Study of Room Temperature Ferromagnetism for Cobalt and Manganese doped ZnO Diluted Magnetic Semiconductor

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Abstract. We report the results of electronic and magnetic properties of poly-crystalline Zn₁₋ₓMₓO (M = Co and Mn) pellets studied by XRD, VSM and XPS. The specimens were synthesized by solid state reaction method using high purity oxides. Samples exhibit Wurtzite hexagonal symmetry and show interesting magnetic properties. The Co (5%) doped sample prepared by heating in air shows a paramagnetic state in agreement with several claims. But the sample prepared by heating in Ar atmosphere depicts ferromagnetic ordering. Addition of 2% Mn in it further enhances its magnetic moment. The specimens ZnCoO (Ar heated) and ZnCoMnO were hydrogenated at 550°C that caused a significant change in their magnetization. The Co doped ZnO shows a robust increment in the magnetic moment but the Mn doping does not seem to respond to hydrogenation. O 1s XPS results show clear evidence of oxygen depletion for the samples prepared by heating in Ar atmosphere and a further depletion upon hydrogenation. Results suggest oxygen vacancies as the basic origin for room temperature ferromagnetism in doped ZnO.

1. Introduction
Researchers have carried out extensive studies of diluted magnetic semiconductors (DMS), in which transition metal atoms are introduced into the lattice, thus inserting local magnetic moments into their lattice [1-6]. But despite a lot of efforts there is no agreement on the presence and the origin of room temperature ferromagnetism (RTFM) in the DMS’s with different morphologies. The experimental results regarding RTFM in Co doped ZnO system, in thin films, bulk, polycrystalline and nanocrystalline samples differ widely. In case of thin films, there are many reports of RTFM, some of which attribute the observed RTFM to Co clustering [7,8]. In some cases RTFM is thought to be intrinsic in nature [9,10]. Double exchange interaction has also been proposed as an alternative explanation of RTFM [11]. There are reports of FM in ZnO:Co bulk samples due to Co clustering [12]. In the case of polycrystalline bulk samples, prepared by the solid-state reaction method, many groups have reported paramagnetic (PM)

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behaviour at RT [13-15]. RTFM in a ZnO:Co system has, however, been reported when the samples were either co-doped with CuO [13] or hydrogenated [14, 15]. The observed RTFM in hydrogenated samples was attributed either to the appearance of Co clusters [14] or oxygen vacancies [15]. We have studied electronic and magnetic properties of single phase polycrystalline ZnCoO and ZnCoMnO samples with 5% Co and 2% Mn concentration, before and after hydrogenation. Low Mn doped (2%) ZnO sample had shown clear evidence of RTFM [16] so it was interesting to see how Co and Mn weigh together in FM ordering. This might be useful to understand some aspects regarding the mechanism of RTFM in DMS’s.

2. Experimental procedure

The Zinc (II) oxide (purity 99.99%), cobalt (III) oxide and manganese (IV) oxide (purity 99.999% each) powders were used to prepare the samples i.e. Zn_{0.95}Co_{0.05}O, Zn_{0.93}Co_{0.05}Mn_{0.02}O. The appropriate amounts of oxide powders were mixed and ground thoroughly for long period (~12 hrs) to ensure homogeneity. The ground mixture was calcined at 500°C for 14 hrs. These were again ground for extended periods and heated at 800°C for 10 hrs raising the temperature slowly in microprocessor controlled furnace. The resulting lumps were again ground and pellets prepared using a hydraulic pressure of ~8 tons. The pellets were sintered at 500°C for ~18 hrs. The samples were hydrogenated for ~ 5 hrs at 550°C in cylindrical quartz tube in a locally fabricated furnace. XRD patterns were collected on a Rigaku x-ray diffractometer equipped with CuKα radiation. The scans were taken from 10 to 90° with a step size of 0.05° and Rietveld profile refinements carried out using FULLPROF Program [17]. We recorded the patterns again for the sintered pellets to rule out presence of any small impurity peaks. But we found negative results and the patterns were found to be exactly repeated with no signature of any such peaks. The hysteresis loops were measured by vibrating sample magnetometer (VSM) at CBPF, Brazil. The O1s core level photoemission spectra were measured using x-ray photoelectron spectrometer at IUC, Indore, India. The pellets were scraped uniformly and spectra recorded after minimizing the feature coming from carbon contamination of the surface (C 1s peak). The vacuum in the chamber was ~4.4 × 10^{-10}Torr. So there was least possibility of samples getting contaminated again still we scraped the samples in situ to ensure uncontaminated surface. Then there was no chance of any carbon coming again on the samples. Final spectra were taken after minimizing the feature coming from carbon contamination of the surface (C 1s peak). No shift was observed due to charging of the samples. Etching or sputtering was avoided due to fear of change of surface composition as these may cause differential removal of some light elements from the surface.

![Figure 1, 2 (a), (b). XRD pattern of ZnO and fitted patterns of Zn_{0.95}Co_{0.05}O (Ar heated) and ZnCoMnO.](image)
3. Results and discussion
3.1 Characterization and crystal structure
Figure 1 shows the indexed XRD pattern of the heat treated pure ZnO powder and figures 2 (a) and (b) show the fitted patterns of only Zn_{0.95}Co_{0.05}O (Ar heated) and Zn_{0.93}Co_{0.05}Mn_{0.02}O recorded at 300K. The patterns show the single phase ZnS type Wurtzite symmetry with no signature of any impurity peak/other phase. The Rietveld refinement were carried out using the P6_{3}mc space group (No.186, Z=2), with each atom in the Wurtzite hexagonal structure residing on the 2b Wyckoff position with the Zn atoms at (1/3,2/3,0) and the O atoms at (1/3,2/3,z) co-ordinates. In the refinement process the Mn and Co occupancies were varied for the two Zn and O sites to locate the exact site of dopants that was very vital. The cell parameters listed in table 1 confirm the single phase nature and stoichiometry of samples.

3.2 Magnetization results
Hysteresis curve for ZnO pellet depicted no sign of any FM ordering, instead it shows a clear diamagnetic character (figure 3). Figures 4 show the hysteresis curves for Zn_{0.95}Co_{0.05}O (prepared by heating in air and that in Ar atmosphere). The Co doped sample prepared by heating in air shows a pure PM state while the sample prepared in Ar atmosphere readily reveal RTFM ordering. The shape of the hysteresis loop for FM samples does not rule out the presence of some para-magnetic (PM) contribution. Therefore, to separate out the PM and the FM contributions we have made fittings to the experimental curves using the method described in our earlier work [16]. Figure 5 displays pure FM contributions for the ZnCoO (Ar heated) sample before and after hydrogenation. The Saturation magnetization (M_s) becomes more than three fold (table 1) and coercivity also increases remarkably upon hydrogenation (figure 5). This is in agreement with the reports that hydrogenation causes a robust increase in Co doped ZnO [14, 15].

![Figure 3](image1.png)
![Figure 4](image2.png)

**Figure 3**
Figure 3, 4. Hysteresis curve for ZnO and that for Zn_{0.95}Co_{0.05}O (Ar heated and air heated) at 300K

Figures 6 show hysteresis curves for Zn_{0.93}Co_{0.02}Mn_{0.02}O sample before and after hydrogenation. Firstly, the FM ordering is found to be significantly higher for the Co+Mn doped sample than that for the pure Co doped sample. The saturation magnetization is found to be much higher than the pure Co doped sample (table 1). This clearly indicates that the FM induction processes are additive for the two dopants. Secondly, the ZnCoMnO sample too shows an increase in magnetic moment upon hydrogenation (nearly two times, table 1) but it is not as much as that was found for ZnCoO. If Mn responded to hydrogenation in the same way as the Co did, the moment should have increased to three times. This implies that Mn ions stay passive and don’t make observable contribution to hydrogenation in FM induction mechanism. To confirm this prediction we checked the effect of hydrogenation on 2% Mn doped ZnO sample separately (reported to show RTFM [16]). But no enhancement in its FM properties was noted upon hydrogenation (not shown, here) confirming our prediction with regard to ZnCoMnO.
3.3. Oxygen 1s XPS data

Our main objective was to find out how oxygen content is varied upon hydrogenation in these samples and whether it can be correlated to their magnetic properties. We employed powerful XPS technique and measured O 1s core level spectra. Prior to measuring the spectra the C 1s peak was minimized by scraping the sample surfaces to get a clean surface. Oxygen 1s spectra are shown in the figure 7 for Ar heated ZnCoO sample. The spectra are asymmetric indicating some surface contamination i.e. possibility of multi-component oxygen species in the near-surface region of the samples. Therefore, spectra were fitted by three Gaussians located at ~531.2, 532.7, 533.5 eV. The high energy peaks centered at about 532.7 and 533.5 eV are due to the chemisorbed oxygen of the surface hydroxyl, –CO\(_3\), absorbed \(\text{H}_2\text{O}\), absorbed \(\text{O}_2\) or mainly due to the surface contamination. However, the most intense first peak at \(~531.2\) eV is due to the O1s contribution from the samples. Our main interest lies in this feature. Figure 8 compares the spectra for ZnCoO samples (air heated, Ar heated and Ar heated hydrogenated). The intensity of O 1s peak clearly lowers in the FM sample heated in Ar than that in PM sample heated in air. Upon hydrogenation the peak lowers further, appreciably, indicating that O content decreases significantly upon hydrogenation in it. The intensities of the first Gaussian (corresponding to Oxygen 1s feature) have been displayed in the inset of
figure 8 for more clarity. The spectra for ZnCoO (Ar heated) and ZnCoMnO (before and after hydrogenation) are shown in figure 9. The intensity under the main peak is nearly same for the ZnCoO and ZnCoMnO showing a comparable O content, but it lower remarkably upon hydrogenation of Co+Mn sample showing a depletion of oxygen.

4. Conclusions and future outlooks

The Zn$_{1-x}$M$_x$O (M=Co, Mn) samples were synthesized and their magnetic and electronic properties investigated using XRD, VSM and XPS techniques. We make following conclusions:

1. We have convincing evidence to confirm that Co and Mn ions induce FM ordering in ZnO lattice and the two have additive effect in inducing of the ordering. The Reitveld analysis has clearly eliminated any second-phase formation as the possible source of the magnetic behavior. Magnetization shoots up further by hydrogenation in Co doped samples but Mn doping stays passive in that regard.

2. Some reports reveal that FM ordering in ZnO originates from defects on the Zn sites and not from oxygen vacancies [18, 19] and oxygen annealing has no effect on magnetic moment, like that in case of TiO$_2$ and HfO$_2$ films. But our findings don’t support this and rather indicate that the observed magnetic behavior is directly related to the presence of oxygen vacancies. These defects might mediate the exchange coupling of Co and Mn spins through electron doping of the matrix and thus cause FM ordering. Our findings point that oxygen vacancies generated, irrespective of the method used, whether by heating during calcination or post heating treatment, play vital role in ordering mechanism, over and above various other possible interactions. This is in agreement with the reports claiming that oxygen deficient samples which show RTFM, turn insulating and non-FM, upon annealing in excess oxygen [20, 21].

3. We are tempted to predict that valency of doped cation should also be important in this regard. The trivalent or higher valent cations would tend to absorb excess oxygen in the lattice, from the charge neutrality viewpoint, therefore, the FM ordering is likely to be quenched in such systems. We plan to measure Zn, Mn and Co 2p XPS spectra to investigate the cationic valence states and try to correlate them to the oxygen contents that will be helpful to understand more conclusively the role of impurity and vacancy states. XAFS, RIXS, XMCD studies are also underway to conclude how changes in electronic structure could correlate to the observed magnetic properties.

References

[1] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science 287 1019
[2] Xueyun Zhou, Shihui Ge, Dongsheng Y, Yalu Z and Yuhua X 2008 J. Alloys and Compounds 463 L9
[3] Cao P, Zhao D X, Zhang J Y, Shen D J, Lu Y M, Fan X W and Wang X H 2007 Physica B 392 255
[4] Zhang Y B, Li S, Tan T T and Park H S 2006 Solid State Commun. 137 142
[5] M Gacic, G Jakob, C Herbot, H Adrian, T Tietze and S Brueck 2007 Phys. Rev. B 75 205206.
[6] H. Yang, L. Zhao, Y. J. Zhang, Y. Wang and H. Liu 2009 J. Alloys and Compounds 473 543
[7] Park J H, Kim M G, Jang H M, Ryu S and Kim Y M 2004 Appl. Phys. Lett. 84 1338
[8] Kim J H, Kim H, Kim D, Ihm Y E and Choo W K 2002 J. Appl. Phys. 92 6066
[9] Kittilstved K R, Norberg N S and Gamelin D R 2005 Phys Rev. Lett. 94 147209
[10] Cui J, Zeng Q and Gibson U J 2006 J. Appl. Phys. 99 08M113
[11] Han X, Wang G, Jie J, Zhan X and Hou J G 2006 Thin Solid Films 491 249
[12] Deka S and Joy P A 2005 Solid State Commun. 134 665
[13] Lin H et al 2004 J Appl. Phys. Lett. 85 621
[14] Wang Y, Sun L, Kong L, Kang J, Zhang X and Han R 2006 J. Alloys and Compounds 423 256
[15] Manivannan A, Dutta, Glaspell G and Seehra M S 2006 J. Appl. Phys. 99 08M110
[16] Singhal R K, Dhawan M S, Gaur S K, Dolia S N, Kumar S, Shripathi T, Deshpande U P, Xing Y T, Saitovitch E and Garg K B 2009 J. Alloys and Compounds 477 379
[17] Rodriguez-Carvajal J 2003 FULLPROF version 3.0.0., Laboratorie Leon Brillouin CEA-CNRS
[18] Hong N H, Sakai J, and Brizé V 2007 J. Phys.: Condens. Matter 19 036219
[19] Iusan D, Sanyal B, and Eriksson O 2006 Phys. Rev. B. 74 235209/1-8.
[20] Ramachandran S, Narayan J and Prater J T 2006 Appl. Phys. Lett. 88 242503
[21] Qingtao P, Kai H, Shibing N, Feng Y, Shumei L, Deyan H 2007 J.Phys.D:Appl.Phys. 40 6829