

Ferromagnetism in inhomogeneous bulk samples of Co-doped ZnO

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ABSTRACT

We report on the effect of different gaseous environments (air, argon and Ar/H₂) on the structural and magnetic properties of Zn_{0.98}Co_{0.02}O synthesized by the solid state reaction route. We have also studied the effect of different annealing times and temperatures on the as synthesized samples. M-H curves of the air sintered and the argon annealed samples show paramagnetic behavior whereas the samples annealed in the hydrogenated argon (Ar/H₂) environment exhibit ferromagnetic property at room temperature. Based on the structural and magnetic properties it has been found that Co metal clusters are responsible for the observed room temperature ferromagnetism (RTFM) in the hydrogenated samples. Copyright © 2012 VBRI Press.

Keywords: Clusters; annealing; electron microscopy; room temperature ferromagnetism.



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Introduction

Recently, diluted magnetic semiconductors (DMSs) attracted tremendous attention due to their possible applications in the development of emerging spintronics based devices [1, 2]. Soon after the theoretical prediction of room temperature ferromagnetism (RTFM) in transition metal doped ZnO by Dietl et al. [3] and Sato et al. [4] lot of research work started on ZnO based DMS. The first report on RTFM in Co-doped ZnO was made by Ueda et al. [5] in thin films of compositions Zn_{1-x}Co_xO (x = 0.05-0.25) prepared by PLD on sapphire substrates. Later, many other groups studied the magnetic properties of Co-doped ZnO by growing the materials in thin film and bulk forms under varying growth conditions, and reported wide variety of results [6-9]. Some groups [10-11] also observed RTFM in Zn_{1-x}Co_xO nanorods. From the results of various groups it appears that the ferromagnetism in the sample relies very much on the growth conditions such as synthesis temperature and gaseous environment during synthesis. In some cases Co metal clusters have been proposed as the source of ferromagnetism [12]. Recently, Lee et al. [13] showed that ZnCo(9.1%)O and ZnCo(5%)O thin films become ferromagnetic when hydrogenated with Ar/H₂ mixed gas, due to the enhanced ferromagnetic spin-spin interaction in the H-Co coupling. Deka et al. [14] reported ferromagnetism in hydrogenated Zn_{0.95}Co_{0.05}O sample, synthesized by solution combustion method and showed that ferromagnetism is induced due to the formation of Co metal during reduction process. Manivannan et al. [15] found ferromagnetism in hydrogenated Zn_{0.95}Co_{0.05}O because of the oxygen vacancies created under

hydrogenation. It has been reported by several groups [16-19] that oxygen vacancies and interstitial Zn defects plays crucial role in introducing ferromagnetism in Co doped ZnO. Jayakumar et al. [20] studied the magnetic properties of $\text{Zn}_{0.85}\text{Co}_{0.05}\text{Li}_{0.10}\text{O}$ system and found that observed ferromagnetism is due to Co metal clusters. Very recently, several groups [21-23] reported RTFM in nanocrystalline ZnO, HfO_2 , TiO_2 and In_2O_3 without introducing any magnetic ions and they thought that defects or oxygen vacancies are responsible for observed ferromagnetism. These results further raise the controversy about the mechanism of origin of ferromagnetism in DMS, i.e., whether it is intrinsic to the materials or due to some secondary phases present in the samples. In the present work, bulk samples of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ have been synthesized via standard solid-state reaction route. The effect of hydrogenation on the structural and magnetic properties of the synthesized materials has been explored. RTFM has been observed in the hydrogenated (Ar/ H_2 annealed) samples. Evidence of formation of Co metal clusters has been found in the hydrogenated samples.

Experimental

Bulk samples of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ were synthesized via the standard solid state reaction route, where first of all appropriate amounts of ZnO and Co_3O_4 were mixed and ground in an agate mortar. The resulting powder was heated at 450 °C for 15 h in air followed by furnace cooling. After this, the resulting material was reground and pelletized. Finally, the pellets were sintered at 700 °C in air for 12 h followed by furnace cooling. Some air sintered samples were annealed in argon for 6 h at 700 °C. Thereafter, argon annealed samples were further annealed at 700 °C in a mixture of argon and hydrogen gas (Ar 90% + H_2 10%) for 1, 3 and 5 h. Similar treatments were given to the samples synthesized by sintering in air at 800 °C. Henceforth for simplicity, the samples synthesized by sintering in air at 700 °C and 800 °C will be represented as D7 and D8, respectively. In the D7 series: D7AR will represent the argon annealed sample, D7AR-1H2, D7AR-3H2 and D7AR-5H2 will represent the argon annealed samples further annealed in Ar/ H_2 atmosphere for 1, 3 and 5 h, respectively. Similarly we have D8 series: D8AR, D8AR-1H2, D8AR-3H2 and D8AR-5H2. The crystal structure of the samples was studied using an X-ray diffractometer (XRD - BRUKER D8 ADVANCE) employing Cu-K_α (1.54 Å) radiation. The temperature dependence of the magnetization (M-T) and magnetic hysteresis (M-H) loops were measured using Vibrating Sample Magnetometer (VSM - Model 155 Princeton Applied Research). Microstructural and chemical analysis of the samples is done using Field Emission Scanning Electron Microscope (FESEM - FEI Quanta 200 ESEM FEG) equipped with an Oxford Inca Energy Dispersive X-ray (EDAX) detector.

Results and discussion

The X-ray diffraction patterns of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ samples of D7 and D8 series annealed in different atmospheres are shown in Fig. 1 and 2, respectively. From Fig. 1, it is clear that most of the diffraction peaks of each pattern correspond to ZnO wurtzite structure. In addition to this,

there are few weak peaks in the patterns of air sintered samples (D7) that correspond to unreacted Co_3O_4 . The peaks corresponding to unreacted Co_3O_4 are also present in D7AR samples. The XRD patterns of the hydrogenated samples, however, show peaks corresponding to CoO and Co metal and there are no peaks corresponding to unreacted Co_3O_4 as observed in the D7 and D7AR samples. The occurrence of Co peaks in the hydrogenated samples suggests that after hydrogenation Co_3O_4 get reduced into Co. The peak corresponding to CoO disappears in D7AR-5H2 samples. Broadly, similar structural characteristics of the samples of D8 series have been found through XRD studies (see Fig. 2). However, there are some noticeable differences in the XRD patterns of the samples of D8 series as compared to that of D7 series. In the XRD pattern of D8 samples there is only one diffraction peak corresponding to unreacted Co_3O_4 whereas there are two peaks in D7 samples. This may be due to higher sintering temperature of D8 samples. In the hydrogenated samples of D8 series only Co metal appears as secondary phase and no traces of CoO phase is observed. Traces of Co metal are observed in all the hydrogenated samples for both the temperatures.

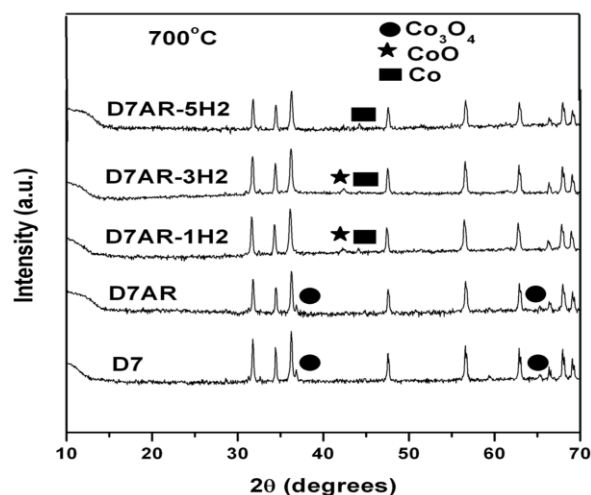


Fig. 1. X-ray diffraction pattern (intensity on logarithmic scale) of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ sintered at 700°C.

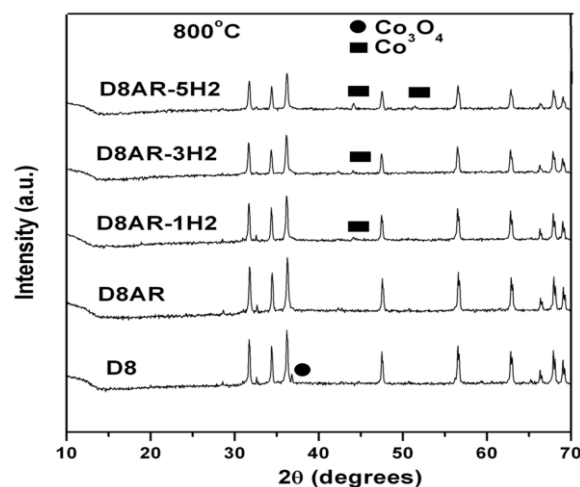


Fig. 2. X-ray diffraction pattern (intensity on logarithmic scale) of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ sintered at 800°C.

Fig. 3 shows the magnetization versus magnetic field (M-H) curves recorded at 300 K for the $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ samples sintered at 700 °C. For the M-H measurements all the samples have been taken in powder form and the diamagnetic contribution from the sample holder has been subtracted. The M-H plots of the D7 and D7AR, show linear variation of magnetization with magnetic field, suggesting paramagnetic behavior of the sample. On the other hand, the M-H curves of the samples annealed in Ar/H_2 (D7AR-1H₂, D7AR-3H₂ and D7AR-5H₂) show presence of hysteresis loops. These results reveal that after annealing in Ar/H_2 the samples become ferromagnetic at room temperature. The variation of Co peak intensity (I_{Co}) obtained from XRD and saturation magnetization (M_s) with annealing time in Ar/H_2 atmosphere of the samples of D7 series is shown in **Fig. 4**.

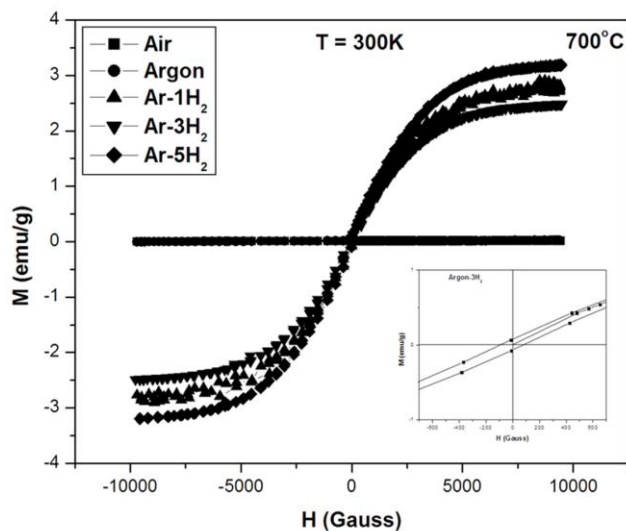


Fig. 3. M-H curves of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ samples sintered at 700°C in different atmospheres.

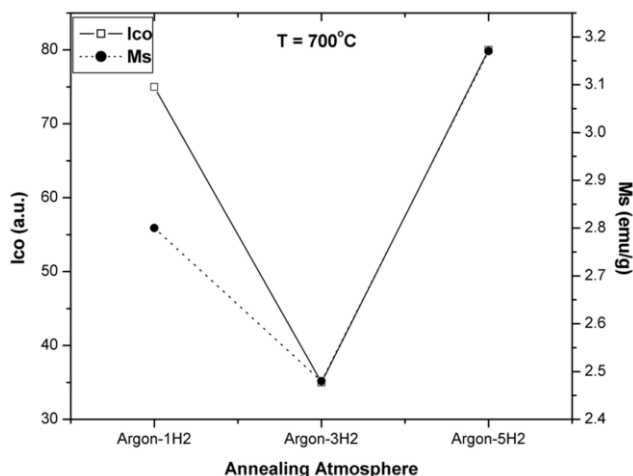


Fig. 4. Variation of I_{Co} and M_s with the different annealing atmospheres at 700°C.

From **Fig. 4**, it is clear that both I_{Co} and M_s have similar variations with annealing time. M-H plots expanded near origin are shown in the inset of **Fig. 3**. The insets show clear splitting in the curves near origin. The magnetization versus magnetic field (M-H) curves measured at 300 K of the $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ samples (D8 series) synthesized by

sintering in air at 800 °C is shown in **Fig. 5**. The M-H curves of the D8 and D8AR shows paramagnetic behavior.

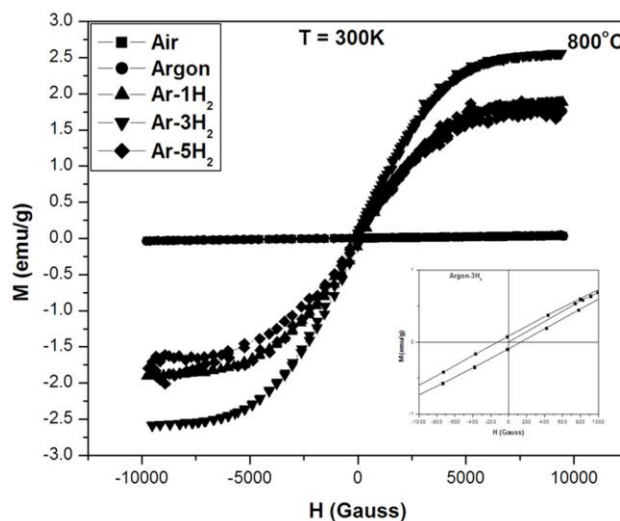


Fig. 5. M-H curves of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ samples sintered at 800°C in different atmospheres.

However, after hydrogenation there is well defined hysteresis loop, suggesting ferromagnetic interactions in the samples as observed for the samples of D7 series. For the samples of D8 series the variation of I_{Co} and M_s with annealing time in Ar/H_2 atmosphere have been shown in **Fig. 6**. I_{Co} and M_s both increase with annealing time up to 3 h and after that I_{Co} increases but M_s decreases. The increase in I_{Co} suggests that concentrations of Co metal clusters increases (visible from XRD and FESEM-EDAX results) as hydrogenation time (t_{H}) increases. This may cause decrease in Co-Co clusters distance below the critical distance and thus promoting antiferromagnetic interaction and hence reduction in the net magnetization of the sample [24]. We found clustering of Co after hydrogenation for both D7 and D8 series of samples but we don't find any correlation of I_{Co} with the hydrogenation time (t_{H}). Intensity of Co cluster depends basically on the microstructure of the samples. All the samples of D7 series have magnetic moment greater than their D8 counterpart because of larger value of I_{Co} of the later. To check the role of Co_3O_4 in producing ferromagnetism in $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$, we make the pure Co_3O_4 pellet by the same procedure as above at 800 °C with $t_{\text{H}} \sim 5\text{h}$. We found that air sintered samples is paramagnetic whereas the hydrogenated sample is ferromagnetic with a strong magnetic moment (see **Fig. 7**). Thus, possibility of reduction of Co_3O_4 into Co is quite high. This further substantiates the possibility of Co clusters in the hydrogenated samples.

The measurement of electrical resistance of the air sintered samples shows high resistance, typically of the order of few mega ohms. The same measurement of the hydrogenated sample shows resistance of the order of few ohms (100-200 Ω). The decrease in resistivity may possibly be due to increase in carrier concentration in the sample or due to the precipitation of Co metal in the sample or both. In order to confirm whether the increase in conductivity is due to increase in carrier concentration or due to precipitation of Co in the hydrogenated samples, we annealed the pure ZnO samples in the hydrogenated argon

(Ar/H₂) at 800 °C for ~ 5 h and measured its resistance. In this case decrease in resistance was very small as compared to Co-doped ZnO. This result suggests that large decrease in resistivity of the hydrogenated Co-doped ZnO is mainly due to formation of small Co metal clusters in the samples.

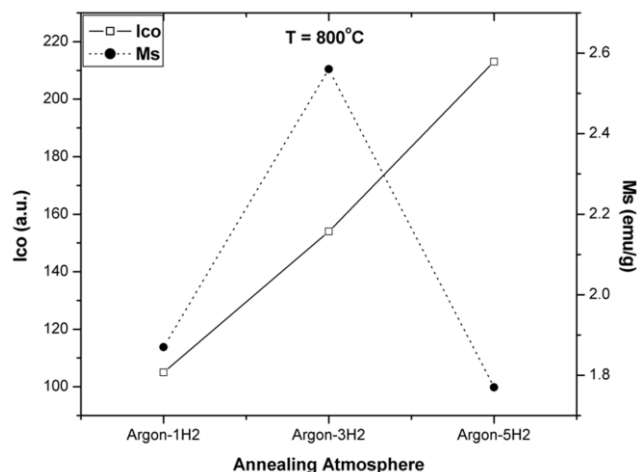


Fig. 6. Variation of I_{Co} and M_s with the different annealing atmospheres at 800°C.

The evidence of formation of Co metal clusters in the hydrogenated samples has also been found during microstructural and chemical analysis of the samples annealed in hydrogenated argon at both the temperatures through FESEM-EDAX. FESEM micrograph and EDAX spectra of air sintered and hydrogen annealed sample for $t_H \sim 5$ h synthesized at 800 °C is shown in **Fig. 8**. EDAX analysis of both the samples indicates the presence of Zn peaks at 1.012 and 8.637 keV, O peak at 0.523 keV and Co peak at 6.929 keV. Au peak at 2.12 keV is coming because gold coating was done on the samples to make them conducting. From the **Fig.**, it is clearly observable that the intensity of Co peak increases as we go from air to hydrogenated samples. Similar, result was observed by Jayakumar et al. [20]. Arrow mark indicates the point where we found Co clusters. These results together with XRD results suggest that the annealing of the samples in Ar/H₂ removes some oxygen from the samples leading to conversion of oxides of Co and Zn into elemental Co and Zn in some portions of the samples. Also, it is clearly visible that as we go from air to hydrogenated argon homogeneity (surface morphology) of the samples decreases which is clear from the FESEM-EDAX results. Thus, we came to conclusion that only the samples having inhomogeneous microstructure possess ferromagnetism. Inhomogeneous microstructure of the Ar/H₂ annealed samples leads to Co enriched area in the ZnO matrix giving rise to Co metal clusters which are responsible for the observed RTFM. The increase or decrease in the net magnetic moment of the sample depends upon the mean Co-Co clusters distance. Similar result is obtained by Tay et al. [25] in Co doped ZnO thin films. Co metal cluster is also visible from the XRD analysis of the Ar/H₂ annealed samples. We found Co clusters in all the Ar/H₂ annealed samples at both the temperatures. But we do not observed any specific trend in the I_{Co} for different t_H at a particular temperature. This is because the probability of formation of Co metal cluster depends on the inhomogeneity in

microstructure of the sample under annealing in Ar/H₂ atmosphere. But since inhomogeneity is probable so does Co clustering in the sample.

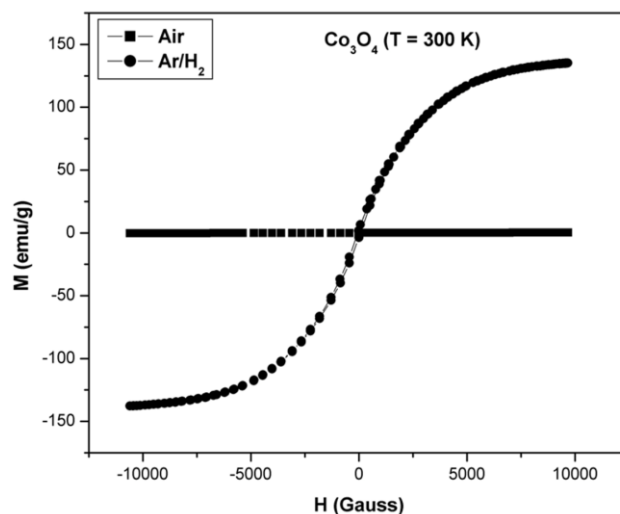


Fig. 7. M-H curves of pure Co_3O_4 samples sintered at 800°C in different atmospheres.

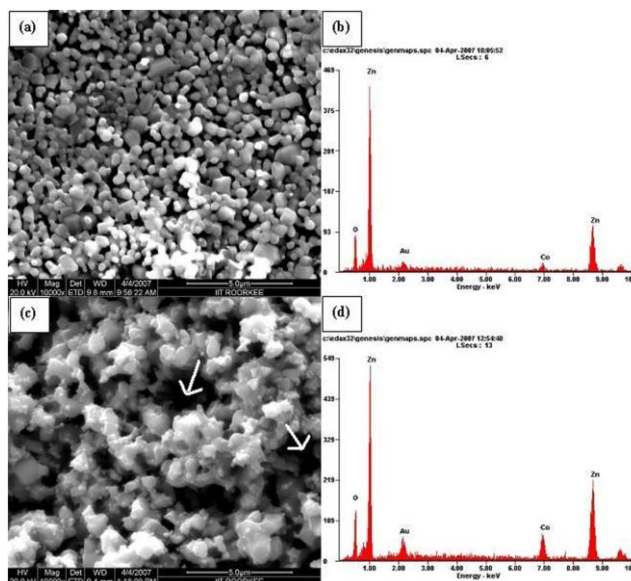


Fig. 8. FESEM micrographs of (a) D8, (c) D8AR-5H2 and corresponding EDAX of (b) D8, (d) D8AR-5H2.

The exact mechanism of ferromagnetism in DMSs is not yet very well understood. However, in the present case Co-metal clusters are responsible for the observed ferromagnetism in the hydrogenated samples of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ at room temperature. Co-metal clusters in the samples are detected by the X-ray diffraction and FESEM-EDAX techniques. The structural characterization of the samples through XRD reveals the presence of Co_3O_4 (antiferromagnetic with $T_N \sim 40$ K) in air sintered and argon annealed samples. CoO, another secondary phase observed in Ar/H₂ annealed samples, is antiferromagnetic with a Neel temperature (T_N) of 291 K. Therefore the observed RTFM in the samples is not due to the presence of any secondary phase other than the Co metal clusters. The sources of origin of ferromagnetism by other mechanisms [20, 26] are also not ruled out.

Conclusion

In the present work, we observed RTFM in the hydrogenated bulk samples of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ and based on the experimental results it has been found that the observed RTFM is mainly due to the presence of Co metal clusters in the hydrogenated samples.

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