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Original Research Paper

Effect of Mn doping concentration on structural, vibrational and magnetic properties of NiO nanoparticles

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ABSTRACT

The $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles were synthesized by chemical precipitation route followed by calcination at 500 °C for 4 h. The prepared samples were characterized by energy dispersive analysis of X-rays (EDAX), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and vibrating sample magnetometer (VSM). Rietveld refinement of XRD data confirms the structural phase purity and XRD patterns are well indexed to NaCl like rock salt fcc crystal structure with *Fm*-3*m* space group. The particle size of Mn doped samples is found to be less than that of pure NiO sample. However, the particle size increases slightly on increasing the Mn concentration due to surface/grain boundary diffusion. The vibrational properties of the synthesized nanoparticles were investigated by Raman and FT-IR spectroscopy. The results of room temperature magnetization (M-H) and temperature dependent magnetization (M-T) measurements are explained with a core-shell model. The synthesized nanoparticles show weak ferromagnetic and super-paramagnetic like behavior at room temperature.

1. Introduction

Recently, transition metal ion doped oxide diluted magnetic semiconductors (DMS) have attracted huge attention in the field of advanced spintronic, magneto-electronic and magneto-opto-electronics [1]. Huge research has been demonstrated on magnetic or non-magnetic transition metal ion doped oxide DMSs which exhibit room temperature ferromagnetism (RTFM) with Curie temperature well above room temperature for their potential application in spintronics [2–4]. One of the most intensively investigated members of metal oxide family, NiO possesses anti-ferromagnetic behavior below Neel temperature of about 523 K [5,6]. NiO nanoparticles with size smaller than 31 nm leads to large anomalous magnetic moments with noticeable coercivity and loop shift at low temperature [7]. The ferromagnetism has been demonstrated in NiO nano-crystalline sample having grain size of 5 nm which is believed to be due to missing bonds and lattice distortion [8]. Although, pure NiO is a Mott- Hubbard insulator with a wide band gap of about 4 eV in bulk form, it shows p-type semiconducting behavior due to presence of Ni^{+2} vacancies or on doping of cations [9–12].

The room temperature ferromagnetism in pure and Fe doped NiO nanoparticles is reported by Mishra et al. [13] and Khemprasit et al. [14]. Swatsitang et al. [15] reported theoretical calculations on the magnetic properties of Mn-doped NiO using density functional theory with generalized gradient approximation (GGA) and plane wave basis. They have shown ferromagnetism in Mn-doped NiO and also shown increase in net magnetization with increase of Mn concentration up to 9.375%. Mallick et al. [16] have synthesized nano-crystalline $Ni_{1-x}Mn_xO$ (x = 0, 0.01, 0.03 and 0.05) with average grain size of 21–28 nm by a chemical route using nickel nitrate hexahydrate and manganese acetate and calcined at 500 °C. They have observed anti-ferromagnetic behavior at 10 K in pristine and 1% Mn doped NiO nanoparticles and super-paramagnetism at room temperature in higher doped samples with average blocking temperature of the order of 180 K. Raja et al. [17] have synthesized $Ni_{1-x}Mn_xO$ (x = 0.00, 0.01, 0.02 and 0.03) nanoparticles by chemical co-precipitation method and found single phase up to 2% Mn-doping concentration. However, RTFM was not observed for their samples ($x \leq 0.02$). Anandan et al. [18] have synthesized $Ni_{1-x}Mn_xO$ (x = 0.00, 0.01, 0.02 and

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0.03) nanoparticles by precipitation route and calcined at 500 °C. They have found anti-ferromagnetic to super-paramagnetic transition up to 2% Mn doping concentration whereas 3% Mn doped sample exhibits weak ferromagnetism at room temperature. Recently, Layek et al. [19] have synthesized single phase $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles up to 6% Mn-doping by low temperature hydrothermal method and calcined at 400 °C. They have observed RTFM in their samples but net magnetization decreases with increase of Mn-doping concentration which contradicts with theoretical calculations done by Swatsitang et al. They also concluded that observed RTFM is an intrinsic property of the material and was not due to any other impurity phases. Bharathy et al. [20] have synthesized single phase $Ni_{1-x}Mn_xO$ (x = 0.0, 0.1, 0.2 and 0.3) nanoparticles up to 30% Mn-doping by sol-gel method. Their samples show weak ferromagnetic behavior at room temperature. Similarly, Sankar et al. [21] have synthesized $Ni_{1-x}Mn_xO$ (x = 0.0, 0.1, 0.2, 0.3 and 0.4) nanoparticles and studied their optical and photocatalytic properties. Therefore, it can be seen that synthesis route plays an important role in structural and subsequently on magnetic properties of Mn-doped NiO nanoparticles. Therefore, a simple, efficient and reproducible method to synthesize Mn-doped NiO nanoparticles having RTFM with significant magnetization is yet to reach the desire grade.

In this present article, we demonstrate the structural, morphological, vibrational and magnetic properties of $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles synthesized by chemical precipitation route with the addition of polymer. Herein, room temperature ferromagnetism is achieved and doping assisted enhanced magnetism is realized for $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles.

2. Experimental details

2.1. Synthesis

$Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles were synthesized by chemical precipitation technique [22] with the addition of polyvinyl-pyrrolidone (PVP) which acts as a capping agent. In the experiment, 20 ml of 0.25 M aqueous solution of metal chloride salts using stoichiometric amount of nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), manganese chloride tetra-hydrate ($MnCl_2{\cdot}4H_2O$) and 100 ml of 0.5 M aqueous solution of sodium hydroxide (NaOH) were prepared in double distilled water separately. Then 0.4 g PVP was dissolved in NaOH solution and heated at 45 °C. The metal chloride solution was added drop wise to the heated NaOH solution under high speed stirring for 2 h. The light green or brownish green solution depending on doping concentration of Mn was observed and was left for 2 h. The resulting light green or brownish green precipitates of ($Ni_{1-x}Mn_x(OH)_2$) (x = 0.00, 0.02, 0.04 and 0.06) was filtered using whatman filter paper and washed twice with deionized water and ethanol to remove the unreacted salts. The samples were dried in a hot air oven at 80 °C for 10 h. The obtained dried materials ($Ni_{1-x}Mn_x(OH)_2$) is then grounded with mortar and pestle. Then, the hydroxide powder of $Ni_{0.98}Mn_{0.02}(OH)_2$ was characterized by TGA/DTG/DTA using Seiko SII-EXSTAR TG/DTA-7200 to study their thermal decomposition properties and to decide proper calcination temperature in order to obtain $Ni_{0.98}Mn_{0.02}O$ nanoparticles.

Fig. 1 represents TGA, DTG and DTA curves of synthesized dried hydroxide powders of $Ni_{0.98}Mn_{0.02}(OH)_2$ recorded for 5 °C min^{-1} heating rate in the N_2 environment from room temperature to 750 °C. The first step was observed at temperature below 150 °C and corresponding weight loss is 12.84%. This step can be associated with the elimination of chemically adsorbed and/or structurally bonded water molecules [23,24]. The second and major

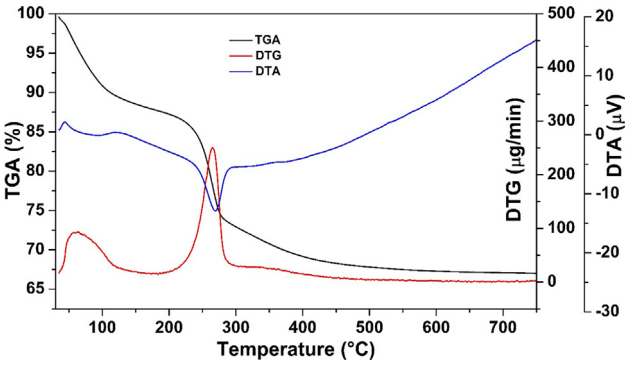

Fig. 1. TGA, DTG and DTA curves of dried powder of $Ni_{0.98}Mn_{0.02}(OH)_2$.

step seen in the temperature range 200 °C to 300 °C, shows weight losses of 17.51%. This step is related to the thermal decomposition of $Ni_{0.98}Mn_{0.02}(OH)_2$ to $Ni_{0.98}Mn_{0.02}O$ [23,24]. Further, thermal decomposition of $Ni_{0.98}Mn_{0.02}(OH)_2$ to $Ni_{0.98}Mn_{0.02}O$ leads to the oxidation of Ni^{+2} or Mn^{+2} to a higher oxidation state like $Ni_{0.98}Mn_{0.02}O_y$ (where y is stoichiometry) [25]. The third and final step marked by sharp decrease in the slope of TGA curve up to 500 °C, shows weight loss of 3.08%. This may correspond to the decomposition of non-stoichiometric $Ni_{0.98}Mn_{0.02}O_y$ to $Ni_{0.98}Mn_{0.02}O$ [23,25] and no further weight loss was observed beyond 500 °C. Therefore, the dried precipitates of $Ni_{1-x}Mn_x(OH)_2$ ((x = 0.00, 0.02, 0.04 and 0.06) was calcined in air at 500 °C for 4 h and black colored $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles are obtained.

2.2. Characterization

The chemical composition of the synthesized $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) samples was studied by EDAX. The structure and phase purity of samples were characterized by XRD using Rigaku powder X – ray diffractometer with Cu K_α radiation (λ = 1.5418 Å). Further, morphology and the crystalline nature of the synthesized nanoparticles were checked by TEM using a Tecnai 20 electron microscope operated at 200 kV. Selected area electron diffraction (SAED) patterns were also recorded for further structural analysis. The vibrational properties of the synthesized nanoparticles was studied by Raman spectroscopy using diode laser (473 nm, 25 mW) as an excitation source at room temperature. Further, the FT-IR spectra of the synthesized $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles were recorded using Perkin Elmer GX instrument. The room temperature isothermal magnetization (M-H) measurements with an applied magnetic field up to 5 T and temperature dependent magnetization (M-T) measurements in the temperature interval 10–350 K with an applied magnetic field of 500 Oe were done using 14T PPMS-vibrating sample magnetometer (VSM).

3. Results and discussion

The EDAX spectra of $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) samples are shown in Fig. 2(a–d). The synthesized samples are stoichiometric and do not contain any other foreign impurity element/impurity. The weight and atomic percentage of the $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) samples is presented in Table 1.

Fig. 3 represents powder XRD patterns of the synthesized $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles along with Rietveld fit. The Rietveld refinement was carried out using full-prof software to determine lattice parameters. The XRD patterns of $Ni_{1-x}Mn_xO$ (x = 0.00, 0.02, 0.04 and 0.06) nanoparticles are well

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