Journal of Advances in Nanomaterials, Vol. 2, No. 2, June 2017
https://dx.doi.org/10.22606/jan.2017.22003

Study of the Hydrogenation and Re-heating of Co-doped In_2O_3 based Diluted Magnetic Semiconductors

Rana Mukherji[1*], Vishal Mathur[1], Arvind Samariya[2], Manishita Mukherji[3]

[1] The ICFAI University, Jaipur, India
[2] S.S. Jain Subodh P.G. College, Jaipur, India
[3] Amity University Rajasthan, Jaipur, India
[*]Email: rana.mukherji@gmail.com

Abstract. In this work, the Co^{2+} ions doping effect on the magnetic behaviour of In_2O_3 nanoparticles (NPs) has been discussed. The $In_{0.94}Co_{0.06}O$ sample was prepared by solid state reaction method. According to XRD, the single crystalline phase was identified as the cubic bixbyite crystal structure and doping effect of prepared NPs. The magnetic study at room temperature (RT) revealed that the prepared Co doped In_2O_3 sample had achieved overlapped paramagnetic (PM) properties defeating the diamagnetic (DM) properties of In_2O_3. Furthermore, it was found that the ferromagnetic (FM) is clearly induced by post-annealing in hydrogen atmosphere at 50 and 300 K. This study also depicts that the sample is finally returned to the PM state after re-heating.

Keywords: Diluted magnetic semiconductors, transition metals, In_2O_3.

1 Introduction

Oxide-based diluted magnetic semiconductors (O-DMSs) have attracted much attention due to prospective in spintronics and magneto-optoelectronic applications. Actually, the oxide semiconductors exhibit various advantages such as wide band gap suitable for applications with short wavelength light, transparency and dyeability with pigments, high n-type carrier concentration, capability to be grown at low temperature even on plastic substrate, ecological safety, durability and low cost [1-9]. In addition, large electronegativity of oxygen is expected to produce strong p–d exchange coupling between band carriers and localized spins. The magnetic properties of doped oxide-based semiconductors were seen to be very sensitive to the fabrication process and the processing conditions. Various theoretical and experimental studies have been proposed on the ferromagnetic, paramagnetic, antiferromagnetic, and spin glass properties of transition metal (TM)-doped TiO_2 [9,10], ZnO [11-16], SnO_2 [17-19], as well as In_2O_3 [20-31].

In_2O_3 is a transparent semiconductor with a wide band gap (3.75 eV) and a cubic bixbyite crystal structure that contains 80 atoms per unit cell. [29]. There are numerous reports on room temperature ferromagnetism (RTFM) in In_2O_3 systems doped with TMs [20–24]. Though, the origin of ferromagnetism (FM) is still controversial and numerous exchange mechanisms have been offered to interpret the origin of magnetism. These mechanisms include Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions, bound magnetic polaron models (BMPs), as well as carrier-mediated and charge transfer FMs [30-35]. At present, only few investigations reported on of Co-doped In_2O_3 nanoparticles. Therefore, it is of prodigious attention to investigate the possibility of ferromagnetic properties in nanoparticle form of Co-doping as it can further understanding of future spintronics devices. In the present work , the samples are prepared by doping Co (6%) into In_2O_3 and the effect of hydrogenation and then re-heating on magnetic properties of the samples.

2 Experimental Details

Stoichiometric amounts of Indium (II) oxide (purity 99.99%: Aldrich) and cobalt (III) oxide (purity 99.999%: Alfa Aesar) powders were used to make $In_{0.94}Co_{0.06}O$ through solid state reaction method. [32].The sample was then exposed for hydrogenation for ~5 hrs at 550 °C in a cylindrical quartz tube in a reduction furnace.X-ray diffraction (XRD) analyses of the samples were taken at 300K through

PHILIPS X'PERT X-ray diffractometer equipped with CuKα radiation. The scans were recorded from 20 to 90° with a step size of 0.02°. The crystal structures were refined using the Rietveld profile refinements program FULLPROF [33]. Field dependent magnetization measurements were ascertained at 300 K and 50 K using vibrating sample magnetometer (VSM).

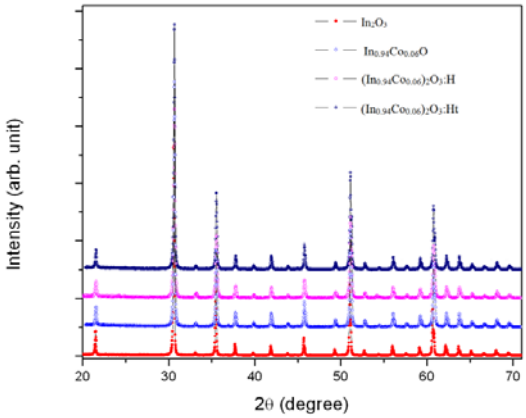

Figure 1a. Indexed XRD patterns of In_2O_3, as-prepared $(In_{0.94}Co_{0.06})_2O_3$, hydrogenated $(In_{0.94}Co_{0.06})_2O_3$:H

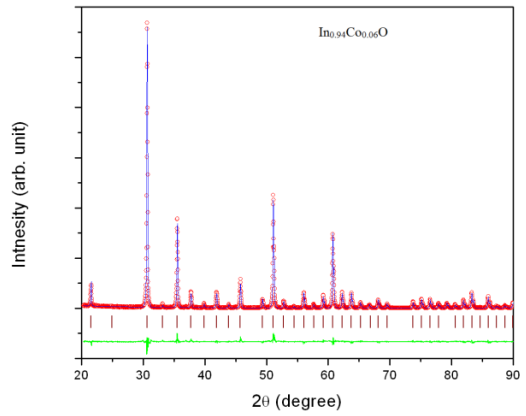

Figure 1b. Refined XRD patterns of the as-prepared sample $(In_{0.94}Co_{0.06})_2O_3$.

3 Results and Discussion

3.1 XRD Data

Fig. 1a shows the XRD patterns of pure In_2O_3, $(In_{0.94}Co_{0.06})_2O_3$ and the hydrogenated $(In_{0.94}Co_{0.06})_2O_3$:H. It is observed that all Bragg peaks are indexed in the cubic bixbyite or C-type rare earth, structure with a lattice parameter a =10.11 Å (space group Ia3, no. 206, PCPDF# 06-0416) without any impurity phase. Rietveld profile refinements of XRD patterns of $(In_{0.94}Co_{0.06})_2O_3$ were analyzed by using the FULLPROF Program (Fig. 1b) [33]. The refinement results ratify that Co^{2+} ions substitute the In^{3+} site and the hydrogenation or long re-heating of the hydrogenated sample did not cause any structural change. A slight cell volume contraction is observed on Co doping (V= 1035.4 Å3 for pure In_2O_3 and V= 1029.5 Å3 for 6% Co doped sample), due to a minor difference in ionic radii of the dopant and the host ions (Co^{2+} :0.745Å and In^{3+} :0.80 Å) [31,32]. Interestingly, upon re-heating of the hydrogenated samples (for 7 or more h) the oxygen contents re-acquire their as-prepared values.

3.2 Magnetization Data

The M-H curves for undoped In_2O_3 sample indicate a strong diamagnetic behavior (Fig. 2). Fig. 3a shows the M-H curves for the as-prepared $In_{0.94}Co_{0.06}O$ recorded at 300 K. The sample shows a paramagnetic behavior when it is doped with Co ($In_{0.94}Co_{0.06}O$) as shown in Fig. 3a.

Hydrogen in In_2O_3 is acting as a shallow donor impurity; it is thus probable to deliver additional conduction electrons. It is observed that the same sample after hydrogenation shows ferromagnetic behavior (Fig. 3b).This exposes that the carrier density improved upon H contamination which might mediate the exchange coupling of the Co spins through electron doping of the matrix which shows a clear visibility of ferromagnetism in agreeing with the other studies [34]. The saturation magnetization (Ms ~ 3.6 emu/g) and the coercivity (~0.0210 T) are significant at 300K (Fig. 3b, Table-2). The enhancing of magnetic properties of the sample with hydrogenation or incorporation of H is already experimentally observed in doped In_2O_3 [1, 8]. In order to estimate the magnitudes of the saturation magnetization, the coercivity and the remanence, the high field (up to 2 T) magnetization measurements were performed for the hydrogenated sample $In_{0.94}Co_{0.06}O$:H at 50 K and 300 K(Figure 4). This shows that magnetization data decreases by small amount that can be attributed from shallow donor hydrogenic model [36] which suggests that on lower temperature (~50 K) hydrogen is in more weakly bound state than 300K.

The coercivity enhances from 0.021 T (at 300 K) to ~0.058 T (at 50 K) of hydrogenated samples 1 and 2 (Figure 4). Both 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 the sample is finally returned to the PM state upon further reheating of nearly seven hours. The probable reason can be described as air annealing may absorb oxygen and decrease the oxygen vacancy concentration. This finding specifies that the oxygen vacancies play a key role in inducing FM.

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 hydrogen atmosphere at 50 and 300 K. Experimental findings confirm that on hydrogenation, the samples have achieved overlapped paramagnetic with ferromagnetic properties defeating the diamagnetic properties of In_2O_3. This study also depicts that the sample is finally returned to the paramagnetic state after re-heating.

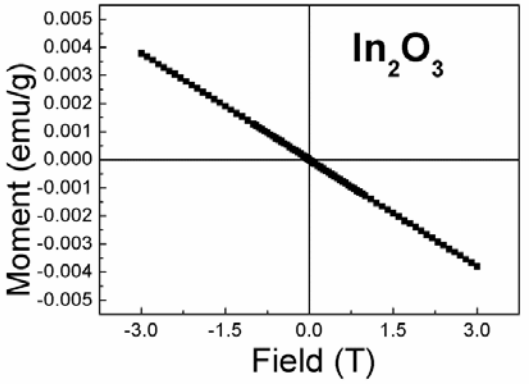

Figure 2. The M-H curves for In_2O_3 showing a diamagnetic state.

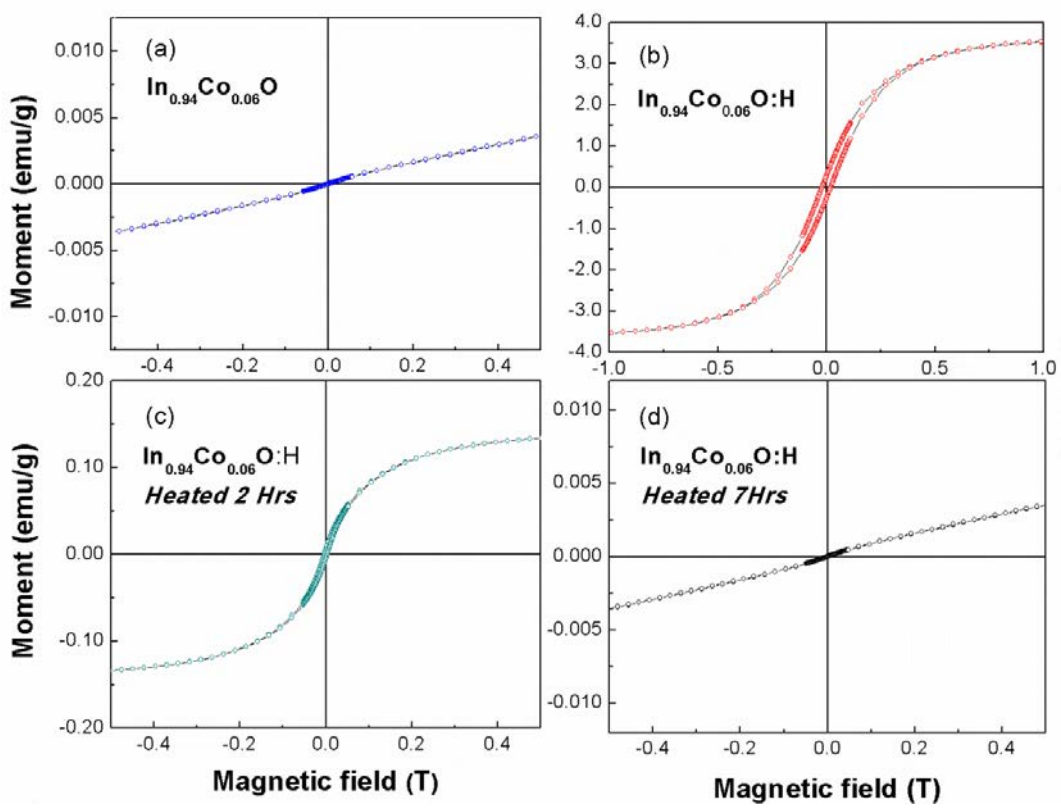

Figure 3. M-H curves recorded at 300 K for **(a)**. As-prepared $In_{0.94}Co_{0.06}O$ **(b).** Hydrogenated $In_{0.94}Co_{0.06}O$ **(c).** Heated 1 sample (2 hrs) $In_{0.94}Co_{0.06}O$ and **(d).** Heated 2 sample (7 hrs) $In_{0.94}Co_{0.06}O$.

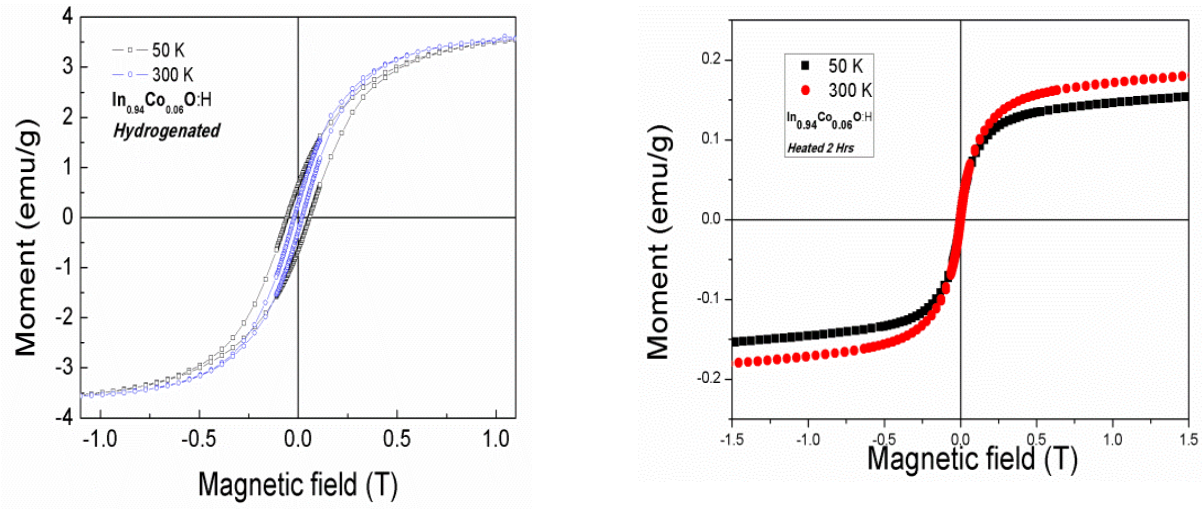

Figure 4. Comparison of M-H curves for hydrogenated samples $In_{0.94}Co_{0.06}O$:H and heated $In_{0.94}Co_{0.06}O$:H at 300 K and 50 K.

Table 1: The magnetic moment, coercivity and retentivity for In_2O_3 and $In_{0.94}Co_{0.06}O$ sample before and after hydrogenation and after the heat treatment.

Sample	Saturation Moment *(emu/g)*		Coercivity *(Tesla)*		Remanence (emu/g)	
	[300 K]	[50 K]	[300 K]	[50 K]	[300 K]	[50 K]
In_2O_3	Dia	Dia	-	-	-	-
$In_{0.94}Co_{0.06}O$	Para	Para	-	-	-	-
$In_{0.94}Co_{0.06}O$:H	3.6	3.52	0.021	0.058	0.285	0.623
$In_{0.94}Co_{0.06}O$ (h*t.2hrs)*	0.180	0.153	0.025	0.017	0.031	0.023
$In_{0.94}Co_{0.06}O$ (*ht.7hrs*)	Para	Para	-	-	-	-

References

1. S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnar, M.L.Roukes, A.Y. Chtchelkanova, D.M. Treger, "Spintronics: A Spin-Based Electronics Vision for the Future" *Science*, vol. 294, no. 5546, pp. ,1488–1495, 2001.
2. S.B. Ogale "Dilute Doping, Defects, and Ferromagnetism in Metal Oxide Systems", *Advance Materials,* doi:10.1002/adma.200903891,2010.
3. T. Dietl , "More than just room temperature" *Nature Materials,* doi:10.1038/nmat2918, 2010.
4. A. A. Dakhel, "Comparative Study of the Hydrogenation of Cu and TM (Mn,Fe,Ni)-Codoped ZnO" *Nanocomposite DMS*, doi:10.1007/s10948-015-2997-6,2015.
5. K.M. Shaif, , R. Vinod Kumar, R.J. Bose, , V.N.Uvais, , V.P Mahadevan Pillai, "Effect of Cu on the microstructure and electrical properties of Cu/ZnO thin films.", *Journal of Alloys and Compounds*, vol. 551 pp 243-248, 2013.
6. C. Xia, F.Wang, C.Hu, "Theoretical and experimental studies on electronic structure and optical properties of Cu-doped ZnO.", *Journal of Alloys and Compounds* , vol. 589, pp 604-608, 2014.
7. N.E. Sung, , S.W. Kang, H.J. Shin, H.K. Lee,I. J. Lee, "Cu doping effects on the electronic and optical properties of Cu-doped ZnO thin films fabricated by radio frequency sputtering.", *Thin Solid Films*, vol. 543, pp 285-288,2013.
8. R. K. Singhal, A. Samariya, S. Kumarb, S. C. Sharma, Y. T. Xing, U. P. Deshpande, T. Shripathid, E. Saitovitchc, "A close correlation between induced ferromagnetism and oxygen deficiency in Fe doped In_2O_3" *Applied Surface Science*, vol. 257, pp 1053–1057., 2010.
9. N. Bao, "Room temperature ferromagnetism study of TiO_2 based magnetic semiconductors by pulsed laser deposition", *Dissertation*. National University of Singapore, 2013.
10. A. Manivannan, G. Glaspell, P. Dutta and M.S. Seehra "Nature of the reversible paramagnetism to ferromagnetism state in cobalt-doped titanium dioxide", *Journal of Applied Physics*, vol. 97, pp 10D325,2005.
11. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, "Zener model description of ferromagnetism in zinc-blende magnetic semiconductors" *Science* , vol. 287 ,no. 5455, pp. 1019-1028, 2000.
12. X.H. Xu, H.J. Blythe, M. Ziese, A.J. Behan, J.R. Neal, A. Mokhtari, R.M. Ibrahim, A.M. Fox, G.A. Gehring, "Carrier-induced ferromagnetism in n-type ZnMnAlO and ZnCoAlO thin films at room temperature" *New Journal of Physics*, vol. 8 , pp 135-144, 2006.
13. A.J. Behan, A. Mokhtari, H.J. Blythe, D. Score, X.H. Xu, J.R. Neal, A.M. Fox, G.A. Gehring, "Two Magnetic Regimes in Doped ZnO Corresponding to a Dilute Magnetic Semiconductor and a Dilute Magnetic Insulator", *Physical Review Letters*, doi:10.1103/PhysRevLett.100.047206, 2008.
14. F. Zhang, D. Chao, H. Cui, W. Zhang , W. Zhang, "Electronic Structure and Magnetism of Mn-Doped ZnO Nanowires", *Nanomaterials*, vol. 5, pp 885-894, 2015.
15. M. Bouloudenine, N. Viart, S. Colis, J. Kortus, A. Dinia, "Antiferromagnetism in bulk $Zn_{1-x}Co_xOZn_{1-x}Co_xO$ magnetic semiconductors prepared by the coprecipitation technique", Applied Physics Letters, doi.org/10.1063/1.2001739,2005.

16. F. Pan, C. Song, X.J. Liu, Y.C. Yang, F. Zeng, “Ferromagnetism and possible application in spintronics of transition-metal doped ZnO films” *Material Science and Engineering,* vol. R 62, pp 1–35,2008.
17. S.B. Ogale, R.J. Choudhary, J.P. Buban, S.E. Lofand, S.R. Shinde, S.N. Kale, V.N. Kullkarni, J. Higgins, C. Lanci, J.R. Simpson, N.D. Browning, S.D. Sarma, H.D. Drew, R.L. Greene, T. Venkatesan, “High Temperature Ferromagnetism with a Giant Magnetic Moment in Transparent Co-doped $SnO_{2-\delta}$ *Physics Review Letters*, doi:10.1103/PhysRevLett.91.077205, 2003.
18. C.B. Fitzgerald, M. Venkatesan, A.P. Douvalis, S. Huber, J.M.D. Coey, T. Bakas, “SnO_2 doped with Mn, Fe or Co: room temperature dilute magnetic semiconductors”, *Journal of Applied. Physics*, vol. 95, pp.7390-7392, 2004.
19. J.M.D. Coey, A.P. Douvalis, C.B. Fitzgerald, M. Venkatesan, “Ferromagnetism in Fe-doped SnO_2 thin films” *Applied Physics Letters*, doi:10.1063/1.1650041, 2004.
20. J. Philip, A. Punnoose, B.I. Kim, K.M. Reddy, S. Layne, J.O. Holmes, B. Satpati, P.R. Leclair, T.S. Santos, J.S. Moodera, “Carrier-controlled ferromagnetism in transparent oxide semiconductors” *Nature Materials*, doi:10.1038/nmat1613.
21. J. He, S.F. Xu, Y.K. Yoo, Q.Z. Xue, H.C. Lee, S.F. Cheng, X.D. Xiang, G.F. Dionneb, I. Takeuchi, “Room temperature ferromagnetic n-type semiconductor in „$In_{1-x}Fe_x)_2O_{3-s}$” *Applied Physics Letters*, vol. 86, pp 052503, 2005.
22. Y.K. Yoo, Q.Z. Xue, H.C. Lee, S.F. Cheng, X.D. Xiang, G.F. Dionneb, S.F. Xu, J. He, Y.S. Chu, S.D. Preite, S.E. Lofland, I. Takeuchi, “Bulk synthesis and high-temperature ferromagnetism of $(In_{3-x}Fe_x)_2O_{5-j}$ with Cu co-doping”, *Applied Physics Letters*, vol. 86, no. 4, pp. 042506, 2005.
23. X.H. Xu, F.X. Jiang, J. Zhang, X.C. Fan, H.S. Wu, G.A. Gehring, “Magnetic and transport properties of n - type Fe-doped In_2O_3 ferromagnetic thin films” Applied Physics. Letters, vol. 94, 212510 , 2009.
24. P.F. Xing, Y.X. Chen, S.S. Yan, G.L. Liu, L.M. Mei, Z. Zhang, “Tunable ferromagnetism by oxygen vacancies in Fe-doped In_2O_3 magnetic semiconductor”, *Journal of Applied Physics*, vol 106, no. 4, pp. 043909-043909-4,2009.
25. R.K. Singhal, A. Samariyaa, S. Kumarb, S.C. Sharmaa, Y.T. Xingc, U.P. Deshpanded,T. Shripathid, E. Saitovitchc, "A close correlation between induced ferromagnetism and oxygen deficiency in Fe doped In_2O_3" *Applied Surface Science*, vol. 257,pp 1053-1057,2010.
26. S.C. Li, P. Ren, B.C. Zhao, B. Xia, L. Wang , "Room temperature ferromagnetism of bulk polycrystalline $(In_{0.85-x}Sn_xFe_{0.15})_2O_3$: Charge carrier mediated or oxygen vacancy mediated" *Applied Physics Letters* , vol. 95, no.10 pp 102101, 2009.
27. B.C. Zhao, H.W. Ho, B. Xia, L.H. Tan, A.C. Huan, L. Wang, "Effect of oxygen vacancy on ferromagnetism and electric transport of bulk polycrystalline $(In_{0.8}Mo_{0.05}Fe_{0.15})_2O_3$." *Applied Physics Letters*, vol. 93, no. 22, pp 2506, 2008.
28. F.X. Jiang, X.H. Xu, J. Zhang, X.C. Fan, H.S. Wu, G.A. Gehring, "Role of carrier and spin in tuning ferromagnetism in Mn and Cr-doped In_2O_3 thin films." *Applied Physics Letters* , vol. 96, pp 052503 2010.
29. N.H. Hong, J. Sakai, N.T. Huong, V. Brizé, "Room temperature ferromagnetism in laser ablated Ni-doped In_2O_3 thin films." *Applied Physics Letters* , vol. 87,pp 102505, 2005.
30. G. Peleckis, X.L. Wang, S.X. Dou, "High temperature ferromagnetism in Ni-doped In_2O_3 and indium-tin oxide." 89 , pp 022501,2006.
31. D. Bérardan, E. Guilmeau, “Magnetic properties of bulk Fe-doped indium oxide”, *Journal of Physics: Condensed Matter*, vol. 19, no. 23, pp 236224, 2007.
32. R.K. Singhal, A. Samariya, Y.T .Xing, S. Kumar, T. Shripathi, U.P. Deshpande , E. Saitovitch , “Electronic and magnetic properties of Co-doped ZnO diluted magnetic semiconductor”. *Journal of Alloys Compound*, vol. 496, pp 324-330, 2010.
33. J. Rodriguez-Carvajal, in: FULLPROF version 3.0.0. Laboratorie Leon Brillouin,CEA-CNRS, 2003.
34. R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides." *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* , vol. 32, no. 5, pp 751-767,1976.
35. J.M.D. Coey, M. Venkateshan, C.B. Fitzgerald,"Donor impurity band exchange in dilute ferromagnetic oxides." *Nature Materials* , vol. 4, no. 2, pp 173-179, 2005.
36. P. D. C. King, R. L. Lichti, Y. G. Celebi, J. M. Gil, R. C. Vilão, H. V. Alberto, J. Piroto Duarte, D. J. Payne, R. G. Egdell, I. McKenzie, C. F. McConville, S. F. J. Cox, and T. D. Veal, “Shallow donor state of hydrogen in

In 2 O 3 and SnO 2: implications for conductivity in transparent conducting oxides." Physical Review B 80, no. 8, pp 081201(1)- 081201(4),2009.

