

Structural and Charge Density Properties of Iron Doped Nickel Oxide Synthesized by Co-precipitation Method

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Abstract: $Ni_{1-x}Fe_xO$ ($x = 0.00, 0.01, 0.02, 0.03, 0.04$) samples were successfully synthesized by co-precipitation method. Room temperature structural properties were analyzed by PXRD studies and Rietveld profile refinement technique. The structural results revealed that the samples assigned by cubic symmetry with $Fm-3m$ space group. Effects of structural properties with respect to the Iron substitutions in NiO matrix was investigated. Charge density profiles of the prepared materials were also investigated by maximum entropy method. From MEM analysis, it found that the ionic nature of Ni-O bond decreased. The surface morphologies were determined by scanning electron microscopic (SEM) measurements.

Keywords: Rietveld refinement, bonding nature, crystal structure, maximum entropy method.

I. INTRODUCTION

In recent decades, the metal oxides have been focused more attracted applications. Nickel oxide materials have paid important attention because of their mechanical, electrical, catalytic and magnetic properties [1-5]. The preparation of metal oxide materials plays vital role in the conversion process of energy [6]. NiO materials are one of the most promising candidates and used in important applications in batteries, capacitors, smart windows, sensors for gas, drug delivery in medical application and magnetic bar codes [7-12]. Nickel oxide material can be synthesized by different methods such as hydrothermal, co-precipitation, electrospinning, reflux methods, etc. [13-16]. The NiO material is a p-type semiconductor with wide energy band gap and it possess magnetic properties such as ferromagnetic, antiferromagnetic, super-paramagnetic behaviour and the magnetic order depending on the size of the particle and synthesis method. Sohaib et al., reported that the NiO is an antiferromagnetic insulating material with a Neel temperature of 523 K [17].

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In this present attempt, $Ni_{1-x}Fe_xO$ ($x=0.00, 0.01, 0.02, 0.03, 0.04$) samples were successfully synthesized by co-precipitation method and the effects of Iron dopant on the structural, morphological and charge density properties. The present report details the effects on structural properties with various doping percentages. The influence of Iron doping on the structural property has been experimentally analyzed via powder X-ray diffraction and Rietveld profile refinements [18]. The primary aim of this work details with the distribution of charges inside the unit cell of the samples. In general, the electronic property of the materials plays a vital role in electrical properties, which helps to know about the bonding nature between constituent atoms. The charge density distribution maps and interatomic chemical bonding futures inside the unit cell of $Ni_{1-x}Fe_xO$ ($x=0.00, 0.01, 0.02, 0.03, 0.04$) samples were reconstructed by maximum entropy method (MEM) [19] by the structure factor evolved by Rietveld profile refinement [18].

II. EXPERIMENTAL

A. Materials synthesis

$Ni_{1-x}Fe_xO$ ($x=0.00, 0.01, 0.02, 0.03, 0.04$) samples were synthesized by co-precipitation method. To prepare the samples, Nickel nitrate was used as starting materials. 0.5 M of Nickel nitrate solution was added with 1M of NaOH solution, which is used as a precipitation agent. The solution was stirred for 2 h and precipitation was washed to remove Na ions and finally dried at 80°C. Further, the doped samples were prepared by the same procedure for all the Iron doped NiO with the addition of Iron nitrate. Finally, the NiO and NiO: Fe samples were calcined at 700°C for 2 h.

B. Materials characterization

The Powder XRD and Rietveld profile refinement method [18] analysis were performed to determine the phase identification of the prepared samples using JANA2006 software [20]. The room temperature PXRD data sets were collected by Burker X-ray diffractometer with $CuK\alpha$ monochromatic radiation from 20°-100° for a step width of 0.02°. Microstructure and surface morphology were done by scanning electron microscopic images (SEM) (Zeiss EVO MA15 Research).

III. RESULTS AND DISCUSSION

A. XRD and Rietveld profile refinement analysis

Fig. 1 shows the powder XRD profiles of Ni_{1-x}Fe_xO (x=0.00, 0.01, 0.02, 0.03, 0.04) samples. All the observed PXRD profiles for pure NiO and NiO:Fe samples assigned by cubic structure with space group Fm-3m. The PXRD patterns are also well matched with standard JCPDS database (Card No. 04-0835) without any trace of addition extra phases. When increasing the dopant, the intensity of the diffraction peaks become reduce and broader due to the Fe ion as shown in fig. 1. The characteristic main peak of the samples shifted towards higher 2θ side for all samples (fig. 1 (b)). This attributed that the substitution of the impurity ions Fe distorts the host NiO matrix. The estimated cell parameters decreased with respect to the substitution of Fe ion in the NiO matrix. The lattice constant ‘a’ for the cubic structure of Ni_{1-x}Fe_xO (x =0.00, 0.01, 0.02, 0.03, 0.04) samples calculated using the following equation [21],

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2 + l^2}{a^2} \right) \tag{1}$$

In order to find more information about crystal structure, the Rietveld refinement has been performed using JANA2006 [20] software by the PXRD data. The fitted profiles of samples with x=0.00, 0.01, 0.02, 0.03, 0.04 compositions are shown in figs. 2 (a)-(e). The results of Rietveld profile refinement with acceptable R-factors such as R_p, R_{obs} and GOF extracted from profile refinement results and the values are given in Table I. From the Rietveld profile refinement [18], it is noticed that the cell parameters increase while increasing Fe substitution. The average crystallite size of samples estimated using Debye-Scherer’s formula [22].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where β is FWHM (full width half maximum of the peak), λ is wavelength and θ is Bragg angle. The calculated average crystallite size (D) values listed in Table I.

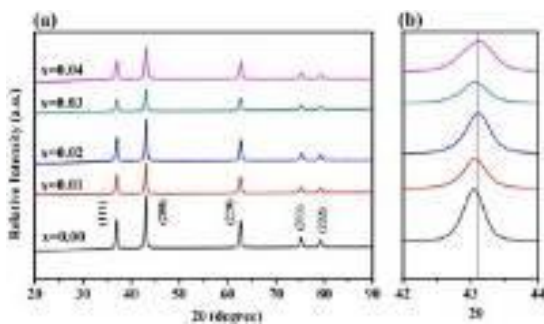


Fig. 1. (a) XRD patterns of Ni_{1-x}Fe_xO (x = 0.00, 0.01, 0.02, 0.03, 0.04) samples (b) Enlarged XRD patterns from 42°-44°.

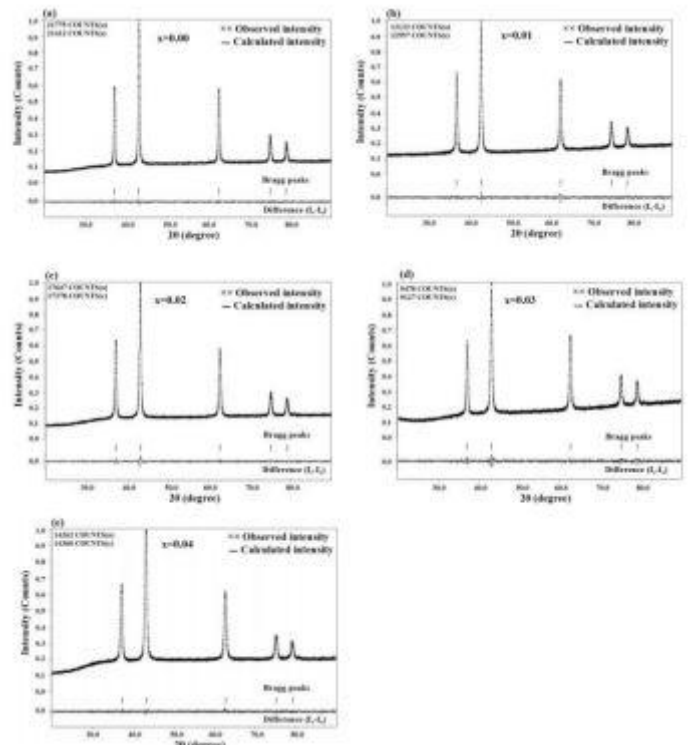


Fig. 2. Fitted X-ray profiles for Ni_{1-x}Fe_xO samples, (a) x = 0.00, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.04

Table-I: Structural parameters of Ni_{1-x}Fe_xO (x = 0.00, 0.01, 0.02, 0.03, 0.04) samples through refinement of powder XRD data

Parameter	x = 0.00	x = 0.01	x = 0.02	x = 0.03	x = 0.04
a = b = c (Å)	4.178(6)	4.179(2)	4.185(9)	4.172(2)	4.178(7)
Volume (Å ³)	72.97(1)	73.02(1)	73.28(1)	72.65(2)	72.97(1)
Density (gm/cc)	6.79	6.78	6.76	6.81	6.78
R _p (%)	1.55	1.85	1.88	2.08	1.46
R _{obs} (%)	0.17	0.13	1.81	0.26	0.33
GOF	1.07	1.12	1.30	1.14	1.02
F(000)	144	144	144	144	144
Thermal parameters					
Ni/Fe	1.15	1.19	1.48	1.26	1.43
O	1.02	0.99	1.07	0.97	1.04
Crystallite size (nm)	28	26	23	24	17

B. Electron density analysis

The charge density distribution studies are very useful to understand the physical properties of the materials, like optical and electrical properties. In this work, the charge densities were calculated inside the unit cell using maximum entropy method [19]. Each unit cell of the sample was divided into 64×64×64 pixels along the three axes and each pixel fixed as F₀₀₀/a₀³ using PRIMA [23] and VESTA [24] software. Figs. 3 (a)-(e) show the charge density analysis with shaded of iso-surfaces inside the unit cell. Fig. 4 (a) shows the 3D structure with (200) shaded plane.

Figs. 4 (b)-(c) show the 2D maps on (200) plane with iso-surface level of 0-1 e/Å³ with a contour interval of 0.04 e/Å³. From the 2D planes, the contour lines show the accumulation of charges between the Ni-O bonds (Figs. 4 (b) - (f)). The contour lines come closer when the substitution of Iron content in the NiO matrix. This authenticates ionic nature of Ni-O bond is decreased. These results are consistent with PXRD data. Figs. 5 (a) and (b) show the 1D charge density profiles along Ni-O bond, which also elucidate length of the bond and mid-bond charge densities and are listed in Table II.

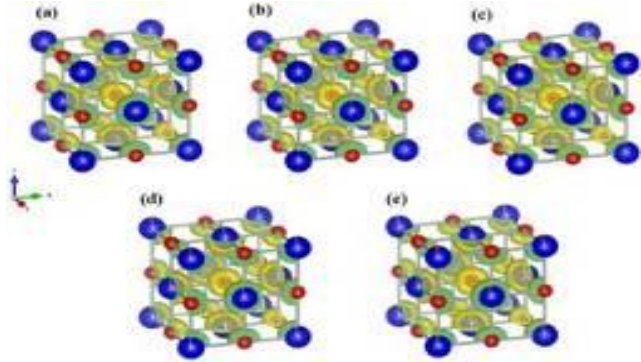


Fig. 3. 3D electron density of Ni1-xFexO samples, (a) x = 0.00, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.04.

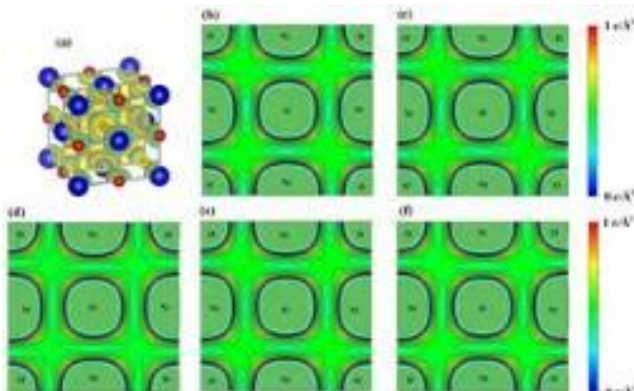


Fig. 4. 3D unit cell of Ni1-xFexO samples with (a) (200) plane shaded and 2D electron density distribution on (200) plane for Ni1-xFexO samples, (b) x=0.00, (c) x=0.01, (d) x=0.02 (e) x=0.03, (f) x=0.04.

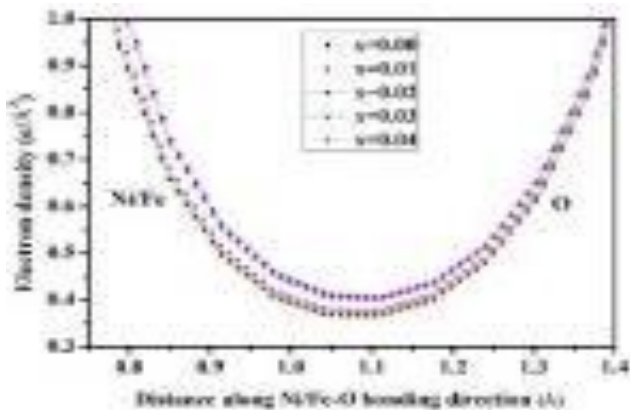


Fig. 5. 1D electron density profiles along the Ni-O bonding directions for Ni1-xFexO samples.

Table-II: Charge density parameters of Ni-O bond for

Concentrations	Ni _{1-x} Fe _x O samples	
	Bond length (Å)	Mid bond electron density (e/Å ³)
x=0.00	2.0894	0.3666
x=0.01	2.0898	0.3664
x=0.02	2.0925	0.4062
x=0.03	2.0863	0.3768
x=0.04	2.0893	0.4016

C. Surface morphology and EDS analysis

Figs. 6 (a)-(e) show the surface morphology images of Ni_{1-x}Fe_xO samples measured by scanning electron microscopy. The SEM images were recorded with magnification of around ×25000. All samples show fractured surface morphology. Figs. 6 (a)-(e) confirm that the substitution of Iron content in the NiO matrix helps to enhance the morphology. With the substitution of the Iron content the particle size of the samples increased with respect to the dopant.

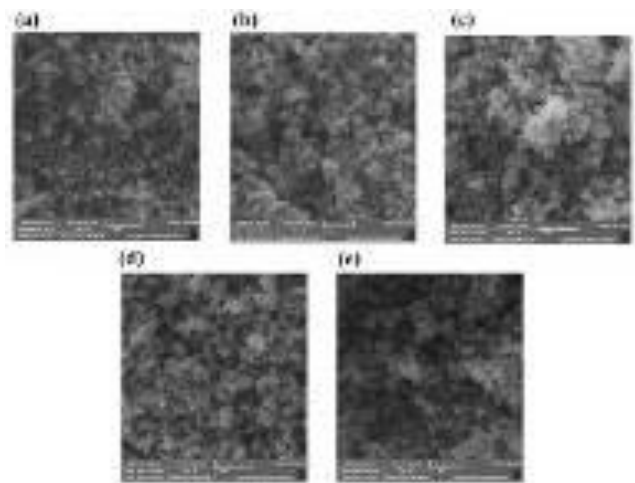


Fig. 6. SEM images of Ni1-xFexO samples (a) x = 0.00, (b) x = 0.01, (c) x = 0.02, (d) x = 0.03, (e) x = 0.04.

IV. CONCLUSION

In this work, Ni_{1-x}Fe_xO (x = 0.00, 0.01, 0.02, 0.03, 0.04) samples were successfully synthesized by facile co-precipitation method. The XRD analysis shows the samples crystallized by cubic structure. The refined structure factors from profile refinement were used to analyze charge density distributions in the samples, bond length and mid bond electron densities through maximum entropy method. The charge densities maps revealed that the Ni-O bonds exhibit covalent in nature. The SEM analyses indicate that the samples are uniform surface morphology.

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