

A Novel Synthetic Route for Green-emitting $Zn_{2-x}Mn_xSiO_4$ Phosphor using Colloidal Silica

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The Mn^{2+} -doped Zn_2SiO_4 phosphor has been used as a luminescent material for lamp and plasma panel display because of its high-luminescent efficiency and chemical stability.¹ The emission of the $Zn_{2-x}Mn_xSiO_4$ at 520 nm is attributed to d-level spin-forbidden transition for Mn(II).²⁻³ According to the earlier literatures, the photoluminescence (PL) process of $Zn_{2-x}Mn_xSiO_4$ phosphors has been characterized by the transition of $3d^5$ electrons in the manganese ion acting as an activation center in the willemite structure. In particular, the transition from the lowest excited state to the ground state, i.e. ${}^4T_1(4G) \rightarrow {}^6A_1(6S)$ transition, is directly responsible for the green light emission.^{4,5}

In the synthesis of $Zn_{2-x}Mn_xSiO_4$, the solid state reaction is difficult to control the distribution of the doped metal ions and the morphology of the particles, and avoid the aggregation of the willemite (rhombohedral structure R3) particles.⁶ In order to overcome these problems, many methods for preparation of the $Zn_{2-x}Mn_xSiO_4$ have been proposed, such as sol-gel method,⁷ polymer precursor method,⁸ spray pyrolysis method,⁹ and hydrothermal method.¹⁰⁻¹³ Especially, sol-gel technique offers several processing advantages over many material production methods, mainly due to purity, homogeneity, lower calcining temperature.^{14,15} In the syntheses of $Zn_{2-x}Mn_xSiO_4$ using sol-gel method, tetraethyl orthosilicate (TEOS) is generally used as a Si-source. However, the reagent has some problems such as organic pollutants and complicated process including hydrolysis step.

In this paper, we present a novel method for preparation of $Zn_{2-x}Mn_xSiO_4$ using a colloidal silica suspension. It is generally accepted that the negative ionic charge is developed on the surface of silica above about pH 7, and nearly zero charge below about pH 2.¹⁶ At low pH where there is little surface charge, the silica surface is covered by a monolayer of hydrogen-bonded water molecules to form silanol. In case that water-soluble polar organic molecules are present, they compete with water for the silanol surface.¹⁶ In sol-gel method using the citric acid, the citric acid molecule loses 3 protons from the three carboxyl groups, which results in the citrate anion. This citrate anions can chelate metal cations like as the interaction between citric acid and colloidal silica. This is the reason why we use colloidal silica solution instead of TEOS for the preparation of $Zn_{2-x}Mn_xSiO_4$, the green-emitting phosphor.

We fabricate $Zn_{2-x}Mn_xSiO_4$ using colloidal silica solution and characterize our samples by various methods, such as X-Ray

Diffraction (XRD), Scanning Electron Microscopy (SEM), and PL measurements.

Experimental Section

$Zn_{2-x}Mn_xSiO_4$ ($x = 0.08$) powders were prepared by sol-gel method using citric acid. The stoichiometric amounts of $Zn(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot xH_2O$ were dissolved in citric acid solution, and then the pH of solutions was adjusted to be 1~2. Subsequently, the colloidal silica (LUDOX AM-30) was dropped into the solution at a rate of approximately 1 mL/min under violent agitation. The transparent sol was gradually changed into the dark-gray powders during the heating on a hot plate at 150 °C. The obtained dark-gray powder was treated for 6 h at temperatures between 800 °C and 1200 °C in the air, and finally all samples were reduced at 800 °C for 4h under the mixture of nitrogen (96%) and hydrogen (4%). For structural refinements, XRD with Cu K α radiation was used (Shimadzu XRD-6000 model). The morphology of phosphor particles was observed by the Scanning Electron Microscopy (SEM) using a Hitachi S-4200 under $V_{acc.} \approx 15$ kV. Specimens for electron microscope were coated with Pt-Rh on carbon tape for 90 s under vacuum. For PL measurements, Fluorometer with a xenon flash lamp was used (Shimadzu RF-5301PC model).

Result and Discussion

Figure 1 shows the XRD patterns of samples treated at temperatures between 800 °C and 1200 °C for 6 h. As shown in Figure 1, the pure willemite phase, Zn_2SiO_4 is formed even at 800 °C, which is comparable to the crystallization temperature of Zn_2SiO_4 , about 1300 °C at solid-state reaction. It should be mentioned that a colloidal silica as a Si-source is effective one in the fine particle synthetic route. In case that water-soluble polar organic molecules are present, they compete with water for the silanol surface. The adsorption onto the silica surface (Si_3OH) involves the relative proportion of hydrocarbon to polar atoms in the molecule.¹⁶ As a citric acid molecule has the three carboxyl groups, it is the CO groups in a citric acid molecule that interacts with the silica surface. Colloidal silica plays an important role in a sol-gel process through the adsorption onto the silica surface. As clearly mentioned above, our interpretation

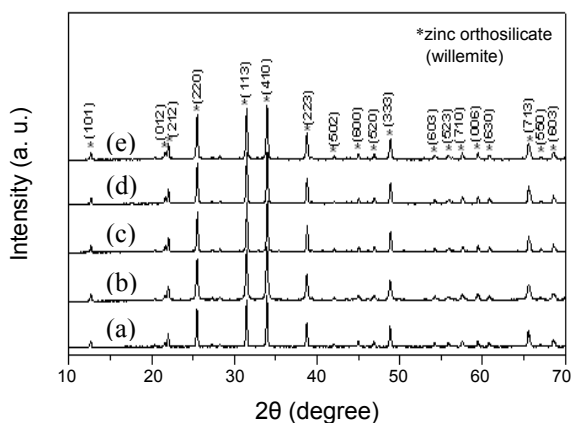


Figure 1. Powder X-ray diffraction patterns of the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ synthesized at various temperature: (a) commercial, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1200 °C.

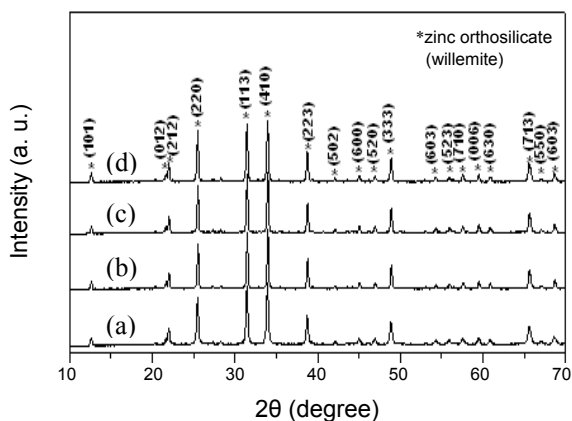


Figure 2. Powder X-ray diffraction patterns of the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ synthesized at 1000 °C as a function of silica contents : (a) commercial, (b) colloidal silica no excess, (c) colloidal silica 10% excess, and (d) colloidal silica 20% excess.

is based on the formation of pure single phase, Zn_2SiO_4 even at a very low temperature of 800 °C.

Figure 2 shows the X-ray diffraction patterns of $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ powders synthesized at 1000 °C as a function of Si contents. As shown in Figure 2, the XRD patterns are agreed well with the standard Zn_2SiO_4 (JCPDS card no. 37-1485) regardless of Si contents within the resolution limits of X-ray diffractometer.

We investigated the size and morphology of the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ particles using SEM. Figure 3 shows the SEM photographs of the samples prepared at different temperature between 800 °C and 1200 °C. The mean sizes of particles prepared at 800 °C, 900 °C, and 1000 °C are approximately 100 nm, 300 nm, and 400 nm, respectively. The particles prepared at 900 °C exhibit only a weak edge-connection of grains with pseudo-spherical shape. With increasing synthetic temperature from 900 °C to 1000 °C, the particles exhibit a more enhanced edge-connection of grains. Moreover, the particles prepared at 1200 °C are most severely agglomerated with irregular-faceted surfaces. Figure 4 shows the SEM images of Zn_2SiO_4 particle prepared as a function of Si contents. The SEM images reveal that the

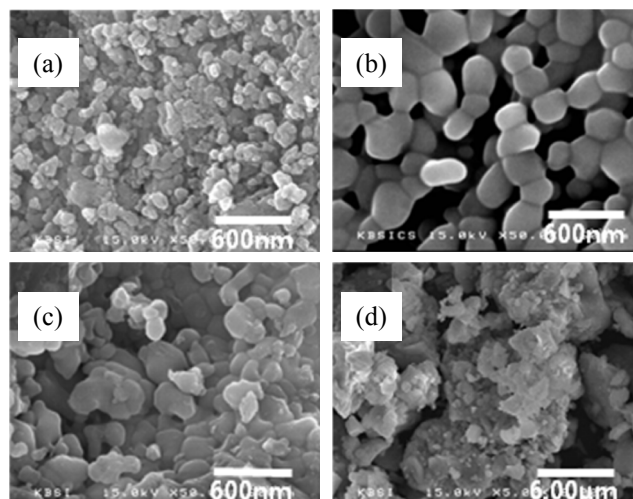


Figure 3. SEM photographs of the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ synthesized at various temperature: (a) 800 °C ($\times 50$ K), (b) 900 °C ($\times 50$ K), (c) 1000 °C ($\times 50$ K), and (d) 1200 °C ($\times 5$ k).

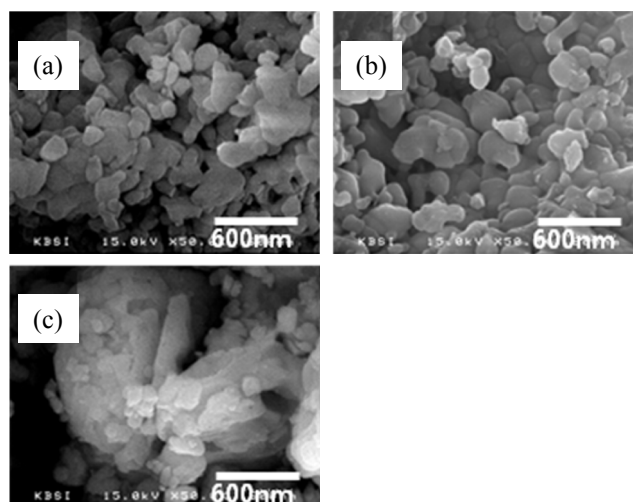


Figure 4. SEM photographs of the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ synthesized at 1000 °C as a function of silica contents : (a) colloidal silica no excess, (b) colloidal silica 10% excess, and (c) colloidal silica 20% excess.

particles are more slightly agglomerated as Si content is increased. Especially, the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ particles are more agglomerated in case of 20% excess of colloidal silica.

It is generally accepted that the green emission centered at 520 nm is due to the presence of Mn^{2+} ions, which strongly depends on the coordination in host lattice.^{2,15} Mn^{2+} has d^5 configuration with high spin ($S = 5/2$). The emission band is assigned to transitions between the spin-orbit components of the ${}^4\text{T}_1$ excited state and the ${}^6\text{A}_1$ ground state.^{2,15,17,18} Figure 5 shows the PL spectra of $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ prepared at different temperature between 800 °C and 1200 °C. All emission spectra were obtained under 254 nm excitation. The PL spectra show that the PL intensity of the $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ phosphor increases as the synthetic temperature increases.¹⁹ It should be mentioned that the degree of the crystallization of $\text{Zn}_{1.92}\text{Mn}_{0.08}\text{SiO}_4$ phosphor is increased as the synthetic temperature rises up. Moreover, the

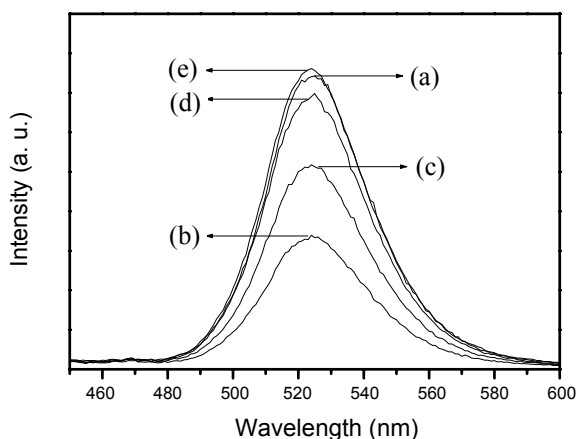


Figure 5. PL emission spectra of the $Zn_{1.92}Mn_{0.08}SiO_4$ synthesized at various temperature: (a) commercial, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1200 °C.

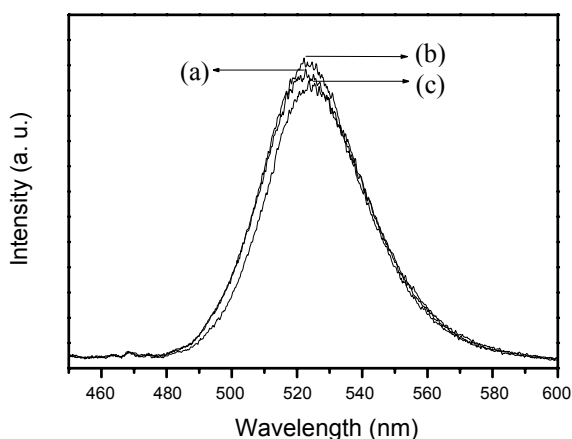


Figure 6. PL emission spectra of the $Zn_{1.92}Mn_{0.08}SiO_4$ synthesized at 1000 °C as a function of silica contents: (a) colloidal silica no excess, (b) colloidal silica 10% excess, and (c) colloidal silica 20% excess.

PL intensity of $Zn_{1.92}Mn_{0.08}SiO_4$ prepared at 1200 °C is remarkable compared to that of the commercial $Zn_2SiO_4:Mn$ (Kasei company, Japan). Figure 6 indicates the variation of PL intensity for $Zn_{1.92}Mn_{0.08}SiO_4$ as a function of colloidal silica content. As shown Figure 6, the excess Si contents in $Zn_{1.92}Mn_{0.08}SiO_4$ phosphors do not induces a considerable change in PL intensity, but a considerable modification in the agglomeration of particles.

As mentioned above, we use a colloidal silica (LUDOX AM-30, solid wt. 30%) instead of TEOS for the preparation of green-emitting $Zn_{1.92}Mn_{0.08}SiO_4$ phosphors. The successful performance of our work has been verified by means of XRD, SEM, and PL measurements on $Zn_{1.92}Mn_{0.08}SiO_4$ phosphors prepared using a colloidal silica.

Conclusions

We have synthesized Mn-doped Zn_2SiO_4 phosphors by sol-gel method using colloidal silica. The adsorption characteristics of the citric acid molecules onto the silica surfaces enables us to use colloidal silica as a Si-source instead of TEOS which is generally utilized for the fine particle synthesis of the silicate based compounds. At a very low temperature (800 °C), we could obtain the single phase of Zn_2SiO_4 , which is remarkable compared to that of the solid state reaction (about 1300 °C). The mean size of particles prepared at 800 °C, 900 °C, and 1000 °C is 100 nm, 200 nm, and 400 nm, respectively. The PL intensity of $Zn_{1.92}Mn_{0.08}SiO_4$ prepared at different temperature between 800 °C and 1200 °C, increases as the synthetic temperature rises up. Moreover, the PL intensity of $Zn_{1.92}Mn_{0.08}SiO_4$ prepared at 1200 °C is remarkable compared to that of the commercial $Zn_2SiO_4:Mn$ (Kasei company, Japan). The PL intensity for $Zn_{1.92}Mn_{0.08}SiO_4$ as a function of colloidal silica content, do not induces a considerable change in PL intensity, but a considerable modification in the morphology of particles.

It might be said that colloidal silica is a promising chemical as a Si-source for the synthesis of fine particle of silicate compounds, instead of TEOS.

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