

Development and processing temperature dependence of ferromagnetism in $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$

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We report the development of room-temperature ferromagnetism (FM), with coercivity $H_c = 2000$ Oe and saturation magnetization $M_s \sim 0.01$ emu/g, in chemically synthesized powders of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ processed at 150°C , and paramagnetism with antiferromagnetic interactions between the Co^{2+} spins ($S=3/2$) in samples processed at higher temperatures $200 \leq T_p \leq 900^\circ\text{C}$. X-ray diffraction data show a decrease in the lattice parameters a and c with T_p , indicating a progressive incorporation of 0.58\AA sized tetrahedral Co^{2+} at the substitutional sites of 0.60\AA sized Zn^{2+} . Diffuse reflectance spectra show three well defined absorption edges at 660, 615, and 568 nm due to the $d-d$ crystal field transitions ${}^4A_2(F) \rightarrow {}^2E(G)$, ${}^4A_2(F) \rightarrow {}^4T_1(P)$, and ${}^4A_2(F) \rightarrow {}^2T_1(G)$ of high spin ($S=3/2$) Co^{2+} in a tetrahedral crystal field, whose intensities increase with processing temperature. X-ray photoelectron spectroscopy shows that the doped Co^{2+} ions in the 150°C processed samples are located mostly on the surface of the particles and they disperse into the entire volume of the particles when processed at higher temperatures. The observations suggest that the FM most likely results from Co^{2+} attached to the surface sites and it is lost in well dispersed samples formed at $T_p > 150^\circ\text{C}$. © 2006 American Institute of Physics. [DOI: 10.1063/1.2173956]

I. INTRODUCTION

A promising way to introduce magnetic functionality into existing semiconductors is to dope them with magnetically active transition metals (TMs). Recent theoretical predictions¹⁻³ proposed TM-doped ZnO as one of the most hopeful candidates for room-temperature ferromagnetism (FM). However, experimental studies in these systems,^{4,5} especially $\text{Zn}_{1-x}\text{Co}_x\text{O}$, have been controversial with reports supporting the possibilities of both intrinsic carrier-mediated FM^{6,7} and magnetic-impurity-cluster-driven mechanisms.⁸ To understand the origin of the observed FM, we carried out a detailed investigation of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ prepared using the sol-gel method in air which would inhibit the formation of ferromagnetic Co clusters, focusing particularly on the role of processing conditions. If any impurity phases were to be formed, they would be oxides of Co, which are all antiferromagnetic (AF) with Néel temperatures T_N below room temperature. Preparation and/or processing temperatures have been a very crucial parameter controlling the occurrence and stability of FM in TM-doped semiconductor oxides.^{9,10}

II. EXPERIMENTAL DETAILS

Appropriate amounts of $0.25M$ $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ and $0.05M$ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (molar ratio $[\text{Co}/(\text{Co}+\text{Zn})] = 0.02$) were stirred together into which a $0.50M$ $\text{NaOH} \cdot \text{H}_2\text{O}$ solution was then added dropwise and held at 65°C throughout the entire reaction, until a pH of 10 was reached. The resulting precipitate was washed and an-

nealed at various temperatures $100 \leq T_p \leq 900^\circ\text{C}$ under vacuum (10^{-3} torr) to obtain $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$. The samples were investigated using x-ray diffraction (XRD), spectrophotometry, x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and magnetometry, the details of which are given elsewhere.^{11,12}

III. RESULTS AND DISCUSSION

XRD patterns of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ samples [Fig. 1(a)] showed strong peaks of wurtzite ZnO at all preparation temperatures $100 \leq T_p \leq 900^\circ\text{C}$. The lattice parameters a and c [Fig. 1(b)], determined using the (102) and (110) peaks, were lower than 3.250 and 5.207\AA , respectively, reported for bulk ZnO. This is presumably due to the incorporation of 0.58\AA sized tetrahedral Co^{2+} at the substitutional sites of 0.60\AA sized Zn^{2+} . With T_p increasing, the lattice parameters decreased and saturated, as shown in Fig. 1(b), suggesting a progressive substitution of Co ions at the Zn sites.

Optical characterization of the $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ powders was carried out by measuring the diffuse reflectance from $300\text{--}800$ nm. Figure 2(a) shows three well defined absorption edges at 660, 615, and 568 nm due to the $d-d$ crystal field transitions ${}^4A_2(F) \rightarrow {}^2E(G)$, ${}^4A_2(F) \rightarrow {}^4T_1(P)$, and ${}^4A_2(F) \rightarrow {}^2T_1(G)$, respectively.^{13,14} The appearance of these transitions clearly suggests that the doped Co^{2+} are in the high spin ($S=3/2$) state and are under a tetrahedral crystal field. The intensity of these transitions increases with T_p , indicating a progressive incorporation of Co^{2+} ions in Zn^{2+} sites. The direct band gap energies were calculated from their diffuse-reflectance spectra using the Kubelka-Munk function¹¹ and found to be 3.15 ± 0.07 eV.

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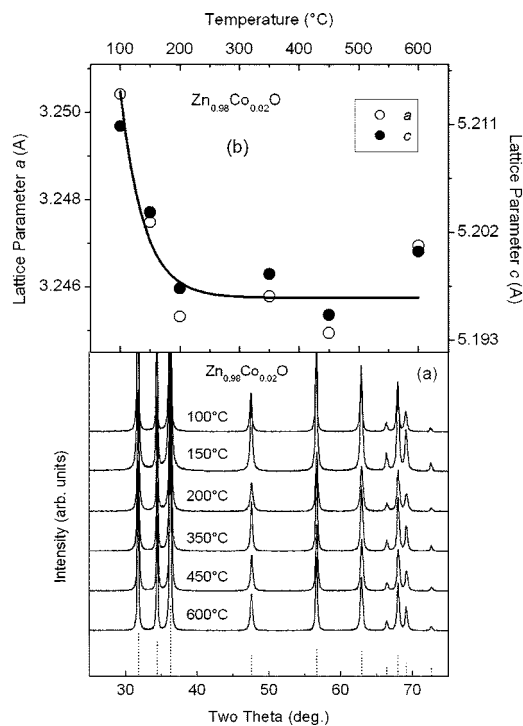


FIG. 1. Panel (a) shows the XRD spectra of Zn_{0.98}Co_{0.02}O samples prepared at various temperatures along with reference lines for wurtzite ZnO. (b) shows the variation of the lattice parameters *a* and *c* calculated from the hexagonal peaks (102) and (110).

TEM measurements showed hexagonal particles with slight changes in the shape and size with T_p . The particles [shown in Fig. 2(i)] were all elongated with aspect ratios ~ 2.0 and average size 60 nm. The energy dispersive x-ray spectroscopy measurements confirmed the Co presence on 150 and 350 °C annealed samples. Electron diffraction patterns from several spots in the samples confirmed the ZnO structure observed in XRD and provided no evidence of any impurity phases.

The Co $2p_{3/2}$ and Co $2p_{1/2}$ regions of the XPS spectra of the Zn_{0.98}Co_{0.02}O samples are shown in Fig. 2(b). Comparing the binding energies of the primary and satellite Co XPS peaks of the Zn_{0.98}Co_{0.02}O samples with those of the Co₃O₄ reference sample, as well as those reported for other Co oxides and metallic Co, ruled out their possible presence in the samples.¹¹ These results also suggest a 2+ oxidation state for Co¹¹ and that Co is indeed incorporated in the ZnO lattice. No measurable change in the Co binding energy is observed with increasing T_p . However, a systematic decrease in Co peak intensity with increasing T_p is evident from Fig. 2(b), although all these samples were prepared by annealing the same reaction precipitate with an intended Co concentration of 2%. This is likely due to an inward diffusion of Co from the particle surface with increasing annealing temperature, considering the surface sensitivity of the XPS technique. The diffusion of dopant ions has been observed in Fe doped SnO₂,¹² in which the dopant undergoes the opposite effect. With the purpose of confirming the possibility of dopant diffusion, XPS spectra were collected from Zn_{0.98}Co_{0.02}O prepared at $T_p=150, 600,$ and 900 °C after removing a 10 nm surface layer from the powder samples attached to a carbon

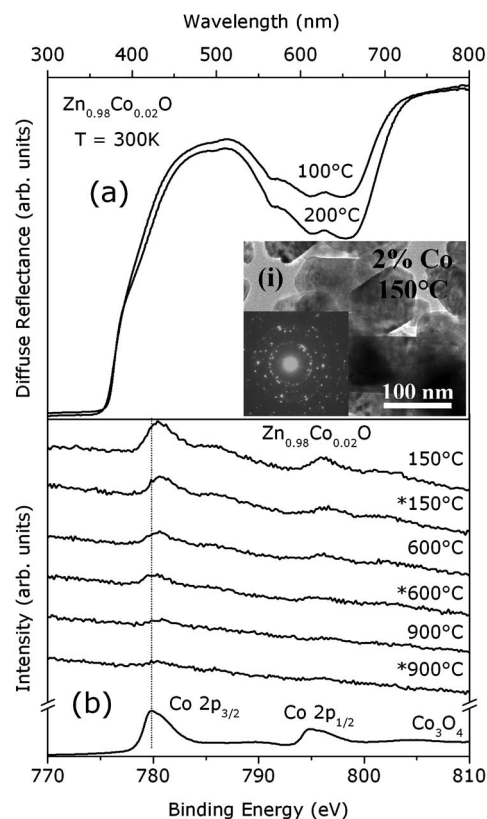


FIG. 2. (a) Room-temperature diffuse reflectance spectra showing the absorption edges at 660, 615, and 568 nm. (i) shows the TEM image along with the electron diffraction pattern obtained from the 150 °C prepared sample. Panel (b) shows the XPS spectra as a function of preparation temperature of Zn_{0.98}Co_{0.02}O. * indicates the data collected from the same sample after removing a 10 nm surface layer. The data obtained from a Co₃O₄ sample, prepared under identical synthesis and processing conditions but with no Zn precursor, is also shown.

tape, employing Ar⁺ ion sputtering [spectra with * in Fig. 2(b)]. These measurements showed a relatively large decrease in the Co concentrations in the sample prepared at 150 °C (from 1.29% in the as-prepared sample to 0.83%). However, the 600 and 900 °C annealed samples did not show a significant change in Co concentration. This fully supports the inward diffusion of Co from the surface. Based on the XRD and optical data discussed before, this suggests that in samples prepared at $T_p \sim 150$ °C, Co ions predominantly occupy the surface sites while they move inward and occupy the substitutional Zn sites when annealed at higher temperatures.

The M vs H data of Zn_{0.98}Co_{0.02}O at 300 K showed a linear variation indicating paramagnetic behavior in all the samples prepared at temperatures $200 \leq T_p \leq 900$ °C. However, the sample prepared at 150 °C displayed an additional saturating FM-like component as shown in inset (i) of Fig. 3(a). In Fig. 3(b), the hysteresis loops of Zn_{0.98}Co_{0.02}O measured at 300 and 5 K are shown which are somewhat asymmetric and indicate a shift to lower fields. Evidently, the loops are superimposed by an overwhelming paramagnetic component, presumably due to isolated Co²⁺ spins. The coercivity and loop shift decreased from 2000 and 670 Oe, respectively, at 300 K to 247 and 41 Oe at 5 K. In many magnetic systems, hysteresis loop shifts are associated with

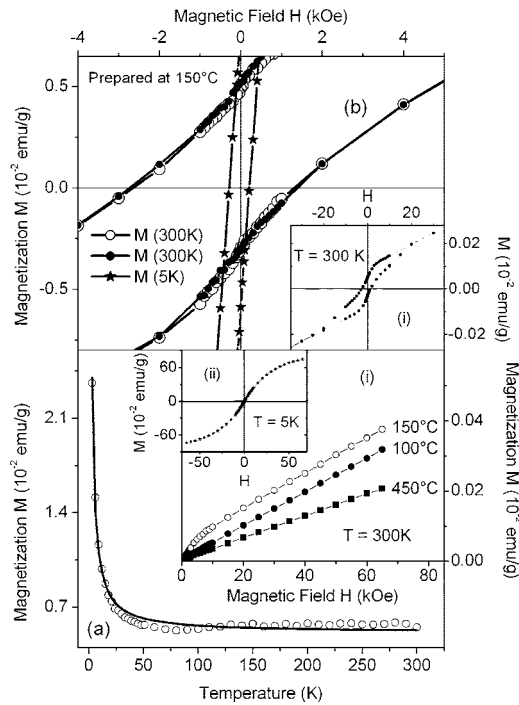


FIG. 3. (a) shows the M vs T data of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ measured with $H=500$ Oe. The solid line is a theoretical fit using the modified Curie-Weiss law (Ref. 12) yielding $\chi_0=1.02 \times 10^{-5}$ emu/g Oe, $C=1.07 \times 10^{-4}$ emu K/g Oe, and $\theta=-0.15$ K. Inset (i) shows the M vs H data measured at 300 K, (ii) shows the complete 5 K hysteresis loop. (b) shows the low-field region of the hysteresis loops obtained from the 150 °C prepared sample at 5 K along with the data from two separate runs at 300 K. The separate runs were done in order to confirm the observed shift in the loops towards the lower fields. These loops illustrate the decrease in coercivity and loop shift from 300 to 5 K. The complete 300 K hysteresis loop is shown in inset (i). The lines joining the data points in all of the figures except Fig. 3(a) are for visual aid.

exchange bias,¹⁵ a phenomenon commonly observed in FM-AF interfaces. In a Co doped ZnO system, the most probable source of loop shift is the possible formation of Co nanoparticles with an exchange coupled CoO surface layer. However, there are four results that do not support this possibility: (i) the changes in coercivity and loop shift with temperature are opposite to what is expected for a Co/CoO system,¹⁶ (ii) there is no peak in M vs T data [Fig. 3(a)] at or below the Néel temperature $T_N=291$ K expected for bulk CoO, (iii) in a Co/CoO system, the exchange bias should not be observed at $T > T_N=291$ K of CoO, and (iv) the preparation of the sample under identical synthesis and annealing/vacuum conditions, but with no Zn precursor, produced pure Co_3O_4 with no FM or exchange bias. It is also important to note that none of the known Co oxides have FM or AF ordering at or above room temperature. It has been shown that small FM and AF regions formed within a sample can result in a measurable exchange bias.¹⁵ If Co doping produces both AF and FM regions of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$, it could result in an exchange bias effect. It has been argued^{12,17,18} that in TM-doped semiconductors, coupling of dopant spins via oxygen vacancies results in FM interactions while those mediated by oxygen ions are AF. Wherever additional Co ions are missing in their closest proximity, the spins might display a paramagnetic behavior, as observed in Fig.

3(a).^{12,17} Based on the results from XPS, XRD, and optical studies, the observed FM ordering is obtained most likely in the surface region (with high surface concentrations of Co) of the 150 °C prepared samples, presumably due to the large number of oxygen vacancies present on the surface. In the core of the particles, the magnetic coupling may be mediated by oxygen ions producing an AF coupling,¹⁷ thus providing the FM-AF interface. The observed decrease in the loop shift when the sample was cooled from 300 to 5 K is an unusual behavior and uncommon in conventional exchange bias system. A possible reason for this anomaly may be magnetic phase changes in the AF and/or FM components between 300 and 5 K. However, the possibility of a weak trace of an unknown metastable binary oxide of Co and Zn undetectable in the XRD XPS, or optical studies contributing to the FM or AF component is not completely ruled out.

IV. CONCLUSIONS

We have shown that $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ powders prepared at 150 °C display FM presumably due to Co^{2+} residing on the surface particles. The powders prepared at temperatures $150 < T_p \leq 900$ °C display only a paramagnetic behavior due to the uniform distribution of Co^{2+} within the material, which reduces their interaction.

ACKNOWLEDGMENTS

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