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SYNTHESIS AND CHARACTERIZATION OF Ni - DOPED ZnO BY CHEMICAL PRECIPITATION METHOD

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ABSTRACT

Ni – doped ZnO nanoparticles were prepared using chemical precipitation methods with aqueous solution of nickel acetate and zinc acetate in the presence of NaOH at room temperature. The prepared nanoparticles' densities, diameters and lengths of the rods can easily be controlled through the concentrations of the dopant Ni²⁺ ions and it is in nanorod form and were incorporated into the Wurtzite structure of ZnO crystal. The effects of Ni doping on the structural and optical properties of ZnO: Ni particles were investigated using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Ultraviolet–Visible (UV) Spectroscopy and Photo Luminescence (PL) spectroscopy.

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INTRODUCTION

Nanocrystalline materials have attracted a wide attention due to their unique properties and potential applications in nano device fabrication. (West *et al.*, 2003).

As one of the important II- VI semiconductors, ZnO materials are of great importance to several applications such as UV light emitters, gas sensors and photo therapy agents, since it have wide band gap of (3.37eV), large exciton binding energy (60 MeV) (Sayed *et al.*, 2006 and Pearton *et al.*, 2003) and semiconductor properties (Xu *et al.*, 2005 and Zhou *et al.*, 2006). It is well known that the changes in optical, electrical and magnetic properties could occur when impurities were added to a wide gap semi conductor thus doping a certain element in to ZnO has become important method to optimize its optical, electrical and magnetic performance, which is crucial for many practical applications.

Recently preparations of various doped ZnO nano structures with different elements have been achieved to improve the electrical, optical and magnetic properties (Yuan *et al.*, 2008). Ni is an one of the important dopants to improve those properties. The nano sized NiO itself has demonstrated acting catalytic (Wang and Zhu *et al.* 2008), magnetic (Uhm *et al.*), electro chromic (Lin *et al.* 2008), optical and electrochemical properties (Wang and Song *et al.* 2005). Furthermore, nickel oxides can be used as transparent p-type semiconducting layer (Satro *et al.*, 1993) and are being studied for applications in smart

windows, electrochemical super capacitors (Srinivasan *et al.*, 1997) and dye sensitized photocathodes (Lindstrom *et al.*, 1999).

Synthesis of Ni doped ZnO nanoparticles can be done by many methods including Hydrothermal (Al-Harbi 2011) method, Co-precipitation method (El-Hilo *et al.*, 2009), Sol- gel method (Elilarasi *et al.*, 2010), and Solvo thermal method (Chengbin jing *et al.*, 2010). In this work chemical precipitation method is used to synthesize Ni – doped ZnO nanoparticles at room temperature.

The aim of the present contribution is the investigation of structures and optical properties of Ni- doped ZnO Wurtzite nanoparticles by XRD, TEM, SEM, FTIR and UV- PL Spectroscopy.

MATERIAL AND METHODS

Chemicals

Zinc acetate, Zn (CH₃COO)₂ · 2H₂O, Ni (CH₃ COO)₂ · 2H₂O, and polyvinylpyrrolidone (PVP MWt 4000) were used, which were obtained from Aldrich, USA. All other chemicals and solvents used in this study were obtained from commercial sources with high purity analytical grade reagent. Double distilled (DI) water was used for the preparation of all reagents.

Synthesis of ZnO: Ni²⁺ nanoparticles

ZnO nanocrystals doped with Ni²⁺ (0.5-2.5 %) ions were prepared by simple chemical precipitation method. The

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reactants were Zn (CH₃COO)₂ · 2H₂O, Ni (CH₃COO)₂ · 2H₂O, and polyvinyl pyrrolidone (PVP mw4000) which were all of analytical purity. Ultra pure deionized water and ethanol (equal volume) were used as the reaction medium. In a typical procedure, ethanol –water mixture solution of 100 ml of 0.2M Zinc acetate and different concentration of nickel acetate in 25 ml water were added by constant stirring using magnetic stirrer. A selected concentration of PVP (1g) was added to the precursor solution, followed by an addition of 0.2M NaOH drop by drop to form the precipitate. The precipitate was washed with water and ethanol for several times and dried in oven for 2hrs at 120°C.

Apparatus

The XRD patterns of the powdered samples were recorded using X PERT-PRO diffractometer with a Cu K_α radiation (λ=1.5406 Å). The size of the crystallite was estimated using the Debye Scherer equation of the major XRD peak. The size and morphology of the nanoparticles were studied using SEM (HITACHI model S-3000H), and TEM (PHILIPS-CM 200; 20-200 kv) microscopes. All samples were prepared by Drop Cost method using carbon coated copper grid. The UV spectra of all the samples in deionized water were recorded using UV-1650PC SHIMADZU spectrometer. Fluorescence measurement was performed on a RF-5301PC spectrophotometer. Emission (350-600 nm) spectra were recorded under the different excitation wavelengths at room temperature. The FT-IR spectra were obtained on an AVATOR 360 spectrometer through KBr pellet technique. Thermo gravimetric and differential thermal analyses (TG-DTA) were carried out with SDT Q 60020 thermometer in air atmosphere.

RESULTS AND DISCUSSION

X-Ray Diffraction Studies (XRD).

The X-ray diffraction patterns of an undoped and nickel doped ZnO samples are shown in Fig.1. The well resolved peaks observed in the X- ray diffraction patterns indicate that the powder samples posses Wurtzite structure of ZnO indexed using Joint Council for Powder Diffraction Standards file (JCPDS 89-1397) (Takuya Tsuzuki *et al.*, 2009).

The average grain size of the pure ZnO: Ni samples were calculated from the full width half maximum (FWHM) of the diffraction peaks using the Debye–Scherrer equation (Deka 2005).

$$D = k\lambda / (\beta \cos\theta)$$

where D= Crystalline diameter,

λ = wave length of X- ray radiation,

β= FWHM and θ is the Bragg angle,

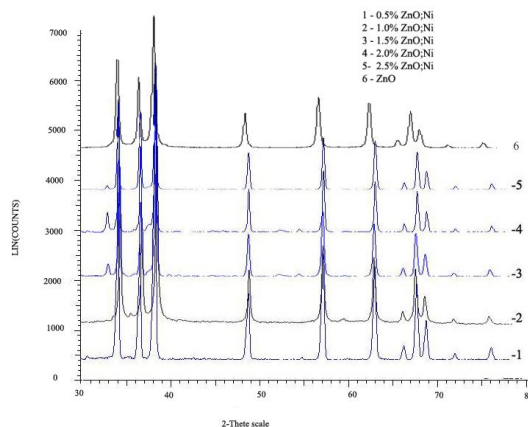


Fig. 1 XRD of ZnO-Ni of Various concentrations

Table 1 Particle size and various concentration of Nickel in ZnO: Ni nanoparticles.

Concentration (0.5-2.5%) (NiO)	Particle size (nm)
0.5	23.0655 Å ^o
1.0	30.1157 Å ^o
1.5	27.5302 Å ^o
2.0	35.0809 Å ^o
2.5	27.0431 Å ^o

Table 2 ZnO: Ni nanoparticles in different size at various temperatures.

ZnO: Ni (1.5%) Nanoparticles at different temperature	Particle size
110°C	28.584 Å ^o
160°C	27.0019 Å ^o
325 °C	27.7739 Å ^o
411 °C	35.0839 Å ^o

By changing the concentration of the dopant and varying the temperature of the reaction medium, the size of the ZnO nanoparticles were vary from 23to35 nm. The increases in size of ZnO is due to Ni ions get substituted in more number on the surface of ZnO.

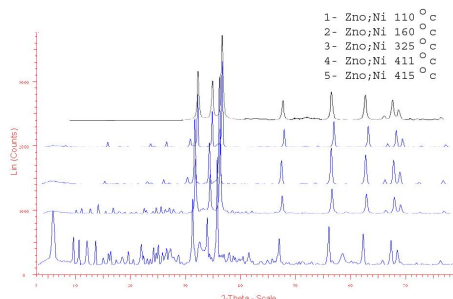


Fig. 2 XRD of ZnO-Ni of Various temperatures.

UV-VISIBLE SPECTROSCOPY

The optical absorption spectra of undoped and nickel doped ZnO samples by UV-Vis spectrophotometer in the range of 200- 600 nm were presented. It is shown in Fig.3. Where it can be seen that the excitonic absorption peak as prepared undoped and nickel doped samples appear from 390nm. But the pure ZnO nanoparticles exhibit a strong near band edge UV emission peak centered at 386nm.

The excitonic absorption peak as prepared undoped and nickel doped samples become broad as the concentration increases. It can be observed clearly from Fig.3 which explains that the absorbance increases when the concentration of Ni increases from 0.5 to 2.5 %.

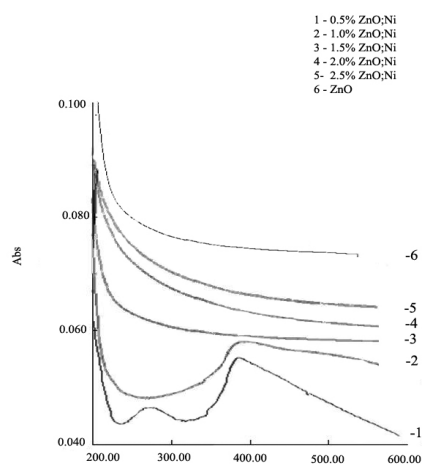


Fig. 3 UV visible spectra of ZnO; Ni

The room temperature optical absorption spectra for the various compositions of ZnO: Ni nanoparticles are shown in Fig.3. Pure ZnO sample shows absorption band edge at 342nm but the band edge shows a shift towards higher wavelength side for the nickel doped samples that indicates that Ni²⁺ ions were incorporated into the ZnO lattice (Thota *et al.*,2006). The inherent reason for red shift in band edge is due to the change of the electron exchange interactions between the band electrons and the localized d electrons of the Ni²⁺ ion (Wang *et al.*,2003) which is also considered as the blossoming of magnetic phase.

PHOTO LUMINESCENCE STUDY

The PL Spectra for the nickel doped ZnO shown in Fig.4 are obtained employing a laser light of 360nm wave length as the excitation source in spectrofluorimeter. The PL spectra in Fig. 4 show three strong peaks occurring around 390 nm (3.16ev), 455nm and 470nm; the first one is in the ultraviolet (UV) region, while other two correspond to violet and blue respectively in visible region. They are certainly due to ZnO as they are present in x= 0 case in Fig.4. It is well known that the UV

emission peak at 3.16ev is described to the near-band-edge emission of ZnO which originates from the recombination of free excitons through an exciton-exciton collision process (Samanta *et al.*,2005). The violet emission around 455nm is related to oxygen vacancies. The blue emission around 470nm may be attributed to negatively charged Zn vacancies (Wang *et al.*,2006)

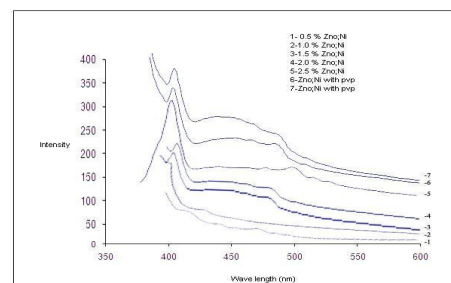


Fig. 4 PL spectra for Ni-doped ZnO sample recorded at Room temperature

FTIR STUDIES

FTIR spectra of Ni doped ZnO nanoparticles are shown in Fig.5. The peak at 3411cm⁻¹ is the stretching vibration of the O-H bond. The absorption bands observed in the ranges from 619 to 699 cm⁻¹ are attributed to the stretching modes of Zn-O (Liu *et al*) in the tetrahedral and octahedral coordinations respectively. The shift in values of vibration frequencies from 460 and 686cm⁻¹ is suggestive of incorporation of Ni in octahedral and tetrahedral sites existing in Wurtzite structure. The shift in frequency is caused by the difference in the bond lengths that occurs when Ni on replaces Zn ion. The bands occurring near 766 and 832 cm⁻¹ are attributed to the vibrations of ZnO-Ni local bonds and defect states respectively.

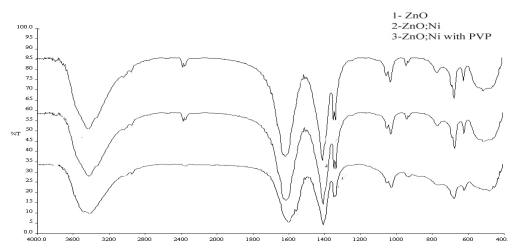


Fig. 5 FTIR spectra of ZnO, ZnO: Ni nanoparticle SEM analysis

Morphology and structure of powders were further investigated by SEM analysis. The SEM micrographs of the ZnO nanoparticles are shown in the fig. (6). It shows that the synthesized ZnO nanoparticles are well dispersed.

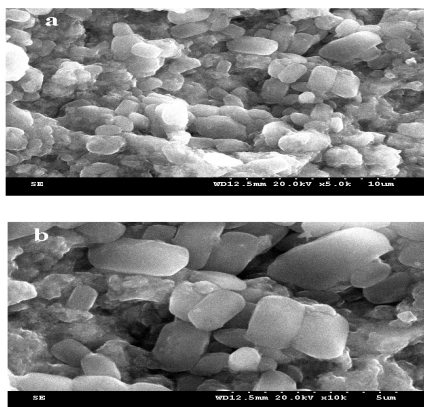


Fig. 6(a, b) SEM Micrograph of ZnO Nanoparticles

TEM ANALYSIS

The morphology and crystalline structure of synthesized particle were examined by transmission electron microscope. The TEM image and the corresponding pattern of Ni-doped ZnO is shown in fig (7). It can be obviously observed that the particle is composed of polycrystalline with grain diameter of about 27 to 35 nm which is in good agreement with that estimated by Debye-scherrer formula based on the XRD pattern. From the fig (7) lattice space of the particle is 0.246 nm, which is slightly less than that (0.280nm) of pure ZnO prepared by bio mineralization process (Chen *et al.*,2006). Because of a smaller size of Ni²⁺ compared to Zn²⁺ the replacement of Zn²⁺ by Ni²⁺ can cause slight decrease in lattice parameter.

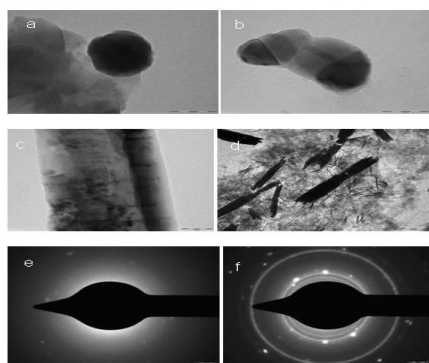


Fig. 7 (a b c d e and f) shows TEM images of ZnO; Ni

This indicates that almost Ni ions in the sample occupied the place of Zn ions. Fig 7(a) reveals the image is looking like nanoball, it confirms the initial stage of the nanorods formation from spherical shape to Wurtzite structure.

Fig 7 (b) and (c) shows the growth of nanorods from nanoballs of the early stage by recombination of many nanoparticles

Fig 7 (d) shows the well crystallized nanorods formation and fig 7 (f) and (e) shows the selected area electron diffraction (SAED) pattern of ZnO nano particles. The diffraction rings composed of dots show that the particles

are well crystallized and can be indexed to corresponding planes respectively, which is in accordance with similar peaks in the XRD pattern.

TGA and DTA STUDIES

TGA and DTA carried out for further confirmation of Ni doped ZnO nano particles. Fig 8 shows the TG and DTA curve of sample Ni doped ZnO. Moderate weight loss for Ni-doped samples up to 100 °C is attributed to the release of absorbing water on the surface. The exothermic events with weight loss about 15 % at about 330 °C result from the thermal decomposition of the organic matters. Zinc acetate can be decomposed completely into ZnO below 333°C fig 8(a). However the residue (i.e., ZnO) is amorphous in nature as identified by XRD. For ZnO-Ni, the result of TG-DTA Fig 8 (b) show that the exothermic reaction takes place between 110°C-430°C accompanied with weight loss from 47 to100 % corresponding to the complete oxidation of carbonaceous matter. The temperature was performed in TGA and DTA of ZnO; Ni nanoparticles up to 1014 °C. It indicates there is no change in structure.

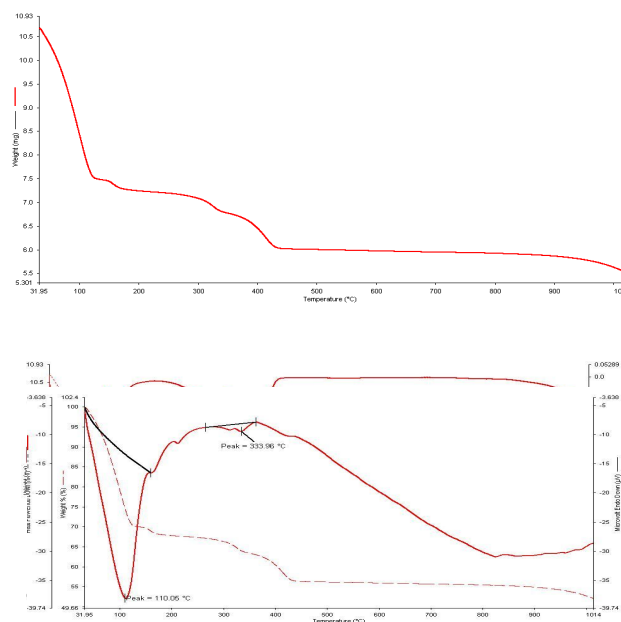


Fig. 8 (a b and c) shows TGA curve of ZnO, ZnO; Ni and ZnO; Ni with pvp

CONCLUSION

To summarize high quality semiconductors Zn_{1-x}Ni_x O nanorods have been synthesized by a simple chemical precipitation method at room temperature. Structural analysis indicated that the prepared products are single crystalline Wurtzite structure, and no other secondary phase was found in the nanorods. Photoluminescence spectra measurement demonstrated that both the pure and Ni-doped ZnO nanorods exhibit a strong near band edge UV emission peak centered at 342 nm. The TGA and DTA curve of ZnO; Ni shows its thermal properties of pure and doped nanoparticles. Combining the optical

properties with thermal properties, the synthesized $Zn_{1-x}Ni_xO$ nanorods may be potentially applied as components to build opto electronics and thermally stable devices.

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