Luminescence properties of ZnS:Cu, Eu semiconductor nanocrystals synthesized by a hydrothermal process*

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ZnS:Cu, Eu nanocrystals with an average diameter of ∼ 80 nm are synthesized using a hydrothermal approach at 200 °C. The photoluminescence (PL) properties of the ZnS:Cu, Eu nanocrystals before and after annealing, as well as the doping form of Eu, are studied. The as-synthesized samples are characterized by X-ray diffraction, scanning electron microscopy, inductively coupled plasma-atomic emission spectrometry, and the excitation and emission spectra (PL). The results show that both Cu and Eu are indeed incorporated into the ZnS matrix. Compared with the PL spectrum of the Cu mono-doped sample, the PL emission intensity of the Cu and Eu-codoped sample increases and a peak appears at 516 nm, indicating that Eu^{3+} ions, which act as an impurity compensator and activator, are incorporated into the ZnS matrix, forming a donor level. Compared with the unannealed sample, the annealed one has an increased PL emission intensity and the peak position has a blue shift of 56 nm from 516 nm to 460 nm, which means that Eu^{3+} ions reduce to Eu^{2+} ions, thereby leading to the appearance of Eu^{2+} characteristic emission and generating effective host-to-Eu^{2+} energy transfer. The results indicate the potential applications of ZnS:Cu, Eu nanoparticles in optoelectronic devices.

Keywords: ZnS:Cu, Eu, nanocrystals, hydrothermal treatment, PL spectra

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1. Introduction

In the last decade, II–VI semiconductor nanoparticles have attracted much attention because of their novel optical and electronic properties, and their promising applications in optoelectronics. Among the family of II–VI semiconductors with a large band gap, zinc sulfide with the addition of an appropriate activator of a few ppm is used as a phosphor and thin-film luminescent material in many fields, such as displays, biological detection, light-emitting diodes, lasers, and quantum dot sensitized solar cells.[1–11] In particular, when doped with transition metals or rare-earth ions, zinc sulfide may provide new opportunities toward the application of nanoparticles as full-color luminescence materials in the UV-visible region.[12–17] Ion Cu^{2+} is known as a high-efficiency green emission activator. Many studies have reported that the doping of the Cu^{2+} impurity in the host lattice can enhance luminescence sensitivity and play an important role in the luminescence process,[18,19] and that the Eu dopant exhibits two doping forms of blue (Eu^{2+}) and red (Eu^{3+}) in ZnS.[20,21] Whether the impurity ions, i.e., rare-earth ions doped into ZnS, are in the matrix lattice or located at the surface remains controversial because of the difference in chemical properties between Zn^{2+} and RE^{3+}.[22] Ageeth *et al.*[23] used old and new synthesis methods to prepare ZnS:Eu, CdS:Eu, ZnS:Tb, and ZnS:Er nanocrystallines, and the results showed that the rare-earth ions were not incorporated into the ZnS host lattice. However, many studies[20,21,24] reported that rare-earth ions were incorporated into ZnS nanoparticles, and the effective energy transfer occurred from the host to the dopants.

ZnS materials have been prepared by some different methods.[25–28] Low-temperature hydrothermal synthesis (150 °C–250 °C) is becoming popular because of the low-cost facility, the capability of the large-scale preparation of materials, and environmental friendliness. The hydrothermal process has also been widely used to prepare crystals of different morphologies, dimensions, and structures.[28–30] However, research on ZnS:Cu, Eu nanocrystals synthesized by the hydrothermal approach has not been published. In this paper, Cu-doped and Cu, Eu-codoped ZnS are synthesized using the hydrothermal approach. The PL emissions before and after annealing are compared, and the doping forms of Eu are also investigated.

2. Experimental details

2.1. Preparation of the ZnS:Cu, Eu nanoparticles

All the reactants were reagent grade. 54 mL of 0.38-M $ZnCl_2$ pure ethanol solution, 2.3 mL of 0.0027 M $CuCl_2$ water solution and 0.063 mL of 0.005-M $Eu(NO_3)_3$ water solution

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were mixed together under magnetic stirring. The molar ratio of Cu/Zn was 3×10^{-4}, and the molar ratio of Eu/Cu was 0.5 in the mixed solution. The solution was dissolved into 0.4 M $(NH_4)_2S$ water solution under stirring and the molar ratio of S/Zn was 3. The pH value of the mixed solution was adjusted to 4.0 by dissolving hydrochloric acid into the solution. The resulting precipitate was placed in a Teflon-lined autoclave of 50 mL capacity. The closed autoclave was then placed into the furnace at a preset temperature of 200 °C for 12 h, and naturally cooled down to room temperature. The resulting precipitate was filtered off and washed once in water. The final product was dried in air at 60 °C for 12 h.

The annealed samples were synthesized from the final product via a hydrothermal treatment at 200 °C for 12 h and then annealed in Ar at 900 °C for 1 h. The detailed experimental parameters are shown in Table 1.

Table 1. Samples and experimental parameters.

Samples	Experimental parameters	Process conditions
S1	$Cu/Zn = 3\times10^{-5}$, Eu/Cu = 0.5	hydrothermally treated at 200 °C for 12 h
S2	$Cu/Zn = 3\times10^{-4}$, Eu/Cu = 0.5	
S3	$Cu/Zn = 3\times10^{-3}$, Eu/Cu = 0.5	
S4	$Cu/Zn = 3\times10^{-5}$	
S5	$Cu/Zn = 3\times10^{-4}$	
S6	$Cu/Zn = 3\times10^{-3}$	
S7	$Cu/Zn = 3\times10^{-4}$, Eu/Cu = 0.5	hydrothermally treated at 200 °C for 12 h and then annealed in Ar at 900 °C for 1 h

2.2. Characterization of the sample

The crystal structure of the nanocrystal was analyzed using X-ray diffraction (XRD) (XRD-6000, Shimadzu Corporation), and the morphology of the sample was characterized using scanning electron microscopy (SEM) (HITACHIS4800 SEM). The content values of Cu and Eu in the samples were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (PROFILE SPEC, USA). The PL measurement was performed by a HITACHI F-4500 spectrophotometer with an excitation wavelength of 337 nm in a wavelength range of 200 nm–900 nm. The emission slit width, the excitation slit width, and the voltage of the photomultiplier tube (PVT) were set to be 1.0/2.5 nm, 1.0 nm, and 700 V, respectively. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural and morphological characterization

Typical XRD patterns of the ZnS:Cu, Eu samples are shown in Fig. 1, and the relevant experimental parameters are listed in Table 1. The diffraction peaks (2θ) at 28.6°, 33.1°, 47.5°, 56.3°, 59.1°, 69.5°, 76.8°, and 79.2° correspond to the (111), (200), (220), (311), (222), (400), (331), and (420) diffraction planes, respectively. The peaks clearly indicate that the synthesized ZnS:Cu, Eu nanocrystals possess a sphalerite structure. No other diffraction peaks are detected, except that the ZnS-related peaks exactly match the standard cubic ZnS JCPDS No. 5-0566. All the peak positions have a slight red shift with the increase in Cu content. Meanwhile, the peak intensity decreases and the full width at half maximum (FWHM) increases slightly. It is demonstrated that the incorporation of Cu^{2+} ions contributes to the reduction in the particle size of ZnS:Cu, Eu because the radius of the Cu^{2+} ion is smaller than that of the Zn^{2+} ion.

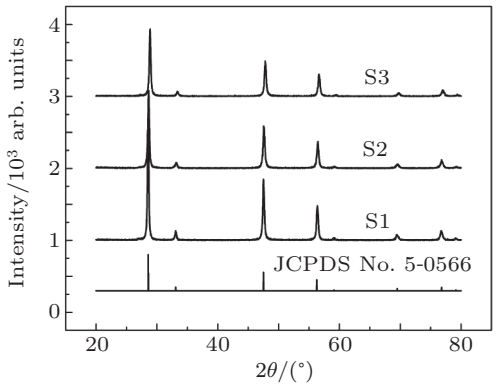


Fig. 1. The XRD patterns of ZnS:Cu, Eu.

Figure 2 shows the SEM images of the ZnS:Cu, Eu nanoparticles (S1, S2, and S3) synthesized by the hydrothermal treatment. All the particles are spherical-like and the average diameter is about 80 nm, while the particle size in S3 slightly decreases compared with that in S1.

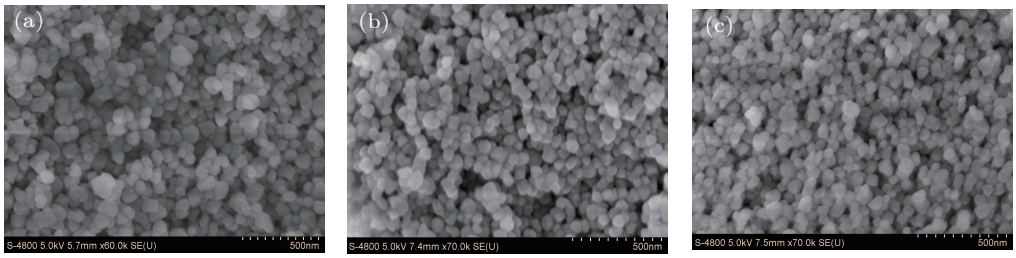


Fig. 2. SEM images of the samples (a): S1, (b): S2, (c): S3.

3.2. Composition analysis

ICP-AES is widely used as a powerful analytical method for the fast, simple, and sensitive determination of trace elements.[31] The content values of Cu and Eu in S2 were determined by ICP-AES as shown in Table 2.

Table 2. Measured Cu and Eu content values in S2.

Measuring elements	Wavelength/nm	Predictive value/μg·g^{-1}	Measured value/μg·g^{-1}
Cu	327.393	195.4	172.6
Eu	381.967	233.7	3

The results show that the detected Cu content is close to the predicted value, however, the measured Eu content is much lower than the predicted value. This may be because Cu is easy to be incorporated into the matrix lattice due to its ion radius being similar to the Zn ion radius. On the other hand, it is difficult for Eu to be incorporated into the matrix lattice because of their different chemical properties.

3.3. PL property

Figure 3 shows the PL spectra of the ZnS:Cu and ZnS:Cu, Eu samples. It is clearly exhibited that all the PL spectra of the samples are broad-band. The PL emission intensity of ZnS:Cu is enhanced with the increase in the molar ratio of Cu/Zn at the beginning, and the strongest luminescence intensity comes from the sample with a Cu/Zn molar ratio of 0.0003 (S5). The PL intensity decreases with the continuous increase in the Cu/Zn molar ratio, owing to the concentration quenching effect. The PL emission band of S5 is centred at 512 nm, and the broad emission band is a Gaussian superposition of blue emission from the recombination of S vacancy-trapped electrons and Zn vacancy or Cu^{+}-trapped holes. The green emission from the S vacancy-trapped electrons and Cu^{2+}-trapped holes[23,32] belongs to the ZnS host emission. It is found that the PL emission spectra of the codoped samples are centred at about 516 nm (S1). The emission intensity increases compared with that of the ZnS:Cu sample. The reasons are as follows: Eu^{3+} as an impurity compensation and a co-activator forms a donor level, as shown in Fig. 4. The luminescence mechanism is basically the same as those of the ZnS:Cu and ZnS:Cu, Tm samples analyzed in our previous work.[33] The strongest luminescence intensity from S1 may be related to the incorporation of an appropriate amount of Eu^{3+}.

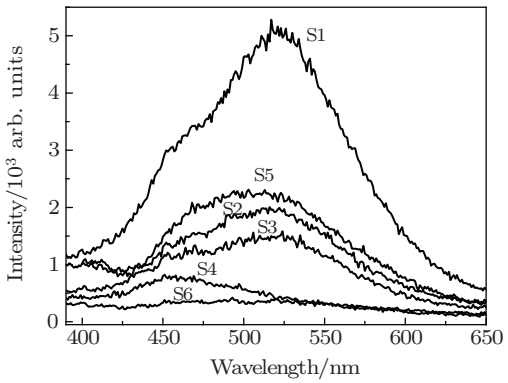


Fig. 3. The emission spectra of ZnS:Cu and ZnS:Cu, Eu nanocrystals ($\lambda_{ex} = 337$ nm).

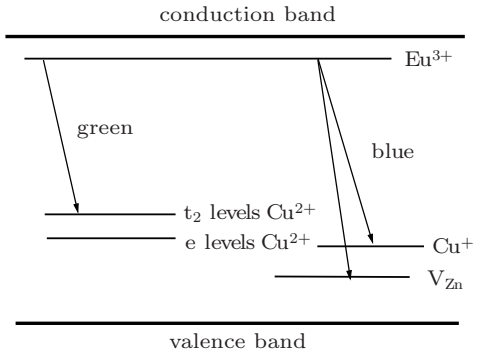


Fig. 4. Energy level diagram of ZnS:Cu, Eu synthesized using the hydrothermal approach.

Figure 5 shows the room-temperature PL spectra of S2 and S7. The inset shows the PL excitation spectrum of sample S7. There are two peaks set at 337 nm and 365 nm in the excitation spectrum, respectively. All the emission spectra are excited by 337 nm in this study. No characteristic peaks of Eu are observed in the excitation spectra of the ZnS:Cu, Eu sample (inset of Fig. 5), indicating that Eu has been incorporated

into the ZnS matrix without surface adsorption. Compared with the as-synthesized sample, the annealed sample has a PL intensity that is increased by four times and a peak wavelength without any red shift. Generally, a red shift appears after annealing, owing to the increase in particle size. However, this is superseded by the production of a large blue shift of about 56 nm, from 516 nm to 460 nm. This should be related only to the dopants. More Cu^{+} interstitial impurities become Cu^{2+}, and thus the green emission is enhanced. An Eu^{3+} reduction forms Eu^{2+} and occupies the Zn^{2+} vacancy, leading to the generation of Eu^{2+} characteristic emission ($4f^{6}5d\rightarrow 4f^{7}$). The blue emission is enhanced and an effective energy transfer may occur between the host and Eu^{2+} characteristic blue luminescence. According to the literature, the observed Eu^{2+} emission spectrum is broad, and the center position of the emission is strongly influenced by the environment.[34] This experimental phenomenon is also confirmed by the fact that the sample can emit blue light when the Eu dopant exists in the form of Eu^{2+} in ZnS. These results are helpful in identifying the doping form of Eu in ZnS, and indicating the potential applications of rare-earth-doped ZnS in optoelectronic devices.

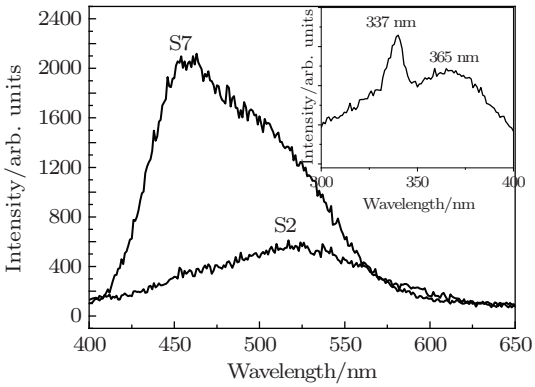


Fig. 5. The PL spectra of S2 and S7 ($\lambda_{exc} = 337$ nm). The inset shows the PL excitation spectrum of S7 ($\lambda_{em} = 460$ nm).

4. Conclusions

Cu mono-doped and Cu, Eu-codoped ZnS nanocrystals are prepared using a hydrothermal approach (200 °C, 12 h). These spherical-like particles are of sphalerite structure and around 80 nm on average in diameter. Each of the PL spectra of ZnS:Cu, Eu nanocrystals has a broad emission band centred at 516 nm, showing that Eu^{3+} ions are incorporated into the ZnS matrix as a recombination center of luminescence. The PL intensity of the annealed sample is increased by four times and the peak has a large blue shift of about 56 nm compared with the un-annealed one. It is indicated that some of the Eu dopants are incorporated into the ZnS matrix in the form of Eu^{2+}. At the same time, an effective energy transfer may occur between the host and Eu^{2+} characteristic ($4f^{6}5d\rightarrow 4f^{7}$) blue emission. The results will be useful for developing an intense nanosized blue–green light source in display applications.

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