Identifying the Sources of Ferromagnetism in Sol-Gel Synthesized

$\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.10$) Nanoparticles

J. J. Beltrán^{1, 2}, C. A. Barrero¹ and A. Punnoose³

¹ *Grupo de Energías Alternativas y Biomasa (GEAB-CIDTEC), Universidad Popular del Cesar, UPC, Balneario Hurtado Via Patillal, Valledupar, Colombia.*

² *Grupo de Estado Sólido, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, UdeA, Calle 70 No 52-21, Medellín, Colombia.*

³ *Department of Physics, Boise State University, Boise, Idaho 83725-1570, USA.*

ABSTRACT

We have carefully investigated the structural, optical and electronic properties and related them with changes in the magnetism of sol-gel synthesized $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.10$) nanoparticles. Samples with $x \leq 0.05$ were free of spurious phases. Samples with $x \leq 0.03$ were found to be with only high spin Co^{2+} ions into ZnO structure, whereas sample with $x = 0.05$, exhibited the presence of high spin Co^{2+} and low spin Co^{3+} . We found that the intensity of the main EPR peak associated with Co^{2+} varies with the nominal Co content in a similar manner as the saturation magnetization and coercive field do. These results point out that the ferromagnetism in these samples should directly be correlated with the presence of divalent cobalt ions. Bound magnetic polaron (BMP) model and the charge transfer

* Corresponding Author E-mail: jjbj08@gmail.com

model are insufficient to explain the ferromagnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanoparticles. The room temperature ferromagnetism (RTFM) may be originated from a combination of several factors such as the interaction of high spin Co^{2+} ions, perturbation/alteration and/or changes in the electronic structure of ZnO close to the valence band edge and grain boundary effects.

Keywords: *Co doped ZnO; XRD; Optical Absorption; EPR; XPS; Room temperature ferromagnetism.*

1. INTRODUCTION

ZnO is a semiconducting material, which has a direct wide-band gap ($E_g \sim 3.3$ eV) at room temperature (RT) with a large exciton binding energy of 60 meV [1]. ZnO is attracting attention because of its multiple applications such as light-emitting diode, transparent conductor oxide, varistor, surface acoustic wave device, piezoelectric transducer, chemical gas sensor, biosensor and as window material for display and solar cells [2]. It is well known that the electrical and optical properties of ZnO can be tuned by modifying its electronic structure via the doping with selective elements. Transition metal (TM) doping in ZnO nanostructures has been proposed as an interesting alternative to develop dilute magnetic semiconductor (DMS) [3]. These DMS materials have attracted much attention as promising functional materials because of the possibility of manipulating, in a controllable way, charge and spin degree of freedom of free carriers in a single substance [4]. These materials must exhibit an intrinsic ferromagnetism at RT or above. By intrinsic ferromagnetism we mean that magnetism originated from the TM doped ZnO itself and not as due to the presence of hidden secondary phases or to clustering of the TM dopant ions

that can be contaminating the sample. To satisfy such system, the foreign atoms should be distributed the most homogeneous manner as possible in the crystalline structure of the host semiconductor substituting at the cation sites. Within the series of TM's, Co has some advantages such as abundance of electronic states and similar ionic radius (Co^{2+}) to that of Zn^{2+} and thus may most effectively tunes both the optical and electronic properties of DMS based on ZnO [5].

The role of Co ions on the magnetism in this TM doped ZnO system has been widely explored both theoretically and experimentally with poor agreement in the reported results. Let us first present some of the reported theoretical studies. Lee and Cheng [6] found that the spontaneous magnetization is not possible in intrinsic Co doped ZnO, and that the ferromagnetic (FM) coupling is short ranged and a high concentration of both Co ions and electron carriers are needed to achieve ferromagnetism. On the other hand, Spaldin [7] and Gopal and Spaldin [8] predicted paramagnetic (PM) behavior in the absence of free carriers, but when holes were introduced by creating Zn vacancies, the FM state may be stabilized. The influence of Co concentration on the magnetic interactions is also not theoretically clear. While some groups reported room temperature ferromagnetism (RTFM) for 25 at.% and lower concentrations (≤ 15 at.%) of Co, other groups reported the absence of FM behavior [9,10].

Now, regarding the experimental investigations, we noticed poor agreement in the oxidation state of Co, the types of structural defects, the kind of observed magnetic behavior, either PM, antiferromagnetic (AFM) or FM, and the physical origin of this

magnetism. Kittilstved and Gamelin [11] and Schwartz *et al.* [12] have studied Co^{2+} doped ZnO thin films and evidenced chemical activation of long-range FM coupling mediated by shallow donor electrons. Lawes *et al.* [13] reported absence of ferromagnetism, but dominant AFM interaction, down to 2 K in bulk $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with $0.02 \leq x \leq 0.15$. Mesaros *et al.* [14] prepared $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x = 0.05, 0.10$, and 0.15) nanoparticles using a wet-chemical synthesis route, and a FM behavior was revealed for the samples, however a possible origin for this magnetic interaction was not provided. Fu *et al.* [15] prepared Co doped ZnO nanomaterials by using a hydrothermal method and suggested that the observed ferromagnetism originates probably from the Co^{3+} enrichment and the coexistence of $\text{Co}^{2+}/\text{Co}^{3+}$ on the particle surface, which may lead to the superexchange or a double-exchange mechanism between those ions. Gandhi *et al.* [16] synthesized Co doped ZnO nanoparticles using a co-precipitation method and reported that the donor defects, such as oxygen vacancies and zinc interstitials, were found to be the main reasons for the observed RTFM. On the other hand, Acosta-Humánez *et al.* [17] studied using EPR some Co doped ZnO nanoparticles prepared by a sol-gel method. The authors reported that the ferromagnetism of these materials is governed by FM coupling among cobalt ions, but a possible microscopic mechanism is not offered. Now, Hays *et al.* [18] studied sol-gel synthesized $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.12$) nanoparticles, and found a PM behavior with increasing AFM interactions as x increased to 0.10. They also reported a weak FM behavior for the sample with $x = 0.12$, and proposed that this high Co concentration and appropriate oxygen stoichiometry may be needed to achieve adequate FM interaction between the Co^{2+} ions. Pal *et al.* [19] explained the ferromagnetism observed above RT in Co doped ZnO nanorods, synthesized by a solvothermal route, using a bound magnetic polaron model and

expected to arise from the intrinsic exchange interaction of Co ions and zinc vacancies, interstitial oxygen related defects. Kumar *et al.* [20] investigated sol-gel synthesized $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.04$) nanoparticles and reported RTFM in the samples which increase with increasing Co concentration. They suggested that the joint effects of the intrinsic exchange interactions arising from oxygen vacancy assisted bound magnetic polarons and the grain boundary effects were responsible for the RTFM in this system. Tahir *et al.* [21] prepared Co doped ZnO nanorods and found that surface defects such as oxygen vacancies are likely a source of RTFM. They mentioned that oxygen vacancies are likely to congregate at low-energy (101) and (100) surfaces, instead of inside the bulk. On the other hand, changes in the magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanoparticles with x ranging from 0 to 0.2 prepared by forced hydrolysis method, was related to changes in the electronic structure of ZnO nanoparticles caused by dopant incorporation [22]. In a recent paper Shatnawi *et al.* [23] investigated the magnetic and optical properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.2$) nanocrystalline particles prepared by solid state reaction method. They attributed the RTFM to the interaction between the localized magnetic moments mediated by the free charge carrier. Clearly, from this short controversial literature review, it is noticed that the FM behavior in this system is closely associated with the different preparation methods, to the differences in dopant concentrations, the oxidation states, the sites that the Co ions occupy and the type of structural defects. Therefore, diverse theories and mechanisms have been proposed to understanding the origin of intrinsic ferromagnetism in Co doped ZnO.

In this paper, we carefully characterize the crystallographic, vibrational, optical and magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.10$) nanoparticles prepared by a sol-gel

method. The main goals are to: (i) search for the oxidation and spin states of Co ions, (ii) discern the participation of Co in the RTFM signal, (iii) infer about the preferred location of the Co (Co^{2+} and/or Co^{3+}) ions in the ZnO lattice, and (iv) to contribute to the understanding of the role of cobalt ions on the magnetic properties of Co doped ZnO.

2. EXPERIMENTAL DETAILS

Co doped ZnO nanocrystallites with different Co nominal contents of 0, 1, 3, 5 and 10 at.%, [$\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.01, 0.03, 0.05, 0.08$ and 0.10)], were prepared by the citrate precursor method based on the modified Pechini process [24]. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, citric acid (CA), ethylene glycol (EG), 5M ammonia solution and deionized water were used for the preparation of the starting sol. First the metal nitrates, in required molar ratios, and CA were dissolved in 200 mL of deionized water with a $\{[\text{Zn}]+[\text{Co}]\}:[\text{CA}]$ molar ratio of 1:3. The resultant sol was gradually heated at 70 °C under constant stirring and then NH_3 aqueous solution was introduced dropwise to maintain a pH of 5, and afterwards EG with EG/CA ratio of 5 was added to the mixture. Thus, the combination of EG and CA results in more stable chelate complex. The solution temperature was increased and kept between 90 and 95 °C, under constant stirring, for ~ 4h, to evaporate water. Finally, the temperature was raised slowly between 100 and 110 °C, to promote the polyesterification and the system was maintained until the bar stirring stopped by itself. In this last step, the solution became more viscous and finally turned into wet gel. The wet gel thus formed was dried at 200 °C in air for 4 h to get rid of volatile components, resulting in a black solid amorphous product known as polymeric precursor. This resulting mass was hand ground in an agate mortar and sieved through 150 μm sieve. This process was repeated until all the black solid material passed through the sieve. In order to

investigate the effect of annealing time on different properties of the sample obtained, this fine powder precursor was divided into two portions and annealed in a tubular furnace at 550 °C (heating rate: 5 °C/min) in air atmosphere for 1 h and 3 h, to obtain two sets of samples. To obtain insight into possible Co impurity phases which might be formed under these synthesis conditions, Co_3O_4 was also prepared following identical synthesis procedures.

X-ray diffraction (XRD) patterns were collected at RT using a Phillips X'Pert X-ray diffractometer with Cu-K α source ($\lambda = 1.5406 \text{ \AA}$) in Bragg-Brentano geometry. The obtained XRD patterns were analyzed by Le Bail refinement using the Rietica program [25], where the peak shapes were described by a pseudo-Voigt function and the background was modeled with a 6-term polynomial. TEM analysis was performed with a FEI Tecnai G2 F20 Super-Twin transmission electron microscope operating at 200 kV after placing a drop of ethanolic colloidal dispersion on carbon-coated Cu grids (200 mesh). Fourier transform infrared (FTIR) spectra of the samples were recorded using FTIR Bruker tensor 27 Spectrophotometer, using the KBr pellet technique, with an experimental resolution of 4 cm^{-1} approximately. RT optical absorption spectra in the ultraviolet and visible light wavelength were measured using an Evolution 600 UV-vis spectrophotometer (Thermo Scientific) fitted with an integrating sphere diffuse reflectance accessory. Electron paramagnetic resonance (EPR) measurements of the powder samples were carried out at 5 K using a Bruker ELEXSYS EPR system equipped with an Oxford liquid helium flow cryostat operating at $\sim 9.4 \text{ GHz}$. Small amounts ($\sim 20 \text{ mg}$) of each powder were placed in quartz tubes and inserted into the microwave cavity of the EPR system. EPR signal from the background quartz tube was measured and subtracted from data. The XPS analyses

were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al-K α X-ray source (1486.7 eV) with an analysis area of 300 x 700 microns. The high energy resolution photoemission spectra were collected using a pass energy of 40 eV, whereas for the survey was of 160 eV. The charge-shifted spectra were corrected using the adventitious C1s photoelectron signal at 284.8 eV. The overlapped bands of XPS spectra were deconvoluted using XPS PEAK41 software. The magnetic properties of the samples were studied using a PPMS (Physical Property Measurement System), Model 6000 (Quantum Design) equipped with a superconducting magnet. The Magnetic measurements were carried out as a function of applied magnetic field of ± 0.5 T and as a function of temperature (5-300 K).

3. RESULTS

3.1 Transmission electron microscopy: Figure 1 shows TEM images of Zn_{0.99}Co_{0.01}O sample taken at different magnifications. These micrographics show that irregular nanoparticles of various sizes less than 100 nm tend to coalesce conforming large agglomerates, which is usually common in this synthesis method [26,27]. In addition, it is also observed that these particles of nanometric scale contain grain boundaries and free surfaces, which may affect the physical properties [28].

3.2 X-ray Diffraction: Figure 2 presents the XRD refined patterns of Zn_{1-x}Co_xO samples annealed for 1 h along with that of Co₃O₄ sample prepared as reference. The hexagonal würtzite ZnO crystal structure was discerned as the only phase in the Zn_{1-x}Co_xO nanopowders with x in the range of $0 \leq x \leq 0.05$, without the appearance of any extra peak. However, additional weak peaks probably, belonging to a spinel Co₃O₄ phase, emerge in

the samples with $x = 0.08$ and 0.10 indicated by the orange vertical bars in the fit. These peaks were more clearly noticed when the y-axis is plotted in logarithmic scale. The result is that this phase accounts for 0.5 and 0.9 wt % in the XRD patterns of $\text{Zn}_{0.92}\text{Co}_{0.08}\text{O}$ and $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ samples respectively. From the magnified regions of the XRD patterns, shown in the top-right panel of Figure 2, it can be noted that for $x \leq 0.05$, the XRD peak positions of Co doped ZnO samples are shifted towards higher diffraction angles with increasing Co concentration. However, for $x > 0.05$, the XRD peaks shifted to lower angles. The lattice parameters of all samples, annealed for 1 h, are displayed in left part of Figure 3. The a and c lattice parameters of ZnO as well as the cell volume gradually decrease with increase in doping concentration and tend to have a minimum at doping concentration of 5at.%. These lattice parameters then increase with further rise in the doping [see panel (a) of Figure 3]. The changes in the cell parameters observed in the present study are very similar to those found by Hays *et al.* in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanoparticles [18]. Parameter L [29] (Zn-O bond length along the c direction) also follows the same trend as shown in panel (b) of Figure 3. In a tetrahedral environment and high spin state, the ionic radii of Co^{2+} and Zn^{2+} are 0.58 and 0.60 Å [30] respectively. It is expected that the lattice parameters tend to decrease slightly with increasing Co concentration in a solid solution $\text{Zn}_{1-x}\text{Co}_x\text{O}$ as observed here (maximum $\Delta a/a$ and $\Delta c/c$ of 9×10^{-4} and 2×10^{-3} respectively). Thus, the ZnO lattice shrinking as x increases to 0.05 indicates that at least 5% of the Zn^{2+} tetrahedral sites in ZnO lattice can be replaced successfully by Co^{2+} ions. Now, the observed increase in the lattice parameters above $x = 0.05$, suggests the additional presence of interstitial Co^{2+} and/or Co^{3+} ions. As shown below from XPS and EPR results low spin trivalent Co ions (ionic radii of 0.685 Å [30]) were detected from 5 at.% Co doped sample onwards, which

can explain the increase in the lattice parameters. Interestingly, the average crystallite size (D_v) [31] increases with increase of Co concentration [see panel (b) of Figure 3]. This result suggests that Co ions in ZnO structure could encourage crystallite growth, speeding up further growth of ZnO grains. Similar changes have been observed by other authors [20,32]. It can be seen from panel (c) of Figure 3 that the R parameter [33] increases and the c/a ratio decreases as x increases to 0.05, and above this nominal percentage a definite trend is not observed, which could be related to the formation of the spinel phase on further doping of Co above 5 at.%.

On the other hand, XRD patterns of Co doped ZnO nanoparticles annealed for 3 h (data not shown) displayed similar diffractions peaks as those observed from samples annealed for 1 h. The fitting showed slightly higher lattice parameters and D_v values in comparison to those for samples annealed for 1 h, with similar trends as shown in the right part of Figure 3.

Summarizing, the lattice parameters calculated from the XRD data indicate that the solubility limit of Co ions in the ZnO wurzite structure for both sets of samples is lower than 8 at.%, but when doping Co above $x = 0.05$, probable segregation of Co_3O_4 might occur.

It is worth mentioning that the Williamson-Hall plot [34] did not show linearity neither in undoped nor in Co doped ZnO samples, however, scattered points were observed which might indicate that this preparation method gives rise to non-homogeneous particle shape and size distributions, as evidenced in the TEM micrographs of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ sample.

3.3 Fourier transformed infrared spectroscopy: Figure 4 shows the FTIR spectra in the wavenumber range of 400-4000 cm^{-1} for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with $x = 0, 0.01, 0.03$ and 0.05 annealed for 1 h. The intense band centered at around 450 cm^{-1} is assigned to antisymmetric stretching vibration of O-Zn-O bonds, which also confirms the wurtzite structure [35]. All spectra exhibit two very weak peaks located at ~ 2850 and 2925 cm^{-1} due to C-H bond bending and stretching respectively and another two weak bands at 1390 cm^{-1} and 1630 cm^{-1} attributed to the antisymmetric and symmetric C=O stretching bond. These modes are commonly associated with the carboxylate functional group, possibly originating from the fragments of the citrate precursor. It is worth mentioning that these bands are not considered as contaminants in the nanoparticles, rather they point out to the presence of adsorbed species on the surface of nanopowders that could influence the properties of ZnO due to potential changes in their surface structure [36]. The intense and broad absorption in the $3100\text{-}3700 \text{ cm}^{-1}$ range is due to the stretching vibration of hydroxyl groups attached on the surface of nanocrystalline powders, indicating the existence of water absorbed on the surface of ZnO nanograins. This possibly could be attributed to the polarity of ZnO. Water dissociation often is favored at ZnO surfaces, leaving OH^- groups and hydrogen (H^+) ions, where the stacking of Zn^{2+} ions in the (0001) plane tends to bind the hydroxyl group and the stacking of O^{2-} ions in the (000 $\bar{1}$) plane tends to be under-coordinated with hydrogen, due to the electrostatic instability of these planes [37]. From Figure 4, it can be observed that the intensity of OH, C-H and C=O bands with respect to the O-Zn-O stretching mode decrease with increasing Co doping. Additionally, it is observed that with increasing Co content from $x = 0.01$ to 0.03 the intensity ratio of OH to O-Zn-O stretching bonds increases and then decreases when x reaches 0.05 . Due to that OH^- group is considered a

potential *n*-type defect in ZnO [38] these results could suggest that possibly intrinsic *n*-type defects may be suppressed with increasing Co content to $x = 0.05$.

3.4 Optical absorption: Optical absorption spectroscopy is considered a versatile tool to reveal electronic transitions when Co^{2+} ions are incorporated into ZnO lattice, substituting for Zn^{2+} at tetrahedral sites of the ZnO wurtzite structure and for studying the effect of Co doping concentration on the band gap of ZnO. RT optical absorption spectra of undoped and Co doped ZnO nanopowders, annealed for 1 h at different Co concentrations as well as Co_3O_4 sample prepared under the same conditions are shown in Figure 5(a). The introduction of Co ions into ZnO lattice led clearly to the appearance of three well defined additional absorption peaks as compared with the spectrum of undoped ZnO. These peaks located around 567, 610 and 655 nm are related to d-d transitions of Co^{2+} involving crystal field levels in a tetrahedral crystal symmetry and can be ascribed to the ${}^6\text{A}_1(\text{F}) \rightarrow {}^4\text{E}(\text{G})$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$, and ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{A}_1(\text{G})$ transitions respectively, where A, E and T are generally designations of intermediate energy bands [21,39,40]. These results support the fact that high spin tetrahedrally coordinated ($3d^7$, $S=3/2$) Co^{2+} ions are substituting at the Zn^{2+} sites in the ZnO structure. From this Figure 5(a) it is evident that the relative intensity and areas under curves of the absorption bands between 525 and 725 nm do increase with increasing Co concentration, indicating increased absorption by the Co^{2+} ions incorporated in ZnO.

To probe further into the details of differences between the samples, we have differentiated the absorbance with respect to the wavelength and the results are depicted in Figure 5(b). Besides the strong absorption peak centered at ~ 380 nm, which arises from ZnO at the band

edge and the peaks related to d-d transitions of Co^{2+} ions, there are two additional humps located at ~ 420 nm and ~ 510 nm in Co doped ZnO samples, as evident in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $x \geq 0.05$. As x increases from 0 to 0.05, the peak at 380 nm sharply decreases and suddenly disappears at $x = 0.03$. On the other hand, the relative intensity of the peak located at 420 nm increases and is shifted to higher wavelengths with increasing x up to $x = 0.05$ and then it remains almost constant on further increasing x . Regarding the broad peak located at ~ 510 nm, this does not change the position with increasing Co^{2+} ions, but weakly increases its intensity. Regarding the physical origin of these two additional humps, Patra *et al.* [41] have proposed that the band located at 420 nm in the spectrum of Co doped ZnO can be assigned to the presence of Co^{3+} ions tetrahedrally coordinated with oxygen corresponding to $5\text{E} \rightarrow {}^5\text{T}_2$ transition. However, this interpretation should be taken with care because according to XPS and EPR results (presented below) the presence of Co^{3+} is only indicated in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples when x reaches 0.05. On the other hand, Schwartz *et al.* [12] have observed a band close to the absorption band edge in Co doped ZnO nanocrystals which has been related to one of the spin-forbidden Co^{2+} ligand-field charge transfer (CT). Similar observations were found by Shi *et al.* in Co doped ZnO nanorods [42]. Therefore, the broad peak located at 420 nm has been commonly assigned to sub-band gap ligand to metal charge-transfer (LMCT) in which the Co^{2+} acts as the CT acceptor and the valence band serves as the CT donor. Thus, Co^{2+} rich zone below band gap can promote ligand field CT and semiconductor band-to-band transitions. Now, the shoulder at 510 nm has been assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ ligand-field transitions of pseudo-octahedral Co^{2+} ions [12,43]. Taking into account XPS, EPR and XRD results, these pseudo-octahedral Co^{2+} ions, present in $x = 0.01$ and 0.03 , could be more easily converted into pseudo-octahedral Co^{3+} ions when x reaches 0.05 and with further increment

of Co doping, the additional broadening of 510 nm peak could indicate the formation of the spinel structure of Co_3O_4 as secondary phase.

The inset in Figure 5(a) shows the band gap (E_g) variation, obtained following the Kubelka-Munk rule [44] as a function of nominal Co content (red solid spheres). The Co_3O_4 sample gave two E_g values, 1.61 and 2.22 eV, similar to those reported in the literature and were lower than the E_g observed in all the Co doped ZnO samples [45]. From inset of Figure 5(a) it can be seen that the band gap decreases with increasing Co concentration, indicating a red shift in the band gap of ZnO as observed by Elilarassi and Chandrasekaran [39] and Hays *et al.* [18]. Our results are also in close agreement to those reported by Qiu *et al.* [46]. They have observed that the decrease of the band gap in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanonorods with $0 \leq x \leq 0.10$ follows the relationship $\Delta E_g = 0.54(e^{-x/0.03} - 1)$ eV where x is Co^{2+} concentration. As shown by the blue solid triangles in the inset of Figure 5(a), the decrease in the band gap with the increase in Co concentration well follows this trend. Origin of the abnormal narrow band gap energies found by Qiu *et al.* [46] was attributed to s,p-d exchange interactions that are proportional to the square of lattice volume. In this work, we have not observed a direct correlation between E_g and the variation of the lattice parameters or cell volumes in Co doped ZnO samples. Therefore, this gradual decrease in the band gap for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with increasing x may be mainly related to the stronger exchange interactions between the localized d electrons of the Co ions substituting for Zn^{2+} ions and the s and p electrons of the host band of ZnO [46–48]. The magnetic impurity d states in DMS, generally appear near the Fermi level [49]. Thereby, the d states of Co ions exhibit splitting under the influence of the tetrahedral

crystal field of ZnO, leading to lower doublet e_g state and a higher energy triplet t_{2g} state. The t_{2g} orbitals which have the same symmetry as the functions xy , yz and zx hybridize well with the p orbitals of the valence band of the host semiconductor, further split into $t_{bonding}$ and $t_{antibonding}$ states, leaving the $t_{antibonding}$ states close to the conduction band (CB) and the $t_{bonding}$ states close to the valence band (VB). The $t_{bonding}$ states participate in bonding and hence are localized. The $t_{antibonding}$ states have higher energy and contain itinerant electrons [49]. Therefore, second-order perturbation corrections to CB and VB are expected [50]. Since the redshift to the band gap is a sum of the absolute value of both corrections and VB and BC, it is deduced that the strong s,p-d hybridization probably lowers the bottom of the conduction band, while heightening the top of the valence band, thus resulting in a band gap narrowing [46].

Optical absorption spectra and the derivative absorbance of $Zn_{1-x}Co_xO$ ($0 \leq x \leq 0.10$) nanoparticles annealed for 3 h showed similar results as those found for the samples annealed for 1 h [(see Figures 6(a) and 6(b)], except that the broad peak located at ~ 510 nm is more evident at $x = 0.03$. In comparison to the samples annealed for 1 h, those annealed for 3 h exhibited slightly smaller band gaps of 3.22, 3.04, 2.86, 2.77, 2.69 and 2.6 eV for $x = 0, 0.01, 0.03, 0.05, 0.08$, and 0.10, respectively, and follows the same trend in the relationship $\Delta E_g = 0.54(e^{-x/0.03} - 1)$, except for the last doping concentration. It is worth mentioning that the areas under the curves of the absorption bands between 525 and 725 nm in Figure 5(a) increase as x increases to 0.05 and then decrease with further rise in the doping, indicating higher Co^{3+} content for $x \geq 0.08$ in these samples annealed for 3 h. As mentioned above, these band gap values are smaller than those for the samples annealed for

1 h, although the latter samples have smaller crystallite sizes. These results may be due to the fact that the structural changes caused by the dopant incorporation and the different annealing times, have a dominant role in the observed changes of the band gap.

3.5 X-Ray Photoelectron Spectroscopy: Figure 7(a) shows full wide-scan X-ray photoelectron spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with $x = 0, 0.01, 0.03$, and 0.05 annealed for 1 h. All of the peaks in undoped ZnO can be ascribed to Zn, O, and C along with their Auger peaks and evidence of any magnetic impurity or TM ions was observed within the detection limit of the XPS system. In Co doped ZnO nanoparticles, weak peaks corresponding to Co was observed in addition to the above peaks, as labeled in the Figure. The Zn $2p_{3/2}$ core level data of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $0.01 \leq x \leq 0.05$ are displayed in Figure 7(b). All the spectra were deconvoluted using a single and symmetric signal located around 1021.3 eV and no significant changes in the chemical shift in comparison to undoped ZnO sample were observed [(see the inset in Figure 7(b))]. The slight change in the binding energy (BE) of Zn $2p_{3/2}$ peak for these samples compared to that of bulk ZnO (1021.8 eV) [51] may be due to the nanometric size of these powders. The observed BE values indicates that Zn atoms retain the bivalent state in tetrahedral sites surrounded by O^{2-} ions. The intensity and relative area under the Zn $2p_{3/2}$ peak progressively decreases upon increasing the Co doping, confirming that the Co^{2+} ions gradually replaces increasing numbers of Zn^{2+} ions. From the survey spectra, similar results were observed when the relative areas under Auger peak Zn $\text{L}_3\text{M}_{4,5}\text{M}_{4,5}$ (490-505 eV) and 3p core region were plotted against x . Figure 7(c) shows the high-resolution XPS of O 1s core level spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $x = 0.01, 0.03$ and 0.05 along with that of Co_3O_4 sample. The inset shows the O 1s core region

of pure ZnO sample. The broad and asymmetric shape of this signal was deconvoluted into two components indicating the presence of two different oxygen species. The first peak with lower BE centered at ~530.2 eV (O 1s-1) is attributed to O^{2-} ions in the hexagonal wurzite ZnO structure which are bound to Zn^{2+} or substitutional Co^{2+} atoms in tetrahedral sites, located mainly in the core region. The second BE peak (531.2-531.5 eV, O 1s-2) may be associated to weakly bound -OH bonds located at the surface of ZnO nanoparticles, as observed in FTIR spectra. Changes in this latter component may be related to changes in the concentration of oxygen vacancies and/or defects on the surface of ZnO nanoparticles and/or oxygen-deficient regions within the matrix of ZnO [52–54]. It is worth mentioning that Co doped ZnO samples did not show chemical shift in the BE of O 1s peaks in comparison to undoped ZnO sample [(see the inset in Figure 7(c)]. With increasing Co doping concentration from $x = 0.01$ to 0.03, the intensity of the O 1s-1 peak decreases and then increases as x reaches 0.05. On the other hand the full width at half-maximum and relative area of O 1s-2 peak remains almost unchanged, from $x = 0$ to 0.05. These observations probably indicate that the oxygen deficiency reaches a maximum at $x = 0.03$. and may also indicate that the distribution of oxygen vacancies and defects on the surface of Co doped ZnO nanoparticles do not vary significantly as Co content increases. Regarding the reference sample, the O1s-1 peak in Co_3O_4 at 529.5 eV, can be assigned to oxygen ions in their respective lattice sites, while the peak located at 532.5 eV (O 1s-3) in Co_3O_4 may be due to $-CO_3$ surface contamination [55]. From these results it is clear that the presence of O1s-1 and O1s-2 peaks in the Co doped ZnO samples highlight the difference in the chemical environment of the oxygen ions in comparison to reference sample.

Figure 7 (d) shows high resolution XPS scans of the Co 2p core electron regions of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0.01 \leq x \leq 0.05$) samples annealed for 1 h and also the spectrum of Co_3O_4 , which is included as reference. The Co 2p core-electron spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with $x = 0.01$ and 0.03 were deconvoluted into two components. The first component lies in the range of 780.9-781.0 eV with spin-orbit splitting (ΔS) of 15.6-15.8 eV, whereas the second component that appears at 786.0-786.2 eV is associated with shake-up satellite peaks (SS). Note that the ΔS values of these Co ions are much higher than those for metallic Co (15.1 eV) or CoO (15.2 eV), but they are close to $\text{Co}(\text{OH})_2$ (15.9 eV) [56] and to Co_3O_4 (15.8 eV for Co^{2+} component). This observation, along with the presence of the strong SS around 5.2 eV of the 2p core level confirms that the valence state of Co ions in the ZnO structures are mainly $2+$ and of high spin and that they are substituting Zn^{2+} at the tetrahedral site surrounded by O^{2-} ions [57]. On the other hand, in the spectrum of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ sample, the introduction of two additional components was necessary to improve the deconvolution considerably. These two new components with main line of 779.7 eV and a ΔS of 15.2 eV and the small SS located at 790.1 eV strongly suggest the presence of Co^{3+} ions [58]. Although, small differences in the BE and ΔS values for Co^{3+} component in $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ in comparison to those for the reference sample (779.3 eV and ΔS of 15.1 eV) were observed, the XPS technique is insufficient to differentiate between Co^{3+} ions in wurzite structure and Co^{3+} in Co_3O_4 due to the overlapping of these Co^{3+} components in XPS spectra. In order to confirm if any secondary phase is present in the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ sample, XRD patterns were recorded with extended accumulation time enhancing the detection limit considerably (data not shown). This pattern did not reveal any phase other than ZnO, even when plotted in logarithmic scale. Additionally, careful analysis of the spectra for $\text{Zn}_{1-x}\text{Co}_x\text{O}$

$x\text{Co}_x\text{O}$ ($0.01 < x < 0.05$) did not show any noticeable change in the peak positions of Zn 2p and O 1s core level upon increasing the Co content, thus ruling out the presence of any impurity phase [59]. According to the Shannon ionic radii Table [30] Co^{3+} exists in octahedral environments and not in tetrahedral ones, then, it is possible to assume that these Co^{3+} ions probably are occupying interstitial and/or superficial sites in ZnO grains, instead of forming any secondary phase. It is highly probable that Co^{3+} ions may be located in the surface of the nanoparticles, where the presence of oxygen vacancies and/or defects is higher. On the other hand, the BE and ΔS of Co^{3+} component in $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ sample is slightly higher than Co_3O_4 suggesting that Co^{3+} ions in wurzite structure have slightly lower symmetry, probably occupying distorted sites in a nearly environment. All these observations from XPS results suggest that Co^{3+} ions could be presumably located in both surface and core-interstitial region, occupying distorted octahedral sites i.e. pseudo-octahedral environment.

3.6 Electron Paramagnetic Resonance: Figure 8 illustrates the experimental EPR spectra recorded at a chosen temperature of 5 K for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with $0.01 \leq x \leq 0.10$ annealed for 1 h. In these types of compounds, the cobalt atoms substitute for the zinc atoms and the neutral charge state is commonly Co^{2+} ($3d^7$ configuration). The spectra are composed of a dominant sharp peak centered at around 1526 G ($g_x = g_y = 4.6$) and a weaker and relatively broad signal at 3015 G ($g_z = 2.2$). These lines are attributed to the perpendicular component ($H \perp c$) corresponding to tetrahedrally coordinated PM Co^{2+} ions substituting at Zn^{2+} sites in the wurzite ZnO structure and its parallel component ($H \parallel c$) respectively, suggesting that the system symmetry is axially distorted [14]. The lines with a g value of ~ 1.96 or

2.004 associated to shallow donors or core-shell vacancies originating from zinc and oxygen vacancies respectively [60,61] were not detected. The weak lines centered around the signal located at 3015 G in the spectrum of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ sample, marked by arrows in the inset (a) of Figure 8, are most likely weak hyperfine splitting of Co ions. As Co doping concentration increases, these weak lines tend to disappear due to increased interaction between the doped Co^{2+} ions. From Figure 8, it can be seen that the 1500 G signal became increasingly broadened (from 130 to 450 G) with increasing Co concentration. This behavior is correlated to the large concentration of spins of the isolated Co^{2+} ions, which is known to contribute to the broadening of the signal. It is well known that the EPR spectra of the Co dopant in the ZnO nanopowders depend strongly on the Co concentration and that the area under the integrated spectrum is proportional to the spin concentration. In order to investigate this variation, the EPR spectra were recorded while keeping all controllable experimental parameters such as microwave power, frequency, field modulation and sample mass identical. Inset (b) of Figure 8 shows the double integration of the corresponding experimental EPR spectra plotted as a function of x . It is noted that initially the EPR signal intensity increases from $x = 0.01$ to $x = 0.03$, reaching a maximum at this concentration and then decreases as x increases further. These results, along with the XPS data discussed above, strongly point out that a significant fraction of the interacting high spin Co^{2+} ($S=3/2$) ions are converted into low spin Co^{3+} ($S=0$) state as x increases from 0.03 to 0.05. As it can be seen in Figures 3(c) with increasing Co concentration from $x = 0.03$ to $x = 0.05$ a strong change in R parameter is observed. Then, when Co ions increases from $x = 0.03$ to $x = 0.05$ causes a higher distortion of lattice, possibly, resulting in the redistribution of electron charge around Co^{2+} ions, which could lead to the presence of the Co^{3+} ions.

Summarizing XRD, optical absorption, XPS and EPR results, there exist a solid solubility limit of Co^{2+} ions in Co doped ZnO $x \leq 0.03$, and some of these Co^{2+} are converted into Co^{3+} for $x = 0.05$, resulting in a mixture of Co^{3+} and Co^{2+} . Upon further increasing the Co doping above 0.05, the Co^{3+} ion concentration exceeds the absolute solid solubility limit. Then, Co^{3+} ions cannot remain dissolved in the ZnO lattice for $x > 0.05$, and so they form an impurity phase containing Co^{3+} ions such as Co_3O_4 .

3.7 Magnetic Measurements: Figure 9 shows RT M vs H curves of all Co doped ZnO samples (along with Co_3O_4) annealed at 550 °C for 1 h. Hysteresis loops of all these samples measured at 5 K showed a linear behavior (data not shown). At RT, it can be seen that with increasing Co concentration, the linear part owing to the PM component increases [(see also Figure 13(b))]. This result is in full agreement with EPR data which also showed an increasing concentration of isolated Co^{2+} ions as x increases. Clear hysteresis loops are observed in the Co doped ZnO samples with $x \leq 0.03$ suggesting the presence of FM interaction at RT. The width of these M vs H curves decreases substantially with further increase in doping concentration, indicating a PM and/or superparamagnetic-like behavior from $x = 0.05$ onwards.

Figure 10 depicts the RT M vs H curves of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.08$) samples annealed for 1 and 3 h, where the linear component has been subtracted ($M - \chi_p H$ vs H), to illustrate the actual M_s and H_c from the FM phase. Here, it is worth mentioning that the pure ZnO sample exhibit a very weak RTFM with saturation magnetization (M_s) of about 0.47 memu/g [62]. The $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $x = 0.01$ and 0.03 evidenced a clear FM behavior while it

decreased for $x = 0.05$. The $\text{Zn}_{0.92}\text{Co}_{0.08}\text{O}$ samples showed a somewhat strange M vs H curve, possibly indicating the presence of an impurity magnetic phase in addition to the dominant Co doped ZnO. On the other hand, the $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ samples were lacking a hysteresis loop, suggesting a superparamagnetic (SP) like behavior [(see lower inset of Figures 10(a) and (b)].

The variation of M_s and H_c as a function of nominal Co content for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.08$) samples annealed for 1 and 3 h are shown in Figure 11(a) and (b) respectively. For the 1 h annealed samples both M_s and H_c parameters increases reaching maximum values for $x = 0.03$ and then decreases as x increases further. Interestingly, the variations of M_s and H_c in these samples show similar trend as the intensity of the EPR signal at 5 K. Now, From Figure 11(b) it is clear that the increment of annealing time decreases the FM behavior for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0.0 < x < 0.05$). The low M_s values and the presence of the PM component observed in these samples suggest that the fraction of the doped Co^{2+} ions participate in the ferromagnetically coupled state is too small, which results in weak ferromagnetism. The highest value of the M_s obtained at 300 K in this work is very much lower than this obtained by Inamdar *et al.* [38] in Co doped in ZnO nanocrystal capped with organic molecules, indicating that the magnetic properties in this system strongly depend on the preparation method, synthesis conditions such as precursors, reactants, reaction/processing/capping, temperature, pH etc Figure 12 shows the temperature dependence of the magnetization for Co doped ZnO samples annealed at 550 °C for 1 h along with that for Co_3O_4 sample in both ZFC and FC conditions at an applied field value of $H = 500$ Oe from 5 to 300 K. The M vs T curves of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples present a concave nature similar to PM materials. On the other hand, ZFC and FC curves of Co_3O_4

sample exhibit a Neel temperature of 35 K confirming its well established AFM behavior. These curves of Co doped X ZnO samples were fitted following the modified Curie-Weiss law[63] $\chi = \chi_o + C/(T + \theta)$, where χ_o represents non-paramagnetic contributions, $C = Nu^2/3K_B$ (N is the number of magnetic ions/g, u is the magnetic moment of the ion, K_B is the Boltzmann constant) and θ is the Curie-Weiss temperature. The values of C and θ [see Figure 13(a)] indicate that the interaction between the disordered paramagnetic-like Co^{2+} spins (χ_p) [see Figure 13(b)], observed in the RT M versus H data are AFM in nature. In Figure 13(b) it can be seen that χ_o increases from $x = 0.01$ to 0.03 and slightly decreases for $x = 0.05$ and then increases again with further doping. The large increase of χ_o in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $x \geq 0.08$ can be due to the presence of Co_3O_4 . The decrease of χ_o for $x = 0.05$ can be associated to the presence of Co^{3+} , while the increase for the samples with $x \leq 0.03$ might be due to the increase of Co^{2+} ions.

4. DISCUSSION

We will summarize the analysis of the different data collected using the various techniques employed in this work. Co doped ZnO samples with $x \leq 0.05$, annealed for 1 h or 3 h are pure and free of spurious phases. Co_3O_4 was the only impurity phase identified in all the Co doped ZnO samples with $x \geq 0.08$. According to the results, we can divide $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples into 3 different groups. The first group with $x < 0.05$ can be considered as true solid solutions with only Co^{2+} ions in the ZnO structure; the second group with $x = 0.05$, where there is evidence of the presence of multivalent Co ions, i.e. Co^{2+} and Co^{3+} without the formation of any impurity phases; and finally, the third group with $x > 0.05$ demonstrate the coexistence of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ and of an impurity phase, most probably Co_3O_4 . In all these samples, there are isolated Co^{2+} ions that do not interact magnetically at RT, resulting in the

observed PM signal, which increases with increasing Co concentration. M vs T curves suggest that some of these disordered Co^{2+} ions in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ are AFM coupled. The RT PM behavior can be explained due to the random distribution of the Co ions, which results in the formation of isolated, pairs and very small clusters of Co ions at dopant concentrations below the percolation threshold and/or magnetically coupled Co ions whose transition temperature are below RT. The AFM signal can be explained by the superexchange interactions between Co^{2+} ions.

Now, let us discuss the possible physical sources of the RTFM signal in our impurity-free samples. Janish *et al.*, from first principles proposed that the superexchange mechanism should lead a FM coupling between two like (i.e., same element and same oxidation state) TM ions in semiconductor hosts, for a 90° metal-anion-metal bond. However, this geometry requirement excludes the conventional wurtzite structure [64]. Additionally, the percentage of Co ions present in these samples is too low to justify the RTFM by any of the known exchange mechanisms. RKKY interaction seems not be responsible of this behavior since gives the impression that semiconducting properties of ZnO are retained and not is converted into a metal with such low doping. Now, the magnetic data revealed that M_s increases with increasing Co content and decreases with increasing annealing time. These results could indicate that percolation of bound magnetic polarons (BMPs) may be responsible for RTFM. Within the BMP model, the large density of oxygen vacancies, which increase with increase in doping concentration, help to produce more BMPs, to yield a greater overall volume occupied by BMPs, leading to the overlap of BMPs and resulting in weak ferromagnetism. With increasing annealing time the number of oxygen vacancies should decrease, therefore reducing the FM interaction. In order to predict if BMP model is

suitable to explain the magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $0.01 \leq x \leq 0.03$, we fitted the M vs H data to the following equation [65] :

$$M = M_0 L(x) + \chi_p H$$

where the first term accounts for the BMP contribution and the second term is due to the observed PM contribution at higher fields. Here, the spontaneous moment of the system is given by $M_0 = Nm_s$, where N is the number of BMPs involved and m_s is the spontaneous magnetic moment per BMP. $L(x) = \cot(x) - (1/x)$ is the Langevin function with $x = m_{eff}H/K_B T$, where m_{eff} is the true spontaneous moment per BMP. At high temperature, the interaction between the BMPs can be ignored and $m_s = m_{eff}$. From Figure 14 it is observed that the Equation fits the experimental data well. The fitting parameters of the two curves are summarized in Table 1. From this table, it is noted that M_0 and χ_p match well with data showed in Figures 10(a) and 13(b) respectively, indicating the quality of the fit. N values which were obtained from M_0 and m_{eff} are around $10^{13}/\text{cm}^{-3}$, which is very small in comparison to required concentration of BMPs ($\sim 10^{20}/\text{cm}^{-3}$) for percolation in ZnO [65]. Thus, the BMPs model is not truly capable of explaining the observed weak RTFM in these Co doped ZnO samples. Thus, it is necessary to consider other models that may be more commensurate with our results.

Now, it was observed that in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ sample with $x = 0.05$, there is a mixed valence of Co ions (Co^{2+} and Co^{3+}) without the presence of impurity phases and a reduction in the M_s .

The charge transfer ferromagnetic model, proposed by Coey *et al.* [66,67] is based on the ability of the doped TM ions to exhibit mixed valence and exchange coupling to provide electrons locally into the conduction band or to accept electrons from it. This model requires the existence of a defect-based band having a peak in the density of states (DOS) close to the Fermi level, a charge reservoir for transferring electrons and an effective exchange integral associated with the defect states. Although there is a charge reservoir for transferring electrons, this model does not seem to influence the FM properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanoparticles considerably. According to XPS results, the Co^{3+} ions formed are presumably decreasing the oxygen-deficient regions. Therefore, possible excess or remnant donor defects cannot contribute to the charge transfer process and only form isolated spin polarons, and the Stoner criterion $N(E_f) > 1/I$ may not be satisfied. The reduction in magnetization in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with $x = 0.05$ can be related to decrease in oxygen vacancies within the matrix of ZnO. The presence of Co^{2+} ions in ZnO produce free charge carriers as well as oxygen vacancies centers. When x reaches 0.05, and Co^{3+} ions are formed, resulting in the annihilation of oxygen vacancies, by reducing the free charge carrier density.

In our previous paper, we discussed the physical origin of the FM signal in Fe-Co co-doped ZnO samples [59]. In that work the integral intensity of the EPR signal corresponding to the Co^{2+} ions was adequately fitted using the Curie law. The results from these fits showed negative Curie-Weiss temperature values suggesting that some Co^{2+} ions were weakly FM coupled. Therefore, we could expect a similar trend in the present samples, because they were prepared in the same way. Moreover, Acosta-Humánez *et al.* [17], Mesáros *et al.* [14] and Raita *et al.* [68] also reported FM coupling of Co ions using EPR in Co doped ZnO

nanoparticles prepared by modified sol-gel methods. Then, the RFTFM in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $x = 0.01$ and 0.03 should directly be correlated with the incorporation of high spin Co^{2+} ions along and the perturbation/alteration and/or changes in the electronic structure of ZnO.

On the other hand, Straumal *et al.*[28] have proposed that the main factor controlling the ferromagnetic behavior of Co doped ZnO is the value of the specific grain boundary area (s_{GB}). According to these authors, the Co doped ZnO becomes ferromagnetic if s_{GB} is higher than a certain threshold value $s_{\text{th}} = 1.5 \times 10^6 \text{ m}^2/\text{m}^3$. The s_{GB} value can be calculated by using the formula $s_{\text{GB}} = 1.65/D_v$, where D_v is the mean crystal size. Our samples shows typical values of $s_{\text{GB}} = 3,7 \times 10^7 \text{ m}^2/\text{m}^3$, which is much higher than s_{th} . Therefore, effects of the grain boundary could also contribute to the RTFM signal in doped nanoparticles.

5. CONCLUSIONS

We investigated in detail the crystallographic, optical, electronic and magnetic properties of sol-gel synthesized undoped and Co doped ZnO nanopowders. Within the detection limit of these techniques, we found that the samples with less than 8 at.% of Co content were free of spurious phases, suggesting that the solubility limit were below that value. For the sample with $x = 0.01$ and 0.03 the high spin Co^{2+} ions replaced the Zn^{2+} ions at the ZnO lattice and for the samples doped with 5 at.% Co, presence of Co^{3+} ions also were detected. For these samples, the bang gap, L and both lattice parameters decrease with increasing Co content, whereas the PM and AFM signals, the average crystallite size and R increase. Interestingly, the variation of M_s showed a similar trend as the intensity of the Co^{2+} EPR signal at 5 K, suggesting that these ions directly contributed to the FM signal. BPM model

is insufficient to explain the RTFM in these Co doped ZnO samples and the charge transfer ferromagnetic model also does not seem to influence the FM properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanoparticles considerably. According to the results obtained in this paper, the FM behavior may be originated from a combination of several factors such as the presence of high spin Co^{2+} ions, the formation of defect levels (free delocalized charge carriers of holes or electrons) close to the valence band edge and grain boundaries effects.

ACKNOWLEDGMENTS

This study was supported in Colombia by CODI-University of Antioquia (Sustainability Program for the Solid State Group 2014-2015 and project IN645CE). Research at Boise State University was supported by NSF CBET 1134468, NSF EAGER DMR-1137419, and ARO W911NF-09-1-0051 grants.

AUTHOR INFORMATION

Corresponding Author

*jjbj08@gmail.com

Author Contributions

All authors have given approval to the final version of the manuscript.

REFERENCES

- [1] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, Recent progress in processing and properties of ZnO, *Progress in Materials Science*. 50 (2005) 293–340.
- [2] Ü. Özgür, D. Hofstetter, H. Morkoc, ZnO Devices and Applications A Review of Current Status and Future Prospects, *Proceedings of the IEEE* 98.7 (2010) 1255–1268.
- [3] R. Janisch, P. Gopal, N.A. Spaldin, Transition metal-doped TiO₂ and ZnO-present status of the field, *Journal of Physics: Condensed Matter*. 17 (2005) R657–R689.
- [4] H. Ohno, Making nonmagnetic semiconductors ferromagnetic, *Science*. 281 (1998) 951–955.
- [5] Z. Jin, T. Fukumura, M. Kawasaki, K. Ando, H. Saito, T. Sekiguchi, et al., High throughput fabrication of transition-metal-doped epitaxial ZnO thin films: A series of oxide-diluted magnetic semiconductors and their properties, *Applied Physics Letters*. 78 (2001) 3824–3826.
- [6] E.-C. Lee, K. Chang, Ferromagnetic versus antiferromagnetic interaction in Co-doped ZnO, *Physical Review B*. 69 (2004) 085205.
- [7] N.A. Spaldin, A search for ferromagnetism in transition-metal-doped piezoelectric ZnO, *Physical Review B*. 69 (2003) 125201.
- [8] P. Gopal, N.A. Spaldin, Magnetic interactions in transition-metal-doped ZnO: An ab initio study, *Physical Review B*. 74 (2006) 094418.
- [9] C.N.R. Rao, F.L. Deepak, Absence of ferromagnetism in Mn- and Co-doped ZnO, *Journal of Materials Chemistry*. 15 (2005) 573.
- [10] A. Risbud, N. Spaldin, Z. Chen, S. Stemmer, R. Seshadri, Magnetism in polycrystalline cobalt-substituted zinc oxide, *Physical Review B*. 68 (2003) 1–7.
- [11] K.R. Kittilstved, D.R. Gamelin, Manipulating polar ferromagnetism in transition-metal-doped ZnO: Why manganese is different from cobalt (invited), *Journal of Applied Physics*. 99 (2006) 08M112.
- [12] D.A. Schwartz, N.S. Norberg, Q.P. Nguyen, J.M. Parker, D.R. Gamelin, Magnetic quantum dots: synthesis, spectroscopy, and magnetism of Co²⁺ - and Ni²⁺-doped ZnO nanocrystals., *Journal of the American Chemical Society*. 125 (2003) 13205–18.

- [13] G. Lawes, A.S. Risbud, A.P. Ramirez, R. Seshadri, Absence of ferromagnetism in Co and Mn substituted polycrystalline ZnO, *Physical Review B*. 71 (2005) 045201.
- [14] A. Mesaros, C.D. Ghitulica, M. Popa, R. Mereu, A. Popa, T. Petrisor, et al., Synthesis, structural and morphological characteristics, magnetic and optical properties of Co doped ZnO nanoparticles, *Ceramics International*. 40 (2014) 2835–2846.
- [15] J. Fu, X. Ren, S. Yan, Y. Gong, Y. Tan, K. Liang, et al., Synthesis and structural characterization of ZnO doped with Co, *Journal of Alloys and Compounds*. 558 (2013) 212–221.
- [16] V. Gandhi, R. Ganesan, H.H. Abdulrahman Syedahamed, M. Thaiyan, Effect of Cobalt Doping on Structural, Optical, and Magnetic Properties of ZnO Nanoparticles Synthesized by Coprecipitation Method, *The Journal of Physical Chemistry C*. 118 (2014) 9715–9725.
- [17] F. Acosta-Humánez, R. Cogollo Pitalúa, O. Almanza, Electron paramagnetic resonance in $\text{Zn}_{1-x}\text{Co}_x\text{O}$, *Journal of Magnetism and Magnetic Materials*. 329 (2013) 39–42.
- [18] J. Hays, K.M. Reddy, N.Y. Graces, M.H. Engelhard, V. Shutthanandan, M. Luo, et al., Effect of Co doping on the structural, optical and magnetic properties of ZnO nanoparticles., *Journal of Physics. Condensed Matter*, Institute of Physics Journal. 19 (2007) 266203.
- [19] B. Pal, S. Dhara, P.K. Giri, D. Sarkar, Room temperature ferromagnetism with high magnetic moment and optical properties of Co doped ZnO nanorods synthesized by a solvothermal route, *Journal of Alloys and Compounds*. 615 (2014) 378–385.
- [20] S. Kumar, S. Basu, B. Rana, A. Barman, S. Chatterjee, S.N. Jha, et al., Structural, optical and magnetic properties of sol–gel derived ZnO:Co diluted magnetic semiconductor nanocrystals: an EXAFS study, *Journal of Materials Chemistry C*. 2 (2014) 481–495.
- [21] N. Tahir, A. Karim, K.A. Persson, S.T. Hussain, A.G. Cruz, M. Usman, et al., Surface Defects: Possible Source of Room Temperature Ferromagnetism in Co-Doped ZnO Nanorods, *The Journal of Physical Chemistry C*. 117 (2013) 8968–8973.
- [22] J. Chess, G. Alanko, D. A. Tenne, C.B. Hanna, A. Punnoose, Correlation between magnetism and electronic structure of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanoparticles, *Journal of Applied Physics*. 113 (2013) 17C302.
- [23] M. Shatnawi, A. M. Alsmadi, I. Bsoul, B. Salameh, G. A. Alna'washi, F. Al-Dweri, et al., Magnetic and optical properties of Co-doped ZnO nanocrystalline particles, *Journal of Alloys and Compounds*. 655 (2016) 244–252.

- [24] Pechini M.P. (1967) US Patent 3,330,697, 11 July 1967.
- [25] C.J. Howard, H. Hunter, B.A. Rietica, A Computer Program for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Australian Nuclear Science and Technology Organization Lucas Heights Research Laboratories.
- [26] P. A. Lessing, Mixed-Cation Oxide Powders via Polymeric Precursors, American Society Ceramic Bulletin. 68 (1989) 1002–1007.
- [27] E.R. Leite, I.T. Weber, E. Longo, J. A Varela, A new method to control particle size and particle size distribution of SnO₂ nanoparticles for gas sensor applications, Adv. Mater. 12 (2000) 965.
- [28] B.B. Straumal, A. A. Mazilkin, S.G. Protasova, P.B. Straumal, A. A. Myatiev, G. Schütz, et al., Grain boundaries as the controlling factor for the ferromagnetic behaviour of Co-doped ZnO, Philosophical Magazine. (2012) 1–13.
- [29] H. Morkoç, Ü. Özgür, General Properties of ZnO, in: Zinc Oxide, Wiley-VCH Verlag GmbH & Co. KGaA, 2009: pp. 1–76.
- [30] Shannon, R. D.; Prewitt, C. T. Effective Ionic Radii in Oxides and Fluorides. Acta Crystallographic. (1969) B25, 925–946. Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. Acta Crystallographic. (1976) A32, 751–767.
- [31] B.D. Cullity, The Structure of Polycrystalline Aggregates, in: Elements of X-Ray Diffraction, Addison-Wesley Publishing Company, Reading, Massachusetts, 1978: p. 259.
- [32] N.M. Basith, J.J. Vijaya, L.J. Kennedy, M. Bououdina, S. Jenefer, V. Kaviyaran, Co-Doped ZnO Nanoparticles: Structural, Morphological, Optical, Magnetic and Antibacterial Studies, Journal of Materials Science & Technology. 30 (2014) 1108–1117.
- [33] M. Gaudon, O. Toulemonde, A. Demourgues, Green coloration of Co-doped ZnO explained from structural refinement and bond considerations., Inorganic Chemistry. 46 (2007) 10996–1002.
- [34] G.K. Williamson, W.H. Hall, X-Ray Line Broadening From Filed Aluminium and Wolfram, Acta Metallurgica. 1 (1953) 22–31.
- [35] S. Kumar, S. Mukherjee, R. Kr. Singh, S. Chatterjee, A. K. Ghosh, Structural and optical properties of sol-gel derived nanocrystalline Fe-doped ZnO, Journal of Applied Physics. 110 (2011) 103508.
- [36] A. Punnoose, K. Dodge, J.W. Rasmussen, J. Chess, D. Wingett, C. Anders,

Cytotoxicity of ZnO Nanoparticles Can Be Tailored by Modifying Their Surface Structure: A Green Chemistry Approach for Safer Nanomaterials., ACS Sustainable Chemistry & Engineering. 2 (2014) 1666–1673.

- [37] D. Stoltz, P. Palmgren, S. Yu, M. Go, U.O. Karlsson, Water Adsorption on ZnO (0001): Transition from Triangular Surface Structures to a Disordered Hydroxyl Terminated phase, J. Phys. Chem. C. 114 (2010) 11157–11161.
- [38] D.Y. Inamdar, A.D. Lad, A.K. Pathak, I. Dubenko, N. Ali, S. Mahamuni, Ferromagnetism in ZnO Nanocrystals: Doping and Surface Chemistry, The Journal of Physical Chemistry C. 114 (2010) 1451–1459.
- [39] R. Elilarassi, G. Chandrasekaran, Influence of Co-doping on the structural, optical and magnetic properties of ZnO nanoparticles synthesized using auto-combustion method, Journal of Materials Science: Materials in Electronics. 24 (2012) 96–105.
- [40] P. Koidl, Optical absorption of Co^{2+} in ZnO, Physical Review B. 15 (1977) 2493–2499.
- [41] M.K. Patra, K. Manzoor, M. Manoth, S.R. Vadera, N. Kumar, Studies on structural and magnetic properties of Co-doped pyramidal ZnO nanorods synthesized by solution growth technique, Journal of Physics and Chemistry of Solids. 70 (2009) 659–664.
- [42] S. Shi, Y. Yang, J. Xu, L. Li, X. Zhang, G.-H. Hu, et al., Structural, optical and magnetic properties of Co-doped ZnO nanorods prepared by hydrothermal method, Journal of Alloys and Compounds. 576 (2013) 59–65.
- [43] J. Li, L. Zhang, J. Zhu, Y. Liu, W. Hao, B. Li, Controllable synthesis and magnetic investigation of ZnO: Co nanowires and nanotubes, Materials Letters. 87 (2012) 101–104.
- [44] A. Escobedo, E. Sánchez, U. Pal, Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures, Revista Mexicana de Física. 53 (2007) 18–22.
- [45] M.Y. Nassar, I.S. Ahmed, Hydrothermal synthesis of cobalt carbonates using different counter ions: An efficient precursor to nano-sized cobalt oxide (Co_3O_4), Polyhedron. 30 (2011) 2431–2437.
- [46] X. Qiu, L. Li, G. Li, Nature of the abnormal band gap narrowing in highly crystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanorods, Applied Physics Letters. 88 (2006) 114103.
- [47] K.J. Kim, Y.R. Park, Spectroscopic ellipsometry study of optical transitions in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys, Applied Physics Letters. 81 (2002) 1420.

- [48] X. Xu, C. Cao, Hydrothermal synthesis of Co-doped ZnO flakes with room temperature ferromagnetism, *Journal of Alloys and Compounds*. 501 (2010) 265–268.
- [49] H. Katayama-Yoshida, K. Sato, Materials design for semiconductor spintronics by ab initio electronic-structure calculation, *Physica B*. 327 (2003) 337.
- [50] Y.D. Kim, S.L. Cooper, M. V. Klein, B.T. Jonker, Spectroscopic ellipsometry study of the diluted magnetic semiconductor system Zn(Mn,Fe,Co)Se, *Physical Review B*. 49 (1994) 1732–1742.
- [51] J. Moulder, J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy: “A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data,”* (1995).
- [52] T. Szörényi, L.D. Laude, I. Bertóti, Z. Kántor, Z. Geretovszky, Excimer laser processing of indium-tin-oxide films: An optical investigation, *Journal of Applied Physics*. 78 (1995) 6211.
- [53] S. Bian, I.A. Mudunkotuwa, T. Rupasinghe, V.H. Grassian, Aggregation and Dissolution of 4 nm ZnO Nanoparticles in Aqueous Environments: Influence of pH, Ionic Strength, Size, and Adsorption of Humic Acid, *Langmuir*. 27 (2011) 6059–6068.
- [54] X. Bie, C. Wang, H. Ehrenberg, Y. Wei, G. Chen, X. Meng, et al., Room-temperature ferromagnetism in pure ZnO nanoflowers, *Solid State Sciences*. 12 (2010) 1364–1367.
- [55] L. Fu, Z. Liu, Y. Liu, B. Han, P. Hu, L. Cao, et al., Beaded Cobalt Oxide Nanoparticles along Carbon Nanotubes: Towards More Highly Integrated Electronic Devices, *Advanced Materials*. 17 (2005) 217–221.
- [56] A.A. Khassin, T.M. Yurieva, V. V Kaichev, V.I. Bukhtiyarov, A.A. Budneva, E.A. Paukshtis, et al., Metal – support interactions in cobalt-aluminum co-precipitated catalysts: XPS and CO adsorption studies, *Journal of Molecular Catalysis A: Chemical*. 175 (2001) 189–204.
- [57] X. Wang, R. Zheng, Z. Liu, H.-P. Ho, J. Xu, S.P. Ringer, Structural, optical and magnetic properties of Co-doped ZnO nanorods with hidden secondary phases., *Nanotechnology*. 19 (2008) 455702.
- [58] J.F. Marco, J.R. Gancedo, J. Ortiz, J.L. Gautier, Characterization of the spinel-related oxides $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ ($x=0.3, 1.3, 1.8$) prepared by spray pyrolysis at 350 °C, *Applied Surface Science*. 227 (2004) 175–186.
- [59] J.J. Beltrán, C.A. Barrero, A. Punnoose, Evidence of Ferromagnetic Signal

Enhancement in Fe and Co Codoped ZnO Nanoparticles by Increasing Superficial Co^{3+} Content, *The Journal of Physical Chemistry C*. 118 (2014) 13203–13217.

- [60] P. Jakes, E. Erdem, Finite size effects in ZnO nanoparticles: An electron paramagnetic resonance (EPR) analysis, *Physica Status Solidi (RRL)*. 5 (2011) 56–58.
- [61] S.K.S. Parashar, B.S. Murty, S. Repp, S. Weber, E. Erdem, Investigation of intrinsic defects in core-shell structured ZnO nanocrystals, *Journal of Applied Physics*. 111 (2012) 113712.
- [62] J.J. Beltrán, C.A. Barrero, A. Punnoose, Understanding the role of iron in the magnetism of Fe doped ZnO nanoparticles, *Physical Chemistry Chemical Physics*. 17 (2015) 15284–15296.
- [63] A. Punnoose, J. Hays, A. Thurber, M.H. Engelhard, R.K. Kukkadapu, C. Wang, et al., Development of high-temperature ferromagnetism in SnO_2 and paramagnetism in SnO by Fe doping, (2005) 1–14.
- [64] R. Janisch, N.A. Spaldin, Understanding ferromagnetism in Co-doped TiO_2 anatase from first principles, *Physical Review B - Condensed Matter and Materials Physics*. 73 (2006) 1–7.
- [65] B. Pal, P.K. Giri, High temperature ferromagnetism and optical properties of Co doped ZnO nanoparticles, *Journal of Applied Physics*. 108 (2010) 084322.
- [66] J.M.D. Coey, K. Wongsaprom, J. Alaria, M. Venkatesan, Charge-transfer ferromagnetism in oxide nanoparticles, *Journal of Physics D: Applied Physics*. 41 (2008) 134012.
- [67] J.M.D. Coey, P. Stamenov, R.D. Gunning, M. Venkatesan, K. Paul, Ferromagnetism in defect-ridden oxides and related materials, *New Journal of Physics*. 12 (2010) 053025.
- [68] O. Raita, A. Popa, D. Toloman, M. Stan, A. Darabont, L. Giurgiu, Co^{2+} Ions in ZnO powders as seen by Magnetic Resonance, *Applied Magnetic Resonance*. 40 (2011) 245–250.

TABLES

Table 1: Fitting parameters extracted from the BMP model.

$\text{Zn}_{1-x}\text{Co}_x\text{O}$	M_o (emu/g)	m_{eff} (emu)	χ_p (emu/gOe)	N (cm^{-3})
$x=0.01$	1.50×10^{-3}	2.61×10^{-16}	5.8×10^{-7}	3.25×10^{13}
$x=0.03$	1.70×10^{-3}	2.97×10^{-16}	2.6×10^{-6}	3.23×10^{13}

FIGURE CAPTIONS

Figure 1: TEM images at different magnifications for nanocrystallites of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ sample annealed for 1 h.

Figure 2: LeBail refinement analysis of XRD patterns of Co doped ZnO samples annealed at 550 °C for 1 h. Semisolid spheres are experimental data, whereas black solid lines represent the fit. The olive lines below represent the difference pattern. The top panel at the right side shows some selected expanded regions in the 31° to 37° 2θ range.

Figure 3: Variation of (a) a and c lattice parameters, (b) Zn–O bond length (L) parallel to the c -axis and average crystallite size (D_v), and (c) lattice distortion degree (R) and c/a ratio as a function of Co content for all Co doped ZnO samples annealed for 1 h (left part) and for 3 h (right part). For a and c lattice parameters error bars are standard deviation of the fit, while error bars of other parameters are standard deviation of the result..

Figure 4: FTIR spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.05$) samples annealed at 550 °C for 1 h.

Figure 5: (a) Optical absorbance spectra of ZnO and Co doped ZnO samples annealed at 550 °C for 1 h. The inset shows the variation of the observed (red solid spheres) and

calculated [46] band gaps (blue solid triangles; see text) with the nominal Co content. (b) Derivative of absorbance spectra with respect to wavelength for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed at 550 °C for 1 h.

Figure 6: (a) Optical absorbance spectra of ZnO and Co doped ZnO samples annealed at 550 °C for 3 h. The inset shows the variation of the observed (red solid spheres) and calculated [46] band gaps (blue solid triangles; see text) with the nominal Co content. (b) Derivative of absorbance spectra with respect to wavelength for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed at 550 °C for 3 h.

Figure 7: (a) Wide survey X- ray photoelectron spectra of undoped ZnO and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $0.01 < x < 0.05$ samples annealed for 1 h. The spectra of the core-electron regions of (b) Zn 2*p*, (c) O 1*s* and (d) Co 2*p* are also shown. The insets in (b) and (c) show core-electron level of Zn 2*p* and O 1*s* region of pure ZnO respectively.

Figure 8: EPR spectra recorded at 5 K of Co doped ZnO samples annealed at 550 °C for 1 h. The inset (a) shows expanded region for $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ sample evidencing hyperfine splitting pointed out by arrows. The inset (b) shows the integrated intensity of the EPR spectra plotted as a function of x .

Figure 9: RT hysteresis loops at 300 K for Co doped ZnO nanoparticles along with Co_3O_4 sample annealed for 1 h.

Figure 10: RT magnetic hysteresis loops (M - χ_p vs H) of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples in the range of $0.0 \leq x \leq 0.08$ annealed at 550 °C for (a) 1 h and (b) 3 h. The insets in (a) and (b) show M - χ_p vs H for $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ samples.

Figure 11: Variations of saturation magnetization (M_s) and coercive field (H_c) with nominal Co concentration of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples in the range of $0.0 \leq x \leq 0.08$ annealed at 550 °C for (a) 1 h and (b) 3 h. The dashed line in Figure 10(a) represents the M_s value of undoped ZnO.

Figure 12: $M(T)$ curves with $H = 500$ Oe for 1, 3, 5, 8 and 10 % Co doped ZnO samples annealed for 1 h. The symbols solid (lines) correspond to ZFC (FC) data. The inset shows ZFC and FC curves for Co_3O_4 .

Figure 13: Changes in (a) Curie constant (C) and Curie-Weiss temperature (θ) and (b) the linear paramagnetic component (χ_p) [(obtained from Figure 10(a)] and non-paramagnetic contributions (χ_o) of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples as a function of x of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed at 550 °C for 1 h.

Figure 14: Initial portion of the M vs H curve fitted with the BMP model [65] for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $0.01 \leq x \leq 0.03$ annealed for 1h. Open symbols are experimental data and the solid lines represent the fit.

FIGURES

Figure 1: TEM images at different magnifications for nanocrystallites of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ sample annealed for 1 h.

Figure 2: LeBail refinement analysis of XRD patterns of Co doped ZnO samples annealed at 550 °C for 1 h. Semisolid spheres are experimental data, whereas black solid lines represent the fit. The olive lines below represent the difference pattern. The top panel at the right side shows some selected expanded regions in the 31° to 37° 2θ range.

Figure 3: Variation of (a) a and c lattice parameters, (b) Zn–O bond length (L) parallel to the c -axis and average crystallite size (D_v), and (c) lattice distortion degree (R) and c/a ratio as a function of Co content for all Co doped ZnO samples annealed for 1 h (left part) and for 3 h (right part). For a and c lattice parameters error bars are standard deviation of the fit, while error bars of other parameters are standard deviation of the result.

Figure 4: FTIR spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0 \leq x \leq 0.05$) samples annealed at 550 °C for 1 h.

Figure 5: (a) Optical absorbance spectra of ZnO and Co doped ZnO samples annealed at 550 °C for 1 h. The inset shows the variation of the observed (red solid spheres) and calculated [46] band gaps (blue solid triangles; see text) with the nominal Co content. (b) Derivative of absorbance spectra with respect to wavelength for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed at 550 °C for 1 h.

Figure 6: (a) Optical absorbance spectra of ZnO and Co doped ZnO samples annealed at 550 °C for 3 h. The inset shows the variation of the observed (red solid spheres) and calculated [46] band gaps (blue solid triangles; see text) with the nominal Co content. (b) Derivative of absorbance spectra with respect to wavelength for Zn_{1-x}Co_xO samples annealed at 550 °C for 3 h.

Figure 7: (a) Wide survey X- ray photoelectron spectra of undoped ZnO and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $0.01 < x < 0.05$ samples annealed for 1 h. The spectra of the core-electron regions of (b) Zn 2p, (c) O 1s and (d) Co 2p are also shown. The insets in (b) and (c) show core-electron level of Zn 2p and O 1s region of pure ZnO respectively.

Figure 8: EPR spectra recorded at 5 K of Co doped ZnO samples annealed at 550 °C for 1 h. The inset (a) shows expanded region for $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ sample evidencing hyperfine splitting pointed out by arrows. The inset (b) shows the integrated intensity of the EPR spectra plotted as a function of x .

Figure 9: RT hysteresis loops at 300 K for Co doped ZnO nanoparticles along with Co_3O_4 sample annealed for 1 h.

Figure 10: RT magnetic hysteresis loops ($M-\chi_p$ vs H) of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples in the range of $0.0 \leq x \leq 0.08$ annealed at 550 °C for (a) 1 h and (b) 3 h. The insets in (a) and (b) show $M-\chi_p$ vs H for $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ samples.

Figure 11: Variations of saturation magnetization (M_s) and coercive field (H_c) with nominal Co concentration of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples in the range of $0.0 \leq x \leq 0.08$ annealed at 550 °C for (a) 1 h and (b) 3 h. The dashed line in Figure 10(a) represents the M_s value of undoped ZnO.

Figure 12: $M(T)$ curves with $H = 500$ Oe for 1, 3, 5, 8 and 10 % Co doped ZnO samples annealed for 1 h. The symbols solid (lines) correspond to ZFC (FC) data. The inset shows ZFC and FC curves for Co_3O_4 .

Figure 13: Changes in (a) Curie constant (C) and Curie-Weiss temperature (θ) and (b) the linear paramagnetic component (χ_p) [(obtained from Figure 10(a)] and non-paramagnetic contributions (χ_o) of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples as a function of x of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed at 550 °C for 1 h.

Figure 14: Initial portion of the M vs H curve fitted with the BMP model [65] for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples with $0.01 \leq x \leq 0.03$ annealed for 1h. Open symbols are experimental data and the solid lines represent the fit.

GRAPHICAL ABSTRACT

The intensity of the main EPR peak associated with Co^{2+} varies with the nominal Co content in a similar manner as the saturation magnetization and coercive field do. These results point out that the ferromagnetism in these samples should directly be correlated with the presence of Co^{2+} ions.