

Structural and Magnetic Properties of Co Doped ZnO Nanoparticles

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Abstract: The Co doped ZnO ($Zn_{1-x}Co_xO$; $x = 0.00, 0.02, 0.06$ and 0.10) nanoparticles were synthesized using the co-precipitation method. Characterization techniques help to determine the different structural and magnetic properties. XRD pattern help to identify the structure of sample and confirms the phase confirmation. FTIR (Fourier transform infrared) characterization help to determine the functional groups present in the sample. It is based on the absorption phenomenon of sample. VSM characterization helps to understand the magnetic properties of samples. The spontaneous magnetization was found to be 0.1 emu/gm for pure ZnO which increases to 0.2 emu/gm with the 10% doping of Co in ZnO.

Keywords: Doping, Magnetic properties, Nanoparticles, Optical properties.

I. INTRODUCTION

In the present scenario, the industries have expanded the rate of synthesis of chemical due to increase demand of chemicals. The industries are responsible for the water pollution as industries drain the large amount of dye waste in nearby rivers and water source. To solve this problem, lot of chemical materials are used but they are too expensive and non efficient. The waste chemicals are ejected in huge amount from textile industry. The non biodegradable wastes are not easier task to remove it from water. It causes the health issues and environmental pollution. Since these highly toxic dyes contain lot of heavy metals ions and suspended solids which are dangerous to all living organism. These toxic dye solution is highly soluble in water and degrade in longer time. There have been efforts made to create in expensive photo catalyst that have potent photocatalytic activity when exposed to solar light. Environmental waste management systems have used a variety of possible photocatalysts based on semiconductor metal oxides, including TiO_2 , ZnO, ZrO_2 , V_2O_5 , Fe_2O_3 etc. [1-3]. The performance of ZnO as a photo catalyst is affected by its morphology, manufacturing method, pH, crystallinity, pollutant composition, irradiation intensity, and used dopants [4-5]. ZnO, however, is not fully utilised as a photocatalyst due to a number of drawbacks. Two significant limitations emerge from ZnO's wide band gap energy which prevents photo absorption in the visible light region.

The first is low photocatalytic efficiency because photo-generated charges recombine quickly. Due to the high risk, the removal of hazardous dyes is very essential. The dye has been degraded due to the photodegradation of nanoscale ZnO. It converts the dye waste into biodegradable product and minerals. The nanoscale particle has massive potential to degrade the organic and inorganic pollutant. These semiconductors photo catalyst has property of producing electron and whole pair when light falls on it. This property is used for reducing the toxicity rather than alteration. Nanoparticles have application in the field of textile. Several fabric properties that are essential to the textile industry such as fabric friction, air permeability, tensile strength, may be impacted by nanoparticles coating.

In this manuscript the Co doped ZnO ($Zn_{1-x}Co_x$; $x = 0.00, 0.020, 0.06$ and 0.10) and nanoparticles were synthesis using co-precipitate method. Their structural, optical and magnetic properties were studied in detail.

II. MATERIALS AND METHODS

A. Synthesis

The Co doped ZnO ($Zn_{1-x}Co_xO$; $x = 0.00, 0.02, 0.06$ and 0.10) nanoparticles were synthesis using the co-precipitate method. Here Zinc Chloride, Cobalt Chloride, Sodium Hydroxide were used as precursor. The Double distilled water was used to dissolve the precursor to form the uniform solution.

The 150 ml solution of zinc chloride formed when the Zinc Chloride precursor of calculated amount is added to double distilled (DD) water with continuous stirring at 130 rpm for 2 min. The magnetic bead was pour in the solution for continuous stirring. For pure ZnO nanoparticle synthesis, there was no additional doping of metal ion.

The prepared NaOH solution using NaCl pallet was added gently to the $ZnCl_2$ solution. The PH of solution observed about 8. Sodium hydroxide (NaOH) was good precipitating agent. Add NaOH drop by drop at constant stirring in the solution and stop it when uniform precipitate is formed. If the PH of solution was not reach to desired value, then again add the NaOH solution slowly.

Let the solution settle, the obtained precipitate was centrifuges in repeated manner at 5000 rpm for 3 min. The centrifuges process was totally repeated in five step in which the precipitate Washed with DD water three times and with acetone two times.

The obtained residue was dried for at 70 °C in oven and grinded with the mortar and pestle to get fine powder.

Finally prepared nanopowder was calcined at 500 °C for 2 hours. The furnace is at high temperature so it takes approximately one day to down. Remove the sample from furnace carefully. Calcination technique helps to remove the impurities that retain in the residue. The sample colour was not changed.

For preparation of Zinc chloride (ZnO) nanoparticle with doping of the metal ions like Co, Make the solution of 150 ml

of $ZnCl_2$ and $CoCl_2$ precursor using the calculated amount of precursor for desired solution formation. Using continuous stirring 130 rpm, the precursor was added in DD water. Mix the zinc chloride and Cobalt Chloride solution and to form precipitate the drop wise addition of NaOH solution was used. Due to addition of $CoCl_2$ different concentration, three more samples were prepared. $CaCl_2$ present in sample in 2% , 6%, 10% of solution of zinc chloride. The centrifuge method helps to separate the residue from the prepared solution. Similar conditions of normal ZnO synthesis were used for this new sample. The residue was dried and grind to get the powder of sample. The powder had stored after calcination at 500 °C for 2 hours in glass bottles. The colour of sample change which indicate the changes in the properties due to doping of metal ion.

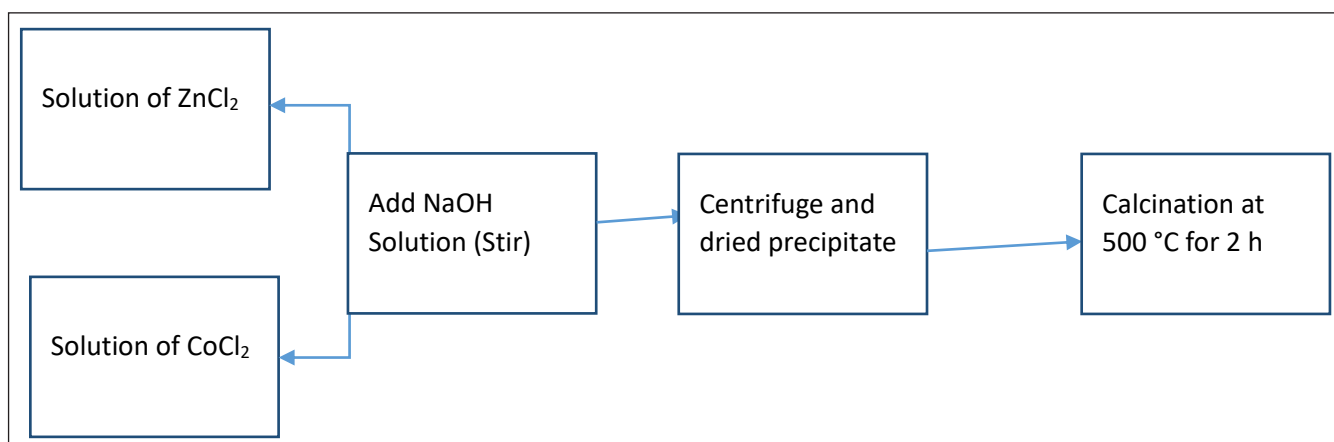


Fig. 1: Symmetric Diagram for the Synthesis of Pure and Co Doped ZnO Nanoparticles



Fig. 2: Image of Pure and Co Doped ZnO Nanoparticles

B. Characterization

In order to understand the material physics, characterization techniques refer to the process by which we can study the different properties of the synthesized compound [6]. To study the structural properties of the synthesized nanoparticles two important tools were used are X-Ray diffractometer (XRD) and Fourier transform infrared (FTIR) [6] and study the optical properties using UV-VIS spectrometer. The magnetic properties of the synthesized nanoparticles were studied using VSM from which we got a hysteresis loop and hence the

saturation magnetization, coercivity and other parameters can be calculated.

III. RESULTS AND DISCUSSIONS

A. X-Ray Diffraction

The diffraction pattern obtained from the XRD measurement contains peaks that correspond to the different crystal planes of the nanoparticles. By analyzing the positions and intensities of these peaks, valuable information can be extracted. The positions of the peaks allow the determination of the crystal structure and lattice parameters of the nanoparticles. The peak widths provide insights into the size and strain within the nanoparticles.

To extract quantitative information, the diffraction pattern is typically analyzed using specialized software. The software compares the experimental diffraction pattern with known reference patterns of different crystal structures, allowing identification and phase analysis. Moreover, peak broadening analysis techniques, such as the Scherrer equation, can be applied to estimate the size of nanoparticles.

The undoped ZnO have wurtzite structure, the variation in intensity observed due to have different doping concentration of Cobalt. The small shift of peak is observed when the ZnO doped with Co. The XRD pattern of the synthesized ZnO nanoparticles revealed diffraction peak at 2 theta angles of 31.8, 34.5, 36.1, 47.6, 56.6, 62.9, and 67.9, corresponding to the (100), (002), (101), (102), (110), (103), and (112) crystallographic planes, respectively, the diffraction peaks were consistent with hexagonal wurtzite crystal structure of ZnO (JCPDS card no. 36-1451).

By applying the scherrer equation to the full-width at half maximum (FWHM) of the (101) diffraction peak, the average crystallite size of the ZnO nanoparticles was determined to be approximately 15.2 nm. The XRD characterization of the synthesized ZnO nanoparticles confirmed the presence of the hexagonal wurtzite crystal structure. The calculated average crystallite size of 15.2 nm indicated that the synthesized nanoparticles possessed a nanoscale dimension, which is favourable for various applications.

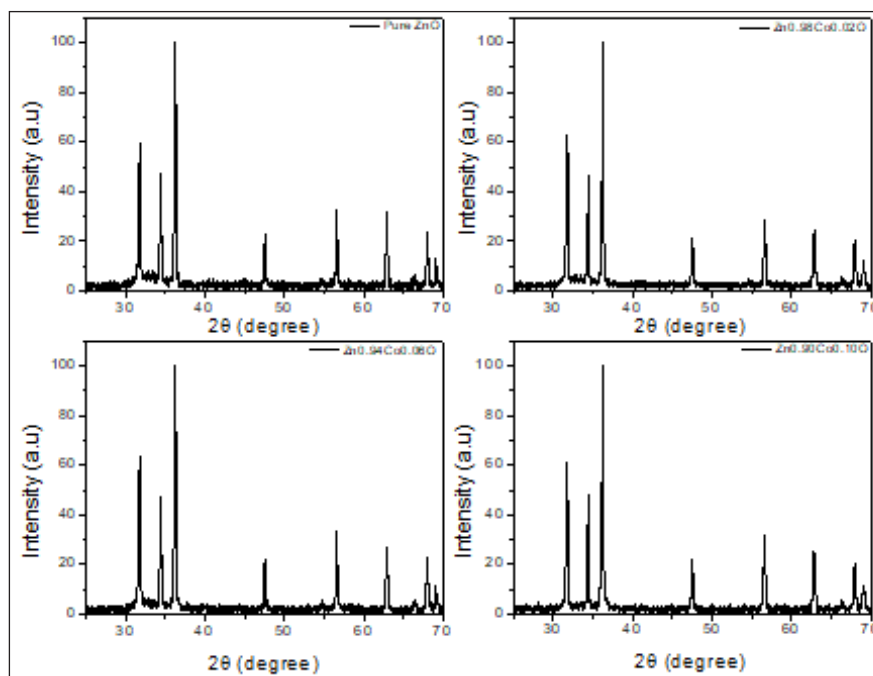


Fig. 3: XRD Plots of Pure ZnO and Co Doped ZnO Nanoparticles Fourier Transform Infrared Spectroscopy (FTIR)

FTIR (Fourier Transform Infrared Spectroscopy) is a widely used analytical technique for characterizing the properties of nanoparticles. It measures the absorption and transmission of infrared light by the nanoparticles, providing valuable information about their chemical composition and structure.

In FTIR, a beam of infrared light is passed through a sample containing nanoparticles. The light interacts with the nanoparticles, causing certain bonds within the particles to vibrate at characteristic frequencies. The amount of light absorbed by the nanoparticles at each frequency is measured, creating a unique fingerprint or spectrum.

By analyzing the FTIR spectrum, one can identify functional groups present in the nanoparticles, determine the types of bonds, and infer the chemical composition. Additionally, FTIR can detect impurities, identify surface modifications, and monitor chemical reactions involving nanoparticles.

To extract meaningful information, the obtained spectrum is compared to reference spectra or databases to identify specific nanoparticles or their components. Quantitative analysis can

also be performed by correlating the intensity of absorption peaks with the concentration of the nanoparticles.

The FTIR (Fourier Transform Infrared) spectroscopy analysis of ZnO nanoparticles and ZnO doped with cobalt nanoparticles revealed distinct vibrational spectra associated with the respective materials. In the case of ZnO nanoparticles, the FTIR spectrum exhibited characteristic peaks at around 380 cm^{-1} and 430 cm^{-1} , which are attributed to the Zn-O stretching vibrations. These peaks indicate the presence of Zn-O bonds in the ZnO nanoparticles. Additionally, a broad absorption band in the range of $3400\text{-}3600\text{ cm}^{-1}$ suggests the presence of surface hydroxyl groups on the nanoparticles.

On the other hand, the FTIR spectrum of ZnO doped with cobalt nanoparticles displayed additional peaks in the range of $500\text{-}700\text{ cm}^{-1}$. These peaks correspond to the Co-O stretching vibrations, indicating the successful doping of cobalt into the ZnO lattice. The presence of these peaks suggests the formation of Co-O bonds, which are characteristic of the doped material.

Overall, the FTIR analysis confirmed the presence of Zn-O bonds in both ZnO nanoparticles and ZnO doped with cobalt

nanoparticles. However, the additional peaks observed in the spectrum of the doped material indicate the successful incorporation of cobalt into the ZnO lattice, providing valuable information about the structural characteristics of the doped nanoparticles.

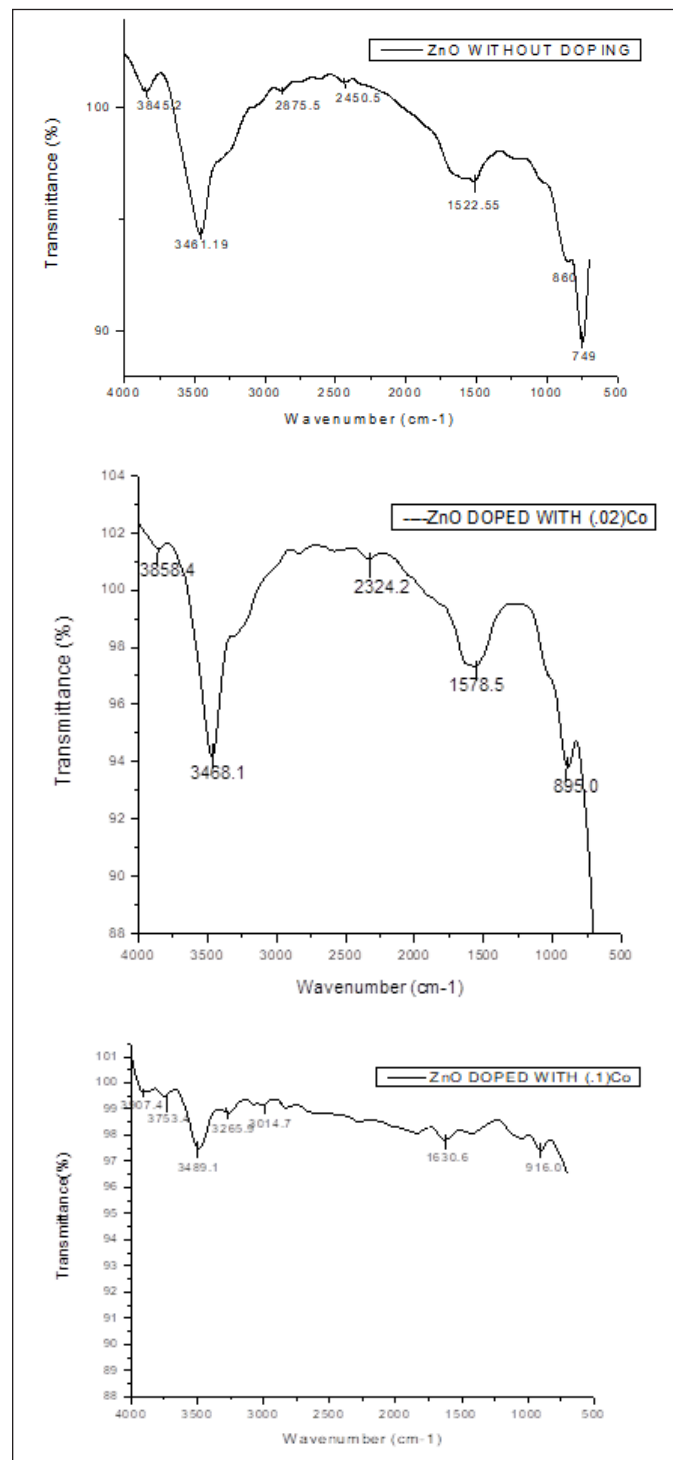


Fig. 4: FTIR Plots of Pure ZnO and Co Doped ZnO Nanoparticles

C. Vibrating Samples Magnetometer (VSM)

VSM, or vibrating sample magnetometry, is a technique used to study the magnetic properties of nanoparticles. It involves subjecting the nanoparticles to an oscillating magnetic field and measuring the resulting magnetization. By analyzing the response of the nanoparticles to the magnetic field, important properties such as the magnetic moment, coercivity, and saturation magnetization can be determined. VSM is particularly useful for characterizing nanoparticles because it can provide insights into their size distribution, magnetic anisotropy, and overall magnetic behavior. By obtaining these properties, researchers can better understand the behavior of nanoparticles and design applications that utilize their unique magnetic properties. Zinc oxide (ZnO) nanoparticles synthesized via the coprecipitation method typically exhibit diamagnetic or weak paramagnetic behavior. The magnetic properties of ZnO nanoparticles depend on their size, crystalline structure, and defect density.

In bulk form, ZnO is diamagnetic, meaning it does not possess any intrinsic magnetic properties. However, when ZnO is prepared in the nanoscale regime, its behavior can change due to quantum confinement effects and surface defects.

In co-precipitation synthesis, ZnO nanoparticles are typically produced by precipitating zinc salts in the presence of a base or a precipitating agent. The resulting nanoparticles can have a wide range of sizes and surface defects, which can influence their magnetic properties.

Most commonly, ZnO nanoparticles prepared via co-precipitation exhibit weak paramagnetic behavior. This arises due to the presence of oxygen vacancies and other defects on the nanoparticle surface. These defects introduce localized unpaired electrons, which give rise to weak paramagnetism. The spontaneous magnetization was calculated to be 0.1 emu/gm for pure ZnO nanoparticles, which increases to 0.2 emu/gm for 10% doping of Co in ZnO nanoparticles.

The incorporation of Cobalt iron into the zinc oxide lattice also impacted the magnetic properties. Magnetic characterization using techniques like vibrating sample magnetometry revealed an increase in magnetization with higher Co doping concentration. This enhancement suggests the successful introduction of magnetic moment stroke Cobalt doping offering potential for applications in magnetic devices and spintronics. Overall the results indicate that Cobalt doping of ZnO nanoparticle is induced to change in their structural, optical and magnetic properties. The red shift in the absorption edge increased optical absorption and enhanced magnetization demonstrate the influence of Co ion on the electronic structure and properties of ZnO. This modification has implications for a wide range of applications including optoelectronics, sensors, and magnetic devices.

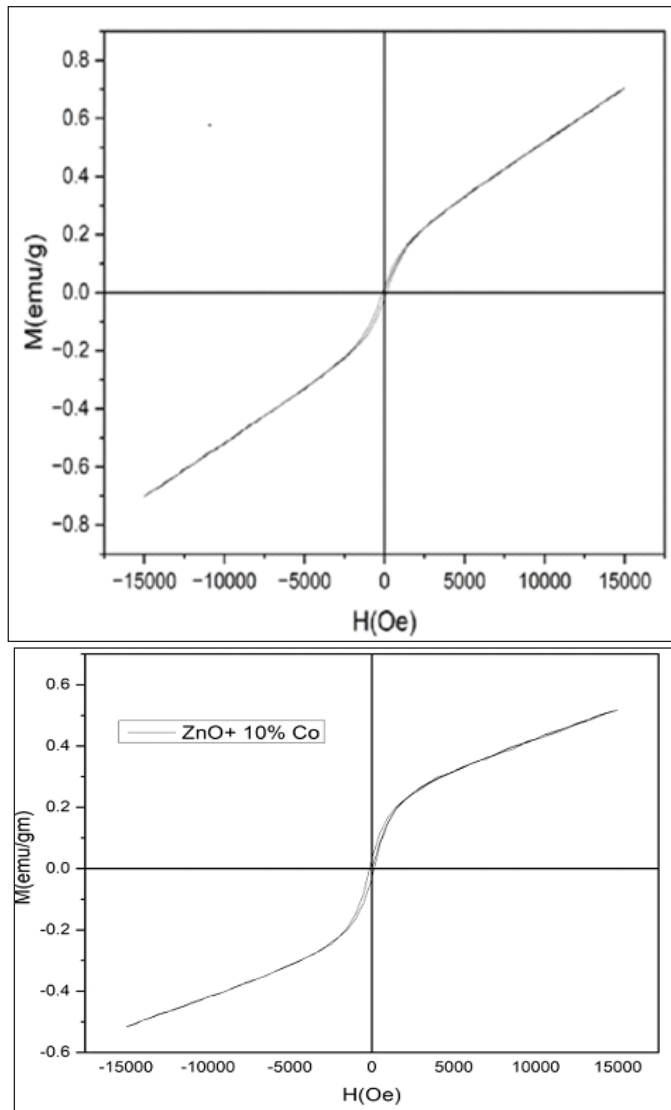


Fig. 5: VSM Plots for Pure ZnO and 10% Co Doped ZnO Nanoparticles

IV. CONCLUSIONS

In conclusion, the report on the characterization of ZnO nanoparticle doped with 2%, 6% and 10% cobalt (Co) doping concentrations reveals significant insights into the properties and potential applications of these co-doped nanoparticles.

Through structural analysis using X-ray diffraction (XRD), it was determined that the crystal structure of the Co doped ZnO nanoparticles remained consistent with pure ZnO, indicated successful incorporation of Co ions into the ZnO lattice without introducing significant structural changes.

Magnetic characterization using techniques such as vibrating sample magnetometry (VSM) demonstrated an increase in magnetization with higher Co doping concentrations. This enhancement in the magnetic properties suggests the successful introduction of magnetic moments through Co doping, which opens up possibilities for applications in magnetic devices and spintronics.

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