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Original Research

Structural and magnetic Properties of Mn, Co, Ni doped ZnO Nanocrystals

Tamirat Tibebu[1], Raghavender A.T[1*], Kebede Legesse Kabeta[1], Anjaneyulu T[2] and Melkamu Biyane Regasa[3]

[1]Department of Physics, College of Natural and Computational Sciences, Wollega University, Post Box No: 395, Nekemte, Ethiopia

[2]Department of Physics, Narasaraopet Engineering College, Narasaraopet - 522 601, Andhra Pradesh, India

[3]Department of Chemistry, College of Natural and Computational Sciences, Wollega University, Post Box No: 395, Nekemte, Ethiopia

Abstract

ZnO is one of the most important semiconductor material for research. It is abundant, cost effective, non-toxic and also it is used in many bio-medical applications. The transition metal(TM) such as manganese (Mn), cobalt (Co) and nickel (Ni) doped zinc oxide (ZnO) nanocrystals are promising candidates for variety of practical application due to their spin of electron that lead to new magnetic, optical and transport properties. TM doped ZnO nanocrystals were synthesized using co-precipitation technique. The structural and magnetic properties were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and vibrating sample magnetometer (VSM) measurements. The XRD of Mn-doped ZnO nanocrystals shows hexagonal structure. The crystal size from the XRD was observed to be 10 nm. FTIR spectra shows strong absorption peaks between 200 - 600 cm^{-1} as a characteristic bands due to the metal ions. The TM doped ZnO nanocrystals shows weak ferromagnetic properties at room temperature. It is well known that, ZnO has large band gap energy about 3.3ev which only absorb light within UV region. TM doped ZnO nanocrystals have very good photo catalytic activities, therefore in our further research work, we plan to investigate different optical properties of these materials.

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***Corresponding Author:**

Raghavender A.T

E-mail:

raghavi9@gmail.com

INTRODUCTION

ZnO is one of the semiconductor materials that is widely used and is key element in many industrial manufacturing process including paint, cosmetics, plastics, battery, electrical equipment, rubber, soap, textile, floor covering and etc. ZnO is the material with a great variety of technological application such as surface acoustic wave devices, piezoelectric transducer, optical wave guides, gas sensor, spin functional devices and ultraviolet light emitter. TM doped dilute magnetic semiconductors (DMS) such as ZnO has recently attracted increasing research attention due to their potential use in spintronic devices (Pearton *et al.,* 2003; Hong *et al*., 2005; Hong *et al*., 2007 and Hong *et al*., 2005). Ferromagnetic properties in TM doped ZnO nanoparticles and thin films have been investigated by several research groups (Martinez *et al.,* 2005; Sato *et al.,* 2002; Hong *et al*., 2005 and Hong *et al*., 2007 etc.). It has been addressed that the origin of ferromagnetism in TM doped ZnO nanoparticles and thin films was due to the introdution of defects during the synthesis process and growth of the films. But, still the origin of ferromagnetism is in debate. Therefore, in order to understand the role of transition metal ions doping in ZnO nanoparticles and to investigate the structural and magnetic properties we carried this present work.

MATERIALS AND METHODS

Mn, Co and Ni doped ZnO nanoparticles were synthesized using coprecipitation technique (Raghavender *et al.,* 2011 and Berhanu *et al.,* 2014). The AR grade sodium hydroxide (NaOH), zinc nitrate hexhydrate (Zn $(NO_3)_2 6H_2O$), manganese (II) nitrate hydrate ($Co(NO_3)_2.6H_2O$), cobalt nitrate hex hydrate (Co $(NO_3)_2 6H_2O$) and nickel nitrate ($Ni(NO_3)_2).6H_2O$) (98%) were used as starting materials. The metal nitrates were dissolved together in minimum amount of deionized water to get a clear solution. NaOH solution was added drop by drop to metal nitrates solution under vigorous stirring. The precipitation occurred immediately to change the reaction solution to dark brown. The entire reaction was carried out at 75 °C for 2 h. The pH of the solution was varied by NaOH. The resulting precipitates were washed with deionized water and ethanol several times. The resulting precipitates was dried at 200 °C for 3h. The structural characterization of precipitates powders was carried out using Philips (France) X-ray diffraction (XRD) system with Ni filter using Cu –Kα radiation (wave length λ = 1.54 A^o). The morphology was verified using FEI Quanta (USA) FEG 200 High Resolution Scanning Electron Microscope (HR-SEM). Further structure was confirmed by ABB Bomem MB 102 (Canada) infrared (FTIR) spectrometer.

The samples were mixed with KBr and made in the form of pellets for IR transmission measurements. Room temperature magnetic properties were investigated using Lakeshore (USA) vibrating sample magnetometer (VSM 7410).

RESULTS AND DISCUSSIONS

Figure.1 shows the typical X-ray diffraction patterns of Mn-doped ZnO nanoparticles. XRD spectra shows the hexagonal structure. The extracted cell parameters of the wurtzite-like phase of sample shows a = 3.253 Å and c = 5.214 Å. These lattice values are very close to the un-doped ZnO. The sharp intense peaks of ZnO confirms the good crystalline nature of $Zn_{0.9}Mn_{0.1}O$ and the peaks originated from (100), (002), (101), (102), (110), (103), (200),(112), (201),(004) and (202) peaks. The particle size calculated by Debye Scherer's formula was observed to be 10 nm. The broad peaks of the synthesized sample confirms very narrow particle size. Except a small amount of un-reacted ZnO, the sample shows the peaks corresponding to $Zn_{0.9}Mn_{0.1}O$.

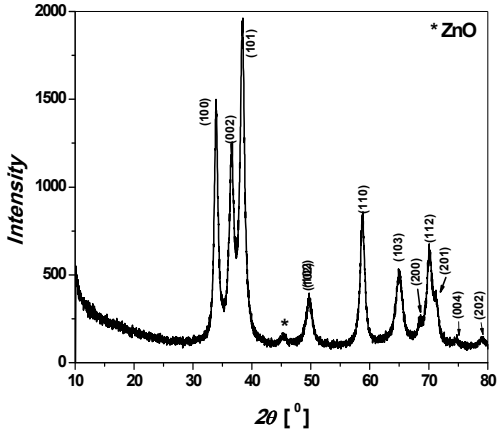

Figure 1: X-ray diffraction patterns of $Zn_{0.9}Mn_{0.1}O$ nanoparticles

The nanoparticles nature of the $Zn_{0.9}Mn_{0.1}O$ was confirmed using the SEM analysis. As the particle size confirmed by the XRD was about 10 nm, due to nanocrystalline nature and narrow particle size, the SEM magnification was not sufficient to see the particle size distribution very clearly. However, as observed from Figure 2 the SEM image shows very narrow particle size.

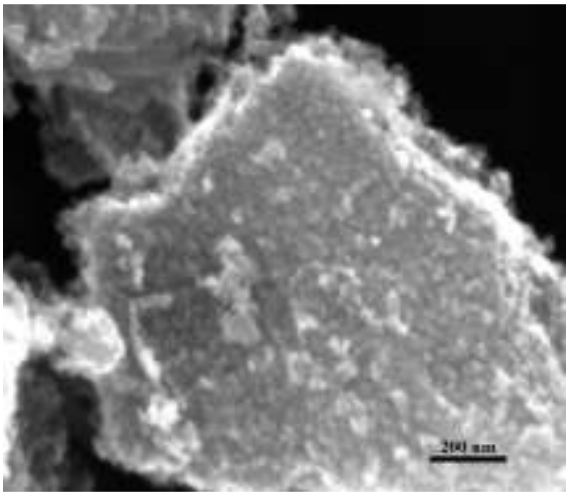

Figure 2: SEM image of $Zn_{0.9}Mn_{0.1}O$ nanoparticles

The structural properties of Mn, Co and Ni doped ZnO nanoparticles were further investigated using IR analysis. Figure. 3 shows the IR spectra of $Zn_{0.9}Mn_{0.1}O$, $Zn_{0.9}Co_{0.1}O$ and $Zn_{0.9}Ni_{0.1}O$ nanoparticles. As observed from Figure. 3, there is strong absorption peak between 200-600 cm^{-1} as characteristic band due to the metal ions doped in ZnO (Wang *et al.,* 1999). $Zn_{0.9}Mn_{0.1}O$, $Zn_{0.9}C0_{0.1}O$ and $Zn_{0.9}Ni_{0.1}O$ nano crystals have strong vibrational mode around 500 cm^{-1} which are assigned to the stretching vibrations of ZnO. The vibrational band in ZnO changes due to Mn, Co and Ni doping. These bands are the characteristics bands corresponding to the synthesized materials. Apart from the main vibrational bands, the bands due to H_2O, nitrates and carboxylic groups are not present in the IR spectra revealing the phase formation and the purity of the synthesized materials.

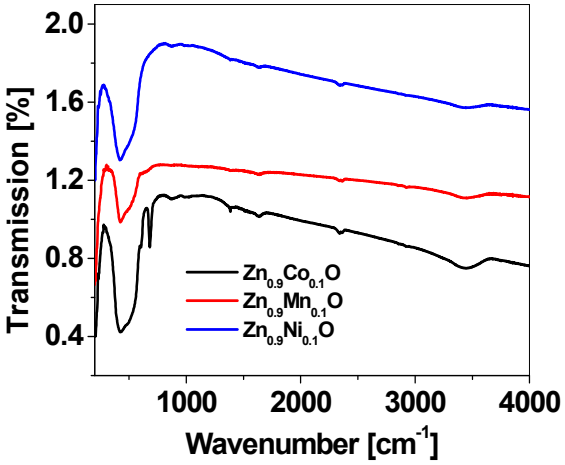

Figure 3: IR spectra of $Zn_{0.9}Mn_{0.1}O$, $Zn_{0.9}Co_{0.1}O$ and $Zn_{0.9}Ni_{0.1}O$ nanoparticles

Figure. 4 shows the room temperature magnetization measurements for $Zn_{0.9}Mn_{0.1}O$, $Zn_{0.9}Co_{0.1}O$ and $Zn_{0.9}Ni_{0.1}O$ nanoparticles. Generally these materials were observed to be paramagnetic or antiferromagnetic at room temperature. These materials shows ferromagnetic properties when they are in thin film form. Often, the presence of secondary phases might contribute for achieving the ferromagnetic properties in the bulk, nano and in thin films. As observed from Figure 4, all the M-H curves shows the room temperature ferromagnetic behavior owing to very small magnetization values. Probably the Curie temperature (T_C) of these materials might be above room temperature (Huang *et al.,* 2009). The M-H curves are very narrow and the magnetization values are very small. Finding the remanence and coercivity was not possible as there are no clear hysteresis loops. The ferromagnetic behavior in the synthesized samples may be due to the several reasons such as, the synthesis technique, synthesis environment, annealing temperature, particle size etc. In the case of TM doped ZnO thin films, defects can be created in order to achieve room temperature ferromagnetic properties (Hong *et al.,* 2005 and Hong *et al.,* 2007). Rabi *et al.,* (2007) for Co and Mn doped ZnO nanopowders, the ferromagnetic properties were not due to secondary phases. The room temperature ferromagnetic properties in TM doped ZnO was observed due to carrier exchange interactions, the large variation in the carrier concentration and magnetic properties were observed to depend on the synthesis technique (Ghosh *et al.,* 2005). Also, the origin of

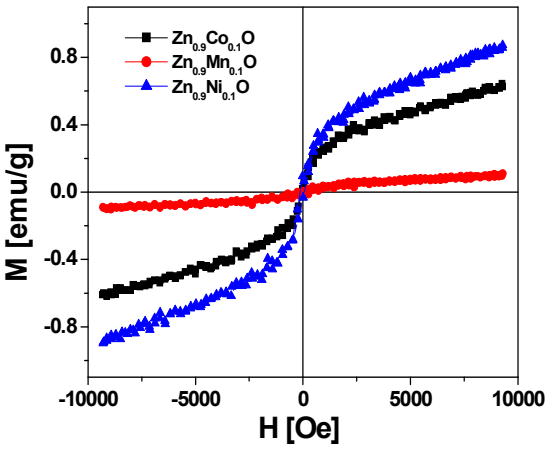

Figure 4: M-H curves for $Zn_{0.9}Mn_{0.1}O$, $Zn_{0.9}Co_{0.1}O$ and $Zn_{0.9}Ni_{0.1}O$ nanoparticles

in the samples is not fully understood. Further experiments will be carried in near future and its results will be reported in detail.

CONCLUSIONS

TM doped ZnO nanocrystals were synthesized using co-precipitation technique. X-ray diffraction patterns shows the formation of TM doped ZnO nanoparticles having particle size around 10 nm. IR measurements showed the structural formation due to TM doping in ZnO. The room temperature magnetic measurements for Mn, Co, Ni doped showed the weak ferromagnetic properties.

Conflict of Interest

Authors declared no conflict of interest.

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