Short Communication

Assessment of the H₂ Followed by Air Sintering of Co-doped In₂O₃ Based Diluted Magnetic Semiconductors

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The study shows the influence of Co doping, sintering in hydrogen atmosphere and re-heating on magnetic properties of In_2O_3 . The $In_{0.97}Co_{0.03}O$ samples were prepared by solid state reaction method. XRD patterns shows that Co ions take position of at the In_3 + sites. The investigations at room temperature (RT) concludes that the Co doped In_2O_3 sample had achieved overlapped paramagnetic (PM) properties conquering the diamagnetic (DM) properties of In_2O_3 . Additionally, it was found that the ferromagnetism (FM) is noticeably induced via H_2 -annealing at 300 K. This study also depicts that the sample is finally reverted to the PM state after further long sintering.

Keywords: Diluted magnetic semiconductors, Transition metals, In₂O₃.

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1. INTRODUCTION

Oxide-based diluted magnetic semiconductors (O-DMSs) have received a prodigious attention in technical communal. They manipulate both of the spin and charge degree of freedoms through contamination of transition elements such as Mn, Fe, Co, Cr, etc. into a host like ZnO, ZnS, In₂O₃, SnO₂, TiO₂ etc [1-6] to develop novel multi-functional spintronics devices. The better applicability of In₂O₃ is owing to its excellent properties like its transparency, cubic bixbyite crystal structure and n-type degenerate semiconducting material with direct band gap of ~ 3.75 eV as compared to other DMSs [7]. The sintering condition plays a crucial role on the magnetic properties of DMSs. It is scholastically verified that the sintering in hydrogen atmosphere boosts the magnetic saturation and coercivity [8, 9].

At present, only few investigations reported on of Codoped In_2O_3 nanoparticles. Henceforth, it is of prodigious attention to investigate the possibility of FM properties in Co-doped In_2O_3 nanoparticles. In the present work, the samples are prepared by doping Co (6 %) into In_2O_3 and studied the effect of H2-sintering and then re-sintering on magnetic properties of the samples.

2. EXPERIMENTAL DETAILS

Solid state reaction method [10, 11] is used to prepare the composition of $In_{0.97}Co_{0.03}O$ using In_2O_3 (purity 99.99%: Aldrich) and Co_2O_3 (purity 99.999%: Alfa Aesar) powders. Now the blended samples are taken in a quartz tube and placed in reduction furnace for post-annealing in the presence of hydrogen for ~10 hours at around 550 °C. Afterward, hydrogenated pallets were further heated for 7h in air. Samples were structurally analysed through X-ray diffraction (XRD) technique at 300 K through PHILIPS X'PERT XRD equipped with CuKa radiation. The scans have been taken from scattering angle 20° to 90° with a step size of 0.02°. The Rietveld profile refinements program, FULLPROF, is used to refine the crystalline structures [12]. Magnetic hysteresis loops were analyzed at 300 K and 50 K via vibrating sample magnetometer (VSM).

3. RESULTS AND DISCUSSION

3.1 XRD Data

Figure 1a shows the XRD patterns of the undoped In_2O_3 , $(In_{0.97}Co_{0.03})_2O_3$ and the hydrogenated $(In_{0.97}Co_{0.03})_2O_3$:H samples. All the Bragg's peaks of the samples are observed well indexed to the single phase cubic bixbyite or *C*-type rare earth of In_2O_3 crystalline which validates the non-occurrence of subordinate phases and Co cluster formation.

FULLPROF Program (space group Ia3, no. 206, PCPDF# 06-0416) [13] is used to assess Rietveld profile refinements of XRD patterns of $(In_{0.97}Co_{0.03})_2O_3$ as shown in Fig. 1b. The refinement results ratify that divalent Co^{2+} (0.745 Å) [14] are readily substituting for In³⁺ (0.80 Å)[15] ,however, a slight cell volume shrinkage is witnessed on doping (V = 1035.4 Å3 for pure In₂O₃ and V = 1029.5 Å3 for 6% Co-doping).

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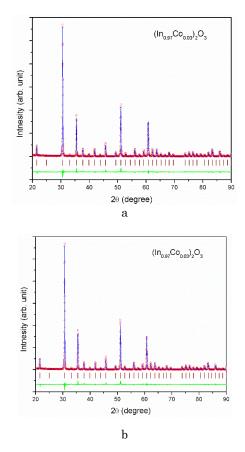


Fig. 1 – XRD patterns of In2O3, $(In_{0.97}Co_{0.03})_2O_3$, hydrogenated $(In_{0.97}Co_{0.03})_2O_3$:H samples (a) Rietveld refinement profiles of XRD of $(In_{0.97}Co_{0.03})_2O_3$ (b)

3.2 Magnetization Data

The M-H loops for undoped In_2O_3 sample indicates a strong DM behavior [16] (Fig. 3). Fig. 3a shows the curves for the $In_{0.97}Co_{0.03}O$ recorded at 300 K. The sample witnesses a PM behavior [17].

Hydrogen in In_2O_3 is acting as a shallow donor impurity; it is thus probable to deliver additional free electrons. Our outcomes (saturation magnetization $(M_s \sim 3.2424 \text{ emu/g})$ and the coercivity (~ 0.0335 T)) evidently show an upswing in concentration of free carriers on hydrogenation (Fig. 3b) which might intermediate the interchange coupling of the Co spins via electron contamination of the matrix. This shows a clear visibility of FM in agreeing with the other studies [8-10]. Both the samples are then heated for approximately two hrs in air at 550 C (heated 1 sample) and appreciable depression in magnetic moment is observed (Fig. 3c). The M-H curve for the heated 1 sample (Fig 3 (d)) shows that

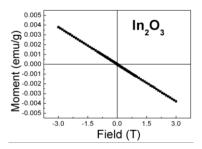
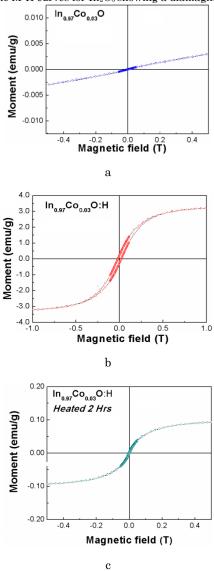


Fig. 2 – The M-H curves for In_2O_3 showing a diamagnetic state



Assessment of the H2 Followed by Air Sintering...

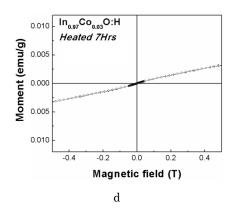


Fig. 3 – M-H loops noted at 300 K for $In_{0.97}Co_{0.03}O$ (a), Hydrogenated $In_{0.97}Co_{0.03}O$ (b), air-sintered 1 sample (2 hrs) $In_{0.97}Co_{0.03}O$ (c) and air-sintered 2 sample (7 hrs) $In_{0.97}Co_{0.03}O$ (d)

the sample is finally returned to the PM state upon further reheating of nearly seven hours. Many investigations also reported that the magnetic parameters improve its performance when the temperature is increased [8, 19, 20].

4. CONCLUSION

The study reveals that pure In_2O_3 is diamagnetic and turns to paramagnetic upon Co doping. The samples were post-annealed in H₂ atmosphere at 300 K. Experimental findings confirms that on hydrogenation, the samples have achieved overlapped PM with FM properties defeating the diamagnetic properties of In_2O_3 . This study is also depicts that the sample is finally resumed to the PM state after re-sintering.

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