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Strong green luminescence of Ni^{2+}-doped ZnS nanocrystals

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Abstract. ZnS nanoparticles doped with Ni^{2+} have been obtained by chemical co-precipitation from homogeneous solutions of zinc and nickel salt compounds, with S^{2-} as precipitating anion, formed by decomposition of thioacetamide (TAA). The average size of particles doped with different mole ratios, estimated from the Debye–Scherrer formula, is about 2–2.5 nm. The nanoparticles could be doped with nickel during synthesis without altering the X-ray diffraction pattern. A Hitachi M-850 fluorescence spectrophotometer reveals the emission spectra of samples. The absorption spectra show that the excitation spectra of Ni-doped ZnS nanocrystallites are almost the same as those of pure ZnS nanocrystallites ($\lambda_{ex} = 308$–310 nm). Because a Ni^{2+} luminescent center is formed in ZnS nanocrystallites, the photoluminescence intensity increases with the amount of ZnS nanoparticles doped with Ni^{2+}. Stronger and stable green-light emission (520 nm) (its intensity is about two times that of pure ZnS nanoparticles) has been observed from ZnS nanoparticles doped with Ni^{2+}.

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During recent decades, the preparation and characterization of materials on the nanometer-size scale have provided not only new physics in reducing dimensions, but also the possibility of fabricating novel materials [1–3]. Nanosized ZnS semiconductor (e.g. ~ 3.6 eV) is commercially used as phosphor and also in thin-film electroluminescent devices [4–6]. The photophysical and photochemical properties of ZnS semiconductor nanocrystals doped with Mn^{2+}, Cu^{2+}, Ag^{+} have been studied recently [7–12]. These doped nanoparticles show interesting properties different from those of bulk materials, such as an increased energy band-gap, which results from size quantization confinement [13]. However, there has not much work on luminescence studies in ZnS:Ni^{2+} semiconductor nanoparticles. For example, theoretical studies of the optical spectra and their pressure dependence for ZnS:Ni^{2+} crystal have been completed by Zheng et al. [15] Here, we present the photoluminescence (PL) characteristics of ZnS nanoparticles doped with Ni^{2+} for the first time. Novel luminescent properties, such as strong green-light emission, have been observed.

1 Experimental

The precipitation of doped ZnS nanoparticles was performed starting from homogeneous solutions of zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), $NiSO_4$ $6H_2O$ at 0.5 M and TAA at 0.5 M for precipitation reaction. The reaction temperature was fixed at 80 °C, and the solutions were acidified to control the decomposition of TAA that generated the sulfide anions. In each experiment, the salt solutions and the TAA solution were separately heated to 80 °C before mixing in a batch reactor with no agitation. A bluish tint appeared after 5 min, indicating the beginning of the nucleation step. The reaction time was fixed at 30 min, after which the hydrolytic reaction of TAA was terminated by rapidly cooling the solution to $< 10\,°C$ in an ice bath. As-precipitated ZnS nanoparticles were then centrifuged at 4000 rpm, washed three times with water to eliminate TAA, and finally washed three times with isopropyl alcohol. The cleaned powders were dried for about 10 h at 80 °C until complete evaporation of the solvent was achieved.

The photoluminescence spectra of the samples were recorded with a Hitachi M-850 fluorescence spectrophotometer. All measurements were carried out at room temperature under ambient atmosphere and the doped ZnS nanocrystal samples were dispersed in isopropyl alcohol so that a 25-mM solution of doped ZnS nanocrystallites was obtained. X-ray powder diffraction (XRD) patterns were recorded by using a Japan Rigaku D/max-rA X-ray diffractometer with graphite monochromatized Cu K_α irradiation ($\lambda = 1.5418$ Å). The absorption spectra of samples were recorded by using an UV–vis spectrophotometer (in a test process, the 25-mM solution of doped ZnS nanocrystallites was obtained by dispersing the sample in isopropyl alcohol).

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2 Results and discussion

The doped mole percent ratios of Ni^{2+} are 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, respectively. The XRD patterns of samples are shown in Fig. 1. It reveals that the particles exhibit a zinc-blende crystal structure. The three diffraction peaks correspond to (111), (220), and (311) planes of the cubic crystalline ZnS, respectively. From XRD analysis, no characteristic peaks of impurity phases have been observed. The average size of particles doped with different dopants, estimated from the Debye–Scheerer formula, is about 2.0–2.5 nm. The average particle-size of ZnS nanocrystals is about 2.20 nm.

Figure 2 shows the absorption spectra of doped and undoped ZnS nanocrystallites. It reveals that the absorption spectra of ZnS nanoparticles are not varied when Ni^{2+} ions are doped in ZnS nanoparticles. Their absorption shoulder is about 308 nm. Therefore, the excitation spectra of doped ZnS nanoparticles are almost the same as those of pure ZnS nanocrystallites (308–310 nm).

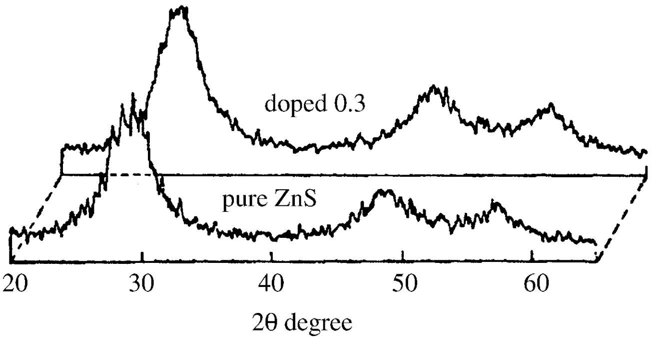

Fig. 1. X-ray diffraction patterns of pure ZnS nanocrystals and doped 0.3% Ni^{2+} (mole ratio) sample

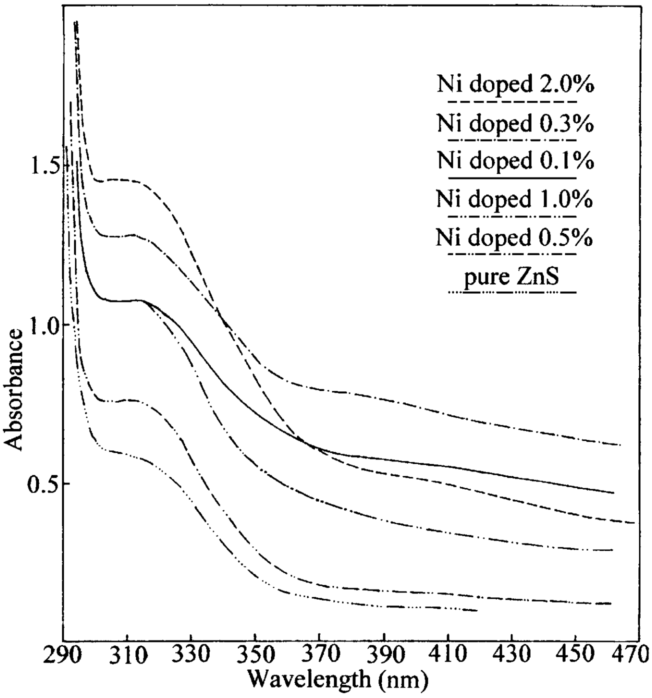

Fig. 2. The absorption spectra of the samples (mean impurity mole ratio)

Figure 3 shows the emission spectra of pure ZnS nanoparticles and ZnS nanocrystallites doped with different mole ratio Ni^{2+}. Their excitation wavelength is 308–310 nm. The doped mole percent ratios are also given in Fig. 3. The emission peak of pure ZnS nanoparticles is at 450 nm. But the emission peaks of doped ZnS nanocrystallites are at 520 nm (green). The fluorescence efficiencies of doped samples are decreased as the doped mole ratio of Ni^{2+} is increased.

Figure 4 shows the energy levels of Ni^{2+} (d^8) impurity in ZnS bulk material calculated by using configuration-interaction (CI) theory applied to a metal-ligand $(NiS_4)^{-6}$ cluster model. They are compared with a ligand-field (LF) theoretical fit in the same figure [18]. The lowest multiplet term ^3F of the free Ni^{2+} ion is split into $^3T_1$, $^3T_2$ and $^3A_2$

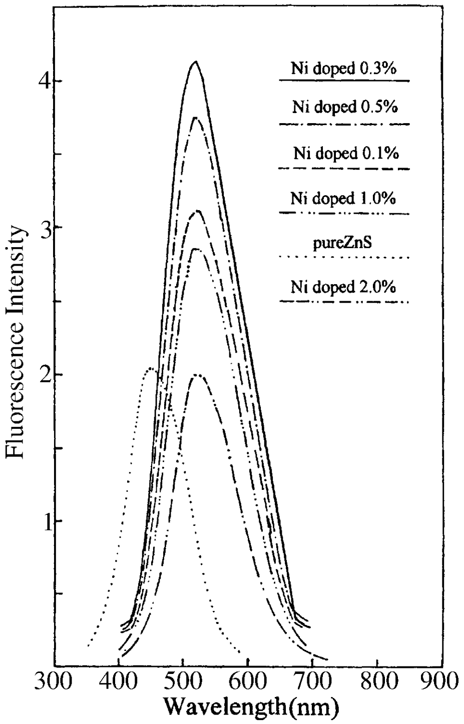

Fig. 3. The emission spectra of the samples ($\lambda_{excitation} = 308–310$ nm), mean impurity mole ratio of Ni^{2+}

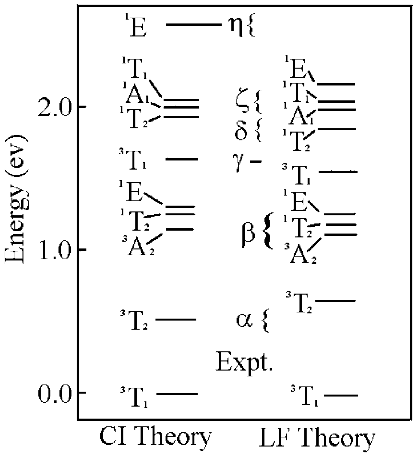

Fig. 4. The energy levels of a Ni^{2+} (d^8) impurity in ZnS bulk material calculated using CI theory applied to a metal-ligand $(NiS_4)^{-6}$ cluster model

through the anisotropic hybridization. Due to the *d–d* optical transitions of Ni^{2+}, the luminescent center of Ni^{2+} is formed in ZnS. However, the luminescent center of Ni^{2+} makes the nonradiative recombination processes increase. It thus limits the quantum efficiency of the luminescence of doped ZnS bulk material [18].

The photoluminescence mechanism of ZnS nanocrystals doped with other metallic ions is very complex. First, the smaller particles have higher surface/volume ratio and more surface states. Therefore, they contain more accessible carriers for PL [17]. These indicate that the surface states are very important for the physical properties especially the optical properties of nanoparticles. In nanoparticles, most ions at the surface are non-saturated in coordination. Electrons and holes may be excited easily and escape from the ions. Many carriers trapped at the surface states or defect sites may be released by photo excitation [14, 16]. So fluorescence efficiencies of nanocrystals are higher than those of bulk material.

In ZnS nanocrystallites doped with Ni^{2+}, first, the luminescent centers of Ni^{2+} are formed. Then due to the *d–d* optical transitions of Ni^{2+}, the green emission band has been observed from ZnS:Ni^{2+} nanoparticles. Because the band-gap structure of ZnS nanocrystallites doped with Ni^{2+} is remarkably different from that of pure ZnS nanocrystallites, the luminescence spectra of doped ZnS nanocrystallites are also varied. Second, since the effect of the luminescent centers of Ni^{2+} in nanometer-scale material is remarkably different from that of bulk materials, the quantum yield for photoluminescence of doped samples can be increased. Because more and more electron–holes are excited and radiative recombination is enhanced, the fluorescence efficiency of the doped samples is remarkably increased.

3 Conclusion

PL experiments show a strong green-light emission band (520 nm) from the Ni^{2+}-doped ZnS nanocrystals at room temperature. The emission band of ZnS nanoparticles is at 450 nm. Also the fluorescence efficiency of Ni^{2+}-doped ZnS nanoparticles is enhanced dramatically and is much higher than that of pure ZnS nanocrystals. The luminescent centers of Ni^{2+} in ZnS nanoparticles are not only changing the emission wavelength of doped samples, but also enhancing the fluorescence quantum yield. When the doped mole ratio of Ni^{2+} is 0.3%, the fluorescence efficiency of Ni^{2+}-doped ZnS nanoparticles is about two times that of pure ZnS nanocrystallites.

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