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Structural, Optical and Magnetic Properties of Ni Doped ZnO Nanostructures Prepared by Co-Precipitation Method

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Abstract: Pure and Ni doped zinc oxide (ZnO) nanostructures have been synthesized by co-precipitation method. The X-ray diffraction reveals that the polycrystalline nature for pure and Ni doped ZnO with the hexagonal wurtzite phase. The photoluminescence (PL) spectra of all the samples exhibited a broad emission in the visible range. The rod shaped structure was observed for Ni doped ZnO by scanning electron microscopy. The energy dispersive X-ray spectroscopic analysis (EDX) confirmed the compositions of the presented elements in pure and Ni doped ZnO. The room temperature magnetic measurement exhibits well defined weak ferromagnetic behaviour for Ni doped ZnO.
Keywords: Photoluminescence, Spectroscopic, Ferromagnetic.

Introduction

The structural, optical and magnetic properties of metal oxide nanoparticles (NPs) are of particular interest for practical applications. Recently, oxide based diluted magnetic semiconductors (DMS) such as transition metal doped semiconductors with room temperature ferromagnetism (RTFM) have been studied for their advanced applications in spintronic devices. ZnO NPs are the wurtzite-phase n-type semiconductors having a wide direct band gap of ~3.37 eV which gives an enormous attraction towards commercial applications. The transition metals doping in semiconductor ZnO facilitates the generation of carrier mediated ferromagnetism [1]. Many reports addressed room temperature ferromagnetic behavior of transition metal [Fe, Mn, Ni, Co, Cr] doped semiconductor oxides and the behavior of ferromagnetism is mainly due to intrinsic defects or impurity phases or ferromagnetic precipitates [2]. Among various synthetic routes, co-precipitation method has been popularly adopted to synthesis ZnO NPs due to its low cost, superior uniformity and high yield of NPs. In this paper, structural, optical and magnetic properties of pure and Ni doped ZnO were presented. The change of magnetic behaviour was identified for Ni doped ZnO.

Experimental Section

Synthesis of pure and Ni doped ZnO was carried out using analytical grade zinc acetate dihydrate [Zn $(CH_3COO)_2$. $2H_2O$], nickel acetate dihydrate [Ni $(CH_3COO)_2.2H_2O$] and sodium hydroxide (NaOH) in as received condition. In the synthesis process, a required amount of zinc acetate was completely dissolved in de-ionized water and a required amount of aqueous NaOH solution was added drop wise to the mixture. Later the

solution with the white precipitate was stirred at room temperature for 30 min, and then kept at 80°C for 5 hours. Thereafter, the white precipitate was washed several times with double distilled water and ethanol. Finally, the precipitate was dried at 120 °C for an hour. The obtained ZnO samples were annealed at 300°C in air for 2 hours. Thus, nanopowder of ZnO was collected and used for further studies. For the synthesis of $Zn_{1-x}Ni_xO$ (x=0.03) NPs, the calculated amount of nickel acetate in water was mixed with zinc acetate solution separately. The required amount of aqueous NaOH solution was added drop by drop to the homogenous mixture to get a white precipitate with pale pink color. A similar procedure adopted for the preparation of pure ZnO NPs was followed for the synthesis of Ni doped ZnO NPs.

Results and Discussion

X-ray diffraction patterns of $Zn_{1-x}Ni_xO$ (x=0, 0.03) NPs are shown in **Figure 1(A)**. The d-spacing of the peaks are well matched with standard data (JCPDS: 89-1397), and corresponding structure of the sample is hexagonal wurtzite. No impurity phase was found in the Ni doped ZnO sample because of the smaller ionic radii of the Ni^{2+} ions (ionic radius: 0.69 Å) are substituted in the inner lattice of Zn^{2+} ions (ionic radius 0.74 Å) [3]. The XRD patterns of Ni doped ZnO are same as that of pure ZnO, showing that small amount of Ni doping did not change the ZnO structure. In order to study the effect of Ni doping, a careful analysis of the position of XRD peaks are carried out and (102) peak is shifted towards lower 2θ value as shown in inset of **Figure 1A**.

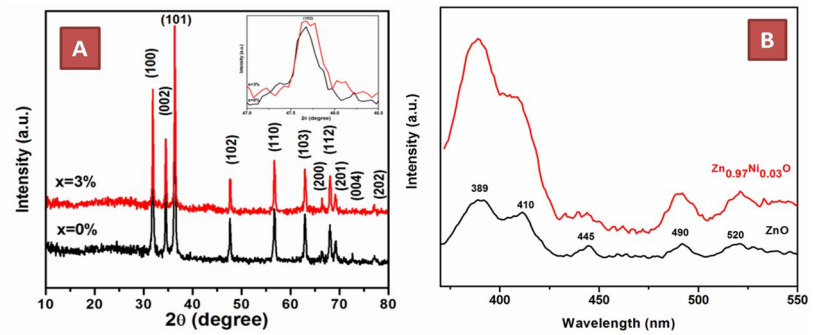

Figure 1. (A) XRD patterns of $Zn_{1-x}Ni_xO$ (0.0 and 0.03) samples. Inset shows the magnified area of (102) peak, (B) PL spectra of $Zn_{1-x}Ni_xO$ (0.0 and 0.03).

Figure 1B shows the room temperature PL spectra of pure and Ni doped ZnO. These spectra were recorded in a spectral range of 340-550 nm with an excitation wavelength of 325 nm. It can be seen from the spectra that different emission peaks were observed such as strong UV emission band around 389 nm and blue and green emissions band at 490, 520 respectively. The emission band around 389 nm is a spontaneous emission peak of ZnO in UV region, which originates from a near-band-edge (NBE) transition of wide band gap of ZnO [4]. Generally, oxygen vacancies are the most common defects in semiconductor oxides and usually act as radiative centers in luminescence processes. These oxygen vacancies are the intrinsic defects in n-type ZnO and can capture electrons and thus form ionized vacancies which act as deep defect donors and result in new energy level, which further influences the optical properties of ZnO [5]. Therefore, the observed green emission at 520 nm is likely related to the oxygen vacancies. The emission peak positions are slightly shifted for the Ni doped ZnO samples. **Figure 2 (A, B)** shows the SEM images of ZnO and Ni doped ZnO samples. Pure ZnO possesses flake like morphology whereas Ni doping changes its morphology to rod like with different diameter and length.

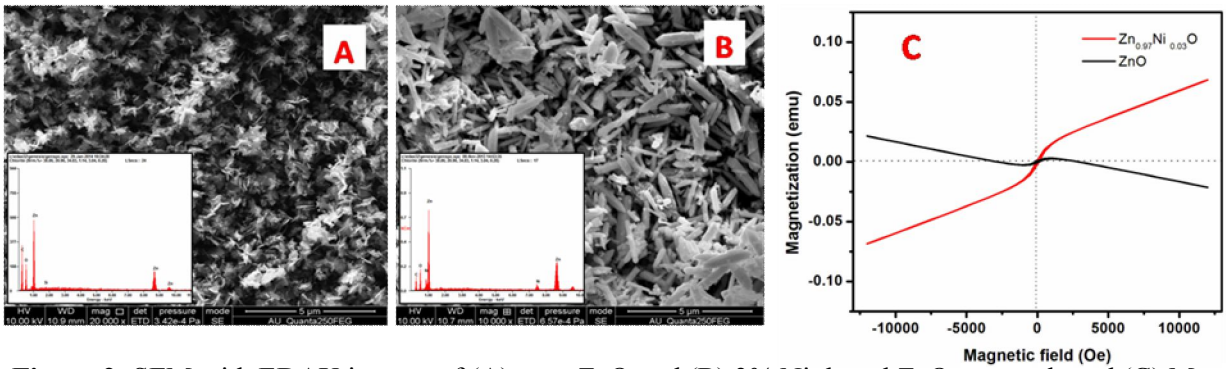

Figure 2. SEM with EDAX images of (A) pure ZnO and (B) 3% Ni doped ZnO nanorods and (C) Magnetic behavior of (A) ZnO (B) $Zn_{0.97}Ni_{0.03}O$ nanorods.

The chemical compositions of synthesized pure and Ni doped ZnO NPs were determined by EDS spectra and are shown in insets of **Figure 2 (A, B)**. These spectra indicated the presence of only Zn, O and Ni. Magnetization versus magnetic field (M-H) curves for $Zn_{1-x}Ni_xO$ (x=0 and 0.03) samples, measured at 300K with maximum applied field of ±1.5 Tesla is used to identify the effect of Ni doping on magnetic properties of ZnO NPs. **Figure 2(C)** exhibit weak ferromagnetic behavior of Ni doped ZnO but the pure sample show only the diamagnetic nature. The existence of diamagnetic behavior for pure ZnO is also referred in the literature [6]. The magnetization observed at 13 kOe is 0.067emu/g for $Zn_{0.97}Ni_{0.03}O$. The changes in M-H loop can be explained on the basis of the magnetic contribution from the orientation of the strong exchange interaction in d-d couple with nickel ions. It is reasonable to point out that the observed ferromagnetism is due to the presence of oxygen vacancies and/or defects in the crystal surface [7].

Conclusion

$Zn_{1-x}Ni_xO$ NPs were successfully prepared by co-precipitation method. The hexagonal (wurtzite) crystalline structure was identified for pure and doped ZnO through XRD analysis and confirmed that Ni^{2+} ions were incorporated into the lattice site of Zn^{2+} ions in ZnO matrix and further confirms that there is no peak corresponds to Ni cluster. Compositional analysis (EDS) ascertained the existence of Zn, O and Ni in the synthesized materials. The PL peak intensities of NBE and green emissions increased with respect to the doping of nickel ions. Vibrating sample magnetometer study clearly showed the diamagnetic behavior of pure ZnO whereas 3% Ni doping in ZnO makes the samples as weak ferromagnetic at room temperature.

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