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Ceramics International 37 (2011) 1341–1344
CERAMICS INTERNATIONAL
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# Developing the properties of new blue phosphors: $TiO_2$-doped $Zn_2SiO_4$

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Received 18 October 2010; received in revised form 5 November 2010; accepted 14 December 2010

## Abstract

$2ZnO + SiO_2 + X$ mol% $TiO_2$ ($Zn_2SiO_4$-$X$-$TiO_2$, $1 \leq X \leq 3$) and $2ZnO + SiO_2 + 3$ mol% $MnO_2$ ($Zn_2SiO_4$-3-$TiO_2$) compositions were prepared using nanoscale ZnO, $SiO_2$, $TiO_2$, and $MnO_2$ particles. The mixing powders were calcined between 1000 °C and 1300 °C in a $N_2$ atmosphere. $Zn_2SiO_4$ was the only phase in the calcined $Zn_2SiO_4$-$X$-$TiO_2$ phosphors. We found that the photoluminescence (PL) properties of synthesized $Zn_2SiO_4$-$X$-$TiO_2$ phosphors revealed these to be blue rather than green. The effects of $TiO_2$ content and calcining temperature on the PL properties of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors were rigorously investigated.

*Keywords:* C. Optical properties; Nanostructures; Photoluminescence spectroscopy

## 1. Introduction

White LEDs hold great potential for application in flat-panel displays, as rapid progress has been made in their material design and fabrication [1]. Among the inorganic phosphors, $Zn_2SiO_4$–$Mn^{+2}$ is a green phosphor well known for its high luminescence efficiency and excellent color purity [2,3]. To date, a great deal of effort has been put into investigating the photoluminescence (PL) properties of rare earth ions ($Tb^{+3}$, $Eu^{+3}$) doped in $Zn_2SiO_4$ phosphors, in order to examine their applications in such areas as field emission displays, plasma display panels, and thin-film electroluminescence devices [4]. In addition to such green phosphors, many other materials have been investigated as blue phosphors, including $Eu^{+2}$-doped $BaMgAl_{14}O_{23}$ [5] and $BaMgAl_{10}O_{17}$ particles [6]. So far, no reports have investigated the PL properties of $TiO_2$-doped $Zn_2SiO_4$ phosphors. We have found that $Zn_2SiO_4$-$X$-$TiO_2$ particles are blue phosphors rather than green. In the present study, we examine the effects of $TiO_2$ content and calcining temperature on the PL properties of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors.

## 2. Experimental procedures

Nanoscale $SiO_2$, ZnO, $TiO_2$, and $MnO_2$ particles were weighed according to the composition formula $2ZnO + SiO_2 + X$ mol% $TiO_2$ ($Zn_2SiO_4$-$X$-$TiO_2$, where $1 \leq X \leq 3$) and $2ZnO + SiO_2 + 3$ mol% $MnO_2$ ($Zn_2SiO_4$-3-$MnO_2$). The average particle sizes of spherical $SiO_2$, spherical $TiO_2$, and irregular ZnO powders were approximately 23 nm, 12 nm, and 72 nm, respectively. The diameter and length distributions of tube-type $MnO_2$ particles were 15–25 nm and 300–800 nm, respectively. After being mixed in acetone and dried, the compositions were calcined from 1000 °C to 1300 °C for 2 h in a $N_2$ atmosphere. The crystalline phases of the calcined particles were analyzed using X-ray diffraction (XRD) patterns. PL properties were recorded in the wavelength range of 250–700 nm on a Hitachi F-4500 fluorescence spectrophotometer, equipped with an emitting light at an excitation wavelength of 215 nm for $Zn_2SiO_4$-$X$-$TiO_2$ particles and 254 nm for $Zn_2SiO_4$-3-$MnO_2$ particles.

## 3. Results and discussion

The XRD patterns of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors are illustrated in Fig. 1 as a function of calcining temperature. With calcining at 1000 °C, no secondary phases or raw material

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doi:10.1016/j.ceramint.2010.12.013

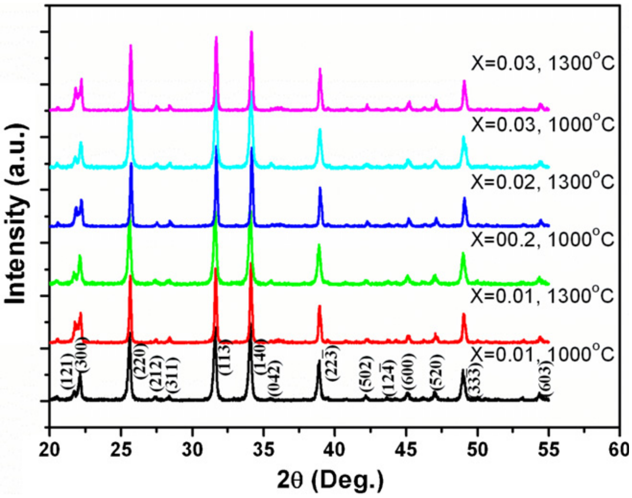

Fig. 1. XRD patterns of calcined $Zn_2SiO_4$-$X$-$TiO_2$ particles.

phases are observable. The rhombohedral structure of $Zn_2SiO_4$ is well formed and all the peaks reasonably correspond to the $Zn_2SiO_4$ phase (JCPDS 37-1485). Fig. 1 also shows that no obvious shifting of the diffraction peaks is observable as the $TiO_2$ content and calcining temperature increase. The ionic radius of $Ti^{+4}$ (0.064 nm) is close to that of $Zn^{+2}$ (0.074 nm) and much larger than that of $Si^{+4}$ (0.040 nm), suggesting that the $Ti^{+4}$ ions will dope onto the $Zn_2SiO_4$ particles and substitute at both $Zn^{+2}$ sites. As the calcining temperature increases from 1000 °C to 1300 °C, the full width at half maximum (FWHM) values of the (1 4 0) diffraction peak of the $Zn_2SiO_4$-$X$-$TiO_2$ phosphors decrease from 0.40–0.47° to 0.25–0.26°, indicating that the degree of crystallization of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors increases with rising calcining temperature.

When $Zn_2SiO_4$-1-$TiO_2$ phosphor is calcined at various temperatures, the logarithmic curves do not readily reveal the differences in maximum emission intensities. To accomplish this, Fig. 2 uses single exponential and non-normalized curves to reveal the PL emission spectra. The emission intensity of

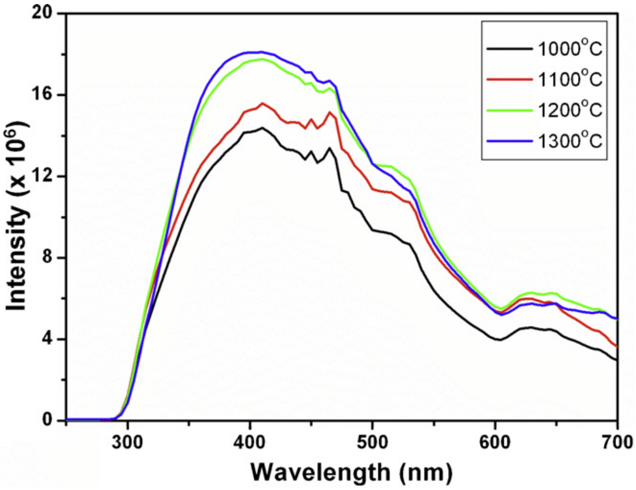

Fig. 2. PL emission spectra of $Zn_2SiO_4$-1-$TiO_2$ phosphor (excitation wavelength 215 nm) as a function of calcining temperature.

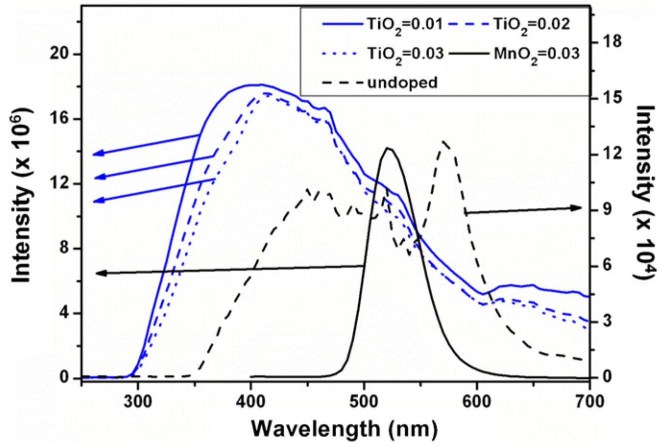

Fig. 3. PL emission spectra of 1300 °C-calcined $Zn_2SiO_4$-$X$-$TiO_2$ phosphors (excitation wavelength 215 nm) and $Zn_2SiO_4$-3-$MnO_2$ phosphor (excitation wavelength 254 nm).

$Zn_2SiO_4$-1-$TiO_2$ phosphor increases with increasing calcining temperature, independent of $TiO_2$ content. As calcining temperature increases from 1000 °C to 1300 °C, the main wavelength of the emission light undergoes a small shift from 406 nm to 409 nm. Thus, the synthesized $Zn_2SiO_4$-$X$-$TiO_2$ phosphors emit blue rather than green light.

Fig. 3 also uses single exponential and non-normalized curves to reveal the emission spectra, because the maximum emission intensities differ widely between undoped $Zn_2SiO_4$ and $Zn_2SiO_4$-$X$-$TiO_2$ (or $Zn_2SiO_4$-3-$MnO_2$) phosphors. The 1300 °C-calcined $Zn_2SiO_4$-3-$MnO_2$ phosphor has the strongest emission spectrum and the only emission band around 525 nm (excitation wavelength 254 nm, maximum emission intensity, $PL_{max}$, $1.42 \times 10^7$). For $Zn_2SiO_4$ particles in the absence of $MnO_2$ and $TiO_2$ dopants a low $PL_{max}$ is observable (excitation wavelength 215 nm, $PL_{max}$ $1.6 \times 10^4$). A strong blue emission spectrum (excitation wavelength 215 nm, $PL_{max}$ 1.72–$1.80 \times 10^7$) is observable in the 1300 °C-calcined $Zn_2SiO_4$-1-$TiO_2$ phosphor. The $PL_{max}$ of the $Zn_2SiO_4$-$X$-$TiO_2$ phosphors

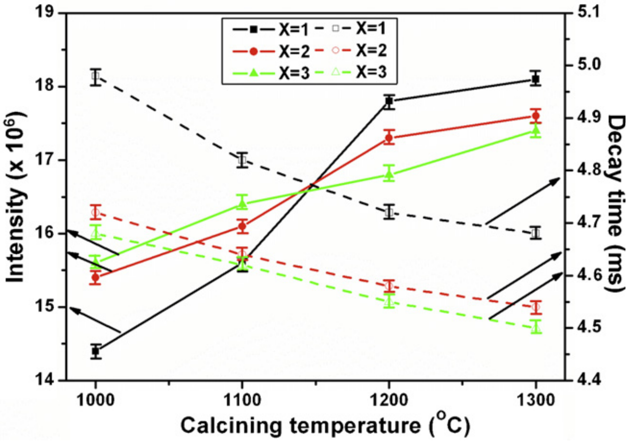

Fig. 4. Emission intensities and decay times of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors as a function of calcining temperature.

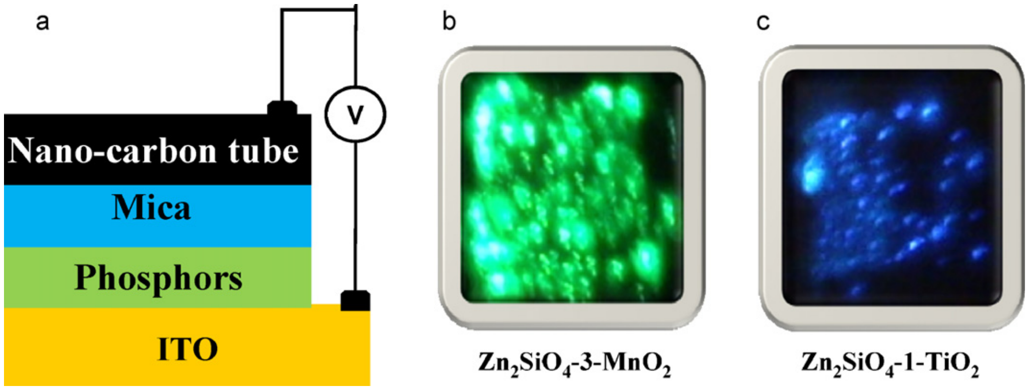

Fig. 5. Photographs of the EL properties of (b) green light emission phosphor ($Zn_2SiO_4$-3-$MnO_2$) and (c) blue light emission phosphor ($Zn_2SiO_4$-1-$TiO_2$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

is higher than that of $Zn_2SiO_4$-3-$MnO_2$ phosphor and much higher than that of undoped $Zn_2SiO_4$ phosphor. Apparently, the variations in the luminescence peaks from green light to blue are attributable to using $TiO_2$ as the dopant in the willemite $Zn_2SiO_4$ crystal structure. The configurations of the PL emission spectra in all the $Zn_2SiO_4$-$X$-$TiO_2$ phosphors were similar apart from small red-shifting in the strongest emission band. The results presented in Figs. 2 and 3 prove that the $Zn_2SiO_4$-$X$-$TiO_2$ particles will produce new blue phosphors, although the mechanism is not yet fully known.

The $PL_{max}$ values of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors are presented in Fig. 4 as a function of calcining temperature. The $PL_{max}$ increases with rising calcining temperature, and the maximum $PL_{max}$ occurs for particles calcined at 1300 °C. Based on our SEM observations, we think this is the result of the $Zn_2SiO_4$-$X$-$TiO_2$ particle sizes increasing with rising calcining temperature. The intensity decay of the PL process can be expressed as follows:

$$I_{em} = I_0 \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where the lifetime $\tau$ refers to the time required for the intensity to drop to $I_0/e$, $I_0$ is the initial intensity, and $I_{em}$ is the intensity at time $t$. Fig. 4 also shows that the lifetimes of $Zn_2SiO_4$-$X$-$TiO_2$ phosphors decrease with increasing calcining temperature and $TiO_2$ content. The calcined $Zn_2SiO_4$-$X$-$TiO_2$ phosphors exhibit decay lifetimes extending from 4.50 ms to 4.98 ms. In $Zn_2SiO_4$–$MnO_2$ phosphors, if too much $MnO_2$ dopant is added a concentration quenching effect occurs, with resulting degeneration of the emission intensity and decay time [7]. As the $Mn^{+2}$ dopant concentration and the calcining temperature increase, the chance for MnO (or $MnO_2$) to substitute for ZnO increases and the concentration of $Mn^{+2}$ ions increases. Energy transfer between $Mn^{+2}$ and $Mn^{+2}$ ions is expected to happen, which will take the excitation energy too far from the absorption location. The $Zn^{+2}$ ions potentially lose their excitation at quenching time, leading to a concentration quenching effect. In this study, it is believed that the addition of $TiO_2$ into $Zn_2SiO_4$ formed $Ti^{+4}$ ions, and that the concentration of $Ti^{+4}$ ions rose as $TiO_2$ content and calcining temperature increased. This concentration quenching effect would also occur in $Zn_2SiO_4$-$X$-$TiO_2$ phosphors, which is why the emission intensity degenerated with increasing $TiO_2$ content at calcining temperatures of 1200 °C and 1300 °C, and the decay time shortened as the $TiO_2$ content and calcining temperature increased.

Fig. 4 reveals another important result—the $PL_{max}$ of 1000 °C-calcined $Zn_2SiO_4$-$X$-$TiO_2$ phosphors is 80% higher than that of 1300 °C-calcined phosphors. These results also prove that high-efficiency $Zn_2SiO_4$-$X$-$TiO_2$ phosphors are obtainable using nanoparticles as precursors, because $Ti^{+4}$ ions easily occupy the sites of $Zn^{+2}$ ions and lead to highly efficient PL properties. Figs. 5(b) and (c) presents photographs of the electroluminescent properties of 1300 °C-calcined $Zn_2SiO_4$-3-$MnO_2$ and $Zn_2SiO_4$-1-$TiO_2$ phosphors, respectively, excited by the electrical-voltage-biased structure shown in Fig. 5(a). Images (b) and (c) prove that we have developed $Zn_2SiO_4$-based phosphors with different luminescence properties by adding different dopants.

## 4. Conclusions

In this study, we prepared $Zn_2SiO_4$-$X$-$TiO_2$ phosphors with satisfactory blue photoluminescence properties. As the calcining temperature was increased from 1000 °C to 1300 °C, the wavelength of the emission light for $Zn_2SiO_4$-$X$-$TiO_2$ phosphors shifted from 406 nm to 409 nm. The phosphors decay lifetimes ranged from 4.50 ms to 4.98 ms, and decreased with increasing calcining temperature and $TiO_2$ content.

## Acknowledgements

The authors will acknowledge to the help of Mr. Jia-Yun Kao in experimental process and financial support of NSC 99-2221-E-390-013-MY2.

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