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Structural, spectroscopic and magnetic characterization of undoped, Ni^{2+} doped ZnO nanopowders

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ABSTRACT

Structural, magnetic and optical properties of undoped and Ni^{2+} doped ZnO nanopowders have been prepared by sonochemical assistance. Powder XRD studies confirm the hexagonal structure of both undoped and Ni^{2+} doped of ZnO nanopowders and its average crystallite sizes are evaluated. Optical absorption and Electron Paramagnetic Resonance spectral data confirmed the site symmetry for Ni^{2+} ions as octahedral. Photoluminescence spectra exhibited the emission bands in ultraviolet and blue regions at an excitation wavelength of 328 nm. FT-IR spectra showed the characteristic vibrational bands of Zn–O. Vibrating sample magnetometer was used for the magnetic property investigations and indicates room temperature ferromagnetism which is intrinsic in nature and attributed to oxygen and/or Zn deficiencies.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted a lot of attention for their potential applications in spintronics. DMSs use both spin and charge of electron for a new class of devices such as spin valves, memory, logic devices, optical isolators, quantum computation and ultra fast optical switches. DMSs are the materials in which transition metal (TM) elements are substituted for a few percent of cations of host semiconductors [1]. Among II–VI semiconductors, ZnO is a potential candidate for fabricating DMSs due to its high solubility for TMs and superior semiconductor properties. ZnO is a wide bandgap of 3.3 eV with a large exciton binding energy of 60 meV and has potential applications in electronics and optoelectronic devices [2]. Sluiter et al. [3] have theoretically predicted that the transition metal ions doped ZnO is ferromagnetic at room temperature. A number of experimental reports are available on ZnO doped with transition metal ions with few conflicting reports [4]. Zhang et al. [5] have reported the evidence of intrinsic ferromagnetism in individual ZnO nanoparticles doped with transition metal ions. The main challenge for this kind of novel materials is to preserve their magnetic character at room temperature in order to be useful for technological applications. According to the ferromagnetic exchange coupling theory, ideal DMSs should have a homogeneous distribution of the magnetic dopants. The presence of any magnetic precipitate in the host semiconductors in the form of secondary phases of the magnetic impurities is unfavorable to the real applications of DMSs and therefore should be avoided [6]. In the exploration of the specific materials, ZnO has been identified as an excellent candidate host semiconductor for supporting room-temperature ferromagnetism.

Doping is a widely used method to improve electrical, optical and magnetic properties of semiconductor compounds, facilitating the construction of many electronic and optoelectronic devices. In transition metal ions, Nickel ion is an important with rich optical properties in different transparent materials and also has the advantage of Ni^{2+} ion is its sensitivity towards their ligand field environment. Furthermore Ni^{2+} (0.69 Å) have same valence compared to Zn^{2+} and its radius is close to Zn^{2+} (0.74 Å).

Some researches on Ni doped ZnO have been reported and results showed that the luminescence properties of ZnO were changed after doping with Ni [7–10]. Various chemical methods have been developed to prepare ZnO nanostructured materials. Most of these materials are synthesized by a traditional solid-state method [11,12], simple solution-based methods such as chemical precipitation [13], sol–gel synthesis [14], and hydrothermal reaction [15].

However, simple and mild routes for the synthesis of nickel ions doped ZnO still need to be explored and the structure of the synthesized powder is becoming a key factor for its application to nanodevices. In recent years sonochemical method is being used in the preparation of many materials by ultrasound technology. Ultrasound waves supply the high energy needed for chemical reactions via the process of acoustic cavitations involving the formation, growth, and implosive collapse of bubbles in the liquid.

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During the cavitational collapse, intense local heating of the bubbles occurs for a few microseconds resulting in high-velocity inter particle collisions whose impact can be used for synthesis [16]. The sonochemical method has several advantages over other methods. Furthermore, it is suitable for large-scale production in terms of rapidity, low cost and low energy demand [17]. Recently authors are reported Co^{2+}, Cu^{2+} and Cr^{3+} doped ZnO nanopowders [18–20]. The site symmetry of transition metal ions (TM) are ascribed as distorted octahedral sites and exhibited room temperature ferromagnetism in ZnO nanopowders. In the present paper, undoped and Ni^{2+} doped ZnO nanopowders were synthesized by sonochemical method and characterized by powder XRD and spectroscopic techniques. Structural, optical and magnetic properties of the prepared materials are discussed in detail.

2. Experimental section

Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), Sodium Lauryl Sulphate, SLS ($C_{12}H_{25}O_4SNa$), Nickel Nitrate ($Ni(NO_3)_2$) and Sodium hydroxide (NaOH) were purchased from Merck Chemicals. All of the chemical reagents used in this experiment were analytical grade and used without further purification. Zinc acetate (2.195 g, 0.01 mol%) was ground for 5 min and SLS (2.018 g, 0.007 mol%) was added to zinc acetate. After the mixture was ground for 5 min, it was stood for 2 h at room temperature. The mixture that was still a solid powder was then mixed with sodium hydroxide pellets (0.89 g, 0.02 mol%) and ground for 30 min. Later 0.03 mol% of nickel nitrate was added to the above mixture. The product was washed several times in an ultrasonic bath with distilled water and alcohol (till the pH of solution becomes neutral) to remove any by-product and SLS. After washing, the solution was centrifuged at 10,000 rotations per minute (rpm) about 30 min. The settled powder was collected and dried in air at 80 °C for 2 h. The similar procedure has been used for the preparation of undoped ZnO nanopowder without using nickel nitrate.

Powder X-ray diffraction pattern of undoped and Ni^{2+} doped ZnO powders were done on PANalytical XPert Pro-diffractometer with Cu*K*α radiation (1.54060 Å). Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscope (EDS/EDX) images for both prepared powders were taken from JEOL JSM 6610 LV. Photoluminescence (PL) spectra of samples were obtained from Horiba Jobin-Yvon Fluorolog-3 Spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources. Fourier Transformed Infra Red (FT-IR) spectra of samples were recorded using ATR accessories on Bruker's Alpha Spectrophotometer in the region of 400–4000 cm^{-1}. Optical absorption spectra were taken from JASCO V-670 Spectrophotometer in the wavelength region of 200–1400 nm. The EPR spectrum was obtained from JEOL JES-TE100 ESR spectrometer operating at X-band frequencies and having a 100-kHz field modulation. The magnetic hysteresis loop was obtained from a Lake Shore 7407 vibrating sample magnetometer (VSM) for the samples.

3. Results and discussion

3.1. XRD analysis

The phase identity and crystallite size of prepared nanopowders were determined by using Powder X-ray diffractometer. Fig. 1 shows the powder X-ray patterns of undoped and Ni^{2+} doped ZnO nanopowders. XRD studies confirmed that the synthesized undoped and Ni-doped ZnO nanopowders were hexagonal wurtzite structure and all the diffraction peaks agreed with the JCPDS card no. 36-1451. Thus, it can be concluded that the doping of Ni does not change the wurtzite structure of ZnO. The pronounced diffraction peaks in XRD pattern clearly shows the crystalline nature and they assigned to the diffraction planes of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1) and (2 0 2). From diffraction data, lattice cell parameters are evaluated for undoped ZnO as $a=0.3259$ nm, $c=0.5229$ nm and for Ni-doped ZnO nanopowder lattice parameters are $a=0.3249$ nm, $c=0.5214$ nm. The lattice parameters of Ni^{2+} doped ZnO nanopowder are slightly less than that of pure ZnO. Although the change is very small, the dopant plays a role in the variation of lattice parameters that gives an indication for the Ni doping in the ZnO crystalline structure since the ionic radii of Ni^{2+} (0.69 Å) is less than that of Zn^{2+} (0.74 Å). Liu et al. reported similar trend of decreasing lattice constants [21]. The crystallite size was estimated for the most prominent XRD peak using Scherrer's formula,

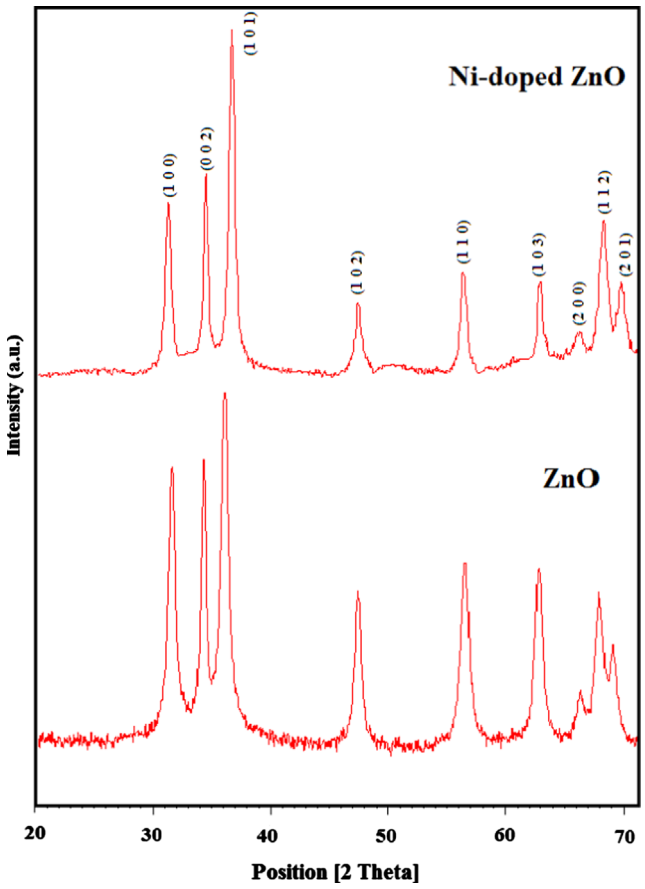

Fig. 1. Powder XRD pattern of undoped and Ni^{2+} doped ZnO nanopowders.

$$t = 0.9\,\lambda/\beta\,\cos\,\boldsymbol{\theta}$$

where t is crystallite size in nm, λ is wavelength of X-ray radiation (1.5406 Å) used, θ is Bragg diffraction angle and β is FWHM intensity. Evaluated values of crystallite size were about 98 nm and 48 nm for undoped and Ni-doped ZnO respectively. The reduction in the particle size is mainly due to the distortion in the host ZnO lattice by the foreign impurity i.e. Ni^{2+} which decreases the nucleation and subsequent growth rate by the addition of Ni concentrations. The micro-strain (e) can be calculated using the formula [22],

$$\text{Micro}-\text{strain}(\varepsilon) = \beta\,\cos\,\theta/4.$$

The calculated values of micro-strain are 0.02×10^{-3} and 1.26×10^{-3} for undoped and Ni-doped ZnO nanopowders respectively. It is observed that the strain value was increased for Ni^{2+}