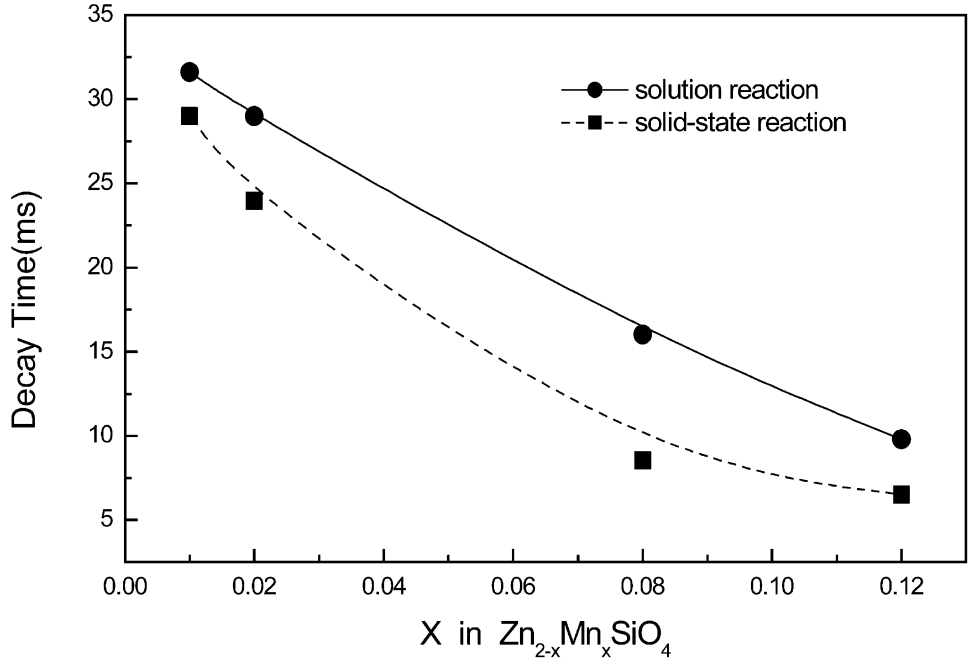

Fig. 10. Decay time of $Zn_{2-x}Mn_xSiO_4$ phosphors prepared with the solid-state reaction (1400 °C) and with the solution reaction method (1200 °C) as a function of Mn concentrations.

relation between the color purity and the emission intensity of the phosphors. Further works would be needed to clarify this result.

Fig. 10 shows the decay time curves for the phosphor samples prepared at 1200 °C with the solution reaction method and at 1400 °C with the solid-state reaction method as a function of Mn concentrations. The decay time corresponds to the time necessary to reach 10% of the maximum of the intensity after the switching off the excitation. The decay time of the solid-state reacted phosphors was slightly shorter than that of the solution-reacted samples. The decay times for both were about 6–9 ms at the Mn concentration of $x = 0.12$. The obtained decay time is suitable for the full color of display device applications. The decay mechanism is not entirely clear. Morell et al. [1] have reported that the decay time may be decreased if there are more de-excited centers which transit to ground state very quickly.

4. Conclusions

$Zn_{2-x}Mn_xSiO_4$ green phosphors were prepared with both the new developed solution reaction method and the conventional solid-state reaction method, and their various properties were compared. The photoluminescent and crystalline properties were investigated as functions of the firing temperatures and manganese concentrations ($x = 0.005$–0.2). Phosphor samples prepared with the solution reaction method that showed better uniformity in particle size than those prepared with the solid-state reaction method. The solution-reacted phosphors are composed of small round shaped grains, about 0.5–1.0 μm in size. On the other hand, the phosphors prepared with the solid-state reaction have a relatively large grain size of 1–2 μm and are rectangular in shape. The emission intensity of the solution-reacted phosphors was higher than that the solid-state reacted ones. From SEM and PSA analysis, it can be concluded that the higher emission intensity in the solution-reacted phosphors may come from the small particle size, their good uniformity and round shape. The firing temperature can be lowered at 1200 °C when the $Zn_{2-x}Mn_xSiO_4$ phosphors are prepared with the solution reaction instead of the solid-state one. The decay time is 6–9 ms for both samples at the Mn concentration of $x = 0.12$.

Acknowledgements

The present research was conducted by the research fund of Dankook University in 2001.

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