Synthesis and photoluminescence of Mn-doped zinc sulfide nanoparticles

Dongyeon Son, Dae-Ryong Jung, Jongmin Kim, Taeho Moon, Chunjoong Kim, and Byungwoo Park

Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

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Mn-doped zinc sulfide nanoparticles were synthesized using a liquid-solid-solution method, as a simple synthetic route for preparing nearly monodispersed nanocrystals with a diameter of 7.3±0.7 nm. The influence of doping concentration for optimum luminescence properties was studied with the nonuniform distribution of local strain and the capping effect. The improved photoluminescence properties of the 450 °C-annealed samples with 1.0 at. % Mn doping are attributed to both the removal of water/organics and the enhanced crystallinity (reduced local strain).

A great deal of attention has been devoted to the preparation and characterization of nanosized semiconductor materials as a class of condensed matter with reduced dimensions. For the effective preparation of the nanoparticles, various synthetic methods have recently been reported, such as sol gel, precipitation, microemulsion, and chemical vapor deposition. However, high-quality nanophosphors have remained a technical challenge for applications in the fields of photonics and electronics.

Zinc sulfide (ZnS) is an important luminescence material, with a band gap of 3.7 eV and is widely used in flat-panel displays, infrared windows, sensors, etc. Since the study on Mn-doped ZnS (ZnS:Mn) nanoparticles in 1994, many researchers have studied the synthetic techniques, luminescence properties, and applications. Especially, several papers have shown that the photoluminescence (PL) properties of ZnS:Mn are highly dependent on the Mn concentration. However, no reports have investigated the Mn-concentration effects simultaneously considering the crystallinity and the degree of capping. To obtain high-quality nanophosphors, it is essential to understand the role of both the local strain (crystallinity) and the water/organic quenching.

In this work, a liquid-solid-solution (LSS) technique, which has many advantages in comparison with other methods, was applied to the preparation of ZnS:Mn nanocrystals. By employing suitable organic agents, nearly uniform-sized ZnS:Mn nanoparticles with a diameter of 7.3±0.7 nm were synthesized. We investigated the optimum condition for luminescence properties with the actual dopant concentration, the nonuniform distribution of local strain, and the capping effect.

The ZnS:Mn nanoparticles were synthesized by the LSS method. Zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O, 0.66 g] was dissolved in distilled water (10 ml) and stirred for complete dissolution. As a sulfur source, 0.225 g of thiourea CH₃CSNH₂ was dissolved in ethanol (10 ml). Manganese nitrate [Mn(NO₃)₂, 0.05 g] was prepared as a Mn precursor in distilled water (2 ml). Zinc acetate solution was added to the autoclave, and manganese nitrate solution was poured into the vessel. Both 0.1 g of sodium linoleate [(C₁₇H₃₃)COOH] was added to the autoclave to control the reaction rate. The autoclave was sealed and heated at 90 °C for 10 h. Then, the resultant was centrifuged, rinsed several times with ethanol, and dried at 60 °C for 5 h. To investigate the Mn-concentration effects, all the samples were annealed at 450 °C for 10 h.

The nanostructures of ZnS:Mn nanoparticles were analyzed by high-resolution transmission electron microscopy (JEM-3000F, JEOL). X-ray diffraction was measured with Cu Kα radiation, and inductively coupled plasma (ICP-1000V, Shimadzu) analysis was performed to determine the chemical composition of the samples. The UV spectrometer was operated with a xenon lamp in the ultraviolet region, and emission spectra were recorded on a spectrophotometer (FP-6500, JASCO). Mass-reduction data were obtained with a thermogravimetric analyzer (TGA), and elemental analysis was performed using a carbon, hydrogen, nitrogen, and sulfur (CHNS) instrument (Flash EA 1112, CEI). The chemical-bond states were analyzed by x-ray photoemission spectroscopy (XPS) with Mg Kα radiation.

Figure 1 shows the TEM images of the 450 °C-annealed ZnS:Mn nanoparticles synthesized by the LSS method. The nanoparticles exhibit nearly uniform-sized shape with a diameter of approximately 7 nm. The inset shows diffraction patterns confirming the crystalline ZnS. In the diluted TEM sample of Fig. 1(b), the crystalline planes of the ZnS:Mn nanoparticles clearly represent the (111) d spacing of 0.312 nm.

We estimated the band gap energy (Eg) of the ZnS:Mn nanoparticles from the UV-vis absorption spectrum. The fitted Eg of the ZnS:Mn nanoparticles was approximately 3.8 eV, which is larger than that of bulk ZnS (3.7 eV) and is

![FIG. 1. TEM images of the 450 °C-annealed ~7 nm diameter ZnS:Mn nanoparticles. The inset in (a) shows diffraction patterns of ZnS. The crystalline planes of the ZnS:Mn nanoparticles exhibit a (111) plane.](image-url)
consistent with the calculated $E_g$ value (3.79 eV) by the Brus equation. The $E_g$ value was estimated by considering the particle size ($7.3 \pm 0.7$ nm), the effective masses ($m^* = 0.25m_e$ and $m^*_b = 0.59m_e$), and the dielectric constant (8.2).

X-ray diffraction patterns of the 450 °C-annealed samples with different Mn concentrations (0, 1, 2, 5, 8, and 10 at. %) are shown in Fig. 2. No secondary phases are present in the ZnS:Mn nanoparticles, and the peak broadening indicates the nanocrystal size and the nonuniform distribution of local strain. However, the actual Mn concentration in the ZnS:Mn nanoparticles was less than the Mn-precursor concentration, being 0, 0.2, 0.3, 1.0, 0.6, and 0.5 at. %, respectively, as confirmed by ICP.

The nanocrystal size and crystallinity (local strain) were estimated from the Scherrer formula of $\Delta k$ vs $k$ [the scattering vector $k = (4\pi/\lambda)\sin \theta$]. The three peaks of (111), (220), and (311) were fitted using a double-peak Lorentzian function for $K_{01}$ and $K_{02}$, for the peak widths $\Delta k$ (full width at half maximum). As shown in Table I, the average sizes of the ZnS:Mn nanoparticles (determined at $k=0$) with different Mn concentrations were $7.3 \pm 0.7$ nm, which was consistent with the TEM data (Fig. 1), and confirmed the nearly uniform-size distribution of the nanoparticles obtained by the LSS method. The PL properties can be influenced by the nanocrystal size. The size effect was minimized in the present study which investigated the doping-concentration effect with the crystallinity and the degree of capping.

Figure 3 represents the PL emission spectra of ZnS:Mn nanoparticles with 325 nm excitation at room temperature. The PL band at ~580 nm is a characteristic emission of Mn$^{2+}$ ion, which can be attributed to a $^4T_{1g} \rightarrow ^6A_{1g}$ transition. However, the Mn-peak position of ZnS:Mn nanoparticles at ~580 nm was blueshifted compared to the bulk, because the crystal-field splitting in ZnS:Mn nanoparticles (with a large surface area) is smaller than that of bulk powders. (The emission of bulk ZnS:Mn for this transition exhibits ~590 nm band.)

The magnitude of PL intensity is consistent with the actual Mn concentration, as shown in Fig. 3(a). Therefore, the ZnS:Mn nanoparticles of 5 at. % Mn (1.0 at. % by ICP) showed a strong Mn-emission band. Interestingly, the actual dopant concentration of ZnS:Mn nanoparticles through the LSS method did not increase in proportion to the amount of Mn precursor, probably due to the interface-limited reaction kinetics of the LSS technique. X-ray diffraction of 10 at. % Mn (0.5 at. % by ICP) sample without rinsing showed a byproduct phase of manganese acetate hydrate (not shown here).

Figure 3(b) shows the PL emission of ZnS:Mn nanocrystals at various annealing temperatures. The actual Mn concentration for all the samples was ~1 at. %. The luminescence intensities were improved as the annealing temperature was increased from 150 to 450 °C, and two probable factors for this PL enhancement are the crystallinity and the degree of capping. Several papers have reported that the PL properties can be affected by improved crystallinity. However, these studies only offered the diffraction-peak broadening as an evidence for the enhanced crystallinity, without considering simultaneously the size, concentration, and capping effect.

![Figure 2](image1.png)  
**FIG. 2.** (Color online) X-ray diffraction patterns of 450 °C-annealed ZnS:Mn nanoparticles as a function of Mn concentrations: 0, 1, 2, 5, 8, and 10 at. %. (The actual Mn concentration is shown in parentheses.) The peak positions and intensities are marked for the cubic ZnS (JCPDS #05–0566).

![Figure 3](image2.png)  
**FIG. 3.** (Color online) Photoluminescence spectra of the 450 °C-annealed ZnS:Mn nanoparticles with different Mn concentrations (left column). The right column shows the PL emission spectra as a function of annealing temperature for the 5 at. % (1.0 at. % by ICP) nanoparticles.

<table>
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<tr>
<th>TABLE I. Nonuniform distribution of local strain and nanocrystal size for the ZnS:Mn nanoparticles as a function of Mn doping concentration and annealing temperature. The local strain was estimated from the slope of $\Delta k$ vs $k$ plot, and the nanoparticle size was determined at $k=0$.</th>
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<tr>
<td>Mn precursor, 450 °C annealing (actual Mn conc.)</td>
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<tr>
<td>Undoped (0 at. %)</td>
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<tr>
<td>1 at. % (0.2 at. %)</td>
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<tr>
<td>2 at. % (0.3 at. %)</td>
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<tr>
<td>5 at. % (1.0 at. %)</td>
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<tr>
<td>8 at. % (0.6 at. %)</td>
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<td>10 at. % (0.5 at. %)</td>
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In this study, the nonuniform distribution of local strain ($\Delta l/d$ with $k=2\pi/d$) in the ZnS:Mn nanocrystals was obtained from the slope of the $\Delta k$ vs $k$ plot. Table I shows the crystallinity data at various temperatures. As the annealing temperature was increased up to 450 °C, the nonuniform distribution of local strain decreased. Therefore, the luminescence properties were improved with the crystallinity (local strain) over a suitable temperature range. The 600 °C-annealed ZnS nanoparticles, however, had no Mn emission peak, due to the diffused-out Mn dopants during phase transition (from cubic zinc blende to hexagonal wurtzite).

The second enhancement factor for the luminescence properties is the reduction of water/organic capping. To examine this effect, both the TGA and the CHNS elemental study were performed. Figure 4 shows the TGA result for the as-synthesized ZnS:Mn nanoparticles. A weight loss of $\approx 4.6\%$ was observed from $\approx 100$ to $\approx 190$ °C (region A), due to the evaporation of residual water adsorbed to the surface of the particles. The lineolate bonding at the surface begins to desorb at $\approx 320$ °C, and a weight loss of $\approx 6.4\%$ was measured up to $\approx 440$ °C (region B). Elemental analysis showed the presence of the carbon and hydrogen quantitatively (inset of Fig. 4). The amounts of carbon and hydrogen decreased gradually with the increasing annealing temperature. The presence of water and organic elements has been reported to degrade the luminescence properties, because they may decrease the efficiency of energy transfer at the surface. (The Mn dopants near the surface can be affected by water/organic within several angstrom range.) In this work, we demonstrated that the PL properties are improved with decreasing degree of capping (water/organic quenching), using TGA and CHNS techniques. However, the exact contribution between the enhanced crystallinity and the removal of water/organics needs to be resolved for luminescence properties.

The XPS spectra for the Zn 2p and S 2p core levels of the ZnS:Mn nanocrystals were measured at different annealing temperatures, as shown in Fig. 5. The marked peak positions are from the standard ZnS sample. In Fig. 5(a), the Zn 2p peaks were slightly shifted by $\approx 1$ eV with the annealing temperature. This peak shift can be explained by the removal of surface absorbates. Therefore, the binding energies of the Zn 2p peaks in the 450 °C-annealed sample were close to the values for the pure ZnS. As shown in Fig. 5(b), the S 2p peak of the room temperature and 150 °C samples had a broad shoulder peak, which can be attributed to the residual water. With the increasing annealing temperature, the broad shoulder peak disappeared, consistent with the elemental analysis as shown in Fig. 4.

In conclusion, ZnS:Mn nanoparticles (7.3±0.7 nm) were synthesized using the LSS technique, as a simple synthetic method. The influence of doping concentration was studied with the actual Mn concentration, the crystallinity, and the capping effect. The results showed that the 1.0 at. % Mn-doped ZnS nanoparticles had a strong Mn emission. The improved photoluminescence properties of the 450 °C-annealed samples with 1.0 at. % Mn-doping are attributed to both the removal of water/organics and the enhanced crystallinity.

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**References**