

## Synthesis and Study of Magnetic Properties of Nano Sized $Zn_{1-x}Co_xS$ with High Doping Concentrations by the Wet Chemical Method

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**Abstract:**  $Zn_{1-x}Co_xS$  nanocrystallites synthesized by the wet chemical method have been studied. X-ray powder diffraction analysis shows that the solid solubility limit of sphalerite  $Zn_{1-x}Co_xS$  can reach  $x = 16\%$ . Further magnetic measurements indicate significant differences for samples with different doping concentrations ratios. Optical properties for samples with high doping concentrations ratios are not investigated because cobalt ions are eliminators of the photoluminescence. Distorted lattice structure and low temperature super-paramagnetism are observed for high doping concentrations samples, while a crystallized structure and abnormal effective magnetic moment ( $3.3 \mu B/Co$ ) are found in low doping concentrations samples.

**Key words:** wet chemical-- super-paramagnetism-concentrations--nano

### INTRODUCTION

Transition metal (TM) doped II–VI and III–V semiconductors have been investigated extensively due to their wide range applications in electroluminescence devices, light emitting displays, optical sensors, etc (Pearson S.J., D.P. Norton, K. Ip, Y.W. Heo and T. Steiner, 2004; Peng W.Q., S.C. Qu, G.W. Cong, X.Q. Zhang and Z.G. Wang 2005). The introduction of magnetic TM into nonmagnetic semiconductors provides possible venues for generation of diluted magnetic semiconductor (DMS) (Peng W.Q., S.C. Qu, G.W. Cong, X.Q. Zhang and Z.G. Wang 2005). The recombination of magnetic spin and electron charge information in a single host may provide promising application in the study of spintronics. Nanometre-sized semiconductors have received great attention due to their unique properties and potential applications in optoelectronic industries (Duan X.F., Y. Huang, J. Wang and C.M. Lieber, 2001; Shipway A.N., E. Katz and I. Willner 2000). The structure, electronic, optical and magnetic properties of nanoparticles can differ from those of their corresponding bulk form due to quantum confinement effects (Guzelian A.A., U. Banin, A.V. Kadavanich, X. Peng and A.P. Alivisatos, 1996; Yoffe A.D., 1993) and surface adsorption effects (Huang F., B. Gilbert, H.Z. Zhang and J.F. Banfield, 2004; Zhang H.Z., B. Gilbert, F. Huang and J.F. Banfield, 2003). Successful doping of magnetic TM in semiconductor nanoparticles yields a new paradigm as a zero dimensional counterpart of the well developed DMS and photoluminescent bulk and thin film systems, which could potentially lead to the fabrication of unusual magneto-optical and magneto-electronic devices (Ohno H., 1998; Furdyna J.K., *et al.*, 2000). Homogeneously substitutional doping is one of the most important goals for achieving novel physical properties in TM doped nano-sized semiconductors. However, the crucial factor determining the doping quality—that is, the mechanism of the doping process—is yet to be thoroughly investigated (Stowell C.A., R.J. Wiacek, A.E. Saunders and B.A. Korgel, 2003) and far from well understood. For TM-doped nanoparticles, the doping situation is strongly correlated to the efficiency of the photoluminescence or magnetism of the nanoparticles. It is suggested that sample preparation conditions can introduce uncontrolled lattice defects, thus affecting the carrier density related physical properties, such as magnetism (Ueda K., H. Tabata and T. Kawai, 2001; Cho Y.M., W.K. Choo, H. Kim, D. Kim, and Y. Ihm, 2002).

Also, instances of phase segregation or other precipitates might lead to abnormal physical properties. In addition, complexity may arise from the dopant ion itself, which has the tendency to be excluded during nanocrystal synthesis in some situations (Radovanovic P.V. and D.R. Gamelin, 2001, Mikulec F.V., M. Kuno,

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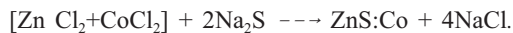
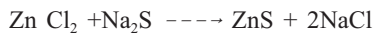
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M. Bennati, D.A. Hall, R.G. Griffin and M.G. Bawendi, 2000). These surface-adsorbed dopants have significant different coordination condition and exchange coupling interactions with the semiconductor band electrons, thus may compromise the target physical properties of the materials. As a nontoxic II–VI semiconductor material, ZnS is considered to be a promising host material. Recent studies of Mn-doped ZnS nanoparticles revealed significant increase of luminescence intensity. The increase of luminescence intensity is attributed to the strong interaction of Mn<sup>2+</sup> d electrons with s–p electrons of the host nanocrystalline ZnS (Bhargava R.N., D. Gallagher, X. Hong and A. Nurmikko, 1994). The sp–d exchange interactions in bulk Co<sup>2+</sup> doped II–VI semiconductors have been found to be much larger than those in the Mn<sup>2+</sup>-doped counterparts (Zielinski M., C. Rigaux, A. Lemaître and A. Mycielski, 1996; Seong M.J., H. Alawadhi, I. Miotkowski and A.K. Ramdas, 2001). Thus, it is plausible that unique magneto-optical and magneto-electronic phenomena may arise from the quantum confinement effect in Zn<sub>1-x</sub>Co<sub>x</sub>S nanocrystalline. Previous work analysed the electronic absorption spectroscopy of low doping level Zn<sub>1-x</sub>Co<sub>x</sub>S nanocrystallites ( $x < 1.5\%$ ), revealing that Co<sup>2+</sup> ion can actually incorporate into the lattice of ZnS nanoparticles (Radovanovic P.V. and D.R. Gamelin, 2001). Though the appropriate doping concentration is a premise for achieving room temperature ferromagnetism of DMS (Antony J., S. Pendyala, A. Sharma, X.B. Chen, J. Morrison, L. Bergman and Y. Qiang, 2005) results related to the synthesis and properties of relatively high doping Zn<sub>1-x</sub>Co<sub>x</sub>S nanocrystallites have not been reported yet. In this study, Zn<sub>1-x</sub>Co<sub>x</sub>S nanocrystallites with high doping concentrations were prepared by the wet chemical method.

## 2. Synthesis:

ZnS nanoparticles were synthesized by an aqueous method similar to that followed by Nosaka *et al.* (Zhang H.Z., B. Gilbert, F. Huang and J.F. Banfield, 2003). Here the molar solution of Zinc chloride (ZnCl<sub>2</sub>) and Sodium sulfide (Na<sub>2</sub>S) are prepared by using double distilled water. Mercaptoethanol (M.E) is used as the capping agent (or surface active agent=surfactant). The chemical route is same for ZnS with only difference that we use ZnCl<sub>2</sub> for ZnS Q.Ds. A three neck reaction flask is used as reaction chamber and reaction takes place under N<sub>2</sub> inert gas to prevent any oxidation effect while reaction is going on. The reaction takes place according to the following equation:

M.E



The final solution will be centrifuged and washed several time with double distilled waters so that salt (NaCl) and other impurities will be washed perfectly. The remaining centrifuged ZnS:Co will be dried under table lamp or at ordinary temperature and powder can be prepared for XRD, PL, is and TEM. The amount of used additive (CoCl<sub>2</sub>), is 1%, 3%,5%,7%,10%to 16% molar volume percentage with respect to the ZnCl<sub>2</sub>.

## RESULTS AND DISCUSSION

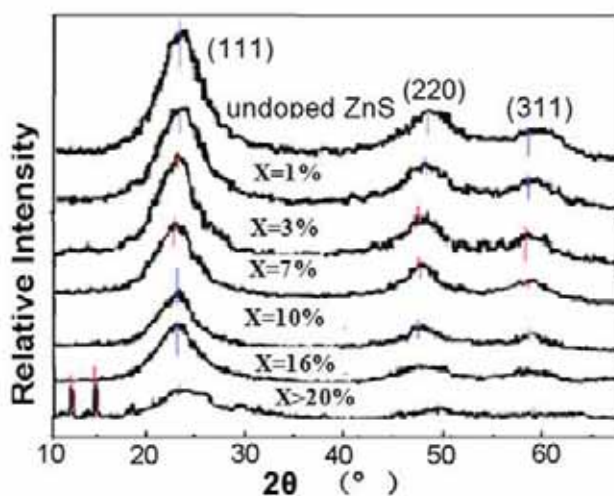
X-ray diffractometry (XRD) was performed using a X-ray diffractometer (model D8Advanced). Cu  $\alpha$  1.54 Å, was used as the source of incident radiation. The XRD patterns of the samples are presented in figure 1. It shows that when the Co<sup>2+</sup> percentage in the starting solution is less than 20%, the XRD patterns of the precipitated samples are in good agreement with ZnS sphalerite patterns. The three diffraction peaks correspond to (111), (220) and (311) planes of the cubic crystalline ZnS with reflections positioned at  $2\theta = 28.6^\circ$ ,  $48.0^\circ$  and  $56.6^\circ$  respectively. Typical wurtzite peaks (100), (101), (102) and (103) have not been observed. Also, no other additional peaks can be found for samples with  $x \leq 16\%$ . When the Co<sup>2+</sup> percentage in the starting solution is greater than 20%, the XRD pattern shows that the material consist of ZnS sphalerite phase as main phase, and unidentified phases as minor phases. The peaks besides ZnS sphalerite peaks cannot be indexed by any existing phases. These peaks may be considered as indications of a new compound.

The crystallite size was estimated from the full width at half maximum of the major XRD peak using the Scherrer equation (Huang T.C., H. Toraya, T.N. Blanton and Y. Wu, 1993).

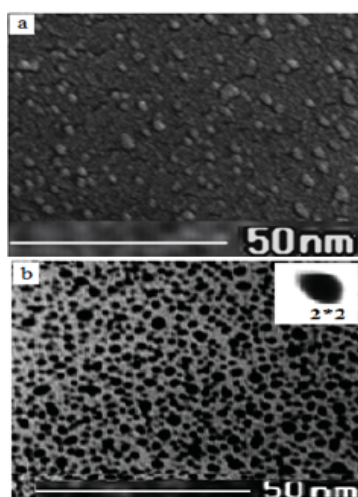
The sizes of Zn<sub>1-x</sub>Co<sub>x</sub>S nanocrystallites are around 2.9 nm when the corresponding coprecipitation ratio is at low level, while they decrease abruptly to 1.5–2 nm at high level. Figure 2 shows typical TEM images of Zn<sub>1-x</sub>Co<sub>x</sub>S nanocrystalline with  $x = 3\%$ ,  $10\%$ . TEM measurement shows that the averaged particle sizes of the three samples are about  $2 \pm 0.5$  nm. In fact, we found the sizes of the nanoparticles are almost the same in TEM observation ( $\sim 3.0 \pm 0.5$  nm), which are much larger than the calculated averaged 2.9 nm or 1.5–2 nm from Scherrer's formula. Previous research in nano-ZnS shows that the difference of the size calculated from

XRD and observed from TEM can be attributed to the distorted lattice structure, where both anion ( $S^{2-}$ ) and cation ( $Zn^{2+}$ ) deviate from standard tetrahedral coordination [Huang F., B. Gilbert, H.Z. Zhang and J.F. Banfield, 2004; Zhang H.Z., B. Gilbert, F. Huang and J.F. Banfield, 2003).

The more deviation existed, the larger distortion in nanoparticles. Here we found that for the low doping concentrations ratios  $Zn_{1-x}Co_xS$  samples, with  $x$  increasing, the calculated average sizes almost keep the same (at 2.9 nm), indicating the distortion level of samples in this stage is less and insensitive to the doping amount. Meanwhile, for high doping concentrations ratios samples, with  $x$  increasing, the calculated average sizes decrease gradually from 2 to 1.5 nm, indicating the distortion of the lattice is larger and is sensitive to the  $Co^{2+}$  concentration increase in the second stage. In this work, Optical properties for samples with high doping concentrations ratios are not investigated because cobalt ions are the eliminators of the photoluminescence; instead we focused on magnetic properties.



**Fig. 1:** X-ray diffraction spectra of  $Zn_{1-x}Co_xS$  nanocrystallites.



**Fig. 2:** TEM image indicates the size of  $2\pm 0.5$  nm with a good size distribution for (a)  $Zn_{95}Co_5S$  and (b)  $Zn_{90}Co_{10}S$  Q.Ds.

#### 4. Magnetic Properties:

The temperature dependence of the susceptibility is shown in figure 3(a) at a constant magnetic field (5 kOe). Inset in figure 3(a) is displayed the inverse susceptibility for samples as a function of temperature, and the plot of  $\chi^{-1}$  versus  $T$  exhibits a linear behaviour above 10 K, indicating the nanoparticles are paramagnetic materials above 10 K. The result is consistent with the Curie–Weiss equation

$$\chi = C / (T + \Theta) \quad (1)$$

where  $\chi$  is the magnetic susceptibility,  $C$  is the paramagnetic Curie constant and  $\Theta$  is the Curie–Weiss temperature. The Curie–Weiss temperatures for all three samples ( $\text{Zn}_{1-x}\text{Co}_x\text{S}$ ,  $x = 0.3\%$ ,  $7\%$ ,  $10\%$ ) are close to zero ( $-7$  to  $-15$  K) by extrapolating the high temperature linear part. This indicates the antiferromagnetic exchange between Co magnetic moments is very weak, especially at temperature above 10 K. The results are different from those of bulk  $\text{Zn}_{1-x}\text{Co}_x\text{S}$ , where large negative Curie–Weiss temperature ( $-50$  to  $-100$  K) as well as strong antiferromagnetic interaction are reported (Chen C.J., W. Gao, Z.F. Qin, W. Hu and M. Qu 1991; Lewicki A., A.I. Schindler, J.K. Furdyna and W. Giriat, 1989).

$$\mu_{\text{eff}} = [3k_B C / (N_A x)]^{1/2} \mu_B \quad (2)$$

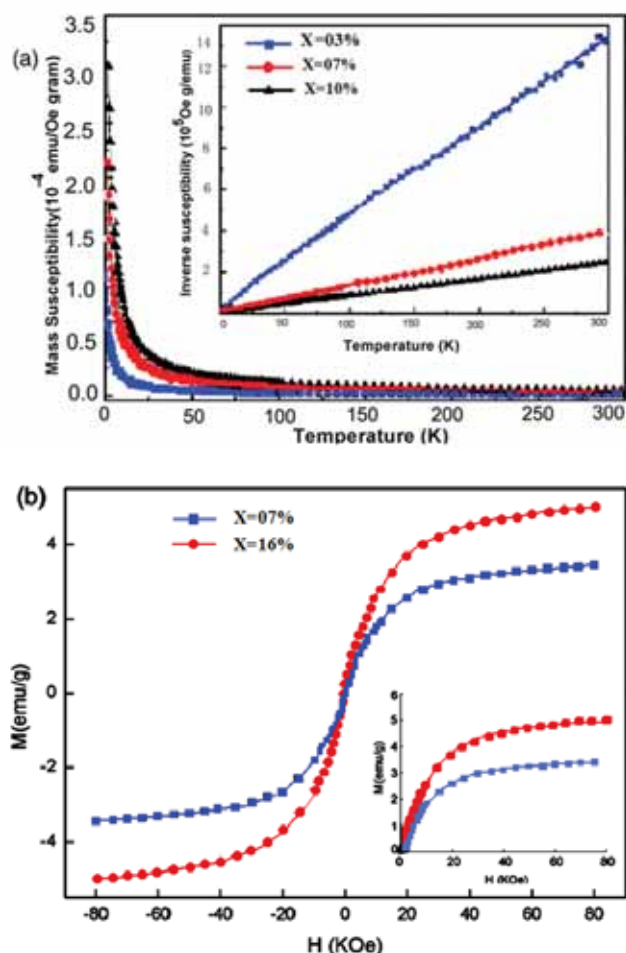
where  $x$  is the atomic fraction of  $\text{Co}^{2+}$  ions,  $N_A$  is the number of metallic ions per unit volume and  $k_B$  is the Boltzmann constant. The effective magnetic moments of  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  with  $x = 3\%$ ,  $7\%$ , and  $10\%$  are  $\mu_{\text{eff}} = 3.3 \mu_B/\text{Co}$ ,  $3.0 \mu_B/\text{Co}$  and  $3.0 \mu_B/\text{Co}$  respectively. It is found that for samples falling in the period of high doping concentrations ratio the  $\mu_{\text{eff}}$  is consistent with the theoretical value ( $3 \mu_B$ ). However, the magnetic moment of low doping concentrations ratio samples is higher than the theoretical value. This large magnetic moment of  $\text{Co}^{2+}$  ions in low coprecipitation ratio samples could not be attributed to the coupling of spin magnetic moment and orbital moment only. Recently, it has been suggested that there is a new source of magnetism in TM doped ZnO film, namely, triplet states associated with two-electron defects (Venkatesan *et al.*, 2004; Yoffe, 1993; Yang *et al.*, 2001). The additional contribution from defect magnetic moments may lead to the abnormal apparent  $\mu_{\text{eff}}$  ( $3.3 \mu_B/\text{Co}$ ) in nanocrystallites. Figure 3(b) shows the 2 K field-dependent magnetization of selected samples  $\text{Zn}_{93}\text{Co}_7\text{S}$ ,  $\text{Zn}_{90}\text{Co}_{10}\text{S}$ . No hysteresis is observed in both samples. It is found that linear  $M$ – $H$  relationships are exhibited at the low field ( $< 10$  kOe), while with the magnetic field increasing further  $M$ – $H$  relationships deviate from the linear behaviour and gradually saturate. This cannot be explained by the Curie–Weiss law, which is only effective when  $\mu_0 \mu_{\text{eff}} H \ll k_B T$ . Thus the more applicable Langevin paramagnetism theory is introduced to explain our results at low temperature. Based on Langevin theory, the magnetization of  $\text{Zn}_{1-x}\text{Co}_x\text{S}$  can be expressed as

$$M = N \mu_{\text{eff}} \left( \coth \frac{\mu_0 \mu_{\text{eff}} H}{k_B T} - \frac{k_B T}{\mu_0 \mu_{\text{eff}} H} \right)$$

Where  $N$  is the number of effective magnetic moments per volume and  $\mu_{\text{eff}}$  is the effective value for this magnetic moment. The  $M$ – $H$  relationship can be fitted well using equation (3) with  $N$  and  $\mu_{\text{eff}}$  as least-squares fitting parameters (figure 3(b)). For  $\text{Zn}_{93}\text{Co}_7\text{S}$  nanocrystallites, though the  $\text{Co}^{2+}$  ion density  $xN_A$  is about  $1.80 \times 10^{27} \text{ m}^{-3}$ , fitting results show that the density of magnetic moments  $N$  is  $3.29 \times 10^{26} \text{ m}^{-3}$ , only  $1/5.5$  of the total  $\text{Co}^{2+}$  ion density, while the effective magnetic moment is  $5.0 \mu_B$ , larger than the theoretical value of a single  $\text{Co}^{2+}$  ion ( $3 \mu_B$ ). Similar results are found in  $\text{Zn}_{90}\text{Co}_{10}\text{S}$  nanocrystallites, where  $N = 4.48 \times 10^{26} \text{ m}^{-3}$  (which is  $1/5.8$  of total  $\text{Co}^{2+}$  ion density), and  $\mu_{\text{eff}} = 5.2 \mu_B$ . The effective magnetic moments for both samples are much larger than the theoretical value of a single  $\text{Co}^{2+}$  ion, while the density of magnetic moments is far less than the density of the magnetic atoms, revealing the existence of superparamagnetism in these samples at low temperature. This superparamagnetism might come from a complex magnetic coupling mechanism, where 5–6 magnetic atoms couple together to form a single superparamagnetism cluster with net magnetic moment of  $\sim 5 \mu_B$ . The magnetic coupling interaction must be very weak and easily destroyed, since when the temperature increases to 10 K the superparamagnetism cannot be observed anymore.

#### 5. Conclusion:

Highly free standing controllable ZnS:Co nanoparticles are synthesized by a chemical method and highly stable monodispersed quantum particles with a good size distribution of 2 nm have been produced. It was shown that when the  $\text{Co}^{2+}$  percentage in the starting solution is less than 20%, the XRD patterns of the precipitated



**Fig. 3:** (a) Temperature-dependent magnetic mass susceptibility measured under a magnetic field of 5 kOe. Inset: inverse susceptibility as a function of temperature for both samples. (b) Magnetization versus applied magnetic field measured at 2 K. Dots, experimental data; line, fitting based on Langevin theory.

samples are in good agreement with ZnS sphalerite pattern. Distorted lattice structure and low temperature super-paramagnetism are observed for high doping concentrations samples. This finding has important implications for DMS materials, in which the magnetic properties may be significantly affected on increasing the doping.

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