



Structural and magnetic properties of Fe doped NiO

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Abstract : Mott-Hubbard anti-ferromagnetic insulator, NiO shows *p*-type semiconducting behaviour due to vacancy at Ni²⁺ site in its bunsenite structure. We report the modification of structural and magnetic order in NiO on Fe doping. NiO samples at different Fe concentrations in the range 0 to 5 at.% have been prepared by chemical co-precipitation and post thermal decomposition method. Both structural and magnetic characterization reveal that with increasing Fe doping concentration, NiO evolves as a magnetically inhomogeneous state out of the parent homogeneous antiferromagnetic state. In addition, structural inhomogeneity was also observed with Fe precipitating to γ -Fe₂O₃ phase, the signature of which could be clearly seen for Fe content beyond 2 at.%. At lower Fe content however, some amount of Fe occupies lattice and interstitial sites in the NiO matrix and drive the latter to acquire ferromagnetic ordering, which was evident from a clear hysteresis loop at 300 K.

Keywords : Dilute magnetic semiconductor, X-ray diffraction, magnetization, NiO.

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1. Introduction

Recent years have seen an upsurge of research in Diluted Magnetic Semiconductor (DMS) materials due to their application in spintronic devices [1]. DMS has charge and spin degrees of freedom in a single substance, leading to novel applications combining magnetic, electronic and optical functionalities. The discovery of room temperature ferromagnetism in Co²⁺ doped TiO₂, Mn²⁺ and Ni²⁺ doped ZnO are due to charge carrier electron, known as *n*-type DMS materials. As compared to the *n*-type DMS systems like transition metal (TM) doped ZnO and TiO₂, there exist a few *p*-type DMS systems, the detailed characteristics of which have not yet been reported. A theoretical prediction by Dietl *et al*, [2] indicates that the curie temperature of *p*-type DMS can be well above that of *n*-type DMS.

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NiO is a *p*-type semiconductor due to vacancy at Ni²⁺ sites [3,4]. It is an antiferromagnetic Mott-Hubbard insulator with Neel temperature, $T_N = 523$ K. The magnetic structure of NiO consists of ferromagnetic sheets of Ni²⁺ parallel to the (111) plane with opposite spin directions in neighbouring sheets. TM doping [5] or reduction of particle size [6] have been shown to disturb the magnetic structure of NiO with evolution of ferromagnetism in some cases.

The hole content in the *p*-type NiO is enhanced on TM doping, which is believed to cause the observed DMS in this system. Nowotny *et al* [7] reported *p*-type properties in Cr doped NiO. Battle *et al* [8] reported that Co doping doesn't induce ferromagnetic ordering in NiO. Instead the T_N increases linearly with Co concentration. Fe doped NiO is a *p*-type material, which has been shown to exhibit ferromagnetism at room temperature [5]. The basic crystal structure of NiO (bunsenite) being different from that of FeO (wustite), Fe doping in NiO matrix is expected to create considerable strain in the latter. The associated modification in Fe doped NiO should therefore influence its magnetic properties. In the present study, we have examined both the magnetic and the structural properties of Fe (0 to 5 at.%) doped NiO. At high Fe concentration, though second phase precipitation leads to formation of γ -Fe₂O₃, the observed magnetization at low Fe concentration (<3 at.%) is found to be a consequence of Fe occupying the NiO matrix both at lattice sites as well as at interstitial positions.

2. Experimental

The Ni_{1-x}Fe_xO samples with *x* varying from 0 to 5 at.% were prepared by chemical coprecipitation method. Stoichiometric amount of Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in distilled water. The hydroxycarbonate precursor was chemically precipitated by slowly adding an aqueous NH₄HCO₃ solution of pH ~8 at room temperature accompanying magnetic stirring. The resultant gels were washed several times with distilled water and ethanol until free of nitrate ions, filtrated and dried in air at 353 K. The dried gels were then calcined at 873 K for 4 hours in air to obtain Fe-doped NiO samples. XRD measurements were done at 300 K using Rigaku Powder Diffractometer with CuK_α radiation. Magnetic properties of different Fe doped NiO samples were studied using Physical Properties Measurement System (PPMS)–VSM.

3. Results and discussion

3.1. Structure and microstructure evolution :

Since the radius of Fe³⁺ ion (0.64 Å) is almost same as that of Ni²⁺ ion (0.69 Å), Fe is expected to substitute Ni in the lattice structure of NiO. XRD plots (Figure 1) show that Ni_{1-x}Fe_xO samples remain single phase for *x* up to 0.02. Due to limited solubility however, second phase precipitation is expected at higher concentrations of Fe in NiO [9]. Appearance of Fe₂O₃ phase beyond 2 at.% and NiFe₂O₄-phase beyond 5 at.% of

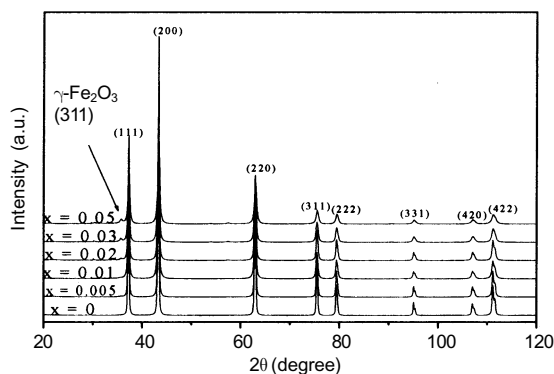


Figure 1. XRD pattern of $\text{Ni}_{1-x}\text{Fe}_x\text{O}$ ($x = 0$ to 0.05).

Fe in NiO has been reported [5]. Our XRD plots for $x > 0.02$ (Figure 1) show that the (311) peak of $\gamma\text{-Fe}_2\text{O}_3$ appear as the second phase. The FCC structure of host NiO phase however does not change on Fe doping. The lattice parameter remains almost same (4.176 \AA) up to 3 at.% Fe doped NiO samples whereas it shows a slight increase for 5 at.% Fe concentration.

Figure 2 shows the increase of line width at different peak positions corresponding to their (hkl) with increasing Fe content in NiO. Wang *et al* [5] from a similar observation of XRD line broadening, calculated particle size using Debye-Sherrer formula and concluded that size of NiO particles reduces from 60 to 35 nm on increasing Fe content from 0 to 2 at.%. The basic crystal structure of NiO (bunsenite), however is

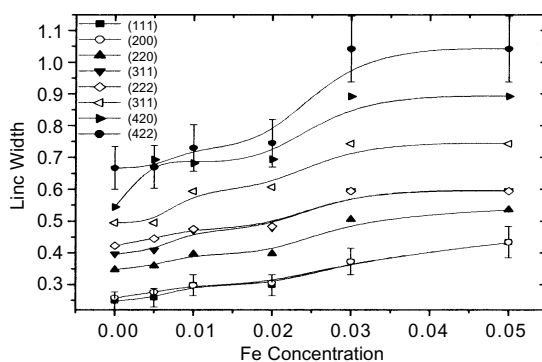


Figure 2. The variation of line width with various Fe concentrations at different peak position indicated by their (hkl) .

different from that of FeO (wustite). Fe doping therefore is expected to create a large amount of strain in NiO lattice. Hence use of Debye-Sherrer formula without taking strain into consideration for calculation of particle size may lead to erroneous result. Apart from the contribution of particle size reduction, defects and disorder in the lattice affect the width of the XRD lines. The increase in XRD line width with increasing Fe content in NiO, for example, can arise due to the following possibilities.

At low concentration, when Fe^{3+} occupies Ni site, two such Fe ions can lead to a vacancy at Ni site [5]. Cr doped NiO also presents a similar scenario [7]. The associated strain at the substituted Fe sites as well as at the vacant Ni site can contribute to line broadening. Another possibility pertains to the widely different basic structure of NiO and FeO. Due to two order of larger nonstoichiometry, δ ($\delta \sim 5 \times 10^{-2}$) in the wustite, $\text{Fe}_{1-\delta}\text{O}$ than that in the bunsenite, $\text{Ni}_{1-\delta}\text{O}$ ($\delta \sim 5 \times 10^{-4}$), the dopant iron governs the defect structure in NiO, while the later acts like an inert matrix. In this dilute wustite phase of NiO, formation of defect clusters consisting of cation vacancies and iron interstitial is well known [10,11]. The basic unit of these clusters consists of four Ni vacancies tetrahedrally coordinating a Fe^{3+} interstitial ion. Such clusters were observed by extended X-ray absorption fine structure analysis [12]. These clusters when isolated from each other would lead to extensive strain generation and line width broadening due to four Ni vacancies for every Fe ion doped at the interstitial site.

Apart from the contribution of strain induced by Fe doping in NiO structure, particle size reduction can lead to broadening of XRD lines as observed by earlier authors [5]. From the broadening of the individual peaks, we calculated the particle size and microstrain values from the Williamson-Hall plot [13]. Particle size shows an almost monotonic decrease with increasing Fe content from 55 nm in pure NiO to 30 nm in 5 at.% Fe doped NiO. The mechanism for the suppression of crystal growth of NiO on Fe doping, which was also observed by Wang *et al* [5] is not clear. The strain on the other hand increases with increasing Fe content and attains a maximum value for 3 at.% Fe in NiO. The rapid increase of strain with increasing Fe content indicates that most of the Fe goes to the interstitial site within this concentration range and produces 4 Ni vacancies for every interstitially doped Fe as discussed earlier. Beyond 3 at.% Fe, the strain decreases indicating strain relaxation due to phase segregation and formation of $\gamma\text{-Fe}_2\text{O}_3$ phase as clearly seen in XRD plot for 5 at.% Fe doped NiO (Figure 1).

3.2. Magnetization :

XRD result indicates that beyond 2 at.% of Fe in NiO, phase segregation leads to formation of $\gamma\text{-Fe}_2\text{O}_3$. We therefore confine the discussion on magnetic characteristics of Fe doped NiO for Fe content up to 2 at.%. Figure 3 shows the temperature dependence of zero field cooled (ZFC) and field cooled (FC) magnetization in a 500 Oe dc field for 2 at.% Fe doped NiO. The inset of Figure 3 shows the difference between FC and ZFC magnetization (ΔM) as a function temperature. The nonzero value of ΔM eliminates the para and diamagnetic contributions to the observed magnetic behaviour leaving only the contribution of hysteretic ferromagnetic regime. Generally, the ZFC susceptibility shows a peak for both superparamagnets and spin glasses. It is usually seen that the temperature dependence of the FC susceptibility becomes saturated below the peak temperature (freezing temperature T_f) for spin glasses and continues to

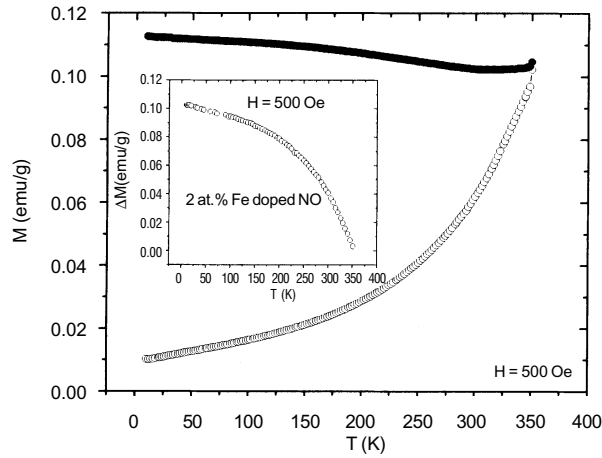


Figure 3. ZFC (open symbol) and FC (solid symbol) magnetization for 2 at.% Fe doped NiO particles as a function of temperature in 500 Oe field. The inset shows the difference between FC and ZFC magnetization as a function of temperature.

increase below that temperature (blocking temperature T_B) for superparamagnets [14]. Nevertheless, glassy behavior in magnetic nanoparticles has also been claimed in which the FC susceptibility continues to increase with decreasing temperature [15]. The peak in ZFC magnetization expected for either spin glass or superparamagnetic phases if present in our system does not appear in the measured temperature range from 10 to 350 K. The FC susceptibility shows a slight decrease with decreasing temperature from 350 K down to 315 K and then increases with further decreasing temperature up to 10 K. The anomaly around 315 K in the FC data suggests [16,17] that some amount of magnetic inhomogeneity might be present in this DMS system.

We now examine any possible contribution that the finite size effect may have to the observed magnetic characteristics in undoped and Fe doped NiO. Average particle size as depicted from Williamson-Hall plot, ranges from 55 nm in pure NiO to 44 nm in 3 at.% Fe doped NiO. Kodama *et al* [6] found anomalous magnetic properties of 31.5 nm NiO particles due to finite size effect. These features are absent in large size NiO particles at room temperature [18]. The 31.5 nm NiO particles show a $T_B \approx 300$ K. In our case, 55 nm dia NiO particles would thus have a T_B much above 300 K. An approximate value of T_B can be calculated from the relation [19]

$$T_B = \frac{KV}{25k_B} \quad (1)$$

where K is the anisotropy constant, k_B is the Boltzmann's constant, and V is the volume of the nanoparticle. The above relation gives

$$\frac{T_{B1}}{T_{B2}} = \frac{V1}{V2} \quad (2)$$

where T_{B1} , T_{B2} and $V1$, $V2$ are the blocking temperature and volume of particles 1 and 2 respectively. Comparing the volume of the NiO nanoparticles with a dia of 31.5 nm, which exhibits T_B around 300 K [6] with the volume of our NiO particles, we find $T_B \sim 1597$ K for the latter. This huge T_B , which is much above the T_N of NiO, implies that our NiO particles would exhibit 2-sublattice antiferromagnetic ordering as in bulk NiO. This is in contrast with the finite size effect in nanoparticles of diameter 31.5 nm and less, where 8-, 6- or 4-sublattice spin configurations arise due to the reduced coordination of surface spins leading to anomalous magnetic properties [6]. Though the particle size of NiO, decreases with increasing Fe content, it is still much above the value required to see finite size effect for particles up to 3 at.% Fe doping. At 3 at.% Fe, the particle size of 44 nm corresponds to a T_B of 818 K, which far exceeds the T_N of NiO. The magnetic characteristics that we see in these particles and particles with lower Fe content having still higher particle size, therefore represent bulk behaviour of Fe doped NiO and not due to finite size effect.

M-H curve obtained from the dc magnetization measurement at 300 K for $\text{Ni}_{1-x}\text{Fe}_x\text{O}$ ($x = 0.01, 0.02$) is shown in Figure 4. A clear hysteresis loop is observed for 2 at.% Fe doped NiO as shown. The appearance of hysteresis loop at room temperature could be due to the ferromagnetic interaction amongst the Fe ions

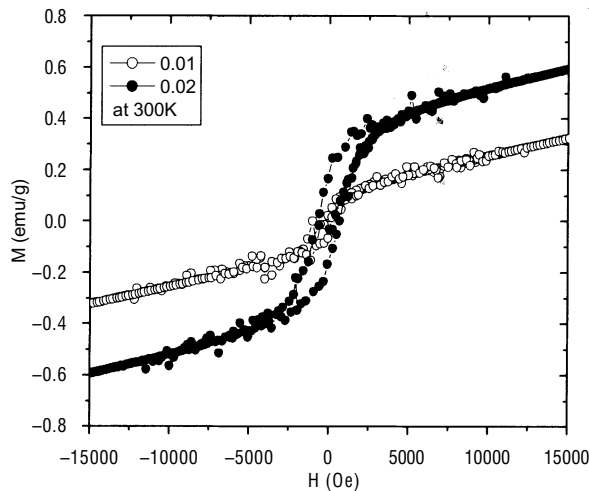


Figure 4. Field dependence magnetization curve for $x = 0.01$ and 0.02 at room temperature.

mediated by the holes, which are created due to interstitial substitution of Fe, which leads to 5 holes for each Fe^{3+} substitution. The hysteresis loop does not saturate up to 40 KOe. It is a common feature that the magnetization of fine particles does not saturate. Kodama *et al* [6] have observed the unsaturation of magnetization up to a field of 60 KOe for 31.5 nm NiO particle at 5 K. In our case the particle as depicted from Williamson-Hall plot is larger than the critical limit to see finite size effect. Rather,

the magnetic inhomogeneity, as suggested from the anomaly of FC magnetization at 315 K may contribute to the observed unsaturation in the hysteresis plot.

4. Conclusion

In Fe doped NiO powder prepared by coprecipitation from nitrate precursors, we show that the size of crystallites monotonically decrease with increasing Fe concentration. The strain on the other hand increases with increasing Fe and attains a maximum value for 3 at.% Fe in NiO. Beyond 3 at.% the strain decreases indicating strain relaxation due to phase segregation and formation of γ -Fe₂O₃. The particles are larger than the threshold value below which finite size effect dominates. The observed magnetic behaviour therefore is a consequence of Fe induced magnetic ordering in the bulk of NiO. In addition some amount of magnetic inhomogeneity also contributes to the magnetic characteristics of Fe doped NiO as evidenced from the temperature dependent magnetization study under field cooled and zero field cooled conditions.

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