

Effects of Water Content in an Ethanol-based Solvent on Sol-gel Synthesis of $Zn_2SiO_4:Mn$ Phosphors

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The effects of initial water content in an ethanol-based solvent during a sol-gel synthesis of $Zn_2SiO_4:Mn$ green-emitting phosphor were studied. The emission intensity and the decay time of the $Zn_{2-x}Mn_xSiO_4$ phosphor were measured according to the different initial water contents in two different precursor combinations. The single-phase formation of the host lattice, the suppression of the residual second phase, emission efficiency, and decay time were studied by changing the initial water content in the ethanol-based solvent during sol-gel synthesis of the $Zn_{2-x}Mn_xSiO_4$ phosphors.

Keywords: phosphor, sol-gel, $Zn_2SiO_4:Mn$

1. INTRODUCTION

$Zn_2SiO_4:Mn$ could be an efficient green-light-emitting phosphor for plasma display panels (PDP) due to its high photoluminescence efficiency and chemical stability. However, it requires a further decrease in decay time before it can be used in real-world PDP green pixel applications.^[1-5] Other blue-light-emitting phosphors for PDP application have been also reported.^[6,7]

The authors previously reported on a simple ethanol-based sol-gel synthesis of nanocrystalline $Zn_2SiO_4:Mn$ phosphor instead of the traditional high-temperature, solid-state reaction with a micron-sized phosphor.^[8] The sol-gel process is considered to be a very flexible low-temperature process for synthesizing nanosized materials.^[9] This process allows the desired composition and a high degree of uniformity to be obtained easily. In the authors' subsequent study,^[10] the effects of zinc and manganese precursors for the sol-gel route were reported. It was found that combinations of zinc acetate and manganese chloride, and combinations of zinc nitrate and manganese acetate, showed the two strongest emission spectra.^[10] In these two studies,^[8,10] only ethanol was used as a solvent, and all processes were carried out in a simple air environment, requiring no further reducing heat treatment.

This paper reports on the results of an ongoing study on the effects of water content in an ethanol-based solvent for the sol-gel route. The initial water content in the solvent was varied. The following five sets of solvents with different water contents were chosen: ethanol 200 ml, ethanol 150 ml

and H₂O 50 ml, ethanol 100 ml and H₂O 100 ml, ethanol 50 ml and H₂O 150 ml, and only H₂O 200 ml.

2. EXPERIMENT

Two sets of combinations of precursors, which showed the strongest emission results from the authors' previous study, were chosen.^[10] One was zinc acetate with manganese chloride, and the other was zinc nitrate with manganese acetate. The initial manganese composition was set to produce a final composition of $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors for each precursor combination.^[10] Fixed molar amounts of zinc precursor and tetraethoxysilane (TEOS) were dissolved in an ethanol-based solvent and stirred for 30 min at room temperature. The manganese precursor and deionized water were then added to the solution, and the solution was stirred an additional 30 min. Finally, NH₄OH was added to the solution to change its initial pH to 11, as in the authors' previous studies.^[8,10] The final solution was dried in air at 60°C for 20 h and transformed into dried amorphous gel powder. The gel powder was fired at 1000°C in air for 1 hr to induce crystallization.

X-ray diffraction (XRD, PANalytical X'Pert PRO) was used to identify the crystalline phases of the sol-gel-synthesized $Zn_2SiO_4:Mn$ phosphors. FE-SEM (Hitachi S-4300) was used to observe the phosphor powder. The photoluminescence spectra were measured using a fluorescence spectrometer (Hitachi F-4500) with a 150 W monochromatized Xe lamp.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the sol-gel-derived

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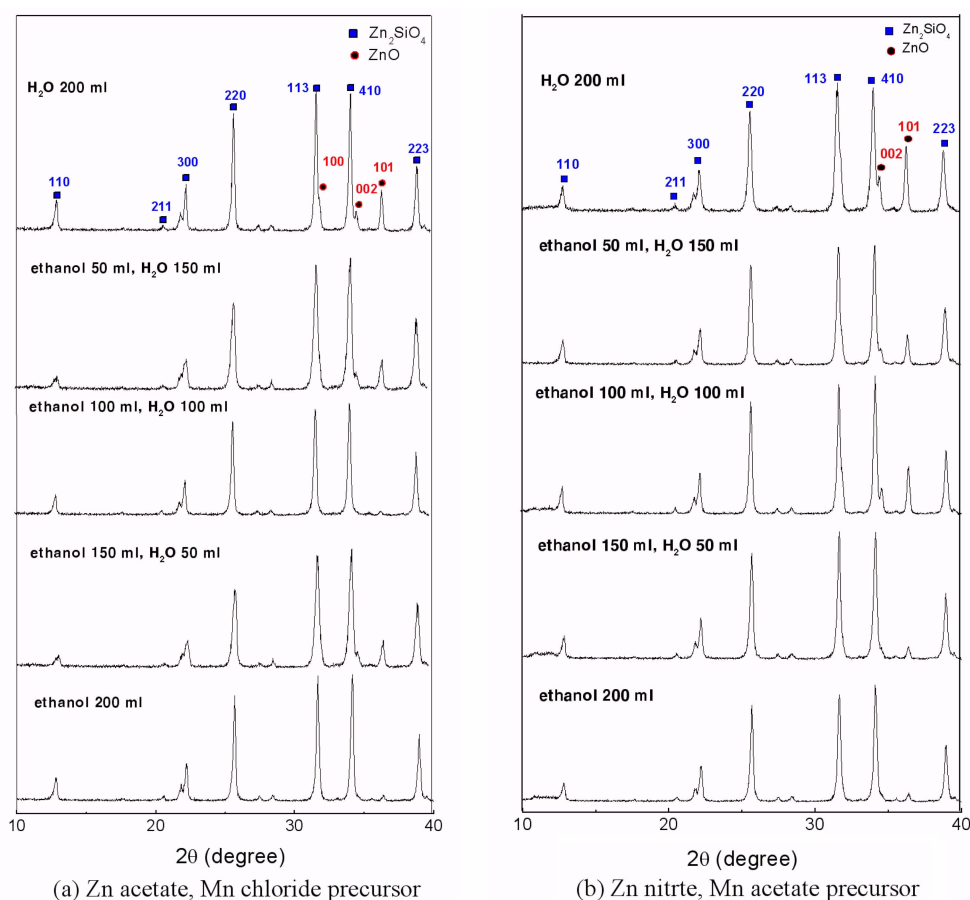


Fig. 1. XRD patterns of sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors with different water contents for the two precursor combinations, (a) zinc acetate and manganese chloride and (b) zinc nitrate and manganese acetate.

$Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors prepared from the ethanol-based solvents with a different initial water content for (a) zinc acetate and manganese chloride precursors and (b) zinc nitrate and manganese acetate precursors. These two combinations of zinc and manganese precursors were chosen because they showed the highest emission intensity in a

previous study.^[10] However, only ethanol was used as the solvent in that study. As shown in Fig. 1, the formation of a residual ZnO phase could be suppressed by controlling the water content in the water-mixed ethanol solvent.

Figure 2 shows FE-SEM images of the sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors fired at 1000°C with dif-

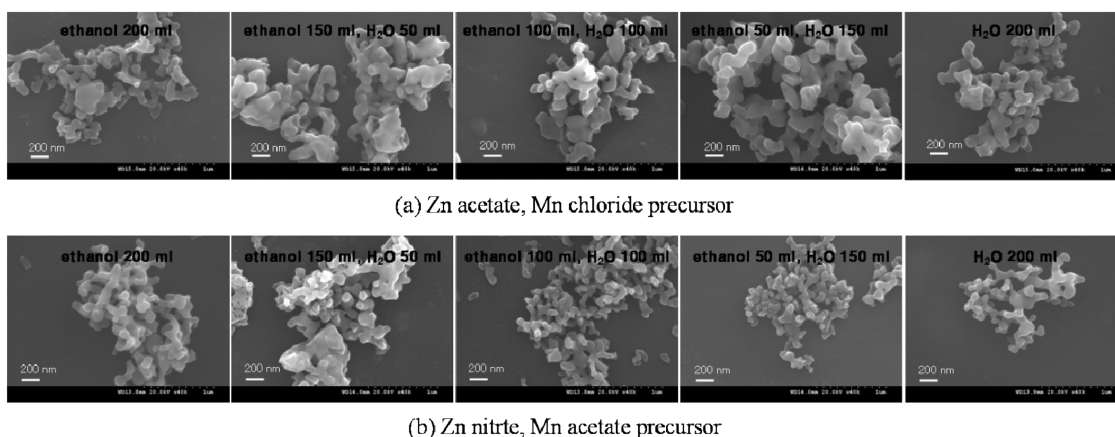


Fig. 2. FE-SEM images of the sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors with different water contents for the two precursor combinations, (a) zinc acetate and manganese chloride and (b) zinc nitrate and manganese acetate.

ferent water contents for the two combinations of precursors, (a) and (b). The images show nanosized $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors between 100 nm and 200 nm in size with an almost spherical or rounded shape.

Figure 3 shows the green emission spectra of the sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors produced in ethanol solvents with different water contents that were excited by 254 nm UV for the two different combinations of precursors. For precursor combination (a), zinc acetate and manganese chloride, the strongest emission band came from the sample produced in ethanol 100 ml and water 100 ml solvent, which also showed the strongest suppression of the residual ZnO phase, as shown in Fig. 1(a). In addition, the intensity was higher than that obtained from the ethanol-only solvent. Therefore, the intensity of $Zn_{2-x}Mn_xSiO_4$ phosphor can be increased by controlling the water content in the ethanol-based solvent while maintaining the suppression of residual ZnO formation. For precursor combination (b), zinc nitrate and manganese acetate, the strongest emission came from the ethanol 150 ml and water 50 ml solvent, which also showed strong suppression of residual ZnO formation, and a higher increased intensity than that of the phosphors produced from the ethanol-only solvent. Therefore, the intensity of the $Zn_{2-x}Mn_xSiO_4$ phosphor can be increased by controlling the water content in the ethanol-based solvent while maintaining the single-phase formation of the $Zn_{2-x}Mn_xSiO_4$ willemite structure.

Figure 4 shows the excitation spectra of the same $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors, focusing on the 524 nm emission shown in Fig. 3, which resulted from a charge transfer mechanism.^[11] The tendency of the relative excita-

tion intensity is similar to that of the emission intensity, as shown in Fig. 3. The strongest excitation band corresponds to the strongest emission sample in Fig. 3.

Figure 5 shows the photoluminescence decay curves of the sol-gel-synthesized $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors with different water contents in the ethanol-based solvent for the two different precursor combinations, (a) and (b). The decay curves represent the phosphorescence lifetimes. The decay time τ was simply measured at the position where the intensity was decreased by $1/e$ of the initial intensity. For precursor combination (a), zinc acetate and manganese chloride in Fig. 5(a), the decay time from the strongest intensity in Fig. 3(a) showed a longer decay time than the phosphors produced in the ethanol-only solvent.

However, for the precursor combination (b) zinc nitrate and manganese acetate in Fig. 5(b), the decay time was decreased to 31 ms for the phosphors produced in the ethanol 100ml and water 100 ml solvent from the 43 ms observed in the phosphors produced in the ethanol-only solvent. These results show that the water-mixed condition produces the strongest emission intensity in Fig. 3(b). In addition, the zinc nitrate and manganese acetate combination has the strongest emission intensity of the six different precursor combinations and the same decay time of 43 ms according to the authors' previous study.

Therefore, the increasing emission intensity and decreasing decay time of the $Zn_{2-x}Mn_xSiO_4$ phosphor synthesized through an ethanol-based sol-gel route can be obtained simultaneously by selecting the appropriate precursor combination and by controlling the water content in the ethanol-based solvent.

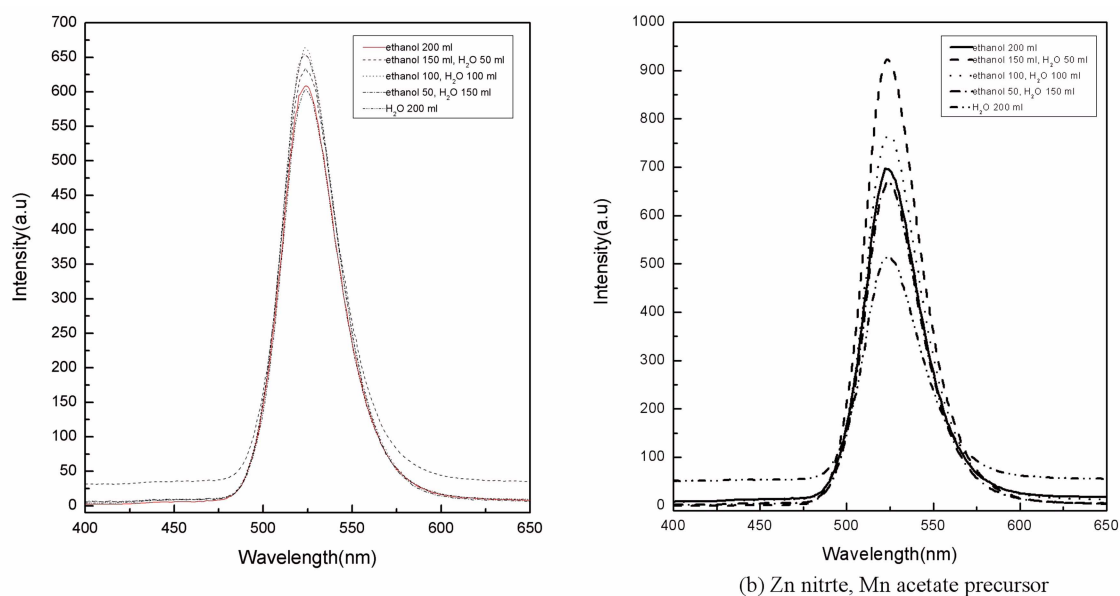


Fig. 3. Emission spectra excited by 254 nm of the sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors with different water contents for the two precursor combinations, (a) zinc acetate and manganese chloride and (b) zinc nitrate and manganese acetate.

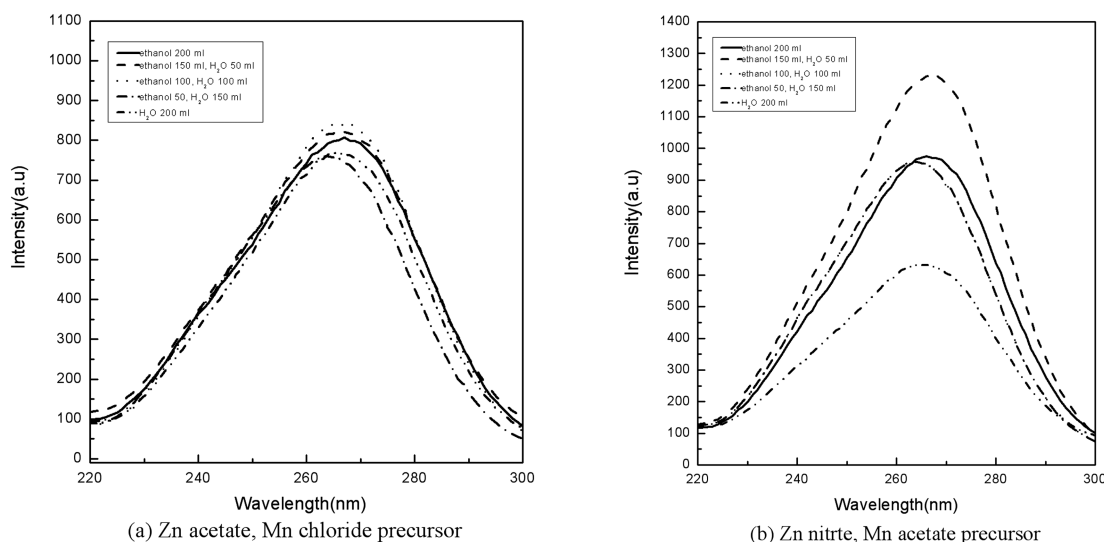


Fig. 4. Excitation spectra of the sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors with different water contents for the two precursor combinations, (a) zinc acetate and manganese chloride and (b) zinc nitrate and manganese acetate. (Emission wavelength was 524 nm.)

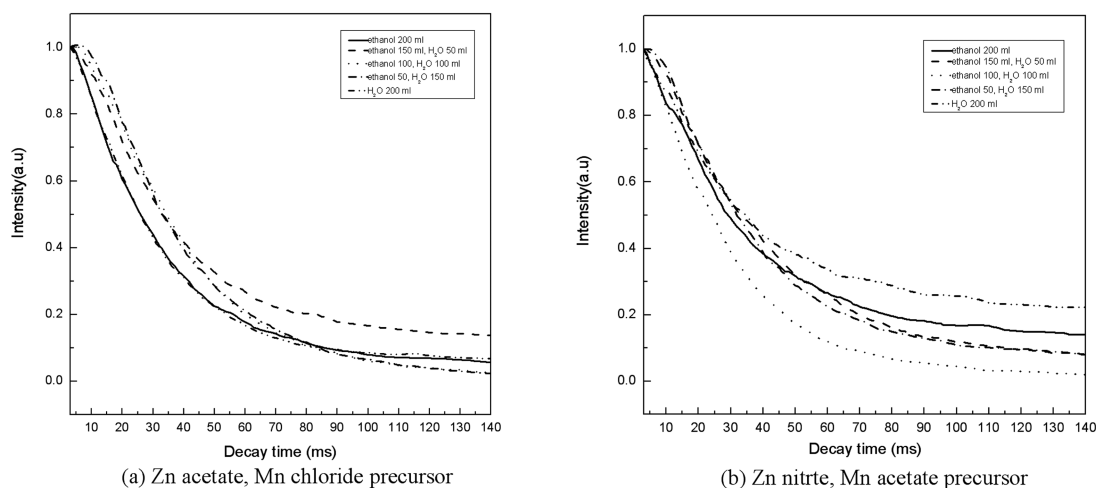


Fig. 5. Photoluminescence decay curves of sol-gel-derived $Zn_{2-x}Mn_xSiO_4$ ($x = 0.04$) phosphors with different water contents for the two precursor combinations, (a) zinc acetate and manganese chloride and (b) zinc nitrate and manganese acetate.

4. CONCLUSION

The effects of initial water content on phosphor synthesis in an ethanol-based solvent were studied. The emission intensity and the decay time of a $Zn_{2-x}Mn_xSiO_4$ phosphor synthesized through an ethanol-based sol-gel route can be optimized by selecting the appropriate precursor combination and by controlling the water content in the solvent. The single-phase formation of the host lattice, the suppression of the residual second phase, emission efficiency, and decay time can be altered by controlling the water content in the solvent during the sol-gel synthesis of $Zn_{2-x}Mn_xSiO_4$ phosphors.

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