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Synthesis of high efficiency Zn_2SiO_4:Mn^{2+} green phosphors using nano-particles

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Abstract

In this study, Zn_2SiO_4:Mn^{2+} luminescent phosphors were prepared by mixing nano-scale ZnO, SiO_2, and MnO_2 particles at the compositions corresponding to $2ZnO + SiO_2 + X$ mol% MnO_2 (Zn_2SiO_4–X-MnO_2, $0.02 \leq X \leq 0.05$). The mixing powders were calcined from 900 °C to 1300 °C in air and in N_2 atmosphere. No matter calcined in air or in N_2 atmosphere, Zn_2SiO_4 was the mainly crystalline phase in particles calcined at 900 °C and was the only phase in particles calcined at 1000 °C and higher. The influences of MnO_2 concentration and calcining atmosphere and temperature on wavelength of luminescence peak and the emission intensity were further intensively investigated. We would show that the calcining atmosphere had no apparent influences on the physical and photoluminescence (PL) characteristics of Zn_2SiO_4:Mn^{2+} phosphors. The MnO_2 content and the calcining temperature were the main reasons to influence the physical and PL characteristics of Zn_2SiO_4:Mn^{2+} phosphors.

Keywords: A. Sintering; C. Optical properties; Nanostructures; Photoluminescence spectroscopy

1. Introduction

In order to realize improved display devices having higher emission efficiency and finer resolution, it is essential to develop fine fluorescent materials that exhibit a high level of luminescence in a stable manner. Zn_2SiO_4:Mn^{2+} particles are well-known phosphors that can be used in plasma displays [1]. Numerous studies had focused on developing chemical reaction methods to prepare highly efficient Zn_2SiO_4:Mn^{2+} phosphors [2–6]. Taghavinia et al. used porous silicon as one of the starting materials and impregnated porous silicon layers with luminescent Zn_2SiO_4:Mn^{2+} particles [2]. Porous silicon was directly involved in the reaction responsible for the formation of luminescent Zn_2SiO_4:Mn^{2+} phosphors. The phosphor particles were obtained inside a transparent porous body, making it possible to activate porous silicon layers with highly efficient phosphors [2]. Kang and Park used the colloidal solution method to fabricate spherical Zn_2SiO_4:Mn^{2+} phosphors with an optimal emission intensity that was 112% that of commercially available materials [5]. Although these chemical methods can be applied to produce fine particles with good luminescence, they have the shortcomings related to complex processing, difficulties in achieving controllability and mass production, and high cost [7–9].

At present, the solid-state reaction method is the most established method used in the mass production of Zn_2SiO_4:Mn^{2+} phosphors. In the past, the Zn_2SiO_4:Mn^{2+} particles were calcined in reducing (N_2) atmosphere to make Zn_2SiO_4:Mn^{2+} phosphors with stronger emission intensities and longer decay times because of the increase of energy transfer effect. The shortcomings of using this method are: (1) it is difficult to process ZnO and SiO_2 for obtaining Zn_2SiO_4 compounds and (2) $MnCO_3$ or MnO_2 are hard to dope into these compounds. Recently, technologies used to process nano-particles have been improved and costs associated with the production of nano-particles have been reduced. In this study, nano-scale ZnO, SiO_2, and MnO_2 particles are used as precursors and solid-reaction process is used to prepare green Zn_2SiO_4:Mn^{2+} phosphors. The photoluminescence (PL) characteristics are investigated and compared with those of the commercially available Nichia's Zn_2SiO_4:Mn^{2+} phosphors. Regardless of the calcinations are carried out in air or in a N_2

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atmosphere, the $Zn_2SiO_4:Mn^{2+}$ phosphors calcined at 1300 °C exhibit PL characteristics and decay times that are superior to those of commercial product fabricated by Nichia Corporation. We will prove that the calcining atmosphere is not an important factor but the dopant content of MnO_2 and the calcining temperatures are the most important factors to influence the PL characteristics of $Zn_2SiO_4:Mn^{2+}$ phosphors.

2. Experimental procedures

Commercial nano-particles were used as the raw materials to investigate the high efficiency $Zn_2SiO_4:Mn^{2+}$ phosphors. Spherical SiO_2 particles (Fig. 1(a)) and irregular ZnO particles (Fig. 1(b)) had grain sizes in the range of 15–35 nm and 50–100 nm, respectively, with average sizes of 23 nm and 72 nm. The tube-typed MnO_2 particles (not shown here) had the diameter of 15–25 nm and the length of 300–800 nm. The nano-scale SiO_2, ZnO, and MnO_2 particles were weighed at the compositions corresponding to $2ZnO + SiO_2 + X$ mol% MnO_2 (Zn_2SiO_4–X-MnO_2), where $0.02 \leq X \leq 0.05$. Then, the slurry method was used to mix the precursors in acetone. After they were mixed and dried, the Zn_2SiO_4–X-MnO_2 compositions were calcined from 900 °C to 1300 °C for 2 h in air or in a N_2 atmosphere. After calcination, the morphologies of calcined particles were observed using scanning electronic microscopy (SEM), and the crystalline phases were analyzed using X-ray diffraction (XRD) patterns. Photoluminescence (PL) characteristics were recorded in the visible range on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150 W Xe lamp emitting light at an excitation wavelength of 254 nm (ultraviolet). The decay times of calcined phosphors were measured using a Tektronix TDS 340A with a Xe flash lamp. The PL characteristics of commercially available $Zn_2SiO_4:Mn^{2+}$ phosphors fabricated by Nichia Corporation were also measured for comparison.

3. Results and discussion

SEM observations reveal that Zn_2SiO_4–X-MnO_2 particles calcined at the same temperature have similar particle sizes,

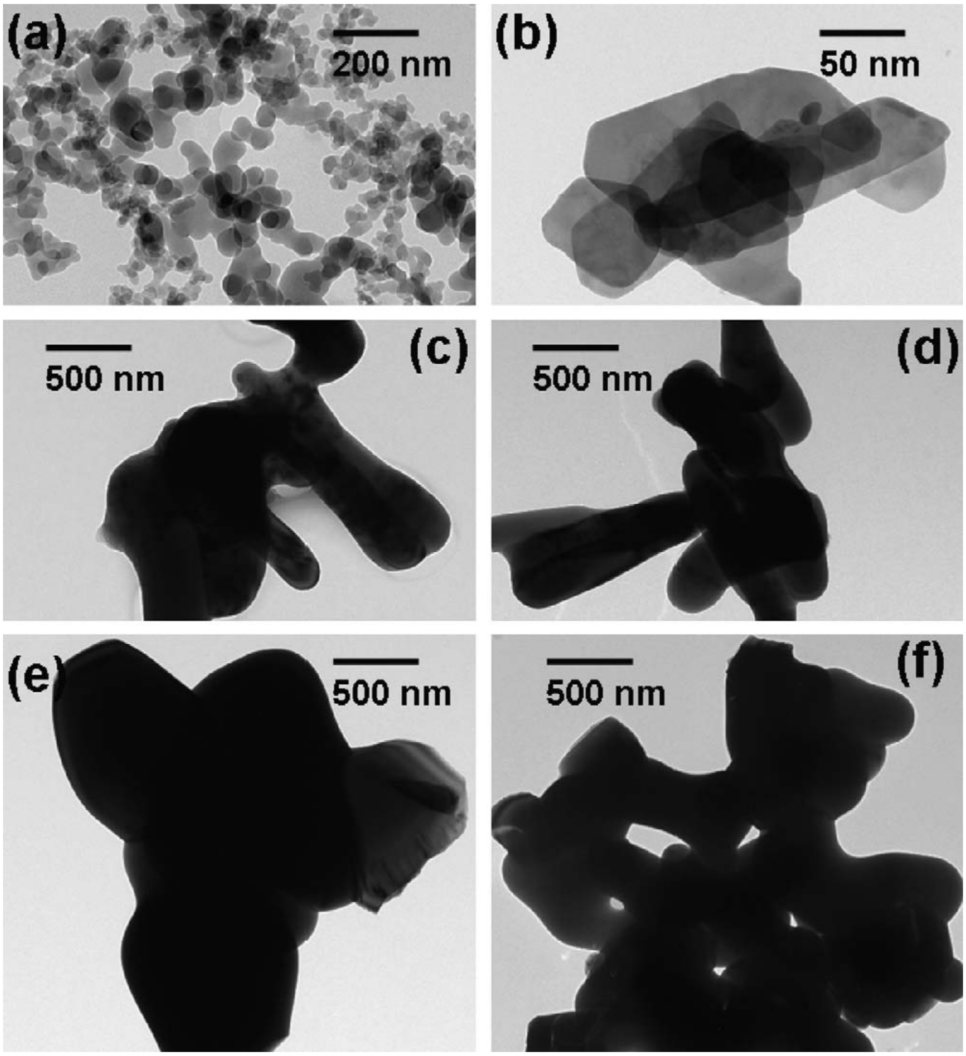

Fig. 1. The SEM micrographs for (a) SiO_2, (b) ZnO, 1100 °C-calcined $Zn_2SiO_4:Mn^{2+}$ particles with (c) 2 mol% and (d) 5 mol% MnO_2, and 1300 °C-calcined $Zn_2SiO_4:Mn^{2+}$ particles with (e) 2 mol% and (f) 5 mol% MnO_2.

regardless of whether the particles are calcined in air or in N_2. Apparently, the calcining atmosphere also has no apparent influence on the agglomeration of nano-particles. The particles calcined at 1100 °C possess the irregular morphologies and have sizes in the nano-scale (0.6–1.2 μm). A comparison between Zn_2SiO_4–2-Mn and (Fig. 1(c)) and Zn_2SiO_4–5-Mn (Fig. 1(d)) reveals that the MnO_2 concentration has no apparent influence on the particle size. In addition, the particles calcined at 1300 °C possess a solid-filled structure and are irregularly agglomerated, with the sizes of Zn_2SiO_4–2-Mn (Fig. 1(e)) and Zn_2SiO_4–5-Mn (Fig. 1(f)) particles being 2.0–3.5 μm and 3.0–4.5 μm, respectively. These results suggest that as higher calcining temperatures are used, the grain sizes of Zn_2SiO_4–X-MnO_2 particles increase with increasing MnO_2 concentration.

Fig. 2 shows the XRD patterns of Zn_2SiO_4–X-MnO_2 phosphors calcined at different temperatures and atmospheres. The XRD patterns clearly reveal that the Zn_2SiO_4, which is reasonably corresponding to rhombohedral Zn_2SiO_4 (JCPDS 37-1485), is the mainly crystalline peaks in particles calcined at 900 °C. ZnO and some unidentified phases coexist and no MnO_x or crystalline silicon is observed. When calcining temperatures are at 1000 °C and higher, only the Zn_2SiO_4 phase is revealed. In order to investigate the dependences of crystalline structures on the calcining temperatures, the full width at half maximum (FWHM) value of (1 4 0) plane is measured. As the calcining temperatures increases from 1000 °C to 1300 °C, the crystalline intensity of (1 4 0) plane increases and the FWHM value decreases from 0.35–0.42° to 0.22–0.26°, and the saturation values for both occur at 1200 °C. These results indicate that the degree of crystallization of Zn_2SiO_4–X-MnO_2 phosphors increases with increasing calcining temperatures. According to the standard JCPD pattern and the previous studies (1 4 0) plane was the main crystalline peak in Zn_2SiO_4. In this study, as the calcining temperatures are 1100 °C and higher, the crystalline intensity of (1 1 3) plane is equal to or larger than that of (1 4 0) plane. The difference in ionic radii of Zn^{2+} (0.074 nm) and Mn^{2+} (0.080 nm) is small, both Zn^{2+} sites with nearest oxygen ions in a slightly distorted tetrahedral configuration can be replaced by Mn^{2+} ions. As nano-scale MnO_2 powder is used as the dopant and the calcining temperatures are 1200 °C and higher, most Mn^{2+} ions will dope into the Zn_2SiO_4 particles and substitute the site of Zn^{2+} ions.

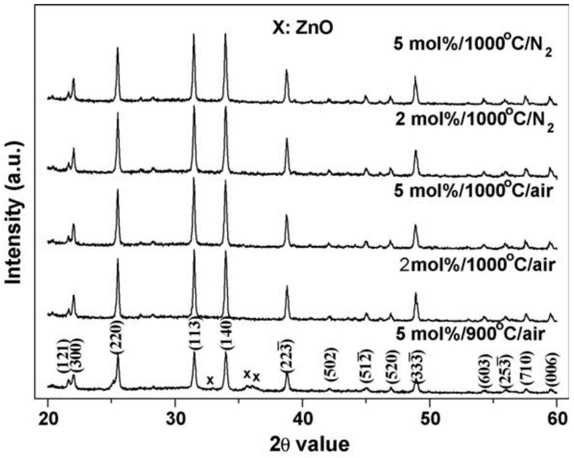

Fig. 2. XRD patterns of calcined Zn_2SiO_4:Mn^{2+} particles.

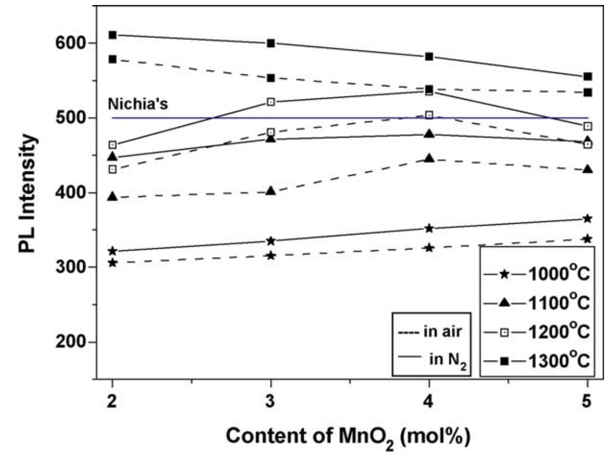

Fig. 3. Emission intensities of calcined Zn_2SiO_4:Mn^{2+} phosphors.

In previous studies, it was difficult to obtain fine luminescent phosphors with improved PL characteristics due to micro-particulation of phosphors with sizes smaller than 1–2 μm, which increased the surface defects and caused the degeneration of emission intensity [10]. The PL emission intensities of Zn_2SiO_4–X-MnO_2 phosphors with various MnO_2 contents are characterized and compared with that of Nichia's phosphor in Fig. 3. The particle sizes of Zn_2SiO_4–X-MnO_2 phosphors increase with increasing calcining temperatures, independent on that the calcining is carried out in air or in N_2 atmosphere. This result will cause that the emission intensities increase with increasing calcining temperatures, and the highest emission intensities are obtained for particles calcined at 1300 °C. Fig. 3 reveals another important result that even calcined at 1000 °C the emission intensities of developed Zn_2SiO_4–X-MnO_2 phosphors are 60% higher than that of commercial Nichia's Zn_2SiO_4–X-MnO_2 phosphor.

Fig. 4 shows the measured emission intensity-decay plots, which can also be used to determine the time required to reach

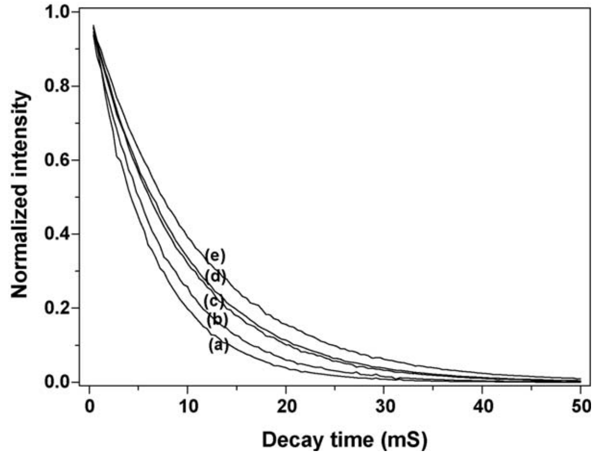

Fig. 4. Decay curves of Zn_2SiO_4:Mn^{2+} phosphors. (a) 2 mol%, 1200 °C in air, (b) commercial product, (c) 2 mol%, 1200 °C in N_2, (d) 4 mol%, 1200 °C in air and (e) 4 mol%, 1200 °C in N_2.

emission intensities of I_o/e. The commercially available phosphor decays to I_o/e in 7.2 ms. It has been reported that the emission decay time depends on the transfer of energy between proximate manganese ions [11]. The concentration quenching effect of $Zn_2SiO_4:Mn^{2+}$ phosphors are existed in the high Zn_2SiO_4 with high dopant of Mn^{2+}, for example higher than 10% of MnO_2 is added [3,5]. Thus, rather than the MnO_2 concentration, the calcining temperature and atmosphere are expected to influence the diffusion-controlled emission decay times. At calcining temperatures of 1200 °C, most Zn_2SiO_4–X-MnO_2 phosphors show decay times longer than that of commercial $Zn_2SiO_4:Mn^{2+}$ phosphor. Fig. 4 also shows that $Zn_2SiO_4:Mn^{2+}$ phosphors calcined in N_2 atmosphere have longer decay times than those in air. Phosphors calcined in air exhibit decay times extending from 4.8 ms to over 14.2 ms and those calcined in N_2 atmosphere extending from 5.4 ms to over 19.8 ms.

In general, increasing MnO_2 dopant content the non-radiative de-excitation processing accompanying the energy transfer will increase. When the Mn^{2+} dopant concentration increases, the energy transfer between Mn^{2+} and Mn^{2+} ions is expected to happen. This will take the excitation energy too far from the absorption location. The Zn^{2+} ions potentially lose the excitation at a quenching time and leads to a concentration quenching effect. This concentration quenching effect will degenerate the PL characteristics, including a decrease in luminescence and the broadness in emission peak. The PL spectra show that using air and N_2 atmosphere as the calcining atmospheres, the Zn_2SiO_4–X-MnO_2 phosphors have the same variations of PL properties. As the calcining temperatures increase from 1000 °C, 1100 °C, to 1200 °C, the maximum emission intensities and longest emission decay times are revealed in the Zn_2SiO_4–5-MnO_2, Zn_2SiO_4–4-MnO_2, and Zn_2SiO_4–4-MnO_2 particles, respectively. Calcined at 1300 °C, the maximum emission intensities and longest emission decay times decrease with increasing MnO_2 content. Because the source materials are nano-particles, MnO_2 can dope into Zn_2SiO_4 and Mn^{2+} ions substitute the Zn^{2+} ions easily. For that as the higher calcining temperatures are used, the concentration quenching effect is revealed in Zn_2SiO_4–5-MnO_2 particles. For that the PL characteristics degenerate in the Zn_2SiO_4–5-MnO_2 particles.

However, the concentration quenching effect has no drastically degenerative effect on the emission intensity and decay time, because the concentration of MnO_2 dopant is lower than 5 mol%. These results in this study also prove that we can get the higher efficient $Zn_2SiO_4:Mn^{2+}$ phosphors by using nano-particles as precursors. Because the Mn^{2+} ions are easy to occupy the sites of Zn^{2+} ions and lead to higher efficient PL characteristics as the chemical reaction methods do. Fig. 1 shows that as 1300 °C is using as calcining temperature, the sizes of $Zn_2SiO_4:Mn^{2+}$ particles increase with increasing MnO_2 content. This result proves that the particle sizes are not the most important reason to influence the PL characteristics of $Zn_2SiO_4:Mn^{2+}$ phosphor. The results in Figs. 3 and 4 also reveal that partial $Zn_2SiO_4:Mn^{2+}$ phosphors obtained at 1200 °C show emission intensities stronger than and decay times comparable to those of commercially Nichia's $Zn_2SiO_4:Mn^{2+}$ phosphor. The all $Zn_2SiO_4:Mn^{2+}$ phosphors obtained at 1300 °C show stronger emission intensities and longer decay times than those of commercially Nichia's $Zn_2SiO_4:Mn^{2+}$ phosphor, regardless of whether they were calcined in air or in N_2.

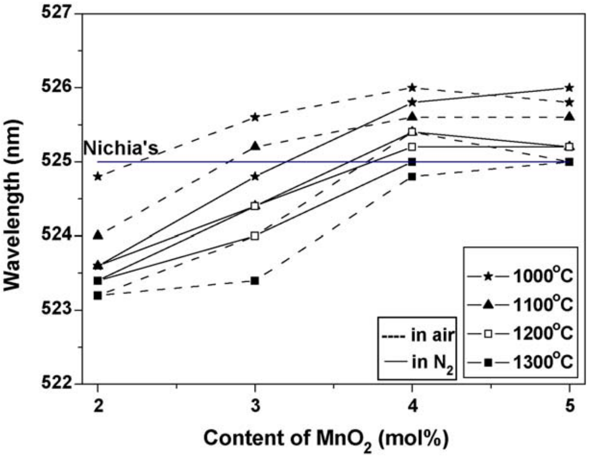

Fig. 5. Wavelengths of luminescence peaks of calcined $Zn_2SiO_4:Mn^{2+}$ phosphors.

The variations in emission intensities, wavelengths (λ), and the bandwidth at half maximum (Δλ) of luminescence peaks can be attributed to the presence of Mn^{2+} cations as dopants in the willemite structure. As the MnO_2 concentrations, calcining temperatures, and atmospheres are changed, the λ values of the luminescence peaks will also change. The λ values of $Zn_2SiO_4:Mn^{2+}$ phosphors developed by Taghavinia et al. [2], Kang and Park [12], and Patra et al. [13] were in the range of 522.4–528.0 nm, 523–526 nm, and 520–534 nm, respectively. Fig. 5 shows the λ values of developed $Zn_2SiO_4:Mn^{2+}$ phosphors, and that (525 nm) of Nichia's phosphor is also revealed. No matter the $Zn_2SiO_4:Mn^{2+}$ phosphors are calcined in air and in a N_2 atmosphere, the λ values are near the 525 nm. As the MnO_2 concentrations are increased from 2 mol% to 5 mol%, the λ values shift toward higher wavelengths, from 523.4 nm to 526.0 nm, and the Δλ values increase from 36 nm to 39 nm, respectively.

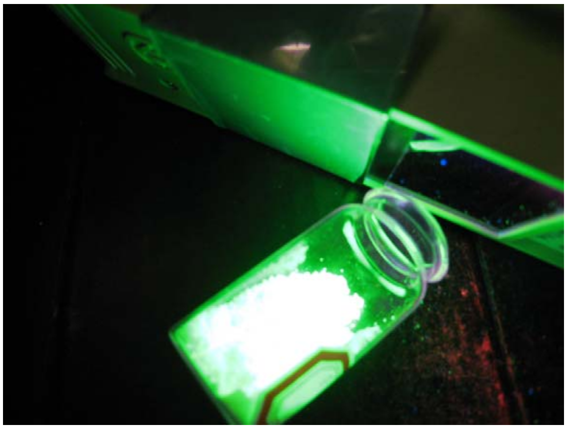

Fig. 6. Photograph for the green light emission of calcined $Zn_2SiO_4:Mn^{2+}$ phosphors.

These results in Figs. 2–5 suggest that too much MnO_2 addition (5 mol%) is not necessary. Because too much MnO_2 addition will broaden the luminescence peaks and decreases the emission intensities. In a word, as using the nano-particles as precursors to synthesize $Zn_2SiO_4:Mn^{2+}$ phosphors, the Mn^{2+} ions can easily substitute the Zn^{2+} ions. For that the PL characteristics are strongly affected by the MnO_2 content and the calcining temperatures, but not affected by the calcining atmosphere. Fig. 6 shows the emission photograph of Zn_2SiO_4–Mn-4 particles calcined at 1200 °C. The photograph proves that $Zn_2SiO_4:Mn^{2+}$ phosphors with very bright emission intensity can easily be obtained by calcining nano-particles.

4. Conclusions

In this study, we had prepared $Zn_2SiO_4:Mn^{2+}$ phosphors with satisfactory green luminescent properties using nano-particles. The developed Zn_2SiO_4–X-MnO_2 particles showed wavelengths characteristic of strong-luminescence particles in the range of 523.4–526.0 nm. Although the $Zn_2SiO_4:Mn^{2+}$ phosphors calcined in N_2 have a higher PL intensity than those calcined in air. Partial $Zn_2SiO_4:Mn^{2+}$ phosphors obtained at 1200 °C and all obtained at 1300 °C showed emission intensities stronger than and decay times comparable to those of commercially Nichia's $Zn_2SiO_4:Mn^{2+}$ phosphor regardless of whether they were calcined in air or in N_2. Zn_2SiO_4–X-MnO_2 particles calcined at 1300 °C showed the maximum emission intensity, which was 22% greater than that of the commercially Nichia's product. The results revealed that nano-particles could be used to mass produce $Zn_2SiO_4:Mn^{2+}$ phosphors with greater efficiency and at lesser cost.

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