Fabrication of Yellow Lighting Phosphor for Low-voltage Display Applications

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Abstract

ZnS:Mn has been studied as a yellow phosphor for the application to fluorescent displays operated at low voltage. It was found that luminescence of Mn^{2+} ion from hexagonal phase of ZnS was suitable for the display applications. The main emission peak was shifted to shorter wavelength when Cu ions were doped. The luminescence color of ZnS:Mn phosphor could be changed with decrease of its brightness.

1. Introduction

As we reported previously, ZnS:Mn is one of the bright and efficient phosphors used in TFEL (thin film electroluminescence) display [1-2]. In the present study, we have studied the ZnS:Mn phosphor for application of the low-voltage fluorescent displays. It is found that the luminescence color of ZnS:Mn is changed from yellow-orange to yellow in Commission Internationale de I'Eclairage (CIE) coordinates as Cu ions were doped. Also, we have tried to increase the luminescence intensity of ZnS:Mn phosphor by controlling a flux material. From our results, low melting point flux material is effective to increase the brightness of ZnS:Mn phosphor.

2. Experimental

2.1 Phosphor synthesis

To synthesize ZnS:Mn phosphor, a conventional method was used. Hexagonal and cubic phases of ZnS powders (average particle size = 3~4 mm) and $MnSO_4 \cdot 5H_2O$ were used as host material and activator, respectively. Chloride containing flux materials such as $ZnCl_2$ and NH_4Cl 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 for 2 h. After sintering, the phosphor was ball-milled with glass bead. The ball-mill condition was set as the mass of the phosphor, glass bead and distilled water were equal. The milling speed was fixed at 100 rpm. After ball-milled, the phosphor was sieved with 400 dots/inch mesh. And small buoyant particles were eliminated during the sieving process.

2.2 Measurement of optical properties

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 spectrometer. Measurement of CL was carried out at excitation energy of 500 eV and a beam current density of 40 $\mu A/cm^2$. The luminescence measurements were conducted on powder samples. On the other hand, low-energy excitation CL was tested at excitation energy of 30 eV. W-filament was used as an electron source of low-energy excitation. In this case, luminescence was measured from phosphor screen. The phosphor screen was made with phosphor paste on the indium-tin-oxide (ITO) coated glass. The phosphor paste was composed of mixture of ZnS:Mn phosphor, conductive material and organic vehicles. After screening process, the phosphor-screened ITO glass was heated at 450°C for 15 min in order to remove the organic vehicles.

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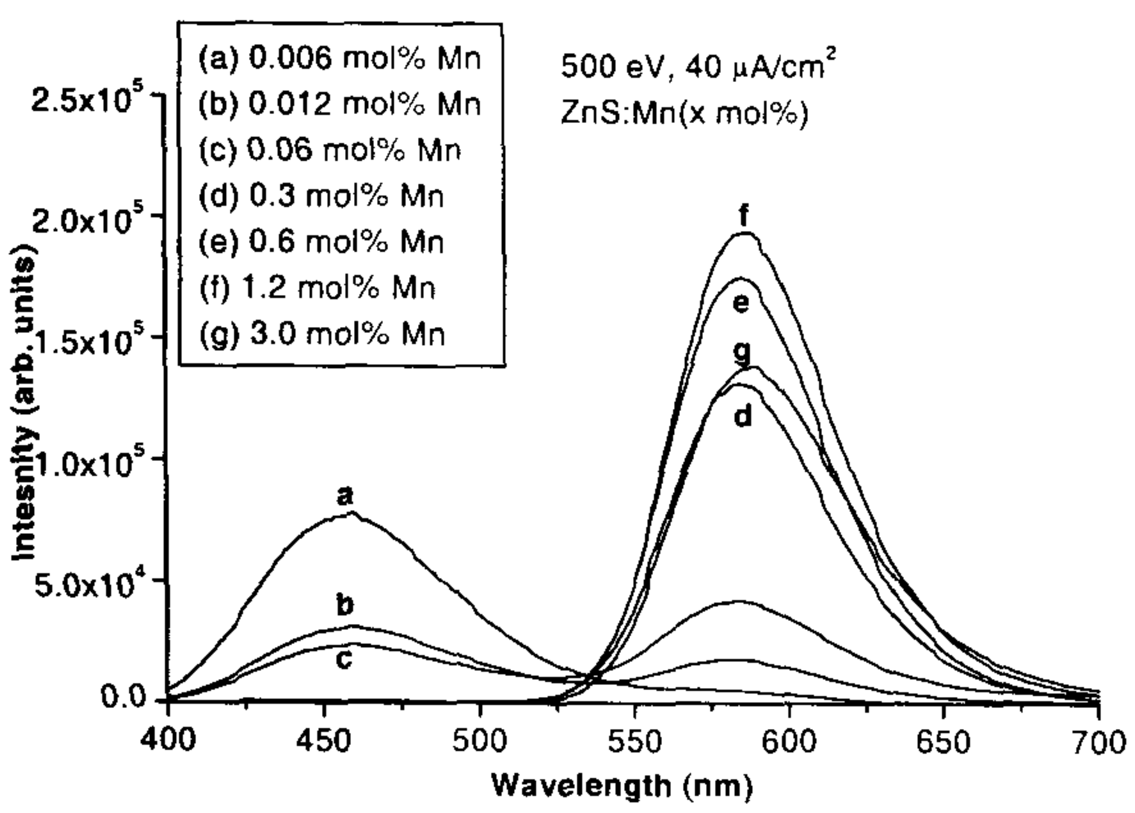
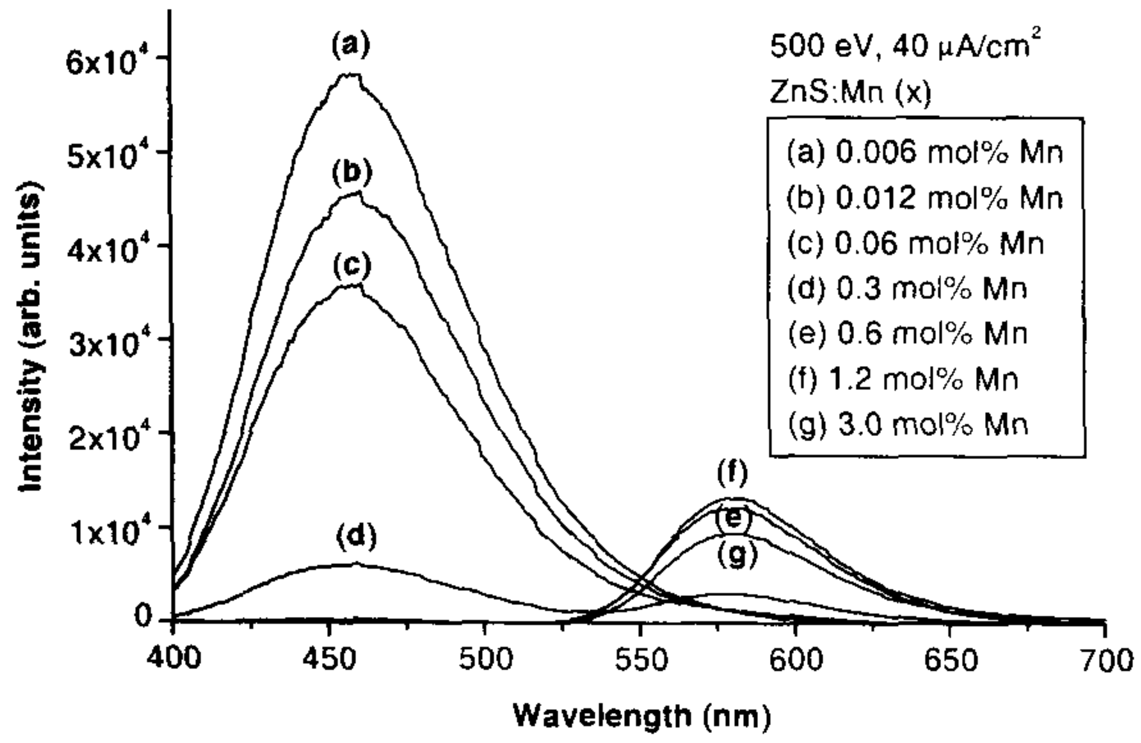
3. Results and Discussion

Figure 1 shows CL emissions of hexagonal and cubic phases of ZnS:Mn phosphors as concentration of Mn ion is varied. The CL was measured at excitation energy of 500 eV and a beam current density of 40 μA/cm^2. When the Mn concentration was lower than 0.3 mol% of host lattice, blue emission appeared, as shown in Fig. 1. 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 intensity of yellow-orange color of emission (*d-d* transition of Mn ion) is enhanced as the concentration of Mn increases in the case of hexagonal phase of ZnS [3-4]. It seems that energy transfer efficiencies are different in each phosphor phase. From the results, the hexagonal phase was focused on our experiments.



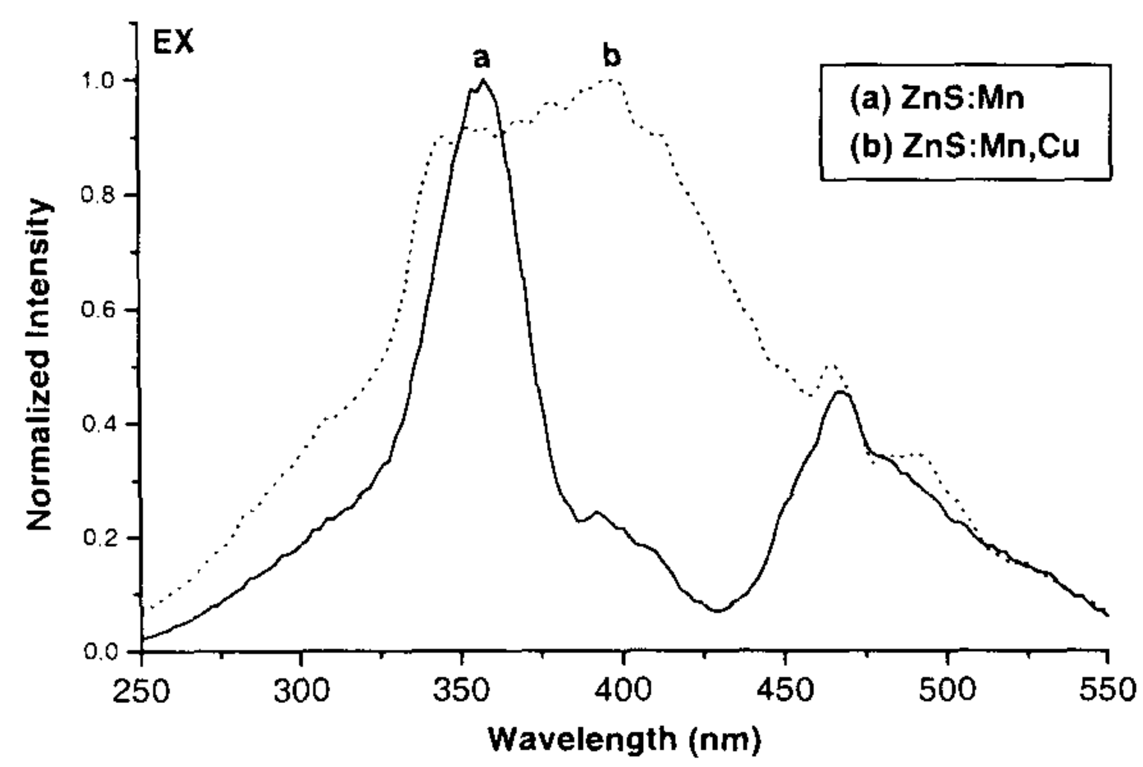
(a)



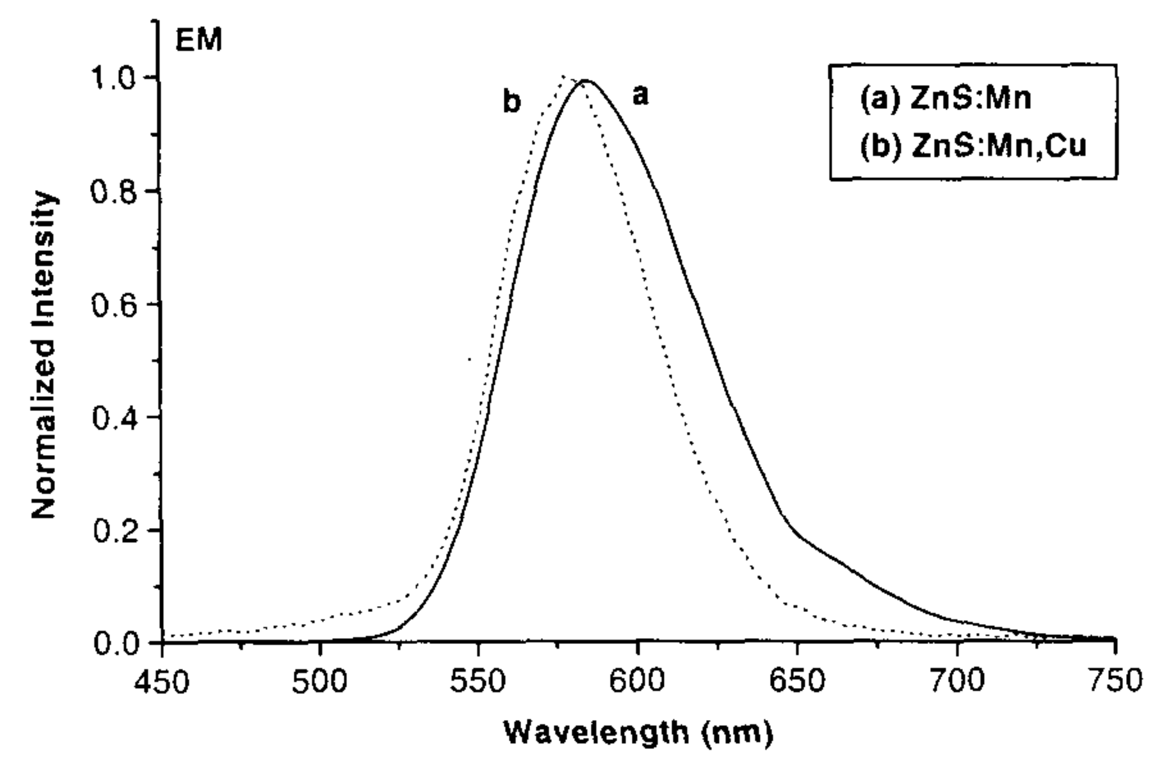
(b)

Fig. 1. CL emission spectra of ZnS:Mn phosphors. (a) hexagonal phase (b) cubic phase.

Fig. 2 shows normalized PL excitation (a) and emission (b) spectra of hexagonal phase of ZnS:Mn and ZnS:Mn,Cu phosphors. From Fig. 2(a), when Cu ion is co-doped, excitation main peak is fairly extended up to 400 nm. However, by introducing Cu ion, the emission peak is shifted to shorter wavelength, as shown in Fig. 2(b).



(a)



(b)

Fig. 2. Normalized excitation (a) and emission (b) spectra of ZnS:Mn and ZnS:Mn,Cu phosphors.

Figure 3 shows CIE coordinates of ZnS:Mn and ZnS:Mn,Cu phosphor, respectively. The ZnS:Mn phosphor shows a yellow-orange emission as shown in CIE coordinate diagram. However, when Cu ion co-doped with ZnS:Mn phosphor, its emission color is changed to yellow without bearing orange color. It can be easily expected to the color changes of the two phosphors because the full wave half maximum (FWHM) of ZnS:Mn is larger than that of ZnS:Mn,Cu about 10 nm and main emission peak of ZnS:Mn,Cu is located at about 579 nm which is shorter wavelength than that of ZnS:Mn, as shown on Fig. 2(b).

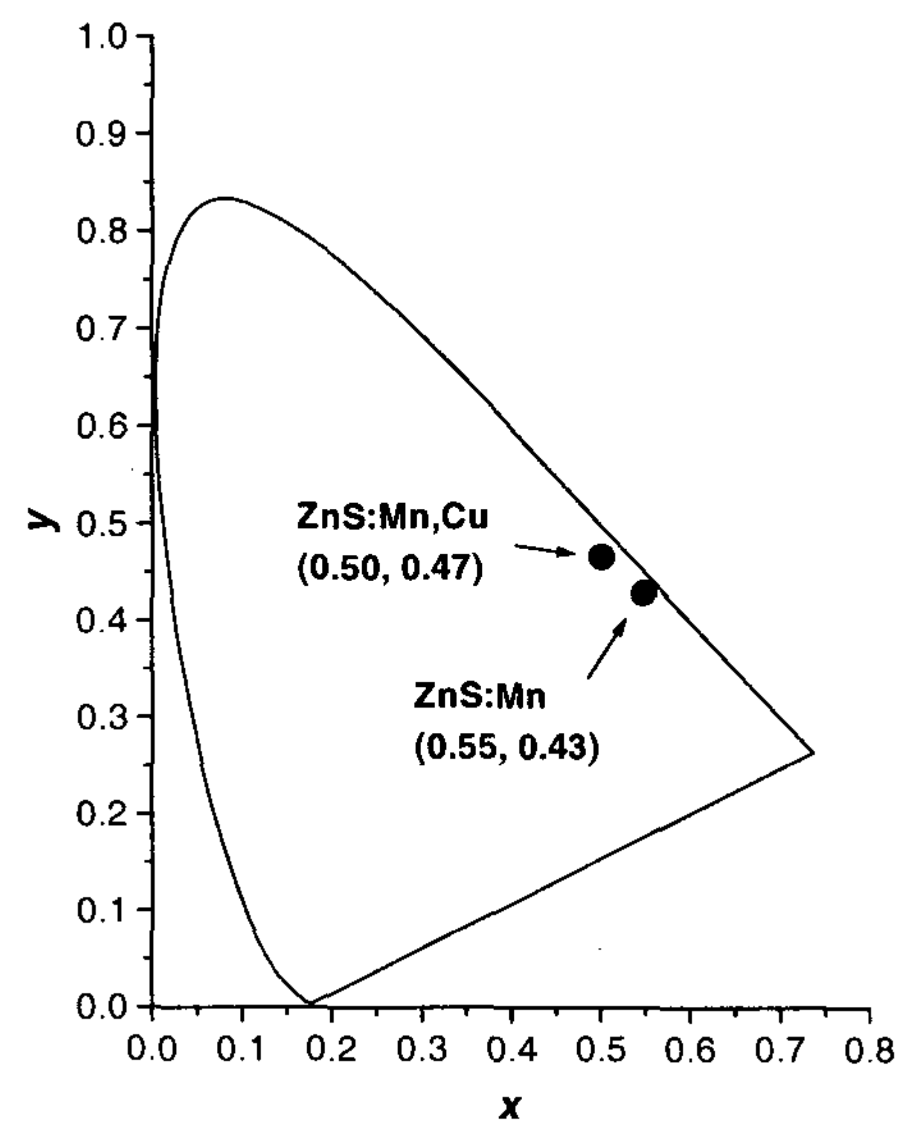


Fig. 3. CIE coordinates of ZnS:Mn and ZnS:Mn,Cu phosphors.

Figure 4 shows CL spectra of ZnS:Mn phosphors synthesized with various flux materials. The CL measurement was performed under excitation energy of 30 eV. In the case of the low-energy excitation CL, W-filament was used as an electron source of low-energy excitation. In the case low-energy excitation, luminescence was measured from phosphor screen. It seems that the luminescence intensity of ZnS:Mn phosphor is dependent on the melting point of flux material, as shown in Table I.

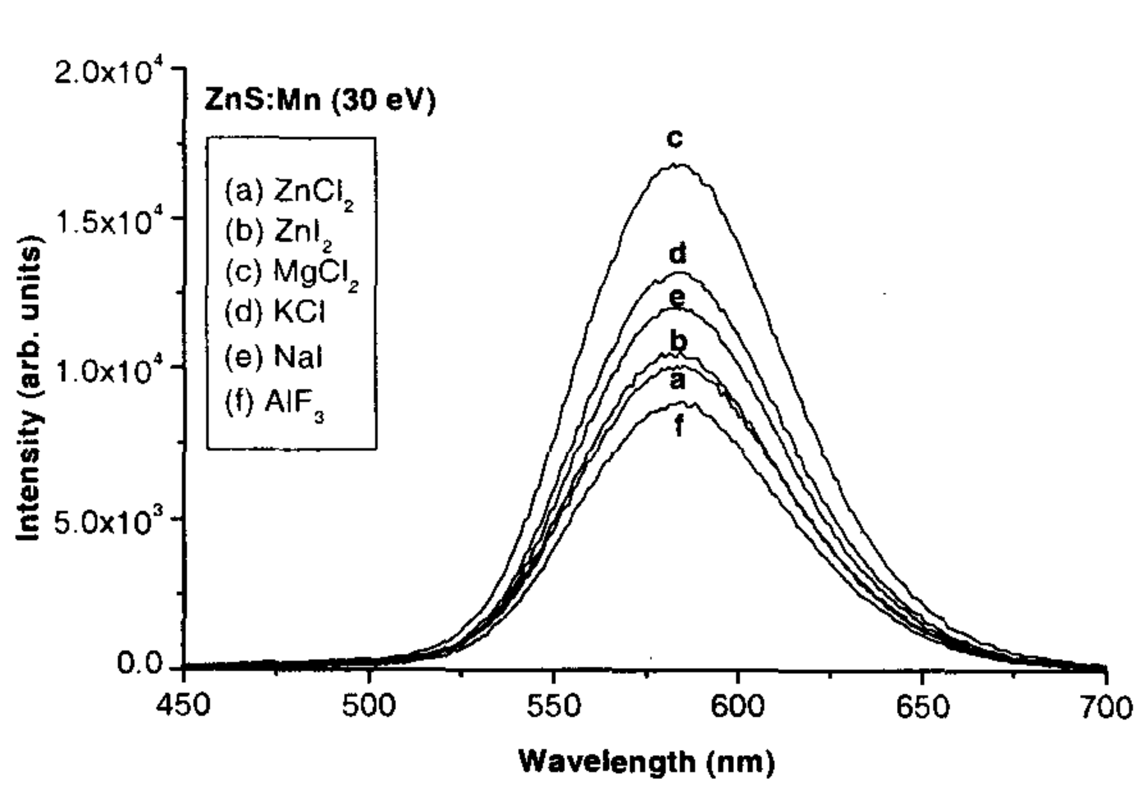
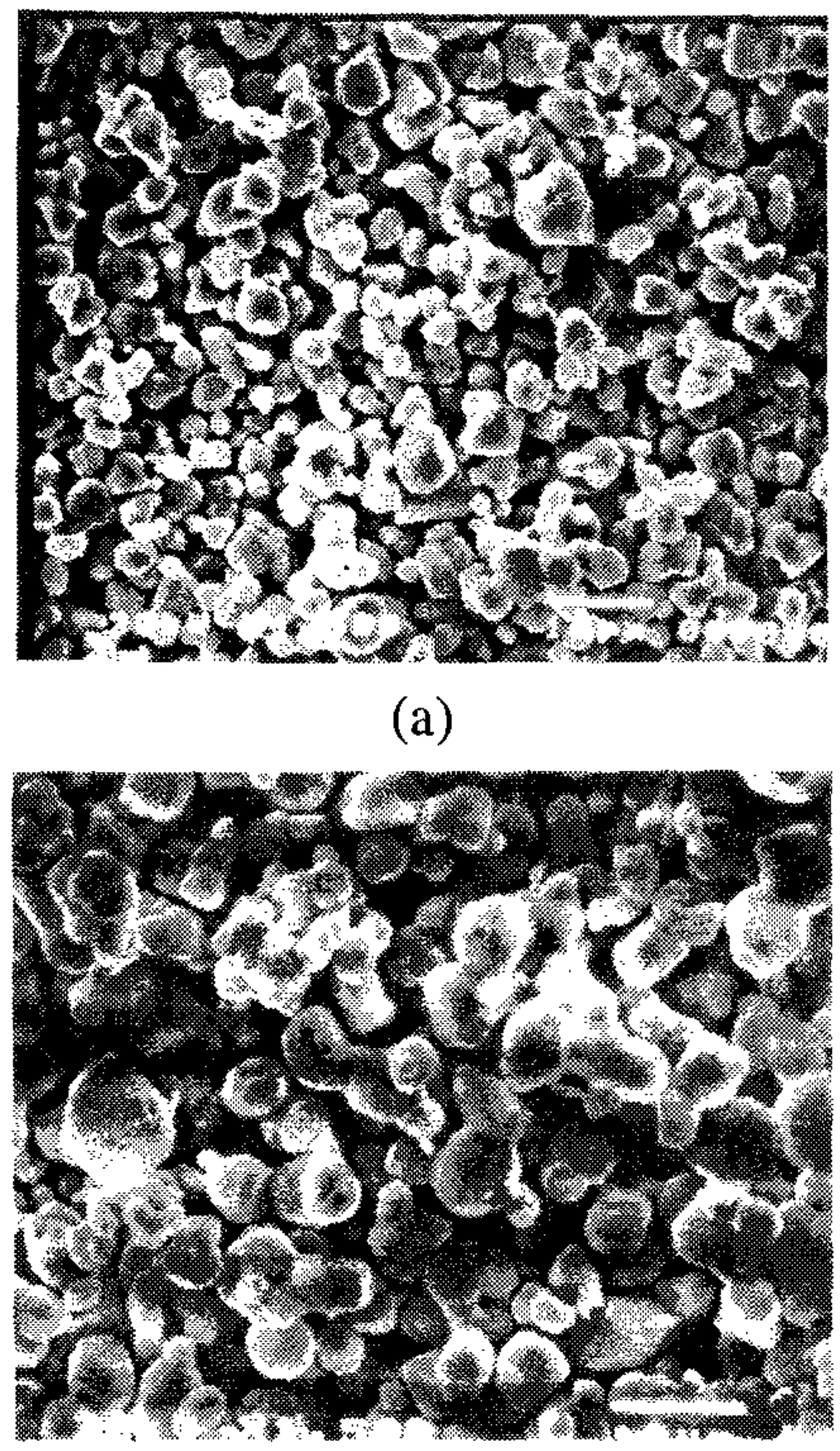


Fig. 4. Low-excitation energy CL emission of ZnS:Mn phosphors with various flux materials.

Table I. Melting points of various flux materials [5].

Flux materials	$ZnCl_2$	ZnI_2	$MgCl_2$	KCl	NaI	AlF_3
m.p.(°C)	275	446	714	771	660	1290

Figure 5 shows SEM images of ZnS:Mn phosphors when heating rate was changed and flux material (NH_4Cl) was used. When the flux material is not used in sintering process, it seems that the increase of the heating rate makes little effect on the growth of the particle size. However, when the flux material is used, the particle growth is affected by the change of heating rate.



(a)

(b)

Fig. 5. SEM images of sintered ZnS:Mn phosphors.

(a) 950°C, 2 h. NH_4Cl added. Heating rate = 4°C/min.

(b) 950°C, 2 h. NH_4Cl added. Heating rate = 7°C/min.

The decrease of low-excitation energy CL is shown as a function of ball-mill time in Fig. 6. The phosphor, which is used in ball-mill test, is the best sample of our experiments. The luminescence intensity was scaled at 1 h-done as unity. The luminescence intensity was decreased as the milling time went on, as shown in Fig. 6. As the milling was processed, relatively large particles remained in the phosphor screen when the phosphor particle monitored by using a SEM.

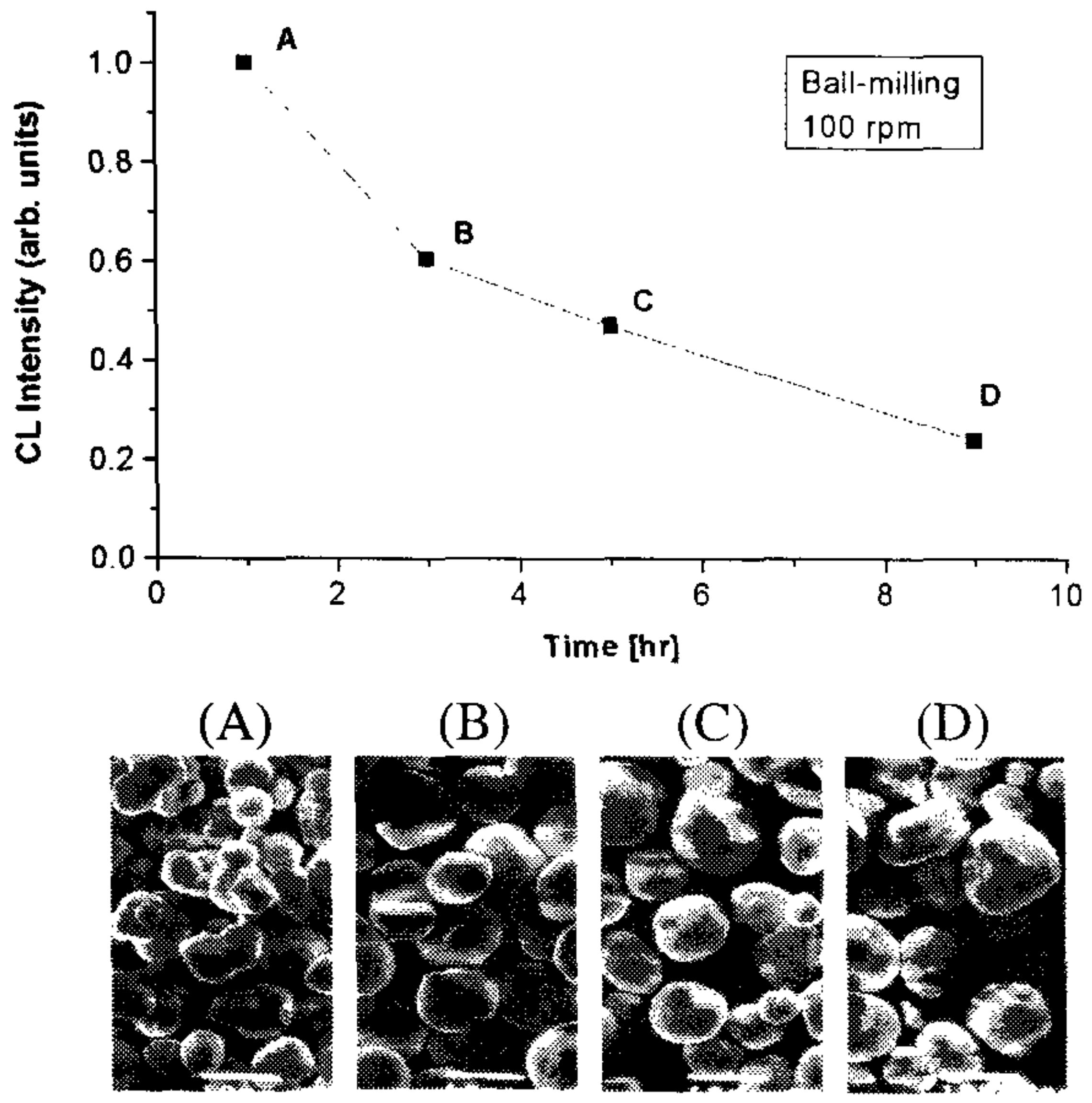


Fig. 6. Decrease of low-excitation energy CL as a function of ball-mill time and SEM images at that time.

4. Summary

ZnS:Mn has been studied as a yellow phosphor for the application to fluorescent displays operated at low voltage. It was found that luminescence of Mn^{2+} ion from hexagonal phase of ZnS was suitable for the display applications. The main emission peak was shifted to shorter wavelength when Cu ions were doped. It was found that the heating rate is important factor to determine the phosphor particle size. From the uniform and small phosphor particle, the phosphor screen is formed efficiently.

5. References

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