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STRUCTURAL AND OPTICAL PROPERTIES OF (NB/CO) CO-DOPED ZNO NAN PARTICLES SYNTHESIZED BY CHEMICAL PRECIPITATION METHOD

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Abstract

In spintronics technologies, diluted magnetic semiconductors (DMS) have to be studied intensively and origins of ferromagnetism in such materials are to be understood clearly. However, it is difficult to understand that whether the ferromagnetism in DMS is intrinsic or due to dopant effects. Therefore, in this work, the microstructure, optical, and magnetic properties of pure ZnO and $Zn_{0.94}Nb_{0.01}Co_{0.05}O$, $Zn_{0.88}Nb_{0.02}Co_{0.10}O$ and $Zn_{0.82}Nb_{0.03}Co_{0.15}O$ Energy band gap calculated from the UV spectroscopy denotes an increasing trend of band gap with increasing dopant concentration in the sample.

Keywords: Diluted Magnetic Semiconductors, Nano crystalline, Crystal Structure, FTIR.

1. Introduction

Diluted Magnetic Semiconducting (DMS) nanoparticles have been studied keenly due to their potential applications in spintronics devices since their unique characteristic of both charge and spin of electrons. These could be potentially used for the fabrication of multifunctional devices such as spin valve transistors [1],

spin light emitting diodes [2], logic devices [3] and non volatile memory have the advantage of rapid data processing, less power consumption, huge capacity and excellent stability than other electronic devices [4-5].

Two key properties of DMS materials are both semiconducting and ferromagnetic properties. The optical and magnetic properties of ZnO nanoparticles are strongly depending upon the dopant, defects, and crystallinity. Therefore, the research community intensively studying DMS materials to realize room temperature ferromagnetism in transition metal (TM) doped semiconductors [1-5].

Recently, doping with TM like Cr, Ce, Ni, Nd, Eu, Gd can tune the semiconducting properties to fabricate novel and unique magneto-electronic and opto-electronic devices [6-7].

Among all the oxide based DMS materials, zinc oxide (ZnO) have been intensively studied due to their large energy gap (3.37 eV) and excitonic binding energy (60meV) greater than traditional semiconducting compounds. Besides, it exhibits unique characteristics such as good optical transparency, chemical and thermal stability, and high voltage – current nonlinearity. Hence, ZnO based DMS nanoparticles can be used in solar cells, magnetic storage devices, modern computers, spintronics, photo luminescent materials, heat mirrors, thin film transistors, gas sensors, good conductor, biomedical and so on [8-9].

So far various methods have been adopted to synthesize TM doped ZnO nanoparticles such as hydrothermal, spray pyrolysis, spin coating, micro emulsion, sol– gel, ball milling, spray pyrolysis,

Electrochemical decomposition, molecular beam epitaxy, thermal evaporation, vapor liquid solid growth, laser-ablation methods, chemical vapor deposition, dip coating, etc. [10-12]. However, most of them are very costly and small scale production, complicate synthesis route, large reaction temperatures, lengthy reaction time, and no stoichiometric compositions. However, chemical co precipitation method is suitable and simple due to their cost effective, low temperature synthesis, large scale production and quick method to prepare Nb/Co co-doped ZnO nano particulate powders. Further, it is able to control over the stoichiometric composition and particle size which can alter the optical, electrical and magnetic properties. In this paper, for the first time, the structural, optical, morphological, and magnetic properties of $Zn_{0.94}Nb_{0.01}Co_{0.05}O$, $Zn_{0.88}Nb_{0.02}Co_{0.10}O$ and $Zn_{0.82}Nb_{0.03}Co_{0.15}O$nanoparticles have been synthesized by the co precipitation method.

2. Sample Preparation

Samples with stoichiometry $Zn_{0.94}Nb_{0.01}Co_{0.05}O$, $Zn_{0.88}Nb_{0.02}Co_{0.10}O$ and $Zn_{0.82}Nb_{0.03}Co_{0.15}O$ were prepared by the chemical co-precipitation technique High purity $ZnCl_2.6H_2O$ (Aldrich99.999%), $CoCl_2 \cdot 6H_2O$(Aldrich99.999%), and $NbCl_5$ (Aldrich99.999%), were weighed and dissolved in de-ionized water. The solutions prepared from the starting materials were taken in a round-bottomed flask fitted with a reflex-cooling tube. Then, an aqueous 500 ml NaOH solution of 5mol/*l* was gradually added to the stoichiometric solution for 30 minutes, in order to achieve a final pH value of 8 at room temperature.

The precipitates containing mixture were allowed to settle for areas on able time and then washed several times with pure water to remove the water-soluble by products (precipitation). Now, the precipitates were filtered out using filter paper of fine pore size and the spongy content in the filter cone was allowed to dry as such. When the moisture content was reduced, the sample could also be dried (calcinations) in a ceramic pan at about 50 ^{o}C to help there Faint moisture and traces of by-products to evolve out of the sample completely. Now the sample was ready for further treatment and study.

3. Employed Characterization Techniques

To verify the composition of resultant powder, inductively coupled plasma optical emission spectroscopy (ICP-OES) technique was carried out. It confirmed the absence of impurities. The optical properties of the crystals were examined between 100 and 1000 nm using LAMBDA-35 UV-Vis spectrophotometer. Differential thermal and thermo gravimetric analysis has been carried out to study the thermal stability for the grown crystals using a simultaneous thermal analyzer TGA7 (Perkin Elmer). The functional groups were observed using Perkin Elmer Spectrum in the range of 500-4000 cm^{-1}. The particle size and morphology were analyzed using transmission electron microscopy (TEM).

4. Results and Discussion

4.1 ICP–OES The Nb/Co co-doped concentrations of the ZnO nanoparticles were analyzed from ICP–OES analysis which found the actual concentration of dopants in the grown crystals. It displays that amount of dopants entered in

4.2Optical absorbance

The band gap (Eg) of the Nb/Co co doped ZnO nanoparticles at 303 K was calculated using the absorbance spectra. This experiment was performed with help of UV– visible spectrophotometer. The UV–visible absorption spectra of the samples are shown in Fig. 1. The band gap energy (Eg) values using Tauc relation is used to estimate the band gap energy (Eg) values and the values are displayed in Fig. 2. The values of E.g. were calculated by taking the intercept of the extrapolation to zero absorption with photon energy axis. The calculated Eg value of the ZnO is 3.18 eV which is lower in than Nb/Co co doped ZnO nanoparticles. This is

well agreed with reported values in Refs. [20-23]. The increase in ZnO band gap is attributed to decrease in particle size with increase in the concentration of oxygen vacancies on ZnO surface [24]. Further, this could be attributed to the Burstein–Moss effect and increase in band gap confirms the incorporation of Nb and Co ions into the ZnO host lattice.

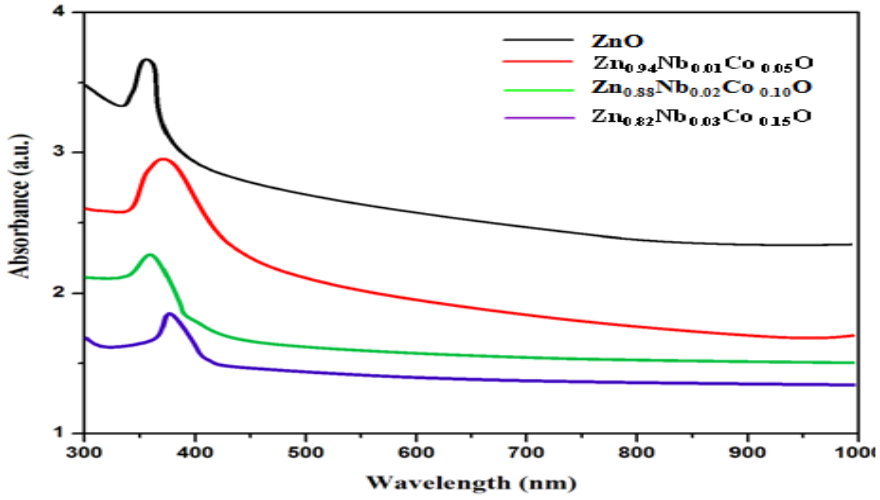

Figure 1. UV–Visabsorption Spectra of Nb/Co codopedZnO nanoparticles at 303 K

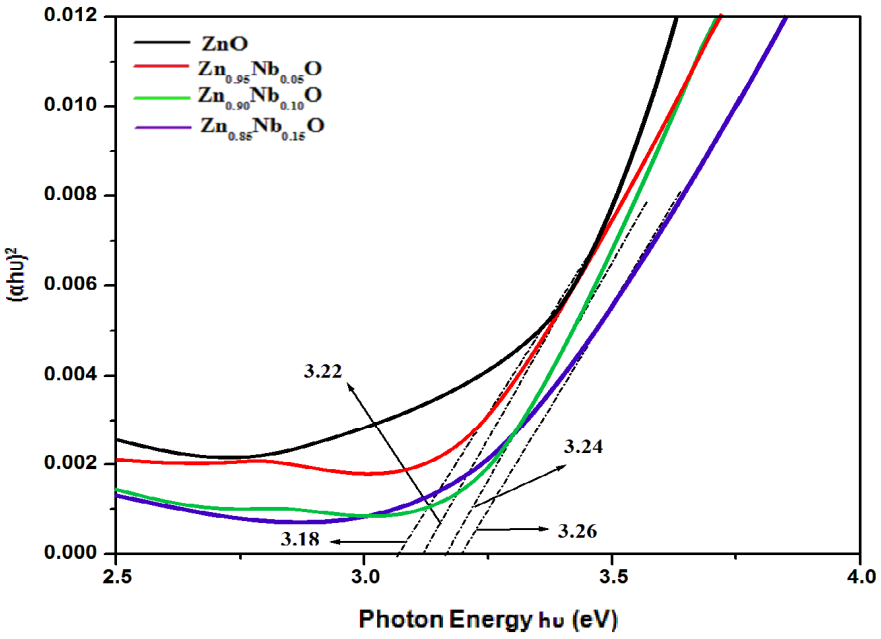

Figure 2 Energy gap value of Nb/Co codopedZnO nanoparticles at 303 K

4.3FTIR study

The FTIR spectra of Nb/Co co-doped ZnO (KBr pellet technique) is shown in Fig. 3 to observe the presence of functional group. The widened peaks were found around at 3487 cm^{-1} and 1565 cm^{-1} respectively. These are associated to O-H stretching and H-O-H bending vibrations due to the presence of H_2O contents on the surface of ZnO and Nb/Co co-doped ZnO nanoparticles as moisture [25]. The minor peak found at 2350 cm-1 and is corresponded to the existence of CO_2 molecules in the air. The two peaks at 1490 and 1615 cm-1 are associated to symmetric and symmetric stretching of carbonyl group (C=O).

A peak observed at 521 cm^{-1} is mainly attributed to the vibration of metal oxide (Zn-O). This is the standard range (400–600 cm^{-1}) for the ZnO nanoparticles [24-25]. No other impurity functional group peaks were found and there by confirm the purity of the samples. Form this studies, it is confirmed the formation of ZnO wurtzite structure,

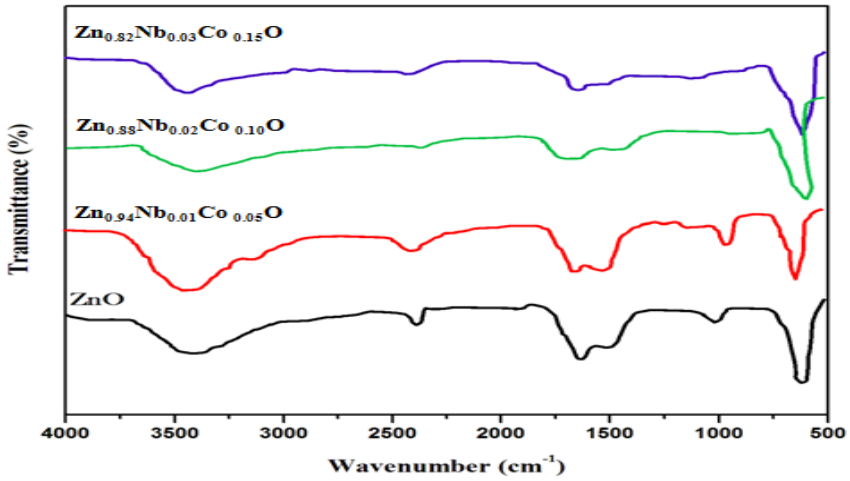

Figure 3 FTIR spectra of Nb/Co codopedZnO nanoparticles at 303 K

4.4TEM Analysis Fig. 4(a) and (b) exhibit the TEM imagesof pure ZnO and Nb/Co co-doped $Zn_{0.82}Nb_{0.03}Co_{0.15}O$ nanoparticles prepared at room temperature. The spherical shaped particles with varying particles size from 40 to 20 nm have been observed.

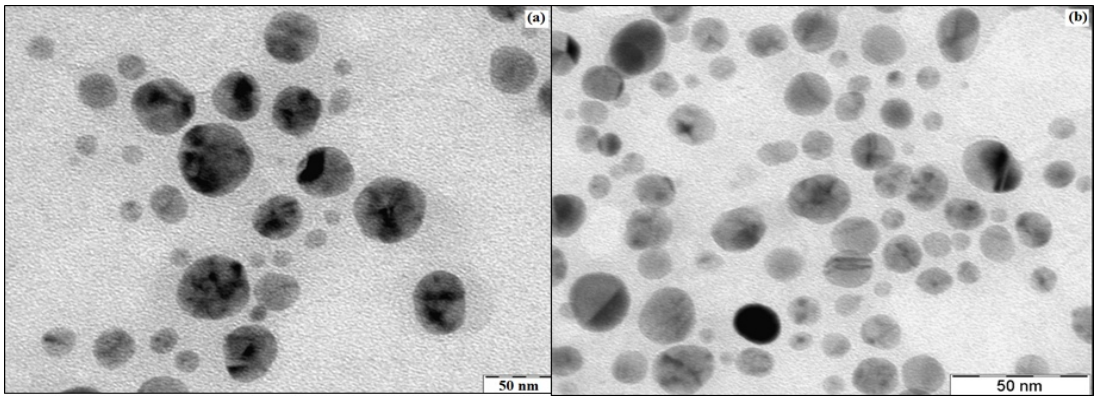

Fig.4. (a) and (b) the TEM images of ZnO and $Zn_{0.82}Nb_{0.03}Co_{0.15}$Onano particles prepared at room Temperature.

5. Conclusions

Nb/Co co-doped ZnO nanoparticles have been successfully synthesized by simple and low temperature chemical co-precipitation method. XRD and UV studies confirm the incorporation of do pant into the ZnO lattice. UV–vis analysis revealed that the band gap increased due to the incorporation of dopants. TEM images of the ZnO and $Zn_{0.82}Nb_{0.03}Co_{0.15}O$ nanoparticles show that the particles are in spherical shape with average particle sizes from 40-20 nm.

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