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# Synthesis of Cobalt (Co) doped ZnO Spintronic Nano Powders by Solution Combustion Method and Their Characterization

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***Abstract*— In this current work, we report the synthesis of transition metal (TM) Cobalt(Co) doped ZnO ($Zn_{1-x}$ $Co_x$ O where x = 0.01, 0.05, 0.1) powders by solution combustion process using urea ($NH_2CONH_2$) as fuel. The synthesized powders were characterized by XRD for phase anlalysis and SEM for microstructure. The powder XRD patterns of the samples confirms the formation of polycrystalline ZnO of hexagonal wurtzite structure by comparing with the standard peaks of JCPDS card no 36-1451. The crystallite size of the powder ranges from 18-30nm when calculated by Scherrer formula. SEM images shows the leaf like ZnO particales of thikness 60nm with 400-600nm length.**

***Keywords*—— *Combustion, Zinc Nitrate, Cobalt Nitrate, Urea.***

## I. INTRODUCTION

Zinc oxide, a II–VI semiconductor, is a known electro-optical and piezoelectric with wide direct band gap (3.3eV) and large removal binding energy material. ZnO is considered as a potential material for a number of applications such as luminescent devices and opto-electronic and as well as chemical sensors [1]. Doping with transitional metal elements leads to many exciting properties of ZnO. Presently, much experimental and theoretical research is focused on dilute magnetic semiconductors (DMS) based on ZnO doped with transition metal ions such as Mn and Co, since the predicted room temperature ferromagnetism in the DMS may be useful in spintronic [2].

Spintronic (spin-based electronics) based on diluted magnetic semiconductor oxides, is presently an active area of examine because spin-based multi-functional electronic devices have several advantages over the conventional charge based devices regarding data-processing speed, non-volatility, and higher integration densities [3]. Ferromagnetic semiconductors have emerge as important materials for spintronic applications [4]. In quantum computing devices, the spin states would be used to construct "qubits," theoretically enable the direction of huge amounts of data. For non-volatile memory storage applications, ferromagnetism is used to store data for extended periods of time. By manipulating spins, rather than charge, it is anticipated that more energy-efficient memory storage will be developed. Recent discoveries of ferromagnetic behaviour in certain dilute magnetic semiconductors DMS have lead to an increased interest in the development and research of these materials. DMSs offer the possibility of optical devices such as spin light emitting diodes spin-LEDs spin-polarized solar cells, and magneto-optical switches. Till now no report has been made of studying the cobalt doped ZnO urea fuel.

The main test for practical application of the DMS materials is the ability of intrinsic ferromagnetism with Curie temperature (TC) at or preferably above room temperature. Much attention has been paid to the magnetic properties of ZnO based DMS materials due to the theoretical prediction by Dietl [5] and Sato [6].

Up to now, various approaches have been applied to prepare TM doped ZnO, such as Sol-gel [7-11], Thermal decomposition solid-state route [12-13], Co-precipitation [14-15], Chemical vapor deposition [16], by using different chemical precursors.

In this work, transition metal Co doped ZnO ($Zn_{1-x}$ $Co_x$ O where $x$ = 0.01,0.05,0.1) powders using urea fuel was synthesized by solution combustion method. Effect of doping concentration on crystallite size is studied.

## II. EXPERIMENTAL DETAILS

### *A. Raw materials used*

Zinc nitrate hexa-hydrate ($Zn(NO_3)_2.6H_2O$). (Universal laboratories), Cobalt nitrate ($Co(NO_3)_3.9H_2O$), (Universal laboratories), Urea ($NH_2CONH_2$).

### *B. Solution Combustion Synthesis of ZnO*

The cobalt (Co) doped ZnO ( $Zn_{1-x}Co_xO$ X = 0.01 , 0.05 , 0.1) powder were prepared by solution combustion process using cobalt nitrate, zinc nitrate as oxidizers and urea as fuel. The oxidizers and fuels were weighed in electonic balance for various doping concentration samples accordingly to Table(I) The amount of oxidizers and fuel were calculated according to stoichiometry calculation as refered Baburao etal (17). The weighed chemicals were dissolved in minimum quantity of water in a beaker and stirred for some time such that solution becomes clear (transparent). The prepared solutions of various doping concentration are shown in fig(1). The homogeneous solution was then introduced into a furnace maintained at a temperature of 500° C. The solution boils and undergoes dehydration followed by decompositions with evolution of gasses ($N_2$ and $CO_2$) then it burns at certain

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minute, and finally get nano crystalline ZnO powder.The synthesized powders were given for the characterization technique, X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD is used to determine the phase formation, crystallite size and SEM is used to determine the micro structure of the powder. The obtained final SCS prepared powders of various concentration are shown in fig(2). The combustion details like nature of combustion combustion time, expected product and obtained product are shown in Table II. And crystallite size is shown in Table III.

Under the equilibrium conditions the reaction equations for preparation of ZnO by urea fuel can be represented as below.

$$(1\text{-}x)Zn(NO_3)_2.6H_2O + xCo(NO_3)_3 9H_20 + 1.66NH_2CONH_2 \rightarrow Zn_{(1-x)}Co_x O + 1.66CO_2 + (2.66+0.5x)N_2 + (9.32+3x)H_2O \quad \ldots\ldots\ldots\ldots (1)$$

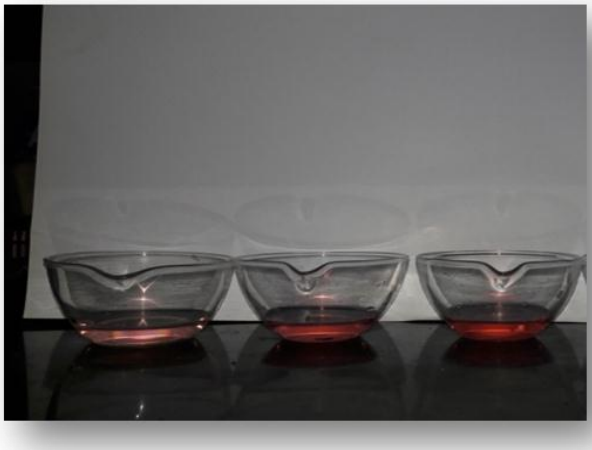

Fig 1. Chemical mixtures of zinc nitrate, cobalt nitrate and urea fuel i,e, (X=0.01 , 0.05 , 0.1 ) before combustion

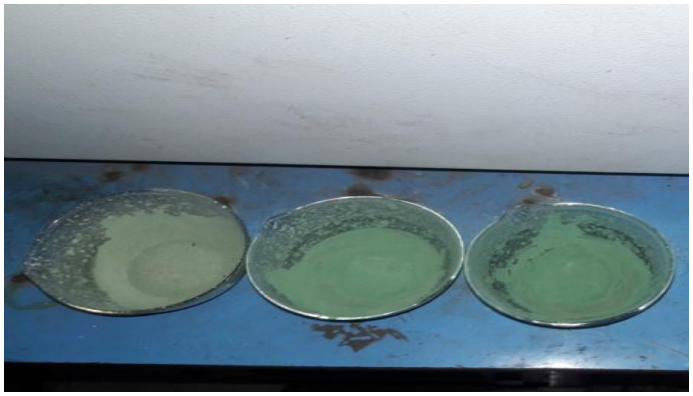

Fig 2 Synthesized powder of ZnO

*C. Phase analysis by X-ray diffraction (XRD)*

X-ray diffraction studies were carried out for phase confirmation and calculating crystallite size of the milled samples, using D8-Advance-Bruker machine with Cu-$K_\alpha$ (wavelength of Cu-$K_\alpha$ ($\lambda$) ~1.5406 Å) radiations for all the measurements. Ni filter was used to attenuate $K_\beta$ lines. The crystallite size of powders was calculated using Scherrer's formula.

$$d = K\lambda / \beta \cos\theta \ldots\ldots\ldots (2)$$

where, $\beta$ is the full width at half maximum (FWHM) of diffracted peaks in degrees,
$\lambda$ stands for wavelength of x-rays,
d stands for the liner dimension of particles in meters,
$\theta$ refers to Bragg's angle in degrees
K' is the shape factor, generally known as a numerical constant and evaluated as 0.93 and depends on shape of crystallites.

## III. RESULT AND DISCUSSION:

Phase analysis of ZnO (Urea fuel) by XRD :

Fig 3-5 show XRD patterns of the Co doped ZnO ($Zn_{1-x}Co_xO$ (where X=0.01, 0.05, 0.1) powder prepared by solution combustion synthesis using urea as fuel at 500°C for all compositions . All the peaks in the XRD pattern of X =0.01,0.05,0.1 of Figure 3-5 respectively are very sharp showing the well crystalline behavior of the powders. The formation of polycrystalline ZnO is confirmed by comparing the peaks with standard peaks of JCPDS card no 36-1451**.** These peaks reveal that all the investigated samples are nano crystalline powder of hexagonal wurtzite structure. The crystallite size of Co doped ZnO powder was 18-30nm when calculated using Scherer's formula. The crystalline size increases with increase in doping concentration

Fig 6. shows the leaf like structure ZnO particales of thikness 60nm with 400-600nm length.

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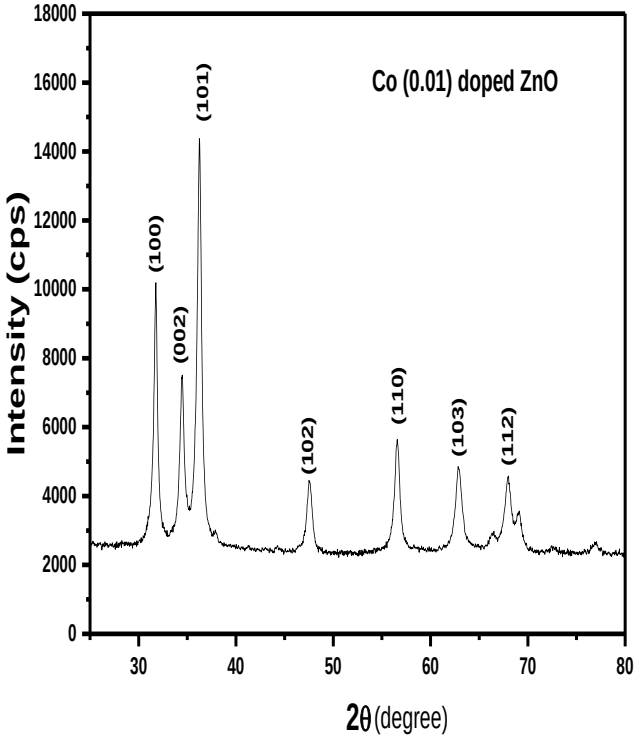


Fig.3 XRD pattern of Co (0.01) doped ZnO

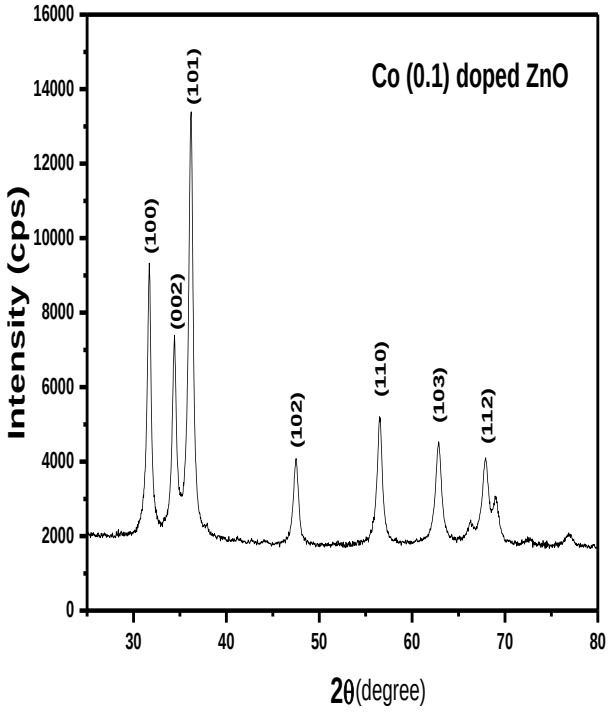


Fig.5 XRD pattern of Co (0.1) doped ZnO

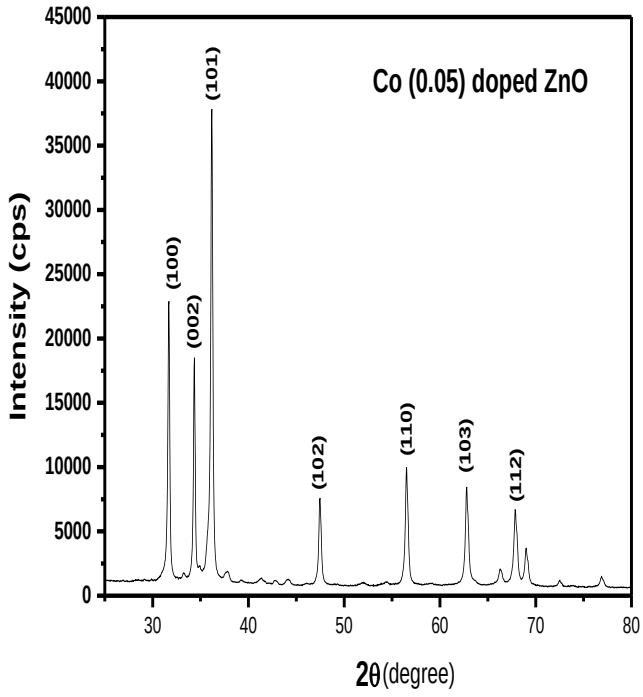


Fig.4 XRD pattern of Co (0.05) doped ZnO

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TABLE. I CHARACTERSTICS OF THE COMBUSTION REACTION TO PRODUCE ZNO

| Sl No | Sample code | Doping % | Samples | Color | Combustion type | Combustion time |
|---|---|---|---|---|---|---|
| 1 | ZNV01 | 1 | (2.94) $Zn(NO_3)_3.6H_2O$ + (0.029) $Co(NO_3)_3.9H_2O$ + $NH_2CONH_2$ | Light green | flame | 5.42min |
| 2 | ZNV03 | 5 | (2.82) $Zn(NO_3)_3.6H_2O$+ (0.145) $Co(NO_3)_3.9H_2O$+ $NH_2CONH_2$ | Light green | flame | 5.23min |
| 3 | ZNV05 | 10 | (2.67) $Zn(NO_3)_3.6H_2O$+ (0.29) $Co(NO_3)_3.9H_2O$+ $NH_2CONH_2$ | Dark green | flame | 5.09min |

TABLE. II AMOUNT OF UREA FUEL AND OXIDIZERS, USED FOR THE COMBUSTION REACTION TO PRODUCE ZNO

| Sno | Doping % | $Zn(NO_3)_3.6H_2O$ in (gm) | $Co(NO_3)_3.9H_2O$ in (gm) | Fuel urea in (gm) | Expected in (gm) | Obtained in (gm) |
|---|---|---|---|---|---|---|
| 01 | 1 | 2.94 | 0.029 | 1.0 | 0.8 | 0.603 |
| 03 | 5 | 2.82 | 0.145 | 1.0 | 0.8 | 0.50 |
| 05 | 10 | 2.67 | 0.29 | 1.0 | 0.8 | 0.455 |

TABLE.III CRYSTALLITE SIZE OF CO DOPED ZNO POWDER

| Doping % | 2θ | β | Θ | cosθ | $d = K\lambda / \beta \cos\theta$ in (nm) |
|---|---|---|---|---|---|
| 1 | 36.42 | 0.49 | 18.21 | 0.9500 | 17.80 |
| 5 | 36.50 | 0.32 | 18.25 | 0.9496 | 27.31 |
| 10 | 36.58 | 0.47 | 18.29 | 0.9494 | 30.46 |

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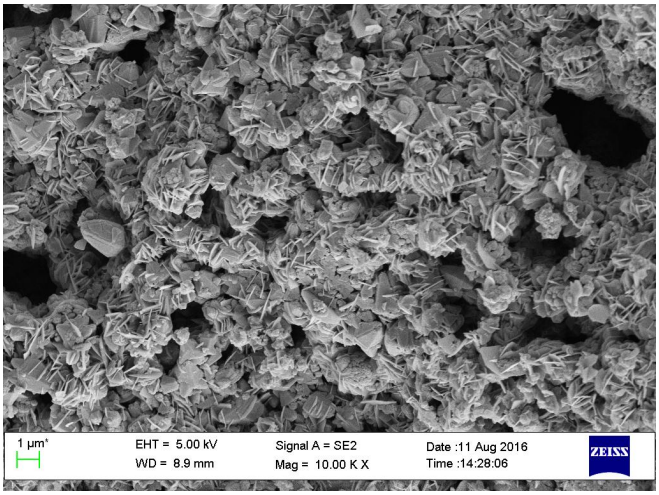
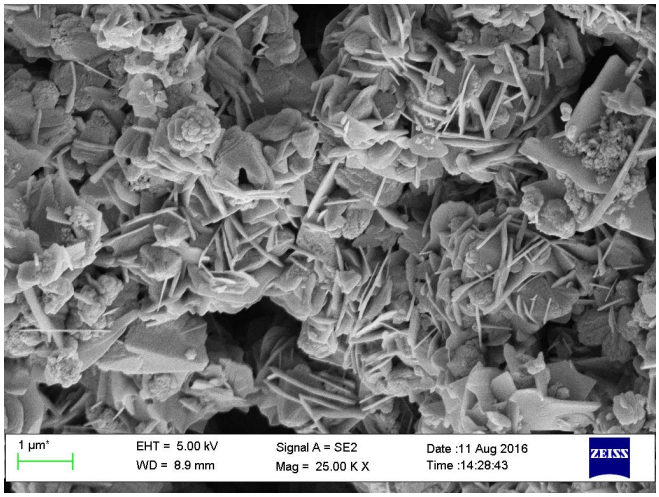
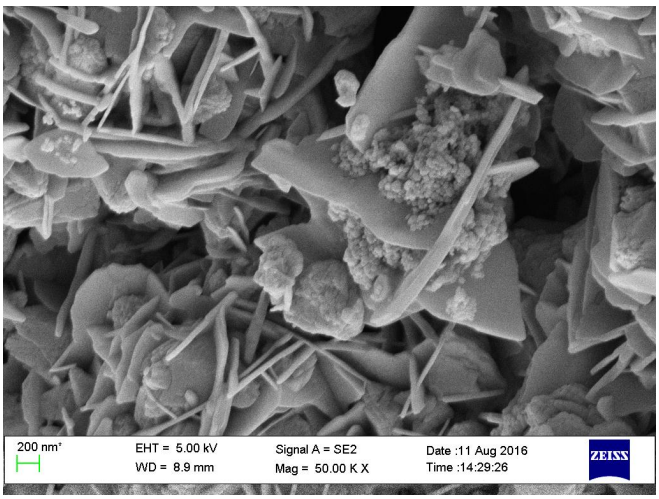


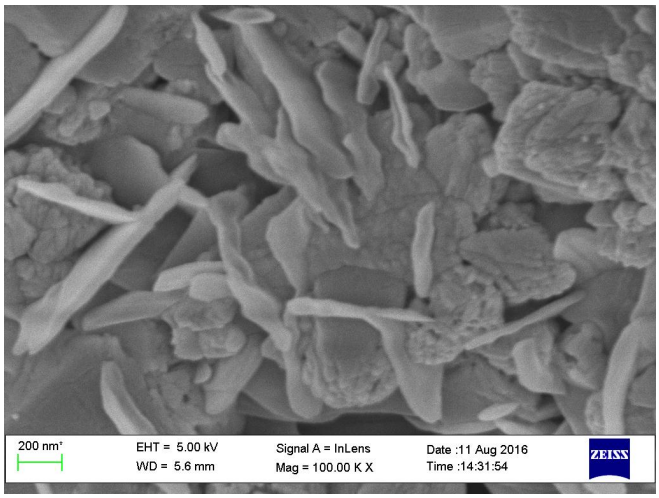

(a) magnification =10 k




(b) magnification =25.0 k




(c) magnification =50.0 k




(d) magnification =100.0 k

Fig 6 SEM images of ZnO sample (0.01) with different magnifiacation

## IV. CONCLUSION

Co doped ZnO ($Zn_{1-x}$ $Co_x$ O (where X=0.01, 0.05, 0.1) powders were synthesized by solution combustion method. The XRD patterns of all the samples show the formation of pure ZnO by comparing with standard (JCPDS card no 36-1451). Up to 10% of Co was soluble in 2 min. No impurity was present in XRD pattern. SEM images shows the leaf like structure ZnO particales of thikness 60nm with 400-600nm length and formed by nano powder of size 18-30nm.

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International Journal of Engineering Research & Technology (IJERT)
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