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Synthesis and Characterization Study of Cobalt Doped ZnO Magnetic Nano-Particles (MNPs)

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ABSTRACT
In this study, 5% cobalt doped ZnO magnetic nano-particles (MNPs) were synthesized using chemical method. The structural, optical and magnetic effect of cobalt doping into ZnO were investigated using X-ray diffraction (XRD), Ultra visible Infra-Red (UV-IR), Photoluminescence (PL) and Superconducting quantum interference device (SQUID) techniques. The structural properties of nano-materials include particle size and lattice strains were estimated by XRD data. Existences of nano-particles in to the samples were verified by Ultra visible absorption technique. The observed hysteresis by SQUID at 5 K revealed the super paramagnetic behavior and temperature dependence magnetization of magnetic nano-particles respectively.
KEYWORDS: Cobalt, ZnO, Magnetic nano-particles, XRD, PL, UV visible, SQUID.

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I INTRODUCTION

Nano-materials have been intensively attracted by the researcher due to their versatile chemical and physical properties compared to that of bulk materials. These materials have already been used for scratch proof eyeglasses, crack-resistant paints and anti-graffiti coatings for walls, transparent sunscreens, stain-repellent fabrics, self-cleaning windows and ceramic coatings for solar cells [1]. The use of magnetic nano-particle materials played vital role of applications due to their unique size. Amongst this, it has variety of potential applications such as medical diagnostics, magnetic immunoassay, waste water treatment, biomedical imaging and information storage etc [2] [3]. The wide band gap semiconductors based magnetic nano-particles have been attracting the researchers for the last few decades due to their potential applications e.g., gas sensor, chemical sensor, biosensor, cosmetics, storage, optical and electrical devices, window materials for displays, solar cells, and drug delivery [4][5]. ZnO is direct band gap semiconductor and has large exciton binding energy (6 meV) due to its exciton emission persists at room temperature as well as higher temperature. The synthesis process of magnetic nano-particles (MNPs) seems to be great challenge for the different kinds of applications. $Zn_{1-x}Co_xO$ nano powders were synthesized by a novel urea-based auto combustion method, the structural and magnetic studies of doped samples revealed the incorporation of co into substitutional ZnO lattice and ferromagnetic behavior respectively [6]. $Zn_{1-x}Co_xO$ $(0 \leq x \leq 0.2)$ nano-particles were prepared by co-precipitation method followed by drying at 200 °C and subsequent annealing at 500 °C. XRD technique showed formation of wurtzite ZnO phase nanostructures, PL spectra revealed emission bands in both UV and visible regions due to the defect centers acting as trap levels and magnetic properties revealed the appearance of ferromagnetic behavior [7]. The optical and magnetic properties of Co-doped ZnO nano-particles were synthesized by the combustion reaction method. XRD and Raman pattern showed the formation of ZnO hexagonal wurtzite phase and a secondary Co_3O_4 phase respectively. Vibrating sample magnetometer measurements exhibited hysteresis loops at room temperature [8].
In this work, un-doped and 5 % cobalt doped ZnO samples were synthesized by chemical method. The synthesized samples were characterized using XRD, PL, UV-IR and SQUID techniques.

II SYNTHESIS DETAILS

Preparation of un-doped and doped ZnO were carried out using Zinc acetate dihydrate, $Zn(Ac)_2.2H_2O$, cobalt acetate tetrahydrate $Co(Ac)_2.4H_2O$ and methanol. The synthesis stepwise procedure described as following:

2.1 Preparation of ZnO

The ZnO was crudly extracted by the heating of methanolic solutions of zinc acetate dehydrate. Zinc oxide solid forms during heating and continues to form during cooling of the solution at room temperature. The formation takes place at a definite temperature of 70^0C. The acetate part acts as a base and the dehydrate part provide the oxygen as a result of disintegration of water molecules.

$$\mathbf{Zn(C_2H_3O_2)_2 + H_2O \rightarrow ZnO(s) + 2HC_2H_3O_2} \quad (1)$$

2.2 Preparation of Cobalt Doped ZnO

The mixture of $Zn(Ac)_2.2H_2O$ in methanol was prepared and with a successive addition of a definite amount of $Co(Ac)_2.4H_2O$. This mixture kept under the influence of constant room temperature (28 ^{o}C) with vigorous stirring for 10 minutes. The solution formed is transparent and clear. Sequentially, the solution is heated under the reflux at 70^{o}C for 12 hours. The precipitate formed was washed 3-5 times with the absolute ethanol to remove the unwanted ions. Later, the washed precipitate was dried at 60^{o}C for 2 hours. The solid formed is blue in color and has the Co^{++} ions. The un-doped and Co-doped ZnO samples were characterized using X-ray diffraction (XRD), Ultra visible Infra-Red (UV-IR), Photoluminescence (PL) and Superconducting quantum interference device (SQUID) techniques.XRD technique (model RIGAKU No.5020289), Ultima-IV with wavelength of 0.1540nm was carried out at Institute of Science, Mumbai. Magnetic properties of magnetization versus temperature (M-T) and magnetization versus applied field (M-H) were carried out using SQUID technique model SQUID 7 Tesla Quantum Design Make MPMS-3(QDUSA) in vibration mode at Tata Institute of Fundamental Research center, Mumbai.

III RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD) Studies

Figure 1(a)-1(b) shows X-ray diffraction pattern of un-doped and Co-doped ZnO samples respectively. It is observed from the Figure that un-doped ZnO sample showed two peaks at 31.33^0 and 33.78^0 assigned for (100) and (002) reflection respectively [Fig.1(a)]. After doping, the diffracted peak attributed (100) observed at 31.96^0 which has shifted (right) by 0.630^0 [Fig.2 (b)]. Whereas, the peak attributed at (002) observed left shift by 0.70^0. The FWHM for 5% Co doped ZnO samples were found to increase than the un-doped sample. The shift in the peak and increase in the FWHM indicates the incorporation of Co^{++} into the lattice of sites of ZnO and decrease of magnetic nano-particle (MNP) size in the sample respectively. Another extra peak observed for co-doped sample at 58.89^0 assigned to (110) reflections. However, this peak was not observed in the un-doped ZnO sample. The average MNPs size has been estimated by Scherrer's formula [9].

$$D = \frac{0.9\lambda}{\beta \cos\theta_B} \quad (2)$$

Where λ is the X-ray wavelength, β is the full width at half maximum of observed peak and θ_B is the Bragg diffraction angle.

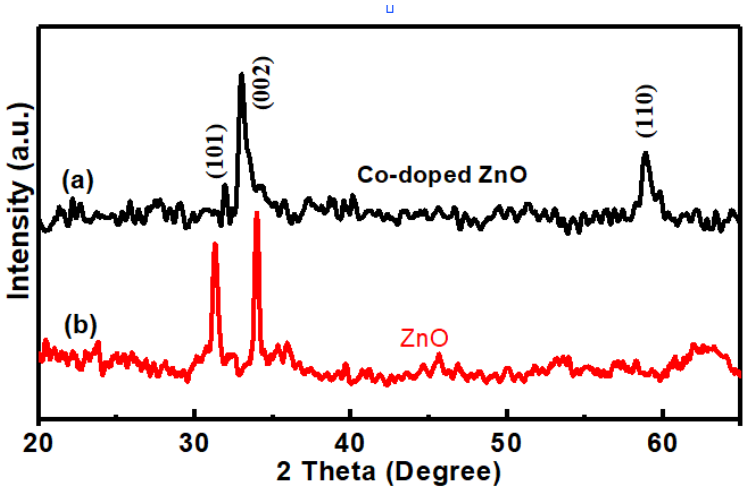

Figure 1: XRD spectra of samples; (a) Un-doped and (b) Cobalt doped ZnO.

The strain present in the implanted samples has been estimated from the peak shift using the relation;

$$\varepsilon = \frac{d_n - d_0}{d_0} \quad (3)$$

Where, d_n and d_0 are inter planar spacing of the doped and un-doped samples respectively. The estimated value of strain in the sample doped with 5% cobalt found to be 0.368. The presence of strain in the sample indicated the cobalt ions into ZnO lattice site substitutionally or interstitially. The estimated full-width at half-maximum (FWHM), peak position of diffraction peaks and crystalline size shown in Table I.

Table I: XRD estimated full-width at half-maximum (FWHM), peak position of diffraction peaks, crystalline size and strain.

Sample	2 theta (degree)	FWHM (degree)	Size (D) nm	Strain
Un-doped ZnO	33.78	0.3450	26.00	-
Cobalt doped ZnO	33.08	0.4370	18.96	0.0305

3.1 UV-Visible Absorption Studies

The UV-visible absorption spectra of 50% Co doped ZnO synthesized using chemical method shown in Figure 2.UV-Visible absorption spectroscopy is useful investigation to reveal the effect of doping on optical properties of nano-particles. The addition of Co as a dopant in the ZnO shifts the absorption wavelength towards the lower side. After doping 5 % of Co into ZnO, the absorption wavelength nano-particle was found at 252 nm [Fig.2]. However, absorption edge wavelength for un-doped ZnO was 369 nm**.** The shifting of edge to lower side indicates the stronger interaction between the dopant and the ZnO nano-particles [10]. The intensity of absorption also increases with the concentration of dopant. The band gap energies of the synthesized nano-particles were calculated by the following relation [11].

$$E_g = \frac{1240}{\lambda} eV \qquad (4)$$

Where, λ- wavelength of nano-particles, the energy band gap of 5% Co doped ZnO sample was estimated to 4.9 eV. However, the band gap of pure ZnO is 3.37 eV. The increase in the energy band gap from 3.37 eV (pure ZnO) to 4.9 eV (50 % Co) appears to originate from active transitions involving 3d levels in Co^{++} ions and strong sp–d exchange interactions between the itinerant 'sp' carriers (band electrons) and the localized 'd' electrons of the dopant [12]. This result also connected the magnetic properties observed in SQUID study as a super paramagnetic behavior of the sample below 19 K.

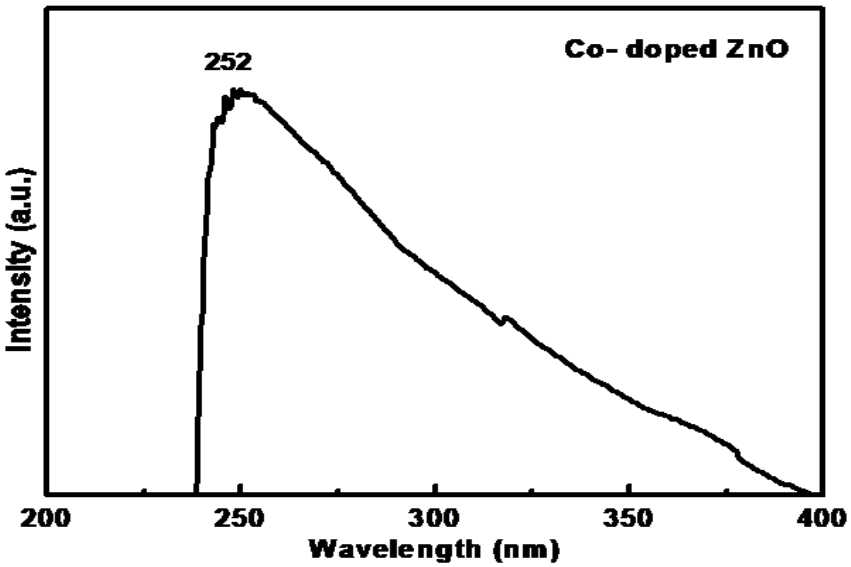

Figure 2: UV-Visible absorbance spectra of 5 % Cobalt doped ZnO sample.

3.3 Magnetic Studies

Figure 3 shows the magnetization versus field (M-H) curve at constant temperature 5 K of cobalt doped ZnO sample. The magnetic properties such as remnant magnetization (R_M) and cursive field (H_C) estimated from this curve were found to be 2.01×10^{-4} (emu/gm) and 6.37 (Oe) respectively [Fig.2 (inset)]. The saturation magnetization not observed in the doped ZnO sample. It may be at higher value of applied field. The observed value of magnetic properties at temperature 5 K for doped sample revealed the super paramagnetic behavior of magnetic nano-particles which is a desirable characteristic of nano-materials [13]. These magnetic properties were found to decrease with increase in the temperature [14].

Figure 4 shows temperature dependent magnetization (M-T) curve at applied field 512 (Oe) of 50% Co doped

ZnO sample. It is seen from the Figure that the magnetizations to be reduced drastically from lower temperature to higher till 19 K, after that reduces gradually. This result observed due to the alignment of number of magnetic dipole moment reduces in the direction of applied field. The extension of this curve intercepts at temperature axis showed Curie temperature (T_C) at 19 K. However, pure ZnO is paramagnetic at room temperature [15].

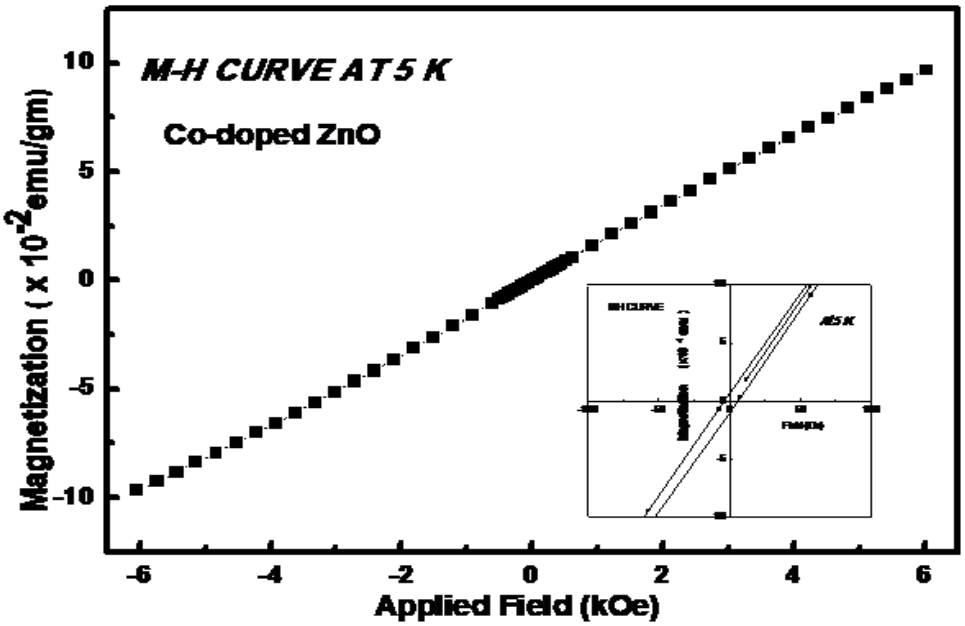

Figure 3: Magnetization versus applied field (M-H) curve at 5 K of Cobalt doped ZnO sample.

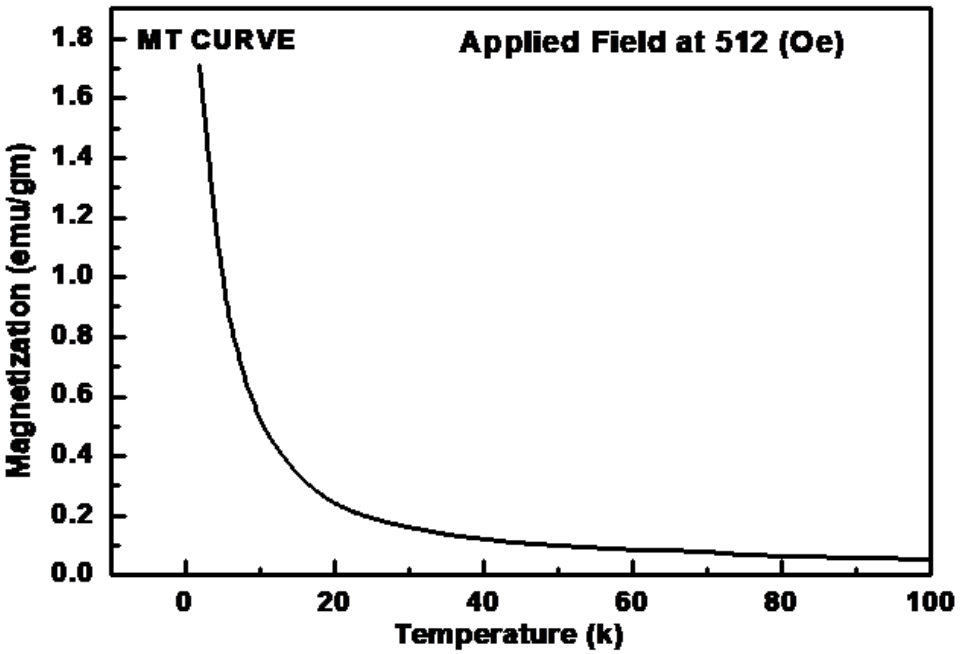

Figure 4: Temperature dependent magnetization (M-T) curve at 512 (Oe) of Co-doped ZnO Sample.

3.2 Photoluminescence (PL) Studies

Figure 5(a)-5(b) shows the room temperature PL spectra of un-doped and 50% Co doped ZnO samples. An intense narrow emission band in the UV spectral range centered at around 372 nm appeared for un-doped ZnO sample. The peak at 372 nm related to the near band edge emission. This emission has been assigned to the free excitonic recombination in ZnO [16]. PL spectra of Co-doped ZnO sample exhibits a broad blue shift in the range from 400 to 418 nm [shown in the inset of Fig.5] attributed due to the shift of the optical band gap in the sample. A blue shift of the band edge reveals the incorporation of Co in the lattice sites in ZnO. This result supports the X-ray analysis of incorporation of Cobalt into the ZnO structure.

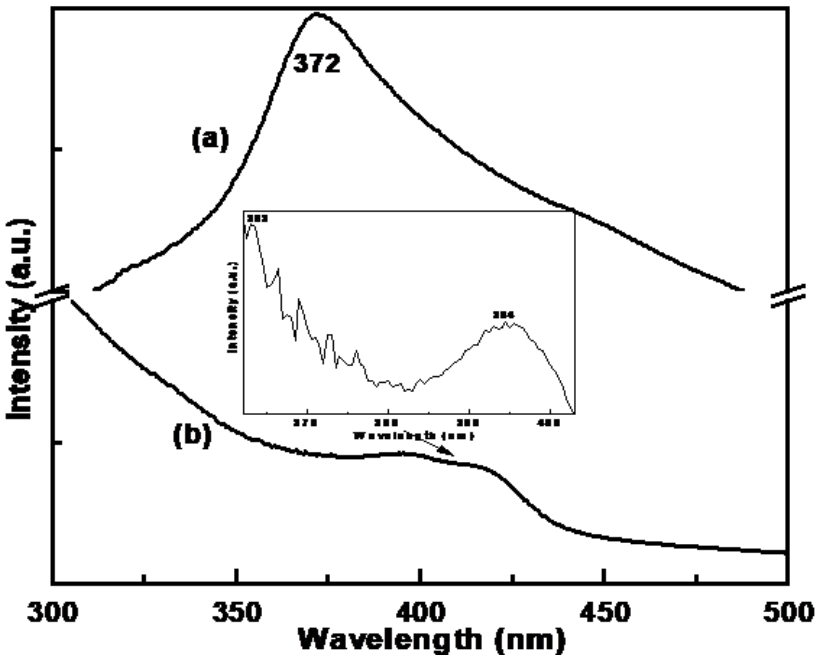

Figure 5: PL spectra of Cobalt doped ZnO sample.

4 CONCLUSIONS

Cobalt doped ZnO magnetic nano-particles were synthesized using chemical method. The SQUID study of cobalt doped ZnO showed the super paramagnetic behavior. UV-Visible absorption spectra showed the absorption wavelength edge and shifting of this edge toward lower side indicates the existence of nano-particles and the stronger interaction between dopant and ZnO respectively. PL spectra showed the blue shift of the band edge reveals the incorporation of Co in the lattice sites in ZnO.

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REFERENCES

[1]. Aravapalli Vanaja, Karumuri Srinivisa Rao, "Effect of Co doping on structural and optical properties of zinc oxide nano-particles synthesized by sol gel method", Advances in Nano-particles, 5, 83-89, 2016.
[2]. Tartaj P, Morales MDD, 'The preparation of magnetic nano-particles for applications in biomedicine', J. Phys D: Appl. Phys., 36, R182–R197, 2003.
[3]. Faraji M, Yamini Y, "Magnetic nano-particles: synthesis, stabilization, functionalization, characterization and applications", Journal on Iran Chem Soc., 7(1), 1–37, 2010.
[4]. Wang Z. L, "Zinc Oxide Nanostructures: Growth, Properties and Applications", Journal of Physics: condensed matter Condensed Matter, 16, R829-R858, 2004.
[5]. Vikash Kumar, Swati Kumari, "structural analysis by rietveld method and its correlation with optical properties of nanocrystalline zinc oride", Adv. Mater. Lett. 2015, 6(2), 139-147, 2015.
[6]. V.Rajendar, K. VenkateswaraRao, "Effect of Co Doping on Structural and Magnetic Properties of ZnO Nano-particles Synthesized by Novel Combustion Synthesis", journal of nano- and electronic physics, Vol. 5 , No 1, 01022 , 2012 .
[7]. S. Fabbiyola, L. John Kennedy, "Synthesis of Co-doped ZnO nano-particles *via* co-precipitation: Structural, optical and magnetic properties"**,** power technology, vol.286, 757-765, 2015.
[8]. T. J. Castro, P. A. M. Rodrigues, "Optical and magnetic properties of Co-doped ZnO nano-particles and the onset of ferromagnetic order", Journal of Applied Physics, 121, 013904, 2017.
[9]. G. Jayalakshmi, N. Gopalakrishnan, "Grain boundary defects induced room temperature ferromagnetism in V doped ZnO thin films", Cryst. Res. Technol. 46, No. 12, 1257 – 1264, 2011.
[10]. A. Geetha, R. Sakthivel **"**Characterization of mg doped zno nano-particles synthesized by a novel green route using azadirachtaindicagum and its antibacterial activity", world journal of pharmacy and pharmaceutical sciences', Volume 6, Issue 8, 1189-1201 (2017).
[11]. A. Geetha, R. Sakthivel, "Green Synthesis of Antibacterial Zinc Oxide Nano-particles Using Biopolymer Azadirachtaindica Gum", Oriental journal of chemistry, 32(2), 2016.
[12]. Talaat M. Hammad , Jamil K. Salem, "Structure, optical properties and synthesis of Co-doped ZnO superstructures", Appl. Nanoscience 3:133–139, 2013.
[13]. Javier Bustamante Mamani, Lionel Fernel Gamarra, Giancarlo Espósito de Souza Brito, "Synthesis and characterization of Fe_3O_4 nano-particles with perspectives in biomedical applications", Material Research, vol.17, No.3, 2014.
[14]. N. S. Pradhan, S. K. Dubey, "Formation of (Ga,Mn)N Dilute Magnetic Semiconductor by Manganese Ion Implantation", International Journal of Engineering and Physical Sciences, vol. 6, 2012.

[15]. G. Clavel, M. G. Willinger, "Solvent dependent shape and magnetic properties of doped ZnO Nanostructures", Advanced Functional Materials, 17, pp. 3159-3169, 2007.
[16]. R. Sanchez Zeferino, M. Barboza Flores "Photoluminescence and Raman Scattering in Ag-doped ZnO Nano-particles", J. Appl. Phys. 109, 014308, 2011.

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