A Study on Feasibility of Hexagonal Phase ZnS:Mn^{2+} Phosphor for Low-voltage Display Applications

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Abstract

Mn doped hexagonal phase of ZnS has been studied as a yellow-orange phosphor for the application to fluorescent displays operated at low voltages. It was found that luminescence from Mn^{2+} was increased as the Mn concentration was increased up to 1.2 mol% of host lattice. This study has been attempted by adding trivalent ions such as Al^{3+} or Bi^{3+} to ZnS:Mn as an agent to do the efficient incorporation of Mn ions into ZnS:Mn lattice, resulting in a significant improvement in the phosphor performance, especially at low voltages.

1. Introduction

ZnS:Mn is one of the bright and efficient phosphors used in TFEL (thin film electroluminescence) display [1]. ZnS:Mn shows a yellow-orange emission of *d-d* transition originated from Mn^{2+} ion [2-3]. The emission color of ZnS:Mn phosphor is useful when the phosphor is stacked on a blue or green emitting phosphor since a white emission could be achieved when the emission colors of two phosphors are mixed. ZnS:Mn phosphor, especially nanocrystal, has been studied recently with interest and attraction from display field [4,5]. To increase its efficiency and brightness, nanocrystalline ZnS:Mn phosphor seems to be suitable for display applications [6-8]. However, as the particle size is reduced to nano-scale, the surface of phosphor becomes unstable. Thus, a polymer material, such as, poly acrylic acid (PAA) is used as a surface stabilizer or luminescence increase [9-11]. In the present study, we have studied the feasibility of ZnS:Mn phosphor for application to the low-voltage fluorescent displays. Also, we have tried to increase the luminescence intensity of ZnS:Mn phosphor by adding a trivalent ion. From our results, trivalent ions such as Al^{3+} or Bi^{3+} turned out a luminescence increase of ZnS:Mn phosphor.

2. Experimental

To synthesize ZnS:Mn phosphor, a conventional method was used. Hexagonal phase of ZnS powder (average particle size = 5 µm) and MnSO$_4$·5H$_2$O were used as host material and activator, respectively. ZnCl$_2$ and NH$_4$Cl were used as fluxes. The raw materials were mixed in water and dried. After drying, sulfur powder was added in the raw materials to compensate for the sulfur deficiency. Sintering was performed at 900~1100°C.

In order to investigate optical properties, photoluminescence (PL) and cathodoluminescence (CL) of ZnS:Mn phosphors were measured at room temperature. The PL was measured by using a photon-counting spectrometer (DARSA-Pro) when Xe-arc lamp was operated at 300 W. The CL was measured using a demountable ultra-high vacuum chamber equipped with a laboratory-built CL spectrophotometer. Measurement of CL was carried out at excitation energy of 500 eV and a beam current density of 40 µA/cm^2. The luminescence measurements were conducted on powder samples.

On the other hand, low-voltage CL was tested at excitation energy of 30 eV. The W-filament was used as an electron source of low-voltage CL test. In this case luminescence was measured from phosphor

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screen, which is composed of mixture of ZnS:Mn phosphor, conductive material and organic vehicles.

3. Results and Discussion

Fig. 1 shows normalized PL excitation (a) and emission (b) spectra of ZnS:Mn phosphors. From Fig. 1(a), the main peak of excitation is located at about 356 nm. As the concentration of Mn was increased, a shoulder peak at about 395 nm was increased. The excitation spectrum is independent of the monitored wavelength except for 0.006 mol% Mn-doped sample.

At the optimal concentration, ZnS:Mn phosphor shows a typical $^4T_1$-$^6A_1$ transition of Mn^{2+} ion and the main emission peak is located at about 585 nm [12]. As the concentration of Mn was increased, the shoulder peak at about 466 nm disappeared in the emission spectra [Fig. 1(b)]. It seems that the peak at 466 nm is related with the self-activation (SA) of ZnS [13].
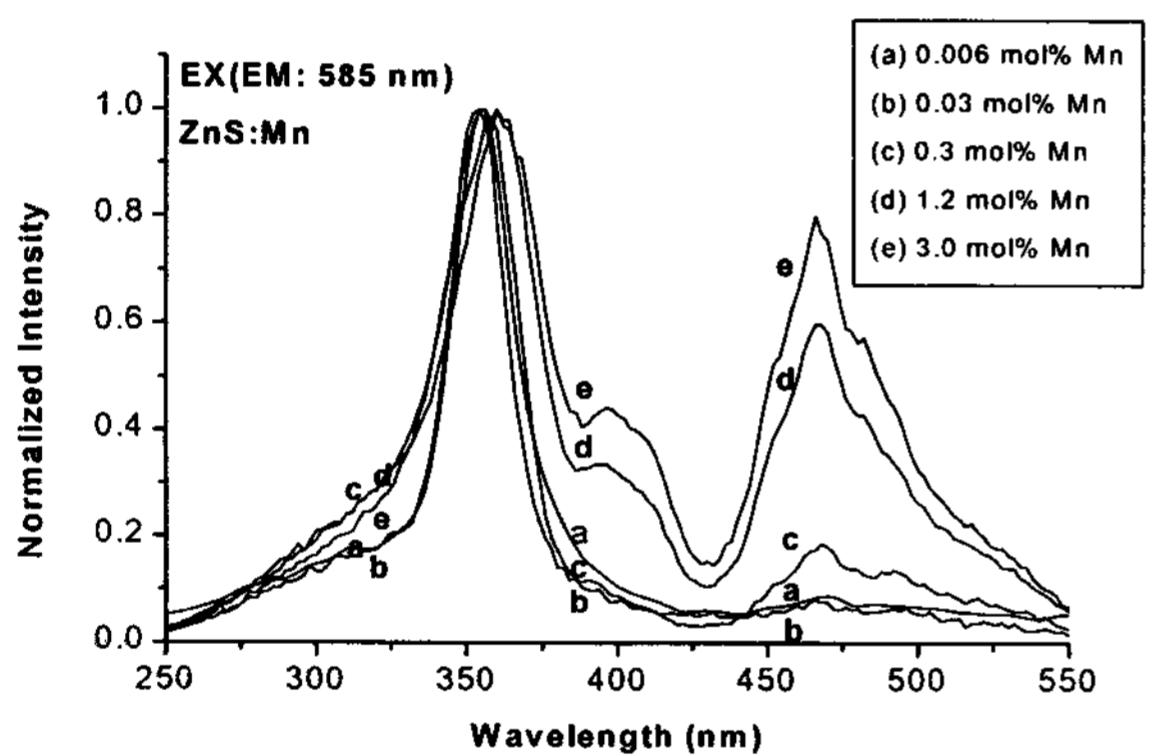
(a)
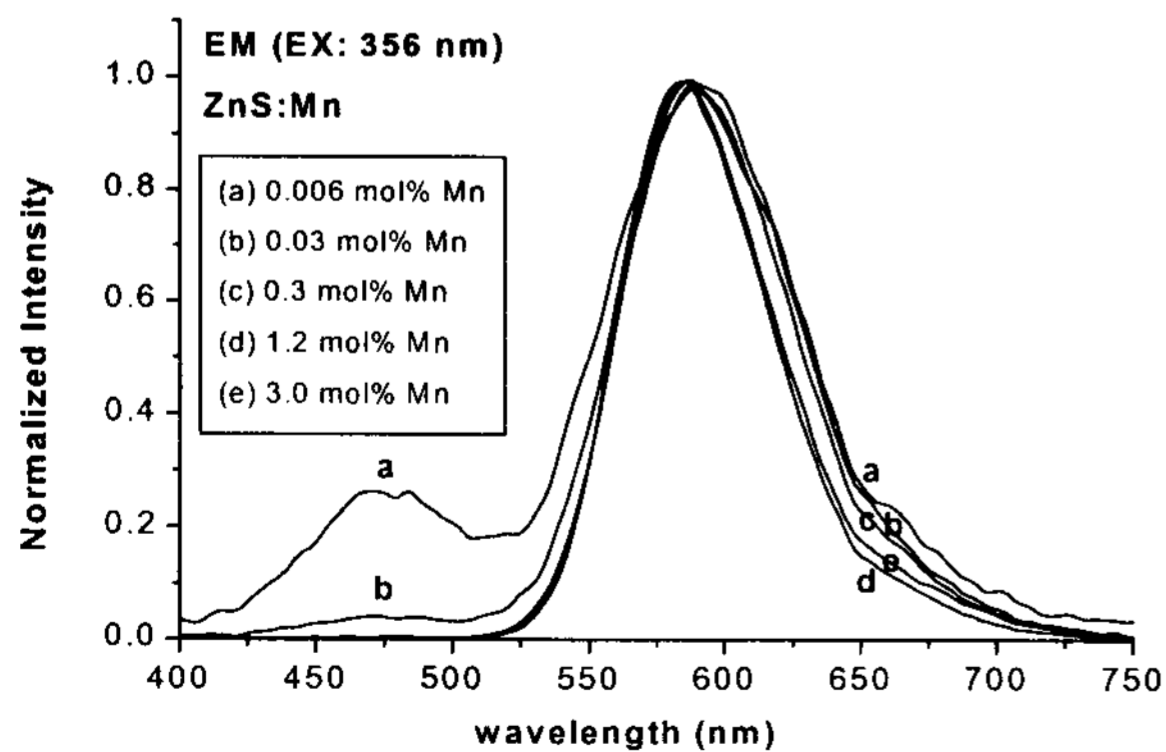
(b)

Fig. 1. Normalized excitation (a) and emission (b) spectra of ZnS:Mn phosphors .

Figure 2 shows CL emissions of ZnS:Mn phosphors as concentration of Mn ion is varied. When the Mn concentration was lower than 0.3 mol% of host lattice, blue emission appeared, as shown in Fig. 2. However, the luminescence of ZnS:Mn shows yellow-orange emission (585 nm) when the concentration of Mn ion reached to 0.3 mol% of host lattice. The CL emission has the same tendency as the PL emission does. It seems that when the concentration of Mn ion is low, luminescence of self-activation (SA) originated from Zn vacancy of ZnS is preferred like the PL emissions [13]. It is thought that as the concentration of Mn increased, the Zn vacancy would be substituted or annihilated by Mn ion. Thus, yellow-orange color of emission appeared originated from d-d transition of Mn ion.
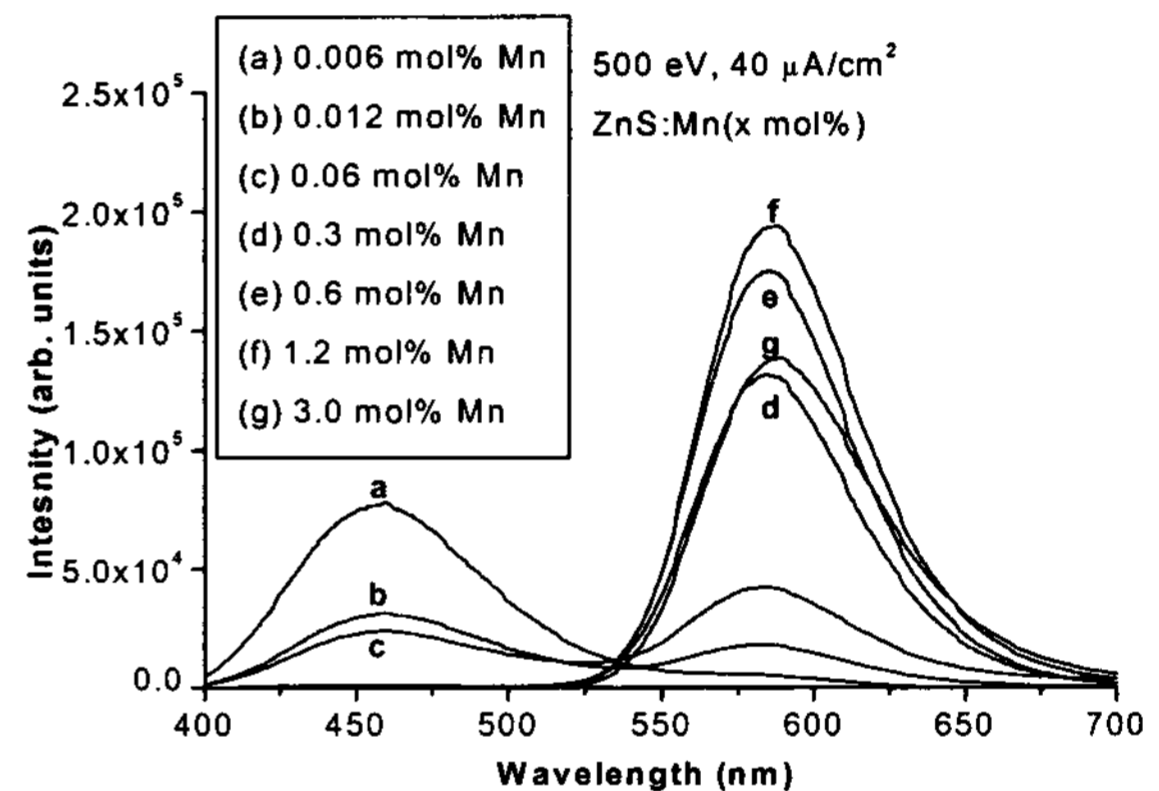

Fig. 2. CL emission spectra of ZnS:Mn phosphors.

Figure 3 shows SEM images of ZnS:Mn phosphors when two different materials were used as fluxes. At synthesis stage, $ZnCl_2$ and NH_4Cl were used as flux materials. When the $ZnCl_2$ was used, the size of sintered particle was not observably changed compared with the raw-material ZnS. However, when the NH_4Cl was used, the size of sintered particle became larger than that of the raw material, as shown in Fig. 3. It seems that coalescence of two or three particles occurred. The physical parameters of the fluxes are listed in Table 1. One can see that the melting points of the two fluxes are below the sintering temperature of the phosphor, as shown in the Table 1. In particular, NH_4Cl sublimes at melting

point. Although the role of flux to the growth of phosphor cannot be explicitly explained at present, it can be thought that NH_4Cl becomes gas phase and acts as flux from the early stage of sintering. Thus, the phosphor particle became large when the NH_4Cl was used as flux.

Table 1. Physical parameters of the fluxes [14]

Flux	Melting Point (°C)	Boiling Point (°C)	Remark
$ZnCl_2$	293	732	-
NH_4Cl	< 340	-	Sublimation without melting
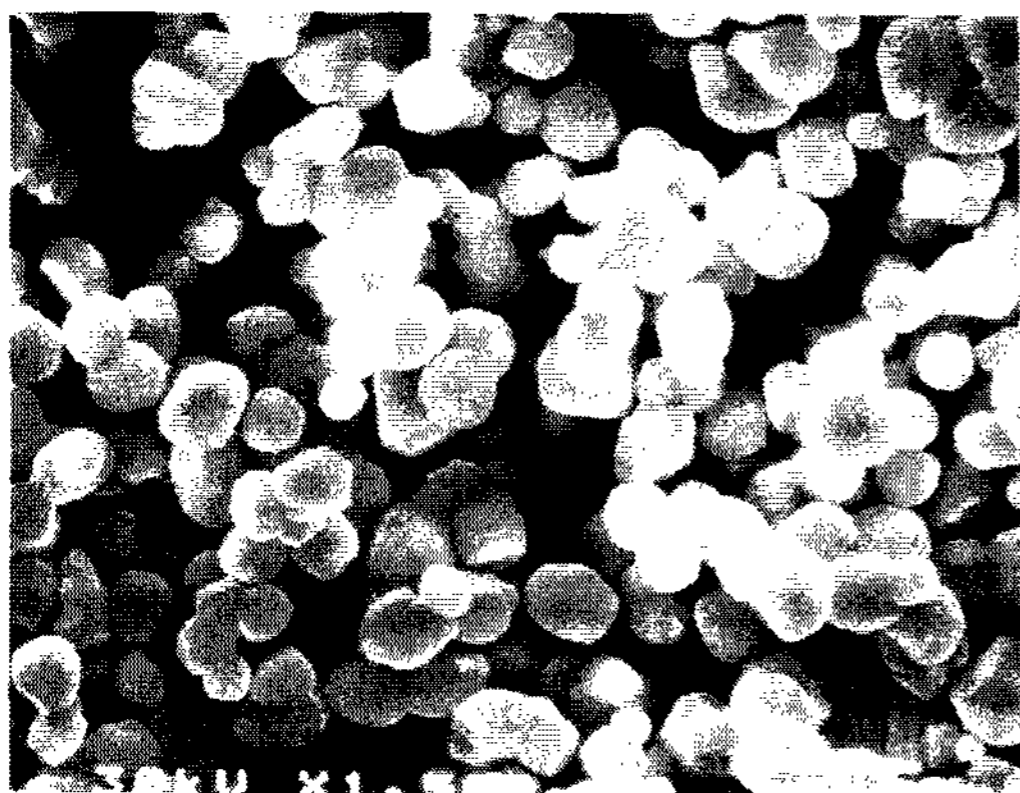
(a)
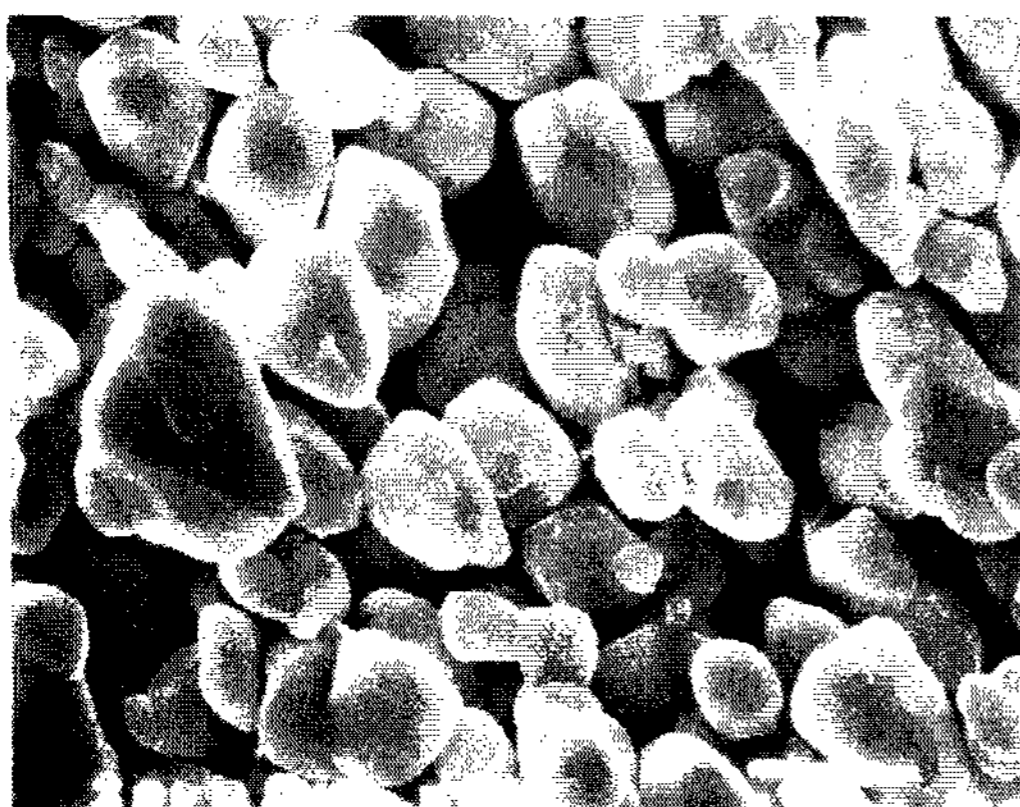
(b)

Fig. 3. SEM images of sintered phosphors. $ZnCl_2$ (a) and NH_4Cl (b) were used as flux materials, respectively.

Figure 4 shows the relative PL emission intensity when the samples are excited with the wavelength of 365 nm. From the figure, the luminescence intensity

of ZnS:Mn was increased when Al^{3+} or Bi^{3+} ions were doped. The exact roles of the ions are not clear at present, but they may act as a luminescence increase of Mn emission.

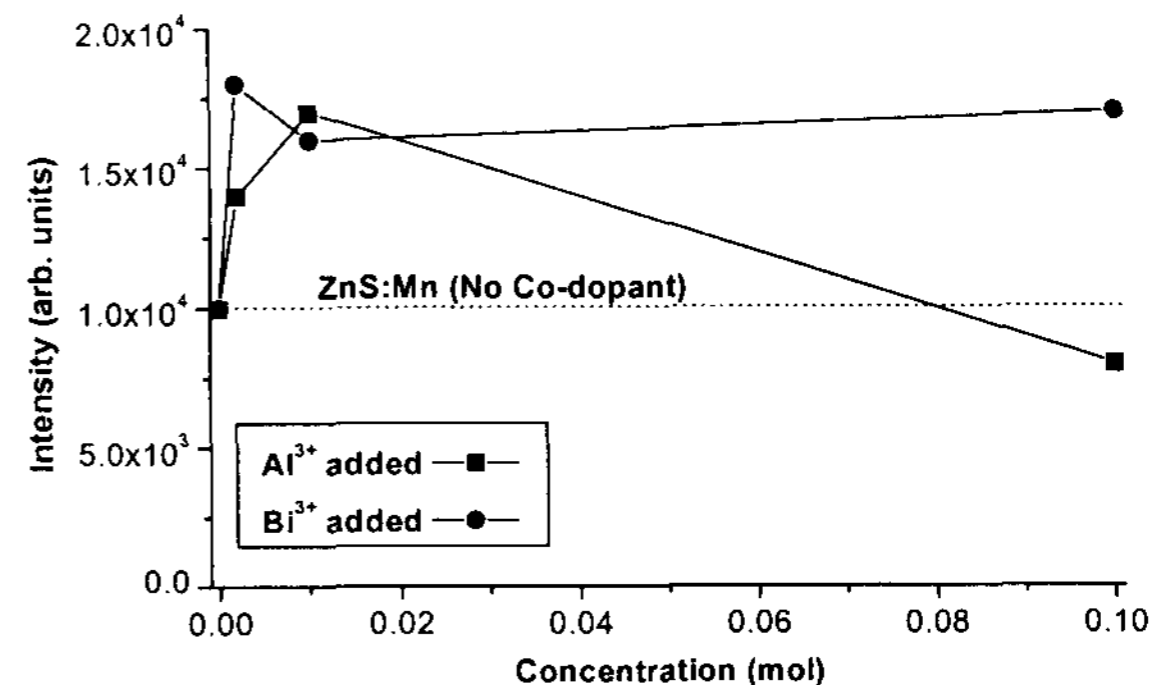Fig. 4. The relative PL intensity of ZnS:Mn,X phosphor (X = Al, Bi).

Figure 5 shows CL emissions of ZnS:Mn phosphors measured at an excitation energy of 30 eV. The phosphor emitted a yellow-orange emission at optimal concentration and it shows the same trend as in the high-energy excitation.
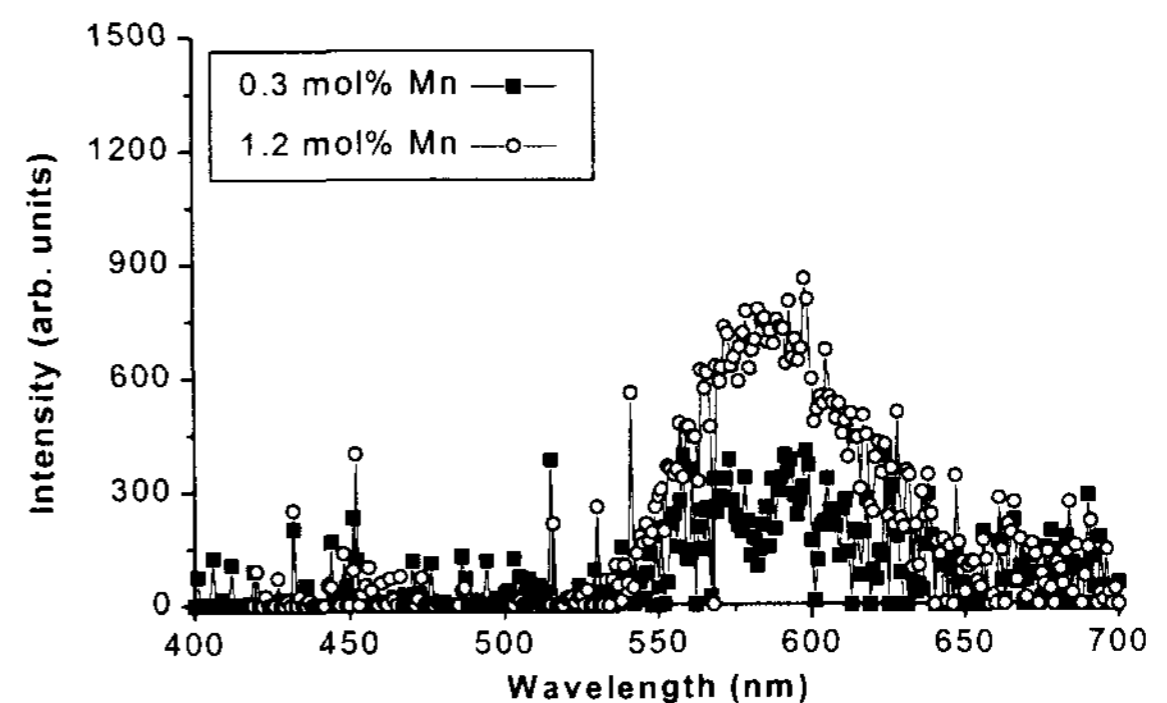

Fig. 5. Low-voltage CL emission of ZnS:Mn phosphors.

4.   Summary and Conclusion

In this work, we have studied the feasibility of hexagonal phase of ZnS:Mn for a yellow-orange phosphor to the application of fluorescent displays. It was found that luminescence from Mn^{2+} was increased up to the optimal concentration of Mn ion. Also, it was tried to increase the efficient

incorporation of Mn ions into ZnS:Mn lattice by adding trivalent ions such as Al^{3+} or Bi^{3+}, which improve the luminescence of phosphor.

5. References

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