Role of Mn^{2+} concentration in the linear and nonlinear optical properties of Ni$_{1-x}$Mn$_x$Se nanoparticles

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ABSTRACT

Ni$_{1-x}$Mn$_x$Se nanoparticles (x = 0.1, 0.3, 0.5, 0.7, 0.9) were successfully synthesized by chemical co-precipitation method and their structural and optical properties were studied using X-ray diffraction, transmission electron microscopy, UV–Visible absorption and photo luminescence spectroscopy. XRD pattern reveals the hexagonal structure of the particles and the peak positions were shifted to higher 2θ values with increase in Mn^{2+} concentration. The average particle size determined from XRD varies from 6 to 11 nm. The UV–Visible absorption spectrum shows absorption edge around the blue region and is red-shifted with increasing Mn^{2+} concentration consequently the optical bandgap energy is decreasing. The PL emission spectrum shows a broad emission around 380 nm, and the intensity of the emission decreases with increase in Mn^{2+} concentration. The nonlinear optical properties of the samples were analysed using Z-scan technique and the samples show optical limiting behaviour and the 2 PA coefficient increases with increasing Mn^{2+} concentration. Overall, manganese concentration influences the linear and nonlinear optical properties of Ni$_{1-x}$Mn$_x$Se nanoparticles.

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1. Introduction

The unique properties of semiconductor nanoparticles have attracted scientists in the past few decades. When comparing with the bulk materials these nanoparticles possess novel electrical and optical properties due to quantum confinement effect leading to their wide applications [1–11]. Nanotechnology can effectively design these promising materials for the applications in various fields such as telecommunications, optoelectronics, catalysis to medicine and bioengineering [12,13]. Semiconductor nanoparticles of transition metal chalcogenides have elicited considerable interest because of their exceptional electronic structure and magneto-optical properties. The variable oxidation states of transition metals make them suitable for wide range of applications and their magnetic susceptibility offers completely new areas of applications [14–18]. The properties of the transition metal selenides are quite different from those of oxides since d electrons in selenides participate in covalent bonding. Such covalent bonding reduces the formal charge on transition metals favouring the formation of metal-metal bonds. Metal-metal interactions indeed play a significant role in determining the properties of many of the transition metal selenides particularly on the electronic structure by means of their transport properties. Such interactions become significant in transition elements selenides of the second and third series [19]. Among the various transition metal chalcogenides, NiSe and MnSe are significant because of their less toxicity of the metallic core compared with other conventional II–VI semiconductors [18,19]. NiSe is a p-type semiconductor with a bulk band gap of 2.0 eV [5,19,20]. Nickel and selenium can form a variety of nickel selenides, including non-stoichiometric compounds because of the valence electronic configuration of Ni (3d^{8}4s^2) and the small difference in electronegativity between Ni (χ = 1.9) and Se (χ = 2.4). At room temperature, there are three stable phases: NiSe$_2$, Ni$_{1-x}$Se (x varies 1.00 to 0.85), and Ni$_3$Se$_2$ [19–23]. These materials are all black semi-conducting solids in fine powder form while the large crystals have silver colour. The nickel selenides are insoluble in all solvents but can be degraded by strongly oxidizing acids. The interesting properties of NiSe nanoparticles make them as a useful

material for catalysis, optical recording, lithium ion cells [5,21–24], laser materials [5,21], energy storage [5], conductivity, sensors and optical fibers. NiSe has been considered as an important material for tandem solar cells and detecting visible radiation [20,21]. It can be treated as an alternative to narrow bandgap semiconductors like cadmium-based semiconductors because of its less toxicity. In order to develop nanomaterials with desired properties ternary nano systems are used instead of binary systems. Using ternary composition it is convenient to find nanoparticles with desired size, bandgap and optoelectronic properties [25].

In this paper, we presented the structural and optical properties of $Ni_{1-x}Mn_xSe$ (x = 0.1, 0.3, 0.5, 0.7, 0.9) nanoparticles synthesized by chemical co-precipitation method for the first time to the best of our knowledge. Because of the ease of processing at ambient conditions and possibility of doping different kinds of impurities with high doping concentrations even at room temperature, co-precipitation method is generally used to synthesis semiconductor nanoparticles [26].

2. Experimental

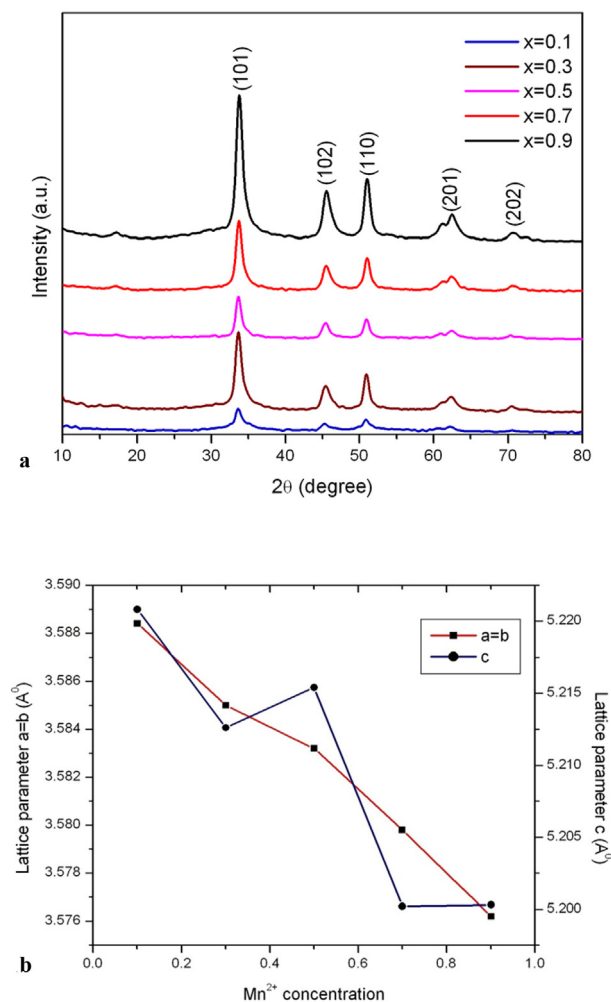### 2.1. Materials

$Ni_{1-x}Mn_xSe$ nanoparticles (x = 0.1, 0.3, 0.5, 0.7, 0.9) are

Fig. 1. (a) XRD patterns of $Ni_{1-x}Mn_xSe$ (x = 0.1, 0.3, 0.5, 0.7, 0.9) nanoparticles. (b) Variation of lattice parameters with Mn^{2+} concentration.

synthesized using chemical co-precipitation method. The starting materials were Manganese Chloride ($MnCl_2$) (CDH), Nickel Chloride ($NiCl_2$) (Merck), Sodium Borohydride ($NaBH_4$) (Merck) and Se powder (Aldrich). All reactants were 99.9% pure and used without further purification.

2.2. Synthesis of NaHSe

Sodium hydrogen selenide solution was prepared by the reaction of sodium borohydride and selenium powder [27]. 80 mg of sodium borohydride was taken in a small beaker and then 1 mL distilled water was added to it. After that 79.9 mg, selenium powder was added to the beaker. The beaker was sealed with a small pinhole exposed to the atmosphere and was placed on ice. The reaction between $NaBH_4$ and Se powder lead to the evolution of hydrogen gas in the flask. After 30 min, the black selenium powder disappeared completely and white crystals appeared in the bottom of the flask. The resulting clear aqueous solution was then transferred into 100 mL of distilled water.

2.3. Synthesis of $Ni_{1-x}Mn_xSe$ nanoparticles

100 mL aqueous solution of 0.1 M nickel chloride and 0.1 M manganese chloride were mixed in a 250 mL beaker at different volume ratios (9:1), (7:3), (5:5), (3:7) and (1:9). 100 mL of sodium hydrogen selenide solution was then added drop by drop to the mixture under constant stirring at room temperature. The colour of the solution was suddenly changed to black and the mixture was stirred for 1 h. The black precipitate was then washed with distilled water for several times to remove the excess organic residues and then dried at 60 °C.

3. Results and discussions

3.1. XRD analysis

Crystallinity and particle size were analysed by X-ray diffraction using PANalytical X-ray Diffractometer with $CuK\alpha$ radiation ($\lambda = 54178$ Å) for 2θ ranging from 10 ° to 80 °. The diffraction patterns of $Ni_{1-x}Mn_xSe$ (x = 0.1, 0.3, 0.5, 0.7, 0.9) are shown in Fig. 1 (a). The broadening of the diffraction peaks indicates the nano dimension of the particles and the position of the diffraction peaks are corresponding to the hexagonal NiMnSe. The major peaks in the diffraction patterns are indexed to (101), (102), (110), (201) and (202) planes (JCPDS Cars No. 89–4831). On increasing the concentration of Mn^{2+} ions, the diffraction peak positions are shifted to higher 2θ values. The shifting of the peak position may be due to the smaller radius of Mn^{2+} (0.82 Å) compared to that of Ni^{2+} (0.83 Å). Replacement of Ni^{2+} ion by Mn^{2+} ion produces lattice strain leading to the decrease in the d-spacing resulting in the shifting of peak positions [28,29].

The lattice parameters of the prepared samples are calculated

Table 1
Calculated values of lattice parameters and particle sizes of $Ni_{1-x}Mn_xSe$ (x = 0.1, 0.3, 0.5, 0.7, 0.9) nanoparticles.

Sample	2θ (degree)	d-spacing (Å)	Lattice parameters (Å)		Particle size (nm)
			a = b	c	
x = 0.1	33.57	2.6669	3.5884	5.2208	9.26
x = 0.3	33.61	2.6642	3.5850	5.2126	9.46
x = 0.5	33.63	2.6624	3.5832	5.2154	10.78
x = 0.7	33.69	2.6580	3.5798	5.2002	10.75
x = 0.9	33.76	2.6530	3.5762	5.2003	5.77