

# Cathodoluminescence Properties of Novel $\text{Mg}_2\text{SnO}_4$ : Mn Phosphor under Low-Voltage Electron Excitation

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## Abstract

The manganese-doped magnesium tin oxide with spinel structure was selected as a green phosphor for FED application and was synthesized by the solid state reaction. Its luminescence properties were investigated under low-voltage electron excitation. The  $\text{Mg}_2\text{SnO}_4$ :Mn phosphor showed green emission with the spectrum centered at 500 nm due to energy transfer from  $^4\text{T}_1$  to  $^6\text{A}_1$  of  $\text{Mn}^{2+}$  ion. Optimum Mn concentration was 0.6 mole % and the decay time was shorter than 10 ms.

**Keywords** : low-voltage, spinel,  $\text{Mg}_2\text{SnO}_4$  : Mn, decay time

## 1. Introduction

In recent years, efficient luminescent materials under low voltage electron bombardment are becoming more and more important for actual and potential applications [1]. High resolution, short decay time, high brightness, and high efficiency are the major requirements of phosphors used in flat panel display devices such as field emission displays (FEDs). The current research interest in the area of luminescence and display technologies is the development of both the novel phosphors and the improved phosphor synthesis techniques. The emission of  $\text{Mn}^{2+}$  activator is strongly dependent on the crystal environment. The tetrahedrally coordinated  $\text{Mn}^{2+}$  ion gives a green emission by forming a weak crystal-field, while the octahedrally coordinated  $\text{Mn}^{2+}$  ion exhibits an orange-to-red emission at usually low temperatures by forming a strong crystal-field [2].

Generally, the oxides with spinel structure ( $\text{AB}_2\text{O}_4$ ) are cubic phase with a large unit cell containing 8A, 16B and 32 oxygen atoms. The A metal ions occupy the tetrahedral interstices and the B metal ions occupy the octahedral sites [3,4]. The host material of the novel green emitting phosphor,  $\text{Mg}_2\text{SnO}_4$  has an inverse spinel structure,  $\text{A}(\text{AB})\text{O}_4$  (A=Mg, B=Sn). Half of the total  $\text{Mg}^{2+}$  ions occupy tetrahedral interstices and the other half of  $\text{Mg}^{2+}$  ions are in octahedral sites with all  $\text{Sn}^{4+}$  ions. When  $\text{Mn}^{2+}$  ions are doped in the  $\text{Mg}_2\text{SnO}_4$  host, they can occupy both tetrahedral sites and octahedral sites. Accordingly,  $\text{Mn}^{2+}$  ions substituted at tetrahedral sites could lead to excellent green emission.

In the present work, the  $\text{Mg}_2\text{SnO}_4$  with a spinel structure was selected as a host material of green phosphor for FED application and it was attempted to prepare  $\text{Mg}_2\text{SnO}_4$ :Mn phosphors by the conventional solid state reaction. According to the other reports, optimized Mn concentration of  $\text{ZnGa}_2\text{O}_4$  is 0.6 mol % under low-voltage [5]. So their luminescent properties under low-voltage electron excitation were compared with the  $\text{ZnGa}_2\text{O}_4$  green phosphor containing 0.6 mol %  $\text{Mn}^{2+}$  activator.

## 2. Experimental

$\text{Mg}_2\text{SnO}_4$ :Mn phosphors were prepared by the solid

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state reaction method. The raw materials were high-purity  $MgO$ ,  $SnC_2O_4$ , and  $MnO$ . The three compounds were mixed thoroughly with an appropriate amount of ethanol at agate mortar and then dried at  $80\text{ }^\circ\text{C}$  for 2 h. The mixture was fired at  $1200\text{ }^\circ\text{C}$  and reheated at the mild reducing atmosphere, 2 %  $H_2$  gas mixed with 98 %  $N_2$  gas. The crystal structure of phosphor was investigated by XRD – Rikaku DMAX-33 X-ray diffractometer. Electron Paramagnetic Resonance (EPR) measurements were recorded using an X-band Bruker ESP 300E spectrometer at 77 K and referenced to DPPH as the g-value standard. Cathodoluminescence spectra were measured by CL spectrometer using an electron beam with the acceleration voltage of 800 V and current of 1.5 mA. Decay curve was measured by using Xenon pulse lamp and oscilloscope.

### 3. Results and Discussion

In this work, the powders obtained by firing in ambient air had pink body color indicate existence of  $Mn^{3+}$  ions. However, the powders reduced finally in 2 %  $H_2$  gas mixture appeared almost in white body color, which points out that all the Mn ions were in the divalent state. In addition, a gray color product was obtained when  $H_2$  content in the reducing gas mixture was more than 2 % because tin component was reduced. No emission from this powder was observed under low-voltage electron excitation. Accordingly, the reduction treatment of specimens fired in ambient air was carried out in 2 %  $H_2$  gas mixture.

To confirm the valence state of Mn ions, EPR spectrum for  $Mg_2SnO_4:Mn$  powder was measured. Fig. 1 shows EPR spectrum of  $Mg_{2-x}Mn_xSnO_4$  ( $x=0.006$ ) powders reduced. EPR spectrum of manganese in the magnesium tin oxide spinel correspond to hyperfine transitions with  $\Delta M_l = 0$  and the fine structure transition with  $\Delta M_s = \pm 1$ ,  $M_s = 1/2$  to  $M_s = -1/2$ . The g value and  $|A|$  value of EPR spectrum were calculated to 2 and  $79 \times 10^{-4} \text{cm}^{-1}$ , respectively. These values were caused by the valence state of  $Mn^{2+}$ . Since the emission center in  $Mg_2SnO_4:Mn$  phosphor is likely to manganese ions, a homogeneous distribution of  $Mn^{2+}$  ions in host material is required. In EPR spectrum of the  $Mg_2SnO_4:Mn$  powder reduced, six hyperfine lines with high resolution are obviously observed. These might be

associated with a homogeneous distribution of manganese. On the other hand, the EPR signal intensity of the phosphor reduced in 2 %  $H_2$  gas is higher, by a factor of 5, than that of powder sample fired in ambient air only. This indicates that the number of the isolated  $Mn^{2+}$  ions by refiring in reducing atmosphere was increased.

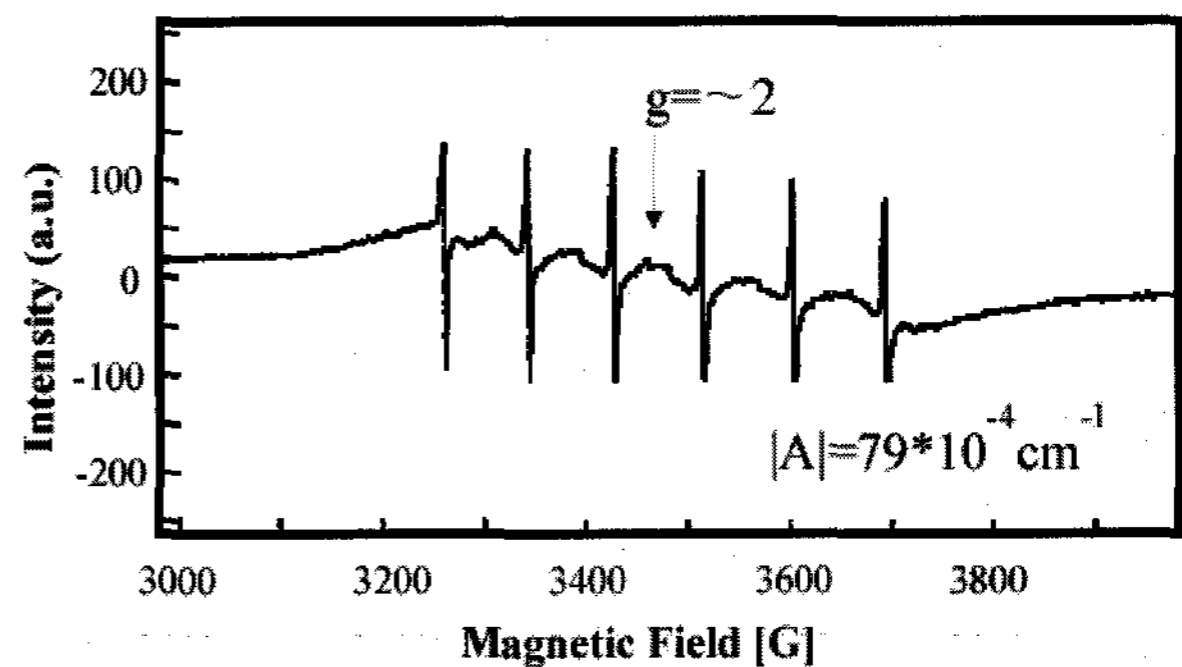


Fig. 1. EPR spectrum of  $Mg_2SnO_4:Mn$  powder.

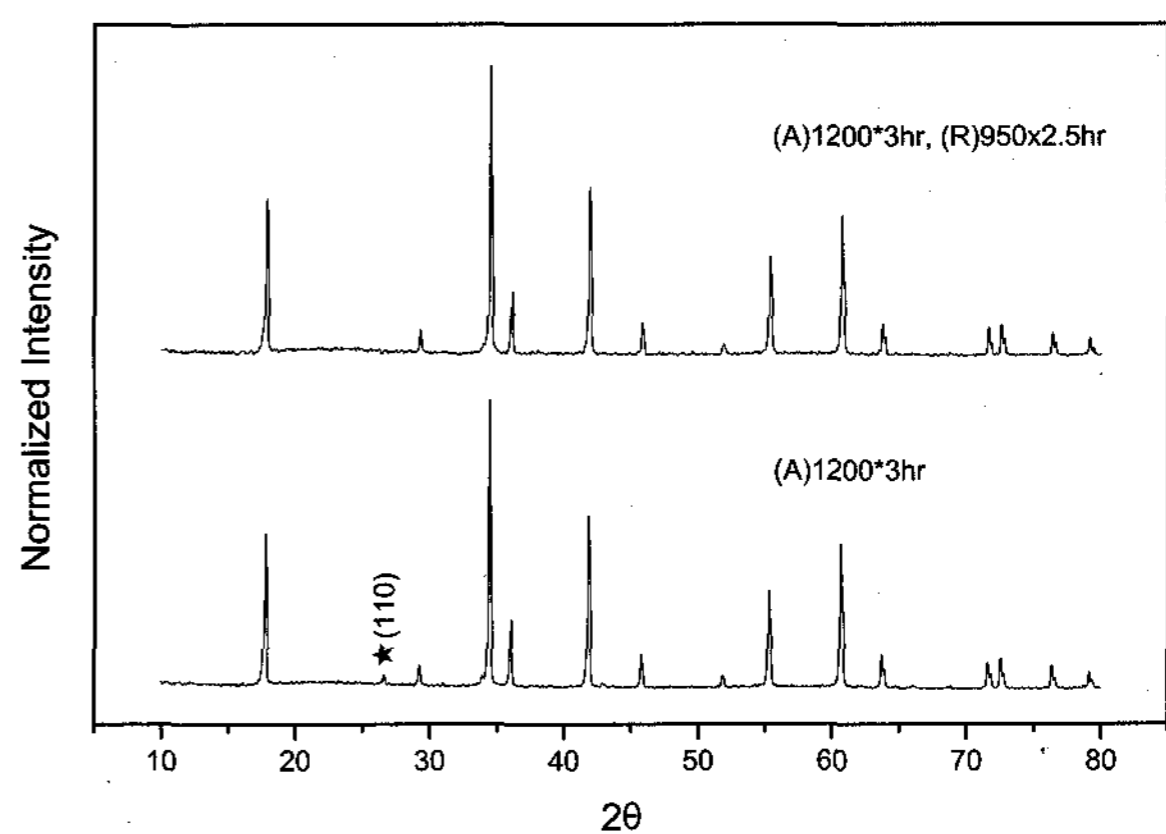
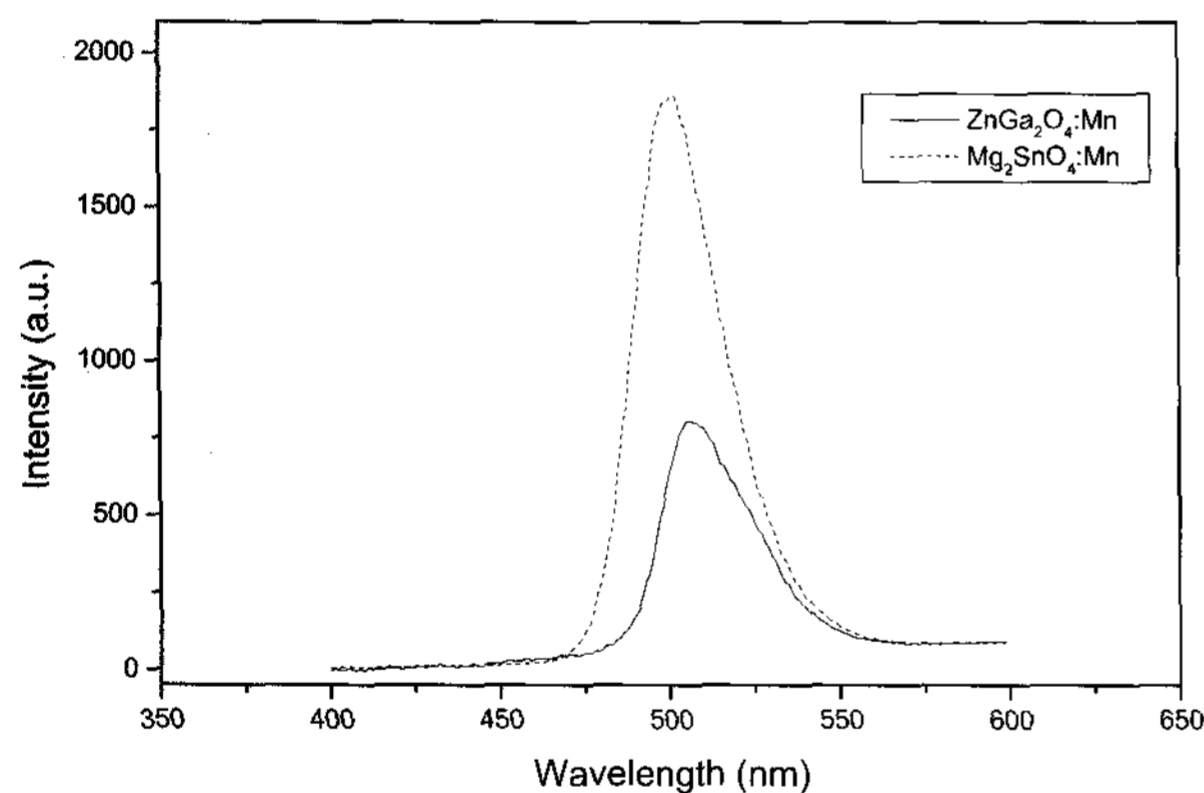


Fig. 2. X-ray diffraction patterns of  $Mg_2SnO_4:Mn$  powders at fired  $1200\text{ }^\circ\text{C}$  and reduced  $950\text{ }^\circ\text{C}$ .

Fig. 2 exhibits X-ray diffraction patterns of  $Mg_2SnO_4:Mn$  powders fired at  $1200\text{ }^\circ\text{C}$  with ambient air and reheated at  $950\text{ }^\circ\text{C}$  with 2 %  $H_2$  gas mixture. In the diffraction pattern of the powder fired at  $1200\text{ }^\circ\text{C}$  in ambient air only, the peak due to the existence of  $SnO_2$  phase was observed. But, no peak of  $SnO_2$  phase existed in the powder reheated in reducing atmosphere after firing in ambient air and only the peaks from  $Mg_2SnO_4$  phase were observed. This is due to the evaporation of the unreacted  $SnO_2$  through reducing treatment. This observation indicates that the single phase of  $Mg_2SnO_4$  was completed by firing at  $1200\text{ }^\circ\text{C}$  and annealing at  $950\text{ }^\circ\text{C}$ .

The CL emission spectra of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  and  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphors under electron beam with 800 V acceleration voltage are expressed in Fig. 3. The doping of 0.6 mole%  $\text{Mn}^{2+}$  in  $\text{Mg}_2\text{SnO}_4$  host material results in excellent green emission centered at 500 nm. The emission process from  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  is the same as that of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor, which 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,  ${}^4\text{T}_1$  to  ${}^6\text{A}_1$ , is directly responsible for the green light emission. In fact, the emission intensity of  $\text{Mg}_{2-x}\text{SnO}_4:\text{Mn}_x$  ( $x=0.6$  mole %) phosphor is much higher than that of  $\text{Zn}_{1-x}\text{Ga}_2\text{O}_4:\text{Mn}_x$  ( $x=0.6$  mole %) phosphor. The  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor exhibits emission spectrum centered at around 505 nm [5]. But, the emission spectrum of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  phosphor due to the strong crystal-field ( $\text{Mg}^{2+}$  ion is smaller than  $\text{Zn}^{2+}$  ion) is centered at 500 nm, which displays green inclining to blue compared to  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor one.

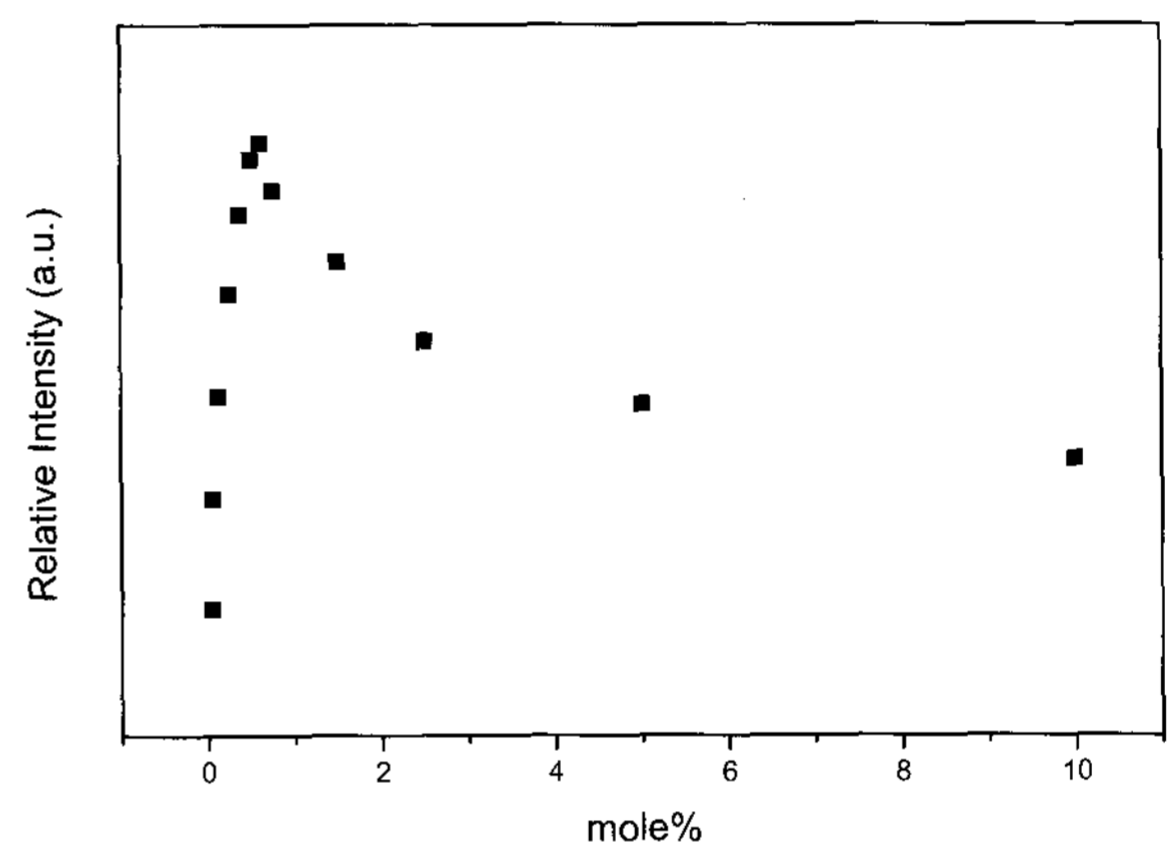


**Fig. 3.** CL emission spectra of  $\text{Mg}_{2-x}\text{SnO}_4:\text{Mn}_x$  ( $x=0.6$  mole %) and  $\text{Zn}_{1-x}\text{Ga}_2\text{O}_4:\text{Mn}_x$  ( $x=0.6$  mole %) phosphors.

To optimize the concentration of activator in  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  phosphor, Mn content was varied from 0.1 mole % to 10 mole %. The Mn content dependence of emission intensity for  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  is shown in Fig. 4. As can be seen in the graph, the emission intensity of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  abruptly augments with the concentration of Mn at the lower Mn content region. It reaches maximum at Mn concentration of 0.6 mole % and then diminishes with increasing Mn content, indicating the concentration quenching [1].

The acceleration voltage dependence of emission intensity for  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  is shown in Fig. 5. Under the

conditions of acceleration voltage of 200 V to 800 V, emission intensities of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  phosphor were compared with those of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  phosphor. When the acceleration voltage is 800 V, relative emission intensity of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  is stronger, by a factor of 2.5, than that of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$ . At 200 V of acceleration voltage, the emission intensity of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  is about 1.5 times as strong as that of  $\text{ZnGa}_2\text{O}_4:\text{Mn}$ . This indicates that the emission intensity of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  phosphor abruptly decreases with decreasing acceleration voltage. However, the emission intensity of  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  compared to  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  under the measured range of acceleration voltage is much stronger.



**Fig. 4.** Mn concentration dependence of emission intensity for  $\text{Mg}_2\text{SnO}_4:\text{Mn}$  under the excitation of electron beam with 1.5 mA-current and 800 V-acceleration voltage.

In general, according to spin selection rule the phosphors doped with manganese activator exhibit a long decay time due to the forbidden transition of  $\text{Mn}^{2+}$  ions. In case of the 2 mole % Mn-doped  $\text{Zn}_2\text{SiO}_4$  phosphor which exhibits the highest emission intensity, the decay time ( $\tau_{10\%}$ ) has been reported to be about 30 ms [6]. To reduce its decay time, Mn concentration is enlarged to c.a. 10 mole % like the commercially available  $\text{Zn}_2\text{SiO}_4:\text{Mn}$  phosphor. Because the isolated  $\text{Mn}^{2+}$  ions in host lattice at a low Mn content causes long decay time while the formation of  $\text{Mn}^{2+}$  ion pairs at a high Mn content reduces the decay time [7]. But the increase of Mn content in  $\text{Zn}_2\text{SiO}_4:\text{Mn}$  accompanies with the decrease in emission intensity. Fig. 6 reveals the measured decay curves of the Mn-doped  $\text{Mg}_2\text{SnO}_4$  and  $\text{ZnGa}_2\text{O}_4$  phosphors. At the 0.6 mole % Mn concentration, their decay curves point out decay time ( $\tau_{10\%}$ ) of shorter than 10 ms. In  $\text{ZnGa}_2\text{O}_4:\text{Mn}$  with a

normal spinel, it is known that Mn ions could occupy both tetrahedral site and octahedral site due to the forming of a disordered spinel. In the  $\text{Mg}_2\text{SnO}_4$ :Mn phosphor, on the other hand, the host material has an inverse spinel structure of  $\text{A}(\text{AB})\text{O}_4$  type and the  $\text{Mn}^{2+}$  ions could occupy the both tetrahedral site and octahedral site [8]. The strongest interaction is between the metal ions ( $\text{M}_t$ ) in tetrahedral sites and the metal ions ( $\text{M}_o$ ) in the octahedral sites, because the  $\text{M}_t\text{-O-M}_o$  distance is relatively short and the angle  $\text{M}_t\text{-O-M}_o$  is large [9]. Accordingly, it could be presumed that the short decay time of  $\text{Mg}_2\text{SnO}_4$ :Mn at relatively low Mn concentration are related with to exchange interaction between the emitting  $\text{Mn}^{2+}$  ions in tetrahedral sites and the non-emitting  $\text{Mn}^{2+}$  ions in octahedral sites.

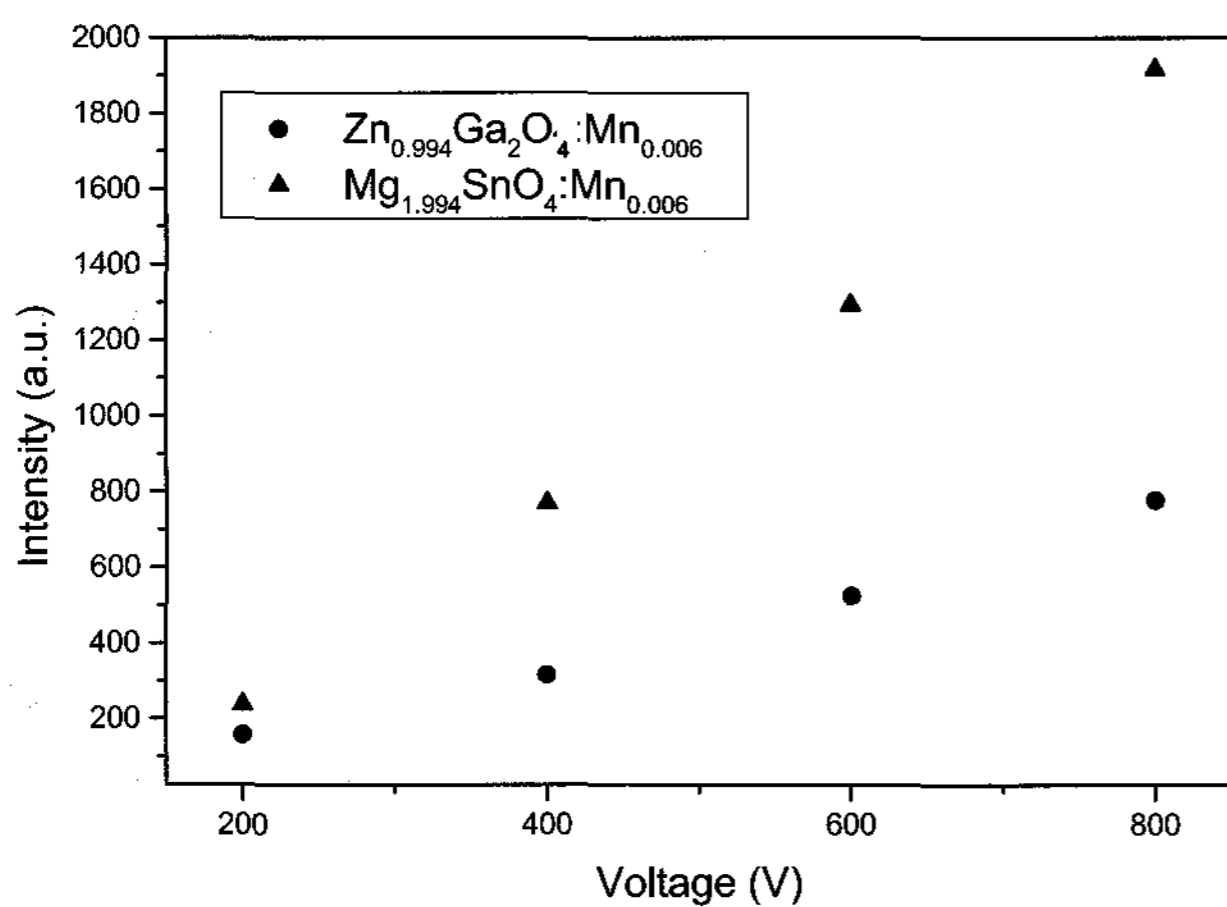


Fig. 5. Comparison of emission intensity for  $\text{ZnGa}_2\text{O}_4$ :Mn and  $\text{Mg}_2\text{SnO}_4$ :Mn phosphors at the various accelerating voltages.

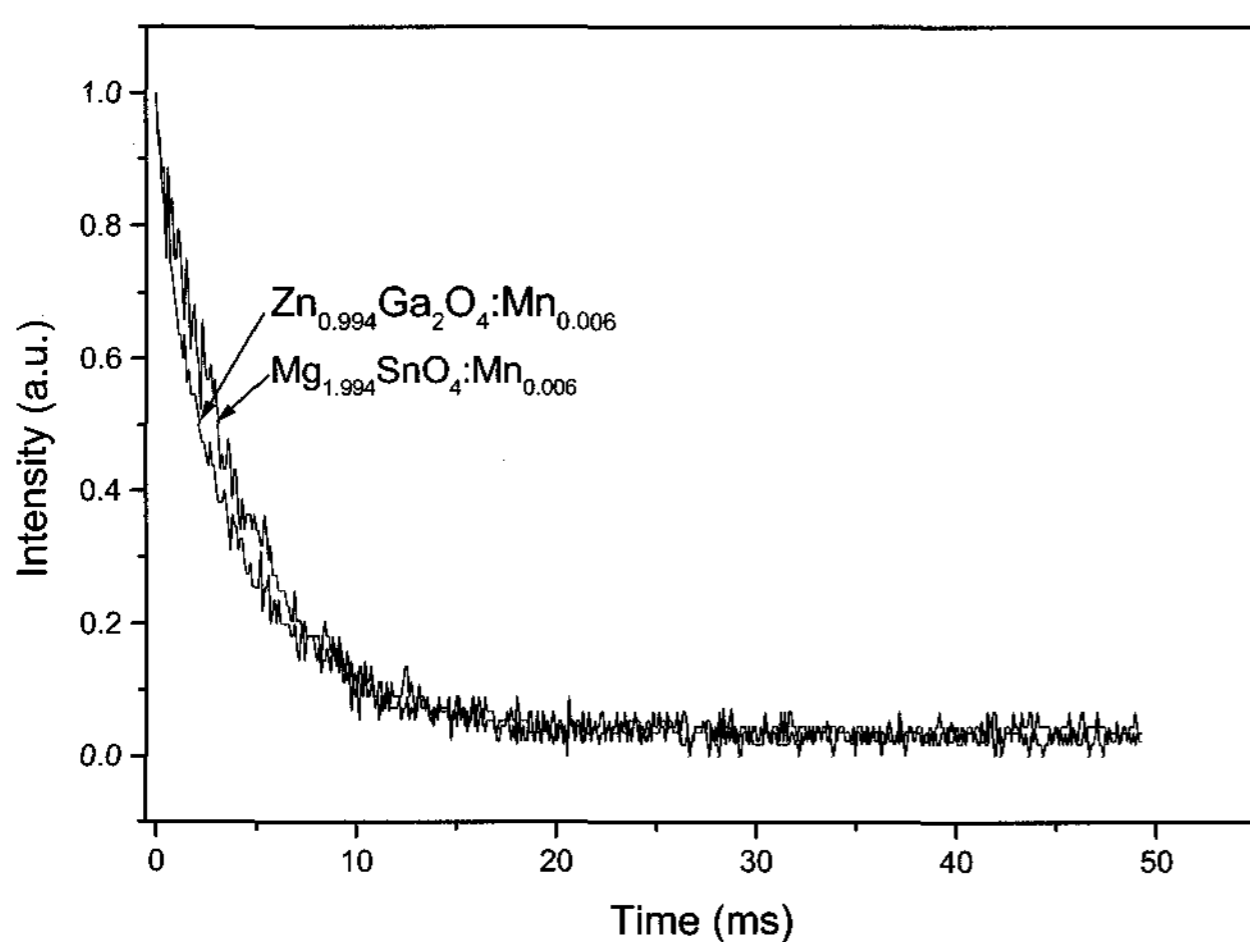


Fig. 6. Decay curves of  $\text{Mg}_2\text{SnO}_4$ : Mn and  $\text{ZnGa}_2\text{O}_4$ : Mn phosphors.

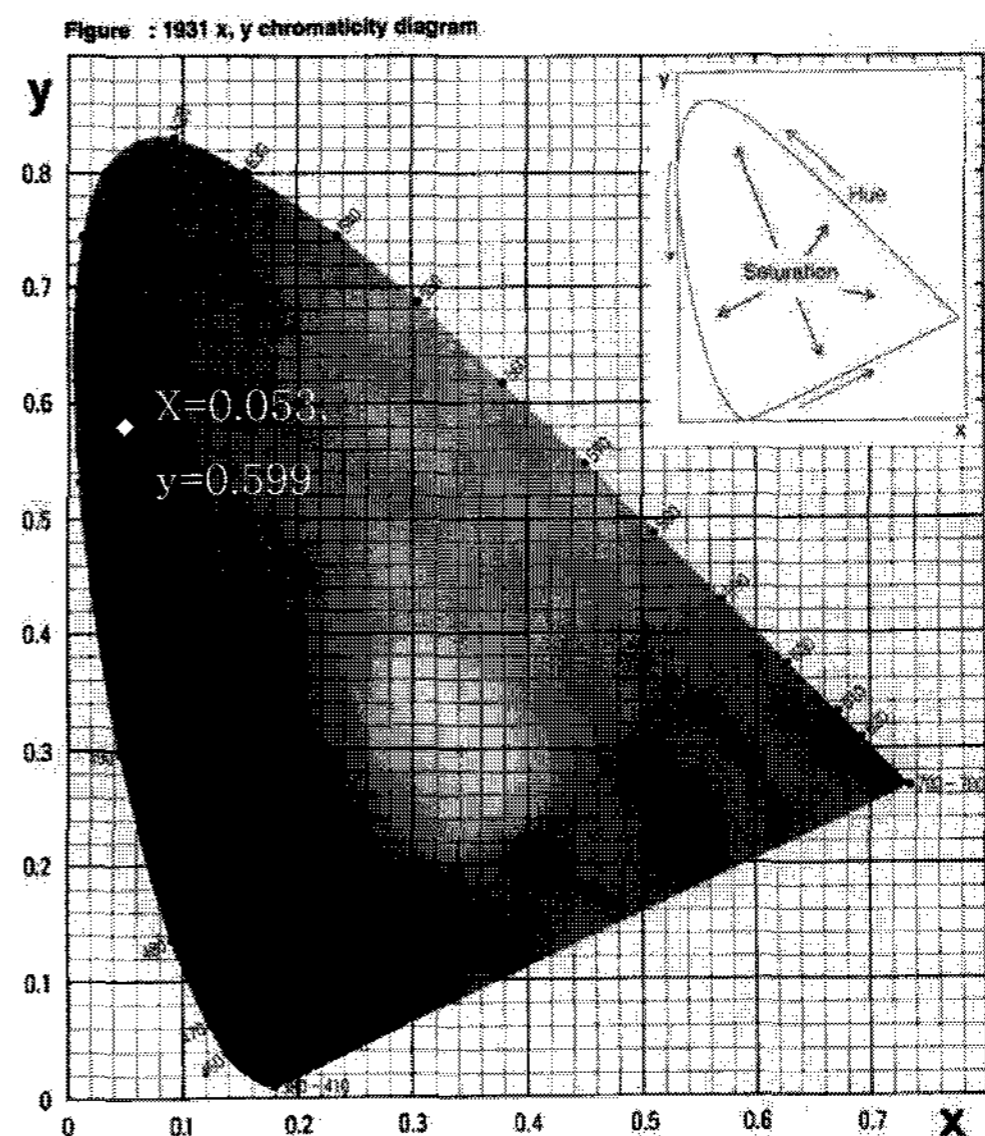


Fig. 7. Chromaticity coordinate of  $\text{Mg}_2\text{SnO}_4$ :Mn phosphor.

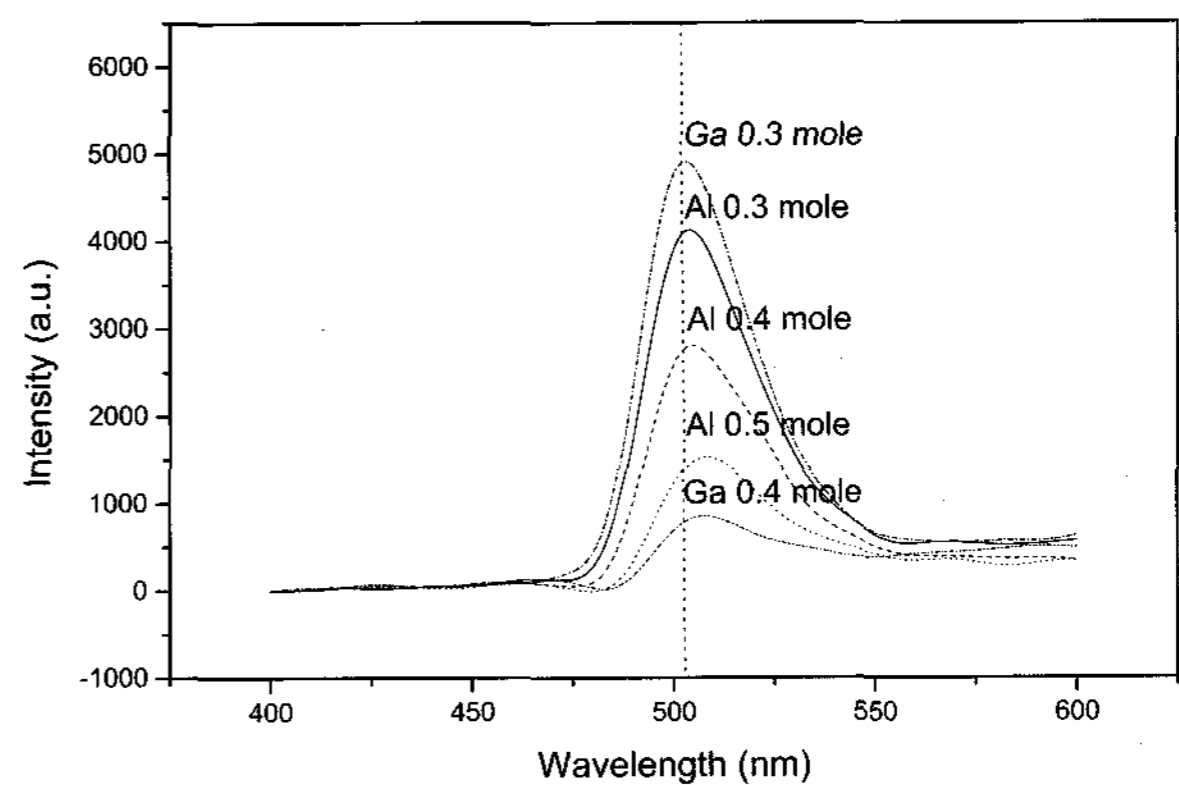


Fig. 8. CL emission spectra of  $\text{Ga}^{3+}$  or  $\text{Al}^{3+}$  co-doped  $\text{Mg}_2\text{SnO}_4$ :Mn phosphors.

Fig. 7 shows the color coordinate of  $\text{Mg}_2\text{SnO}_4$ :Mn on the CIE chromaticity diagram. As can be seen, the color coordinate of  $\text{Mg}_2\text{SnO}_4$ :Mn phosphor is measured to  $x=0.053$  and  $y=0.599$ . On the other hand, it has been reported that the chromaticity value of  $\text{ZnGa}_2\text{O}_4$ :Mn phosphor is  $x=0.118$  and  $y=0.745$  [10]. Accordingly, the color of the emitted light of  $\text{Mg}_2\text{SnO}_4$ :Mn phosphor is more bluish than that of the  $\text{ZnGa}_2\text{O}_4$ :Mn phosphor. As previously mentioned, such disparity in the color coordinate of two phosphors has possibly to do with the difference in the crystal-field by the different environment surrounding  $\text{Mn}^{2+}$  ions.

Because  $\text{Mg}_2\text{SnO}_4$ :Mn phosphor does not exhibit monochromatic green emission, there is a need to shift the emission center to the long wavelength further. From

this point of view, various electronic and structural features can be considered. For the  $Mn^{2+}$  with  $d^5$  configuration, a red shift of the emission can be induced to increase the crystal field. The increase of crystal field is expected to be achieved by substitution of smaller isovalent cation or more highly charged cation for  $Mg^{2+}$  ion [11]. For this purpose,  $Al^{3+}$  and  $Ga^{3+}$  ions are substituted to Mg sites, respectively. As shown in Fig. 8, the emission intensity decreases consecutively with increasing  $Ga^{3+}$  (or  $Al^{3+}$ ) concentration, but a red shift of the emission peak in  $Mg_2SnO_4:Mn$  phosphor occurs. When 40 mole % of  $Ga^{3+}$  is doped, the emission peak is centered at 505 nm wavelength. This implies that substitution of  $Ga^{3+}$  or  $Al^{3+}$  for  $Mg^{2+}$  in  $Mg_2SnO_4:Mn$  produces a stronger crystal field and a red shift in the emission. A detailed study on the emission mechanism for the  $Ga^{3+}$  or  $Al^{3+}$  co-doped  $Mg_2SnO_4:Mn$  is currently in progress.

#### 4. Conclusion

Novel green phosphor with the chemical formula of  $Mg_{2-x}SnO_4:Mn_x$  has been synthesized by the conventional method. The single phase of  $Mg_2SnO_4:Mn$  phosphor is formed by firing at 1200 °C in ambient air and refiring at 950 °C in mild reducing atmosphere. The optimum concentration of  $Mn^{2+}$  showing the maximum intensity under the electron beam excitation was 0.6 mole %. On the other hand, it was presumed that the short decay time of  $Mg_2SnO_4:Mn$  at a relatively low Mn content was originated with the exchange interaction between the  $Mn^{2+}$  ions in tetrahedral sites and the  $Mn^{2+}$  ions in octahedral sites of inverse spinel structure. Also, the substitution of  $Ga^{3+}$  or  $Al^{3+}$  for  $Mg^{2+}$  in  $Mg_2SnO_4:Mn$  produced a red shift with the decrease in emission intensity.

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