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EFFECT OF Fe DOPING IN NiO SEMICONDUCTOR NANOPARTICLES AND STUDIES ON THEIR STRUCTURAL, MAGNETIC AND OPTICAL PROPERTIES: SYNTHESIZED VIA THE PRECIPITATION PROCESS

K. Anandan* & V. Rajendran**
* Department of Physics, AMET University, Chennai, Tamilnadu
** Department of Physics, Presidency College, Chennai, Tamilnadu

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Abstract:

Pure and Fe-doped NiO nanoparticles were synthesized via the simple precipitation process. The metal ion (Fe) was doped in order to study the influence of structural, magnetic and optical properties, which were analyzed using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, vibrating sample magnetometer (VSM), ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) emission spectroscopy techniques. Analytical results demonstrated that the nanocrystalline nickel oxide is in cubic crystalline phase and doping with Fe could decrease the crystallite size and has been modified the magnetic and optical properties of the final products.

Key Words: Semiconductor, NiO, Dopant & Optical Properties

1. Introduction:

In recent years, NiO nanoparticles as a kind of functional material has attracted extensive interests due to its novel optical, electronic, magnetic, thermal, and mechanical properties and potential application in catalyst, battery electrodes, gas sensors, photoelectronic devices, and so on [1–7]. In these applications, it is still needed for synthesizing high-quality and ultrafine powders with required characteristics in terms of their size, morphology, microstructure, composition purity, crystallizability, and so on, which are the most essential factors which eventually determine the microstructure and performance of the final products. Furthermore, it is considered to be a model semiconductor with p-type conductivity, due to its wide band-gap energy 3.7 eV [8]. It can exhibit different properties on doping with foreign elements, since; this is one of the most common methods for the extensive modification of the properties of NiO [9, 10]. Therefore, it is very important to control the powder properties during the preparation process. Among the different process to prepare NiO nanoparticles, the precipitation process can control the grain size, crystalline phase, particles morphology and surface chemistry of the products [11]. Doping of the transition metal elements at the Ni site modifies the magnetic, optical and to some extent structural properties, and opens up the possibility of exploiting this material for Diluted Magnetic Semiconductor (DMS) functionality. In the present research work, pure and Fe metal ion doped NiO nanoparticles were prepared, by using the simple precipitation process, and a review on the evolution of structural, magnetic and optical properties of NiO.

2. Experimental Procedure:

2.1 Materials: The nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$, purity 99.9 %), sodium hydroxide (NaOH, purity 99 %), iron (III) chloride ($FeCl_3$, purity 99 %) and distilled water used in this work were analytical grade reagents, without any further purification.

2.2 Synthesis of Pure and Fe Doped NiO Nanoparticles: Pure and Fe doped NiO samples were synthesized by the simple precipitation process, and all the chemicals used in this work were analytical grade reagents, without any further purification. In a typical process, 0.1 M of nickel acetate tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$) was dissolved in 100 ml distilled water under vigorous stirring. After a few minutes of stirring, greenish precipitates were formed by adding 0.2 M of sodium hydroxide (NaOH) pellets to the above solution. The obtained precipitates were collected and washed with distilled water and absolute ethanol several times, to remove the soluble impurities and dried at 120°C for 10 hrs. Further, a light green colored NiO sample was obtained by calcining the dried precipitate at 450°C for 1hr. The same procedure was followed for the preparation of the Fe doped NiO sample, with the addition of 1 mol % of iron (III) chloride ($FeCl_3$).

2.3 Characterization of the Samples by Different Techniques: The crystalline size and structures of the samples were characterized by X-ray diffraction on a rotating-target X–ray diffractometer (JSO-DEBYFLEX 2002) equipped with monochromatic high intensity CuKα1 radiation (λ = 0.15406 nm, 40 kV, 100 mA). The samples were scanned in the range of 20 to 70° (2θ), with a scanning rate of 0.005°/s and step size of 0.02°. The functional groups of the samples were recorded by FTIR spectroscopy on the Nicolet 205 spectrometer in the range of 4000 – 400 cm^{-1}. The magnetic properties were measured in a BHV-55 magnetometer, (Riken, Japan) at room temperature. The optical absorption spectra of the samples were obtained from a Varian Cary 5E spectrophotometer in the range of 200–800 nm. The photoluminescence emission spectra were carried out on a Fluoromax-4 spectrofluorometer with an Xe lamp as the excitation light source.

3. Results and Discussion:

The structural properties of pure and Fe-doped NiO were studied by the XRD analysis. Fig. 1 shows the XRD patterns of the pure and Fe-doped NiO samples calcined at 450ºC. The calcined samples exhibit peaks at correspond to the (111), (200) and (220) planes for the cubic phase of nickel oxide, which was confirmed from the JCPDS card no. 04-0835, and indicates the good crystallinity of the obtained nanoparticle [12]. Moreover, it is clear that there are no extra peaks due to iron metal oxides, implying that the transition metal ions get substituted at the Ni site without changing the cubic structure. Furthermore, it is interesting to note that on doping of Fe content, the intensity of the XRD peaks decreases and FWHM increases, which is due to the decreasing crystallite size. The average crystallite size (D) was calculated from the dominant diffraction peak (200) by Debye Scherrer's formula, as given below

$$D = k\lambda/\beta\cos\theta$$

Where D is the average nanocrystallites size, λ is the radiation wavelength (0.154 nm), β is the full-width at half-maximum intensity, θ is the diffraction angle. The average crystallite sizes of the pure and Fe-doped NiO nanoparticles were calculated as 29.23 and 22.08 nm, respectively.

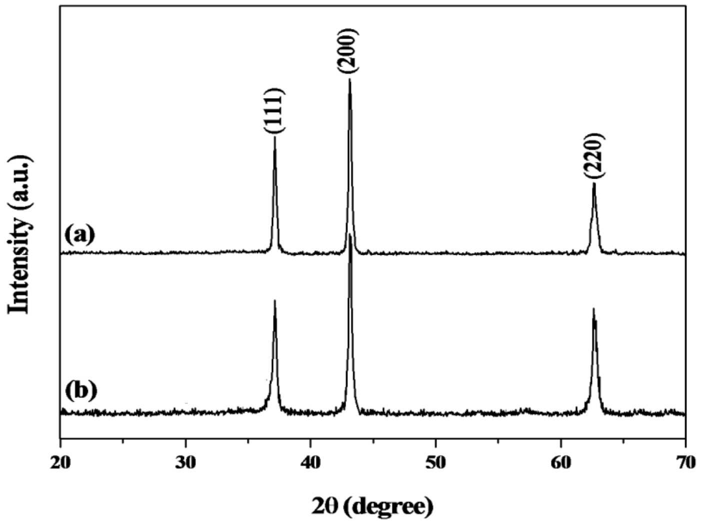

Figure 1: XRD patterns of the prepared (a) pure and (b) Fe-doped NiO nanoparticles calcined at 450ºC.

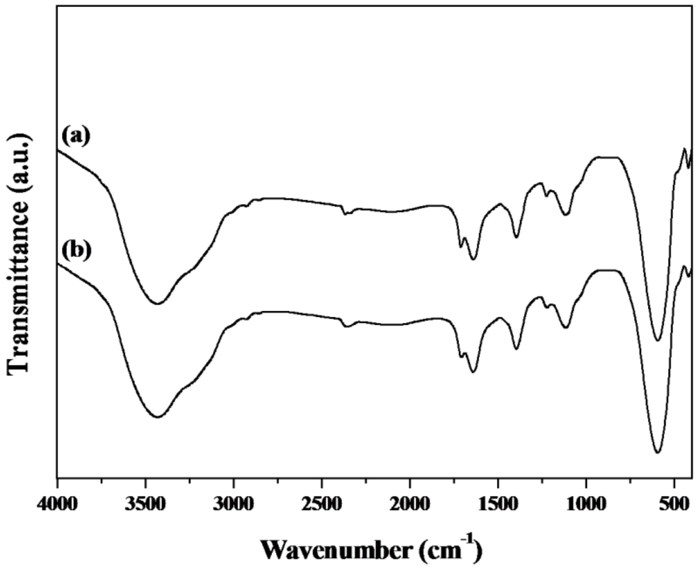

Figure 2: FTIR spectra of the (a) pure and (b) Fe-doped NiO samples dried at 120°C.

FTIR spectroscopy is a useful tool to understand the functional group of the as-prepared samples. Fig.2 shows the FTIR spectra of pure and Fe-doped NiO samples dried at 120ºC. The bands located at ~3434 and 1637 cm^{-1} correspond to the stretching and bending vibrations of the –OH groups [13]. The weak band observed at 2354 cm^{-1} is assigned to the C–H vibrations of the organic residuals. The weak bands observed at ~1391 and 1114 cm^{-1} are assigned to the C–H vibration of the organic residuals, asymmetric stretching vibration of the coordinated carboxylate group and deformation vibration of C=O, respectively [14]. Metal oxides; NiO; generally give absorption bands below 1000 cm arising from inter-atomic vibrations. The peak at 589 cm^{-1}

corresponds to the metal-oxygen vibrational modes of NiO compounds having a sharp and high intense peak, which gave clear evidence about the presence of the crystalline NiO [15]. There were no additional absorption peaks observed in the spectra with the addition of Fe, indicating its homogeneous dispersion in the support material. This is in good agreement with the results of the XRD analysis.

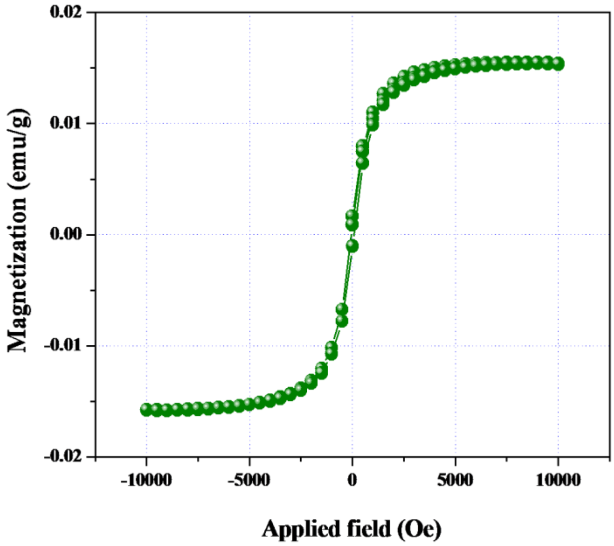

Figure 3: Room temperature magnetization hysteresis loops of Fe doped NiO nanoparticles.

The magnetic property of Fe-doped NiO nanoparticles has been measured. It has been reported that when the size of the particles is reduced to the nanoscale region, the antiferromagnetic material NiO can exhibit different magnetic properties like, superparamagnetism and ferromagnetism [16, 17]. Fig. 3 shows the hysteresis loops of Fe-doped NiO nanoparticles at 300 K. It can be seen that NiO nanoparticles present a ferromagnetic behaviour due to its nanoscale region size although bulk NiO is antiferromagnetic [18]. Therefore, the transition metal Fe influences the magnetic properties of NiO nanoparticles and it is an important class of materials used for spintronic devices [19].

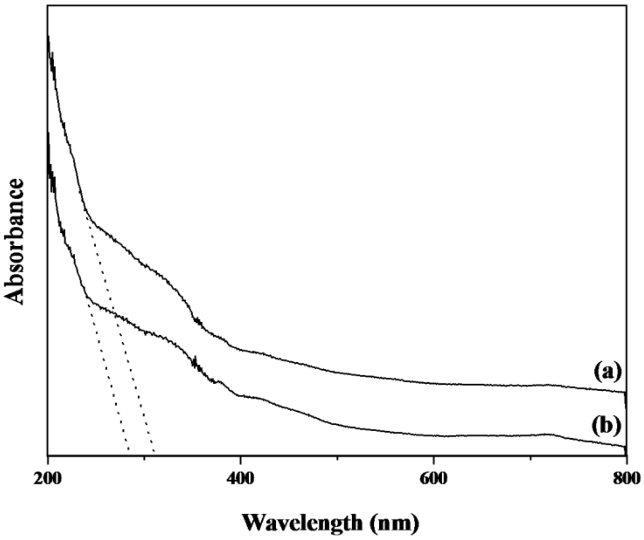

Figure 4: UV-vis absorption spectra of (a) pure and (b) Fe-doped NiO nanoparticles calcined at 450ºC.

Absorption and photoluminescence spectroscopies are powerful non-destructive techniques to explore the optical properties of prepared pure and Fe-doped NiO semiconducting nanostructures. Fig. 4 represented the UV–vis absorption spectra of the samples. The absorptions in the UV region are observed at wavelengths about 311 and 285 nm for the samples pure and Fe-doped NiO nanoparticles, respectively. These absorptions in the UV region are attributed to band gap absorption in NiO [20]. It has been observed that the absorbance tends to increase in the lower region with the Fe doping, which revealed that the absorptions were blue shifted, and the quantum confinement effect was observed for the prepared Fe-doped NiO nanoparticles [21]. The obtained band gaps of the samples were 3.98 and 4.35 eV for the pure and Fe-doped NiO nanoparticles, which are larger than those of the bulk NiO [8]. It is clear that the particle size decreases when the band gap increases; the increase in the band gap suggests that the size of the nanoparticles influences the optoelectronic properties of the materials, and can be tuned by the doping of metal ion.

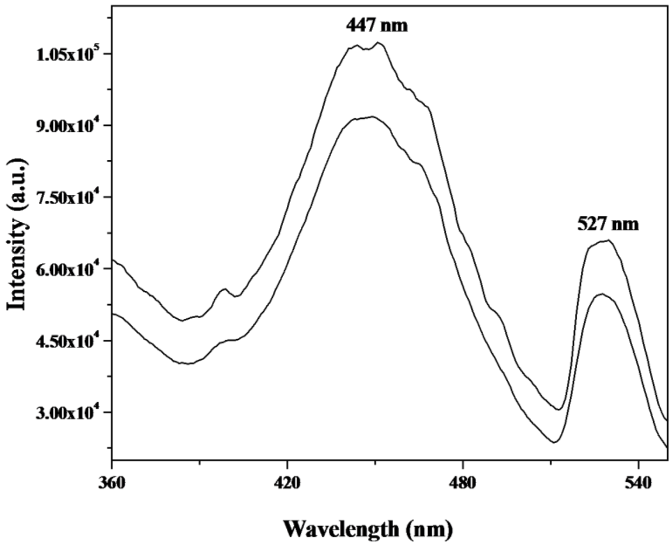

Figure 5: Photoluminescence emission spectra of (a) pure and (b) Fe-doped NiO nanoparticles calcined at 450ºC.

Nanostructured materials have a higher density of crystalline defects, such as stacking faults, oxygen defects etc., than their bulk counterparts. In this case, the photoluminescence emission peak can be attributed to such crystal defects within the NiO matrix. Fig. 5 shows the photoluminescence emission spectra of pure and Fe-doped NiO samples. The broad and strong emission peaks located at 447 and 527 nm dominates the PL spectra for the samples. The broad blue emission peak at 447 nm is due to various surface defects resulting from oxygen and nickel vacancies. The strong visible emission peak located at 527 nm is attributed to the radiative recombination of photo-generated holes with electron, occupying the singly ionized oxygen vacancy assigned to V_o and $Ni_{(in)}$ [22]. In particularly, the Fe-doped NiO nanoparticles were obtained in high intensity, which may be due to the lower crystalline size and presence of the higher oxygen vacancies. Hence, the properties of the broad blue and strong visible emission peaks indicate the high purity and perfect crystallinity of the prepared samples. From the results, it is clear that the Fe doping play a vital role in modifying the optical properties of the NiO nanomaterials. Further, it can be concluded that the doping of metal ion play an important role not only in tailoring the size of NiO nanostructures, but, also in altering and enhancing the magnetic and optical properties of NiO nanomaterials. We believe that the crystalline size and optical properties of the NiO nanostructures play important roles in optoelectronic devices. Therefore, the prepared pure and Fe-doped NiO nanoparticles are promising candidates for luminescent, nano-photonic and optoelectronic applications.

4. Conclusion:

Pure and Fe-doped NiO nanoparticles were successfully synthesized using precipitation process. The XRD and FTIR results exhibit the cubic phase structure of the samples and no impurity phase was observed. It has been found that with introduce of Fe metal into NiO, there is a decrease in the crystallite size. The Fe-doped NiO nanoparticles exhibit ferromagnetic behaviour at room temperature, although NiO bulk is antiferromagnetic material. Optical band gap was found to vary from 3.98 to 4.35 eV with doping suggesting the reduction in particle size as a result of doping. The photoluminescence study showed an increase in the luminescent emission with the Fe doping. Finally, structural, magnetic and optical studies conclude that the Fe ion was successfully incorporated into the lattice position of Ni in NiO matrix and the process may be used to modulate the band gap and particle size and hence the material may be used in opto-electronic devices.

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