Synthesis of Magnesium (Mg) doped Zinc Oxide (ZnO) Nano Powders by Solution Combustion Method and Their Characterization

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ABSTRACT
In this current work, we report the synthesis of Magnesium (Mg) doped ZnO (Zn_{1-x} Mg_x O where x = 0.02, 0.06 and 0.1) powders by solution combustion process using Glycine ($C_2H_5NO_2$) 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 17-26nm when calculated by Scherrer formula. SEM images shows the zinc oxide nanopowders are highly porous and spongy in nature with agglomerate size ranges from 178nm to 244.6nm.

Keywords—— Solution Combustion, ZnO, Glycine, XRD

I. INTRODUCTION

Oxides are now a smart choice and basis of advanced and multifunctional devices [1]. Device fabrication and synthesis using oxides semiconductor have become more important recently because the physical properties are size dependent and can be tuned. Among oxide semiconductor family, ZnO is a wide bandgap material (3.37eV at room temperature) with large exciton binding energy (60 meV) and strong photocatalytic, optical, and piezoelectric properties. They are used in solar cells, photocatalysis and antibacterial active material [2], gas sensors [3], and UV (Ultraviolet) light emitting/detecting devices [4]. ZnO is also an integral part of green luminescence phosphor in fluorescent devices [5]. UV sensors are widely used in different applications, such as pollution monitoring, flame sensing, early missile plume detection, and other advanced military applications [6]. Different types of Si-based photodetectors are already available in the market and are very sensitive with low noise and quick response [5]. However, applications are limited as some need ultrahigh vacuum or high voltage supply (i.e., in photomultipliers) or time dependent degradation and lower efficiency [7]. To overcome this advantages new material such as diamond, SIC, Oxide semiconductors and nitrates are a focus of research. Also chemical and thermal stability at operating conditions are far better than conventional materials more ever their optical properties are slightly temperature dependent[8-9]. One of the possible materials which fulfills most of these requirements is ZnO. Their fore it has been studies extensively recently to further explore its potential applications in electronics and opto electronics [10].

Up to now, various approaches have been applied to prepare Mg doped ZnO, such as Sol-gel [11-15], Thermal decomposition solid-state route [16-17], Co-precipitation [18-19], Chemical vapor deposition [20], by using different chemical precursors.

II. EXPERIMENTAL DETAILS

A. Raw materials used

Zinc nitrite hexahydrate ($Zn(NO_3)_26H_2O$), Magnesium nitrate hexahydrate ($Mg(NO_3)_26H_2O$, Glycine($C_2H_5NO_2$)

B. Solution Combustion Synthesis of ZnO

The magnesium (Mg) doped ZnO ($Zn_{1-x}Mg_xO$ X = 0.02, 0.06, 0.1) powder were prepared by solution combustion process using Magnesium nitrate, zinc nitrate as oxidizers and glycine as fuel. The oxidizers and fuels were weighed in electronic balance for various doping concentration samples accordingly to Table (I) The amount of oxidizers and fuel were calculated according to stoichiometry calculation as referred Baburao et al[21-25]. 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 homogeneous solution was then introduced into a furnace maintained at a temperature of 500^0 C. The solution boils and undergoes dehydration followed by decompositions with evolution of gasses (N_2 and CO_2) then it burns at certain 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 various steps of SCS prepared powders are shown in fig (1). 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 Glycine fuel can be represented as below.

$(1-x)Zn\ (NO_3)_2.6H_2O + xMg\ (NO_3)_2 6H_20 + 1.11\ NH_2CH_2COOH \rightarrow$
$Zn_{(1-x)}\ Mg_x\ O + 2.22\ CO_2 + (0.55+1)N_2 + (2.775+6)H_2O$ ……...(1)

Solution Kept In Furnace

After 2 minutes

After 3 Minutes

After 4 minutes

Completion of Process

Sample after combustion

Figure 1: Images of Solution combustion of Mg doped 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 Miniflex II desktop x-ray diffractometer machine with Cu-K_α (wavelength of Cu-K_α (λ) ~1.5406 Å) radiations for all the measurements. Ni filter was used to attenuate K_β lines. The crystallite size of powders was calculated using Scherrer's formula.

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

where, β is the full width at half maximum (FWHM) of diffracted peaks in degrees,
λ stands for wavelength of x-rays,
d stands for the liner dimension of particles in meters,
θ 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 (Glycine fuel) by XRD: Fig (2-4) show XRD patterns of the Co doped ZnO (Zn_{1-X} Mg_X O where X=0.02, 0.06, 0.1) powder prepared by solution combustion synthesis using glycine as fuel at 500°C for all compositions. All the peaks in the XRD pattern of X =0.02, 0.06, 0.1 of Figure (2-4) 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 17-26nm when calculated using Scherer's formula. The crystalline size increases with increase in doping concentration Fig (5) shows the zinc oxide nanopowders are irregular shaped, highly porous and spongy in nature with agglomerate size ranges from 178nm to 244.6nm.

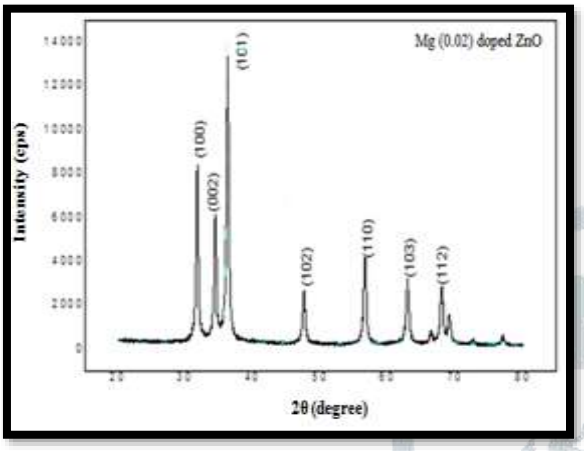


Fig 2: XRD pattern of 2% Mg doped ZnO powder

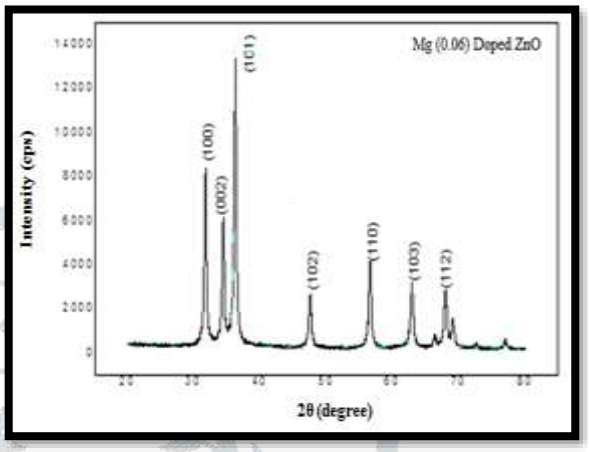


Fig 3: XRD pattern of 6% Mg doped ZnO powder

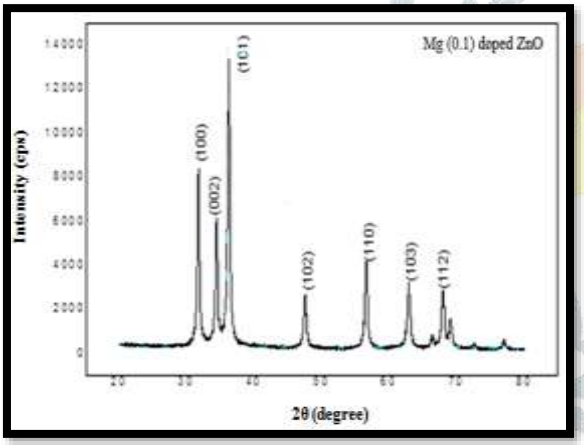


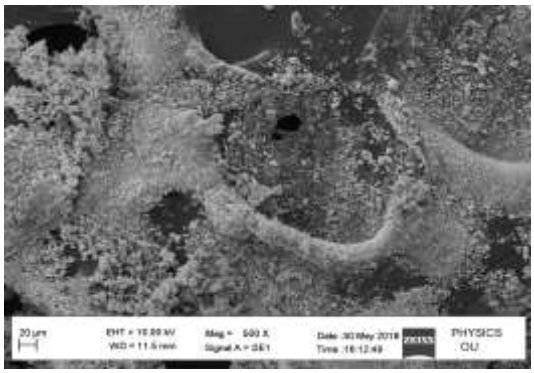
Fig 4: XRD pattern of 10% Mg doped ZnO powder

Table I: Characteristics of the combustion reaction to produce ZnO

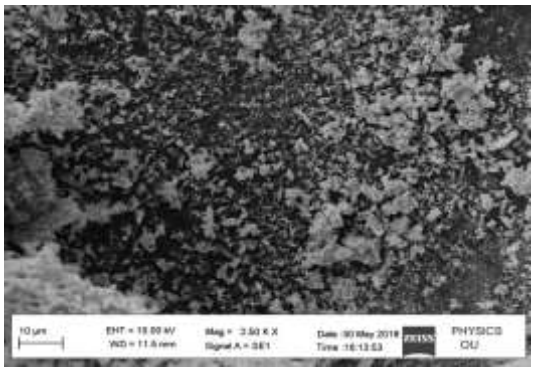
Sl No	Sample code	Mg Doping %	Samples	Color	Combustion type	Combustion time
1	ZN02	2	(5.8308) $Zn(NO_3)_2.6H_2O$ + (0.1025) $Mg(NO_3)_2.6H_2O$ +1.665 NH_2CH_2COOH	Creamish white	Layer	4.25min
2	ZN06	6	(5.5928) $Zn(NO_3)_2.6H_2O$+(0.3076) $Mg(NO_3)_2.6H_2O$ +1.665 NH_2CH_2COOH	Creamish white	Layer	4.21min
3	ZN10	10	(5.3548) $Zn(NO_3)_2.6H_2O$+(0.5128) $Mg(NO_3)_2.6H_2O$ +1.665 NH_2CH_2COOH	Creamish white	Layer	4.08min

Table II: Amount of Glycine and Oxidizers, used for the combustion reaction to Produce ZnO								
Sl no	Code	Doping % of Mg in ZnO	$Zn(NO_3).6H_2O$ (in gms)	$C_2H_5NO_2$ (in gms)	$Mg(NO_3)_2$ $6H_2O$(in gms)	Obtained (in gms)	Expected (in gms)	% Yield
1	ZN02	2%	5.8308	1.665	0.1025	0.298	1.62	18.39
2	ZN06	6%	5.5928	1.665	0.3076	0.318	1.62	19.62
3	ZN10	10%	5.3548	1.665	0.5128	0.320	1.62	19.75

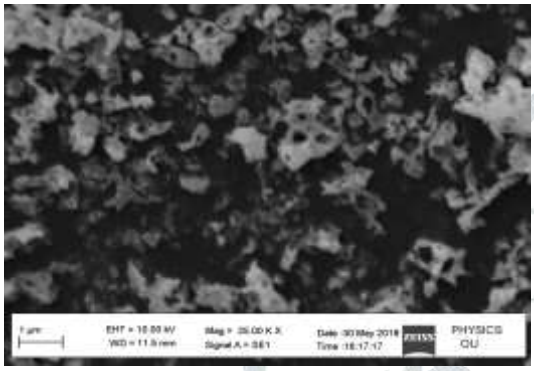
Table III: Crystallite size of Mg doped ZnO powder						
Sl no	Doping %	2Θ	β	Θ	cosΘ	d=kλ/β cosΘ in (nm)
1	2	36.48	0.48	18.24	0.9497	17.43
2	6	36.50	0.32	18.25	0.9496	26.28
3	10	36.62	0.47	18.31	0.9493	17.82



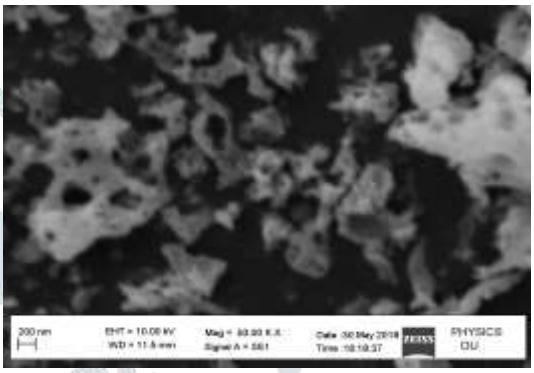
(a) Magnification = 500X



(b) Magnification = 2.50KX



(c) Magnification = 25KX



(d) Magnification = 50.00KX

Fig 5: SEM Images of ZnO sample (0.02) with different magnification

CONCLUSION

Mg doped ZnO (Zn_{1-x} Mg_x O (where X=0.02, 0.06, 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). No impurity was present in XRD pattern. SEM images shows the zinc oxide nanopowders are irregular shaped, highly porous and spongy in nature with agglomerate size ranges from 178nm to 244.6nm.

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