Effect of Doping of Transition Element-Nickel (Ni) in ZnO Nanoparticle

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Abstract - Zinc Oxide (ZnO) is the best versatile material because of its diverse properties and functionality. Doping of transition metals like Cr,Cd,Ni,Fe,Mn,Co,Cu etc provides an effective way to enhance various properties of ZnO nanoparticles,which is essential for their technological applications. In our work ,undoped and Ni doped ZnO nanoparticles were prepared using different methods and the results were compared. Undoped ZnO nanoparticles were prepared using chemical precipitation method, whereas Ni doped ZnO nanoparticles were prepared using co-precipitation method. Both the samples were characterized by UV-Vis spectroscopy. Ni doped ZnO nanoparticles were also characterized by X-Ray Diffraction (XRD). The lattice parameter (a) was found to be 0.428 nm and the crystallite size was found to be 20.57 nm. The band gap of undoped ZnO was found to be 3.40 eV and that of Ni doped ZnO was found to be 3.43 eV. The particle size calculated using effective mass approximation method for undoped ZnO and Ni doped ZnO came out to be 3.91nm and 3.47nm respectively. It was observed that the band gap enhances and the particle size reduces as ZnO is doped with transition metal (Ni). Therefore when ZnO is doped with transition metal (Ni),the absorption edge shifts towards lower blue region.

Keywords: Transition metal, ZnO nanoparticles, Doping, Ni doped ZnO, UV-Vis spectroscopy, X-Ray Diffraction.

I. INTRODUCTION

In recent years, the interest in nanomaterials is rapidly gowing due to their smaller size and high surface to volume ratio [1]. ZnO is a attractive nanomaterial due to its direct band gap (3.37 eV) and quantum confinement properties. It has a large scale of applications such as cosmetics, electronic and piezoelectric devices, drug delivery, batteries, food additive, sensors etc [2]. It belongs to II-VI group of periodic table and it is non-toxic. It has piezoelectric property that is highly useful for the fabrication of various devices such as electromagnetic coupled sensors and actuators [3].

Doping of transition metals in ZnO optimizes the optical, electronic, electrical and magnetic properties that are useful for various practical applications [4]. Nickel is one of the transition metal to improve those properties. At room temperature, nickel has a slow rate of oxidation and thus has a ccorrosion resistant property. Nickel shows ferromagnetic behavior at room temperature and is used in products like plating, rechargeable batteries, smart windows ,electric guitar strings, etc [5].

Undoped and Ni doped ZnO nanoparticles can be synthesized by many methods including sol-gel, hydrothermal, solvo thermal, co-precipitation and chemical precipitation method. In our work, we have used chemical precipitation method to synthesize undoped ZnO and co-precipitation method to synthesize Ni doped ZnO.

The aim of our present work is to analyze the effect of doping of transition metal (Ni) on ZnO nanoparticles by UV-Vis spectrophotometer.

II. CHEMICALS

Undoped ZnO was synthesized using AR grade Zinc Acetate dehydrate [(CH3COO) 2 Zn. 2H2O], Potassium hydroxide (KOH) , thioglycerol,Di-methylene sulfoxide (DMSO), methanol and distilled water.

Whereas the synthesis of Ni doped ZnO was carried out using zinc acetate dihydrate [Zn(CH3COO)2. 2H2O], nickel acetate dihydrate [Ni (CH3COO)2.2H2O] and sodium hydroxide (NaOH) in as received condition.

III. SYNTHESIS OF UNDOPED AND Ni DOPED ZnO NANOPARTICLES

A. Synthesis of undoped ZnO Nanoparticles

Undoped ZnO nanoparticles were prepared using chemical precipitation method. 0.2 M of Zinc Acetate dehydrate was first dissolved in 20 ml DMSO and distilled water and magnetically stirred for 30 minutes. Then 1.2 M of KOH in 10 ml ethanol was drop wise added and stirred for 5 minutes. We have used 0.12 ml of thioglycerol as a capping agent and magnetically stirred for one hour till the solution turns milky. In a few hours, the reaction was completed and the nanoparticle was precipitated by centrifugation. Finally the solution was washed and dispersed in methanol for UV–Vis spectroscopy experiments.

After that, the obtained precipitate was filtered and dried in oven for 3 hours at 150oC. After sufficient drying, the precipitate was crushed to fine powder.

In the preparation of ZnO nanoparticles, the chemical reactions involved were:

$Zn\ (CH_3COO)_2 + KOH \rightarrow Zn\ (CH_3COO)\ (OH) + KCH_3COO$
$Zn\ (CH_3COO)\ OH + KOH \rightarrow ZnO + KCH_3COO + H_2O$

B. Synthesis of Ni doped ZnO Nanoparticles

For the synthesis of Ni doped ZnO, 0.2 M of nickel acetate in 100ml water was mixed with 0.2 M zinc acetate in 100 ml separately. Then 1.2 M aqueous NaOH solution was added drop by drop to the homogenous mixture to get a white precipitate with pale green color. Later the solution was stirred for 3 hours and then kept it in oven at 700 C for 5 hours. After this, the precipitate was washed several times with double distilled water and ethanol. Finally, the precipitate was dried at 1000C for 2 hours.

IV. CHARACTERIZATION

The characterization of undoped and Ni doped ZnO nanoparticles was assured by determining the optical spectra.The particle size was determined that shows the presence of nanoparticles having size of 3.91 nm for undoped and 3.47 nm for Ni doped ZnO. It was analyzed that the band gap is enhanced and the particle size reduces on doping. The absorption edge was fairly shifted towards blue region and also the band gap is enhanced corresponding to bulk ZnO. From, X-ray diffraction measurements, it is confirmed that particle size is in nanometer range. The major peak in the XRD pattern was used to determine the crystallite size.

V. RESULTS AND DISCUSSION

A. UV-Vis Spectroscopy

The UV-Vis spectrum of undoped and Ni doped ZnO nanoparticle is shown in figure 1 and 2 respectively.

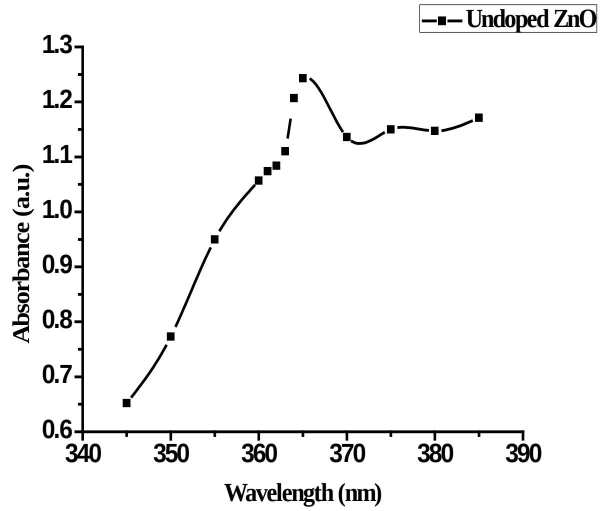

Fig.1: UV-Vis spectrum of Undoped ZnO nanoparticles prepared by chemical precipitation method.

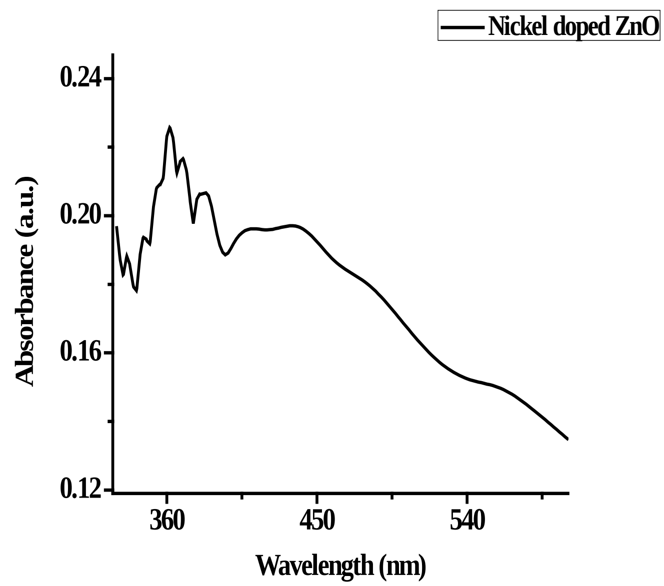

Fig.2: UV-Vis spectrum of Ni doped ZnO nanoparticles prepared by co-precipitation method.

The particle size (R) of both the samples were calculated using effective mass approximation formula [6]-

$$E = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left\{\frac{1}{m_e} + \frac{1}{m_h}\right\} - \frac{1.8e^2}{\varepsilon R}$$

Where E is the band gap of synthesized nanoparticle, Eg is the bulk band gap of ZnO (3.3eV), R is the radius of particle, m_h is the effective mass of hole (for ZnO, it is 0.49 m_o), ε is the dielectric constant of material (for ZnO, it is 9.1) ,m_e is the effective mass of electron (for ZnO, it is $0.28m_o$), and h is Planck's constant.

Fig.3: Ni doped ZnO nanoparticles

Fig.4:Pure ZnO nanoparticles

The values of Band gap (Eg) and particle size calculated is as listed in Table 1.

Table 1: Average particle size and band gap variation of undoped and Ni doped ZnO nanoparticles.

S.no.	Band gap (Eg) eV	Particle Size (nm)
Undoped ZnO	3.40	3.91
Ni doped ZnO	3.43	3.47

B. X-Ray Diffraction

The structural properties of nanoparticles can be analyzed using X-Ray Diffraction. The X-ray Diffraction pattern of Ni doped ZnO nanoparticle is shown in Figure 5. The XRD pattern obtained gives strong peak at 36.30° whose corresponding plane is (111) respectively. The major peak (111) in the XRD pattern was used to determine the crystallite size. The graph (Fig.5) plotted between the incident angle (2Θ) and intensity (au) shows the various intensities of transmitting waves of Ni doped ZnO over an appropriate angle range from 20 to 80. The lattice parameter (a) was found to be 0.428 nm and the crystallite size was found to be 20.57 nm.

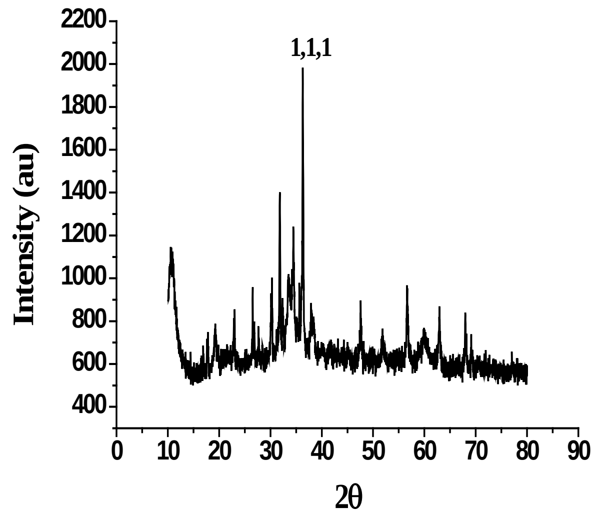

Fig.5: XRD of Ni doped ZnO nanoparticles

Now Using above graph, we can determine Miller Indices (h,k,l) at different peak angles and also can calculate its lattice parameter (a).

Peak	2θ(^{0}) (from X-ray Graph)	θ	$Sin^2θ$	$\frac{Sin^2θ}{Sin^2θmin}$	$\frac{Sin^2θ}{Sin^2θmin}$ xN	$h^2+k^2+l^2$	(h,k,l)	a (nm)
1.	36.30	18.15	0.097	1.299	3.86	3	(1,1,1)	0.428

The lattice parameter (a) of nanoparticles were calculated using –

$$a = \frac{\lambda}{2\sin\theta}\sqrt{h^2 + k^2 + l^2}$$

Where a is lattice parameter and h,k,l are miller indices.

With the help of obtained XRD data, the crystallite size of nanoparticles were calculated using Debye-Scherer formula-

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where: D is crystallite size, λ is wavelength of X-ray radiation i.e., 0.154nm, β is Full Width at Half Maximum (FWHM) in radian obtained at most intense peak and θ is Bragg angle.

The value of FWHM, crystallite size and miller indices are shown in Table 2.

Table 2: Table shows the XRD analysis for Ni doped ZnO nanoparticle.

S.No.	Peaks at 2θ	FWHM β (in degree)	Crystallite size (nm)	Miller Indices h,k,l
1	36.30°	0.37	20.57 nm	(1,1,1)

The lattice parameter (a) was found to be 0.428 nm and the crystallite size was found to be 20.57 nm.

VI. CONCLUSION

In summary, Undoped and Ni doped ZnO nanoparticles were synthesized successfully using chemical precipitation and co-precipitation method [7]. The crystallite size and lattice parameter of Ni doped ZnO nanoparticles were determined using the X-Ray Diffraction pattern. The UV-Vis spectroscopy confirmed the formation of nanoparticles with nickel doping. It can be seen that the band gap enhances and the particle size decreases with nickel doping. the band gap values of undoped and Ni doped ZnO nanoparticles changes from 3.40 to 3.43 eV on doping. These values exhibit a blue shift in band gap which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles. Doping of ZnO with transition metal such as Ni will result in larger surface area and reduction in the particle size of ZnO nanoparticles [8].

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