Cadmium (Zinc) Manganese Sulfide Nanocrystalline (Cd$_{1-x}$Mn$_x$S and Zn$_{1-x}$Mn$_x$S) Dilute Magnetic Semiconductors. Synthesis, Annealing, and Effects of Surface Oxidation on Magnetic Properties

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Abstract. Cd$_{1-x}$Mn$_x$S and Zn$_{1-x}$Mn$_x$S dilute magnetic semiconductor nanocrystals were prepared in aqueous and non-aqueous solutions by simple precipitation methods with x values ranging from 0.1 to 0.5. X-ray powder diffraction showed the as-prepared sample crystal sizes were about 2-3 nm with the Wurtzite cubic structure. After thermal annealing, the crystals converted to the hexagonal wurtzite structure as the crystal size reached 100-200 nm. The magnetite ions on the surface were very easily oxidized in the air and were the cause of an antiferromagnetic transition at near 37 K.

INTRODUCTION

In recent years considerable interest has been drawn to nanometer sized materials in chemical and physical research, and many papers have been published about their unique physical and chemical characteristics. Among them, the synthesis and optical/electrical study of semiconductor nanoparticles with size of 1-20 nm play a very important role in materials research. Their properties can be dramatically different from bulk materials and have many potential applications in photonics, catalysis, and electronic/optical materials.

Nanoparticles of any material can have properties different from the bulk for two major reasons: quantum size effects and surface/interface effects. Quantum size effects occur because the finite number of atoms in a nanoparticle causes the electronic bands to resolve into a finite number of states. Surface/interface effects become important because the fraction of surface atoms becomes appreciable. For example, for a 3 nm diameter particle approximately half the atoms are on the surface. The surface is, of course, different than the bulk, due to different coordination, lattice relaxation, and reconstruction of electronic states.

Several methods of synthesis have been developed. Solution methods can be divided into aqueous and non-aqueous. Generally, non-aqueous synthesis can provide smaller size and narrower size distributions. Whatever the solvent chosen, a good way to obtain nano-sized particles is to provide them a stable compartmentalization environment for synthesis and growing. Molecular, polymers, zeolites, glasses, and biological vesicles have been used successfully, as they trap the nanocrystals to yield a stable, isolable material.

Dilute Magnetic Semiconductors (DMSs)

Semiconductors with small fractions of cations replaced by magnetic ions are called dilute magnetic semiconductors. Since these materials have many special magnetic and optical properties, a great deal of research has been carried out in this field in the last twenty years. Most researchers focus on II−VI compounds doped with Mn, like Cd$_{1-x}$Mn$_x$S, Zn$_{1-x}$Mn$_x$S, Hg$_{1-x}$Mn$_x$S, and the corresponding selenides and tellurides. The unique properties of these compounds come from the interaction of the spin-induced magnetic moment of the Mn$^{2+}$ ions with the electronic bands of the semiconductor lattice.

There have been a few studies of nanoscale DMS materials. Bandamavuye et al. studied the low temperature magnetic properties of Cd$_{1-x}$Mn$_x$S nanoparticles. They found that the spin-glass freezing temperature decreased with decreasing size, and there was a

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EXPERIMENTAL METHODS

Nanocrystals of CdS, MnS, and ZnS MnS were prepared by an aqueous solution forced precipitation method. Structural analysis was carried out by powder X-ray diffraction (XRD), and magnetic measurements by using a SQUID magnetometer.

Synthesis of CdS, ZnS, and ZnS MnS DMS Nanocrystals

The starting materials were 98% Cd(NO₃)₂·4H₂O, 98% Mn(NO₃)₂·4H₂O, 98% Na₂S·9H₂O, 98% Zn(NO₃)₂·6H₂O, and ACU grade ethylene glycol, all purchased from Aldrich Co. Absolute methanol was obtained from Fisher. All materials were used as received. The water used in the synthesis was deionized and bubbled with argon for at least 2 h before the experiment to expel dissolved oxygen. All manipulations were carried out in a glovebox filled with argon.

The reaction solution was prepared by dissolving a certain amount of, for example, Cd(NO₃)₂·4H₂O and Mn(NO₃)₂·6H₂O in deionized water according to the desired molar ratio of Cd:S, that is, the x value. Na₂S·9H₂O was dissolved in deionized water to prepare an anion solution of S⁻, such that the total molarity of S⁻ equaled the combination of the molarity of Cd²⁺ and Mn²⁺. The pH value of the cation solution was adjusted to between 2 and 3 by adding a few drops of dilute nitric acid, which was necessary since the Na₂S is basic and the mixture had to be maintained near neutral. We found pH control was very important during synthesis in aqueous solutions. The pH value of the final mixture had to be 4~7. If the pH was less than 3, H₂S gas would form and escape, and if the pH was more than 6, Mn(OH)₂ would precipitate, causing the yield of CdS, MnS to be low. Orange-yellow precipitates were formed immediately after mixing, and the mixture was stirred for an additional half-hour to complete the reaction. The color of the products depended on the amount of Mn²⁺ ions added. More Mn would change the color from orange to yellow. Stirring was stopped to allow the precipitate to settle, the water was decanted, and the powder was filtered with a fine nitro and washed several times with deionized water. The precipitate was transferred into a desiccator with Drierite, and evacuated overnight.

Samples of CdS, MnS, and ZnS MnS were prepared according to the following stoichiometric equations:

(1) \( (1-x)\text{CdS} + x\text{MnS} + S^2- \rightarrow \text{Cd}_x\text{Mn}_{1-x}\text{S} \)

(2) \( (1-x)\text{ZnS} + x\text{MnS} + S^2- \rightarrow \text{Zn}_{1-x}\text{Mn}_x\text{S} \)

Different x values were used, such as x = 0.3, 0.5, 0.8. The total volume of liquid after mixing was about 200 mL.

We employed cadmium and manganese compounds of nitrate, chloride, and acetate as starting materials, all of which worked well. However, for acetates (AC), the pH changed less after mixing since it formed a buffer solution of HAC·AC. The size of the un-precipitated crystals varied with different ions: acetate usually resulted in the largest particle size while chloride the smallest, however, the size seemed to be unrelated to the manganese content.

Non-aqueous syntheses were carried out in methanol and ethylene glycol following the same procedure, but with no need to adjust the pH before mixing. The products were washed with methanol, then water, and dried under vacuum.

The synthesis of ZnS MnS DMS was essentially the same as with the cadmium compounds. One example of ZnS MnS, X in aqueous solutions was prepared in the following way: 3.13 g (19.3 mmol) Zn(NO₃)₂·6H₂O, 1.29 g (4.5 mmol) Mn(NO₃)₂·6H₂O were dissolved in 100 mL deionized and deaerated water, and dilute HNO₃ was added drop by drop to adjust the pH to 3.0. 0.6 g (15 mmol) Na₂S·9H₂O was dissolved in another 100 mL deionized, deaerated water, then added to the ZnS MnS solution while stirring, and a precipitate was formed immediately. The solution was stirred for another half-hour before it was filtered and washed three times with 50 mL water. The powder was dried under vacuum. The yield varied from 98% to 99%. The whole procedure was carried out under argon gas protection, and the final dried sample was stored in a drybox filled with argon.

Crystal Size Modification through Annelaling

Thermal annealing was used to increase the crystal size and reduce defects sites, and these treatments resulted in sharper signals in the powder XRD spectra. The size of the nanocrystal domain could be enhanced from 2-3 nm to almost bulk size (~500nm). The transition from cubic to hexagonal wurtzite structure was completed when the crystal size reached 100-120 nm. Since the CdS, MnS, and ZnS MnS products are all air sensitive, we employed a vacuum (<10 mtorr Hg) during the heating process. The melting point of CdS products of size 2 nm is about 500 °C, so annealing was done below 450 °C to avoid melting and recrystallization.

The samples were placed in a quartz tube connected with the vacuum line at room temperature, and the valve was
opened slowly in apply the vacuum gradually. This slow procedure was necessary to avoid washing the fine particles into the vacuum line. The tube was then placed in an oven with a temperature controller, raising the temperature to 100°C for 4 h. After this course, the powder was collected, washed by an aqueous solution of acetic acid, filtered through a 0.45-mm pore size filter, and dried at 60°C. The powder was then used for further analysis.

**Structural Characterization and Magnetic Measurements**

Powder X-ray diffraction was carried out on a Siemens 3000 Diffractometer. The radiation source was Cu Kα with wavelength $\lambda = 1.54 \text{ Å}$. The scanning mode was continuous with step size 0.001° and rate 2.0° per min. Most scanning ranges were from 2θ = 20° to 60°. The sample was mounted on an amorphous plastic sample container.

The size of the crystallites was determined by Scherrer's formula:

$$D = \frac{0.94\lambda}{B \cos(\theta)}$$

where $\lambda$ is the wavelength of X-rays (1.54 Å in this case), $B$ is the full width at half maximum of the diffraction peak (radians), and $\theta$ is the Bragg angle of the peak on the 2θ scale.

Magnetic measurements were carried out on a Quantum Design MPMS2 SQUID magnetometer. The sample was cooled by liquid helium and the sample temperature could be varied from 1.7 K to 400 K. For the measurement with zero-field cooling (ZFC), the sample was cooled from room temperature to 5 K without any applied field, and then cooled to 1.7 K with a field of 100 Oe. For the field cooling measurements (FC), the sample was cooled from room temperature to 5 K with a field of 100 Oe, and then cooled to 1.7 K with a field of 100 Oe.

**RESULTS AND DISCUSSION**

**Cd$_{1-x}$Mn$_x$S and Zn$_{1-x}$Mn$_x$S DMS Nanocrystallities**

Structural Analysis

The as-prepared Cd$_{1-x}$Mn$_x$S and Zn$_{1-x}$Mn$_x$S DMS nanocrystallities made from aqueous or non-aqueous solutions were powders, and we used powder X-ray diffraction to analyze their crystal sizes, compositions, and 3-D structures.

The size of the crystal was calculated with Scherrer's formula, eq 3. Since the spectra of the as-prepared samples normally had very fuzzy and wide peaks, the sizes measured were not very accurate. For Cd$_{1-x}$Mn$_x$S, the half-maximum widths of the peaks (2θ) were measured for several samples and averaged.

**Figure 1** shows the XRD spectra of as-prepared nanocrystallites of Cd$_{1-x}$Mn$_x$S made from cadmium and manganese chloride, a typical example. This is a zinc-blende structure of CdS with three obvious peaks, (111), (220), and (311). The average crystal size was calculated to be 2.7 ± 0.5 nm.

The actual amount of manganese incorporated in the CdS crystallities was roughly determined by Vegard's law, which states that incorporation of CdS with Mn$^{2+}$ ions will cause the XRD peaks to shift towards MnS's values, and that the extent of shifting is linearly proportional to the molar ratio of manganese/cadmium. The as-prepared samples exhibited very fuzzy and broad XRD peaks, which made it quite difficult to measure the shift, so we had to anneal the sample to obtain sharper peaks (due to increased crystal size).

**Figure 2** shows an example of Cd$_{1-x}$Mn$_x$S particles prepared from 0.15 M cadmium and manganese nitrates in aqueous solution. The as-prepared sample crystal size was about 3.0 ± 1.0 nm. Then the sample was divided into two portions, and annealed at 200°C for 3 h and 14 h separately. The color of the annealed samples changed from orange to dark red, which indicated a change of the band gap width with the increase of crystal size. From the XRD spectra, it can be seen that the (111) peak of the as-prepared sample gradually drifted to three peaks upon annealing, which indicated the crystal structure changed from cubic (zinc-blende) to hexagonal (wurtzite). The (111) evolved into three peaks with the crystal change from zinc-blende to wurtzite, which is why we did not calculate the crystal size based on (111). Also, the (103) peak of wurtzite structure started to appear as the size grew.

![Graph](https://example.com/graph.png)

**Fig. 1.** Portion of XRD spectra of Cd$_{1-x}$Mn$_x$S as-prepared nanocrystallites made from cadmium and manganese chloride, crystallite size = 2.7 ± 0.5 nm.

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We found that the manganese/cadmium ratios of the products calculated from Vegard's law were sometimes lower than expected from the reactant concentrations (see below, however). For example: to make Cd₄MnₓS, we set the Cd-Mn molar ratio at 7:3, but the XRD spectra with Vegard's law showed the x value of the resultant sample to be only about 0.19 instead of 0.3. In another sample where we expected the x value to be 0.2, the Vegard's law result was only 0.35. These results are illustrated in Fig. 3.

The possible reason is that not all the manganese ions are incorporated into the crystalline; a disproportionate amount may reside on the surface and have no effect on the inside crystal lattice. The XRD spectra cannot yield information about the amount of surface manganese since it can only probe the whole lattice.

To test this hypothesis some samples were washed with dilute nitric acid (pH 2.5) after the synthesis and then washed with deionized water. The acid-washed sample looked the same as the unwashed. Furthermore, we found that the acid-washed and unwashed samples had very similar XRD spectra, as shown in Fig. 4. After annealing, there was a large difference in the XRD peak shift (relative to CaS) between the acid-washed and unwashed samples, as shown in Fig. 5. The acid-washed samples showed a smaller shift, hence less Mn²⁺. What happened during the annealing?

One possible explanation follows, and it should be remembered that the XRD peak shifts here only indicate the lattice space changes inside the crystal by introducing Mn²⁺ into the CaS lattice. It is proposed that the acid wash removed the manganese ions on the surface, but the Mn²⁺ inside the crystal remained untouched, so there was no big difference for the as-prepared samples' spectra. The annealing process causes the particles to increase in size, which reduced the relative amount of surface material (which is ~50% of the total when d=3 nm). Thus some of the surface must come inside. Since the surface was depleted of Mn by the acid, the depleted surface gets mixed with the interior.

However, an additional pathway for Mn²⁺ diffusion was also found. If the precipitated particles were left in the reaction bath and stirred for about 0.5 h, the x values determined from the reactant concentrations and
Vegards laws agreed within error. This is consistent with a slow diffusion process at room temperature for the Mn to enter the particles.

**Magnetic Properties**

The magnetic properties of our DMS materials were found to vary with their method of preparation and handling in the environment. Results for Cd$_2$ and Zn$_2$ MnS were essentially the same. For Cd$_2$, MnS particles were prepared in aqueous solution and then exposed to the atmosphere. Magnetization curves shown in Fig. 7 result from heat treatment of the particles after exposure to the atmosphere. The slight divergence of the zero field cooled and field cooled magnetization below -14 K is an indication of the spin-glass state. This transition also occurs in the bulk material, near 18 K, and is known to decrease in temperature with decreasing particle size.

If the particles prepared in aqueous phase precipitation are exposed to the atmosphere, magnetization curves shown in Fig. 7 result from heat treatment of the particles after exposure to the atmosphere. The slight divergence of the zero field cooled and field cooled magnetization below -14 K is an indication of the spin-glass state. This transition also occurs in the bulk material, near 18 K, and is known to decrease in temperature with decreasing particle size.

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Wei's temperature implying that the transition at 37 K is due to an antiferromagnet. This behavior is in contrast to that seen for samples prepared in a methanol solution and then treated with dodecane thiol while still in the reaction bath. These particles when exposed to air show a magnetization behavior essentially identical to the unexposed sample. Fig. 6. From this we infer that the dodecane thioligated to the surface of the nanoparticles and thereby protected them from oxidation.

The oxidation products of Mn⁺⁺ could be MnO or MnO₂, since both are antiferromagnets. The Neel temperatures for the antiferromagnetic transition of these substances in the bulk are 1/18 K and 64 K, respectively. These do not agree with our measured value of 37 K, but the manner in which a Neel temperature might change with size is not known.

Annealing the oxidized sample caused the nanocrystals to grow and the transition to decrease in intensity. The height of the peak was roughly inversely proportional to the size of crystals (Fig. 8). This might be caused by the decreasing of the specific surface area as crystal size increases.

CONCLUSIONS

Dilute magnetic semiconductors of nanocrystals Cd₉₅Mn₉S and Zn₉₅Mn₉S were prepared by forced precipitation in aqueous solution. The manganese on the surface of the crystals is rather quickly oxidized in air at room temperature, precautions need to be taken during and after synthesis. The oxidation causes an antiferromagnetic transition at 37 K, and the height of the transition peak is inversely proportional to crystal size (which is attributed to lower surface areas and therefore fewer manganese ions are available for oxidation). Ligation with dodecane thiol protects the particles from oxidation.

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REFERENCES AND NOTES