



Evidence of defect-mediated magnetic coupling on hydrogenated Co-doped ZnO

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ABSTRACT

Hydrogenated bulk $Zn_{1-x}Co_xO$ samples were synthesized via standard solid-state reaction route with Co molar concentrations up to 15 at.%. Magnetic characterization demonstrates a room temperature ferromagnetic behavior associated to a paramagnetic Curie–Weiss component. Detailed microstructural analysis was carried out to exclude the presence of extrinsic sources of ferromagnetism. The magnetization increases linearly as a function of Co concentration. Hall measurements reveal an insulating character for the whole set of samples. In this context, the defect mediated magnetic coupling between the Co atoms under the scope of the bound magnetic polarons model is used to interpret the observed room temperature ferromagnetism.

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1. Introduction

The theoretical prediction of room temperature ferromagnetism (RTFM) in transition metal (TM) doped large band gap semiconductors [1] promoted the research on such kind of systems as one of the most active and attractive topic in materials science and condensed-matter physics. The manipulation of both charge and spin of carriers in semiconductors turns the development of spintronic devices with all its new functionalities attainable. In this direction, a huge effort has been concentrated on TM-doped oxide semiconductors as ZnO, TiO₂ and SnO₂ [2–4]. In spite of the extensive investigations, the origin of the observed RTFM remains inconclusive and controversial. Early works on such systems attributed the observed RTFM to a carrier-mediated mechanism [5]. However, there is a growing consensus that defects play an important role to drive the ferromagnetic behavior. In this scenario, the main theoretical models proposed to describe the origin and properties of ferromagnetism suppose that electrons introduced by donor defects into the conduction band [6] or forming bound magnetic

polarons (BMP) [7] mediate ferromagnetic couplings between TM ions. Another important model, attempting to explain the observed RTFM in undoped systems [8], assigns the ferromagnetic response to spins of electrons residing on point or extended defects, the called d^0 ferromagnetism [9].

In the present work we report a study of the structural and the magnetic properties of hydrogenated $Zn_{1-x}Co_xO$ bulk samples with Co molar concentrations up to 15 at.%. Our previous work showed that the presence of substitutional Co on ZnO matrix was not a sufficient condition to achieve RTFM [10]. Besides, recent reports presented direct evidences of the correlation between the concentration of oxygen vacancies (V_O) and the observed RTFM [11–14]. As pointed by Kohan et al., oxygen/zinc vacancy is the main defect in the ZnO matrix under zinc/oxygen-rich conditions [15]. Therefore, V_O can be introduced into the system by annealing the samples in oxygen-poor atmospheres. This effect can be enhanced using a reduction gas to perform the annealing; in the case of using hydrogen gas, the annealing process is called hydrogenation [16]. The hydrogenation of our paramagnetic set of samples [10] added a ferromagnetic phase, confirming reports of robust enhancement of magnetization at room temperature, especially for Co-doped ZnO systems, under this annealing process [17,18]. The hydrogenation is intended to be responsible to introduce a

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properly density of defects in the structure of the samples that couples ferromagnetically the magnetic moments of the dopants.

2. Experiment

Polycrystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x = 0.08, 0.12$ and 0.15) bulk samples were prepared by standard solid state reaction method following procedures described in Ref. [10]. These samples were here labeled as-prepared samples and only present a paramagnetic behavior. The as-prepared samples were then annealed in an atmosphere of Ar (95%) and H_2 (5%) for 3 h at 600°C . The effects of hydrogenation on the structural properties were investigated by X-ray diffraction (XRD) recorded in the range of $2\theta = 30\text{--}70^\circ$ with steps of 0.01° at 3 s/step. Structural analysis was performed using the Rietveld method as implemented by the software General Structure Analysis System (GSAS) package with the graphical user interface EXPGUI [19,20]. The microstructure and the composition distribution were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and an energy dispersive X-ray spectrometry (EDS). Co K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) was used to determine the valence state and to evaluate the environment of Co in the ZnO lattice. The measurements were performed in the transmittance mode at the XAS beamline from the Brazilian Synchrotron Light Laboratory (LNLS), Campinas, Brazil. Magnetic measurements were performed using a superconducting quantum interference device magnetometer (SQUID).

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction (XRD) results for the whole set of samples with the refined Rietveld pattern. The observed peaks correspond to those expected for polycrystalline wurtzite ZnO. Furthermore, the line-widths of the diffraction peaks are relatively quite narrow, revealing the good crystallinity quality of the samples. No additional phases were observed within the XRD detection limit (Fig. 1(b)). The Rietveld refinement initiated with

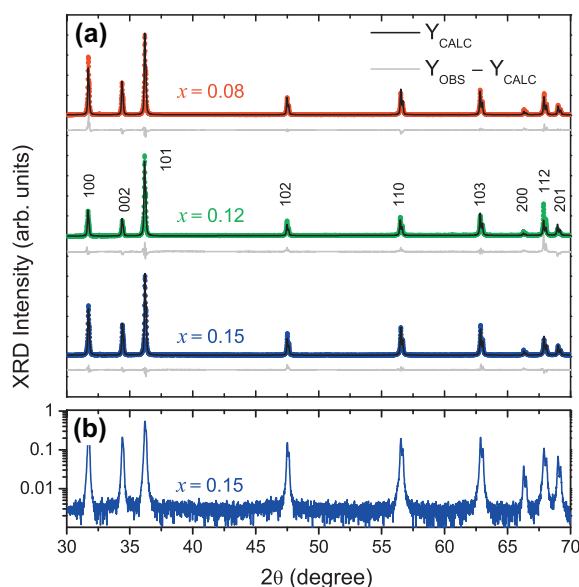


Fig. 1. (a) Refined XRD diffractograms of polycrystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}$ bulk samples. Each figure shows the observed pattern (symbols), Rietveld calculated pattern (solid line), and the goodness of the fit or residual pattern (at the bottom). (b) Same diffraction pattern obtained for sample $x = 0.15$ presented in (a), but in a logarithmic scale to highlight the absence of diffraction peaks associated to secondary phases.

Table 1
Structural data for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples obtained through the Rietveld refinement. O_{occup} is the oxygen occupation factor, χ^2 is the square of goodness-of-fit indicator, and R_{WP} is the refinement quality parameter.

Sample (x)	a (Å)	c/a	V (Å ³)	z (O)	O_{occup}	χ^2	R_{WP}
0.08	3.25164(1)	1.6009	47.665(2)	0.3825(2)	0.984(4)	3.31	3.80
0.12	3.25385(1)	1.5993	47.714(1)	0.3823(2)	0.980(5)	3.52	2.41
0.15	3.25269(1)	1.5998	47.680(1)	0.3825(4)	0.985(4)	2.91	2.90

Zn^{+2} and O^{-2} atoms located at $(1/3, 2/3, 0)$ and $(1/3, 2/3, z)$, respectively. The fitted curves match quite well with the experimental data. Table 1 presents the determined cell parameters along the atomic positional parameters, all this data are quite similar to those reported for pure ZnO [21]. Tetrahedrally coordinated Co^{+2} has an ionic radii of 0.58 \AA and would not introduce high order unit cell distortions when substituting the tetrahedrally coordinated Zn^{2+} that has a close ionic radii of 0.60 \AA [22]. These results indicate the Zn substitution by Co in the ZnO host matrix. Another important result of Rietveld refinement is the oxygen occupation factor (O_{occup}), which can give us an estimative of the concentration of the V_{O} . Taking into account the error in the determination of this parameter, we can say that the obtained V_{O} content is almost constant, 1.7% (0.017), for the whole set of samples. This result is reasonable, since all the samples were synthesized and annealed in the same conditions.

In order to probe the possible presence of secondary phases or chemical phase separation, high-resolution transmission electron microscopy (HRTEM) studies were performed on cross-sectional samples prepared by standard mechanical polishing followed by Ar^+ -ion milling at 4.5 kV under 8° angle (Gatan PIPS system) for about 30 min. HRTEM characterization was performed on a JEOL JEM 2100 URP, operated at 200 keV. Fig. 2(a) presents an example of HRTEM images acquired for the sample with higher Co content ($x = 0.15$). We can see that the distance between neighboring planes is about 0.25 nm, related to the (101) crystallographic plane of wurtzite ZnO, as observed in XRD (Fig. 1). To improve the statistical analysis of the HRTEM studies we have also taken a series of scanning electron microscope (SEM) images over large areas of the polish surface of the sample ($x = 0.15$). The images were acquired using a backscattered electron detector (BSE) of a SEM-LV JEOL JSM 5900 that has a resolution down to 3 nm at 30 kV (Fig. 2(b)). The effective Co concentrations of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples (x_{E}) were also measured by energy dispersive X-ray spectrometer (EDS) and are presented in Fig. 2(c) as a function of the nominal Co concentration (x_{N}). The values x_{E} are explicitly presented in Table 3. We observe a good agreement between the measured and the nominal concentration values. It is worth to point that electron microscopy results do not reveal any evidence of crystallographic secondary phase or local aggregation of Co ions (Co-rich nanoclusters), strongly suggesting that the studied samples are in diluted state in the Co concentration range up to 15%, in good agreement with XRD results.

XANES spectra at room temperature showed in Fig. 3(a) give information on the coordination symmetry and the valence of ions incorporated in a solid. All samples exhibit similar K-edge white line shapes to those previously reported for tetrahedrally coordinated TM-doped ZnO [23]. The valence of the dopant ions can be analyzed by comparing their resulting edge structure to those obtained from reference samples (metallic Co, CoO and Co_2O_3). The XANES results undoubtedly indicate that Co on our samples assumes predominantly the 2+ oxidation state, which corroborates the XRD, HRTEM and SEM results.

Fig. 3(b) and (c) shows the extended X-ray absorption fine structure (EXAFS) oscillations and their correspondent Fourier transforms (FT), respectively. The EXAFS data were obtained at Co K-edge for the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples, a Co foil and Co oxides pow-

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