Cadmium (Zinc) Manganese Sulfide Nanocrystalline ($Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$) Dilute Magnetic Semiconductors. Synthesis, Annealing, and Effects of Surface Oxidation on Magnetic Properties

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Abstract. $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ 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 zinc blende cubic structure. After thermal annealing, the crystals converted to the hexagonal wurzite structure as the crystallite size reached 100–120 nm. The manganese 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 photochemistry, 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 condination, lattice relaxation, and reconstruction of electronic states.[1]

Several methods of synthesis have been developed.[2–5] Solution methods can be divided into aqueous and non-aqueous. Generally, non-aqueous synthesis can provide smaller size and narrower size distribution. Whatever the solvent chosen, a good way to obtain nano-sized particles is to provide them a stable compartmentalization environment for synthesis and growing. Micelles, polymers, zeolites, glasses, and biological vesicles have been used successfully, as they trap the nanoclusters to yield a stable, isolable material.

Dilute Magnetic Semiconductors (DMS)

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 $Cd_{1-x}Mn_xS$, $Zn_{1-x}Mn_xS$, $Hg_{1-x}Mn_xS$, and the corresponding selenides and tellurides. The unique properties of these compounds comes from the interaction of the spin-induced magnetic moment of the Mn^{2+} ions with the electronic bands of the semiconductor lattice.[6]

There have been a few studies of nanoscale DMS materials. Bandaranayake et al. studied the low temperature magnetic properties of $Cd_{1-x}Mn_xS$ nanoparticles.[1,7] They found that the spin-glass freezing temperature decreased with decreasing size, and there was a

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*Authors to whom correspondence should be addressed. E-mails: Klabunde—kenjk@ksu.edu; Sorensen—cmsorensen@ksu.edu minimum at about 5.0 ± 2.5 nm. Below that point the spin glass could not be observed.

Pileni and coworkers prepared $Cd_{1-x}Mn_xS$ in inverse micelles and studied the electronic and optical properties.[8] The authors found that the highest value of x was about 0.3, that is, only about 30% Mn could be incorporated into the crystal. EPR studies showed that the linewidth strongly decreased with decreasing manganese composition. The hyperfine structure was observed at very small x values, showing stronger Mn–Mn interaction as x increased, and that the Mn ions were randomly distributed without forming islands.

Optical properties were also studied with UV-VIS absorption and photoluminescence. The obvious exciton peak showed the quantum size effect, in that the band gap energy decreased as particle size increased. Constant particle variation of the value of x caused the band gap to decrease and then increase. The variation became larger as particle size decreased. The authors explained this phenomenon by hybridation of the Mn^{2+} orbital with the band structure of CdS and the interaction exchange became stronger as the crystallite became smaller.[9,10]

EXPERIMENTAL METHODS

Nanocrystals of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ were prepared by an aqueous solution forced precipitation method.[1,11] Structural analysis was carried out by powder X-ray diffraction (XRD), and magnetic measurements by using a SQUID magnetometer.

Synthesis of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ DMS Nanocrytals

The starting materials were: 98% $Cd(NO_3)_2{\cdot}4H_2O$, 98% $Mn(NO_3)_2{\cdot}6H_2O$, 98+% $Na_2S{\cdot}9H_2O$, 98% $Zn(NO_3)_2{\cdot}6H_2O$, and A.C.S. 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 glovebag filled with argon.

The reaction solution was prepared by dissolving a certain amount of, for example, $Cd(NO_3)_2{\cdot}4H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$ in degassed water according to the desired molar ratio of Cd:Mn, that is, the x value. $Na_2S{\cdot}9H_2O$ was dissolved in degassed water to prepare an anion solution of S^{2-}, such that the total molarity of S^{2-} equaled the combination of the molarity of Cd^{2+} and Mn^{2+}. 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 Na_2S is basic and the mixture had to be maintained near neutral. We found pH control was very important during synthesis in aqueous solution.[11] The pH value of the final mixture had to be 4–7. If the pH was less than 3, H_2S gas would form and escape, and if the pH was more than 8, $Mn(OH)_2$ would precipitate, causing the yield of $Cd_{1-x}Mn_xS$ to be lower. 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 Mn^{2+} ions added. More Mn would change the color from orange to yellow. Stirring was stopped to allow the precipitate to settle, water was decanted, and the powder was filtered with a fine frit and washed several times with degassed water. The precipitate was transferred into a desiccater with Drierite, and evacuated overnight.

Samples of $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ were prepared according to the following stoichiometric equations:

$$(1-x)Cd^{2+} + xMn^{2+} + S^{2-} \rightarrow Cd_{1-x}Mn_xS \qquad (1)$$

$$(1-x)Zn^{2+} + xMn^{2+} + S^{2-} \rightarrow Zn_{1-x}Mn_xS \qquad (2)$$

Different x-values were used, such as x = 0.1, 0.3, 0.5. 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 as-prepared crystals varied with different anions: 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 $Zn_{1-x}Mn_xS$ DMS was essentially the same as with the cadmium compounds. One example of $Zn_{0.7}Mn_{0.3}S$ in aqueous solution was prepared in the following way: 3.13 g (10.5 mmol) $Zn(NO_3)_2{\cdot}6H_2O$ and 1.29 g (4.5 mmol) $Mn(NO_3)_2{\cdot}6H_2O$ were dissolved in 100 mL deionized and degassed water, and dilute HNO_3 was added drop by drop to adjust the pH to 3.0; 3.6 g (15 mmol) $Na_2S{\cdot}9H_2O$ was dissolved in another 100 mL deionized, degassed water, then added to the Zn:Mn solution while stirring, and a pink 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 89% to 97%. The whole procedure was carried out under argon protection in a glovebag, and the final dried sample was stored in a drybox filled with argon.

Crystal Size Modification through Annealing

Thermal annealing was used to increase the crystal size and remove defect sites, and these treatments resulted in sharper signals in the powder XRD spectra. The size of the nanocrystal domain could be enlarged from 2–3 nm to almost bulk size (>300 nm). The transition from cubic zinc blende to hexagonal wurzite structure was completed when the crystal size reached 100 to 120 nm.[11,12] Since the $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ products are all air-sensitive, we applied a vacuum (≤10 micron Hg) during the heating process. The melting point of CdS particles of size 2 nm is about 500 °C, so annealing was done below 450 °C to avoid melting and recrystallizing.

The samples were placed in a quartz tube connected with the vacuum line at room temperature, and the valve was opened slowly to apply the vacuum gradually. This slow procedure was necessary to avoid sucking the fine particles into the vacuum line. The tube was then placed in an oven with a temperature controller. Annealing time and temperature depended on the desired particle size. For example, heating as-prepared $Cd_{0.6}Mn_{0.4}S$ at 300 °C for 12 h increased the particle size from 2.5 nm to 12 nm. The annealed sample was then cooled slowly to room temperature. During this process, the sample was always kept under vacuum or under argon protection.

Structural Characterization and Magnetic Measurements

Powder X-ray diffraction was carried out on a Scintag 2000 Diffractometer. The radiation source was Cu Kα with wavelength 1.54 Å. The scanning mode was continuous with step size 0.01° and rate 2.0° per min. Most scanning ranges were from $2\theta = 20°$ to $60°$. The sample was mounted on an amorphous plastic sample container.

The size of the crystal D was determined by Scherrer's formula:[13]

$$D = 0.94\lambda/(B\cos(\theta)) \qquad (3)$$

λ—Wavelength of X-ray (1.54 Å in this case)
B—Width at half maximum of the diffraction peak (radians)
θ—Diffraction angle of the peak on the 2 θ scale.

Magnetic measurements were carried out on a Quantum Design MPMS2 SQUID magnetometer. The SQUID 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, then a magnetic field of 100 Oe was turned on, and the magnetization was measured while the temperature rose from 5 K to 80 K. For the field cooling measurement (FC), the sample was cooled from room temperature to 5 K with an applied field of 100 Oe, then treated the same as in ZFC.

As always, the sample was well protected from air during the loading process and was put into a gelatin capsule sample holder within a glovebag filled with argon and placed in the SQUID as fast as possible.

RESULTS AND DISCUSSION

$Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ DMS Nanocrystallites Structural Analysis

The as-prepared $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ DMS nanocrystallites made from aqueous or non-aqueous solution 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 sample normally had very fuzzy and wide peaks, the sizes measured were not very accurate. For $Cd_{1-x}Mn_xS$ the half-maximum widths of the peaks (220) and (311) were measured for several samples and averaged.

Figure 1 shows the XRD spectra of as-prepared nanocrystals of $Cd_{0.5}Mn_{0.5}S$ 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 nm.

The actual amount of manganese incorporated in the CdS crystallites was roughly determined by Vegard's law,[6] 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 first to obtain sharper peaks (due to increased crystal size).

Figure 2 shows an example of $Cd_{0.8}Mn_{0.2}S$ particles prepared from 0.15 M cadmium and manganese nitrates in aqueous solutions. 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 with the increase of crystal size. From the XRD spectra, it can be seen that the (111) peak of the as-prepared sample gradually divided 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 wurzite, which is why we did not calculate the crystallite size based on (111)). Also, the (103) peak of wurtzite structure started to appear as the size grew.

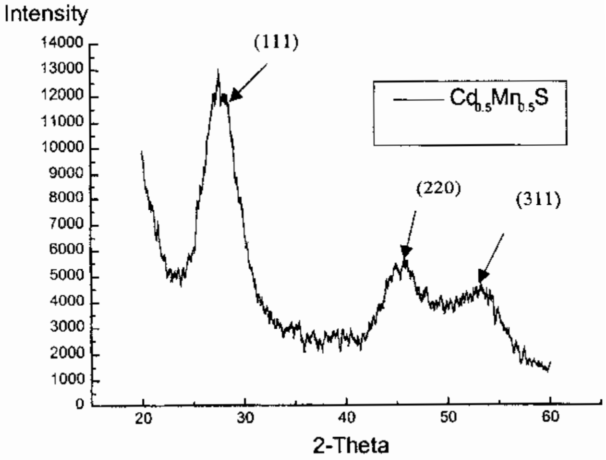

Fig. 1. Portion of XRD spectra of $Cd_{0.5}Mn_{0.5}S$ as-prepared nanocrystals made from cadmium and manganese chloride, crystallite size = 2.7 ± 0.5 nm.

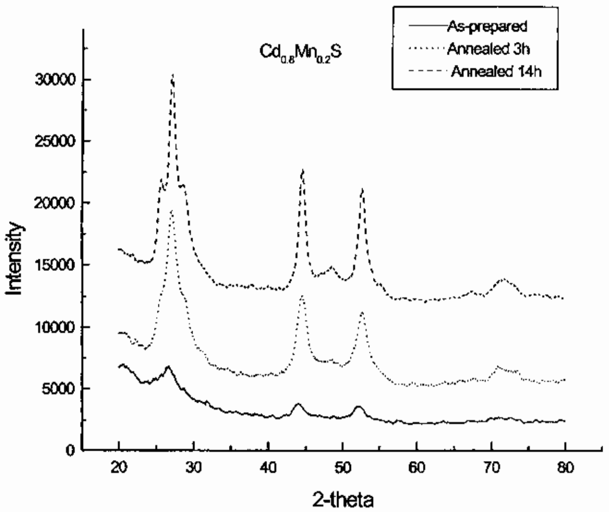

Fig. 2. $Cd_{0.8}Mn_{0.2}S$ sample XRD spectra before and after annealing at 200 °C.

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 $Cd_{0.7}Mn_{0.3}S$, 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 0.5, 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 crystallites; 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 degassed, 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 CdS) between the acid-washed and unwashed samples, as shown in Fig. 5. The acid-washed samples showed a smaller shift, hence less Mn^{2+}. 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 Mn^{2+} into the CdS lattice. It is proposed that the acid wash removed the manganese ions on the surface, but the Mn^{2+} 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 $d \simeq 3$ 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 Mn^{2+} 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

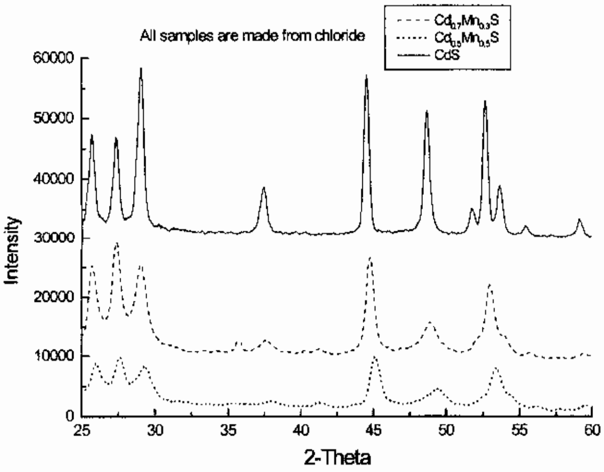

Fig. 3. XRD spectra of CdS standard (annealed at 400 °C for 10 h), $Cd_{0.7}Mn_{0.3}S$. (annealed at 400 °C, 9 h, Vegard x value ~0.19), and $Cd_{0.5}Mn_{0.5}S$ (annealed at 400 °C for 10 h, Vegard x value ~0.35).

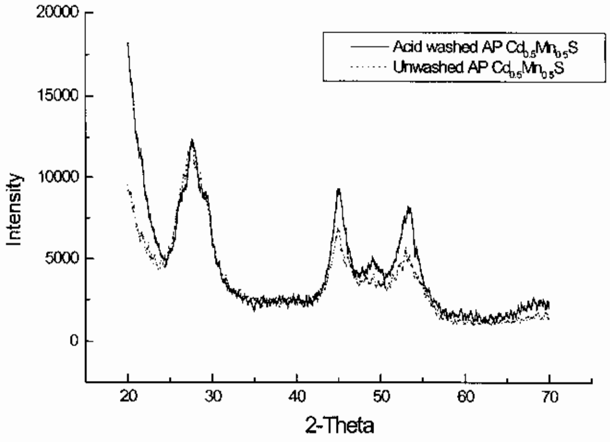

Fig. 4. XRD spectra of as-prepared acid-washed and unwashed.

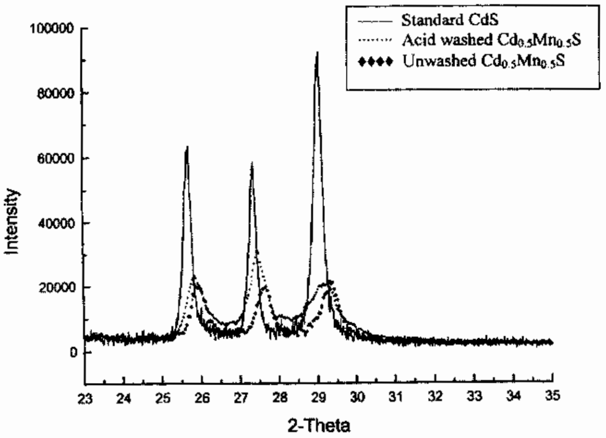

Fig. 5. Part of the XRD spectra of annealed acid-washed and unwashed $Cd_{0.5}Mn_{0.5}S$.

Vegards laws agreed within error.[7,11] This is consistent with a slow diffusion process at room temperature for the Mn^{2+} 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_{1-x} and $Zn_{1-x}Mn_xS$ were essentially the same. If care was taken to avoid exposure of the nanoparticles to air, a spin-glass transition was seen.[7] An example is shown in Fig. 6 for as-prepared $Cd_{0.5}Mn_{0.5}S$ particles. The slight divergence of the zero field cooled and field cooled magnetizations 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.[7]

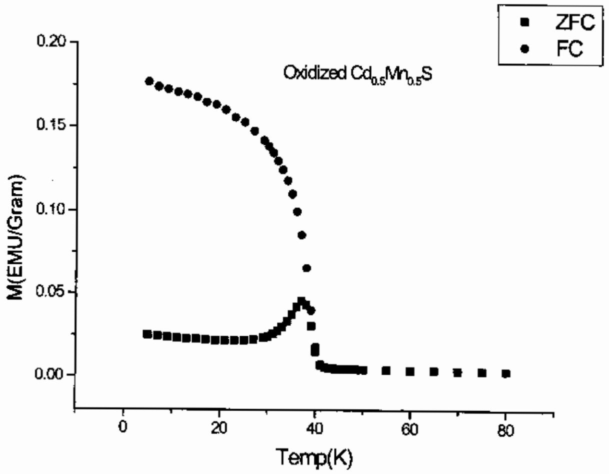

Fig. 7. ZFC (square) and FC (circle) magnetization of oxidized $Cd_{0.5}Mn_{0.5}S$ particles with size 3–4 nm, measured under a field of 100 Oe.

If the particles prepared in aqueous phase precipitation are exposed to the atmosphere, magnetization curves shown in Fig. 7 result. These data differ greatly from those in Fig. 6 in two major ways: (1) a peak in the ZFC curve near 37 K and (2) the overall magnetization is almost two orders of magnitude larger. This was true for both the Cd- and Zn-based compounds. The peak near 37 K and divergence of the ZFC and FC curves imply a magnetic transition. The data for T > 37 K follow a Curie–Weiss Law, with a negative Curie–

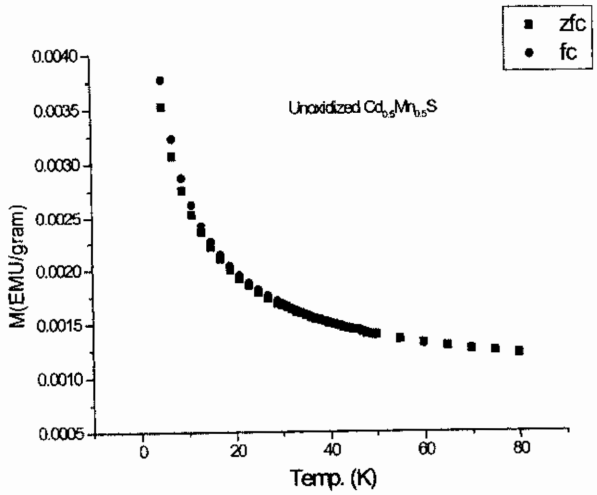

Fig. 6. ZFC (square) and FC (circle) magnetization of as-prepared, unoxidized $Cd_{0.5}Mn_{0.5}S$ particles with size 3–4 nm, measured under a field of 100 Oe.

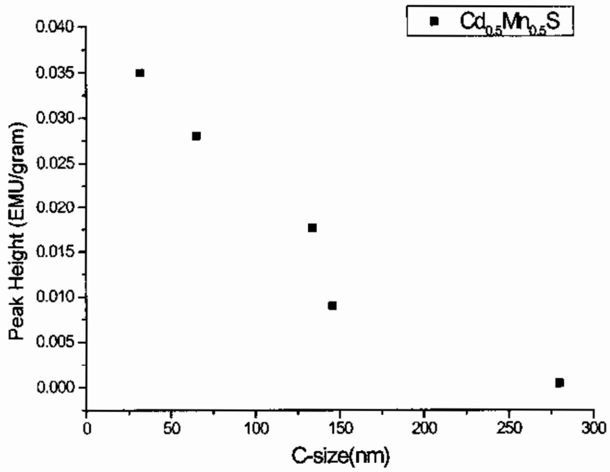

Fig. 8. Transition peak height in magnetization curves vs. crystallite size.

Weiss 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 showed magnetization behavior essentially identical to the unexposed sample, Fig. 6. From this we infer that the dodecane thiol ligated to the surface of the nanoparticles and thereby protected them from oxidation.

The oxidation products of Mn^{2+} could be MnO or MnO_2, since both are antiferromagnetic. The Neel temperatures for the antiferromagnetic transition of these substances in the bulk are 118 K and 84 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 peak 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 $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ 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, so 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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