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Structural and optical properties of NiO and Mn doped NiO nanparticles

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ABSTRACT

$Ni_{1-x}Mn_xO$ ($x = 0.0$ - 0.05) nanoparticles were successfully prepared by precipitation method at room temperature Prepared samples were characterized by structural, optical, microstructure and magnetic properties. X-ray diffraction analysis confirmed that Mn ions substitution of NiO lattice with FCC structure. The average crystalline size found to decrease from 42 to 34 nm. Optical analysis show increase in band from 4 -3.8 eV by strong quantum confinement effect with blue shift in the absorption spectra range of 325 – 290 nm. FTIR spectra confirmed the formation of Ni-Mn-O.

Key words: NiO nanoparticles, Optical properties, quantum confinement effect, NiO lattice

1.Introduction

Over the past decades, scientific and research community have shown their great interest on transition metal oxides as these are used in various applications because of their specific catalytic, optical, electrical and magnetic properties and also due to their easy, safe, environmental friendly, cost Recently, nanosized semiconductor metal oxides are gradually gaining attention due to its extraordinary optical and electrical properties.[1]Many researches are working in transition metal doped nickel oxide (NiO) for a wide range of applications in optoelectronics application. It is widely used in many areas such as sensing devices, chemical micro sensors, gas sensors biological detection , agriculture, medical, manufacturing of spintronic devices, superconductors ,solar cells and anti ferromagnetic layer.[2] Nickel Oxide having cubic structure is a unique material for fundamental investigations and practical applications. Being a p-type semiconductor, NiO are important transition metal oxide due to its stunning advantages as high theoretic capacity (670 mAhg^{-1}), inexpensive,

nontoxic nature, easily produced and readily stored [3]. Nickel Oxide (NiO) as an important p - type transition metal semiconductor with narrow band gap and has attracted increasing interest for its potential applications in many fields. Moreover, NiO is one of the most important catalysts among other metal oxides, and is widely used in environmental catalysis and antibacterial applications. However, for such applications, the chemical and physical properties of NiO are strongly dependant on its size, morphology, specific surface area and sometimes are robustly dependent on the preparation methods. A verity of transition metal doped oxides, such as TiO_2, ZnO, Cu_2O, SnO2, In_2O_3. The transition metal oxide nanocrystals (NiO) are noticeably comparable to those for thin films .Experimental verification of room temperature ferromagnetism of the transition metal oxide nanocrystals as a function of their crystallite size can be expected to have many implications in understanding the origins of room temperature ferromagnetism in DMS nanostructures.[4]Therefore, we chose NiO as the target material because it has lattice, magnetic and structural similarities to that of transition metal oxides (CoO, FeO, and MnO) that could be possible component oxides in DMSs .Mn and Co doped NiO nanocrystals with two different compositions were prepared systematically by the chemical co-precipitation technique. The nickel oxide (NiO) nanoparticle, as a kind of functional material, has attracted extensive interest, due to its novel optical, electronic, magnetic, thermal, and mechanical properties, and potential applications as a catalyst, and in battery electrodes, gas sensors, electrochemical films, photo electronic devices.

2.2 Method

In the past decades, various methods have been proposed to produce NiO nanoparticles with different sizes and shapes such as thermal oxidation sono chemical, combustion and quick─

In these applications, it is still needed for synthesizing high quality and ultrafine powers with the required characteristics, in terms of its size, morphology, microstructure, composition purity, crystallizability, and soon, which are the most essential factors that eventually determine the microstructure and performance of the final products. In the present study, we examine the evaluation of structure and optical properties of NiO nanoparticles on Mn doping (5 at%). We show that Mn doping does not modify the cubic structure and lattice parameters of NiO .The present work is aimed to study the effect of Mn doping on the Structural properties of NiO nanocrystals by means of x-ray diffraction pattern. Optical properties of NiO nanocrystals using UV-Vis absorption and transmittance spectrum. Crystal defects NiO nanocrystals with the help of photoluminescence spectrum. For this reason the NiO and Ni (5%wt) doped NiO nanocrystals has been synthesized by precipitation method at room temperature.

2. Synthesis of NiO and Mn doped NiO nanoparticles

2.1 Materials

. For the preparation of Ni_1-xMn_xO nanostructures, the materials used were Nickel chloride [$NiCl_2.6H_2O$]99 %), Manganese acetate [$MnCH_3COO\ 6H_2O$], Sodium hydroxide (NaOH, 98%), absolute ethanol (CH_3CH_2OH, 99.9%) and double distilled water (Jairavik, New Delhi). All Chemicals used in the presents work were of analytical grade and used without further purifications.

precipitation. Among these processes, precipitation method is a facile way, which attracts considerable interest in industries because of low energy and temperature, inexpensive and cost-effective

approach for large-scale production and good yield.

2.3 Sample Preparation

Briefly, for undoped NiO nanoparticles, 5 gms of Nickel chloride was dissolved in in the mixture of 50ml distilled water and 50 ml ethanol in a conical flask and magnetically stirred at 50 ˚C for 15 minutes to get the uniformly concentrated Nickel chloride solution. Equally, 5 gms of sodium hydroxide was dissolved in the mixture of 50ml distilled water and 50 ml ethanol. These two solutions were prepared separately. Then the sodium hydroxide solution was added drop wise to the Nickel chloride solution under constant stirring of 400 rpm at the same 50 ˚C for 2 hrs. The solution turned into a light green and the precipitation formed in the solution was separated by filtering then washed eight times with double distilled water and ethanol. The NiO nanoparticles obtained. It was dried at 80 ˚C for 4 hours in a hot oven to remove water molecules from the product.

$Ni_{1-x}Mn_xO$ (where x = 5 %) samples were synthesized by adding appropriate amount of Manganese acetate dihydrate to the Nickel chloride in the 100 ml distilled water and ethanol mixture solution. The molar ratio of Mn and Ni [x =Mn / (Mn + Ni)] was kept at about for preparing 5% Mn-doped NiO, respectively. Simultaneously, 5 g of NaOH was dissolved in 50 mL of anhydrous ethanol. Thus, prepared NaOH solution was kept at boiling temperature and the mixed solution of Manganese acetate dihydrate and Nickel chloride were dropped slowly into the NaOH solution for 1

hr and then cooled to room temperature. Following this, the precipitate was kept in an ultrasonic bath for 30 min. The precipitate was repeatedly washed with ethanol to remove unwanted ions, and the obtained white precipitate was dried in a vacuum oven at 100 ℃ for get Mn-doped NiO nanopowders. Polyethylene glycol (MW: 400) was used as capping agent in both undoped NiO and $Ni_{1-x}Mn_xO$ samples. Finally, it was annealed at 400℃ for 3h.

2.4 Characterization

The structure and phase purity of the $Cu_{1-x}Ni_xO$ (x = 0.0, 0.01, 0.03, 0.05 and 0.07) nanoparticles were studied by powder x-ray diffraction method (XRD) using a Philips PW- An on-line data acquisition and handling system facilitated automatic JCPDS library search and match for phase identification purpose.. The absorption and transmittance properties of the samples were studied by ultraviolet-visible (UV-Vis) spectrometer (Perkinelmer, Lambda 35) in the wavelength range from 200 to 1100 nm at room temperature. 1710 x-ray diffractometer with CuKα radiation (λ = 1.54056 Å) in the 2θ range of 10-80° at room temperature.

The photoluminescence (PL) spectrum was recorded at room temperature with a He-Cd laser line at 325 nm used as an excitation wavelength by means of spectrophotometer (Kimon, SPEC-14031 K, Japan).To identify the functional groups and to confirm the presence of Ni ions, the samples were examined with Fourier Transform Infrared Spectrometer (FTIR; RX1 PERKINELMER: USA) at a resolution of 2 cm^{-1}.

3. Result and Discussion

3.1. Structural Analysis of NiO and Mn Doped Nio Nanoparticles

The synthesized samples were characterized for their crystallographic structure by X-ray diffraction filtered with Cukα radiation. (λ=1.5406Å).The intensity data were collected over at 2θ range of 20° - 80ºand the same is shown in figures. The sharp and most intense peaks observed here indicate that the synthesized undoped and Mn doped NiO nanoparticles are high crystalline nature with single phase. The strong diffraction peaks appear at 2ɵ = 37.23º, 43.27º, 62.83º, 75.34º and 79.35º corresponding to (111), (200), (220), (311), and (222) planes respectively.

The crystallite size of the particles was calculated from Debye-Scherer's equation.[6]

$$D = \frac{0.9\,\lambda}{\beta cos\theta}$$

Where, λ - is the wavelength *(1.5406 A°).*

β - is the Full Width at the Half Maximum of the line (FWHM).

θ - is the diffraction angle obtained from 2θ value. The crystalline size has been calculated for the highest intensity peak along the (200) plane is 42.8 nm Again, the lattice constant of the crystal has been calculated using the formula.[7]

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

The calculated lattices parameter to be $a = b = c= 4.1830$ A°.
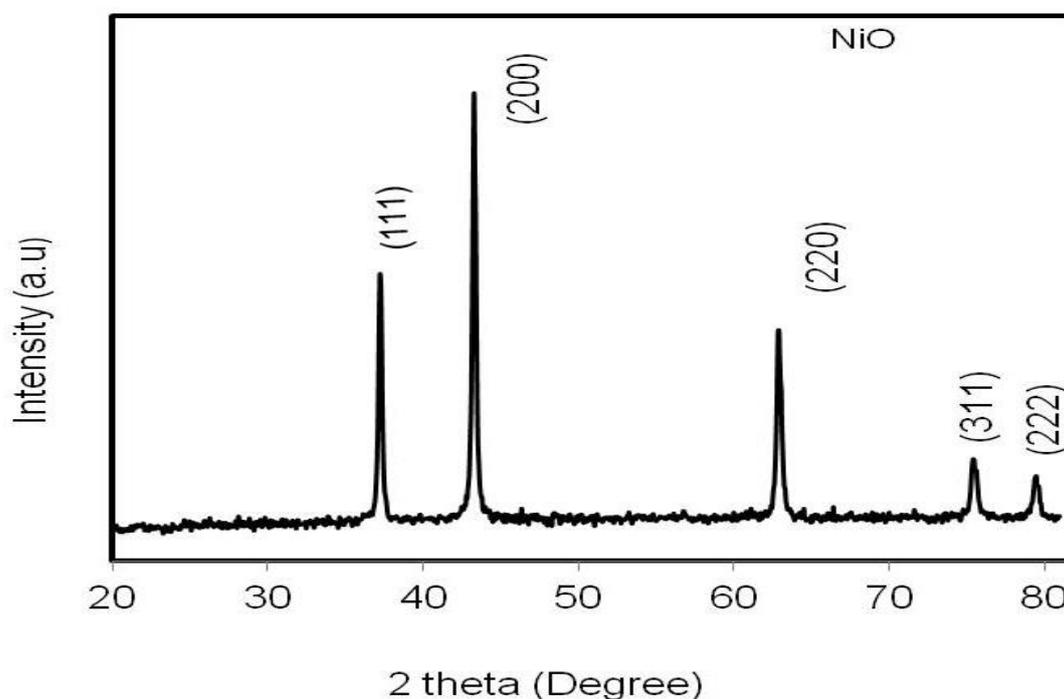
Fig.1.1: X-ray diffraction pattern of undoped NiO nanoparticle
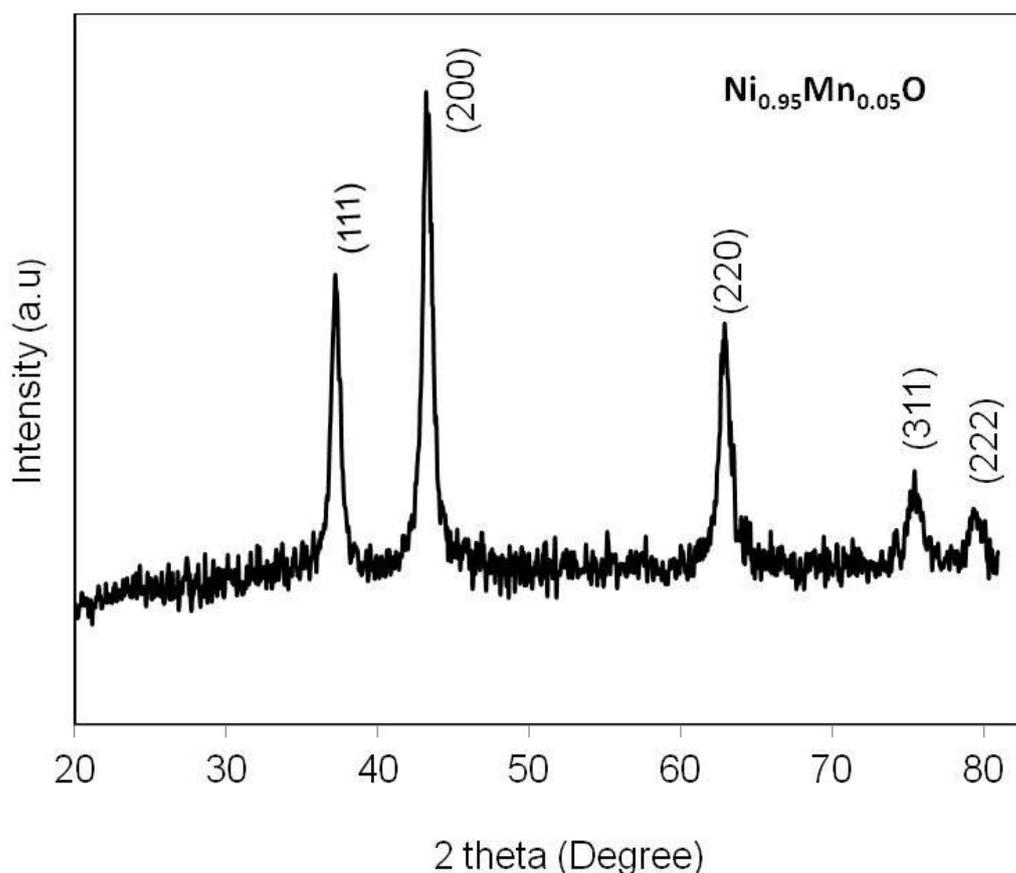
Fig.1.2: X-ray diffraction pattern of Ni₀.₉₅Mn₀.₀₅O nanoparticles

Figure 1.2 illustrates the XRD pattern of the $Ni_{0.95}Mn_{0.05}O$ sample recorded at room temperature. The diffraction pattern were recorded at 2θ = 37.22°, 43.11°, 62.88°, 75.3° and 79.30° corresponding to (111), (200), (220),(311) and (222) planes respectively . No secondary phase was detected, there by indicating that the Mn dopant must be incorporated into the lattice as a substitution atom. Average particle size calculated from the highest diffraction peaks along the (222) plane is 34.20 nm. The lattice parameter is *a=b=c=* 4.1772 A° The grain size, 2θ value, inter planer distance (d), FWHM, lattice constant are compared shown in Table 1.1.

Table 1.1 Average particle size(D) calculated from XRD. Position of (222) peak, Inter planer distance (d), FWHM, Lattice parameter, Number of unit cells presents in the grain.

Sample	Position of (111)peak 2θ	Inter planer distance 'd'(nm)	FWHM	Grain size 'D' nm	lattice parameter (nm)*A*
NiO	43.27	2.090	0.1968	42.80	4.1830
Ni₀.₉₅Mn₀.₀₅O	43.11	2.098	0.2460	34.20	4.1772

Above table indicates that the particle size of NiO / Mn doped NiO nanoparticles depends upon the FWHM. XRD patterns of Mn doped NiO samples are consistent with the spectrum of NiO confirming the high purity of the product. All XRD diffraction peaks of NiO and Mn doping powder are shown in a good agreement with FCC structure reported in JCPDS data card no.65 - 3358 of NiO. From the XRD pattern, it is evident that Mn doped NiO particles exhibit good crystalline nature.

3.2 UV-Vis SPECTRUM OF Nio/Mn DOPED Nio NANOPARTICLES

UV-Visible spectroscopy is a powerful non-destructive technique to explore the optical properties of semiconducting nanoparticles. The optical properties of NiO and Mn doped NiO nanoparticles have been analyzed with methanol as a solvent. The absorption spectrum of NiO and Mn doped NiO in methanol solution in the UV-Vis range is presented in figure 1.3 and 1.4. In our study the optical absorption spectra of undoped sample were recorded between 200 - 800 nm .

UV–visible absorption spectra of NiO nanoparticles are shown in figure 5.3. The absorption band of the NiO nanoparticles have been shows a red shift due to the quantum confinement of the excitants present in the sample compare with bulk NiO particles. This optical phenomenon indicates that these nanoparticles show the quantum size effect..The corresponding band gap energy of absorption maximum λ_{max} for all the samples could be determined using the equation [8]

$$E_g = \frac{hc}{\lambda_{max}}$$
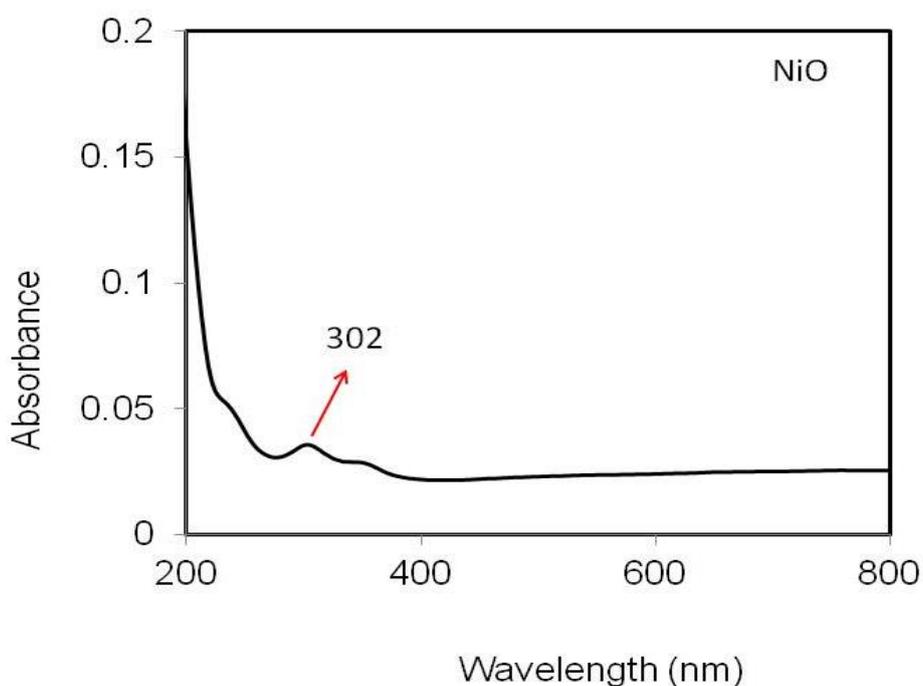
Figure 1.3: UV-Absorption spectra of undoped NiO nanoparticles
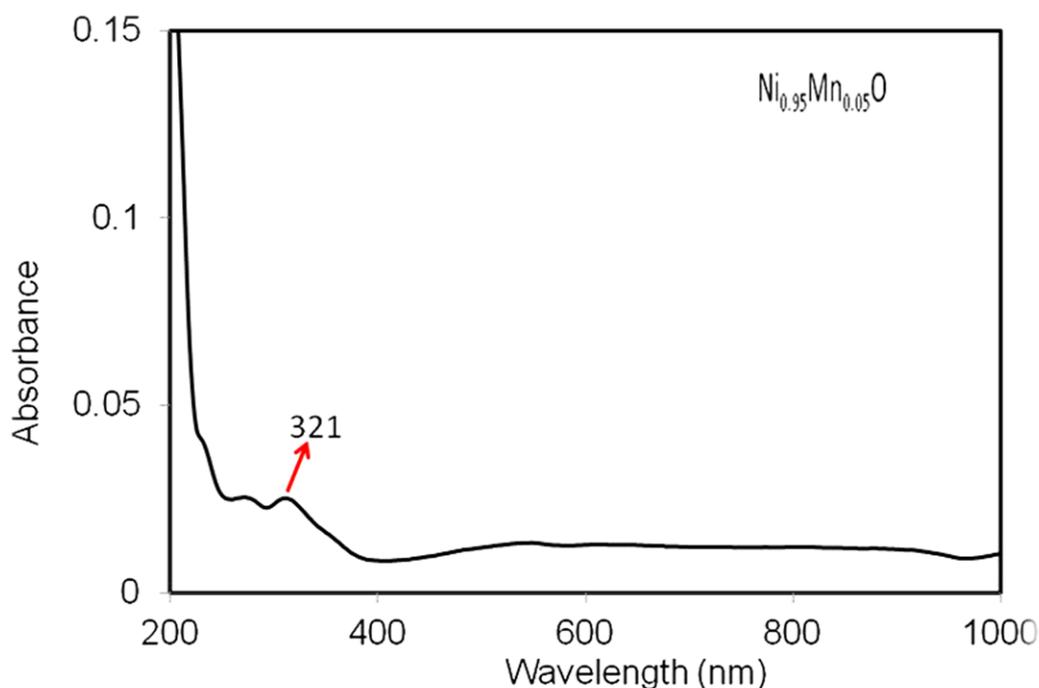
Figure 1.4:UV-Absorption spectra of $Ni_{0.95}Mn_{0.05}O$ nanoparticles

In which h is the Planck constant, c is the light speed, and E_g is the absorption band gap. The maximum absorption of the nanoparticles shows at 302 nm and band gap energy was calculated to be 4.eV

The UV–visible absorption spectrum of $Ni_{0.95}Mn_{0.05}O$ nano particles is shown in figure 1.4. Although the wavelength of our spectrometer is limited by the light source, the absorption band of the Mn doped NiO Nanoparticles have been recorded at 200 nm to 1000 nm. The maximum absorption peak appeared at around 321 nm and its band gap value is around 3.8 eV. Therefore, the UV-Vis analysis confirms that the Mn doping in NiO reduces the energy gap of the
NiO nanoparticles.

3.3 Fourier Transform Infrared Spectrum

FTIR is a technique used to obtain information about the chemical bonding in a material. It is used to identify the elemental constituents of a material sample. The observed spectrum reveals that almost all the peaks are identical in both samples.

The figure 5.5 and 5.6 shows the FTIR spectrum of the undoped NiO and Mn doped NiO nanoparticles respectively presented and in the range of 400 to 4000 cm^{-1} . It can be seen that the peaks corresponding to the vibration modes of crystal structure and functional groubs.There is no more impurities from this spectrum analysis which shows several significant absorption peaks However, the peaks appeared at 2935 cm^{-1}, 1700 cm^{-1}, 1044 cm^{-1}, and 494 cm^{-1} for undoped NiO and Mn doped NiO the peaks presented at 3370 cm^{-1}, 2923 cm^{-1}, 1715 cm^{-1}, 1445 cm^{-1} ,1019 cm^{-1} and 499 cm^{-1} respectively. [9]
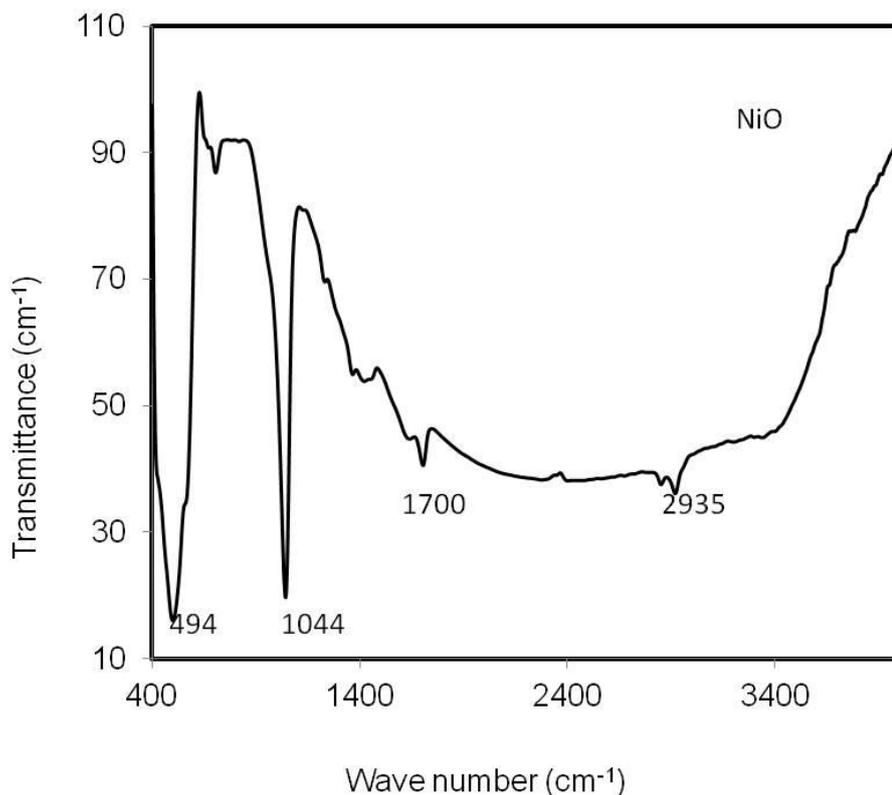
Figure 1.5:FTIR profiles of undoped NiO Nanoparticles

Figure 1.6: FTIR profile of $Ni_{0.95}Mn_{0.05}O$ Nanoparticles
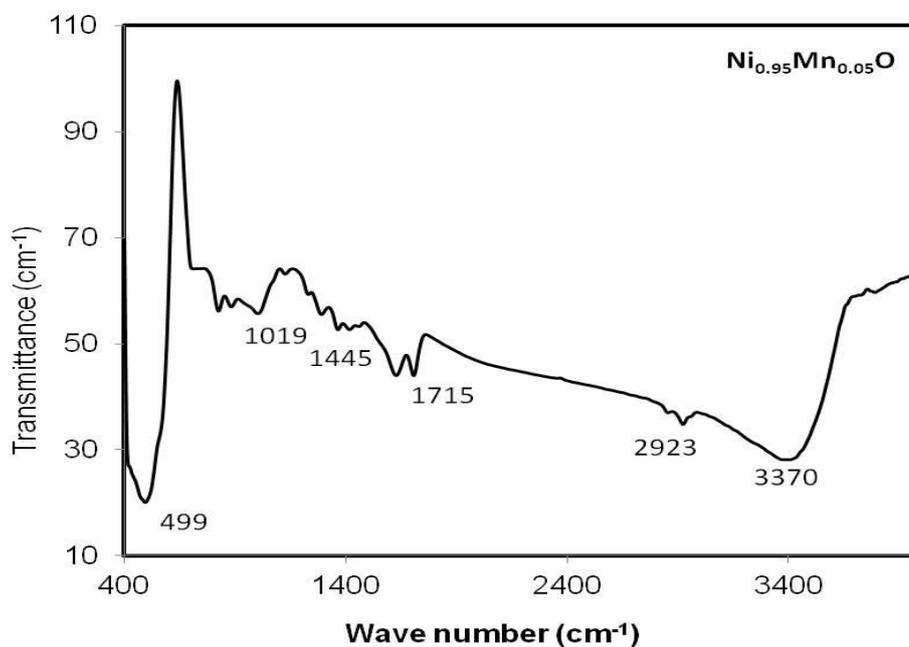
The first broad absorption band centred at 3370 cm^{-1} is attributed to the stretching vibration of O-H group for Mn doped NiO this is absent for undoped NiO. Similarly, peak 2935 cm^{-1} and 2923 cm^{-1} is associated with O-H-O bending vibration mode.

In addition, the peak around the 1715 cm^{-1} and 1700 cm^{-1} indicates the presence of carbonates. The observed vibration mode at 1445 cm^{-1} can be assigned to the carboxylate group which is absent in NiO nanoparticles. The peaks around 1044 cm^{-1} and 1019 cm^{-1} depict the stretching vibration of

Table 1.2: IR peaks and their assignments

C-O . Finally, the broad absorption at 494 cm^{-1}

Assignments	Wavenumber (cm^{-1})	
	NiO	Ni$_{0.95}$Mn$_{0.05}$O
Hydroxyl group	___	3370
O-H-O band	2935	2923
C=O band	1700	1715
-COO group	___	1445
C-O vibration	1044	1019
Stretching vibration of NiO/Mn	497	494

and 499 cm^{-1} assigned to Ni-O stretching vibration mode. The broadness of Ni-O absorption band at

494 cm^{-1} confirms that the Ni-O nanoparticles are crystallized. Irrespective of the dopant of Mn, the peaks shifted towards the higher frequency of 499cm^{-1} that confirms the presence of Mn ions are doped with the synthesized sample.

3.4 Photoluminescence Studies

Photoluminescence is light emission from any form of matter after the absorption of photons (electromagnetic radiation). It is one of many forms of luminescence (light emission) and is initiated by photo excitation (excitation by photons).The photo luminescence spectrum of the NiO is shown in figure 1.7. There are three distinct emission bands in the spectra one peak is at 360 nm UV regions and another two peaks are 421 nm and 458 nm respectively. The undoped NiO nanoparticles peak is low intensity compared to Mn doped NiO.
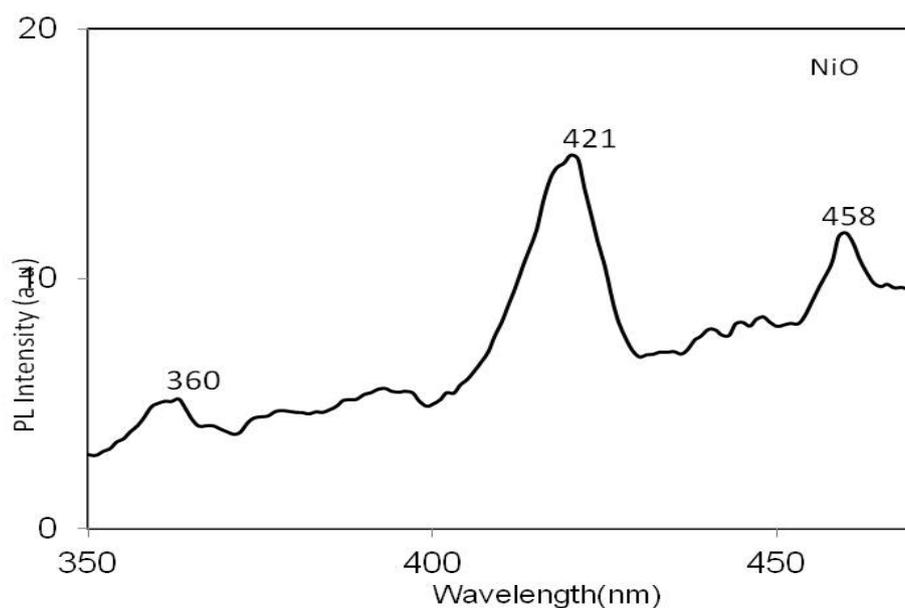
Figure 1.7: Photoluminescence spectra of undoped NiO nanoparticles
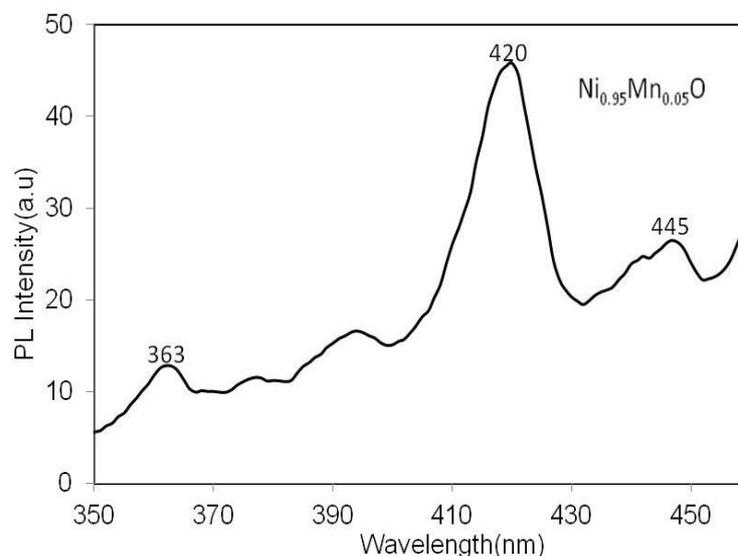
Figure 1.8: Photoluminescence spectra of Ni$_{0.95}$Mn$_{0.05}$O nanoparticle

All the samples mainly have two emission peaks. A violet one centered at around 420 nm, blue around 445 nm.The mechanism of violet emission peak is from exaction recombination formed by electrons in the conduction band and holes in valence band, and blue emission peaks hear the center of 420 to 445 nm are from the transition between shallow donor level formed by V$_0$ and top valance band level .[10]

4. Conclusions

Undoped and Mn doped NiO nanoparticles have been synthesized through chemical precipitation method at room temperature. We report on the effect of Mn doping on the structural and optical properties of NiO nanoparticles. Findings are the formation of cubic phase of undoped and Mn doped NiO were confirmed from the XRD patterns where Mn^{2+} ions substituted Ni^{2+} ions. The crystallite size ranged from 42.8 nm to

34.2 nm. It was observed that the particle size was a decreases when dopant of Mn. By FT-IR spectra, we further confirmed the purity of the prepared samples. 5% Mn doped NiO doped samples showed a red shift in the optical band gap, which can be assigned to the quantum confinement effects. There was a significant decrease in the energy band gap of Mn doped NiO nanoparticles from 4.0 eV to 3.80 eV.

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