

Research Article

Magnetic property of $Zn_{0.8}Co_{0.2}O$ Diluted Magnetic Semiconductors by Auto Combustion Method

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Abstract

Polycrystalline $Zn_{0.8}Co_{0.2}O$ diluted magnetic semiconductors were synthesized by auto combustion technique from aqueous solutions of Zn and Co acetates using polyethylene glycol as catalyst. A complete series of Co (II) substituting Zn(II) was studied, from the structural point of view, by XRD and FTIR. The X-ray diffraction patterns of the films showed that the Co-doped ZnO powder exhibit wurtzite crystal structure. Magnetic hysteresis loops were observed at room temperature, indicating that ferromagnetism can be realized with Co doping into ZnO. Optical absorption measurements showed absorption bands indicating the presence of Co ions in substitution of Zn ions. The calculated band gap value of 2 at% Co doped samples was found to be around 3.37 eV. The morphology and crystal line size of the synthesized powders were evaluated by field emission scanning electron microscopy and transmission electron microscopy (TEM).

Keyword: Magnetic Nanoparticle, XRD, UV-visible, FESEM, TEM, VSM

1. Introduction

Dilute magnetic semiconductors (DMS) have attracted a great deal of attention due to the exciting features they offer for spintronic studies and possible applications. The term "spintronics" refers to utilizing the spin-degree of freedom of an electron apart from its charge-degree-of-freedom. Dilute magnetic semiconductors are materials in which a fraction of the cations is replaced by magnetic ions, and they exhibit complex and interesting electrical and magnetic properties which are tunable.

In recent years, various physical and chemical techniques such as mechanosynthesis route, pulsed laser deposition, spray pyrolysis, gas flow sputtering, sol-gel method, hot pressing, hydrothermal technique (S. Ghosh et al, 2010, Shanying et al, 2010 etc). have been successfully employed for the synthesis of $Zn_{0.8}Co_{0.2}O$ nanoparticles. The aim of this work is the preparation and structural, optical and magnetic characterization of $Zn_{0.8}Co_{0.2}O$ powder.

In this paper, we present a simple auto combustion method to produce $Zn_{0.8}Co_{0.2}O$ nanopowder, using zinc acetate dihydrate and cobalt acetate tetrahydrate as precursors. We have produced single phase $Zn_{0.8}Co_{0.2}O$ Nano powder of uniform surface morphology and good crystalline quality with average particle size ~20 nm.

The rest of the paper has been structured as follows: Feature extraction of the test cases is discussed in section 2. In section 3, not only was analysis of data investigated,

but also morphology of sample has been proposed. The last part concludes the paper.

2. Experimental

$Zn_{0.8}Co_{0.2}O$ has been synthesized by an auto combustion technique. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and the fuel urea (CH_4N_2O) in appropriate amount were first dissolved in 100 mL of double distilled water. Then, add polyethylene glycol ($CH(OCH_2)_nCH_2OH$) was slowly introduced to solution under vigorous stirring. After 30 min, the solution completely converted to a highly viscous gel. Then the beaker vessel was transferred into microwave oven to complete the combustion reaction after about 10 min and also calcined at the temperature of 300°C for 2 hr to obtain the Nanoparticles.

The structural characterization of the samples was done by X-ray diffraction (XRD, Bruker D8 Advance, Germany). Particle size analyzer by HORIBA SZ-100 is used to measure the average size of the particle. Thermal analysis and weight loss of the sample are observed by S-II EXSTAR-6300, India. Fourier transform infrared spectroscopy was used as well by FTIR, PERKIN ELMER, India. Reflectance optical measurements have been performed at room temperature using conventional ultraviolet-visible spectrometer. The magnetic properties of the samples were investigated by using DLS 1600. The morphology of the $Zn_{0.8}Co_{0.2}O$ was revealed by field emission scanning electron microscopy (FESEM):

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ULTRA-55 system, India). Transmission electron microscopy (TEM, JEM-2100, Jeol, India) equipped was used to analyses the detailed structure and composition of the products.

3. Result and discussion

3.1 Crystal Analysis: XRD patterns of the calcined $Zn_{0.8}Co_{0.2}O$ Nano powder shows in Fig. 1, which can be indexed as the $Zn_{0.8}Co_{0.2}O$ wurtzite structure in the standard data (JCPDS 36-1451). Eight peaks centered at $2\theta = 31.8^\circ, 34.44^\circ, 36.28^\circ, 47.59^\circ, 56.65^\circ, 62.92^\circ, 68.01^\circ$ and 69.17° , which correspond to diffraction planes of (1 1 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (4 4 0), (1 0 3), (2 0 0) and (1 1 2) respectively, are detected. The average particle size for $Zn_{0.8}Co_{0.2}O$ sample has been calculated from X-ray line broadening using the Scherrer formula: $D = \frac{0.9\lambda}{\beta \cos\theta}$, where D is the Crystalline size, β the full width at half-maximum in radian, θ the angle of the diffraction peak and λ is the X-ray wavelength. We obtain a crystalline size value of 20 nm.

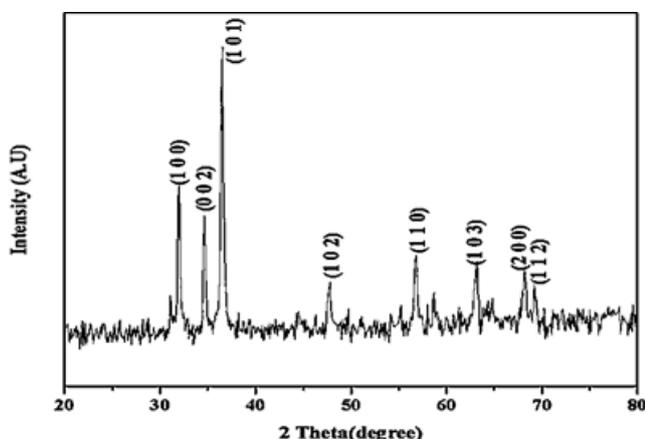


Fig.1. XRD pattern for $Zn_{0.8}Co_{0.2}O$ nanopowder synthesized by Solution Combustion Synthesis method

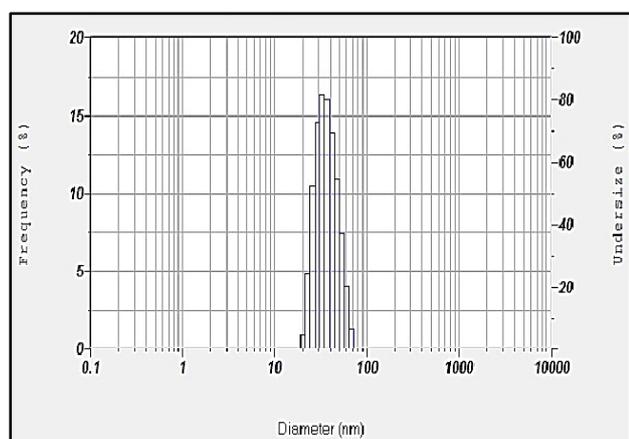


Fig.2. Results of Nano Particle Size Analysis for $Zn_{0.8}Co_{0.2}O$ synthesized by Solution Combustion Synthesis method

The size of the Nano powders in this analysis measured with Nano Particle Size Analyzer (SZ-100) the average particle sizes. Figure 2 Shows those $Zn_{0.8}Co_{0.2}O$ particles possess a narrow distribution with an average effective diameter of 45 nm. Particle size of $Zn_{0.8}Co_{0.2}O$ is done by particle size analyzer (SZ-100). Small amount of sample dissolved in ethanol then sonicated to form clear solution. The particle size which was estimated by particle size analyzer (SZ-100) is greater than the particle size which was estimated by XRD. The obtained particle size is 21nm.

3.2 Thermal analysis: Figure 3 indicates the thermogravimetric curve of the $Zn_{0.8}Co_{0.2}O$ powder precursor after calcination at $300^\circ C$. Thermal analysis of $Zn_{0.8}Co_{0.2}O$ sample was carried out in air atmosphere. The TG curve in Fig. 3 shows weight loss percentage and first weight loss percentage that has sharp slope (in the range $40-90^\circ C$), indicating the formation of crystalline solid phases [8]. The second stage of weight loss percentage has been observed 0.69% in the range of $200-550^\circ C$ which is related to disappear of impurity and third stage is about 1.2% in temperature range $550-800^\circ C$ due to the decomposition of Co-Zn oxalate to $Zn_{0.8}Co_{0.2}O$.

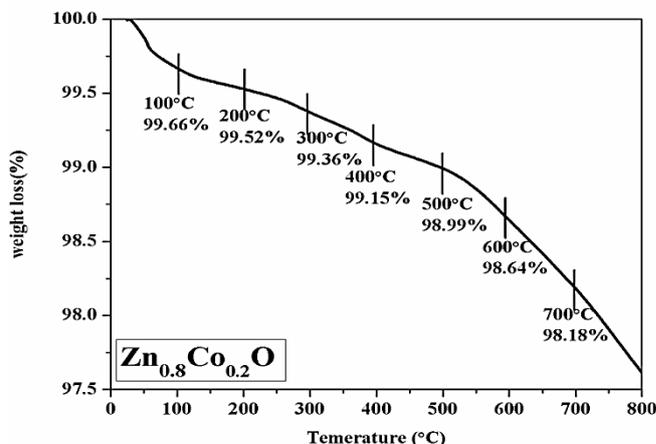


Fig.3. TG-DTA curve for nano crystalline $Zn_{0.8}Co_{0.2}O$

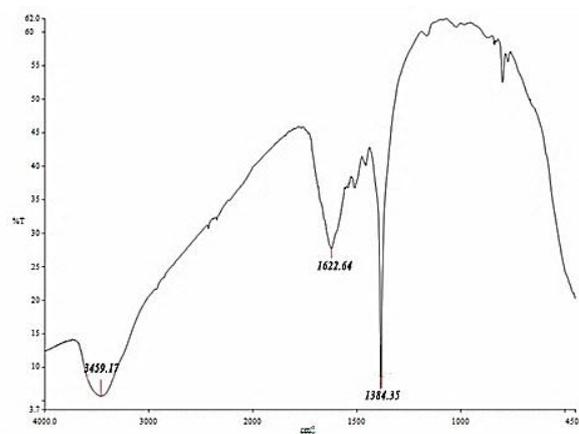


Fig. 4. FT-IR spectra of Nano crystalline powders of $Zn_{0.8}Co_{0.2}O$ calcined in air at $300^\circ C$ for 2 h.

3.3 Fourier Transform Infrared Spectroscopy Analysis: The FTIR spectra measurement of fresh $Zn_{0.8}Co_{0.2}O$ Nanoparticles in the range of $4000-450\text{ cm}^{-1}$ are shown in Figure 4. Absorption bands at $\sim 3460\text{ cm}^{-1}$ represent O–H mode. Absorption bands at $\sim 1622\text{ cm}^{-1}$ and at $\sim 1384\text{ cm}^{-1}$ correspond, respectively, to stretching mode of asymmetric and symmetric C=O bonds of zinc acetate in pure and un-irradiated $Zn_{(1-x)}Co_{(x)}O$ nanopowder that at $\sim 680\text{ cm}^{-1}$ is the stretching mode of ZnO (R.F. Silva et al,2002, H. Li et al,2004).

3.4 UV-Visible: The UV–VIS absorption spectra of the Nano crystalline $Zn_{0.8}Co_{0.2}O$ powder are shown in Figure 5. The band gap energy for the $Zn_{0.8}Co_{0.2}O$ sample appears at $\sim 3.37\text{ eV}$. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the value of the optical band gap. The Tauc relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as

$$(\alpha h\nu) = A (h\nu - E_g)^n$$

Where, A is a constant, E_g is the band gap of the material and exponent n depends on the type of transition. Here, the transitions are direct so it can be taken as $n=1/2$. For, $n = 1/2$ direct transitions, substituting the ‘n’ value in the above equation it changes into

$$(\alpha h\nu)^2 = A^2 (h\nu - E_g)$$

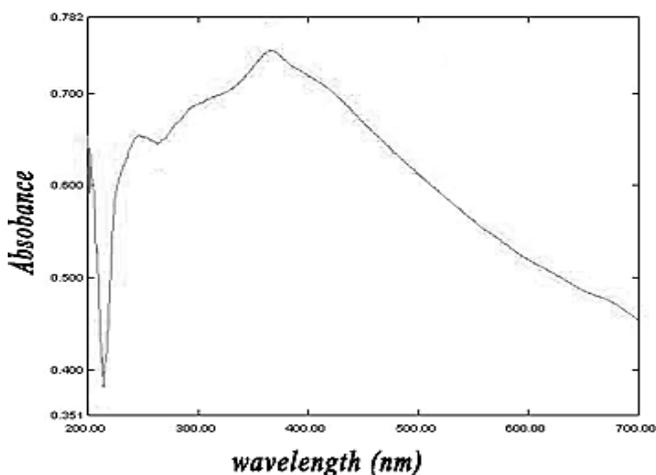


Fig. 5. Room-temperature optical absorbance spectra of Nano crystalline powder of $Zn_{0.8}Co_{0.2}O$ calcined in air at 300°C for 2 h.

3.5 Morphology: The morphology of the Nano crystalline $Zn_{0.8}Co_{0.2}O$ powders as revealed by FESEM (Figure 6a) shows that the powder of $Zn_{0.8}Co_{0.2}O$ consist of nanoparticle with particle size and nanorods with diameters of $\sim 0.22\ \mu\text{m}$ and $3.7\ \mu\text{m}$ in length. The morphology and structure of the Nano crystalline $Zn_{0.8}Co_{0.2}O$ sample were further investigated by TEM. TEM observations (Figure 6b) reveal that the spherical

particles with hexagonal wurtzite structure formed by the aggregation of small crystallites.

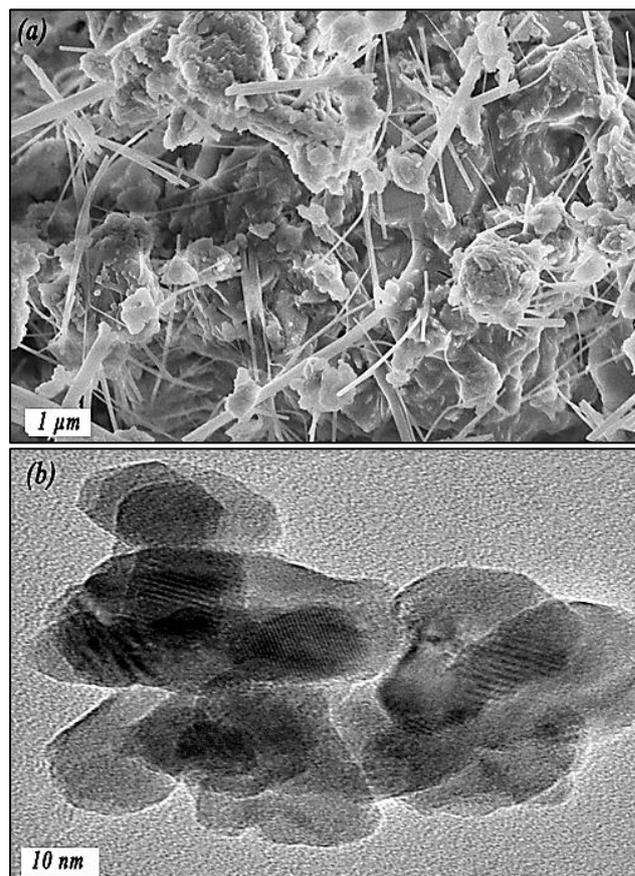


Fig. 6.(a, b) FESEM micrograph and TEM image of Nano crystalline powders of $Zn_{0.8}Co_{0.2}O$ calcined in air at 300°C for 2 h.

3.6 Vibrating Sample Magnetometer (VSM) Analysis: The measurement of magnetization vs field (M–H) curves on the as-deposited $Zn_{0.8}Co_{0.2}O$ powder was carried out at 300°C by VSM system at room temperature with a magnetic field applied parallel to the plane of the powder.

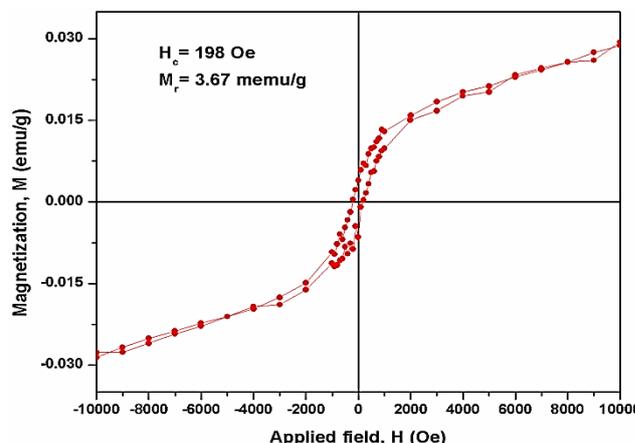


Fig.7. The hysteresis loops of the $Zn_{0.8}Co_{0.2}O$ nanoparticles measured at room temperature.

As shown in Figure 7, because both the M–H curves of the films have clear ferromagnetic loops, the Curie temperature (T_c) of these films would be higher than at least the room temperature. Hysteresis loops with a coercive field $H_C \sim 198$ Oe ($1 \text{ Oe} = 79.57747 \text{ Am}^{-1}$) can be observed at V, showing obvious ferromagnetic characteristic. The remanence magnetizations of $\text{Zn}_{0.8}\text{Co}_{0.2}\text{O}$ are about 3.67 emu/g.

Conclusion

Nano crystalline powders of $\text{Zn}_{0.8}\text{Co}_{0.2}\text{O}$ diluted magnetic semiconductors were successfully synthesized by a novel auto combustion synthesis method and it is successfully doping Co in ZnO nanoparticles their structures, morphology and magnetic properties were investigated. The XRD patterns and FT-IR spectra suggested the formation of wurtzite nanocrystals in the powders after calcination at 300°C . Thermal analysis was done by Thermal gravimetric-Differential thermal analyzer which shows weight loss percentage. Optical measurements using UV–visible spectrometer showed band gap value of 2 at. % Co doped samples was found to be around 3.37 eV. FESEM shows that the powder of $\text{Zn}_{0.8}\text{Co}_{0.2}\text{O}$ consists of nanoparticles with particle sizes and nanorods and TEM image indicate spherical particles with hexagonal wurtzite structure.

Acknowledgments

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Reference

- S. Ghosh, K. Mandal (2010), Study of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($0.02 \leq x \leq 0.08$) dilute magnetic semiconductor prepared by mechanosynthesis route, *Journal of Magnetism and Magnetic Materials*, Vol.322, NO. 14, pp. 1979- 1984
- Shanying Yang, B.Y.Man, M.Liu, C.S.Chen, X.G.Gao, C.C.Wang, B.Hu (2010), Structural, optical and magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ dilute magnetic semiconductors thin films by pulsed laserdeposition, *Physica B: Condensed Matter*, Vol. 405, No.18, pp. 4027- 4031
- E. Bacaksiz, S. Aksu, B.M. Basol, M. Altunbaş, M. Parlak, E. Yanmaz (2008), Structural, optical and magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin films prepared by spray pyrolysis, *Thin Solid Films*, Vol. 516, No, 21, pp. 7899- 7902
- H. Sakuma, Y. Watanabe, K. Aramaki, K.S. Yun, K. Ishii, Y. Ikeda, H. Kondo (2010), Microstructure and magnetic properties of Co-doped ZnO films deposited by gas flow sputtering, *Materials Science and Engineering: B* Vol. 173, N. 1-3, pp. 7-10
- Yow-Jon Lin, Chia-Lung Tsai, Wei-Chung Chen, Chia-Jyi Liu, Lance Horng, Yu-Tai Shih, Zhi-Ru Lin, Jia-Feng Wang (2008), Mechanisms of enhancing magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films prepared by the sol–gel method, *Journal of Crystal Growth* Vol. 310, No. 16, pp. 3763- 3766
- Lin Wensong, Fang Ningxiang, Ouyang Chenxin, Wang Wei (2010), Magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ bulks prepared by hot pressing, *Materials & Design*, Vol. 31, No. 4, pp. 1731- 1733
- M. Bouloudenine, N. Viart, S. Colis, A. Dinia (2004), Bulk $\text{Zn}_{1-x}\text{Co}_x\text{O}$ magnetic semiconductors prepared by hydrothermal technique, *Chemical Physics Letters*, Vol. 397, No. 1-3, pp. 73-76
- S. Thota, T. Dutta, J. Kumar (2006), On the sol–gel synthesis and thermal, structural, and magnetic studies of transition metal (Ni, Co, Mn) containing ZnO powders, *Journal of physics: condensed matter*, Vol. 18, No. 8, pp. 2473.
- R.F. Silva, M.E.D. Zaniquelli (2002), Morphology of nanometric size particulate aluminium-doped zinc oxide films, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 198–200, pp. 551-558.
- H. Li, J. Wang, H. Liu, C. Yang, H. Xu, X. Li, H. Cui (2004), Sol–gel preparation of transparent zinc oxide films with highly preferential crystal orientation, *Vacuum*, Vol. 77, No. 1, pp. 57-62.