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Synthesis and structural analysis of cobalt doped zinc nanoparticles

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Abstract: *Nano science and nanotechnology involves studying and working with matter on an ultra small scale from sub nanometer to several hundred nanometers. The synthesis of nano particles has been considered as a preferred field in the nanotechnology sector due to size dependent properties of the materials. The wide band gap semiconductors like ZnO (3.3 eV) has gained a lot of attention among semiconductor materials due to their potential applications in optoelectronic devices in the visible and UV regions. In this paper, the structural parameters of pure and cobalt substituted ZnO nanoparticles sintered at 450^0C have been analysed to utilize them in the technological based applications using X-ray diffraction (XRD) technique.*

Keywords: *Structral parameters, ZnO, Cobalt, Nanoparticles, XRD*

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I. Introduction

In recent years, nano-crystalline ZnO has gained a special interest, because of possibilities for modification and control of various ZnO-based nanostructures. Moreover, it has a wide band gap, large exciton binding energy, abundant in nature, environment friendly and inexpensive bioluminescent material and ultraviolet(UV) lasing [1,2]. Also the aqueous precursor derived ZnO material is a reliable option for organic semiconductors and amorphous silicon materials to be applicable in transparent thin film transistors at low temperatures [3], light-emitting diodes [4], diode lasers [5], drug delivery [6], photo detectors [7] optical modulator wave guides [8], photovoltaic cells [9], phosphor [10], varistors, biosensors [11] and data storage & bioimaging [12], photodiode [13] piezoelectric transducers [14] and other usages such as doped- ceramic compounds [15]. Nano structured ZnO, nanorods or nanowires in particular, have attracted research, primarily due to their large surface area for applications in sensors and detectors, their light confinement in nano-lasers, and their freedom in lateral parameters for more sensitive piezoelectric devices. For all such purposes, the growth of ZnO nano scale material by a chemical route is to be followed. Most of the present methods rely strongly on ZnO grain manipulation techniques while drying and sintering the hydrated zinc oxide precipitates. Also, the defect structure in the evolution process of nano materials has to be given major attention as there is a strong evidence that defects play a vital role in ferromagnetic order in such materials and the ferromagnetic coupling can be mediated by carriers.

II. Experimental Details

2.1 Synthesis of ZnO Nanoparticles:

The glass wares have been first cleaned and rinsed with distilled water and then dried. All the materials and solvents have been weighed with help of electronic weighing balance and mixed in cleaned round bottom flask. In order to synthesize pure ZnO nanoparticles and cobalt doped ZnO nanoparticles by co-precipitation method. Zinc acetate and cobalt acetate have been used as precursors. Double distilled water has been used as a solvent and different concentrations of dopants have been incorporated. To start with, zinc acetate and cobalt acetate in proposed ratios are mixed well in 5 ml of double distilled water and the obtained solution has been stirred well using magnetic stirrer for about 1 hour to get an almost clear solution. After complete dissolution, ammonia solution is added drop by drop to get the precipitates of zinc oxide nanoparticles. The precipitates are filtered and then dried in oven at 100 ^{0}C temperature for about an hour and annealed at 450 ^{0}C temperature for two hours in a furnace and allowed to cool to room temperature yielding cobalt doped ZnO nanoparticles. During drying, $Zn(OH)_2$ is completely converted in to ZnO. With similar technique ZnO nanoparticles have been prepared without doping. The prepared ZnO nanoparticles have also been characterized for their nano structural properties.

TABLE 1: Synthesis of ZnO Nanopowder in Basic Medium

Sample 1- ZnO Base:

Chemical name	Mole required	Material taken
Zinc acetate	0.0250	5.4873gm
Ammonia solution	------	

Doping of Cobalt (Co)

Sample 2- ZnO: 5% Co :

Chemical name	Mole required	Material taken
Zinc acetate	0.0250	5.2128 gm
Cobalt acetate	0.0250	0.31135 gm
Ammonia solution	-------	5-10 ml

Sample 3- ZnO: 10% Co :

Chemical name	Mole required	Material taken
Zinc acetate	0.0250	4.9385 gm
Cobalt acetate	0.0250	0.6227 gm
Ammonia solution	--------	5-10 ml

Sample 4- ZnO: 15%Co:

Chemical name	Mole required	Material taken
Zinc acetate	0.0250	4.6642 gm
Cobalt acetate	0.0250	0.9341 gm
Ammonia solution	--------	5-10 ml

2.2 Characterization techniques:

X-ray diffraction (XRD):

X-ray diffraction pattern for the ZnO nanoparticles has been recorded using an X-ray diffract meter using Cu K_α radiation of wavelength $\lambda = 0.1541$nm. X-ray diffraction is one of the primary techniques used by mineralogists and solid state chemists to examine the physiochemical makeup of unknown solids and helps to determine the crystal structures and lattice parameters. This method is exploited for qualitative and quantitative phase diagram determinations of unknown substances alongwith determination of the nature of polycrystalline aggregates like particle size, perfection etc.

III. Result And Discussion

3.1 Structural Analysis

The structural parameters of pure and cobalt substituted (different concentration) ZnO nanoparticles sintered at 450^0C have been determined using X-ray diffraction (XRD) Fig.1 shows XRD patterns of pure and cobalt substituted (0-15%) ZnO nanoparticles. The diffraction peaks correspond to the planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (002) and (004) [16]. It has been observed from the obtained pattern that all the sintered samples have hexagonal (wurtzite) crystal structure. These planes are in good agreement with the standard XRD peaks of crystalline bulk ZnO having hexagonal wurtzite structure. In all XRD patterns, the (101) peak is dominant and its intensity is higher than those of the other peaks which indicates that growth of this particular orientation is preferred. The positions of diffraction peaks of Co-doped ZnO gradually change with doping thus revealing the interesting changes in *d* values, lattice parameters (*a*, & *c*) and lattice volume *V.* It also has been observed that XRD peaks get broadened with rise in cobalt content. Not any extra peak of cobalt oxide or any other impurity phase has been observed. It indicates the single phase presence in the samples with absence of a secondary phase. There is slight shift in reflection peaks of the diffraction pattern of cobalt substituted ZnO nanoparticles to lower angle than those of pure zinc oxide nanoparticles. It shows the Co^{2+}ions incorporation into Zn^{2+}sites. However, an insight analysis of the position of the XRD peaks (as shown in Fig. 2), indicates shifting of peaks towards lower angle with a rise in cobalt content. The change in the position of peaks (100) (002) and (101) clearly shows that cobalt ions occupy the zinc sites in the zinc oxide matrix [14].

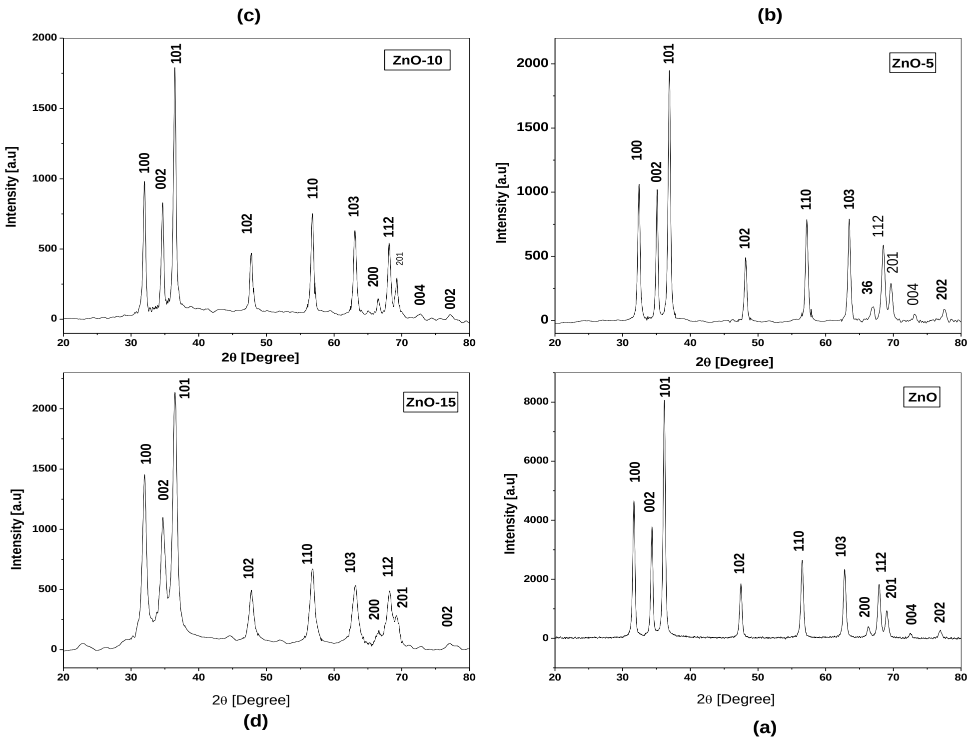

Figure 1: XRD patterns of pure and Cobalt substituted ZnO nanoparticles.

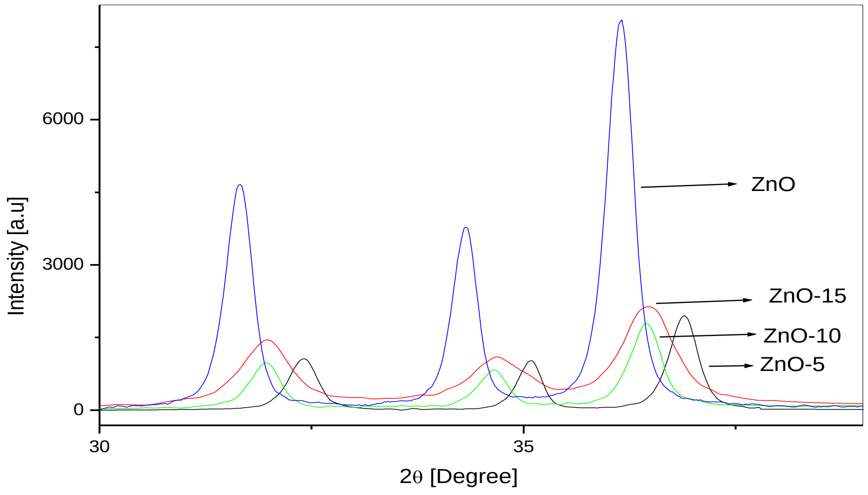

Fig.2: Shifting of [100], [002], [101] peaks with the $Zn_{1-x}Co_xO$ samples

3.2 Lattice Parameters

It is well known fact that the lattice parameters show a remarkable change with addition of different dopants. In doping, ionic radii plays an important role. If the ionic radii of dopants are higher or lower than the host lattice, then lattice parameters of host increase or decrease to accommodate it. In this study, the lattice parameters go on increasing with rise in cobalt content in $Zn_{1-x}Co_xO$ nanoparticles due to lesser ionic radius of Co^{2+} ions than those of Zn^{2+}ions. However, the lattice parameters increase up to 15% cobalt addition. But a decrease in lattice constant has been reported by Abrishami *et.al* [17] with metal ion doping in ZnO nanometer sized crystals in contrast to the observed increase in present study. This is attributed to the different ionic radius (0.58 Å) of Co^{2+} in tetrahedral configuration to that of Zn^{2+} (0.60 Å) [18]. The values of lattice parameters are listed in table 2 and have shown in Fig.3.

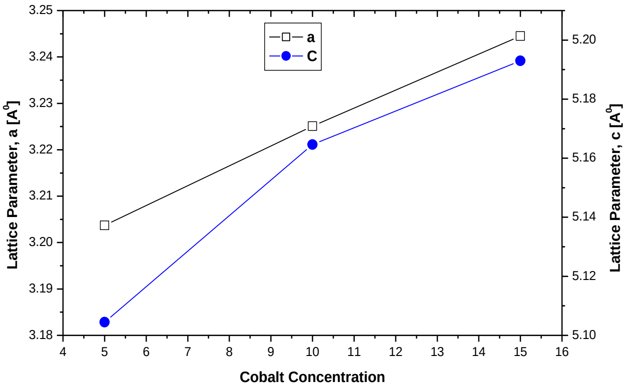

Fig.3 Lattice parameters versus cobalt concentration of the prepared samples

TABLE 2: Lattice parameters of ZnO: Co (5%, 10%, 15%)

Sample Code	**Lattice parameters**			**Volume [Å]^3**	**APF (%)**
	a (Å)	c(Å)	c/a		
ZnO	3.2449	5.2231	1.6096	47.63	75.15
ZnO-5	3.2037	5.1045	1.5933	45.37	75.85
ZnO-10	3.2251	5.1646	1.6014	46.52	75.47
ZnO-15	3.2445	5.1930	1.6006	47.34	75.51

3.3 Volume of Unit Cell

The volume of unit cell has been calculated using the equation

$$V = \frac{\sqrt{3}}{2} a^2 c$$

where a & c are lattice parameters. It has been found that the volume of unit cell increases with rise in cobalt content which may be attributed to an increase in the lattice parameters a and c and the values of unit cell volume are given in Table 2. It indicates that cobalt ions have moved to zinc sites available in the structure.

3.4 Atomic Packing Fraction (APF)

Atomic packing fraction (APF) has been calculated using formula and has been listed in table2

$$APF = \frac{2\pi a}{3\sqrt{3}c}$$

Where a and c are lattice parameters [19]. It is found that the APF first decreases with increasing cobalt content which may due to the reduction of voids of samples. The APF of bulk hexagonal ZnO materials is about 74% but in this study the APF of $Zn_{1-x}CoO_x$ nanoparticles is more than 75% which depicts that APF in nanocrystals is slightly greater than that of bulk materials. This is attributed to the size effect in the nanocrystalline samples. The APF increases with increasing cobalt content in $Zn_{1-x}CoO_x$ nanoparticles which indicates a homogenous substitution of cobalt ions in the zinc sites of ZnO structure.

3.5 Average Crystallite Size (D)

XRD peak profile analysis is a simple and powerful method to evaluate the peak broadening with crystallite size and lattice strain caused by dislocation. The average crystallite size has been estimated using Scherrer's formula [20].

$$D = \frac{K\lambda}{\beta_{hkl}\cos\Theta}$$

Where D is the average crystallite size in nanometers, K is a constant or shape factor equal to 0.9, λ is the wavelength of the radiation (1.54056 Å with Cu K_α radiation), β_{hkl} represents the peak width at half maximum intensity and θ is the peak position. The average crystallite size is in the range of 8-24 nm which decreases with increasing cobalt content in $Zn_{1-x}Co_xO$ nanoparticles. It may be due to the small grain growth of cobalt doped zinc oxide nanoparticles which is not present in pure ZnO nanoparticles. The values of average crystallite size are listed in Table 3.

3.6 Bond Length

The Zn–O bond length (L) is given by

$$L = \sqrt{\left(\frac{a^2}{3} + \left(\frac{1}{2} - u \right)^2 c^2 \right)}$$

where u is the positional parameter in the wurtzite structure and measures the amount which each atom gets displaced with respect to the next [21-22] and ‘u’ is given by

$$u = \frac{a^2}{3c^2} + 0.25$$

It has been observed that the value ‘u’ increases in such a way that the four tetrahedral distances almost remain nearly constant by distorting tetrahedral angles. The Zn–O bond length calculated according to this study is 1.9463 Å to 1.9739 Å; whereas the reported Zn–O bond length in the unit cell of ZnO and neighboring atoms is 1.9767 A° [2]. There is a good agreement of the calculated & actual bond length which supports the results of present study. The value of bond length is given in Table 3.

TABLE 3: Particle size and bond length of ZnO:Co

Sample	[hkl]	2θ (Degree) Observed	FWHM (Degree) Observed	d_{XRD} Observed (Å)	d_{jcpds} (Å)	Particle size (nm)	Bond length (Å)
ZnO	[002]	31.64	0.353	2.8099	2.8135	23.1364	1.9777
	[002]	34.31	0.337	2.6116	2.6025	24.3530	
	[101]	36.14	0.355	2.4825	2.4751	23.3016	
ZnO:5%Co	[100]	32.23	0.373	2.7743	2.7964	22.0000	1.9463
	[002]	35.12	0.310	2.5522	2.6027	26.6140	
	[101]	36.89	0.373	2.4340	2.4751	22.2139	
ZnO:10%Co	[100]	31.80	0.334	2.7927	2.7964	21.8597	1.9624
	[002]	34.50	0.459	2.5821	2.6027	24.1303	
	[101]	36.47	0.345	2.4545	2.4751	21.0215	
ZnO:15% Co	[100]	32.01	0.329	2.8097	2.7964	12.2484	1.9739
	[002]	34.70	0.342	2.5968	2.6027	08.9875	
	[101]	36.57	0.395	2.4611	2.4751	11.9913	

3.7 Strain

The strain-induced broadening in powders, caused by crystal imperfection and distortion has been calculated using the formula,

$$\varepsilon = \frac{\beta_{hkl}}{4Tan\theta}$$

XRD pattern of the prepared samples (shown in Fig.2). It depict that FWHM of the reflection peaks changes after addition of dopant cations as mentioned in Table 3. This indicates the growth of the crystallites or changes in the crystal strains. There is also a slight shift in peak positions, and their FWHM in the samples having different cobalt content as compared to the un-doped ZnO nanoparticles. This shift corresponds to the strain of the compound and replacement of some zinc cations with cobalt. It has been reported in the literature that with addition of foreign particle in the crystal lattice, a strain and defect(s) are produced in the lattice which may result in reduction of crystal quality.

TABLE 4: Strain, dislocation density and specific surface area of ZnO:Co

Sample	**[hkl]**	**Strain**	**Dislocation Density 10^{-3} (nm)$^{-2}$**	**Specific Surface Area**
ZnO	[100]	0.00540	11.83	46.2600
	[002]	0.00477	10.68	43.9487
	[101]	0.00474	10.68	45.9317
ZnO: 5%Co	[100]	0.00561	2.07	48.6491
	[002]	0.00427	1.41	40.2150
	[101]	0.00480	2.03	48.1810
ZnO: 10%Co	[100]	0.00538	2.08	48.7321
	[002]	0.00479	1.52	44.3150
	[101]	0.00493	2.16	49.2532
ZnO: 15%Co	[100]	0.00499	2.09	48.9615
	[002]	0.00488	1.72	44.3543
	[101]	0.00520	2.26	50.9137

3.8 Dislocation density

Dislocation is a crystallographic defect or irregularity within a crystal structure and the dislocation density is a measure of the dislocations which are present in a specific quantity of a material. It is defined as the length of dislocation lines per unit volume of the crystal and is calculated using.

$$\delta = \frac{1}{D^2}$$

Where D is the crystallite size. It has been shown that the dislocation density increases while crystallite size decreases with increasing strain and ultimately reach saturation values. The dislocation density of the prepared samples has been given in Table 4.

3.9 Specific surface area

It is a property of solids defined as the total surface area of a material per unit of mass and can be used to determine the type and properties of a material. The values obtained for specific area depend on the method of measurement. The specific surface area can be calculated from particle size given by

$$S = 6 \times 10^3 / D \times \rho$$

The specific surface area increases with cobalt incorporated as shown in Table 4.

IV. Conclusion

Nanoparticles of ZnO undoped and doped with cobalt with different concentration have been successfully prepared by chemical precipitation method. The XRD patterns obtained confirmed the formation of wurtzite hexagonal ZnO nanostructures without any impurities. The calculated value of lattice constants are a=b= 0.325 nm and c=0.52 nm nearly equal to standard value and relative d- spacing for lattice planes (100), (002) and (101) are nearly equal. The sizes of ZnO particles are in the range of 8-24 nm which have been determined using Debye Scherrer'formula. The Co doped ZnO nanoparticles decrease with increase in concentration of cobalt. The Zn-O bond length calculated is changed from 1.9777 to 1.9739 Å with Cobalt concentration (5-15%). The volume, density and specific surface area also change with incorporation of cobalt.

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