Absence of ferromagnetism and strong spin-orbital coupling in polycrystalline In and Co codoped Zn\(_{1-x}\)Co\(_{0.075}\)In\(_x\)O oxide

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

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Polycrystalline samples of In and Co codoped ZnO (Zn$_{1-\chi}$In$_{\chi}$Co$_{0.075}$O; 0.010 ≤ $\chi$ ≤ 0.020) oxide were prepared by solid-state synthesis technique. Phase purity and structural parameters were determined by means of the Rietveld analysis technique. The results show that both Co and In substitute properly into Zn positions. In doping, increased bulk conductivity of the samples at room temperature indicates an increase of charge carrier concentration. Magnetic measurements were performed using a quantum design PPMS. Effective magnetic moment ($\mu_{eff}$) calculations showed a strong orbital contribution to the value of $\mu_{eff}$, increasing with an increase of In content ($\chi$).

Index Terms—Paramagnetic materials, spintronics.

I. INTRODUCTION

Ferromagnetism in semiconductor materials is an important area of research. The possibility of combining magnetic and semiconductor properties in a single material could lead to new applications in spintronics. Some of the most promising candidates are DMSs (Diluted Magnetic Semiconductors), which are alloys with magnetic elements that are embedded in a semiconductor matrix. These materials can exhibit semiconducting and magnetic properties simultaneously. DMSs are alloys with magnetic elements that are embedded into semiconductor materials. After reported ferromagnetism (FM) at relatively high temperatures in Mn-doped GaAs [3], a great deal of effort was put into finding new semiconductor materials that can exhibit a ferromagnetic feature. Some theoretical works predicted that room-temperature (RT) FM can be achieved in this family of materials. While most groups failed to observe the FM state in ZnO, several reports [9], [10] were published claiming that FM was present in their samples. Yan et al. [11] observed FM in their Mn and Co codoped thin films at 290 K, and Ueda et al. [4] reported that their pulsed laser-deposited thin films showed FM at 280 K. However, in the latter case, reproducibility of the data was poor.

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

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

II. EXPERIMENT

Polycrystalline samples were prepared by "rapid oxalate decomposition" technique [13]. Zinc oxalate dihydrate (ZnC$_2$O$_4$·2H$_2$O), cobalt (II) oxalate dihydrate (CoC$_2$O$_4$·2H$_2$O), and indium (III) oxalate decahydrate (In$_2$(C$_2$O$_4$)$_3$·10H$_2$O) were used as source materials. The precursor powders were mixed in the mortar and put into a preheated furnace at 1223 K for 20 min in air. Then, powders were reground, pressed into rectangular pellets, and sintered at 1523 K in air for 10 h, followed by annealing in argon for 12 h at 1250 K. Phase purity and structural parameters were analyzed by means of X-ray diffraction (XRD) analysis technique using Cu $K_\alpha$ irradiation (Philips PW-1730). Structure refinements were carried out employing Rietveld analysis using Rietica software [16]. Resistivity of the pellets was measured by a standard four-probe technique using the physical property measurement system (PPMS, Quantum Design). Magnetic properties were determined by means of a quantum design PPMS.
of our samples were investigated over a wide temperature range of 10 K to 340 K, utilizing the magnetic property measurement system (MPMS XL, Quantum Design) and applying a 2000-Oe magnetic field for magnetization versus temperature data collection. Chemical compositions of the samples were obtained by applying a scanning electron microscope (SEM)-EDS analysis technique (Leica Stereoscan 440).

III. RESULTS AND DISCUSSION

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

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

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

In order to analyze the chemical composition of our samples, we performed SEM-EDS analysis. For samples, the nominal formula was Zn$_{0.90}$In$_{0.05}$Co$_{0.05}$O which is the actual chemical content of Zn:In:Co$= 0.902 : 0.017 : 0.08$. Calculated chemical compositions for other samples were also close to the nominal ones, which indicated that our samples maintain stoichiometry as it is described by nominal formula.

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

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

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

This indicated that magnetic ions in the lattice are coupled antiferromagnetically (AFM). An increase in In content slightly decreased $\Theta$ values, i.e., $\Theta(x=0.010) \approx -160 \text{ K}$ and $\Theta(x=0.015) \approx -190 \text{ K}$, probably due to an increase in carrier concentration, which led to a higher number of ion-coupled AFM.

The effective magnetic moment ($\mu_{\text{eff}}$) of the Co ion was calculated from Curie–Weiss fits in the linear part of the curves. The obtained $\mu_{\text{eff}}$ values for samples with $x = 0.010$ and 0.015...
were 5.47 and 5.89 $\mu_B$, respectively. If the spin (S)-only contribution to the $\mu_{\text{eff}}$ is considered and Co is assumed to be in a Co$^{2+}$ high spin ($e^{4}t^2_2$) state [16], the calculated $\mu_{\text{eff}}(S) = 3.87\,\mu_B$. However, our values are significantly higher. Therefore, we assumed that for our In–Co codoped samples, strong orbital contribution must be taken into account. In fact, we calculated $\mu_{\text{eff}}(S + L) = 6.64\,\mu_B$ (both spin (S) and orbital (L) contribution were considered). This is in a good agreement with obtained $\mu_{\text{eff}}$ values for Co ion. Since $\mu_{\text{eff}}$ increased with increasing In content ($x$), we think that a higher concentration of itinerant carriers makes orbital contribution to the $\mu_{\text{eff}}$ stronger. Supporting this idea, $\mu_{\text{eff}}$, calculated from a linear part of the $1/\chi$ curve in carrier-poor Mg-Co codoped ZnO samples [18] was much lower, i.e., $\mu_{\text{eff}} = 3.04\,\mu_B$, which indicated that the orbital contribution to the $\mu_{\text{eff}}$ in that case is negligible.

Low-temperature (10 K) magnetization ($M$) as a function of applied magnetic field ($H$) is shown as an inset in Fig. 4. Obviously, we can conclude that there is no presence of any sort of FM or any evidence of hysteresis. All samples show identical paramagnetic behavior following Curie–Weiss law at close to RT. The Weiss temperatures ($\theta$) were negative for all samples decreasing with an increase of In content ($x$). The calculated values of $\mu_{\text{eff}}$ for samples with $x = 0.10$ and $0.015$ were 5.47 and 5.89 $\mu_B$, respectively. This corresponded to the tetragonal Co$^{2+}$ high spin ($e^{4}t^2_2$) state with a strong orbital contribution to the effective magnetic moment. Although carrier concentration was successfully increased, we did not observe any sort of FM. We conclude that the carrier-induced FM model does not work for our samples.

IV. CONCLUSION

In summary, polycrystalline samples of In and Co codoped Zn$_{1-x}$In$_x$Co$_{0.075}$O ($0.010 \leq x \leq 0.020$) were synthesized by a solid-state synthesis technique. Structural analysis showed that samples are of a pure wurtzite-type ZnO phase. A 1% change in In doping level significantly decreased bulk resistivity of the samples at RT ($x = 0.010$) and $x = 0.020, \rho \sim 7.9$ k$\Omega$cm and $\sim 0.2$ k$\Omega$cm, respectively. This was direct evidence that higher carrier concentration was achieved. SEM-EDS analysis showed that actual chemical compositions of the samples are close to nominal ones. All of the samples showed paramagnetic behavior following Curie–Weiss law at close to RT. The Weiss temperatures ($\theta$) were negative for all samples decreasing with an increase of In content ($x$). The calculated values of $\mu_{\text{eff}}$ for samples with $x = 0.10$ and $0.015$ were 5.47 and 5.89 $\mu_B$, respectively. This corresponded to the tetragonal Co$^{2+}$ high spin ($e^{4}t^2_2$) state with a strong orbital contribution to the effective magnetic moment. Although carrier concentration was successfully increased, we did not observe any sort of FM. We conclude that the carrier-induced FM model does not work for our samples.

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