

## Photoluminescence properties of non-rare earth $\text{MgAl}_2\text{O}_4 : \text{Mn}^{2+}$ green phosphor for LEDs

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A non-rare earth elements-based  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  green phosphor for LED applications was synthesized by a solid-state reaction method. X-ray diffraction analysis revealed that the synthesized phosphors have a spinel-type  $\text{MgAl}_2\text{O}_4$  phase and any secondary phase formed by the  $\text{Mn}^{2+}$  addition was not detected. The prepared  $\text{MgAl}_2\text{O}_4 : \text{Mn}^{2+}$  phosphors showed a single intense broadband green emission in the range from 500 to 560 nm excited by near UV to visible blue light. The green emission mechanism was found to be attributed to the spin-forbidden d-d transition ( ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ ) of  $\text{Mn}^{2+}$  by a schematic investigation in terms of energy transfer in  $\text{Mn}^{2+}$  ion. As the  $\text{Mn}^{2+}$  concentration increased, the emission intensity increased up to 3.0 mol% and then decreased at higher concentrations as a result of concentration quenching, while the peak wavelength continuously moved to the longer wavelengths. Dynamic light scattering (DLS) and field-effect scanning electron microscopy (FE-SEM) characterization showed the 3 mol%  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  phosphor particles have an irregularly round shape and uniform size distribution with an average particle size of 1–2  $\mu\text{m}$ .

**Key words:**  $\text{MgAl}_2\text{O}_4 : \text{Mn}^{2+}$  phosphors, Solid-state reaction, Green phosphors, Optical properties, LEDs.

### Introduction

In the recent times, white-light-emitting diodes (LEDs) have attracted increasing attention due to their superior features such as high efficiency, compactness, long operation lifetime and environmental friendliness. It is well known that there are two ways to manufacture white LEDs [1–3]. One is the combination of multiple LED chips with different colors. Because of the different lifetime and stability of each chip, the color temperature and luminous efficiency of white light gradually deteriorate. The other way of getting white light is using a single chip to excite phosphor materials. The combination of a yellow-emitting  $\text{YAG} : \text{Ce}^{3+}$  phosphor and blue emitting LED chip is the conventional and world-wide commercial approach [4]. But, due to lack of a red color component, the color rendering index (CRI) of this type of white LEDs is poor. In order to solve this problem, a variety of phosphors that can emit different colors of light under near UV or blue light excitation has been developed [5].

Most phosphors are oxides, sulfides, oxysulfides, oxynitrides or nitrides doped with transition metals,

particularly, rare-earth (RE) ions. These RE ions play a crucial role in controlling the color of the light emitted by these phosphors. The emission of light from the RE ions is mostly due to electric and magnetic dipole optical transitions within the  $4f^7$  manifold, but it may also be interconfigurational in nature, involving configurations such as  $4f^{n-1}5d$  [6]. Most of these RE ions, nevertheless, are very expensive. In addition, some chlorides, citrates, and oxides of these RE elements are toxic and harmful [7], which greatly limits their applications. Consequently, the search for less-expensive “green” phosphors that do not contain RE ions has been a long-standing and important issue in new phosphor development [8].

A lot of work has been done on the synthesis and characterization of transition metal ions-doped  $\text{MgAl}_2\text{O}_4$ . The  $\text{Mn}^{2+}$ - or the  $\text{Cr}^{3+}$ -doped  $\text{MgAl}_2\text{O}_4$  were reported many years ago [9]. Most of interests about these kinds of spinel have been focused on the laser activity [10]. As the substrate material,  $\text{MgAl}_2\text{O}_4$  performs well under various CVD conditions owing to good thermal and chemical stabilities, and low lattice mismatch to III-V semiconductors [11]. Besides, the transition metal ions-doped  $\text{MgAl}_2\text{O}_4$  shows strong emission in a wide range of visible spectrum [12] and can be used as highly luminous phosphors for packaging of white LEDs. Hence, the application of these transition metal ions-doped  $\text{MgAl}_2\text{O}_4$  in white LEDs is a meaningful subject.

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In this paper, we report a non-rare earth elements-based  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  green phosphor for LED applications. The  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  phosphors were synthesized via a simple solid state reaction method and the particle characteristics, photoluminescence properties and related luminescent mechanism were investigated.

## Experimental

$\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  phosphors were synthesized by a solid-state reaction method [13]. Doping concentration of Mn was controlled from 1.0 to 9.0 mol%. Stoichiometric mixtures of highly pure raw  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MnCO}_3$  materials were thoroughly mixed by ball-milling and then calcined in air at  $1400^\circ\text{C}$  for 6 hrs. After heat treatment, the powder samples were mildly ground before PL measurements. The phase purity of the synthesized powders was identified by X-ray diffraction (XRD) analysis with  $\text{Cu-K}\alpha$  radiation operated at 40 kV and 30 mA. The UV photoluminescence (PL) and photoluminescence excitation (PLE) spectra were collected at room temperature (RT) using a fluorescence spectrometer (FS-2) in the range of 480–600 nm and 250–500 nm, respectively. Particle morphology and size distribution were recorded using scanning electron microscopy (SEM) and particle size analyser (PSA).

## Results and Discussion

Fig. 1(a) shows the XRD patterns of  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  calcined at  $1400^\circ\text{C}$  for 6 hrs with various  $\text{Mn}^{2+}$  ion concentrations. The prominent peaks correspond well to the spinel-type  $\text{MgAl}_2\text{O}_4$  phase (JCPDS # 21-1152). Any impurity or secondary phase was not detected, implying that single crystallized  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  with various  $\text{Mn}^{2+}$  concentrations up to 9.0 mol% can be obtained by the solid-state reaction method.

Based on the effective ionic radii of the cations with different coordination numbers (CN) [14] and electronic charge difference between  $\text{Mg}^{2+}$  ion and  $\text{Al}^{3+}$  ion, it can be expected that  $\text{Mn}^{2+}$  [ $r(\text{Mn}^{2+}) = 0.66 \text{ \AA}$ , when  $\text{CN} = 4$ ] ions are preferably substituted into the  $\text{Mg}^{2+}$  sites [ $r(\text{Mg}^{2+}) = 0.57 \text{ \AA}$ , when  $\text{CN} = 4$ ] instead of the  $\text{Al}^{3+}$  sites [ $r(\text{Al}^{3+}) = 0.53 \text{ \AA}$ , when  $\text{CN} = 6$ ]. Note that the corresponding lattice constant becomes larger when the  $\text{Mg}^{2+}$  ions are substituted by the  $\text{Mn}^{2+}$  ions with a larger ionic radius than that of  $\text{Mg}^{2+}$ . In Fig. 1(b), the (311) peaks shift to lower  $2\theta$  angle, indicating the expansion of the lattice constants when  $\text{Mn}^{2+}$  ions are substituted into the  $\text{Mg}^{2+}$  ion sites.

The excitation (PLE) and emission (PL) spectra of a synthesized  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  samples are shown in Fig. 2. In excitation spectra of Fig. 2(a) at 520 nm emission, the strong excitation peak at 260 nm was ascribed to the strong dipolar  $e \rightarrow t_2$  transition of  $\text{Mn}^{2+}$  ion in  $\text{MgAl}_2\text{O}_4$  structure [15]. Other strong excitation bands due to the  $\text{Mn}^{2+}$  transitions are observed around 365, 385, 430

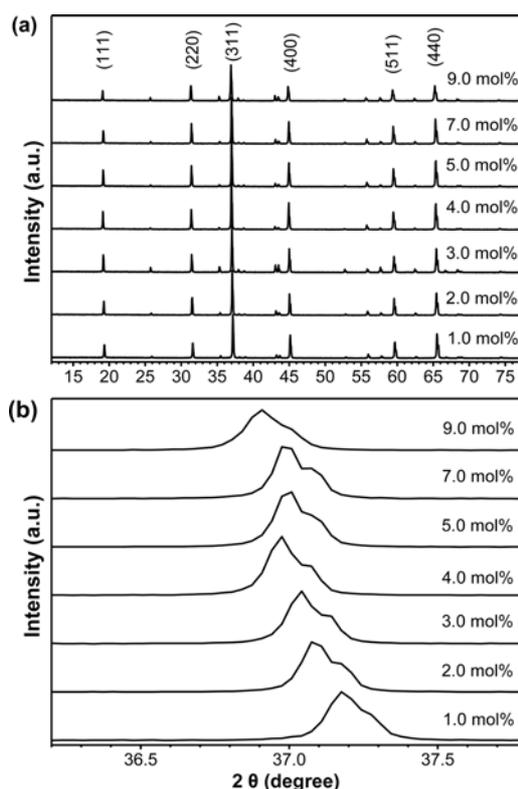


Fig. 1. XRD patterns of  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  with various  $\text{Mn}^{2+}$  ion concentrations.

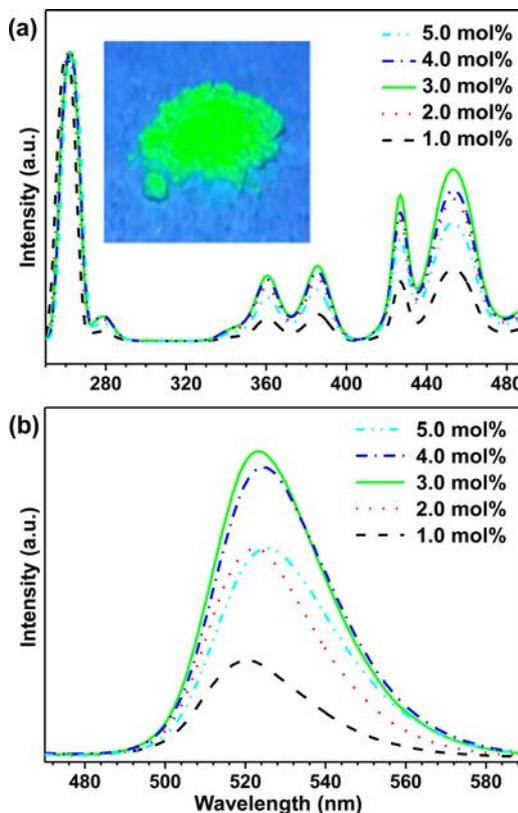
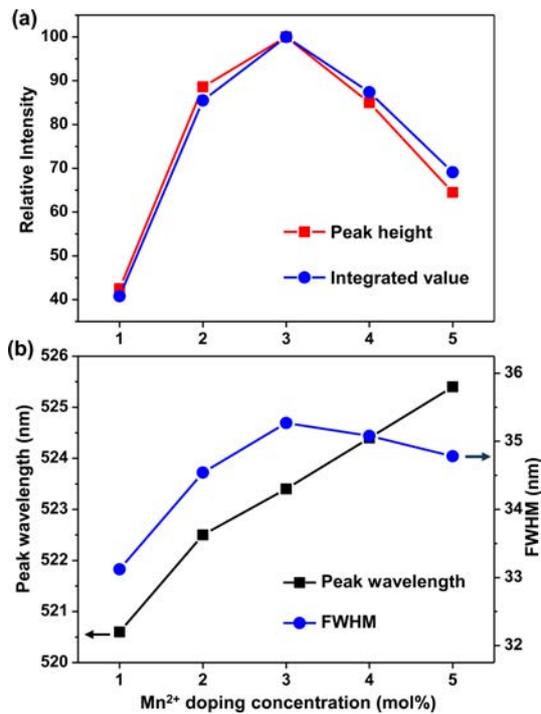


Fig. 2. (a) PLE ( $\lambda_{\text{em}} = 520 \text{ nm}$ ) and (b) PL ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ) spectra of  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  with various  $\text{Mn}^{2+}$  ion concentrations. Inset of (a) shows an image of the 3 mol%  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  exhibiting visible green emission excited at 365 nm.



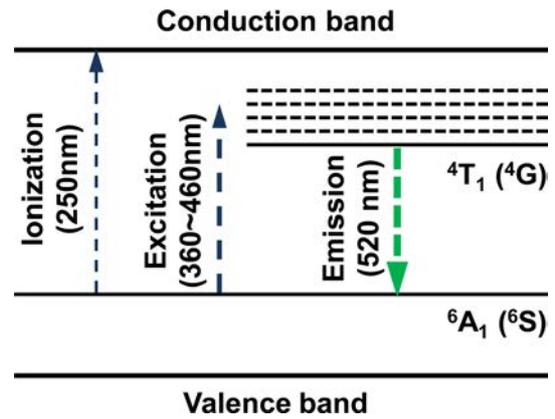
**Fig. 3.** Relative PL emission intensity (a) and peak wavelength with FWHM (b) of Mn<sup>2+</sup>-doped MgAl<sub>2</sub>O<sub>4</sub> with various Mn<sup>2+</sup> doping concentrations.

and 455 nm, corresponding to the transitions of Mn<sup>2+</sup> ion from ground level <sup>6</sup>A<sub>1</sub>(<sup>6</sup>S) to <sup>4</sup>E(<sup>4</sup>D), <sup>4</sup>T<sub>2</sub>(<sup>4</sup>D), [<sup>4</sup>A<sub>1</sub>(<sup>4</sup>G), <sup>4</sup>E(<sup>4</sup>G)], <sup>4</sup>T<sub>2</sub>(<sup>4</sup>G) and <sup>4</sup>T<sub>1</sub>(<sup>4</sup>G) excited levels, respectively [16].

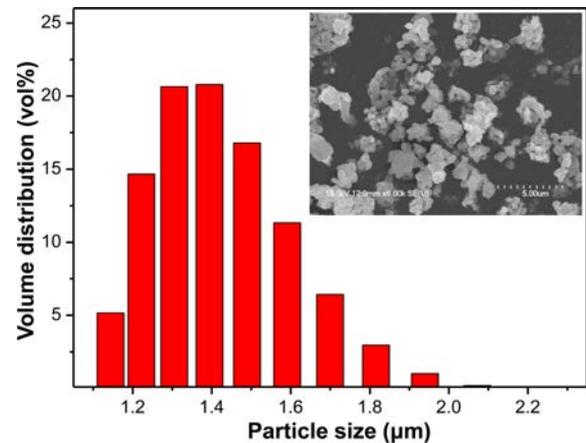
Moreover, the PL spectrum (500-560 nm) excited at 365 nm consists of one broad symmetric band attributed to the spin-forbidden d-d transition (<sup>4</sup>T<sub>1</sub>(<sup>4</sup>G) → <sup>6</sup>A<sub>1</sub>(<sup>6</sup>S)) of Mn<sup>2+</sup> and centered in the wavelength range of 520-525 nm depending on the Mn doping concentration in MgAl<sub>2</sub>O<sub>4</sub>: Mn<sup>2+</sup> [15, 16]. Both the peak position and the shape of the emission spectrum were similar and independent of excitation wavelengths (365, 385, 430 and 455), which indicates there is only one emission center in the phosphor and confirms that the activator ions (Mn<sup>2+</sup>) occupy only equivalent positions in the MgAl<sub>2</sub>O<sub>4</sub> host lattice.

The dependences of PL intensities of MgAl<sub>2</sub>O<sub>4</sub>: Mn<sup>2+</sup> phosphors with various doping concentrations of Mn<sup>2+</sup> (from 1.0 to 5.0 mol%) excited at 365 nm is shown in Fig. 3(a). The PL intensity increased with increasing Mn<sup>2+</sup> concentration until a maximum intensity is reached at the 3.0 mol%, and then it decreased as a result of concentration quenching [17].

Another interesting aspect of the Mn<sup>2+</sup> doping is red-shift of the emission peak position and broadening of bandwidth as confirmed in Fig. 3(b). As the Mn<sup>2+</sup> concentration increases, the peak position continuously moves to the longer wavelength while full-width-at-half-maximum (FWHM) shows a similar trend to the PL intensity. This may be due to some changes produced in



**Fig. 4.** Energy level scheme describing the green light emission process for MgAl<sub>2</sub>O<sub>4</sub>: Mn<sup>2+</sup> phosphor.



**Fig. 5.** Particle size distributions and a typical FE-SEM micrograph (inset) for the 3 mol% Mn<sup>2+</sup>-doped MgAl<sub>2</sub>O<sub>4</sub> phosphor.

the crystal field around Mn<sup>2+</sup> which causes the splitting of 3d electrons. The energy transfer probability of the Mn<sup>2+</sup> from higher levels to lower levels of 3d increases with Mn<sup>2+</sup> doping concentration. This makes it possible that higher Mn<sup>2+</sup> concentration lowers the emission energy for transfer from the higher 3d to the lower 3d state, and hence increases the bandwidth and shifts emission peak position to longer wavelength [18].

The green emission mechanism can be referred to the process schematically shown in Fig. 4. The electrons at the <sup>6</sup>A<sub>1</sub>(<sup>6</sup>S) ground state of Mn<sup>2+</sup> ions are excited to the conduction band or higher energy state than <sup>4</sup>T<sub>1</sub>(<sup>4</sup>G), and the free electrons in the excited state relax to the <sup>4</sup>T<sub>1</sub>(<sup>4</sup>G) excited state through a non-radiative process. This is followed by radiative transitions from the <sup>4</sup>T<sub>1</sub>(<sup>4</sup>G) excited state to the <sup>6</sup>A<sub>1</sub>(<sup>6</sup>S) ground state accompanied by green emission at near 520 nm [19].

Moreover, the emission intensity (*I*) per activator ion is given by the equation,  $I/x = K[1 + \beta(x)]^{Q-1}$ , where *x* is the activator concentration; *Q* = 6, 8 or 10 is for dipole-dipole, dipole-quadrupole or quadrupole-quadrupole interaction, respectively; and *K* and *β* are constants for the same excitation condition for a given host crystal [20]. The plot of log(*x*Mn<sup>2+</sup>) vs log [*I*/*x*Mn<sup>2+</sup>] in the samples excited

365 nm was linear and the slope was  $-0.84$ . By using the above equation, the  $Q$  value obtained was 5.63, which was approximately equal to 6. The result indicates that the dipole-dipole interaction is the major mechanism for concentration quenching of the central  $\text{Mn}^{2+}$  emission in the  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  phosphors.

Fig. 5 shows particle size distributions measured by dynamic light scattering (DLS) and a typical SEM image for the  $\text{Mn}^{2+}$  3 mol% doped phosphor powder. The phosphor powder has an average particle size of 1-2  $\mu\text{m}$  with a tight distribution profile. Each particle has an irregularly round shape and uniform size distribution. The phosphor characteristics are also dependent on the average particle size, size distribution and particle morphology. As the  $\text{Mn}^{2+}$  3 mol% doped phosphor powders synthesized in this work exhibit fine particle size with high uniformity, less scattering effect on their photoluminescence efficiency is expected.

### Conclusions

The non-rare earth elements-based  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  green phosphors have been synthesized via a solid-state reaction route and a systematic study on the effect of  $\text{Mn}^{2+}$  doping concentration on their photoluminescence properties have been carried out. The  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  phosphor showed the major excitation peaks around 365, 385, 430 and 455 nm, which are assigned to the radiative transition from the first state  ${}^6\text{A}_1({}^6\text{S})$  to  ${}^4\text{E}({}^4\text{D})$ ,  ${}^4\text{T}_2({}^4\text{D})$ ,  $[{}^4\text{A}_1({}^4\text{G})$ ,  ${}^4\text{E}({}^4\text{G})]$ ,  ${}^4\text{T}_2({}^4\text{G})$  and  ${}^4\text{T}_1({}^4\text{G})$  of  $\text{Mn}^{2+}$  ions. Under excitation at near UV and blue lights, the  $\text{MgAl}_2\text{O}_4:\text{Mn}^{2+}$  exhibited a strong single band of green emission peaking at 525 nm and the optimum doping concentration of  $\text{Mn}^{2+}$  was found to be 3 mol%. These results demonstrate that the  $\text{Mn}^{2+}$ -doped  $\text{MgAl}_2\text{O}_4$  powder can be applied as a good green phosphor material for white LED using near UV or blue LEDs as the excitation source.

### Acknowledgments

This work was supported by the Korea Foundation for

the Advancement of Science & Creativity (KOFAC), and funded by the Korean Government (MOE).

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