CHIN. PHYS. LETT. Vol. 28, No. 11 (2011) 116103

Structural and Magnetic Studies of $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ *

Murtaza Saleem[1**], Saadat A. Siddiqi[1,2], Shahid Atiq[1], M. Sabieh Anwar[3]

[1] *Centre of Excellence in Solid State Physics, University of the Punjab, Quaid-e-Azam Campus, Lahore-54590, Pakistan*
[2] *Interdisciplinary Research Centre in Biomedical Materials (IRCBM), COMSATS Institute of Information Technology, Defence Road, Off Raiwind Road, Lahore, Pakistan*
[3] *School of Science and Engineering (SSE), Lahore University of Management Sciences (LUMS), Opposite Sector U, D.H.A. Lahore-54792, Pakistan*

(Received 8 July 2011)

Single-phase $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples were prepared by a novel combustion method. X-ray diffraction studies exhibit the pure phase wurtzite structure of doped ZnO. Energy dispersive x-ray analysis confirms the incorporation of dopants into the host material. Scanning electron microscopy shows the ordered morphology in both of the samples. Temperature-dependent resistivity analysis describes the expected semiconducting behavior that is similar to the parent ZnO materials. Room-temperature magnetic measurements reveal the absence of ferromagnetism in Co-doped ZnO, while the Co and Al co-doped sample displays apparent room-temperature ferromagnetic behavior. The decrease of resistivity and presence of ferromagnetic behavior in Al-doped ZnCoO system corroborate the significant role of free carriers.

PACS: 61.46.Hk, 75.50.Pp, 47.70.Pq, 75.75.−c DOI:10.1088/0256-307X/28/11/116103

Atoms of transition metals (TMs) partially substitute the cation sites of host semiconductor materials to produce diluted magnetic semiconductors (DMSs). Recently, these materials have attracted a great deal of interest due to their potential applications in spin based or spintronic devices.[1−3] The achievement of room-temperature (RT) ferromagnetic behavior in DMSs has been considered to be a very important issue. After the early reports of ferromagnetism in DMSs,[4,5] TM-doped Ⅲ–Ⅴ and Ⅱ–Ⅵ semiconductors have remained under discussion among the scientific community. Among these semiconductor materials, ZnO has been included as one of the best research candidates for the fabrication of DMSs because of its various outstanding properties. Moreover, ZnO has prospective applications in different optical and electronic devices.[6]

Although there have been several research reports on TM-doped ZnO thin films and poly-crystalline bulk samples synthesized by various techniques, most of the results exhibit controversies. Ueda *et al.*[7] reported RT ferromagnetic behavior in ZnCoO thin films grown using the pulsed laser deposition (PLD) technique. The magnetic properties of Co-doped ZnO films were attributed to the concentration of Co ions and carriers. Cho *et al.*[8] observed that rapid thermal annealing under vacuum led to a marked increases in Curie temperature and carrier concentration. That, in turn, raised the RT ferromagnetism in CoFe-doped ZnO films. Biegger *et al.*[9] reported the oxygen-vacancy-induced ferromagnetism in ZnCoO thin films, grown under oxygen-poor conditions, using magnetron sputtering. Contrarily, Lin *et al.*[10] attributed the enhanced magnetic moment to the increase in Co concentration and the number of Zn vacancies present in oxygen-rich Co-doped ZnO films, prepared by sol-gel technique. Recently, Lu *et al.*[11] observed that as-deposited ZnCoO thin films were non-magnetic, whereas RT ferromagnetism was witnessed in a ZnCoO system when annealed in Ar atmosphere. However, Jin *et al.*[12] have not found any ferromagnetic behavior in TM (Cr to Cu) doped ZnO thin films, prepared using laser molecular beam epitaxy (LMBE).

Similarly, absence or presence of RT ferromagnetism in TM-doped ZnO bulk samples has also been acknowledged by different researchers. Deka *et al.*[13] prepared poly-crystalline Co-doped ZnO samples using a low-temperature auto-combustion technique. Ferromagnetic behavior with Curie temperature above RT was found in these samples. Bouloudenine *et al.*[14] did not observe any ferromagnetic interactions in Co-doped ZnO nano-crystalline powder samples, synthesized with hydro-thermal method. It was reported that free carriers strongly influenced the magnetic behavior of the ZnCoO system. Deepak *et al.*[15] also reported the absence of net ferromagnetic behavior in ZnCoO powder samples, prepared with decomposition method at low temperature. Sharma *et al.*[16] observed paramagnetism in air sintered and ferromagnetism in the ZnCoO sample annealed in Ar/H_2 environment. Duan *et al.*[17] suggested that an insufficient concentration of donor electrons might be the cause of the absence of ferromagnetism in Co-doped ZnO. Cong *et al.*[18] achieved ferromagnetism only in a

*Supported by the Higher Education Commission (HEC) of Pakistan under the indigenous Ph.D. fellowship 5000 Scheme.
**Corresponding author. Email: murtaza092@yahoo.com
© 2011 Chinese Physical Society and IOP Publishing Ltd

ZnCoO sample annealed in Ar atmosphere. Through first principle calculations, Chen *et al.*[19] predicted the shift of anti-ferromagnetic to ferromagnetic behavior by introducing additional defects in the system. Xu *et al.*[20] detected paramagnetism with weak anti-ferromagnetic exchange interactions in the Co-doped ZnO system, synthesized by using the sol-gel method. Recently, Dinesha *et al.*[21] achieved RT ferromagnetism in a single-phase Fe and Co co-doped ZnO material, prepared by the solution-combustion method. These controversies among researchers for the magnetic behavior of the ZnCoO system seem to be very sensitive to preparation techniques, crystal structure and type of dopant. In this work, we attempt to produce Co doped ZnO and Co-Al co-doped ZnO in pure phase form in order to explore the exact magnetic behavior of these compositions. Moreover, the outcome of Al^{3+} substitution at Zn^{2+} sites is also briefly discussed.

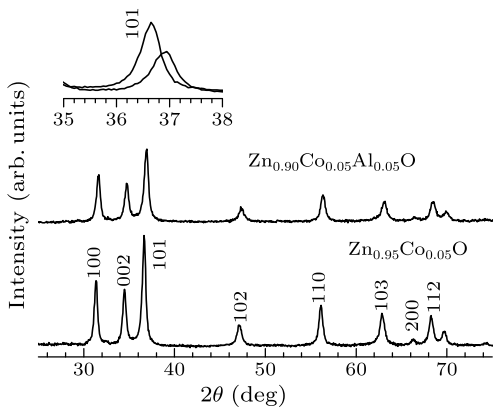

Fig. 1. XRD patterns of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples.

$Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ bulk samples were prepared using the solution combustion method. Nominal stoichiometric compositions of zinc nitrate [$(Zn(NO_3)_2{\cdot}6H_2O$], cobalt nitrate [$(Co(NO_3)_2{\cdot}6H_2O$] and citric acid ($C_6H_8O_7$) with 1:2 metal nitrates (MN) to citric acid (CA) ratio were dissolved in 100 ml de-ionized water. All utilized chemicals were of analytical research grade purity. The pH of the prepared solution was measured and maintained at 4 by adding liquid ammonia [NH_3]. This solution was continuously stirred and heated at 200℃. The temperature was raised to 300℃ after attaining the xerogel. The xerogel was converted into fine powder after a self-propagating extensive exothermic reaction. A large amount of gas was evolved during this reaction. Another composition was synthesized in a similar way using an additional chemical, aluminum nitrate [$Al(NO_3)_3{\cdot}6H_2O$)], of analytical purity. The as-burnt samples of powder were mixed and ground to form the pellets using a hydraulic press, these pellets were then sintered at 600℃ for 2 h in a muffle furnace (Ogawa Seiki). X-ray diffraction (XRD) patterns were obtained using a Panalytical X'Pert Pro multi-purpose diffractometer (MPD) for structural studies. The XRD was operated at 40 kV and 40 mA with Cu K_{α_1} radiation ($\lambda = 1.540598$ Å) using a step scan size of 0.02. A S-3700 N (Hitachi Japan) scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) system was employed for compositional and morphological analysis. SEM was operated at 20 kV in SEI mode and micrographs were obtained at magnification of 15000. Temperature-dependent electrical properties were determined by using a two-point-probe setup. The magnetic hysteresis (M–H) loops for magnetic studies were acquired by a 7404-Lakeshore vibrating sample magnetometer (VSM) at RT.

Table 1. Calculated values of lattice parameters and crystallite sizes.

Sample	a (Å)	c (Å)	**Crystallite size (nm)**
$Zn_{0.95}Co_{0.05}O$	3.2901	5.3177	54.35
$Zn_{0.90}Co_{0.05}Al_{0.05}O$	3.2651	5.2464	39.33

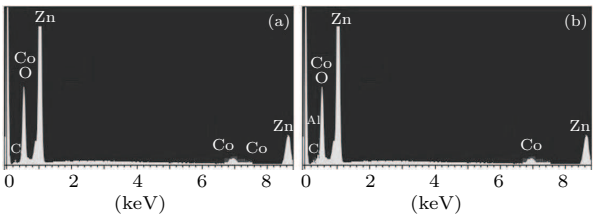

Fig. 2. EDX spectra of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples.

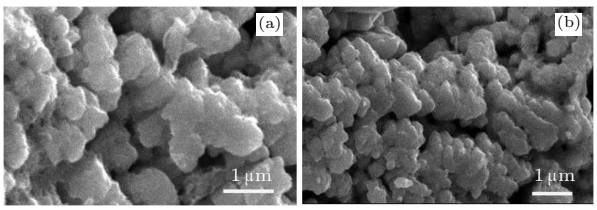

Fig. 3. SEM micrographs of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples.

Figure 1 shows the XRD patterns of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples. Both materials show a hexagonal wurtzite structure similar to ZnO, which is exactly in agreement with previous reports that the structure of host ZnO is normally preserved when lightly doped with TMs.[22,23] This shows that dilute doping of Co or Co+Al in ZnO does not disturb the ZnO space group $P6_3mc$ crystal system. Furthermore, no other second or impurity phase is detected. Hence, it is found that Co and Al ions have partially substituted the host Zn sites without deforming the crystal structure. Moreover, XRD patterns indicate different peak positions, intensities, as well as width in the Co and (Co+Al)-doped ZnO samples as shown in the inset of Fig. 1. This variation

is expected because of the difference in ionic radii of various dopants. It is well recognized that lattice constants are affected by the defect concentration.[24,25] The doping of Co or Co+Al in ZnO might produce some deformation in structure. The atomic radius of Al (0.535 Å) is less than that of Zn (0.74 Å),[26] which manifests as a shrinkage in the lattice parameters a and c, as shown in Table 1. The estimated average crystallite size was calculated by considering the x-ray peak broadening of the most intense diffraction peak (101) for both samples, using the Scherrer formula[27] $D_{hkl} = \frac{k\lambda}{\beta \cos\theta}$. Here θ is the Bragg angle, λ represents the wavelength (λ=1.5405 Å) of Cu K_α radiation, $D_{h,k,l}$ denotes the average crystallite size and β is the full-width at half-maximum (FWHM) in radian. The evaluated sizes of the sample crystallites are listed in Table 1. The size of crystallites decreases with doping of Al. This effect can be easily correlated with the decrease in lattice parameters, owing to smaller ionic radius of the Al substituting Zn, thus causing slight distortions in the Al-doped ZnO lattice leading to a smaller particle sizes.

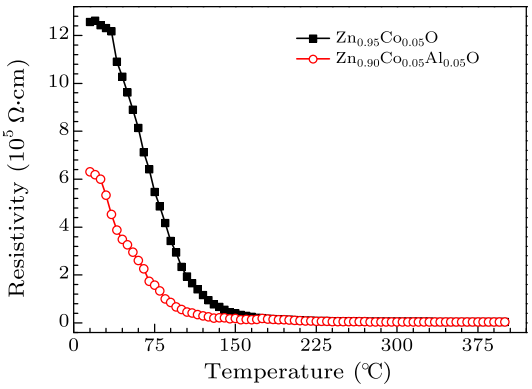

Fig. 4. Temperature versus resistivity graph of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples.

The elemental composition of Co and (Co+Al)-doped ZnO is extracted from EDX, which corroborates the elemental incorporation of Co and Al, as shown in Figs. 2(a) and 2(b). The EDX spectra of the samples reveal the presence of Zn, Co, Al and O, and their contents are in close agreement with the elemental compositions of the dissolved reactants.

Figures 3(a) and 3(b) show the SEM micrographs of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples, respectively. These SEM micrographs indicate the high-quality crystals in both the samples. The grains seem to be mostly uniform in size and shape. They demonstrate the formation of high crystallanity of the samples with the solution combustion method. The size of grains in the (Co+Al)-doped ZnO sample is clearly less than Co-doped ZnO.

The resistivity of both samples decreases with the increase of temperature. It depicts the semiconductor nature of the materials, as shown in Fig. 4. The presence of Zn^{2+} interstitials and oxygen vacancies in ZnO matrix is mainly responsible for n-type conductivity. It is directly related to the concentration of carriers or electrons. The substitution of Al^{3+} at Zn^{2+} sites introduces an extra valence electron in the matrix. Maldonado *et al.*[28] reported in a quantum mechanical study that doping of Al in ZnO generates electron-polarons of a large radius. The n-type conductivity is significantly enhanced due to these polarizable conduction electrons. It is well established[29,30] that Al substitution at Zn sites in the ZnO system increases the concentration of carriers, resulting in a decrease of electrical resistivity. Therefore, the (Co+Al)-doped sample exhibits a low value of resistivity than Co-doped ZnO.

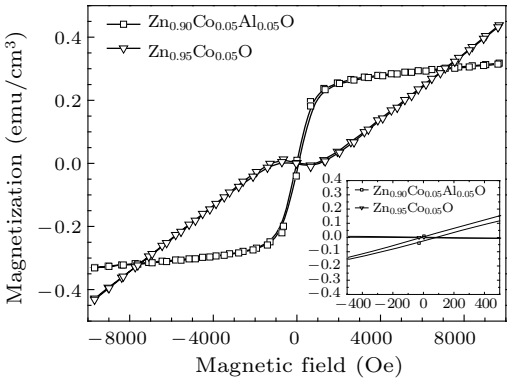

Fig. 5. Magnetic hysteresis (M–H) loops of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples.

The RT magnetic properties of the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.05}Al_{0.05}O$ samples were investigated by VSM. The magnetic hysteresis (M–H) loops were obtained by applying a magnetic field of 10 kOe, as shown in Fig. 5. No ferromagnetic behavior was detected in the Co-doped ZnO sample. However, a marked RT ferromagnetism is evident from the loop of the (Co+Al)-doped ZnO sample. It has been confirmed that crystallization quality strongly influences the magnetic behavior.[31] SEM micrographs show the fine quality of crystals in both the samples. However, the absence of magnetic behavior in simple Co-doped ZnO is attributed to the insufficient concentration of carriers, which is in accordance with a work reported previously.[32] It has also been reported that ferromagnetism may originate from Co_3O_4 such as secondary phases in the ZnCoO system.[33] No impurity or second phase appear in both the samples. According to the Ruderman–Kittel–Kasuya–Yoshida (RKKY) theory,[34,35] ferromagnetic interactions in DMSs arise from the exchange interactions between local spin-polarized electrons (for instance, the electrons of Co^{2+} ions) and conductive electrons. The double exchange[36] and the mean field Zener model[37] have also been reported for the possible mechanisms behind the ferromagnetic behavior of Co-doped ZnO

based DMSs. Moreover, it was also observed that ferromagnetism in the ZnCoO system might arise due to simple Co substitution at Zn sites[38] or oxygen vacancies.[39] Hence, the origin of RT ferromagnetism in ZnCoO DMS is still a somewhat controversial subject. Recently, Zhang and co-workers[40] predicted that Al plays an important role for the achievement of ferromagnetism in a ZnCoO system via first principle calculations. Free carriers (electrons) play a vital role in the establishment of a magnetic phase and hence the ferromagnetism in ZnO doped with magnetic impurities. The magnetic moment and coercivity values evaluated from the M–H loop of the (Co+Al)-doped ZnO sample were observed to be 0.0044 $\mu_{\rm B}$/Co and 88.29 Oe, respectively. Hence, it can be concluded by correlating the electrical and magnetic measurements that free carriers are responsible for the RT ferromagnetic behavior in the Al-doped ZnCoO system.

In summary, the role of Al in a ZnCoO system for the achievement of RT ferromagnetism has been investigated. The ZnCoO and Al-doped ZnCoO samples are synthesized by using an inexpensive solution combustion method and characterized by XRD, EDX, SEM, temperature-dependent resistivity measurements and VSM for the study of structural, compositional, morphological, electrical and magnetic properties, respectively. It is observed that the wurtzite-type hexagonal structure of ZnO is not disturbed by the dilute dopants, besides variations in the unit cell dimensions. The additional doping of Al in ZnCoO strongly influences the concentration of free carriers, as is evident from the decrease in temperature-dependent resistivity. Consequently, ferromagnetic interactions observed at RT are attributed to the generation of sufficient free carriers with doping of Al in ZnCoO.

References

[1] Ohno H, Chiba D, Matsukura F, Omiya T, Abe E, Dietl T, Ohno Y and Ohtani K 2000 *Nature* **408** 944
[2] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 *Science* **291** 854
[3] Sharma P, Gupta A, Rao K V, Owens F J, Sharma R, Ahuja R, Guillen J M O, Johansson B and Gehring G A 2003 *Nature Mater.* **2** 673
[4] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 *Science* **287** 1019
[5] Sato K and Yoshida H K 2000 *Jpn. J. Appl. Phys.* **39** L555
[6] Yang P D, Yan H Q, Mao S, Russo R, Fohnson F, Saykally R, Morris N, Pham F, He R R and Choi H J 2002 *Adv. Funct. Mater.* **12** 323
[7] Ueda K, Tabata H and Kawai T 2001 *Appl. Phys. Lett.* **79** 988
[8] Cho Y M, Choo W K, Kim H, Kim D and Ihm Y E 2002 *Appl. Phys. Lett.* **80** 3358
[9] Biegger E, Fonin M Rudiger U, Janben N, Beyer M, Thomay T, Bratschitsch R and Dedkov Y S 2007 *J. Appl. Phys.* **101** 073904
[10] Lin Y J, Tsai C L, Chen W C, Liu C J, Horng L, Shih Y T, Lin Z R and Wang J F 2008 *J. Cryst. Growth* **310** 3763
[11] Lu Z L, Bian X F, Zou W Q, Xu M X and Zhang F M 2010 *J. Alloys Compd.* **492** 31
[12] Jin Z, Fukumura T, Kawasaki M, Ando K, Saito H, Sekiguchi T, Yoo Y Z, Murakami M, Matsumoto Y, Hasegawa T and Koinuma H 2001 *Appl. Phys. Lett.* **78** 3824
[13] Deka S, Paricha R and Joy P A 2004 *Chem. Mater.* **16** 1168
[14] Bouloudenine M, Viart N, Colis S and Dinia A 2004 *Chem. Phys. Lett.* **397** 73
[15] Rao C N R and Deepak F L 2005 *J. Mater. Chem.* **15** 573
[16] Sharma V K and Varma G D 2008 *Cryst. Res. Technol.* **43** 1046
[17] Duan L B, Chu W G, Yu J, Wang Y C, Zhang L N, Liu G Y, Liang J K and Rao G H 2008 *J. Magn. Magn. Mater.* **320** 1573
[18] Cong C J, Hong J H and Zhang K L 2009 *Mater. Chem. Phys.* **113** 435
[19] Xiang C, Dan H, Wen J D and Yu J Z 2009 *Phys. Lett.* A **373** 391
[20] Qingyu X and JunY 2010 *Physica* B **405** 1216
[21] Dinesha M L, Jayanna H S, Mohanty S and Ravi S 2010 *J. Alloys Compd.* **490** 618
[22] Chuanwei C, Guoyue X, Haiqian Z and Yan L 2008 *Mater. Lett.* **62** 1617
[23] Guangqing P, Changtai X, Linjun W, Xing L, Xinbing J and Jun X 2007 *Scripta Mater.* **56** 967
[24] Park S Y, Kim P J, Y P Lee, Shin S W, Kim T H, Kang J H and Rhee J Y 2007 *Adv. Mater.* **19** 3496
[25] Li X L, Wang Z L, Qin X F, Wu H S, Xu X H and Gehring G A 2008 *J. Appl. Phys.* **103** 23911
[26] Lotus A F, Kang Y C, Walker J I, Ramsier R D and Chase G G 2010 *Mater. Sci. Eng.* B **166** 61
[27] Guangqing P, Feng W, Changtai X, Jungang Z, Xing L and Jun X 2008 *Curr. Appl. Phys.* **8** 18
[28] Maldonado F and Stashans A 2010 *J. Phys. Chem. Sol.* **71** 784
[29] Shou Y K, Wei C C, Fang I L, Chin P C, Hao C K, Shing C W and Wen F H 2006 *J. Cryst. Growth* **287** 78
[30] Vitoratos E, Sakkopoulos S, Anestis C, Spiliotopoulos J, Govender K, Boyle D S and O'Brien P 2005 *Ionics* **11** 259
[31] Jing M, Weichang H, Ruiying L and Huaizhe X 2008 *Mater. Lett.* **62** 403
[32] Duan L B, Chu W G, Yu J, Wang Y C, Zhang L N, Liu G Y, Liang J K and Rao G H 2008 *J. Magn. Magn. Mater.* **320** 1573
[33] Xueyun Z, Shihui G, Dongsheng Y, Yalu Z and Yuhua X 2008 *Physica* B **403** 3336
[34] Sharma V K, Xalxo R and Varma G D 2007 *Cryst. Res. Tech.* **42** 34
[35] Priour D J, Hwang E H and Sarma S D 2004 *Phys. Rev. Lett.* **92** 117201
[36] Li B B, Shen H L, Zhang R, Xiu X Q and Xie Z 2007 *Chin. Phys. Lett.* **24** 3473
[37] Yang J H, Zhao L Y, Ding X, Yang L L, Zhang Y J, Wang Y X and Liu H L 2009 *Mater. Sci. Eng.* B **162** 143
[38] Zhang X M, Mai W, Zhang Y, Ding Y and Wang Z L 2009 *Solid State Commun.* **149** 293
[39] Singhal R K, Arvind S, Xing Y T, Sudhish K, Dolia S N, Deshpande U P, Shripathi T and Saitovitch E B 2010 *J. Alloys Compd.* **496** 324
[40] Zhang T, Song L X, Chen Z Z, Shi E W, Chau L X and Zhang H W 2009 *Appl. Phys. Lett.* **89** 172502