Synthesis of Ni doped ZnO Nanopowders by Solution Combustion Method Using Glycine as Fuel

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ABSTRACT

Ni doped ZnO ($Zn_{(1-x)}$ Ni_x O, x = 0, 2, 4 and 6%) nanopowder have been synthesized by solution combustion method. Using Zinc nitrate Hexahydrate $Zn(NO_3)_2.6H_2O$ and Nickel nitrate Hexahydrate $Ni(NO_3)_2.6H_2O$ as oxidizer and glycine as fuel $C_2H_5NO_2$. The synthesized powders were characterized by X-ray Diffraction(XRD) for phase analysis, Scanning Electron Microscopy(SEM) for microstructure analysis and Energy Dispersive X-ray Spectroscopy (EDX) for elemental analysis. Synthesized powder shows well crystalline behavior the formation of phase pure crystalline ZnO is confirmed as comparing the peaks with standard peaks of JCPDS (card no. 36-145). SEM shows the particles of irregular shape and size, they are randomly oriented agglomerated and the pores can also be observed. The crystallite size of the powder ranges between 23-25nm, when calculated using Scherer formula. EDX spectra confirmed the presence of Zn, O and Ni elements in composition of prepared samples.

Keywords— Solution Combustion, Zinc Oxide, glycine.

I. INTRODUCTION

Materials which have at least one dimension in the size range of 1-100nm are called nanomaterials. Nanomaterials. have wide Application and properties, ranging from electronic via ceramic to catalyst due to their special properties, which are fundamentally dictated by size, composition and structure [1]. In the recent years semiconductor nanomaterials have pulled in much consideration because of their potential innovative application such as storage devices, optoelectronics, nanoelectronics and photonic devices [2-6]. Zinc Oxide (ZnO) is type of semiconductor having band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [7].ZnO discovers applications in different fields, for example, antireflection coatings, straightforward anodes in sun based cells, bright (UV) light producers, diode lasers, Varistors, piezoelectric gadgets, spintronics, surface acoustic wave spread, and furthermore in detecting of gas [8].ZnO doped with using different type of metallic ions like Sn, Ga, Al, and Sc and Y in order to improve its transparent conductive oxide properties [9-10].Transition metal doping into the ZnO lattice can change its optical, electrical, magnetic and catalytic properties, Various investigations have provided details regarding the enhanced optical and attractive properties of ZnO with transition metal [11-12].Many research groups and scientists have reported for the generation of ZnO nanostructures such as hydrothermal methods [13], laser ablation [14], sol–gel method [15], electrochemical depositions [16], thermal decomposition [17], chemical vapor deposition [18], and combustion method [19-20] but till now few groups have reported ZnO synthesis by solution combustion method; it is fast, easy and simple process and it gives homogeneous product, involves low cost equipment and raw materials [21].SCS is an effective method for synthesis of nanoparticles till now no one reported synthesis of ZnO doped with Ni using Glycine as fuel by solution combustion synthesis. In the present investigation, we have used the solution combustion technique to prepare transition metal Ni doped ZnO (Zn_{1-x} Ni_xO, where x = 0, 2, 4, 6%) powder using Glycine as fuel.

II. MATERIALS AND METHOD

A. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$). (Nice laboratories), Nickel nitrate hexahydrate ($Ni(NO_3)_3.6H_2O$), (Nice laboratories), Glycine,($C_2H_5NO_2$).

B. Synthesis

Ni doped ZnO (Zn_{1-x} Ni_xO, where x = 0, 2, 4, 6%) powders were prepared by solution combustion process by using Zinc nitrate Hexahydrate Zn $(NO_3)_2.6H_2O$ and Nickel nitrate Hexahydrate $Ni(NO_3)_2.6H_2O$ as oxidizer and glycine as fuel $C_2H_5NO_2$. All chemicals used were of analytical grade purity, were weighed according to the table I.

Table I: Amount of glycine fuel and oxidizers, used for the combustion reaction to produce ZnO

Sl. No	Doping of Ni in ZnO %	$Zn(NO_3)_2.6H_2O$ in (gm)	$Ni(NO_3)_2.6H_2O$ in (gm)	Fuel glycine in (gm)	Expected in (gm)	Obtained in (gm)	Yield In (%)
1	0	5.948	0.000	1.664	1.62	0.17	10.49
2	2	5.829	0.116	1.664	1.62	0.15	9.25
3	4	5.710	0.232	1.664	1.62	0.13	8.02
4	6	5.59	0.348	1.664	1.62	0.10	6.29

Chemicals were dissolved in minimum amount of water further this mixture of chemicals was taken and stirred continuously using Magnetic stirrer to ensure complete dissolution. The stirred solution is introduced into a preheated furnace which is maintained at a temperature of 500^0C. Initially the solution boils for certain period of time and it carries on with rise in the temperature. The combustion process initiates and at the end of the process we get the final product with the liberation of other gases. After the complete combustion takes place nanocrystalline powder is obtained.

= 1 The amount of oxidizers and fuel were calculated according to the stoichiometry calculation as referred Baburao at all [22]. Using below formula.

$\frac{\text{Fuel (F)}}{\text{Oxidizer (O)}}$ = 1 Stichometeric ratio

Where $\frac{F}{O}$ = fuel to oxidizer ratio = $\frac{\text{No.of moles of fuel} * \text{reducing valency of fuel}}{\text{No.of moles of oxidiser} * \text{oxidizing valency of oxidizer}}$

The combustion reaction feature and the combustion process details such as expected product, yield obtained, amount of chemicals taken, moles of chemical precursor, number of moles of fuel taken and the combustion details like nature of combustion, time, color of the flame, flame type, are shown in detail in Table I-II.

Table II: Characterization of the combustion reaction to produce ZnO

Sl No	Sample code	Doping of Ni in ZnO %	Samples	Color	Combustion type	Combustion time
1	**ZnNi0**	0	(5.948) $Zn(NO_3)_2.6H_2O$ + (0.000) $Ni(NO_3)_2.6H_2O$ + (1.664)$C_2H_5NO_2$	Off white	Layer	4.44min
2	**ZnNi2**	2	(5.829) $Zn(NO_3)_2.6H_2O$+ (0.116) $Ni(NO_3)_2.6H_2O$+ (1.664)$C_2H_5NO_2$	Light green	Layer	5.26min
3	**ZnNi4**	4	(5.710) $Zn(NO_3)_2.6H_2O$+ (0.232) $Ni(NO_3)_2.6H_2O$+ (1.664)$C_2H_5NO_2$	Light Dark green	Layer	5.50min
4	**ZnNi6**	6	(5.59) $Zn(NO_3)_2.6H_2O$+ (0.348) $Ni(NO_3)_2.6H_2O$+ (1.664)$C_2H_5NO_2$	Dark green	Layer	5.62min

C. Characterization Techniques

The final product and the phase purity of the nickel doped ZnO powder samples were examined by X-ray diffraction analysis (XRD) equipped with (CuK α radiation, k = 1.5412 A °).

The mean crystallite sizes were estimated using the Scherer formula,

$d = (\frac{0.9\lambda}{\beta\cos\theta})$

$\lambda=1.5412*10^{-10}$

where :

D is average crystallite diameter,

k is the wavelength of X-ray radiation,

β is full width at half maximum (FWHM)

θ is Bragg angle.

The lattice constants were obtained from the XRD data using hexagonal lattice parameter formula.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}$$

Where:
d is difference between planes of atoms.
h,k,l are all miller indices
a and c lattice constant of Ni doped ZnO.
Data of average a, c, and crystallite size of Ni doped ZnO shown in table-III. SEM is used for microstructure analysis of powder. EDX technique used for elemental analysis or chemical characterization of sample.

III. RESULTS AND DISCUSSIONS

The crystal structure of the samples was investigated by analyzing the X-ray Diffraction (XRD) data The X-ray diffraction patterns of Solution combustion synthesis (SCS) synthesized samples of Ni doped ZnO (Zn_{1-x} Ni_xO where X=0, 2, 4, 6%) were shown in Figure 1-4.XRD spectra depicts the characteristic peaks corresponding to reflection planes (100), (002), (101), (102), (110), (103) and (112) of wurtzite structure of ZnO, which is confirmed by comparing the peaks with standard peaks of JCPDS card no 36-1451. However, no impurity phases were detected in XRD pattern of Ni 0, 2, 4% doped ZnO show in figure1-3 and remaining ratios such as Ni of 6 % from the XRD data figure 4 shows the separation of NiO from ZnO lattice with peak at 2θ=43° which is confirmed by JCPDS (card no. 22-1189). The average crystallite size of the nickel doped ZnO powders were estimated from XRD using Scherrer's equation. Average Crystallite size of obtained powders was 23-25 nm when measured using Scherer formula.

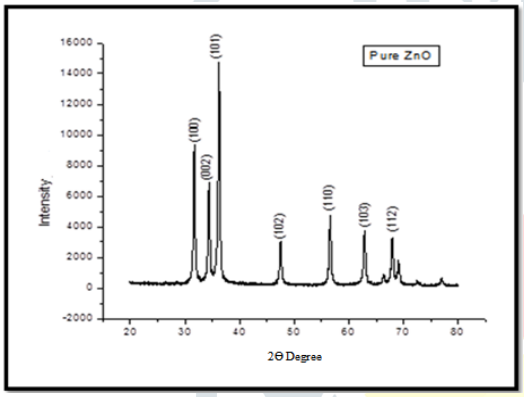


Figure 1: XRD pattern of 0% Ni doped ZnO powder

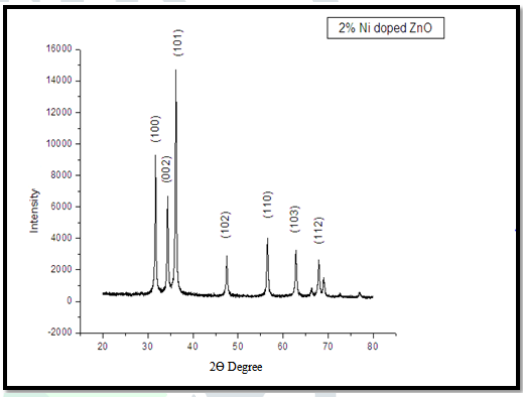


Figure 2: XRD pattern of 2% Ni doped ZnO powder

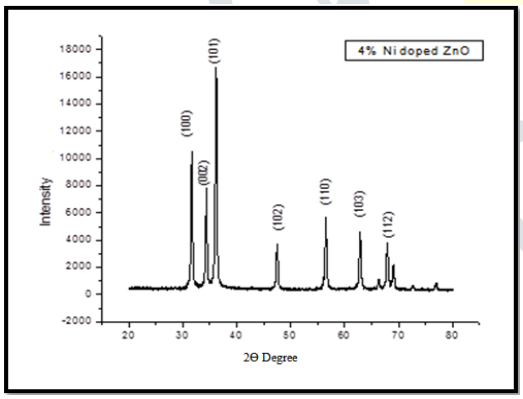


Figure 3: XRD pattern of 4% Ni Doped ZnO powder

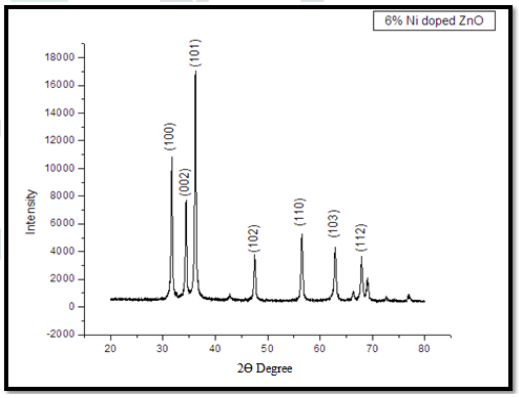
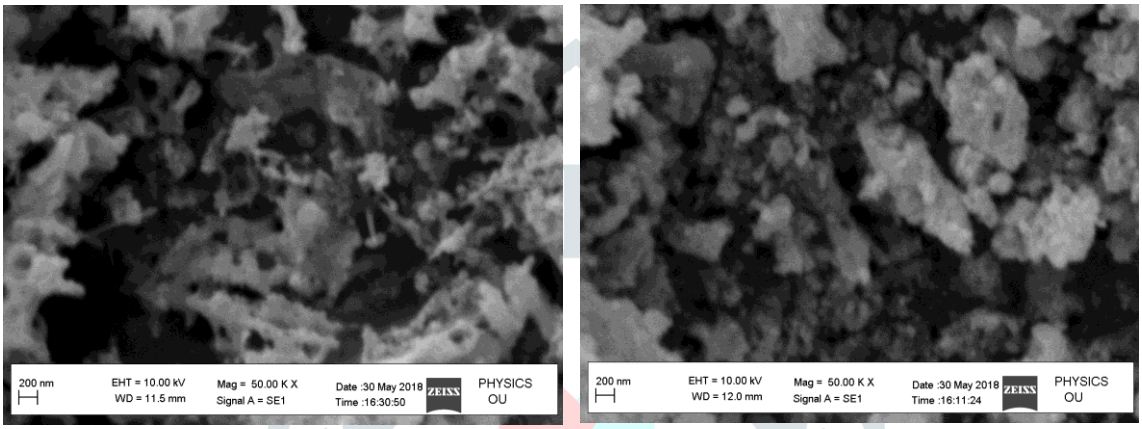


Figure 4: XRD pattern of 6% Ni Doped ZnO powder

Table III: Data of average a, c, and crystallite size of Ni doped ZnO

Sl no	Doped (%)	Average a in A°	Average c in A°	Crystallite size in nm
1	0	3.23	5.19	23
2	2	3.15	5.26	25
3	4	3.25	5.17	24
4	6	3.25	5.21	24

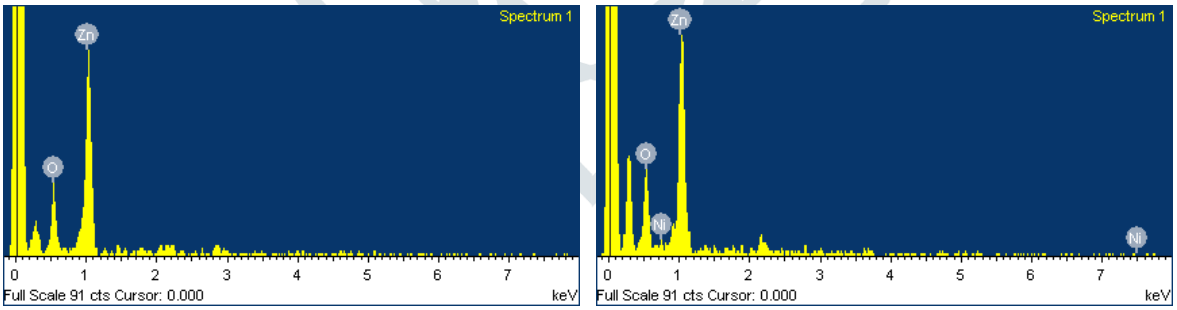
Scanning Electron Microscopy (SEM)is one of the techniques for the topography study of the samples and it gives important information regarding the growth mechanism, shape and size of the particles. The surface morphology of the Ni doped ZnO nanoparticles are as shown in Fig. 5a-b. The entire SEM picture clearly shows the average size of the nanoparticles is the order of nanometer size. It is observed that the particles are irregular in shape and size, they are randomly oriented agglomerated and the pores also can be observed. The porosity due to the many gases are evolved in solution combustion synthesis due to this the porosity is formed in the product which of fluffy mass.



a) Magnification at 50.00k of 0 % Ni doped ZnO b)Magnification at 50.00k of 2 % Ni doped ZnO

Figure 5 : SEM images of ZnO nanopowder

The elemental analysis of Ni doped ZnO powders has been carried out using the energy dispersive X-ray spectroscopy (EDX) Fig 6-a and 6-b show the EDX spectra of 0% and 2% Ni doped ZnO respectively. Fig 6-a shows absence of Ni peak and fig 6-b shows the presence of Ni element peak. Fig 6a-b both show the absence of an impurity other than Zn, Ni and O.



a) EDX spectrum of 0% Ni doped ZnO b) EDX spectrum of 2% Ni doped ZnO

Figure 6: EDX Spectrum of ZnO nanopowder

IV. CONCLUSION

$Zn_{1-x}Ni_xO$ (x = 0, 2, 4, 6%) nanoparticles have been successfully synthesized by solution combustion method. The XRD observations reveal the hexagonal wurtzite structure of Ni-doped ZnO and doping of Ni 0, 2,4,6% does not change the wurtzite structure of ZnO, Hence Ni^{2+} substitutes Zn^{2+} site into the crystal lattice. The presence of NiO as a secondary phase for 6% Ni^{2+} doping level. The XRD patterns of all the samples show the formation of pure ZnO by comparing with standard JCPDS card no 36-1451. SEM images of the 0 and 2% Ni doped ZnO nanopowders show formation of porous agglomarates and irregular shape of ZnO. Particle size ranges from 159nm to 265nm.EDX spectra confirms the presence of Zn, O and Ni.

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