

2005

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Publication Details

This article was originally published as: Peleckis, G, Wang, XL and Dou, SX, Absence of ferromagnetism and strong spin-orbital coupling in polycrystalline $\text{Zn}_{1-x}\text{Co}_{0.075}\text{In}_x\text{O}$ oxide, IEEE Transactions on Magnetics, October 2005, 41(10), 2739-2741. Copyright IEEE 2005.

Absence of Ferromagnetism and Strong Spin-Orbital Coupling in Polycrystalline In and Co Codoped $\text{Zn}_{1-x}\text{Co}_{0.075}\text{In}_x\text{O}$ Oxide

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Polycrystalline samples of In and Co codoped ZnO ($\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$; $0.010 \leq x \leq 0.020$) oxide were prepared by solid-state synthesis technique. Phase purity and structure refinement done by means of the Rietveld analysis technique shows that both Co and In substitute properly into Zn positions. In doping, increased bulk conductivity of the samples at room temperature indicates an increase of charge carrier concentration. All samples showed paramagnetic behavior following Curie–Weiss law at close to room temperatures, with short range antiferromagnetic interaction with $\Theta \approx -200$ K. Effective magnetic moment (μ_{eff}) calculations showed a strong orbital contribution to the value of μ_{eff} , increasing with an increase of In content (x).

Index Terms—Paramagnetic materials, spintronics.

I. INTRODUCTION

COEXISTENCE of semiconducting and ferromagnetic properties is the top feature for a material that is considered for “spintronic” applications [1]. Diluted magnetic semiconductors (DMS) [2] are a group of materials that can exhibit semiconducting and magnetic properties simultaneously. DMSs are alloys with magnetic elements that are embedded into semiconductor material. After reported ferromagnetism (FM) at relatively high temperatures in Mn-doped GaAs [3], a great deal of effort was put into finding new semiconductor materials that can exhibit a ferromagnetic feature. Some theoretical works predicted that room-temperature (RT) FM can be observed in transition metal-doped ZnO [4], [5] or TiO_2 [6]. Consequently, these theoretical findings induced huge practical research in this field.

ZnO is one of the most promising candidates among presently researched DMS materials. It is a very well-known wide bandgap (3.3 eV) semiconductor having wurtzite-type structure. For spintronics, several groups theoretically suggested that RT FM could be observed in Mn-doped ZnO [7], yet p type. On the other hand, other reports [8] suggest that Fe–Co–Ni-doped n -type ZnO may exhibit FM even at room temperature. Experimental data reported on this matter is very controversial, and no firm conclusion can be made if RT FM is achieved in this family of materials. While most groups failed to observe the FM state in ZnO, several reports [9], [10] were published claiming that FM was present in their samples. Yan *et al.* [11] observed FM in their Mn and Co codoped thin films at 290 K, and Ueda *et al.* [4] reported that their pulsed laser-deposited thin films showed FM at 280 K. However, in the latter case, reproducibility of the data was poor.

Some groups claim that the ferromagnetic state is originated from Co metal clusters [12]. Supporting this idea, no FM was observed in polycrystalline samples [13]. Deficiency in charge carriers could be one of the reasons why FM is not observed in polycrystalline samples. This reasoning would be in good agreement with the carrier-induced FM mechanism [14], suggesting that in order to observe FM appropriate itinerant carrier concentration must be maintained. However, recently Yin *et al.* [15] reported that their thin films of Co doped ZnO ($\text{Zn}_{1-x}\text{Co}_x\text{O}$) were insulating but showing RT FM. Thus, they argue the mechanism of carrier-mediated FM [14] stating that another mechanism could be considered as an origin for RT FM.

Since group III elements such as Al, Ga, or In are well-known electron dopants for ZnO, in our study we chose In as an additional carrier source for codoped ZnO. We report on structure and magnetic properties of n -type In and Co codoped ZnO ($\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$; $0.010 \leq x \leq 0.020$) oxide.

II. EXPERIMENT

$\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$ ($0.010 \leq x \leq 0.020$) polycrystalline samples were prepared by “rapid oxalate decomposition” technique [13]. Zinc oxalate dihydrate ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), cobalt (II) oxalate dihydrate ($\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and indium (III) oxalate decahydrate ($\text{In}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$) were source materials for Zn, Co, and In, respectively. The precursor powders were mixed in the mortar and put into a preheated furnace at 1223 K for 20 min in air. Then, powders were reground, pressed into rectangular pellets, and sintered at 1523 K in air for 10 h, followed by annealing in argon for 12 h at 1250 K. Phase purity and structural parameters were analyzed by means of an X-ray diffraction (XRD) analysis technique using $\text{Cu } K_\alpha$ irradiation (Philips PW-1730). Structure refinements were carried out employing Rietveld analysis using Rietica software [16]. Resistivity of the pellets was measured by a standard four-probe technique using the physical property measurement system (PPMS, Quantum Design). Magnetic properties

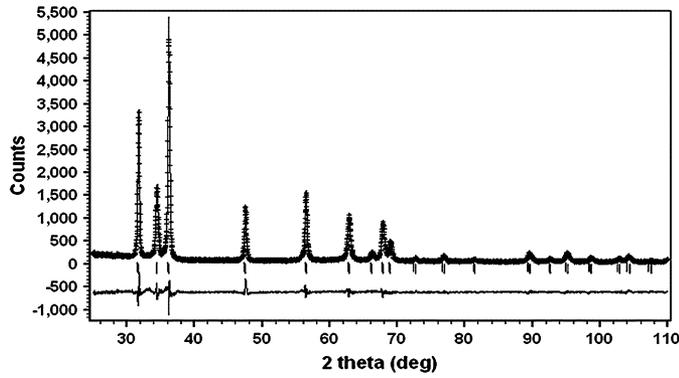


Fig. 1. XRD pattern for $\text{Zn}_{0.91}\text{In}_{0.015}\text{Co}_{0.075}\text{O}$ sample, refined by Rietveld analysis technique.

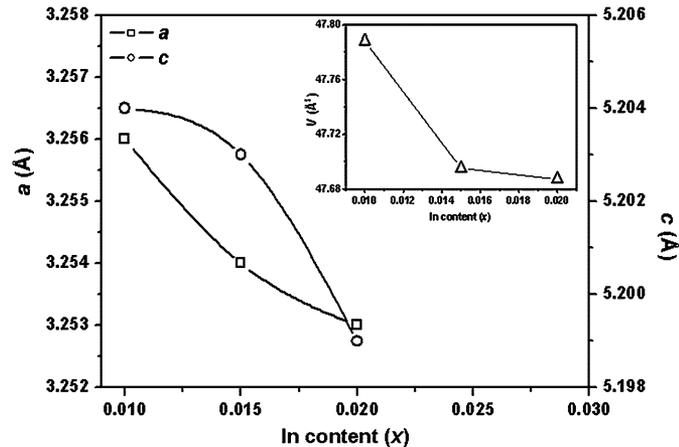


Fig. 2. Dependence of lattice parameters a and c and unit-cell volume (V) on In content (x) obtained by Rietveld refinement. (a) Lattice parameters a and c . Inset: Unit-cell volume (V) versus In content (x).

of our samples were investigated over a wide temperature range of 10 K to 340 K, utilizing the magnetic property measurement system (MPMS XL, Quantum Design) and applying a 2000-Oe magnetic field for magnetization versus temperature data collection. Chemical compositions of the samples were obtained by applying a scanning electron microscope (SEM)-EDS analysis technique (Leica Stereoscan 440).

III. RESULTS AND DISCUSSION

Fig. 1 shows the Rietveld analysis pattern for the $\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$ ($x = 0.015$) phase. XRD patterns showed that all samples are of ZnO wurtzite ($P6_3/MC$ space group)-type structure. No impurity phases were identified in the XRD patterns.

The results of the Rietveld analysis on crystal lattices are shown in Fig. 2, where dependences of lattice parameters a and c and unit cell volume (V) are plotted against the In doping level (x). We can see that incorporation of In into the ZnO lattice caused a shrinkage of both lattice parameters a and c .

The observed decrease in unit-cell volume is unexpected, since the ionic radii of In is slightly bigger than that of Zn ($r_{i(\text{Zn})}^{2+} = 0.60 \text{ \AA}$ and $r_{i(\text{In})}^{3+} = 0.62 \text{ \AA}$ [17]). On the other hand, it suggests that formation of a Co^{3+} species that is smaller than Co^{2+} is possible ($r_i(\text{Co}^{3+}) = 0.55 \text{ \AA}$, $r_i(\text{Co}^{2+}) = 0.58 \text{ \AA}$), due to an In-induced electronic misbalance.

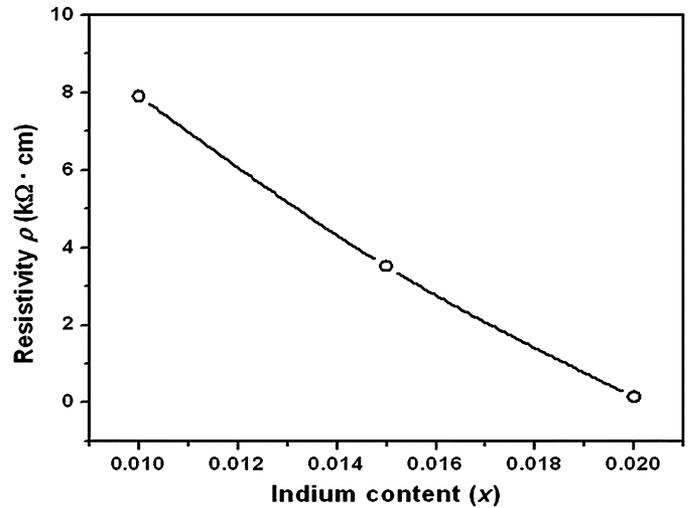


Fig. 3. Resistivity (ρ) of $\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$ ($x = 0.010, 0.015, \text{ and } 0.020$) samples as a function of In doping level (x) at RT (295 K).

In order to analyze the chemical composition of our samples, we performed SEM-EDS analysis. For samples, the nominal formula was $\text{Zn}_{0.91}\text{In}_{0.015}\text{Co}_{0.075}\text{O}$ which is the actual chemical content of Zn:In:Co = 0.902 : 0.017 : 0.08. Calculated chemical compositions for other samples were also close to the nominal ones, which indicated that our samples maintain stoichiometry as it is described by nominal formula.

In our parallel work on Co-only doped $\text{Zn}_{1-y}\text{Co}_y\text{O}$ samples, we observed that all of the samples are insulating. Even after long-time high-temperature (1300 K) argon annealing samples lost their conducting property, Co content y was higher than 5% of nominal Zn content. Therefore, we checked on bulk resistivity of In codoped samples at RT. Dependence of bulk resistivity (ρ) on In content (x) at room temperature is shown in Fig. 3.

In contrast to Co-only doped samples, In doping decreased ρ of the samples quite significantly. For a sample with In content $x = 0.010$, bulk resistivity at RT was $\sim 7.9 \text{ k}\Omega\text{cm}$, while an increase in In content up to $x = 0.020$ caused a sharp decrease in resistivity down to $\sim 0.2 \text{ k}\Omega\text{cm}$. Consequently, we assumed that carrier concentration in the material was successfully increased, which is a requirement for carrier-induced RT FM.

Fig. 4 represents the dependence of inversed molar magnetic susceptibility ($1/\chi$) on temperature (T) for the samples with $x = 0.010$ and 0.015 . As we can see, samples show paramagnetic behavior following Curie-Weiss law at close to RT, which is consistent with the reported data [16]. The Θ values, obtained by extrapolation of fit in the linear part of curves up to an intersection with the T axis (Fig. 4), were all negative.

This indicated that magnetic ions in the lattice are coupled antiferromagnetically (AFM). An increase in In content slightly decreased Θ values, i.e., $\Theta_{(x=0.10)} \approx -160 \text{ K}$ and $\Theta_{(x=0.015)} \approx -190 \text{ K}$, probably due to an increase in carrier concentration, which led to a higher number of ion-coupled AFM.

The effective magnetic moment (μ_{eff}) of the Co ion was calculated from Curie-Weiss fits in the linear part of the curves. The obtained μ_{eff} values for samples with $x = 0.010$ and 0.015

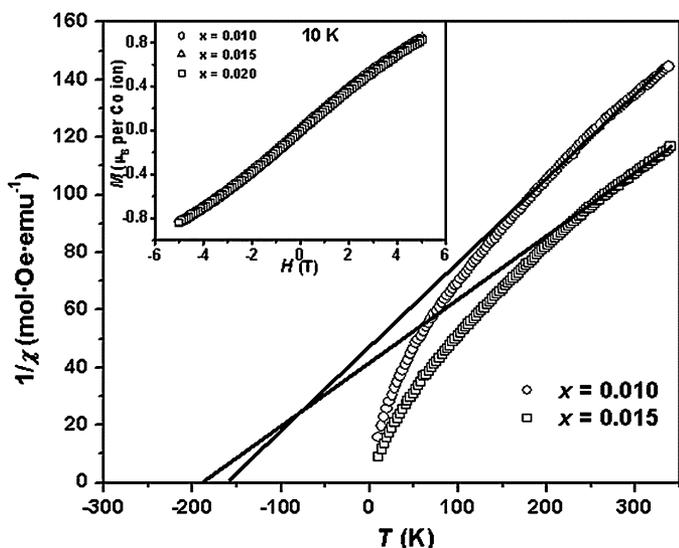


Fig. 4. Inverted magnetic susceptibility ($1/\chi$) versus temperature (T) of $\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$ ($x = 0.010, 0.015$) samples. Solid lines correspond to Curie-Weiss fittings extrapolated up to intersection with T axis. Inset: Dependence of magnetization (M) per magnetic ion on applied magnetic field (H) at a constant temperature of 10 K. M is expressed in μ_B

were 5.47 and $5.89 \mu_B$, respectively. If the spin (S)-only contribution to the μ_{eff} is considered and Co is assumed to be in a Co^{2+} high spin ($e^4t_2^3$) state [16], the calculated $\mu_{\text{eff}}(S) = 3.87 \mu_B$. However, our values are significantly higher. Therefore, we assumed that for our In-Co codoped samples, strong orbital contribution must be taken into account. In fact, we calculated $\mu_{\text{eff}}(S + L) = 6.64 \mu_B$ (both spin (S) and orbital (L) contribution were considered). This is in a good agreement with obtained μ_{eff} values for Co ion. Since μ_{eff} increased with increasing In content (x), we think that a higher concentration of itinerant carriers makes orbital contribution to the μ_{eff} stronger. Supporting this idea, μ_{eff} , calculated from a linear part of the $1/\chi$ curve in carrier-poor Mg-Co codoped ZnO samples [18] was much lower, i.e., $\mu_{\text{eff}} = 3.94 \mu_B$, which indicated that the orbital contribution to the μ_{eff} in that case is negligible.

Low-temperature (10 K) magnetization (M) as a function of applied magnetic field (H) is shown as an inset in Fig. 4. Obviously, we can conclude that there is no presence of any sort of FM or any evidence of hysteresis. All samples show identical behavior under applied magnetic field. Indium doping did not introduce any changes to the magnetic moment as the Co contents were fixed. The moment is only $0.8 \mu_B$ -Co in a 5-T magnetic field, indicating AFM interactions coexisting with paramagnetism. Although the FM is found to be absent in our bulk samples, we cannot rule out the possibility that the FM in In and Co codoped ZnO thin film samples prepared by pulsed laser deposition or other film fabrication technique could be realized.

IV. CONCLUSION

In summary, polycrystalline samples of In and Co codoped $\text{Zn}_{1-x}\text{In}_x\text{Co}_{0.075}\text{O}$ ($0.010 \leq x \leq 0.020$) were synthesized by

a solid-state synthesis technique. Structural analysis showed that samples are of a pure wurtzite-type ZnO phase. A 1% change in In doping level significantly decreased bulk resistivity of the samples at RT ($x = 0.010$ and $x = 0.020$, $\rho \sim 7.9 \text{ k}\Omega\text{cm}$ and $\sim 0.2 \text{ k}\Omega\text{cm}$, respectively). This was direct evidence that higher carrier concentration was achieved. SEM-EDS analysis showed that actual chemical compositions of the samples are close to nominal ones. All of the samples showed paramagnetic behavior following Curie-Weiss law at close to RT. The Weiss temperatures (Θ) were negative for all samples decreasing with an increase of In content (x). The calculated values of μ_{eff} for samples with $x = 0.10$ and 0.015 were 5.47 and $5.89 \mu_B$, respectively. This corresponded to the tetragonal Co^{2+} high spin ($e^4t_2^3$) state with a strong orbital contribution to the effective magnetic moment. Although carrier concentration was successfully increased, we did not observe any sort of FM. We conclude that the carrier-induced FM model does not work for our samples.

ACKNOWLEDGMENT

The work of X. L. Wang was supported by the Australian Research Council under Discovery Project DP0558753. G. Peleckis would like to thank the University of Wollongong for providing IPRS and UPA for his Ph.D. studies.

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