

Synthesis of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ using SiOx as an oxidation inhibitor

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A $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor was synthesized using SiOx as an antioxidizing reagent of Mn^{2+} . The phosphor was efficiently excited by near UV light in a range of 220 - 350 nm, and emitted a green light around 525 nm. The sample showed green emission about 1.2 times higher than that of the one synthesized by a conventional solid state reaction method.

Key words: Phosphor, SiOx, $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$.

Introduction

Manganese-doped zinc silicates are well known as green phosphors for high luminescent efficiency and chemical stability [1-2]. $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ has been widely used as a green phosphor in plasma display panels (PDPs), cathode ray tubes (CRTs) and fluorescent lamps [3-13]. Commercial phosphors such as P1 and P39 have been known to be very efficient green light emitters for lamp and CRT application. The photoluminescence process of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ has been characterized by the transition of $3d^5$ electrons in the manganese ion acting as an activating center [14-16]. Under the UV excitation at 254 nm, the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor shows a bright green emission peak located at 525 nm. The emission band at 525 nm is due to the spin-forbidden ${}^4\text{T}_1({}^4\text{G})$ - ${}^6\text{A}_1({}^6\text{S})$ transition of the $3d^5$ electronic configuration of isolated Mn^{2+} [17-18]. This phosphor has a strong excitation band in the wavelength range of 200 - 280 nm. Accordingly, $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ is a very promising phosphor for various applications. The Mn ion can take multivalent states such as divalent, trivalent and tetravalent. When Mn is doped into the willemite Zn_2SiO_4 lattice, the Mn ion substitutes predominantly for a Zn site surrounded with four oxygens in divalent state and shows green emission. Accordingly, only divalent Mn ions are required for $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ to emit green light. However, there is a possibility for the Mn^{2+} to be oxidized to Mn^{4+} , when the sample is synthesized by firing in air [19-20]. When $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ is fired in reducing atmosphere, however, the phosphor is decomposed and Zn component is volatilized. The emission intensity of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ could be improved when the doped Mn is stabilized in divalent state. Therefore, we focus on the use of SiOx

as an antioxidizing reagent to keep the Mn ions in divalent state. SiOx ($x = 1.2$ - 1.6) can work as a reducing material. Actually, emission intensity of the silicate phosphor such as $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ was improved by using SiOx, and it was found that SiOx had the potential to suppress the oxidation of Mn^{2+} to Mn^{4+} and Mn^{3+} [21].

In this study, we report synthesis of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ using SiOx as an oxidation inhibitor. The $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor synthesized using SiOx showed intense green emission than that of the sample synthesized by the conventional solid state reaction method.

Experimental

The samples were synthesized by a solid state reaction method. The starting materials were ZnO (Kojundo Chemical, Laboratory Co. Ltd. 4N), SiO_2 (Wako Pure Chemical, Ltd. 3N) and MnCO_3 (Kojundo Chemical, Laboratory Co. Ltd. 3N). The materials were stoichiometrically weighed out and then mixed by wet-blending in acetone. The mixture was then fired in alumina boats at 1200 °C in air. After calcination, SiOx powder (Shin-Etsu Chemical Co., Ltd. KSO-9013) was added in several concentrations to the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ sample obtained above, and then mixed by dry-blending. Finally, the mixture was fired in alumina boats at 1200 °C in air.

The crystal phase of the synthesized powder was identified by X-ray powder diffraction (MX-Labo; Mac Science, Ltd.) operating at 40 kV and 25 mA using Cu $\text{K}\alpha$ radiation. The data were collected at a step-scanning mode in the 2θ range of 10 - 70 degrees with a 0.02 degree step width. The luminescence spectra were measured at room temperature using a fluorescent spectrophotometer (FP-6500; Jasco Inc.) equipped with a 150 W Xenon lamp. The phosphors were observed with a scanning electron microscope (JEOL JMS-5310LV).

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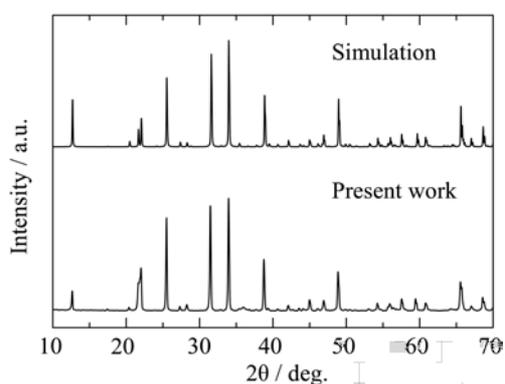


Fig. 1. The XRD pattern of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor synthesized by the novel method using SiO_x . A simulated pattern calculated from the structural data of ICSD is also shown as a reference.

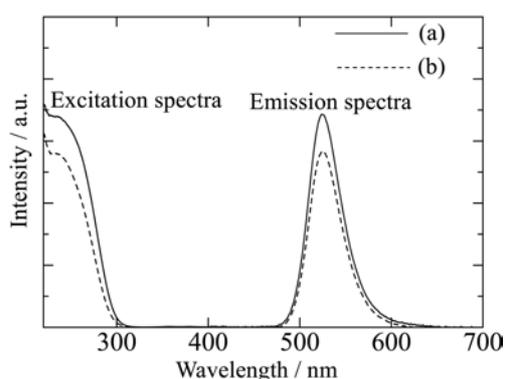


Fig. 2. The excitation and emission spectra of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors synthesized by the novel method using SiO_x (a) and the conventional method (b).

Result and Discussion

Fig. 1 shows the XRD pattern of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor synthesized by the novel method using SiO_x as a reducing agent. A simulated pattern of the same phosphor was calculated from the structural data of ICSD (Inorganic Crystal Structure Data base). All the diffraction peaks of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ sample were in agreement with those of the ICSD data (No.16172) for the standard reference, and it revealed that the sample was obtained in a single phase form without any impurities.

The excitation and emission spectra of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors synthesized by the novel method using SiO_x and by the conventional method at room temperature are shown in Fig. 2. These phosphors were excited by the UV light in the range of 220 - 300 nm, and emitted at around 525 nm. The emission band at 525 nm is attributed to the spin-forbidden ${}^4\text{T}_1\text{-}{}^6\text{A}_1$ transition of the $3d^5$ electronic configuration of isolated Mn^{2+} . The relative emission intensity of the phosphor synthesized using SiO_x was about 120% of that of the same phosphor synthesized by the conventional solid state reaction method. It is considered that SiO contained in the SiO_x powder plays the role of the oxidation inhibitor in the present process.

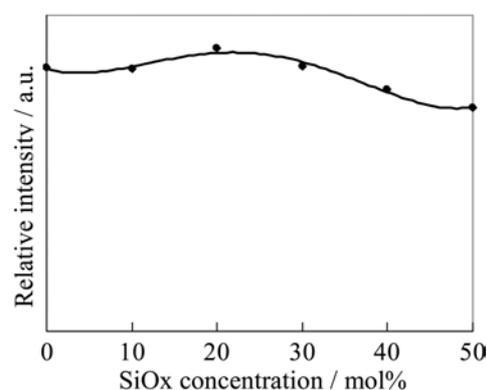


Fig. 3. SiO_x concentration dependence on the emission intensity of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ synthesized by the novel method using SiO_x .

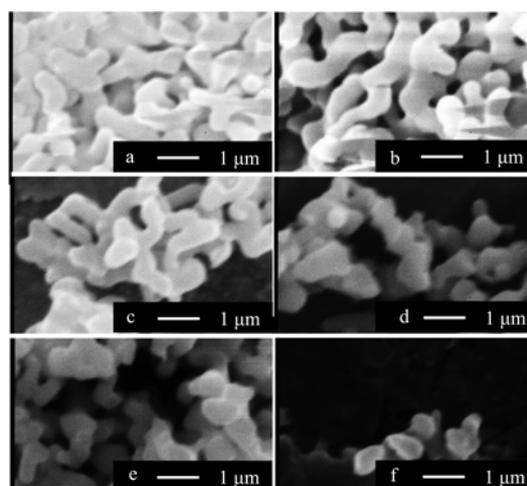


Fig. 4. SEM images of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors synthesized by the conventional method (a) and the novel method using SiO_x in different concentrations (b: 0.1, c: 0.2, d: 0.3, e: 0.4, and f: 0.5 mol% SiO_x).

Fig. 3 describes the SiO_x concentration dependence on the green emission intensity of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor. When the SiO_x concentration was greater than 20 mol%, the green emission intensity gradually diminished. Therefore, the optimum SiO_x concentration is 20 mol%. Excessive amount of SiO_x induced the deviation from the stoichiometric composition of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, and as a result, the green emission intensity was decreased. On the contrary, addition of an appropriate amount of SiO_x , which works as an antioxidantizing reagent, gives a positive effect to increase the green emission intensity.

Fig. 4 shows an SEM images of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphors synthesized by the conventional method and the present novel method using SiO_x . The average particle size of these samples was about 0.5 - 1.0 μm and the morphology was spherical shape. When SiO_x was added to $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, particle growth was not recognized. This indicates that there was no flux effect for SiO_x to grow the grain size. Therefore, it is considered that SiO_x worked as an oxidation inhibitor of Mn^{2+} in the Zn_2SiO_4 matrix, and as a result, the emission intensity of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ was improved. Also,

it is expected that SiOx can be used as a promising oxidation inhibitor for the synthesis of various silicate phosphors such as $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ and $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$.

Conclusions

We synthesized a green-emitting silicate phosphor, $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$, using SiOx as an antioxidative reagent. The sample emitted green light about 1.2 times higher than that of the same $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor synthesized by the conventional process. It has been elucidated that synthesis of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ using SiOx as an oxidation inhibitor is an effective technique. This method using SiOx will be a good technique for the synthesis of several silicate phosphors.

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