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Research articles

Structural and magnetic properties of NiO-MnO_2 nanocomposites prepared by mechanical milling

B. Balaraju[a], S. Kaleemulla[b,*], C. Krishnamoorthi[c]

[a] Thin Films Laboratory, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, Tamilnadu, India
[b] Thin Films Laboratory, Center for Crystal Growth, Vellore Institute of Technology, Vellore 632014, Tamilnadu, India
[c] Center for Nanotechnology, Vellore Institute of Technology, Vellore 632014, Tamilnadu, India

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ABSTRACT

Manganese added nickel oxide composite nanoparticles (1 − x)NiO-xMnO_2 (x = 0.00, 0.5, 0.10, 0.15 & 1.0) were prepared using mechanical milling and subjected to different characterization techniques to study their structural, optical and magnetic properties. The microstructures, surface morphology, crystallite size of the nanoparticles were studied using X-ray diffractometer (XRD), field emission scanning electron microscopy (FE-SEM). From these it was found that the nanoparticles were in cubic structure. Secondary phases were observed with increase of Mn concentration. The crystallite size of the particles was calculated using Scherer's relation and found that the nanoparticles were in the range of 25–35 nm. The magnetic properties of the composite nanoparticles were studied at room temperature and at 100 K using vibrating sample magnetometer (VSM) in the applied field range of ± 75 kOe. The MnO_2 nanoparticles exhibited paramagnetic nature at room temperature. The NiO nanoparticles exhibited soft ferromagnetic nature and strength of magnetization increased with applied external magnetic field (± 50 kOe). The Mn doped nickel oxide composite nanoparticles also exhibited soft ferromagnetism at room temperature and at 100 K. The strength of magnetization increased with increase of Mn concentration and the composite nanoparticles at x = 0.15 ($Ni_{0.85}Mn_{0.15}O$) shown the highest magnetic moment of 6 emu/g at 100 K. The temperature dependent magnetic moments for (1 − x)NiO-xMnO nanoparticles at different x values were also discussed in detail.

1. Introduction

Currently as the technology is moving towards low dimensional devices, great importance has been given on compound semiconductors which are best suited for the present technology. High importance is being put on low dimensional semiconductors. For the past few years high attention is paid on the production of novel nanostructured metal oxide materials. Over the past ten years, extensive studies were carried out on semiconductors in the form of bulk material. Due to introduction of nanotechnology and their applications, continuous efforts are being put on various semiconductors in the quantum well, quantum wire and quantum dot. These nanostructures were extensively studied for electromagnetic absorption application [1,2].

In the sequence, nanoparticles of all materials find various applications due to their peculiar mechanical, thermal, electrical, optical, magnetic properties. The nanoparticles are exhibiting quite better properties than that of bulk material. These nanoparticles with size in the nanometric scale in the everyday life has increased continuously and, in particular, magnetic nanoparticles have find in potential applications that go from the use in the development of reliable large data storage devices, magneto-recording, resistive switching, supercapacitors and biomedicine [3–7]. In this quest, many oxide nanoparticles were studied and reported their peculiar electrical and magnetic properties. Among the various nanomaterials, metal oxides have attracted increasing technological and industrial interest. Over the past few years, NiO nanoparticles are finding much importance due to their outstanding electrical, magnetic and catalytic properties [8,9]. Further, it is known that the bulk nickel oxide exhibits antiferromagnetic nature whereas nickel oxide nanoparticles exhibit a variety of magnetic properties such as spin glass, superparamagnetism and weak ferromagnetic depending on the size of the nanoparticles [10,11]. The interesting properties at nanoscale were attributed to size of the particles and surface effects [12,13]. Semiconductor nanoparticles such as indium oxide (In_2O_3), tin oxide (SnO_2), zinc oxide (ZnO), etc were studied extensively due to their important properties such as optical transmittance, high electrical conductivity and good chemical stability [14]. Among the different oxide semiconductors, nickel oxide nanoparticles find much interest due to its wide range of applications such as

* Corresponding author.
E-mail address: skaleemulla@gmail.com (S. Kaleemulla).

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electrode, lithium ion batteries, resistive switching, dye synthesized solar cell and electrochromic devices, etc [15–17].

For the past few years research is being carried out on magnetism and magnetic interaction in fine nanoparticles of NiO as they find in novel magnetic properties. The challenge before the researchers is to control the size of the nanoparticles as the size and surface morphology strongly decide the magnetic properties of the nanoparticles. The size dependent magnetic properties of NiO were studied by Richardson et al. [18]. Further, it was suggested that the fine NiO should exhibit either weak ferromagnetism or superparamagnetism. In this sequence, different synthesis methods such as chemical precipitation, sol-gel, hydrothermal [19,20], solvothermal, emulsion, thermal decomposition were applied to prepare the nanoparticles [21–24]. Among the different synthesis methods, solid state reaction is one of the best and simplest methods to obtain homogeneous nanoparticles. The bottom up and top down are the two best methods applied for the synthesis of nanoparticles. Bottom up synthesis method has been applied in most of the reported articles and suggested that the magnetic properties of nanoparticles are complex due to interplay between finite size, surface and interface effects. But till today very few articles have been published on synthesis of pure and Mn doped NiO nanoparticles using top down approach. This motivated us to perform systematic investigations on the evolution of NiO nanostructure through top down approach and understand the structural and magnetic properties.

Similarly the effects of size and impurity concentrations were studied here systematically to understand the reason for significant enhancement in the magnetization values between pure and doped composite NiO nanoparticles.

2. Experimental details

Pure and Mn doped NiO composite nanoparticles (1 − x)NiO-xMnO_2 (x = 0.00, 0.05, 0.10, 0.15 & 1.0) were prepared by simple and low cost solid state reaction. Commercially available MnO_2 and NiO (M/S Sigma-Aldrich 99.99% pure) were accurately weighed in required proportions and converted into fine powders using an Agate mortar and pestle. The grinding of the mixtures was carried out for 16 h for all the Mn concentrations. The powder samples were made into pellets and sintered in vacuum at a temperature of 800 °C. Then the sintered pellet was made into fine powders and subjected for different characterizations. Then the synthesized nanoparticles were subjected for various characterization techniques to study the microstructure, chemical, spectroscopic and magnetic properties.

X-ray diffraction (X-ray diffractometer, D8 Advance, BRUKER) was used to establish structural aspects crystal structure, crystallite size, lattice constant, etc. Energy dispersive analysis spectroscopy (EDAX with SEM) (OXFORD instrument incapenta FET X3) was used to know the chemical composition and surface morphology of the synthesized powder samples. Fourier Transform Infrared (FT-IR) Spectroscopic analysis was carried out using FT-IR Spectrophotometer (SHIMADZU) to determine the functional groups and to find the existence of impurities. Magnetic properties were studied at room temperature using Vibrating sample magnetometer (Lake Shore-7410).

3. Results and discussions

Fig. 1(a) shows the X-ray diffraction (XRD) patterns of the MnO_2, NiO and (1 − x)NiO-xMnO_2 nanoparticles at x = 0.00, 0.05, 0.10, 0.15 & 1.0. The first layer of the figure gives the XRD patterns of the MnO_2. The diffraction peaks such as (310), (211), (301), (431), (521), (002) and (312) were observed at 28.75°, 37.35°, 42.85°, 56.66°, 59.41°, 64.86°, and 72.46°, respectively. These diffraction peaks exactly coincided with that of tetragonal structure of MnO_2 [JCPDS No. 44-0141]. The second layer of the Fig. 1(a) shows the XRD profiles of pure nickel oxide (NiO). The diffraction peaks such as (222), (400), (440) and (622) were found at 37.7°, 43.2°, 62.58°, 75.01°, and 79.10°. All

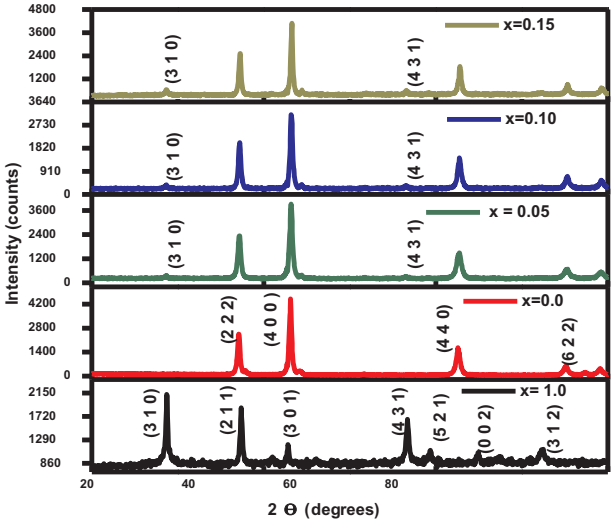

Fig. 1(a). XRD profiles of (1 − x)NiO-xMnO_2 nanocomposites at x = 0.00, 0.05, 0.10, 0.15 & 1.0.

these diffraction peaks were exactly coincided with that of cubic structure of NiO [JCPDS # 73-1519]. Among all the diffraction peaks, (400) was the predominant peak indicating the growth of the nanoparticles took place along (400) direction.

The 3, 4 & 5 layers of the Fig. 1(a) shows the XRD profiles of (1 − x) NiO-xMnO_2 nanoparticles at x = 0.05, 0.10, 0.15. Here also diffraction peaks such as (222), (400), (440) and (622) were found at 37.7°, 43.2°, 62.58°, 75.01°, and 79.10°. The intensity of the diffraction peaks decreased with increase of doping concentration as shown in Fig. 1(b). In general, the intensity of the diffraction peaks decreases greatly with the increase of doping concentration, indicating a loss of crystallinity due to lattice distortion. The (400) diffraction peak of NiO shifted towards the higher diffraction angles with increase of doping concentration. The shift in diffraction angle can be seen clearly in Fig. 1(b).

However, in addition to these diffraction peaks which belong to NiO, two more diffraction peaks such as (310) and (431) were also observed at 28.6° and 56.6° in (1 − x)NiO-xMnO_2 nanoparticles at x = 0.05, 0.10, 0.15. These diffraction peaks belong to impurity MnO_2. The intensity of the (310) diffraction peak increased with increase of Mn concentration from x = 0.05 to x = 0.15. From the figure it can be seen that the intensity of the diffraction peaks related to NiO decreased with increase of Mn concentration. No other impurity phases such as Mn_2O_3, MnO_2, or $NiMn_2O_4$ were found in the (1 − x)NiO-xMnO_2 with increase of Mn concentration from x = 0.05 to x = 0.15. It seems that

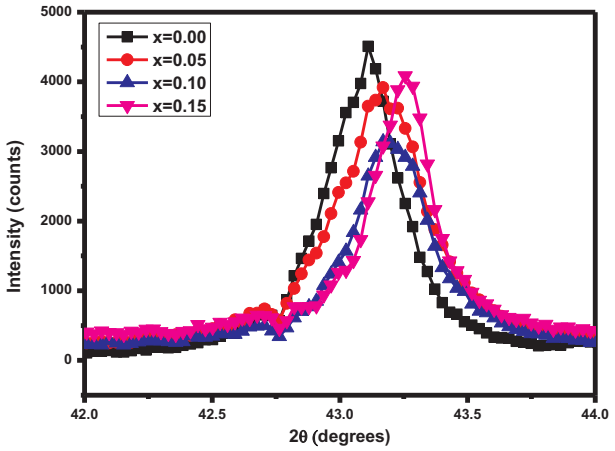

Fig. 1(b). XRD profiles of (1 − x)NiO-xMnO_2 nanocomposites at x = 0.00, 0.05, 0.10 and 0.15.