

## Luminescence enhancement of Zn(Cu<sub>0.01</sub>Cd<sub>0.02</sub>Mg<sub>0.02</sub>)S phosphor

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### 1. Introduction

Because ZnS is a kind of wide band gap II–VI compound semiconductor materials ( $E_g \sim 3.6$  eV), and its excellent energy band characteristic, ZnS becomes a good host material. Owing to the remaining disadvantageous problems of ZnS and doped ZnS phosphors such as weak luminescence intensity and short luminescence lifetime, some researchers have attempted to improve luminescence properties by co-doped method, such as Cu<sup>2+</sup>-Mn<sup>2+</sup>, Cu<sup>2+</sup>-Pb<sup>2+</sup>, and Ni<sup>2+</sup>-Mn<sup>2+</sup> [1-3]. But multi-dopants which are added for enhancing luminescence intensity usually result in another color peak owing to added dopants. Therefore, it remains a significant challenge for us to develop much enhanced luminescence properties of co-doped ZnS phosphor by introducing multi-metal ions into ZnS nanocrystallites without another distinct different peak formation.

### 2. Experimental

Firstly, 10 mmol zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>), 0.1 mmol copper acetate (Cu(CH<sub>3</sub>COO)<sub>2</sub>), 0.2 mmol cadmium acetate (Cd(CH<sub>3</sub>COO)<sub>2</sub>) and 0.2 mmol magnesium chloride (MgCl<sub>2</sub>) were dissolved in water. And then, 10 mmol ethylenediamine tetraacetic acid (EDTA) was used as dispersant in the solution. Secondly, appropriate amount freshly prepared Na<sub>2</sub>S solution was added dropwise to the above mixture, the mixture was maintained at 40 °C for 2 h under strong stirring. Thirdly, the precipitation was separated from solution by centrifugation, and then they were washed twice with distilled water and ethanol, respectively. At last, the prepared phosphors were vacuum dried at 60 °C for 24 h.

### 3. Results and discussion

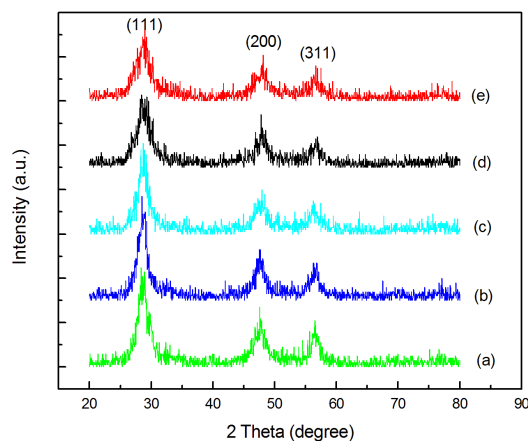


Fig. 1 X-ray diffraction patterns of (a) pure ZnS, (b) ZnS:Cu (2%), (c) ZnS:Cd (1%), (d) Zn(Cu<sub>0.01</sub>Cd<sub>0.02</sub>)S and (e) Zn(Cu<sub>0.01</sub>Cd<sub>0.02</sub>Mg<sub>0.02</sub>)S samples.

The XRD patterns of un-doped, doped and co-doped samples were shown in Fig. 1. It was clearly revealed that all samples exhibit a zinc-blended crystal structure. The three diffraction peaks were corresponding to (111), (200), and (311) planes of the cubic crystalline ZnS, respectively. According to the line width analysis of the (111) diffraction peak based on the Scherrer formula [4], the average sizes of particles doped with different dopants have been estimated as 2-4 nm. From XRD analysis, no characteristic peaks of impurity phases have been observed in doped samples.

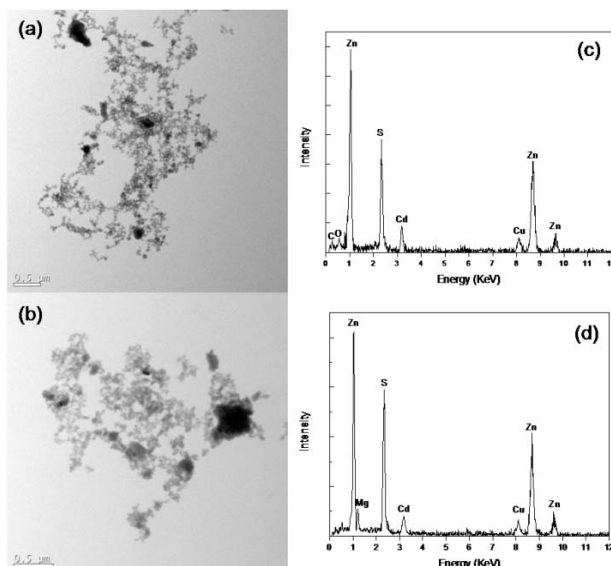


Fig. 2 TEM micrographs of co-doped samples (a)  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02})\text{S}$  and (b)  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})\text{S}$ , and the corresponding EDX spectra of samples (c)  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02})\text{S}$  and (d)  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})\text{S}$ .

Figs. 2 (a) and 2 (b) showed TEM images of  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02})\text{S}$  and  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})$  samples, which revealed that the particles were evenly distributed in system as clusters. It can be also observed that they are roughly around 30-40 nm in diameter. The corresponding EDX spectra of sample  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02})\text{S}$  and  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})$  were plotted in Figs 2 (c) and 2 (d). From these patterns, peaks of impurity elements which corresponding to  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  ions can be observed, so it was proved that these impurity ions were doped in ZnS host successfully as components of  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02})\text{S}$  and  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})$  phosphors.

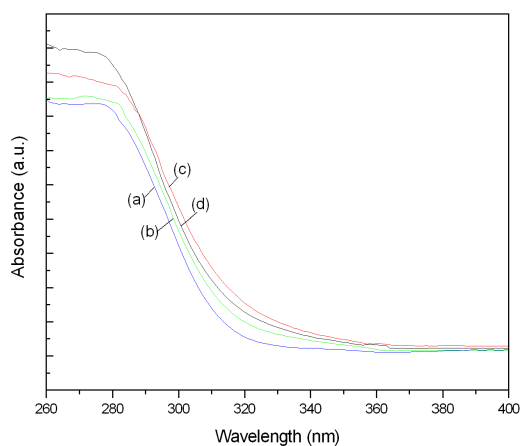


Fig. 3 UV absorption spectra of (a) ZnS, (b) ZnS:Cu, (c)  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02})\text{S}$  and (d)  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})\text{S}$ .

The UV absorption spectrum of ZnS doped with copper is shown in Fig. 3. The bulk ZnS peak was shown at about 340 nm ( $E_g=3.66$  eV). But the absorption spectra of ZnS and doped ZnS samples were observed at 290–305 nm, which indicated the existence of a narrow size distribution of quantum particles of prepared samples. The existing experimental correlation between band edge and quantum dot size can be used to estimate band gap and size of samples [5]. The band gap of samples were at about  $4.16\pm 0.1$  eV.

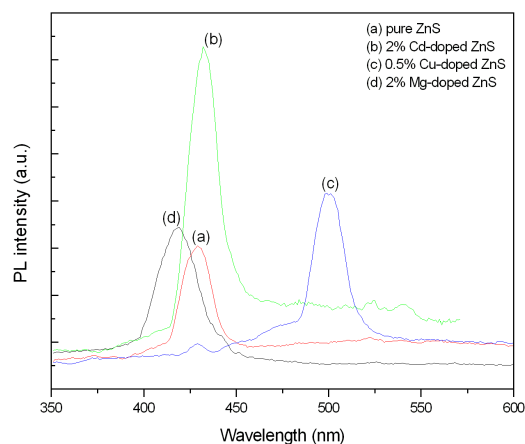


Fig. 4 Photoluminescence spectra of (a) ZnS, (b) ZnS: Cd(2%), (c) ZnS: Cu(0.5%) and (d) ZnS: Mg(2%) samples at an excitation wavelength of 340 nm.

Fig. 4 showed the PL spectra of pure ZnS, Cd<sup>2+</sup>-doped and Cu<sup>2+</sup>-doped ZnS samples. For pure ZnS nanocrystallites, blue emission band centered at 430 nm can be observed, which arises from recombination of vacancies. After doped, the luminescent centers of doped ZnS nanoparticles were transferred to impurity ions, which result in the emission red-shift. Emission peak of Cd<sup>2+</sup>-doped sample was at 440 nm and Cu<sup>2+</sup> doped sample emitted at about 503 nm. The PL intensity of doped ZnS samples increased as comparing with pure ZnS. It could be explained that impurity ions reduced electron- or hole- trapped surface levels on ZnS, which lead to luminescence intensity increases [6].

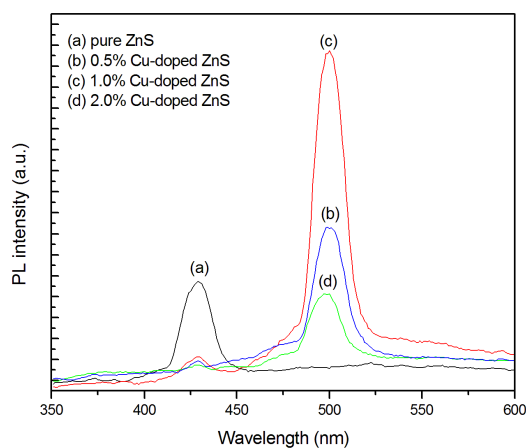


Fig. 5 Photoluminescence spectra of ZnS:Cu with different Cu<sup>2+</sup> contents at excitation wavelength of 340 nm.

Photoluminescence spectra of ZnS and ZnS:Cu nanoparticles using an excitation wavelength of 340 nm were shown in Fig. 5. Comparing with ZnS nanoparticles, the emission wavelength of Cu-doped ZnS was extended to low energy. It was obvious that both emissions from ZnS and Cu<sup>2+</sup> centers can be observed in ZnS:Cu nanoparticles. The one centered at about 430 nm was same as observed in ZnS nanoparticles. The other one which centered at 500–510 nm just comes from Cu<sup>2+</sup> as has been observed in ZnS:Cu nanoparticles. Luminescence enhancement of ZnS phosphors doped with Cu<sup>2+</sup> is corresponded to the doping concentration. The Cu-doped ZnS phosphors had the highest emission intensity when the concentration of Cu<sup>2+</sup> increased to 1 mol%. But if concentration further increased over 1 mol%, luminescence intensity of sample would decrease due to concentration quenching [7].

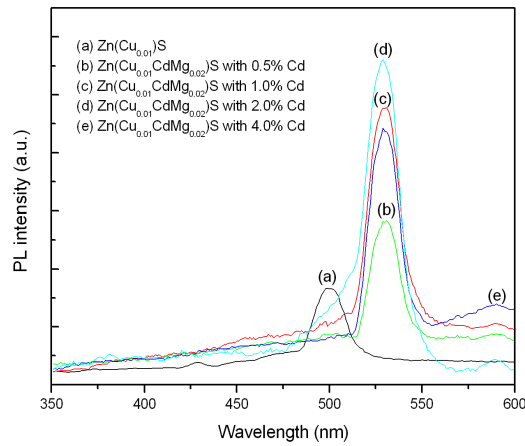


Fig. 6 Photoluminescence spectra of  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_y\text{Mg}_{0.02})\text{S}$  with different  $\text{Cd}^{2+}$  contents at an excitation wavelength of 340 nm.

Fig. 6 showed emission spectrum of ZnS nanocrystallites co-doped with  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$ . Comparing with Cu-doped ZnS sample, it revealed an emission band centered at 533 nm with a little red-shift but keeping same color. PL intensity of ZnS nanoparticles co-doped with  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  was remarkably increased comparing to those of Cu-doped ZnS and pure ZnS nanocrystallites. This result could be derived from the fact that because the gap band structure of  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_y\text{Mg}_{0.02})\text{S}$  nanocrystallites is remarkably different from those of Cu-doped and pure ZnS nanocrystallites, the luminescence spectra of  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_y\text{Mg}_{0.02})\text{S}$  nanoparticles are also varied. Due to the co-effect of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$ , more and more electron-holes are excited and radiative recombination is enhanced, luminescence efficiency of co-doped samples is remarkably increased [8].

Fig. 7 showed decay time curves for pure ZnS and  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_z)\text{S}$  phosphors. Comparing with ZnS bulk materials, ZnS-based nanoparticles have short lifetime because of quantum efficiency [9]. For  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})\text{S}$  phosphor, there is a decay time about 37.2  $\mu\text{s}$  were obtained with 2%  $\text{Mg}^{2+}$  content, whereas in the case of pure ZnS nanoparticles decay time was about 20  $\mu\text{s}$ . By addition of  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  ions, it could be possible to decrease luminescence decay rate and to increase luminescence lifetime of ZnS:Cu phosphor effectively. This was explained that  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  ions successfully decrease the overlap of electron-hole, extend the radiative recombination process of localized excitons, and block the nonradiative transition paths to some extent.

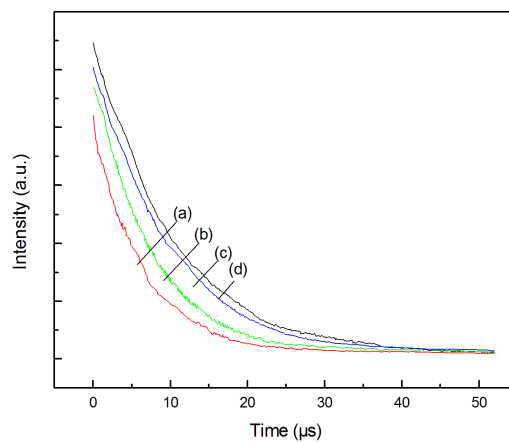


Fig. 7 Decay curves of (a) ZnS and  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_z)\text{S}$  with different  $\text{Mg}^{2+}$  contents recorded at room temperature.

#### 4. Conclusions

In this paper,  $\text{Zn}(\text{Cu}_x\text{Cd}_y\text{Mg}_z)\text{S}$  nanoparticles were synthesized as a desirable phosphor by a co-precipitation method. From XRD and EDX patterns, it could be confirmed that  $\text{Zn}(\text{Cu}_x\text{Cd}_y\text{Mg}_z)\text{S}$  phosphors were synthesized successfully.  $\text{Zn}(\text{Cu}_x\text{Cd}_y\text{Mg}_z)\text{S}$  nanocrystallites revealed an emission band centered at 533 nm with a little red-shift but keeping same color. PL intensity of  $\text{Zn}(\text{Cu}_x\text{Cd}_y\text{Mg}_z)\text{S}$  nanocrystallites was remarkably increased comparing to those of  $\text{Cu}^{2+}$  only doped and pure ZnS nanocrystallites. When the concentration of  $\text{Cd}^{2+}$  reached to 2%, luminescence intensity was about 6 ~ 8 times that of un-doped ZnS. From results of decay curve,  $\text{Mg}^{2+}$  doping could improve PL decay time obviously. Lifetime of phosphor was prolonged by 75% at  $\text{Mg}^{2+}$  content of 2 ~ 4%. From experimental results, the optimum molar ratio of dopants was obtained as  $\text{Zn}(\text{Cu}_{0.01}\text{Cd}_{0.02}\text{Mg}_{0.02})\text{S}$ .

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