

# Synthesis and Ferromagnetic Properties of Lightly Doped Nanocrystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}$

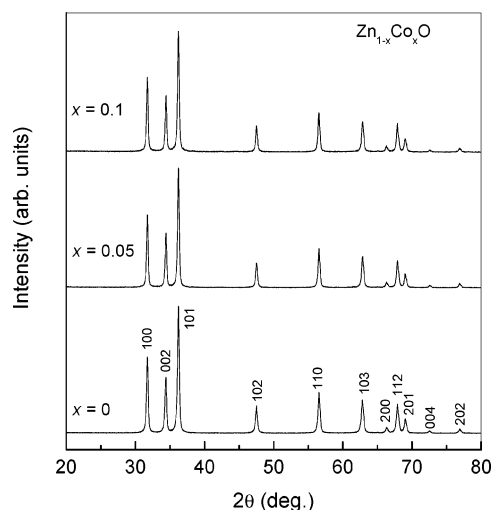
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The discovery of ferromagnetism in wide band gap ferromagnetic semiconductors, obtained by doping small amounts of magnetic impurities in the semiconductors, has raised tremendous scope for the study of these materials for applications such as in spintronics.<sup>1</sup> However, the discovery of ferromagnetism in transition metal ion doped oxide semiconductors, ZnO and  $\text{TiO}_2$ , is of particular importance in terms of their various possible applications. Whereas the diluted magnetic semiconductors (DMS) based on III–V or II–VI semiconductors show ferromagnetism only at very low temperatures, the oxide based DMSs have been shown to be ferromagnetic at higher temperatures. This has raised further scope for the development of the oxide-based DMS materials for future technological applications. One of the important aspects of these materials is their optical transparency, enabling them to be suitable candidates for magneto-optical applications. Ferromagnetism at or close to room temperature has been reported in ZnO doped with small amounts of  $\text{Co}^{2+}$ .<sup>2–4</sup> However, for practical applications, it is desirable that the materials should be ferromagnetic much above room temperature. All the studies reported on Co-doped ZnO have been made on thin films fabricated by different methods. On the basis of these studies, it has been shown that  $\text{Co}^{2+}$  can be substituted for  $\text{Zn}^{2+}$  in ZnO up to 20% without any modification in the structure. However, there are no reports so far on the synthesis and studies on the magnetic properties of polycrystalline  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ . We have attempted the synthesis of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  in polycrystalline form by a low-temperature combustion method of synthesis, as this method is known to produce single-phase oxide compositions, due to the atomic-level mixing of the starting components in solution.<sup>5</sup> The aim of the present study is to see whether ferromagnetism, observed in thin-film samples of Co-doped ZnO, can be obtained in powder samples also, because the ferromagnetic polycrystalline materials are useful for many device applications. Moreover, if the polycrystalline material can be produced as nanoparticles, this will be of particular importance for their use in ferrofluids, biomedical applications, and



**Figure 1.** Powder X-ray diffraction patterns of  $x = 0, 0.05$ , and  $0.1$  in polycrystalline  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ .

magnetic recording, etc. In this communication, we show that ferromagnetism up to 770 K is observed in the nanocrystalline powders of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ , for small concentrations of Co,  $x < 0.1$ .

Nanocrystalline  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  ( $x = 0, 0.05, 0.1$ ) powder samples were synthesized by an auto-combustion method. High-purity Zn was dissolved in dilute nitric acid and was mixed with a water solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , taken in the corresponding molar ratio of Zn and Co in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ . To the mixed solution of the metal nitrates, a water solution of glycine was added, taking 2 mol of glycine per mol of metal ion.<sup>6</sup> The final solution was evaporated on a hot plate till it formed a thick mass which subsequently underwent auto-combustion to give a fine powder. The fine powder samples thus obtained were characterized by powder X-ray diffraction using a Philips 1730 diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å) and by magnetization measurements as a function of magnetic field and temperature using a EG&G PAR 4500 vibration sample magnetometer. Particle morphology was studied using a JEOL model 1200 EX transmission electron microscope.

Powder X-ray diffraction (XRD) patterns of the as-synthesized samples obtained without and with different amounts of Co in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  ( $x = 0.05, 0.1$ ) are shown in Figure 1. The powder XRD pattern of ZnO corresponds to the wurtzite structure of ZnO. The XRD patterns for  $x > 0$  show that the ZnO structure is not disturbed on substitution of Co. No additional peaks due to any impurity are observed for  $x = 0.05$  and  $0.1$ . The average particle size for all three compositions is obtained as  $\sim 40$  nm, calculated from X-ray line broadening using the Scherrer formula,  $t = 0.9 \lambda / \beta \cos \theta$ , where  $t$  is the particle diameter in Å,  $\beta$  is the half-maximum line width, and  $\lambda$  is the wavelength of X-rays.<sup>7</sup> A transmission electron micrograph of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ , shown in Figure 2, indicates that most of the individual

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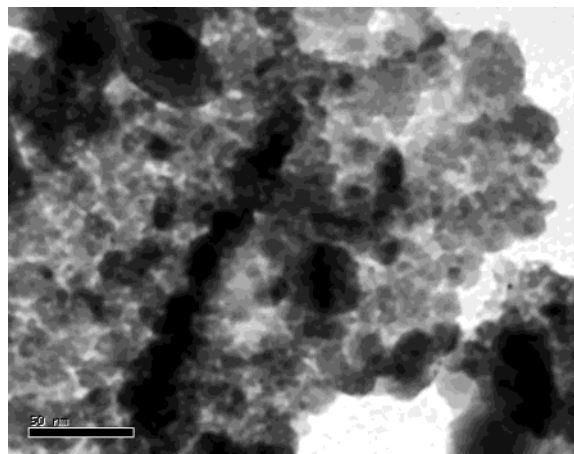
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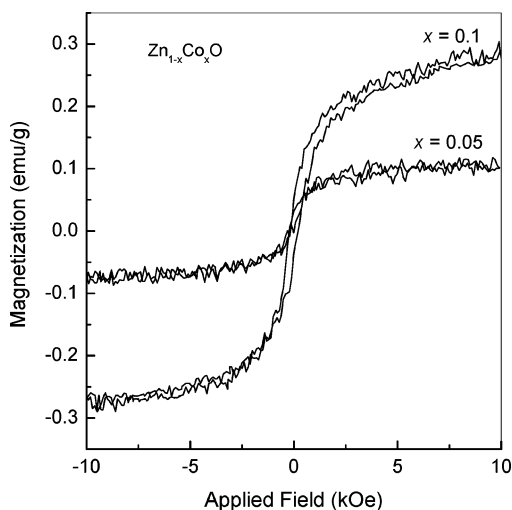
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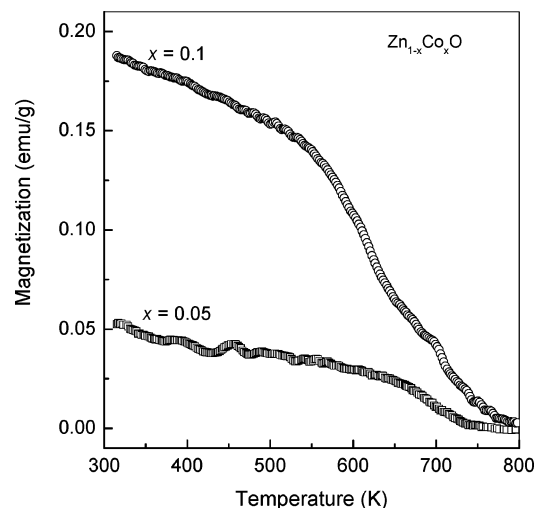
**Figure 2.** Transmission electron micrograph of  $x = 0.1$  in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ .



**Figure 3.** Magnetization of the Co-substituted compositions as a function of field, measured at 300 K.

platelike particles are of the size 5–10 nm. The larger average particle size obtained from XRD studies may be due to the presence of bigger clusters, as seen in the micrograph.

Figure 3 shows the magnetization of the two Co-doped compositions, as a function of magnetic field, measured at room temperature. Saturation magnetization of 0.06 and 0.25 emu/g, at 10 kOe, is observed for  $x = 0.05$  and 0.1, respectively. As no indication for the presence of Co in the powder XRD patterns is observed, and ferromagnetism is observed even for smaller Co concentrations in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ , it can be concluded that the ferromagnetism in the Co-doped compositions originates on doping  $\text{Co}^{2+}$  at the Zn sites in ZnO due to the localized  $d$ -electrons in  $\text{Co}^{2+}$ . However, as the magnetization is increased continuously at higher magnetic fields and the coercivity is almost negligible for both samples, and also considering the very small size of the particles, as evidenced from TEM measurements, the observed magnetic behavior can be described as superparamagnetic.



**Figure 4.** Temperature variation of magnetization for  $x = 0.05$  and 0.10, measured using a magnetic field of 5 kOe.

Figure 4 shows the temperature dependence of magnetization of the two different Co-doped compositions. Magnetic transitions are observed at 740 and 770 K, respectively, for  $x = 0.05$  and 0.1. This is similar to the results reported by Ueda et al.,<sup>2</sup> where all compositions below  $x < 0.2$  showed a magnetic transition close to 300 K. The magnetic transition temperature of Co metal is 1388 K,<sup>8</sup> and therefore, the magnetic transition observed at  $\sim 750$  K, in the present case, is due to ferromagnetism in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  and not due to the formation of Co metal clusters. Moreover, the powder X-ray diffraction patterns did not show any sign of impurity phases. From XPS studies on ferromagnetic  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ , Lee et al found that the doped Co in the wurtzite structure is in the 2+ formal oxidation state.<sup>3</sup> The magnetic transition temperature observed in the present work on the nanocrystalline samples is much greater than those reported on thin film samples. The broad magnetic transition observed is due to the superparamagnetic nature of the fine particles.

The present results of the studies on polycrystalline samples of nanosized  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  show that ferromagnetism can be obtained in polycrystalline material when small amounts of Co are substituted in ZnO. Magnetization and  $T_c$  increase with increasing  $x$  due to presence of localized spins in the substituted  $\text{Co}^{2+}$ . Ferromagnetism is observed in polycrystalline  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  up to  $\sim 750$  K, for the first time, making the material suitable for many practical applications.

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