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SYNTHESIS AND CHARACTERIZATION ON THE LUMINESCENCE PROPERTIES OF MANGANESE DOPED ZnS NANOCRYSTALS

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ZnS and manganese doped ZnS (ZnS:Mn^{2+}) nanocrystals were prepared by adding Na_2S to the solutions of zinc oleate and zinc oleate mixed with $Mn(NO_3)_2$. It was done by thermal decomposition using auto-clave method. The aging of the complexes in auto-clave resulted in ZnS and Mn^{2+} doped ZnS nanoparticles. The diameters of both nanoparticles were determined as approximately 10.3 ± 2.1 nm from XRD line widths and TEM images. The ZnS:Mn^{2+} nanoparticles emitted at 500 nm ~ 650 nm ($\lambda_{max} = 575$ nm) in contrast to ZnS nanoparticles. The luminescence Intensity of ZnS:Mn^{2+} highly depend on the amount of Mn^{2+} added.

Keywords: luminescence; ZnS:Mn^{2+}; ZnS

INTRODUCTION

Optical properties of semiconductor nanocrystallites have been investigated, since these materials have a potential application to nonlinear optical devices. The luminescence properties of nanosized luminescent semiconducting particles are substantially different from those of bulk crystalline materials. The band gap energy increases as particles become smaller, such small particles emit visible luminescence intensity much stronger than bulk crystals. Bhagrava *et al.* have reported that the luminescence enhancement of manganese doped ZnS results from an efficient energy transfer from the ZnS host to Mn^{2+} ions facilitated by

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mixed electronic states [1]. The hybridization of atomic orbital of ZnS and d orbital of Mn^{2+} was also suggested to be responsible for the relaxation of selection rules for the spin-forbidden $^4T_1$-$^6A_1$ transition of Mn^{2+} [1]. In this paper, we report the preparation and optical properties of ZnS and Mn^{2+} doped ZnS semiconductor nanoparticles. The synthesis was done by thermal treatment oleate complexes of them using auto-clave. The aging of zinc oleate and manganese doped zinc oleate in auto-clave resulted in ZnS and Mn^{2+} doped ZnS nanoparticles. It was found that the Mn^{2+} luminescence intensity depended highly on the amount of Mn^{2+} doped.

EXPERIMENT

Chemicals

Manganese (II) nitrate hydrate ($Mn(NO_3)_2$, 98%) and sodium sulfide (Na_2S, absolute) were obtained from Aldrich Chemical. InC. and zinc chloride ($ZnCl_2$, extra pure), and sodium oleate ($C_{17}H_{33}COONa$, extra pure) were obtained from Junsei Chemical Co., Ltd.

Preparation of ZnS and ZnS:Mn^{2+}

ZnS and ZnS: Mn^{2+} were prepared by thermal decomposition of Zinc oleate and manganese doped zinc oleate complex using auto-clave. A 2.23 g (7.34 mmol) of sodium oleate was dissolved in 100 ml of water. And 0.5 g (3.67 mmol) of zinc chloride and 0.285 g (3.65 mmol) of Na_2S were added into the sodium oleate aqueous solution under the constant stirring for 2 hr. The mixture was slowly heated from room temperature to 300°C at 60°C/30 min. After reaching the desired temperature, it was held at 300°C for 2.5 hr and cooled to room temperature. The product color was gray. The reaction product was diluted with methanol and filtered through membrane filter (0.45 μm). The synthetic method of ZnS:Mn^{2+} was similar to that of ZnS. Before the addition of Na_2S, various concentration of $Mn(NO_3)_2$ and sodium oleate was added to zinc oleate solution. The next process was the same at that of ZnS. ZnS:Mn^{2+} was prepared by various concentration of $Mn(NO_3)_2$; ZnS:Mn^{2+} I was synthesized with 3.67 mmol $Mn(NO_3)_2$, ZnS:-Mn^{2+} II was synthesized with 2.57 mmol $Mn(NO_3)_2$, ZnS:Mn^{2+} III was synthesized with 1.84 mmol $Mn(NO_3)_2$, ZnS:Mn^{2+} IV was synthesized with 0.18 mmol $Mn(NO_3)_2$.

Apparatus

ZnS and ZnS:Mn^{2+} nanoparticle size were determined with Transmission Electron Microscope (TEM) (JEOL, JEM-2010) and analysis of the line

width of the X-ray diffraction (XRD) (Philips, X'Pert-MPD system). TEM samples were prepared on the 400 mesh copper grid coated with carbon. A drop of the nanoparticle solution was placed on the copper grid and dried in air. The size distribution of the particles was determined from enlarged photographs of the TEM image. The average size of the crystals was also estimated with XRD using Debye-Scherrer equation. The crystal structure was studied with XRD. And analysis of element was confirmed by TEM-Energy dispersive X-ray (TEM-EDX). The emission spectra were recorded on a Luminescence Spectrometer (Perkin-Elmer, LS50B) and the absorption spectra were on UV-vis spectrometer (Varian, Cary 1C).

RESULT AND DISCUSSION

ZnS and ZnS:Mn^{2+} were synthesized successfully by thermal decomposition of Zinc oleate and manganese doped zinc oleate complex with auto-clave and their crystal structures are confirmed by XRD patterns as Figure 1. The discernible peak in Figure 1(a) can be indexed to (111),

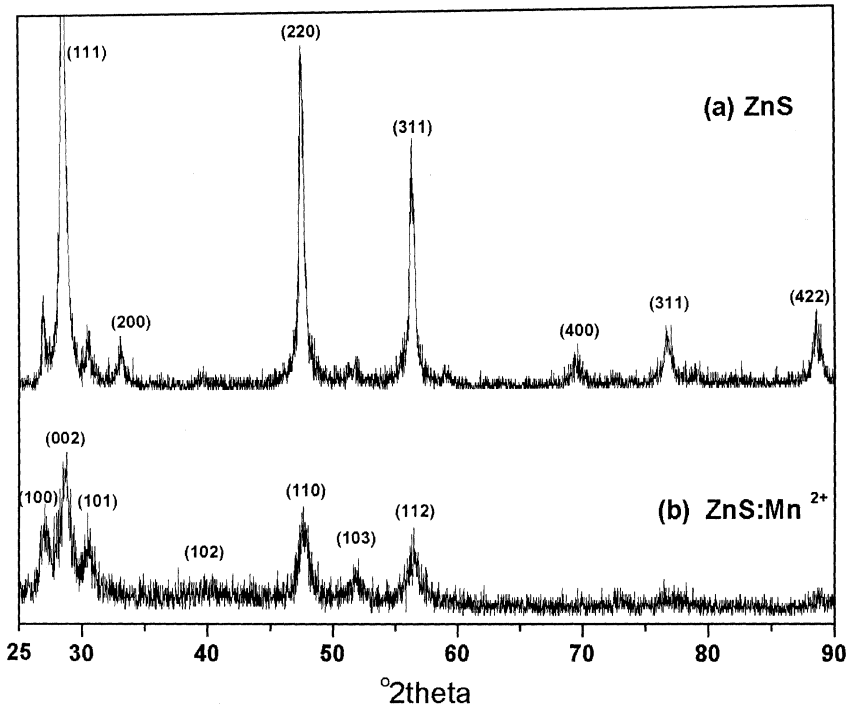

FIGURE 1 X-ray diffraction patterns of ZnS and ZnS:Mn^{2+}.

TABLE 1 Energy Dispersive X-ray Data of ZnS:Mn^{2+}; (a) ZnS:Mn^{2+}I, (b) ZnS:Mn^{2+}II, (c) ZnS:Mn^{2+}III, (d) ZnS:Mn^{2+}IV

	Elmt	Element %	Atomic %
(a)	S	29.88	46.36
	Mn	1.08	1.63
	Zn	68.32	52.00
	Total	100.00	100.00
(b)	S	29.60	45.97
	Mn	2.72	2.46
	Zn	67.69	51.57
	Total	100.00	100.00
(c)	S	39.68	56.10
	Mn	15.16	13.01
	Zn	44.56	30.90
	Total	100.00	100.00
(d)	S	28.59	44.83
	Mn	1.59	1.46
	Zn	68.82	53.71
	Total	100.00	100.00

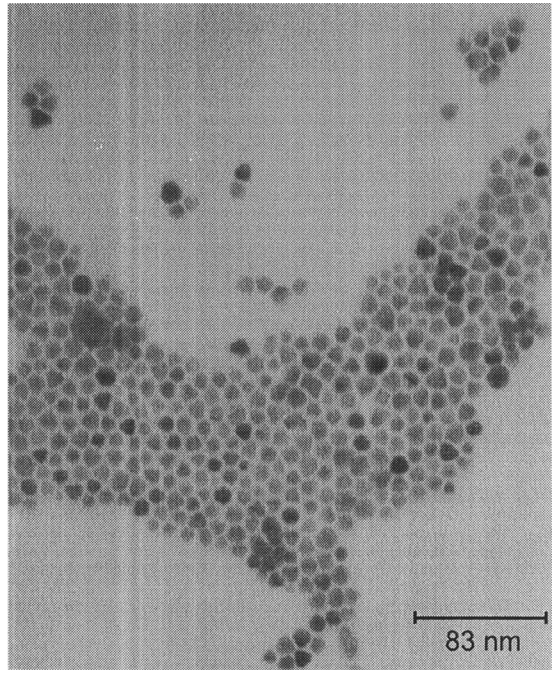

FIGURE 2 Transmission electron microscopic image of ZnS.

(200), (220), (311), (400), (311) and (422) planes, which corresponds to that of sphalerite structure of ZnS (JCPDS card no. 01-0792), and the discernible peaks in Figure 1(b) can be indexed to (100), (002), (101), (102), (110), (103) and (112) planes, which corresponds to that of wurtzite structure of ZnS (JCPDS card no. 75-1534). The amount of Zn, S, Mn in

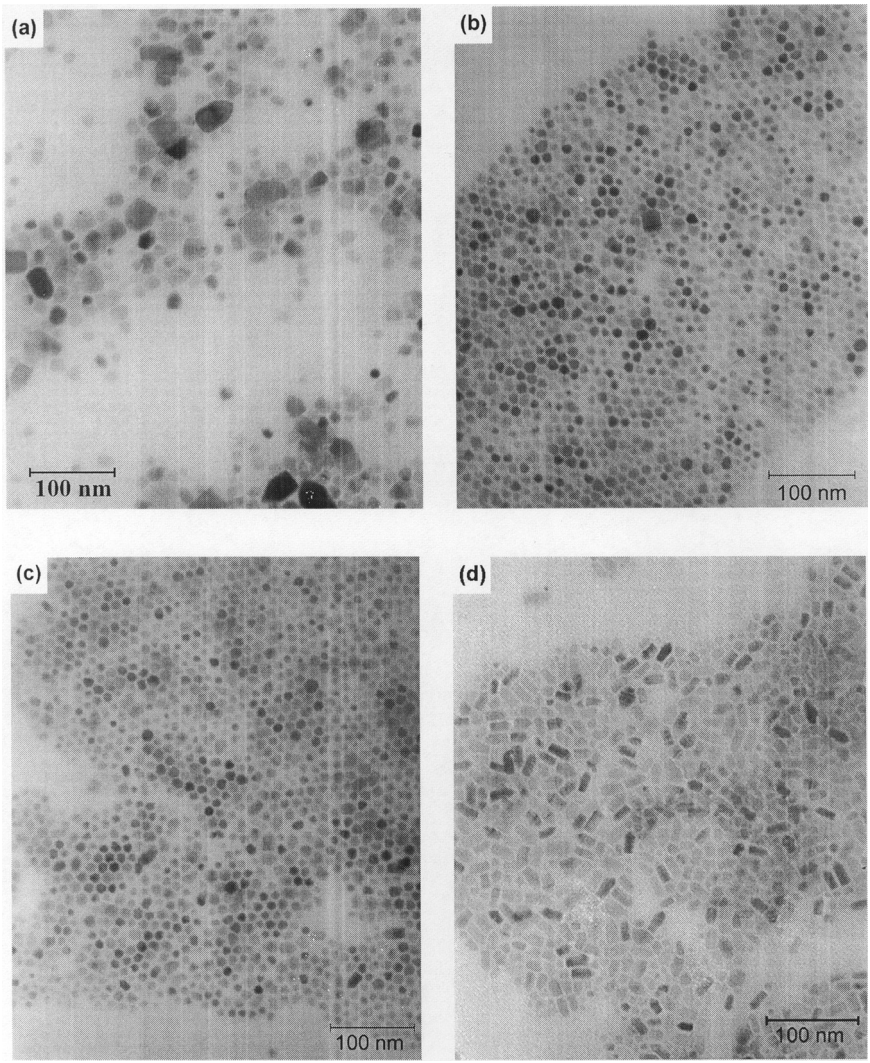

FIGURE 3 Transmission electron microscopic images of ZnS:Mn^{2+}; (a) ZnS:Mn^{2+}I, (b) ZnS:Mn^{2+}II, (c) ZnS:Mn^{2+}III, (d) ZnS:Mn^{2+}IV.

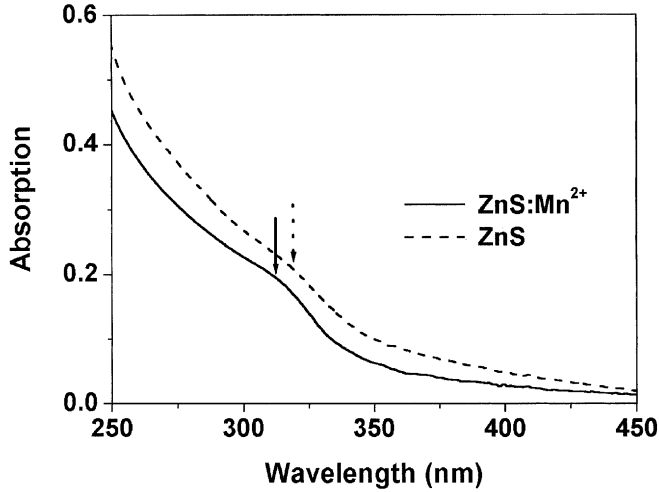

FIGURE 4 UV-vis absorption spectra of ZnS and ZnS:Mn^{2+}.

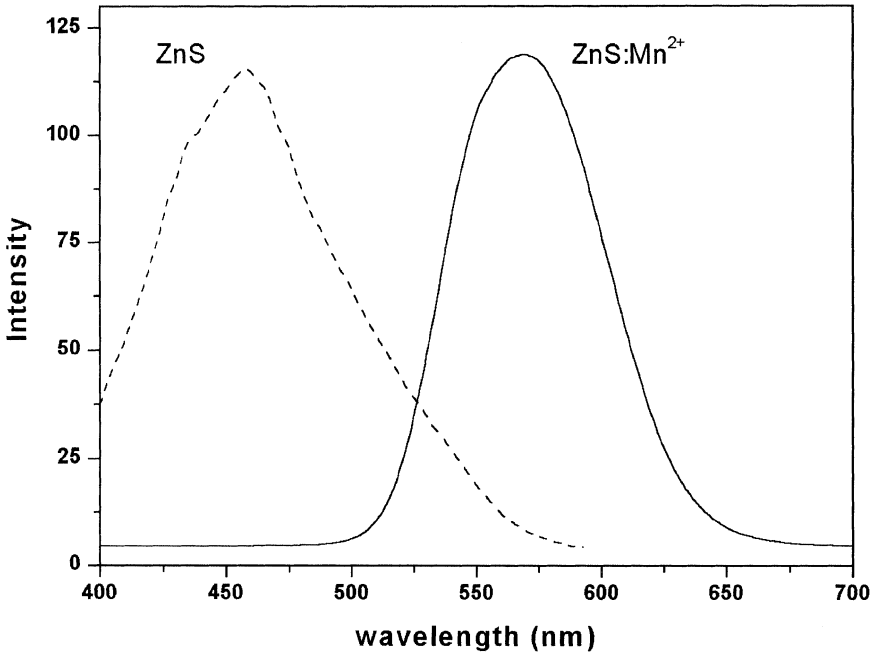

FIGURE 5 Photoluminescence emission spectra of ZnS ($\lambda_{ex} = 319\,nm$) and ZnS:Mn^{2+} ($\lambda_{ex} = 312\,nm$).

the ZnS:Mn^{2+} was confirmed by TEM-EDX and the element and atomic percentage were shown Table 1. The amount of the Mn^{2+} in ZnS:Mn^{2+} was changed with the different concentrations of added $Mn(NO_3)_2$. When the amount of the Mn^{2+} in ZnS:Mn^{2+} was 0.328 g (1.84 mmol), amount of the Mn^{2+} in ZnS:Mn^{2+} was the largest. The nanoparticles of ZnS and ZnS:Mn^{2+} was depicted in the TEM image of Figures 2 and 3. Since we synthesized violently ZnS:Mn^{2+} by auto-clave method, the particle size was not regular. The diameter was determined as 8 nm ~ 13 nm from the TEM image. As shown in Figure 3, the particles of ZnS:Mn^{2+} II and III was monodispersed and the particle shape was spherical in contrast with ZnS:Mn^{2+} I and IV. The absorption and photoluminescence emission spectra of ZnS and ZnS:Mn^{2+} are shown Figure 4 and Figure 5, respectively. ZnS and ZnS:Mn^{2+} nanoparticles showed optical absorptions at $\lambda_{abs.} = 319$ nm and 312 nm, respectively. ZnS nanoparticle showed an emission band at 457 nm ($\lambda_{exc.} = 319$ nm) and ZnS:Mn^{2+} nanoparticle showed an emission band at 575 nm ($\lambda_{exc.} = 312$ nm). The orange emission bands of ZnS:Mn^{2+}

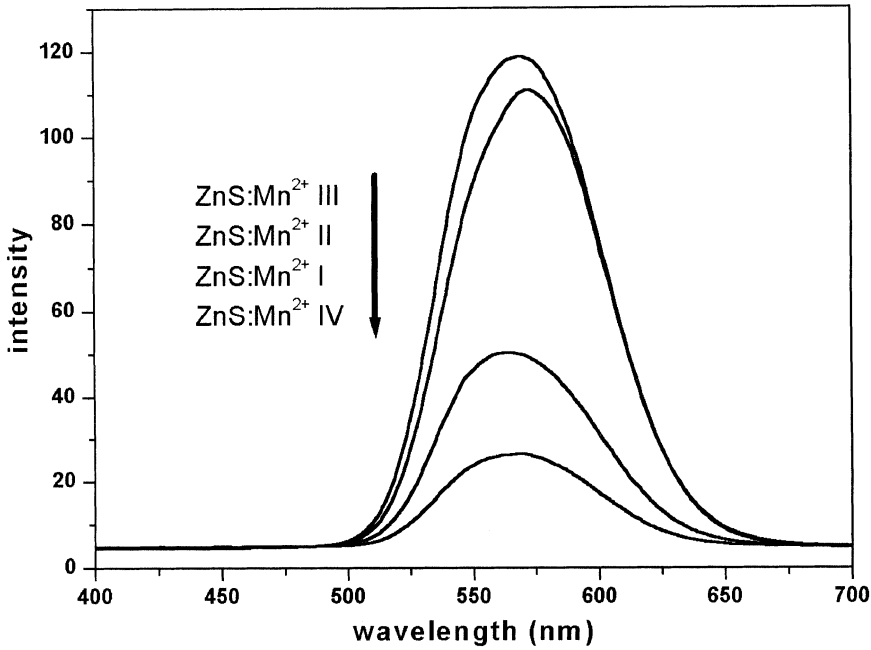

FIGURE 6 Photoluminescence emission spectra of ZnS:Mn^{2+} with different concentration of $Mn(NO_3)_2$; ZnS:Mn^{2+}I was synthesized by 3.67 mmol $Mn(NO_3)_2$, ZnS:Mn^{2+}II was synthesized by 2.57 mmol $Mn(NO_3)_2$, ZnS:Mn^{2+}III was synthesized by 1.84 mmol $Mn(NO_3)_2$, ZnS:Mn^{2+}IV was synthesized by 0.18 mmol $Mn(NO_3)_2$.

in Figure 5 were attributed to the Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ transition of the ZnS nanocrystal host [3,4]. Figure 6 shows that the emission intensity of ZnS:Mn^{2+} depends on the amount of added Mn^{2+}. The ZnS:Mn^{2+} III which have the largest amount of Mn^{2+} in the ZnS:Mn^{2+} from Table 1 shows the largest emission intensity. This is consistent with the previous report by Koshravi *et al* [6]. The highest intensity of ZnS:Mn^{2+} III can be also attributed to the monodisperse state of nanoparticle and homogeneous nanoparticle size. This is obviously shown by comparative TEM images of Figure 3.

CONCLUSION

ZnS and ZnS:Mn^{2+} nanoparticles were prepared by thermal annealing using auto-clave. But the size and shape was irregular, since the particles was synthesized rapidly at high temperature and pressure with auto-clave. The emitting band ZnS:Mn^{2+} showed red shift from that of ZnS and results in the emission band at 500 nm ~ 650 nm. These luminescence properties of ZnS:Mn^{2+} not only photoconductor, transistors and sensor etc. but also light wavelength modification.

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