Co Valence by K-Edge X-ray Absorption Spectroscopy, Magnetic Properties, and Structure of Polycrystalline Bulk $Zn_{1-x}Co_xO$

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We report on magnetic properties and a Co K-edge X-ray absorption spectroscopy (XAS) study of polycrystalline bulk $Zn_{1-x}Co_xO$ ($x = 0.10, 0.15, 0.17$) samples. All samples show paramagnetic behavior and no ferromagnetism was observed. XAS results showed that for all samples the valence of Co is 2+. Spin state assessment derived from Currie–Weiss fitting indicated a possible spin state transition from Co^{2+} high spin to Co^{2+} low spin. Calculated μ_{eff} values for samples with $x = 0.10$ and 0.15 indicated an orbital contribution to the effective magnetic moment of the Co ion.

***Index Terms*—Paramagnetic materials, spintronics.**

I. INTRODUCTION

DURING THE last decade, materials for spintronics or magnetoelectronics were studied widely because of their unique characteristics of using charge and/or spin of electrons simultaneously. Diluted magnetic semiconductors (DMS) [1] are one of the most promising candidates, not only due to their broad applications fields, but also flexibility for spin injection and bandgap tunability, which is essential for spin lifetime. DMS materials are formed when conventional semiconductors are doped with transition-metal (TM) ions.

ZnO is a well-known transparent wide bandgap II–VI semiconductor having a wurtzite structure. Dietl *et al.* [2] theoretically predicted large magnetization and high Tc in ZnO oxide, while Sato *et al.* [3] theoretically suggested that the ferromagnetic state in Mn- or Co-doped Zn-DMS can be stabilized. Experimental results on TM-doped ZnO oxide are very controversial. Mainly room temperature ferromagnetism was found in thin films grown by pulsed laser deposition technique. In fact, Mn-doped ZnO films showed room temperature ferromagnetism [4], [5] and paramagnetic behavior [6]. However, there are contradicting reports on Co-doped ZnO; some report ferromagnetism [7], [8], while others report antiferromagnetic behavior [9], [10]. Poor reproducibility of the data, i.e., ~10%, suggests that probably ferromagnetism in Co-doped ZnO thin films is not an intrinsic property of the material. Recently, there have been reports published [11], [12] that found Co clusters in prepared thin films that could be the reason of observed ferromagnetism. In addition to this, no room temperature ferromagnetism was found in polycrystalline samples [13], [14], which also supports the idea that room temperature FM is not an intrinsic property of the material.

The mechanism of formation of FM states in DMS materials is still unclear. It seems that the most probable cause of induction of FM states in DMS materials is a high concentration of holes that are essential for long range exchange between magnetic ions. However, it is well known that in order to obtain double exchange interaction in the material, the presence of multivalence species of magnetic ions is essential. Yet in the reports that are already published, authors assume that valence state of Co is 2+ [15], [16]. However, no direct systematic study on cobalt valence in ZnO was reported. Therefore, a detailed and systematic study on structure and Co valence state in Co-doped ZnO is essential, if one wants to explain the origin of ferromagnetism as a cause of double exchange interaction between magnetic ions. In this paper, we report on structural magnetic properties and the Co-valence state study by K-edge X-ray absorption spectroscopy (XAS) for polycrystalline Co-doped ZnO oxide ($Zn_{1-x}Co_xO$; $0 \leq x \leq 0.17$).

II. EXPERIMENT

To obtain Co-doped ZnO polycrystalline samples with various Co doping levels $x = 0.1, 0.15$, and 0.17, we applied a "rapid oxalate decomposition" technique. $Zn(C_2O_4)_2 \cdot yH_2O$ and $Co(C_2O_4) \cdot yH_2O$ precursors were prepared by precipitation reaction between Zn, Co acetates, and anhydrous oxalic acid ($H_2C_2O_4$). Formed pinkish precipitates were washed with distilled water and dried at 60 °C in a vacuum furnace. Precursors then were put into preheated furnace for 20 min at 950 °C in air. Dark green powders were formed, and the color intensified with an increase of x in the samples. The structure of the prepared samples was analyzed by means of an X-ray diffraction (XRD) analysis technique using a PW-1730 (Philips) diffractometer, with Cu K_α irradiation. Structure refinements were done by means of Rietveld analysis technique using Rietica software. Magnetic properties of the samples were analyzed using a magnetic property measurement system (MPMS) XL (Quantum

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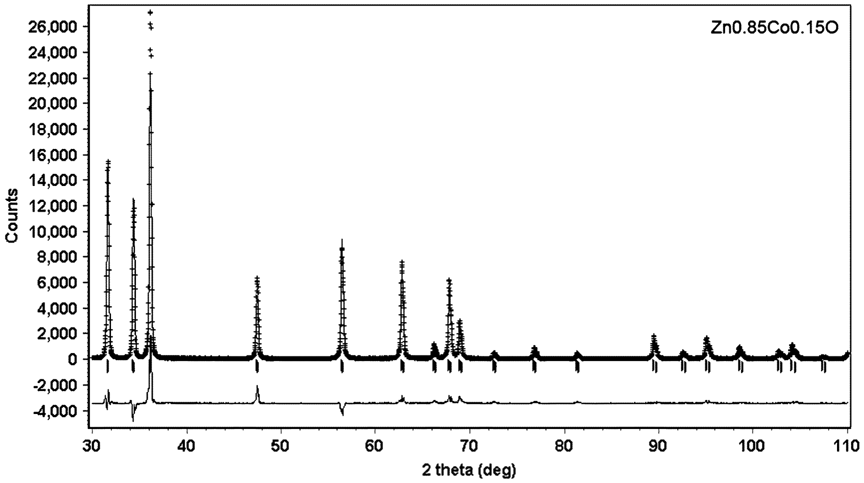

Fig. 1. XRD pattern for $Zn_{0.85}Co_{0.15}O$ sample, refined by Rietveld analysis technique.

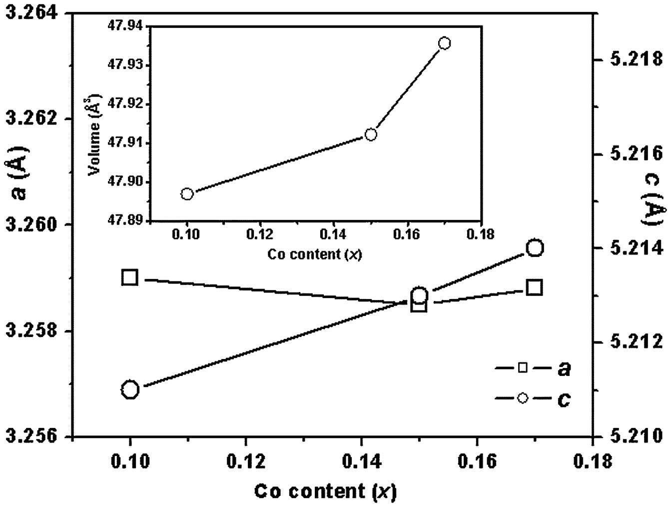

Fig. 2. Dependence of lattice parameters a and c on Co content (x) obtained by Rietveld refinement. Inset: unit-cell volume (V) as a function of Co content (x).

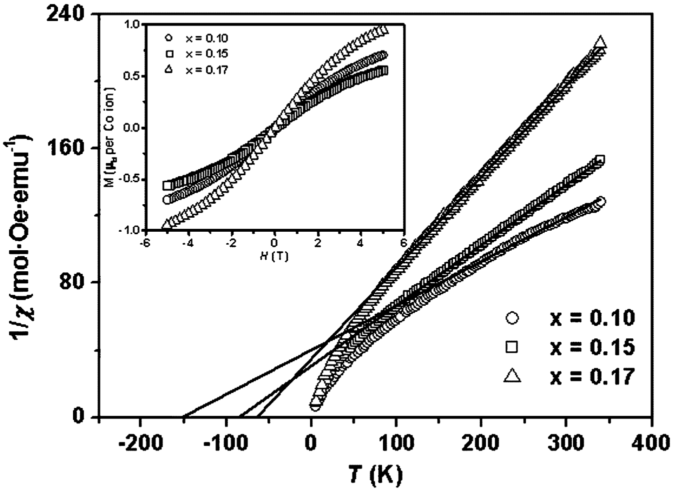

Fig. 3. Inversed magnetic susceptibility $(1/\chi)$ versus temperature (T) of $Zn_{1-x}In_xCo_{0.075}O$ $(x = 0.010, 0.015)$ samples. Inset: magnetization (M) versus applied magnetic field (H) loops at 10 K temperature.

Design). Co X-ray absorption near edge structure spectroscopy (XANES) results were obtained using a synchrotron beamline at the Synchrotron Radiation Research Centre (SRRC, Taiwan).

III. RESULTS AND DISCUSSION

Fig. 1 shows the Rietveld analysis pattern for a polycrystalline $Zn_{0.85}Co_{0.15}O$ sample. All the peaks in the pattern can be indexed according to the ZnO wurtzite phase. Negligible amounts of Co_3O_4 impurity were observed for samples with $x = 0.10$ and 0.15.

Dependences of lattice parameters a and c (Fig. 2) and unit cell volume (V) (inset in Fig. 2) on Co content (x) obtained from Rietveld refinements are represented. The lattice parameter c elongates with increasing Co content (x) in the samples, while lattice parameter a remains rather constant. The unit cell volume (V) increases with increasing Co content (x) as well. This result is consistent with the data reported by Kolesnik *et al.* [13]. However, elongation of the c lattice parameter in our samples is opposite to the result reported in [13]. The observed elongation of the c lattice parameter and increase in unit cell volume cannot be attributed to the presence of Co^{3+}, since the ionic radii of this ion is smaller. This anomaly in the expected structural change is still not understood clearly.

Inverse magnetic susceptibility $(1/\chi)$ as a function of T is represented in Fig. 3. The measurements were done on warming in the field of 2000 Oe (ZFC). The inset in Fig. 3 shows magnetization (M) versus applied magnetic field (H) loops for the same set of samples at 10 K. The topmost curve corresponds to $x = 0.17$, while the curve on the bottom corresponds to $x = 0.10$.

At close to room temperatures, the magnetic behavior of the samples follows the Curie–Weiss law for paramagnetic materials. By linear fitting and its extrapolation up to an intersection with the temperature axis, we obtained Θ values for the Curie–Weiss law. All obtained Θ values for our samples were negative, indicating antiferromagnetic interactions among magnetic ions. The higher the doping level x becomes, the more positive the value of Θ becomes, i.e., for $x = 0.10$ and $0.17, \Theta = -95$ K and -72 K, respectively.

Using the relationship of the slope C in $1/\chi$ curves with effective magnetic moment μ_{eff}, we have calculated the effective

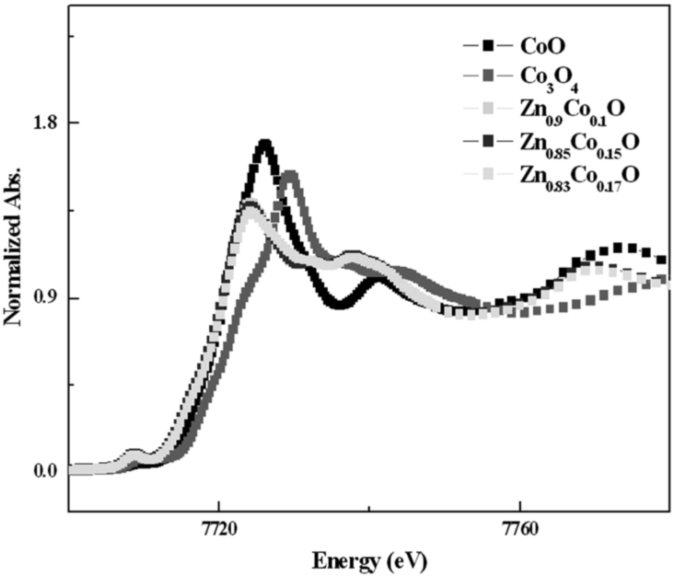

Fig. 4. Co K-edge X-ray absorption spectroscopy for $Zn_{1-x}Co_xO$ ($x = 0.10, 0.15$, and 0.17) samples. CoO and Co_3O_4 are reference materials for Co^{2+} and Co^{3+}, respectively.

magnetic moment (μ_{eff}) in our samples. First, for the calculations of μ_{eff}, we considered a spin only contribution to the effective magnetic moment. In the case of a sample with $x = 0.17$, we calculated $\mu_{\text{eff}} = 3.81\ \mu_B$, which corresponds to that of tetragonal Co^{2+} in high spin state ($e^4 t_2^3$), while μ_{eff} values for samples with Co content $x = 0.10$ and 0.15 are much higher ($\mu_{\text{eff}} = 4.81$ and $4.70\mu_B$, respectively). This result suggested that an orbital contribution to the μ_{eff} should play a significant role. Theoretically calculated $\mu_{\text{eff(S+L)}}$ for Co^{2+} HS was $6.64\mu_B$, while the above-mentioned μ_{eff} for $x = 0.10$ and 0.15 samples was 4.81 and $4.70\mu_B$, respectively. The μ_{eff} values are higher than those when a spin only contribution to the effective magnetic moment is assumed ($\mu_{\text{eff(S)}} = 3.87\ \mu_B$). From the other side, the obtained result suggests that the orbital contribution to the μ_{eff} is not very strong. In addition to that, we have noticed that close to 0 K, there is a small linear part in the $1/\chi$ curves. The calculated effective magnetic moment for a sample with $x = 0.17$ was very close to that of a Co^{2+} low spin state (LS) ($\mu_{\text{eff}} = 2.52\ \mu_B$). For the other two samples, $x = 0.10$ and 0.15 was higher, but below the calculated values for the Co^{2+} HS state with or without orbital contribution ($\mu_{\text{eff}} = 3.02$ and $2.82\mu_B$, respectively). These findings indicate that there is a possible spin state transition when the temperature is close to 0 K, and clearly the orbital contribution to μ_{eff} in this temperature disappears.

In order to determine the valences of Co in a direct approach, we performed X-ray absorption near edge spectroscopy (XANES) of Co K-edge studies of our samples. Fig. 4 shows XAS curves for $Zn_{1-x}Co_xO$ samples with included reference materials for Co^{2+} and Co^{3+} ions, which were CoO and Co_3O_4, respectively.

From the obtained data, we can see that all samples are close to the CoO curve, which suggests that a Co valence state in all of our samples is 2+. The above-mentioned results of XANES measurements strongly agree with all reported data that stoichiometry, oxidation states, and homogeneity are as suggested by the formula $Zn_{1-x}Co_xO$. These results showed that there is no multivalence species of Co in our samples, which could lead to ferromagnetism that is based on a double exchange interaction mechanism. However, this model might work for a typical DMS such as GaAs:Mn films, which were fabricated under nonequilibrium process conditions [17].

IV. CONCLUSION

In summary, polycrystalline bulk samples of Co-doped $Zn_{1-x}Co_xO$ $(0 \leq x \leq 0.17)$ oxide were prepared. All samples were of ZnO single phase having wurtzite-type structure. Magnetic properties of the samples measured showed that they are all paramagnetic, following the Curie–Weiss law at close to room temperatures. The Curie–Weiss temperatures become more positive with increasing Co content in the samples, i.e., $x = 0.10$ and $0.17, \Theta = -95$ and -72 K, respectively. A possible transformation from Co^{2+} HS to Co^{2+} LS was observed for samples with $x = 0.10$ and 0.15 when $T \rightarrow 0$ K. No trace of a multivalence species, essential for double exchange interaction-based ferromagnetism, of Co ions was found in our samples. Extensive research on Co valence in the ferromagnetic thin films is crucial.

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