OPTICAL PROPERTIES OF UNDOPED ZINC OXIDE AND NICKEL DOPED ZINC OXIDE

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Abstract

The main aim of the research work is to study the optical properties of undoped ZnO and Ni doped ZnO. Undoped ZnO and Ni doped ZnO were prepared by using a co-precipitation method. The prepared undoped ZnO and Ni doped ZnO were characterized by Thermogravimetric-Differential Thermal Analysis(TG-DTA), X-ray Diffraction (XRD), Fourier Transform Infra-red (FT IR) spectroscopy, Energy Dispersive X-ray (EDX) spectrometry and Scanning Electron Microscopy (SEM) analyses.TG-DTA analysis of the synthesized undoped ZnO and Ni doped ZnO were carried out to determine the appropriate calcination temperature. From XRD analysis, it was observed that the average crystallite sizes of the prepared undoped ZnO and Ni doped ZnO were 28 and 22 nm, respectively. In FT IR spectra of undoped ZnO and Ni doped ZnO powder, the prominent peak of OH stretching, H-O-H bending and M-O stretching vibrations were observed. Morphological studies were conducted using SEM to confirm the uniform distribution of particles. UV-Visible spectrum showed the absorbance peaks in the 200-800 nm region. From UV-Visible spectral data, it was found that the band gap values of undoped ZnO and Ni doped ZnO are 2.7 and 2.8 eV, respectively.

Keywords: co-precipitation, optical properties, Ni doped ZnO, band gap

Introduction

Semiconductor nanoparticles are gaining much attention due to its peculiar physical and chemical properties. Metal oxide are widely used in commercial products such as catalysts, cosmetics, microelectronic devices, semiconductors, sporting goods, and textiles.

The optical properties of nanocrystalline semiconductors have been studied extensively in recent years. As the size of the material becomes smaller and the band gap becomes larger, this changes the optical and electrical properties of the material, making it suitable for new applications and devices. Among them, the widely accepted method to modify the electrical and optical properties of a semiconductor is the addition of impurity atoms, or doping (Devi and Velu., 2015).

Nanoparticles of ZnO are used in a variety of applications. They can be used as UV absorbent, antibacterial treatment material, catalytic agent and as an additive material in several industrial products. It is currently being used in the fabrication of solar cells, gas sensors, luminescent materials, transparent conductors, heat mirrors and coatings (Ghosh *et al*., 2015).

ZnO nanoparticles can be prepared on a large scale at low cost by simple solution based method, such as chemical precipitation, sol-gel synthesis, and hydrothermal reaction. Many of the earliest synthesis of nanoparticles were achieved by co-precipitation of sparingly soluble products from aqueous solution followed by thermal decomposition of those products to oxides. Co-precipitation method is a promising alternative synthesis method because of the low process temperature and easy to control the particle size. Some of the most commonly substances used in coprecipitation operations are hydroxides, carbonates, sulphates and oxalates.

The aim of this study is to investigate optical properties of undoped ZnO and Ni doped ZnO by using the co-precipitation method.

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Materials and Methods

Sample collection

Zinc sulphate heptahydrate, nickel (II)sulphate hexahydrate, ethylene glycol and sodium hydroxide were procured from BDH. Distilled water was used as the solvent in all analyses.

Preparation of Undoped Zinc Oxide and Nickel Doped Zinc Oxide by Co-Precipitation Method

The common salts $ZnSO_4.7H_2O$ (0.97 mol) and $NiSO_4.6H_2O$ (0.03 mol) were used as zinc and nickel precursors. Zinc sulphate was dissolved in distilled water. Next, the nickel sulphate for a final composition of NiO to ZnO were calculated and added to the solution. Then these solutions were mixed during continuous stirring. Next, 100 mL of 1 M NaOH solution was slowly added to the mixture under constant stirring until the pH of the solution reached to 10. During addition of NaOH solution, precipitates were started to appear. After addition of NaOH, 10 mL ethylene glycol was added immediately. The final solution was then stirred for 20 h at room temperature, so that homogeneity could be maintained. Then the sample was washed with distilled water several times until the pH was 7. After washing the sample was dried at 120 °C. The sample obtained was ground to make fine particles and it was calcined at 500 °C for 4 h in the muffle furnace. Finally, Ni doped ZnO powder was obtained. For the preparation of undoped ZnO, the same procedure as above was applied **(**Chauhan *et al.,* 2017**).**

Characterization of the Prepared Undoped ZnO and Nickel Doped Zinc Oxide Samples

Thermal properties of the prepared undoped ZnO and Ni doped ZnO were investigated by TG-DTA. The powder X-ray diffraction method was used to study the structural properties and the phase purity of the samples. The functional group of prepared undoped ZnO and Ni doped ZnO were identified using FT IR. The elemental composition of the prepared undoped ZnO and Ni doped ZnO were studied by using EDX analysis. The surface morphology of the prepared undoped and Ni doped ZnO were examined by SEM. The optical properties of prepared undoped ZnO and Ni doped ZnO were studied by UV-vis spectrophotometer in the range of 200 to 800 nm. Thermogravimetric analysis of sample was performed by using TG-DTA analyzer, (Hi-TGA 2950 model). The temperature was the range between 0 °C and 600 °C under nitrogen gas (at a rate of 50 mL/min). X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat.No 9240 J 101, Japan. Copper tube with nickel filter was used. The diffraction pattern was recorded in terms of 2θ in the range of 10-70 °. FT IR spectrum was recorded in the range of 4000-400 cm^{-1} by using 8400 SHIMADZU, Japan FT IR spectrophotometer. The scanning electron microscopy (SEM) images were obtained by using JSM-5610 Model SEM, JEOL-Ltd., Japan. The energy dispersive X-ray analysis was carried out using Phenom, Pro-X. The UV-Visible spectra of powder samples are observed in the 200-800 nm range by using UV-Visible spectrophotometer. The energy band gap was determined by using the relationship;

$$\alpha = A\,(h\upsilon - E_g)^n$$

"Where," $h\upsilon$ is photon energy, α is Absorption coefficient ($\alpha = 4\pi k/\lambda$), k is the absorption index or absorbance, λ is wavelength in nm, E_g is energy band gap, A is constant and the exponent n depends on the transition. The value of (n = 1/2, 3/2, 2, or 3 depends on the nature of the electronic transition (1/2 for allowed direct transition, 2 for allowed indirect transition, 3/2 and 3 for forbidden direct and forbidden indirect transitions, respectively).

Results and Discussion

Undoped ZnO and Ni doped ZnO powder were prepared by using co-precipitation method. The resultant prepared samples were characterized by modern techniques (TG-DTA, XRD, FT IR, EDX and SEM).

Thermal Analysis of the Prepared Undoped ZnO and Ni Doped ZnO

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) thermograms of prepared undoped ZnO and Ni doped ZnO are shown in Figure 1. Weight loss percent of undoped ZnO and Ni doped ZnO are listed in Table 1. TGA curve of prepared undoped ZnO and Ni doped ZnO indicated the two stages of decomposition (Figure 1). Endothermic peaks observed at 91 °C and 150 °C for undoped ZnO and Ni doped ZnO with 1.96 and 2.82 % weight loss were due to the evaporation of loosely bound water of the samples. Endothermic peaks observed at 288 °C and 268 °C for undoped ZnO and Ni doped ZnO with 10.20 and 15.66 % weight losses, respectively, were due to the decomposition of $Zn(OH)_2$, which was formed by absorption of water, and then was converted to ZnO and Ni doped ZnO. Total weight loss of undoped ZnO and Ni doped ZnO were given in Table 1.

XRD Analysis of the Prepared Undoped ZnO and Ni Doped ZnO

The powder x-ray diffraction methods are used to study the structural properties and the phase purity of the samples. Figures 2 shows the XRD pattern of prepared undoped ZnO and Ni doped ZnO. The average crystallite sizes of prepared samples were calculated using the Debye Scherrer equation.

$$D = k\lambda/\beta Cos\theta$$

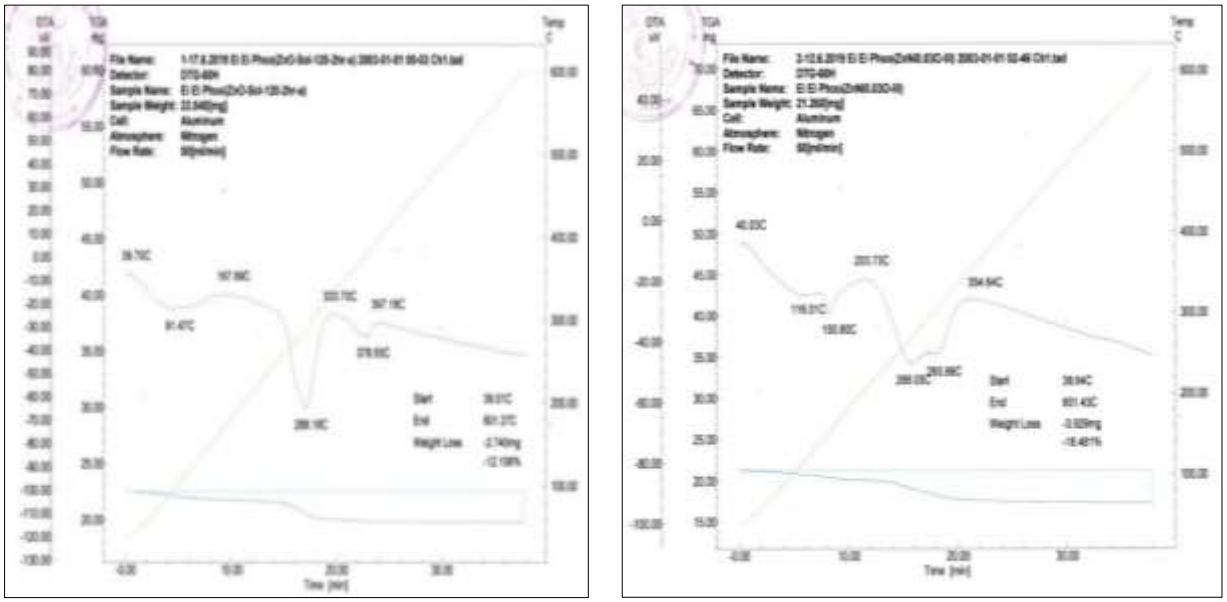
Where k is constant equal to 0.94, D and λ are the crystallite size in nanometers and wavelength of the radiation (1.54056 Å for Cu K_α radiation), respectively. B and θ are the peak width at half-maximum intensity (FWHM) and peak position, respectively. The volume of unit cell for hexagonal system has been calculated from the following equation.

$$V = 0.866a^2c$$

The bond length L for Zn-O is given by $L = \sqrt{(\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2)}$. The parameter *u* in the Wurtzite structure is given by $u = \frac{a^2}{3c^2} + 0.25$.

The average crystallite size of undoped ZnO is found to be 28 nm. The average crystallite size for Ni doped ZnO was found to be 22 nm which is lower than 28 nm for undoped ZnO. Interestingly, doping of Ni^{2+} shows no additional peaks, which confirms no additional impurity phase formation. The lattice parameters a and c for undoped ZnO and Ni doped ZnO are presented in Table 2. The change in a and c lattice parameters are observed due to Ni- doping. The decrease in lattice parameters can be attributed to the replacement of larger Zn^{2+} ions with smaller Ni^{2+} ions.

The wurtzite structure attained from the diffraction peaks indicate that Ni^{2+} is successfully incorporated into the ZnO lattice, which further means no changes in the crystal lattice by the Ni doping.

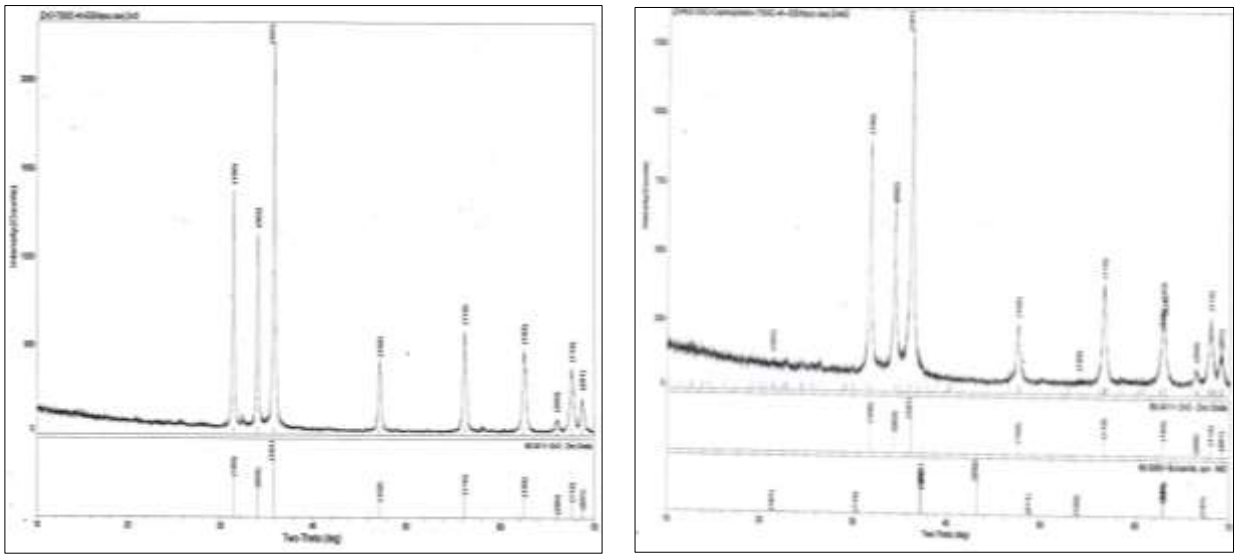


(a) (b)

Figure 1 TG-DTA thermograms of prepared (a) undoped ZnO and (b) Ni doped ZnO

Table 1 Total Weight Loss Percent of Prepared Undoped ZnO and Ni Doped ZnO from TG-DTA Analyses

Sample	Temperature Range(°C)	Nature of Peak	Weight Loss (%)	Total Weight Loss (%)
Undoped ZnO	38-170 170-450	endothermic	1.96 10.20	12.16
Ni doped ZnO	38-170 170-450	endothermic	2.82 15.66	18.48



(a) (b)

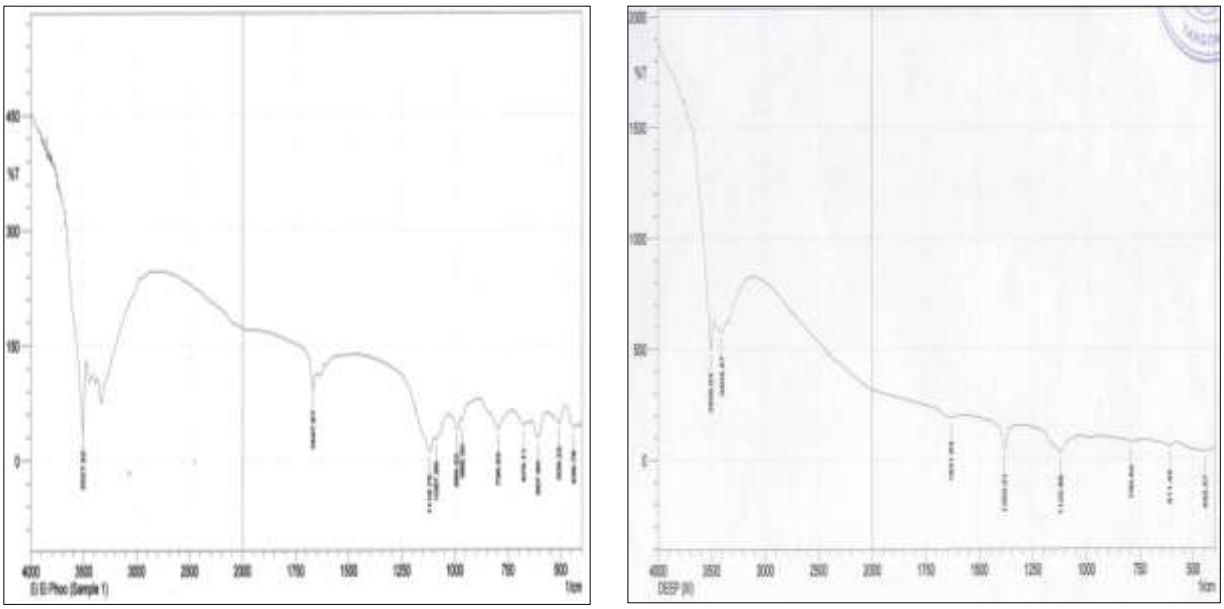
Figure 2 XRD patterns of prepared (a) undoped ZnO and (b) Ni doped ZnO

Table 2 XRD Analyses of Prepared Undoped ZnO and Ni Doped ZnO

Samples	c	a=b	c /a	Crystallite Sizes from XRD (nm)	Crystallite Sizes from Debye- Scherrer formula (nm)	Volume (Å)^3	Zn-O bond length (Å)
Undoped ZnO	5.2345	3.2852	1.5934	30	28	48.92	1.99
Ni doped ZnO	5.2051	3.2494	1.6019	23	22	47.59	1.98

FT IR Analysis of the Prepared Undoped ZnO and Ni Doped ZnO

Figure 3 shows the FT IR spectra of prepared undoped ZnO and Ni doped ZnO. The assignment data is summarized in Table 3. In the spectra of prepared undoped ZnO and Ni doped ZnO, the peak observed at 3439 cm^{-1} and 3404 cm^{-1} for undoped ZnO and Ni doped ZnO, respectively, correspond to O-H stretching vibration and the peak at 1628 cm^{-1} and 1631 cm^{-1} for undoped ZnO and Ni doped ZnO, repectively, correspond to H-O-H bending vibration which are related to the absorbed water on the surface of nanomaterial. Another intense absorption peak at 435 cm^{-1} and 445 cm^{-1} for undoped ZnO and Ni doped ZnO, respectively are related to the stretching vibrations of the Zn-O bond (Table 3) (Silverstein *et al*., 2003; Nakamoto, 1970).



(a) (b)

Figure 3 FT IR spectra of the prepared (a) undoped ZnO and (b) Ni doped ZnO

SEM Analysis of the Prepared Undoped ZnO and Ni Doped ZnO

Figure 4 shows the morphological differences between the prepared undoped ZnO and Ni doped ZnO. The SEM images reveal the formation of homogeneous and uniformly distributed particles. The average crystallite size was found to decrease by doping Ni into the ZnO matrix. The decrease in the crystallite size is mostly ascribed to the formation of Ni-O-Zn on the surface of the doped nanoparticles, which prevents the growth of crystal grains and assists separation of particles.

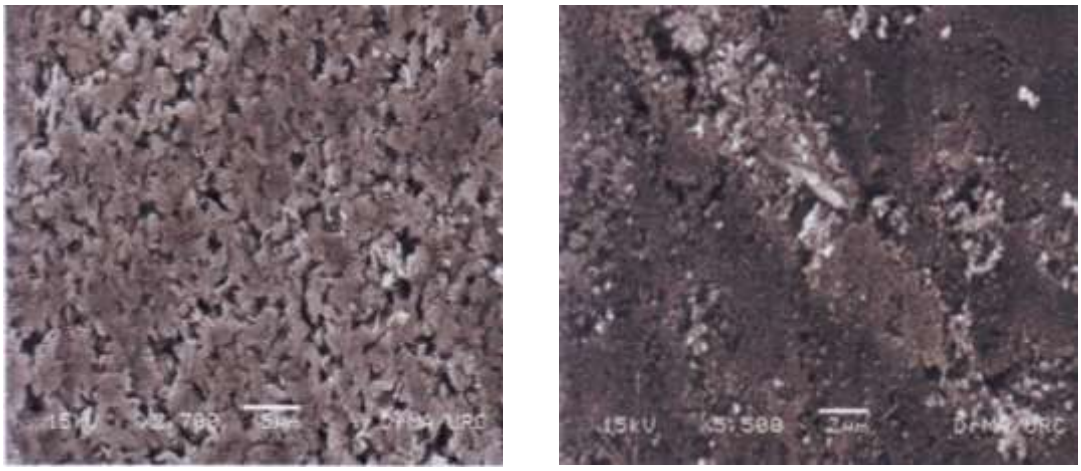
EDX Analysis of the Prepared Undoped ZnO and Ni Doped ZnO

The chemical compositions of prepared undoped ZnO and Ni doped ZnO were measured by EDX spectra and shown in Figure 5. The EDX shows signals of all the expected elements Zn, O and Ni, which confirms the presence of Ni^{2}+ ions which are substituting the Zn^{2+} ions in the Zn matrix.

Table 3 FT IR Band Assignments of the Prepared Undoped ZnO and Ni Doped ZnO

Observed wavenumber (cm^{-1})		*Literature wavenumber (cm^{-1})	Band Assignment
Undoped ZnO	Ni doped ZnO		
3439	3404	3500-3200	O-H stretching
1628	1631	1655-1630	H-O-H bending
607	611	650-420	Zn-O stretching (or)
435	445		Ni-O stretching

*(Silverstein *et al*., 2003; Nakamoto, 1970)



(a) (b)

Figure 4 SEM micrographs of the prepared (a) undoped ZnO and (b) Ni doped ZnO

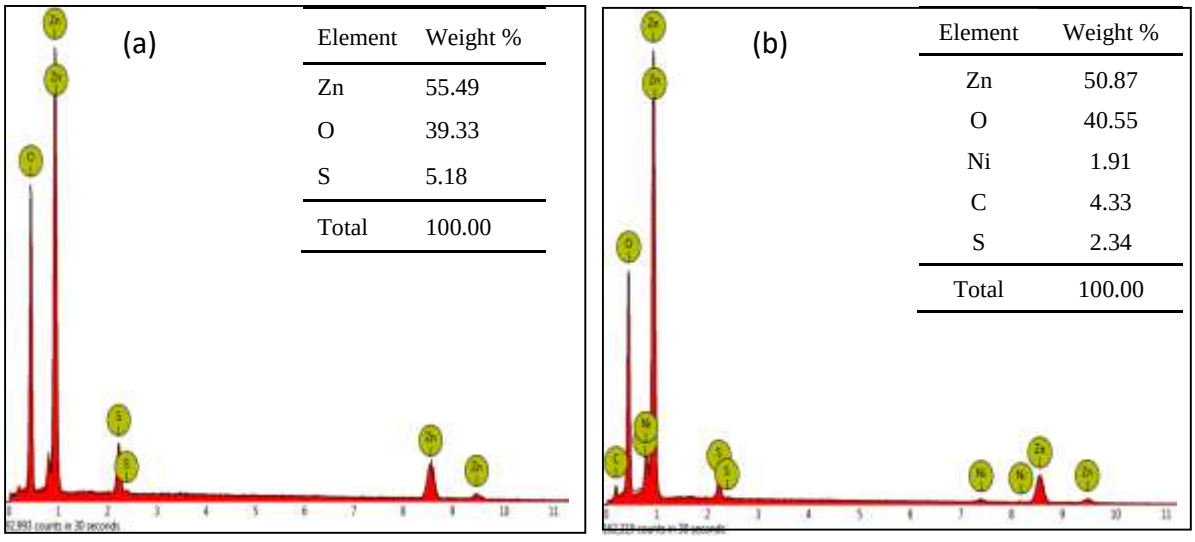


Figure 5 EDX spectra of the prepared (a) undoped ZnO and (b) Ni doped ZnO

UV-vis Analysis of the Prepared Undoped ZnO and Ni Doped ZnO

In UV-vis absorption spectra, peaks are found at 382 and 370 nm for undoped ZnO and Ni doped ZnO, respectively, as shown in Figures 6 (a) and (b). The position of the absorption spectra was observed to shift toward the shorter wavelength side for Ni doped ZnO. This indicates that the band gap of ZnO material increases with the doping Ni^{2+} ions.

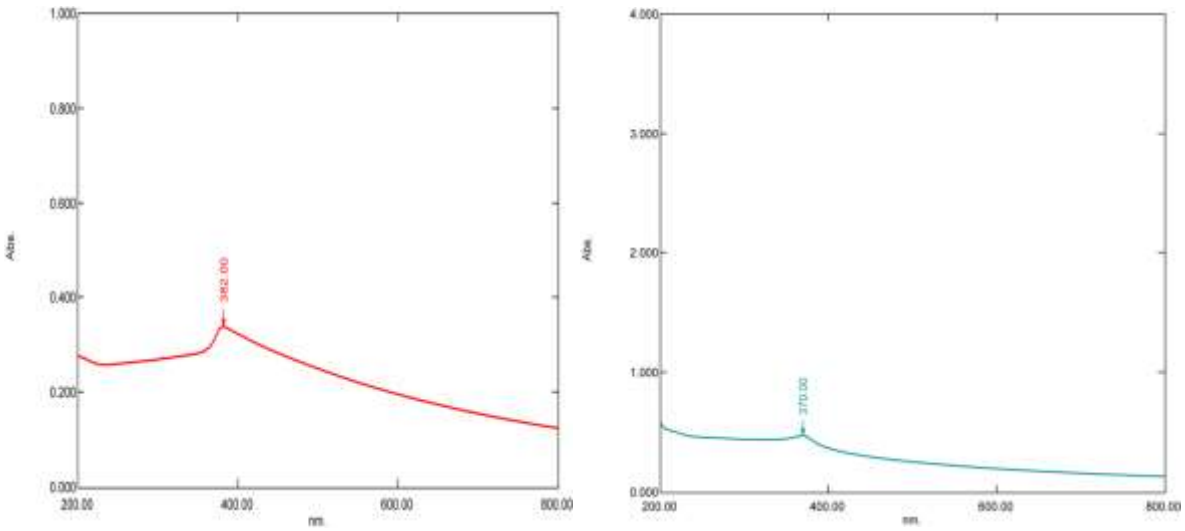
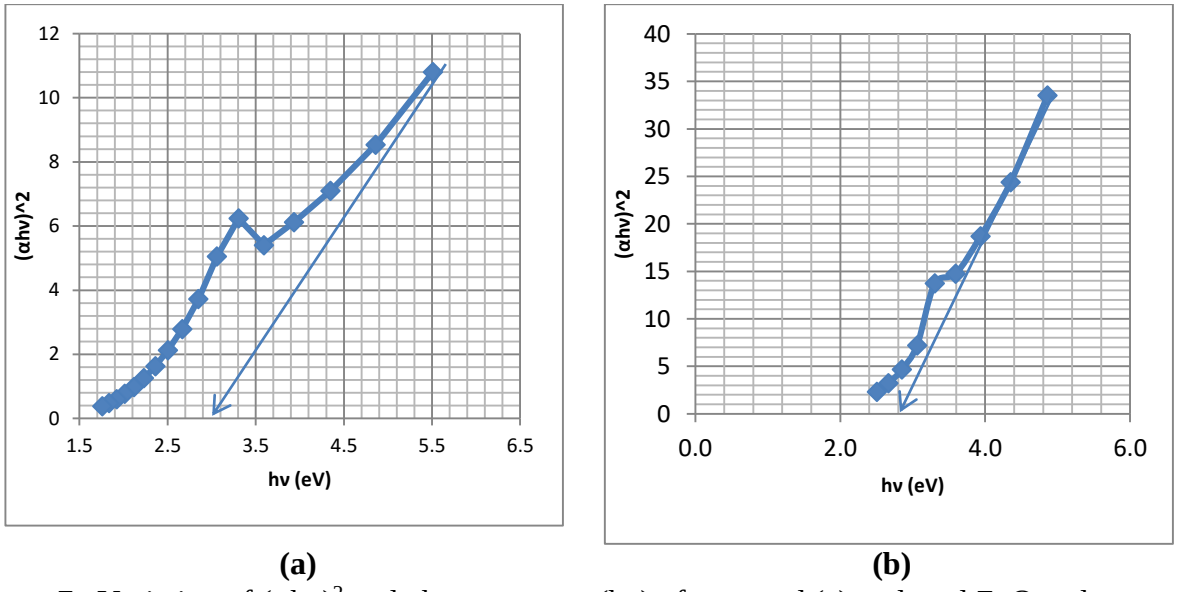


Figure 6 UV-visible spectra of the prepared (a) undoped ZnO and (b) Ni doped ZnO



(a) **(b)**

Figure 7 Variation of $(\alpha hv)^2$ and photon energy (hv) of prepared (a) undoped ZnO and (b) Ni doped ZnO

Optical Properties

The relationship between absorption coefficient, the energy of the incident photon (hv) and near absorption edge of semiconductors is given by the Taucs' relation. The electronic transition is represented in Figure 7. The optical energy band gap E_g is determined by extrapolating the straight portion of this plot to the photon energy in x-axis and it reveals that the value of band gaps were found to be 2.7 eV and 2.8 eV for undoped ZnO and Ni doped ZnO. The decrease in the band gap may be due to the sp-d exchange interaction present between the band electrons and the localized d electrons of the substituted divalent ions (Abood *et al*., 2017).

Conclusion

In this study, the structural and optical properties of prepared undoped ZnO and Ni doped ZnO were prepared by using chemical co-precipitation method. Structural investigation of the undoped ZnO and Ni doped ZnO showed a decrease in lattice parameter. Optical properties and band gap were determined by UV-Visible spectra. The energy band gap values for prepared undoped ZnO and Ni doped ZnO were found to be decreased from 2.7 to 2.8 eV. The observations of Ni doped ZnO reveal that this sample can be chosen as a semiconductor material to be used as photocatalyst.

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