

# High Luminance $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphors Prepared by Homogeneous Precipitation Method

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## Abstract

Manganese-doped  $\text{Zn}_2\text{SiO}_4$  phosphors well known as a green emitter with high luminescence efficiency were prepared by the homogeneous precipitation method, and their photoluminescence properties under vacuum-ultraviolet (VUV) excitation were investigated.  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphors obtained by this method have exhibited a high luminance of property and a spherical shape of particles. In particular, the green emission intensity of zinc orthosilicate prepared as containing around 2 mole% of manganese was much stronger than that of the commercial  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphor, while the decay time was longer. However, addition of  $\text{Al}^{3+}$  and  $\text{Li}^+$  into  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  composition has significantly diminished the decay time of the phosphor without much degradation of the emission intensity.

**Keywords :** Zinc silicate, homogeneous precipitation, spherical, vacuum UV, decay time

## 1. Introduction

Because of its high luminous efficiency,  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  has been widely used as a green emitting phosphor in the display industry, and more recently this phosphor has been used in the construction of plasma display panels (PDP). Commercial phosphors such as P1 and P39 have been known to be a very efficient green emitter for lamp and CRT application. Unfortunately, these phosphors have a demerit in that the emission is spin forbidden, resulting in too long decay time for plasma display applications. Zinc orthosilicate having the formula of  $\text{Zn}_2\text{SiO}_4$  has a willemite structure (space group R3). The willemite lattice has two inequivalent  $\text{Zn}^{2+}$  sites, both having four nearest neighbor oxygen ions in a slightly distorted tetrahedral configuration [1]. The substitution of  $\text{Zn}^{2+}$  sites by  $\text{Mn}^{2+}$  ions results in excellent green

emission. The emission process from this material is attributed to a d-level spin-forbidden transition for the  $\text{Mn}^{2+}$  ions acting as an activating center. In particular, the transition from the lowest excited state to the ground state,  ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ , is directly responsible for the green light emission. In addition, the decay behavior is governed by the energy migration between the Mn centers [2]. In this respect, the energy transfer rate and the corresponding critical distance deserve special consideration.

On the other hand, the efficiency of phosphors has been improved by both novel and improved synthesis techniques [3-4]. The luminescent properties of phosphors are highly dependent on the particle size and crystal structure. Thus the preparation parameters for producing phosphor may be examined to achieve better luminescent properties. Generally,  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphor is synthesized in powder by the solid-state reaction techniques, which involve high temperature firing, resulting in the agglomeration of particles. The subsequent crushing and ball milling processes often damage phosphor surfaces resulting in the degradation of the luminescent performance [5]. For this reason, some recent investigations have addressed development of alternative synthetic method, and more homogeneous

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phosphors with improved luminance have been achieved by the preparation methods such as sol-gel processes [6-8]. Phosphors for the high efficiency require optimizing parameters such as particle size, shape of phosphors, and uniform distribution of activators in the host lattice. This requirement can be met by a wet chemical synthetic method, which would give uniform particle size with good crystallinity. Furthermore, it is thought that such a wet synthetic method would be amenable to homogeneous doping with activator to afford luminescent materials. Therefore, we have been investigating phosphor syntheses by wet chemical techniques and tried to improve their luminescent properties.

In the present work, it was attempted to prepare  $Zn_2SiO_4$ :Mn phosphors by the homogeneous precipitation method and their luminescent properties were compared with the commercial zinc silicate phosphor (P1-GIS, Kasei Optonix, LTD). The synthesis of  $Zn_2SiO_4$ :Mn was conducted to Mn concentrations with 0.005 to 0.05 mole% at 147 nm excitation, which was chosen based on the concentration quenching data, as will be described later in the discussion section, for better luminescent properties could be achieved.

## 2. Experimental Procedure

### 2.1 Sample preparation

In general, a homogeneous precipitation method has been used for the preparation of ceramic powders in multi-component systems. Since it is difficult for Zn and Si components to coprecipitate in a solution at one time, without composition fluctuation, two-stage precipitation process in which Si and Zn components are precipitated by stepwise successively was designed for the present work. This synthetic method was used for preparing phosphors having the formula of  $Zn_{2-x}Mn_xSiO_4$  with  $x$  ranging from 0.005 to 0.05. The raw materials used were high-purity tetraethyl orthosilicate (TEOS, 98%, Acros Organics),  $Zn(NO_3)_2 \cdot 6H_2O$  (99.999%, Aldrich), and  $Mn(NO_3)_2 \cdot 6H_2O$  (99.99%, Aldrich). TEOS was dissolved into a mixed (9:1) solution of ethanol and water, and then kept at room temperature for 2 h. In this step, hydrated silicon oxide ( $SiO_2 \cdot xH_2O$ ) seems to be precipitated. The precipitate was suspended into 2 M-zinc nitrate solution containing manganese nitrate. Then, oxalic acid solution as a precipitant to precipitate Zn and Mn components

was added in this suspension followed by the addition of diethylamine to raise or lower pH to 8. Zn (Mn) oxalate precipitate is formed in this step. The resultant precipitate was filtered, washed, and allowed to dry. This precursor fired at 1050 °C in the air and then reheated at 850 °C in the mild reducing ambient of 5%  $H_2/N_2$  gas mixture. All the obtained powders had white body color, which indicates that all the manganese ions were in the divalent state.

### 2.2 Characterization

Crystalline phases and phase change of phosphors prepared were characterized by powder X-ray diffraction (XRD) using a Rigaku DMAX-33 X-ray diffractometer with  $Cu-K\alpha_1$  radiation and by thermal analysis using a Dupont SDT-2960 TG-DTA analyzer at a heating rate of 10 °C/min. The morphology of the phosphor particles was observed by field emission scanning electron microscopy (FE-SEM) using a Philips XL-30S. Photoluminescence measuring system was set up in order to achieve VUV excitation, which includes D2 lamp ranging from 100 to 300 nm, vacuum chamber, excitation monochromator with sodium salicylate powder, emission monochromator, photomultiplier tubes, and a controlling unit. All the emission spectra were obtained under the excitation of 147 nm, so that the PL characteristics in the similar environment to the actual PDP application could be investigated. The decay curves were measured using Xenon flash lamp, preamplifier, and oscilloscope. The wavelength of pumping source is 355 nm, which can be achieved by the monochromator equipped in front of the lamp. The pulse duration (half width) is 6  $\mu$ sec, which is short enough for our sample.

## 3. Results and Discussion

### 3.1 Preparation characteristics

The precursor, which is the mixture of zinc oxalate and hydrated silicon oxide produced according to two precipitation stages was made to undergo thermal decomposition to zinc orthosilicate powder. The conversion reaction of the precursor to the phosphor was investigated prior to the attempt of preparing manganese-doped materials. The thermal analysis results for the phosphor prepared by the homogeneous precipitation

method, which were examined from room temperature to 1200°C, are given in Fig. 1. The DTA curve exhibits sharp endothermic peaks near 160°C and 390°C. The peaks near 160°C and 390°C originated, respectively, from the evaporation of the water incorporated into the precursor powder and the dissociation of oxalate groups, which induced the weight loss. On the other hand, the sharp exothermic peak shown at 410°C should be attributed to the crystallization to zinc oxide. The TG analysis for the phosphor formation reveals a facile weight loss which begins at ca.130°C and is completed at 400°C. No further significant weight loss is observed from 420°C to 1200°C. In the DTA curve, no appearance of a sharp exothermic peak is shown at higher temperature region than 420°C. This indicates that the crystallization to the phosphor takes place slowly in this sample.

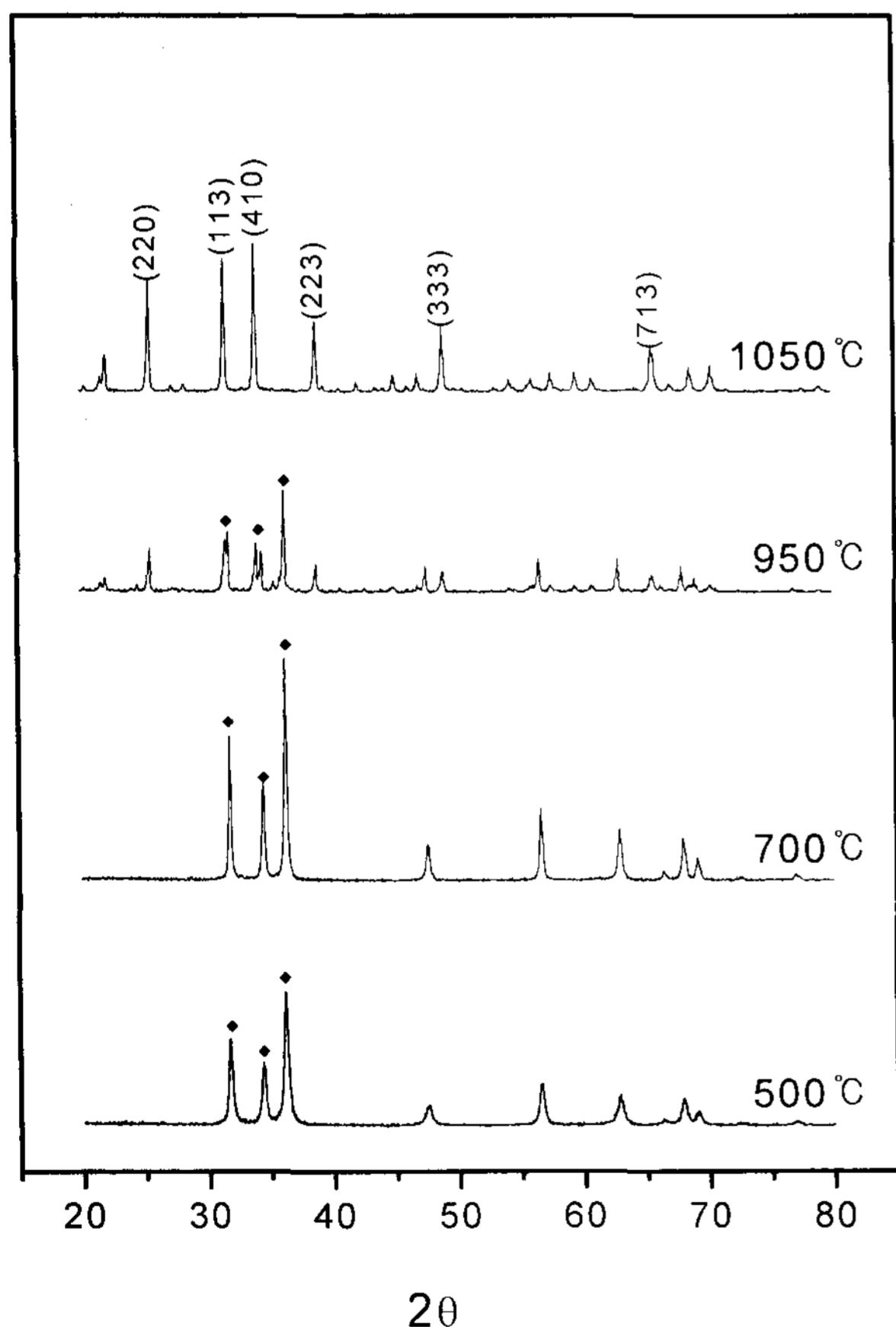


Fig. 1. TG and DTA curves for  $Zn_2SiO_4:Mn$  phosphor prepared by homogeneous precipitation method.

Fig. 2 shows XRD patterns of  $Zn_2SiO_4:Mn$  powders obtained by the homogeneous precipitation method fired at various temperatures. In the diffraction patterns of

samples fired at lower temperature than 700°C, only the peaks due to ZnO phase are observed. At 950°C, the peaks of the ZnO phase and also the main peaks from (220), (113), and (410) planes of  $Zn_2SiO_4$  phase are clearly observed, so the formation of  $Zn_2SiO_4$  starts from 950°C. It is obvious that the single phase of zinc orthosilicate was formed by firing at 1050°C. On the other hand, the presence of the peaks originated from silicon oxide phase could not be definitively identified from the X-ray diffraction patterns. From the results of thermal analysis and XRD patterns it can be noted that the Mn-doped  $Zn_2SiO_4$  phosphor is completed at 1050°C by way of ZnO and amorphous silica phases from the precursor.

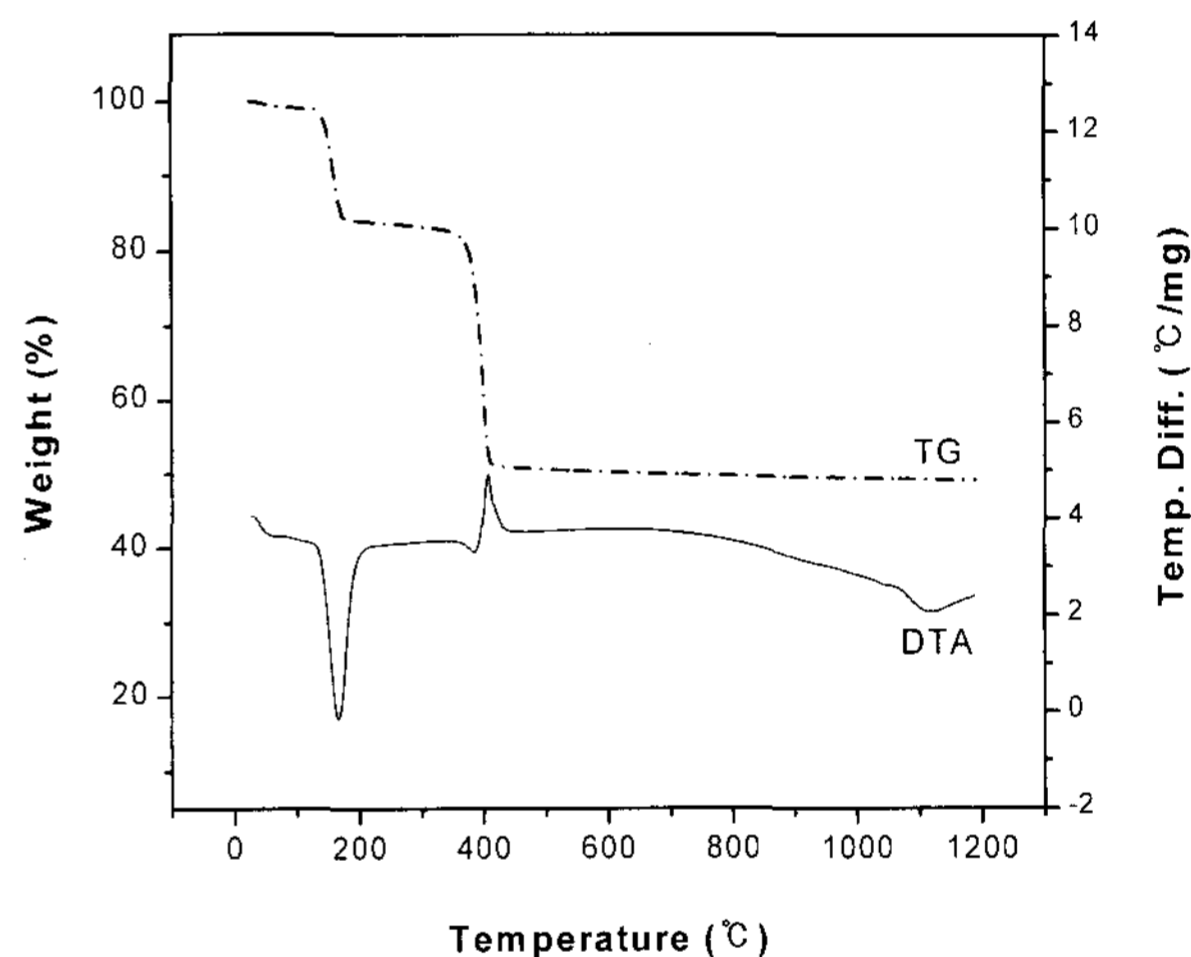
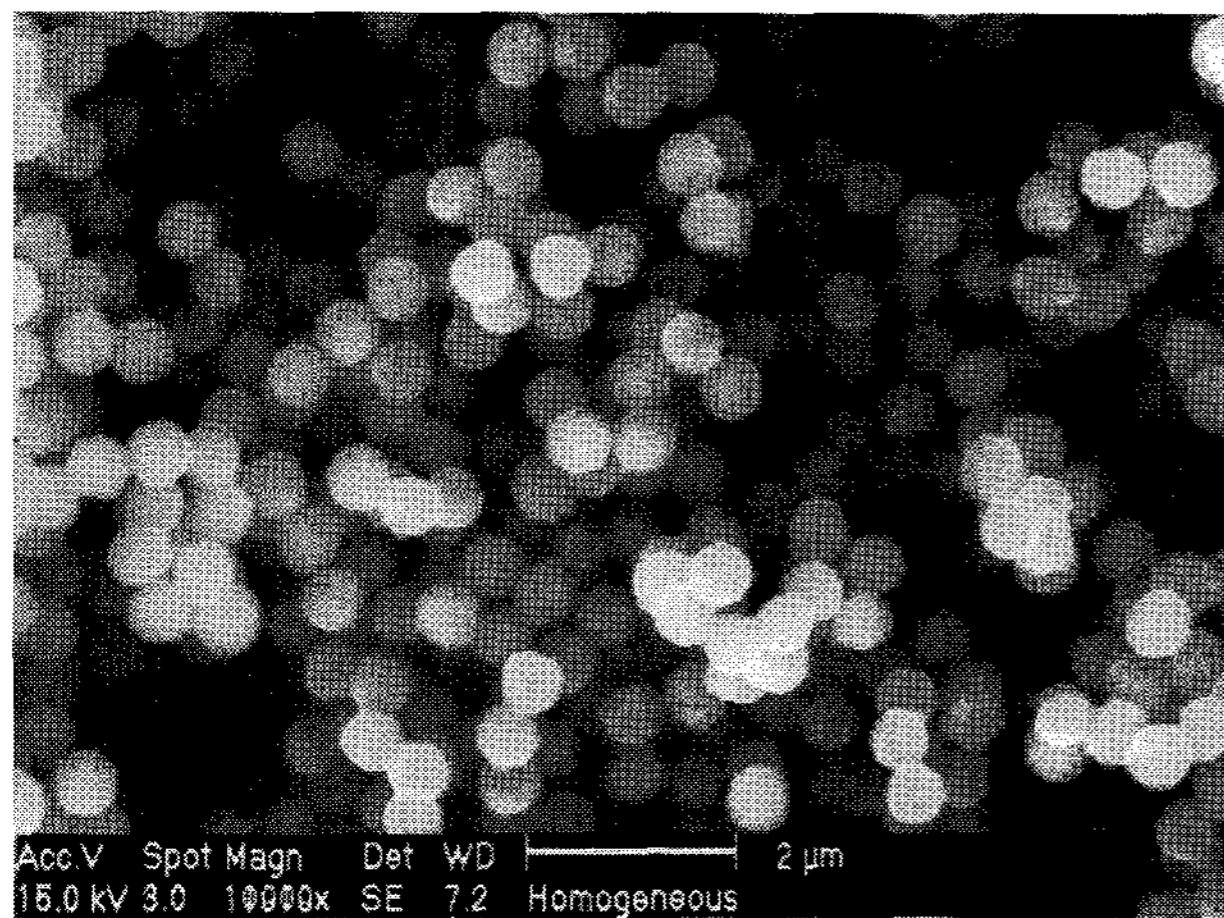
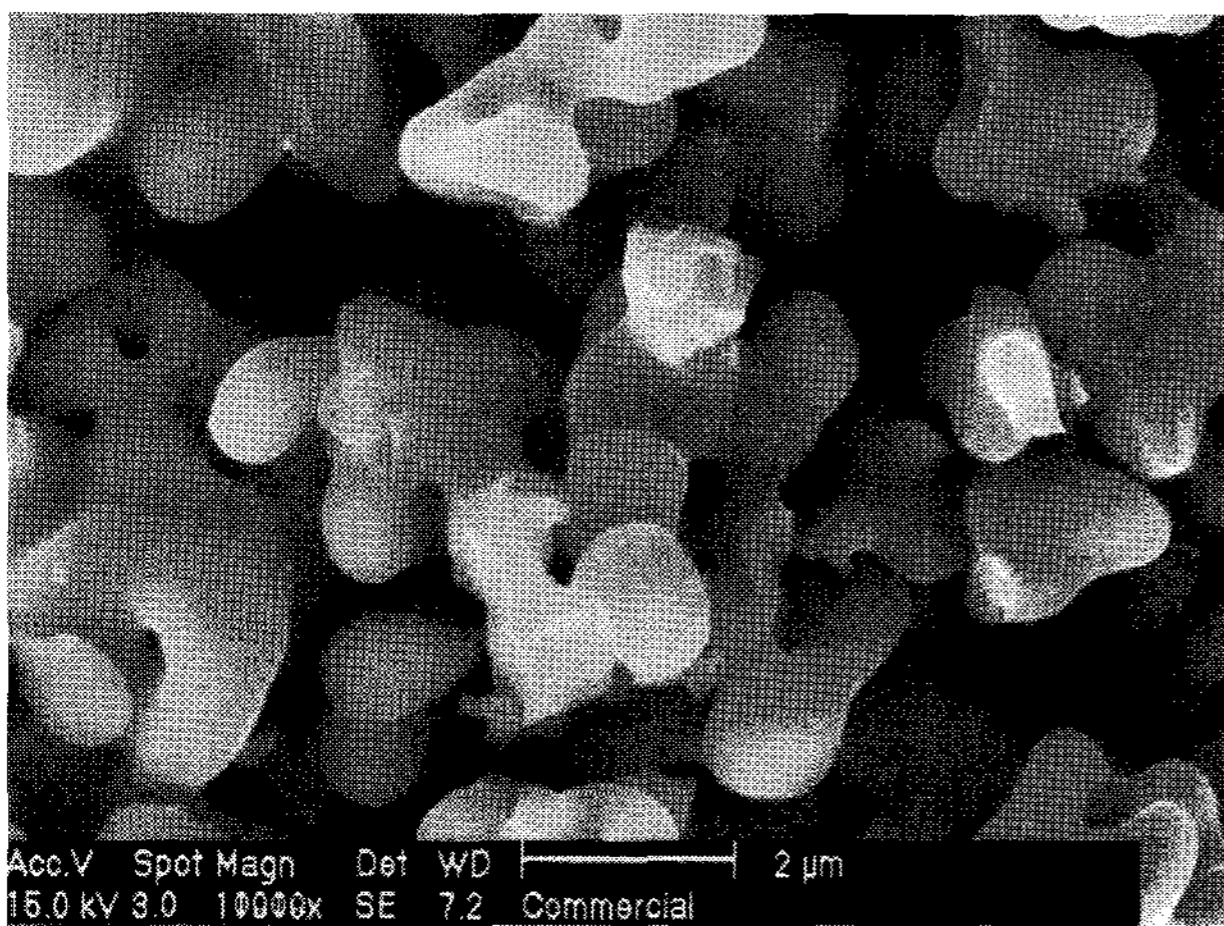


Fig. 2. XRD patterns of  $Zn_2SiO_4:Mn$  powders fired at various temperatures. (The marks indicate ZnO phase.)

The SEM photographs of the  $Zn_2SiO_4:Mn$  phosphor prepared by the homogeneous precipitation method as well as the commercial phosphor are expressed in Fig. 3. The morphology observed is the same for all phosphors synthesized by the above method. The phosphor particles synthesized appear particle size of 0.5  $\mu m$  to be well-dispersed and spherical shape, whereas the commercial ones show irregular and agglomerated. This difference in the morphologies of phosphor particles have influenced a disparity in the luminance of phosphors, since it has been shown that damage to or defects of the phosphor results in a decline of emission intensity [5]. In addition, a spherical shape of the phosphor particles will probably be suitable for the deposition of the phosphors on the glass panel.



(a)

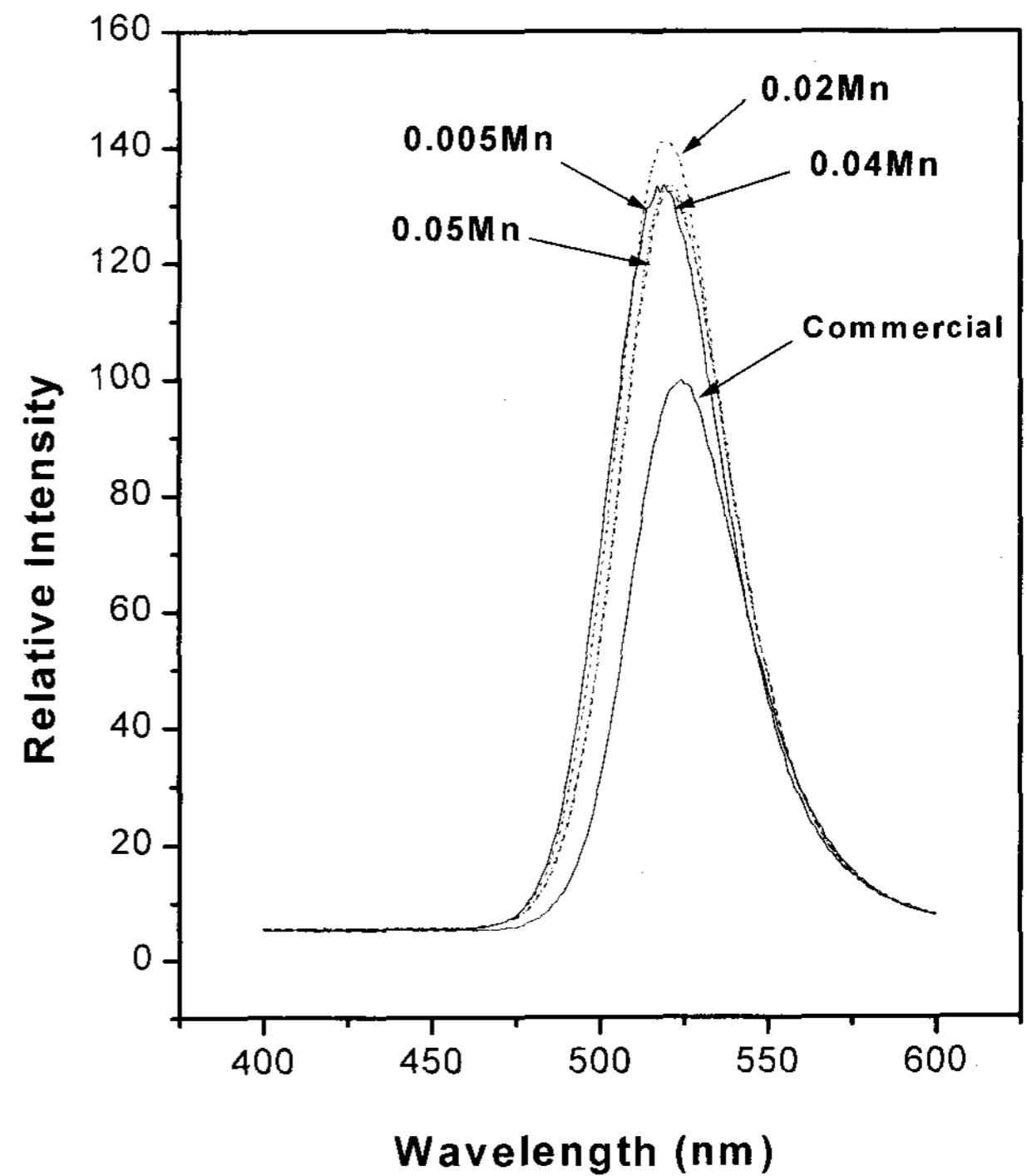


(b)

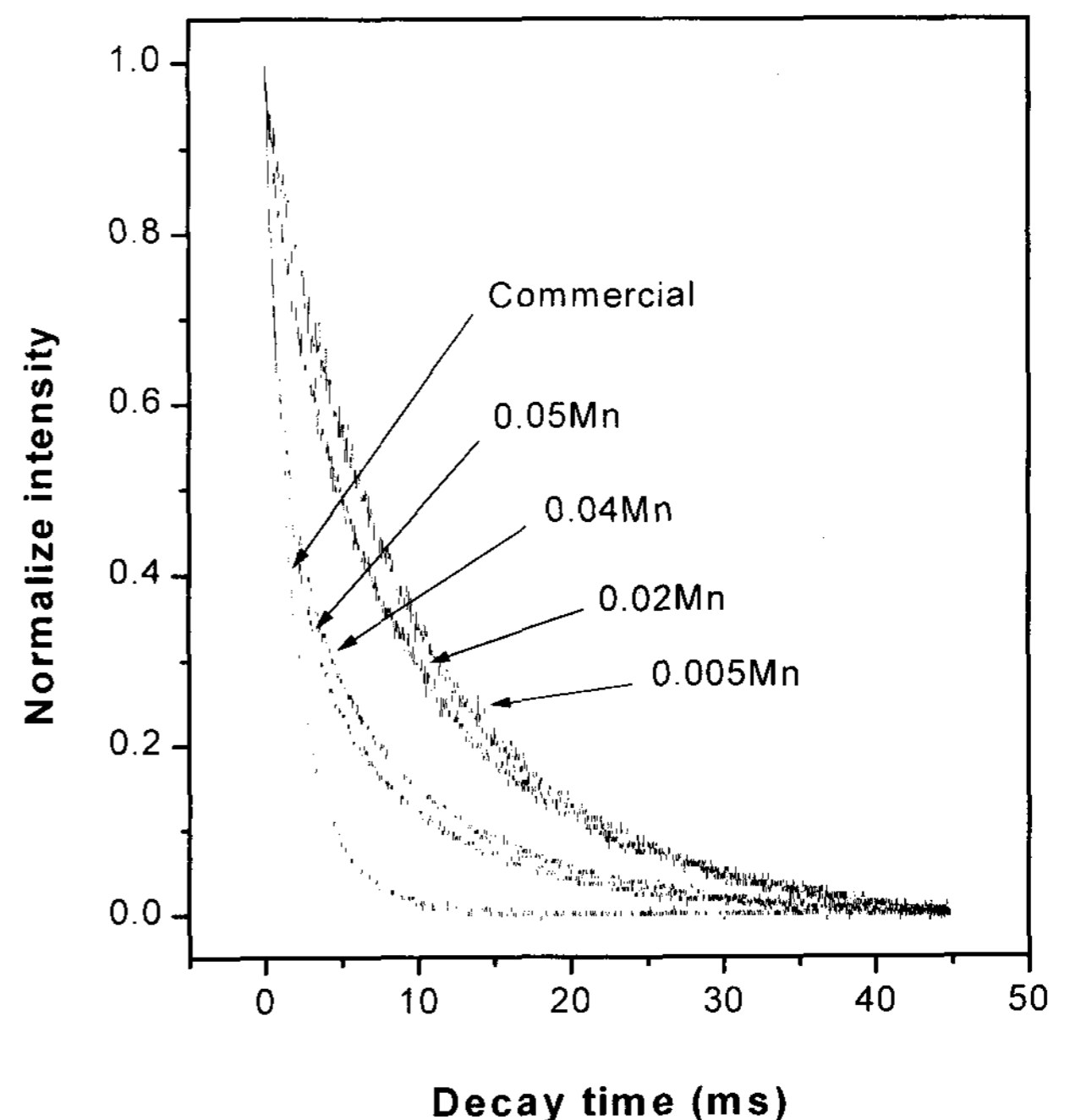
Fig. 3. SEM photographs of  $Zn_2SiO_4:Mn$  phosphors prepared by the homogeneous precipitation (a) and of the commercial phosphor (b).

### 3.2 Luminescence characteristics.

In  $Zn_2SiO_4:Mn$  phosphors, the luminescence behavior with respect to Mn concentration is of particular interest both theoretically and practically. The concentration quenching behaviors have been measured by some research groups, both under the Mn ion's direct excitation at 400~500 nm [9] and the conventional UV excitation at 254 nm [10]. However, the VUV excitation makes it possible to get closer to the actual PDP environment so that one can realize that the luminescence behavior in this condition is different from the conventional excitation condition. As shown in a previous paper [11], we investigated the emission spectra of  $Zn_{2-x}Mn_xSiO_4$  measured as variation of Mn concentration under the Mn's direct excitation (423 nm), UV excitation (254 nm), and VUV excitation (147 and



(a)



(b)

Fig. 4. The emission spectra (a) and the decay curves (b) of  $Zn_2SiO_4:Mn$  phosphors synthesized as various Mn contents.

162 nm). The critical Mn concentration, which manifests the concentration of maximum intensity, was estimated to be about 2 mole% under the VUV excitation, whereas 12 mole% was found when excited at 254 nm and 423 nm. Thereupon, it could be noted that the concentration quenching arises at relatively low Mn concentration

TABLE 1. The VUV PL properties of the synthesized and the commercial  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphors.

Mn content (mole %)	Relative emission intensity(a.u.)	Wavelength (nm)	Decay time ( $\tau_{10\%}$ , ms)	Color coordinate	
				X	Y
0.5	133	519	29	0.219	0.702
1.0	139	519.5	27	0.221	0.707
1.5	139	520	25	0.222	0.708
2.0	141	520.5	23	0.223	0.709
2.5	140	521	21	0.223	0.710
3.0	139	521	19	0.224	0.710
3.5	138	521.5	17	0.224	0.709
4.0	134	522	15	0.226	0.705
5.0	132	522.5	12	0.227	0.701
Commercial	100	524	5	0.240	0.639

when excited under the VUV region. In addition, the critical distance value obtained from the concentration quenching data was compared with that estimated from the calculated spectral overlap. By comparing these values, it was suggested that while the Mn-Mn interaction is a controlling factor at lower energy excitation, the energy transfer from the host lattice to the Mn ions could be a governing factor in the case of VUV excitation.

The resultant PL properties including the emission spectra and the decay curves of the  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphors synthesized are shown in Figures 4(a) and (b) in comparison to the commercial phosphor. For each phosphor composition examined, only one large band centered at around 520nm is observed. The corresponding relative maximum intensity, wavelength, decay time ( $\tau_{10\%}$ ), and color coordinates are presented in Table 1. The  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphors produced as various Mn concentration ( $0.005 < x < 0.05$ ) reveal stronger emission intensity than the commercial one while there is still a need to reduce decay time. Among the others, the luminance of phosphor composition having the Mn content of 2 mole% is improved to about 40% compared to that of commercial phosphor. Also, we have produced the same composition of phosphors by the conventional method. Consequently, both the emission intensities of the phosphors prepared by the solid-state reaction were lower than those prepared by the homogeneous precipitation method. This disparity in the emission intensities upon preparation methods is possibly concerned with the difference in the homogeneous distributions of activator ions and/or the contamination

of impurities. Both the PL properties, on the other hand, are highly dependent on the level of Mn doping such as reported earlier in the literature [9]. This implies that while the luminance exhibits a maximum at a certain point, the decay time decreases consecutively with increasing Mn content. When the Mn concentration increases, the maximum of the emission band is shifted toward longer wavelength. Accordingly, the color of the emitted light becomes more yellowish. This phenomenon can be explained by a diminution of the crystal field, which the substitution of  $\text{Zn}^{2+}$  sites by  $\text{Mn}^{2+}$  ions with a larger ion size, results in a distortion of the  $T_d$  sites [10]. As can be seen in Table 1, at the lower Mn content region of below 1 mole%, the emission intensity is augmented because a higher number of Mn ions, which are the light emitting centers, could be excited. At Mn content region between 1 and 3.5 mole%, the emission intensity of phosphors reveals relatively a high value without a significant fluctuation, because the number of excited centers increases but that of emitting centers does not change considerably. At the higher Mn content region than 4 mole%, the emission intensity decreases abruptly according to a concentration quenching effect. However, the decay time reduces with increasing Mn content from 29 ms to 12 ms at the whole Mn region examined. This effect can be interpreted as follows. That is, the return of de-excitation centers to the ground state, due to the increase of the number of nonradiative ones, is very quick and results in a reduction of the decay time.

In  $\text{Zn}_2\text{SiO}_4\text{:Mn}$  phosphors, in general, it is possible to lessen the decay time by increasing the Mn concentration. However, because of the accompanying energy transfer,

nonradiative de-excitation processes will prevail and the efficiency of phosphor will diminish according to concentration quenching. As the Mn concentration is increased, the competition between a higher number of excited centers and a lower radiative efficiency will determine the optimal Mn concentration. Actually, some research groups have performed these studies [9-10]. And, it has been suggested that an optimum Mn content region ( $0.05 < x < 0.11$ ) could be suitable for the PDP application, in which favorable luminance and decay time can be expected. There is, however, still a need to improve luminance further. In the point of view, we reported [12] that both Mg and Cr incorporation into the 8 mole% Mn-doped  $\text{Zn}_2\text{SiO}_4$  proffer a favorable influence on photoluminescence properties under conventional UV excitation. In particular, Mg enhances the intensity of green emission and Cr shortens the decay time. The enhancement of emission intensity of  $\text{Zn}_2\text{SiO}_4$ :Mn,Mg could be interpreted by the transition from 3s and 3p electron of Mg ions to manganese level of spin-up state, while the contraction of decay time of  $\text{Zn}_2\text{SiO}_4$ :Mn,Cr by the energy transfer between Mn and Cr ions. However, the Mn concentration adopted in the present investigation for the further improvement in luminance under VUV excitation is defined to the region from 0.5 to 5 mole%. Unfortunately, the introduction of co-dopants such as Mg and Cr into the  $\text{Zn}_2\text{SiO}_4$ :Mn compositions adopted in this investigation gave a substantial influence on neither the emission intensity nor the decay behavior under VUV excitation. Recently, it was reported [13] that the co-doping with  $\text{Ba}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}/\text{Li}^+$ , and  $\text{Gd}^{3+}/\text{Li}^+$ , which are presented as a substituent for zinc site, has significantly decreased the decay time of the  $\text{Zn}_2\text{SiO}_4$ :Mn phosphor. Based on these results, we have carried out the synthesis of the phosphor compositions of the (Al,Li) co-doped  $\text{Zn}_2\text{SiO}_4$ :Mn by the homogeneous precipitation method described above. Since the 2 mole% Mn-doped  $\text{Zn}_2\text{SiO}_4$  composition have exhibited the highest emission intensity under VUV excitation at 147 nm, all the co-doping processes were applied on that composition, thereby leading to more improved properties.

The emission spectrum and the decay curve of the  $\text{Zn}_2\text{SiO}_4$ :Mn,Al,Li phosphor are represented in Figures 5(a) and (b) in comparison to the undoped  $\text{Zn}_2\text{SiO}_4$ :Mn phosphor. As can be seen in Figure 5(a), the emission intensity of phosphor having the composition of

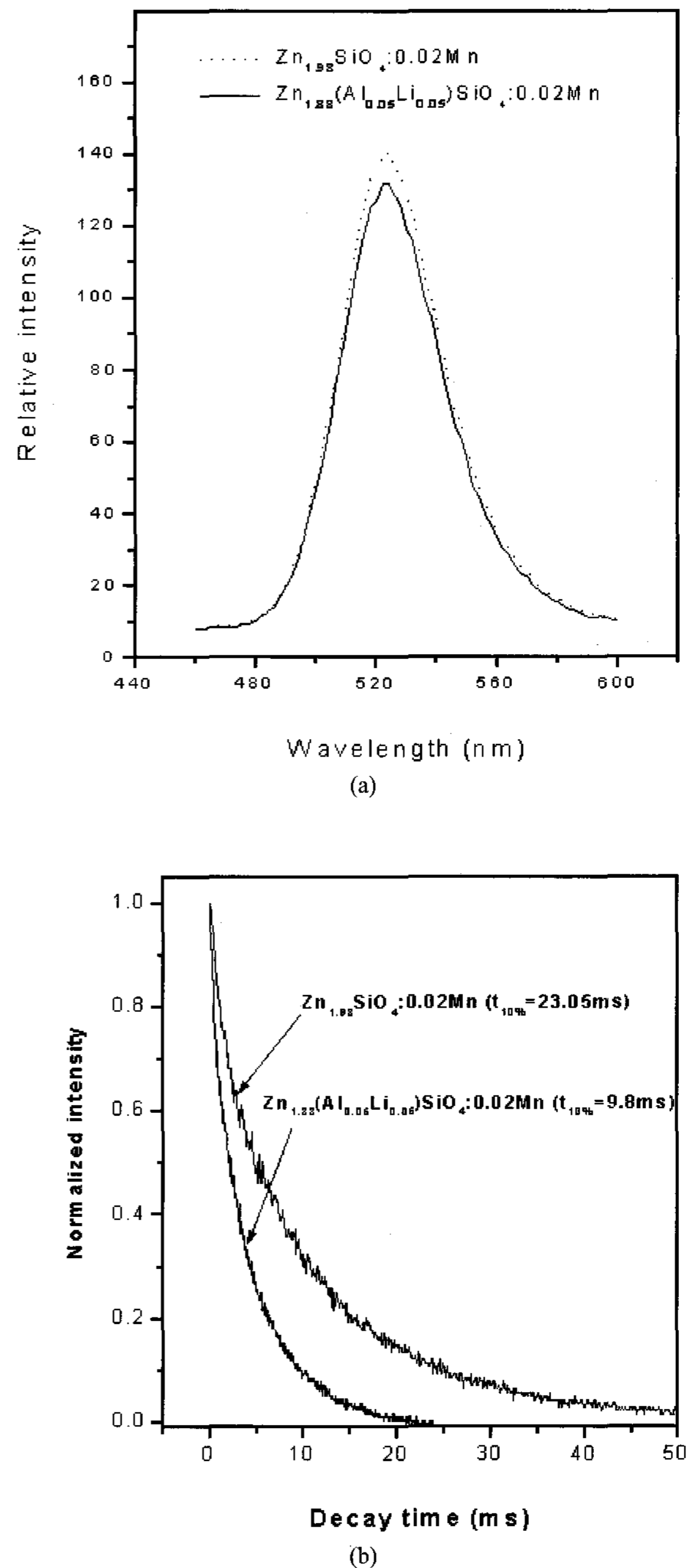


Fig. 5. The emission spectra (a) and the decay curves (b) of the (Al, Li) co-doped  $\text{Zn}_2\text{SiO}_4$ :Mn phosphor and the undoped  $\text{Zn}_2\text{SiO}_4$ :Mn phosphor.

$\text{Zn}_{1.88}(\text{Al}_{0.05}\text{Li}_{0.05})\text{Mn}_{0.02}\text{SiO}_4$  reveals about 95% of the relative intensity for  $\text{Zn}_{1.98}\text{Mn}_{0.02}\text{SiO}_4$  composition. The decay time of the phosphor is shorter than 10 ms. These results indicate that the co-doping with Al and Li offers an advantageous influence, which is a diminution of the decay time and a retention of the high luminance. A detailed study on the decay mechanism for the (Al,Li) co-doped  $\text{Zn}_2\text{SiO}_4$ :Mn is currently being made to obtain a plausible interpretation.

#### 4. Conclusions

In the present work,  $Zn_2SiO_4:Mn$  phosphor preparation was designed by the homogeneous precipitation method to improve the luminescent properties. We have demonstrated that this synthetic method is an excellent technique to zinc orthosilicate, in that the phosphor synthesized appears spherical-shaped particles and has the high luminance. The following conclusions were obtained from this study. The designed method featured a high luminance of phosphors and their spherical shape in the morphology. The green emission intensities of phosphor compositions in around 2 mole% of Mn concentration were about 40% higher than that of the commercial  $Zn_2SiO_4:Mn$  phosphor, while the decay time was longer. However, when Al and Li were incorporated into  $Zn_2SiO_4:0.02Mn$  composition, the decay time of the phosphor has significantly shortened without much degradation of the emission intensity. Accordingly, the (Al,Li) co-doped  $Zn_2SiO_4:Mn$  phosphor prepared by the homogeneous precipitation method have a good luminescent properties with high luminance and fast decay time, which are possibly acceptable for PDP application.

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