Structural and Optical Study of Oxygen Irradiated Rare Earth Doped Nickel Ferrite

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Abstract. In present work, NiFe2O4 nanoparticles doped with 4% Ce ions were synthesized by chemical route using nitrates of iron, nickel and cerium with citric acid. Irradiation with swift heavy ions can modify the properties of ferrites significantly. Modification depends upon type of ion, energy and fluence used for irradiation. Presently NiCe0.04Fe1.96O4 sample was irradiated with 100 MeV O7+ beam at fluencies of 1×1012 ions/cm2, 5×1012 ions/cm2, 1×1013 ions/cm2 and 2×1013 ions/cm2. All samples (pristine and irradiated) were characterized by XRD, FTIR, Raman and UV-Vis spectroscopy. XRD patterns and FTIR spectra confirmed the spinel structure of sample. XRD parameters like crystallite size, lattice parameter, strain etc. were calculated, which show significant change only at the fluence of 5×1012 ions/cm2. UV-Vis spectra show two direct band gaps corresponding to low and high spin in all samples. Band gap was found to be higher for sample irradiated at 2×1013 ions/cm2 fluence in comparison to pristine sample. It is found that irradiation with 100 MeV oxygen affect the structural parameters in random way while optical band gap shows increasing trend with fluence.

1. Introduction
Ferrites are ferrimagnetic oxides which contain iron oxide as the main constituent with distinct metal oxides. These attractive functional materials have received incredible attention among the material scientists because of their excellent magnetic and electrical properties. Ferrites have wide range of applications in the fields of magnetism, electronics, magneto-electronics, optoelectronics, electrochemical science, and biotechnology etc. [1-3]. Among all ferrites cubic spinel ferrites (MFe2O4 where M is a divalent metal ion) are very important and are studied because of their unique magnetic, electrical and optical properties with relative cost-effectiveness. These essential qualities make them suitable for both conventional and innovative applications. Spinel ferrites have a face centered cubic lattice of oxygen ions, forming tetrahedral (A) and octahedral (B) sites that may be occupied either by M2+ and Fe3+ ions. Nickel ferrite (NiFe2O4) is one of the most important cubic spinel ferrite. It possesses high saturation magnetization, low conductivity, high electrochemical stability, catalytic behavior and relatively high permeability. These properties make nickel ferrite excellent material for inductors and transformer cores, power transformers in electronics and telecommunication industry [4, 5]. Researchers are focusing towards modifying the existing properties of materials to improve the technological applications in numerous fields. It has been observed that introducing small amount of dopant into the spinel lattice gives rise to significant variations in the structure and morphology of ferrites. Rare earth ion (R) substituted spinel ferrites have received much more prominence due to its captivating extensive applications. The R–Fe (3d–4f coupling) interaction along with 3d-3d interaction in ferrites produces structural distortion which induces lattice strain and significant change in the structure and morphology of ferrites. In this way substitution of these ions strongly affects the electrical, optical and magnetic behavior of ferrites. Several studies have been conducted and are
ongoing to see the effect of doping with different rare earth elements in ferrites [6-9]. These studies have shown remarkable changes in the structural, magnetic, electrical and optical properties of ferrites after rare earth ion substitution.

Swift heavy ion irradiation (SHI) is also an effective tool for modification of properties of materials. Modification depends upon type of ion species, charge state, energy and fluence used for irradiation. The fast heavy ions interact with material and lose energy due to inelastic collision with electrons (known as electronic stopping $S_e$) and due to elastic collision with nucleus (known as nuclear stopping $S_n$). It has been observed that $S_e$ plays dominating role in determining the properties of irradiated materials by producing different type of defects in the material. When the threshold value of electronic stopping power ($S_{eo}$) is higher as compared to the value of electronic stopping power ($S_e$), then point/cluster defects are produced in the system otherwise latent tracks/columnar defects are produced [10]. Thus, SHI produces material of different microstructure depending on the amount of energy deposited in the material. Since, properties of ferrites are very much sensitive to the microstructure; hence, there has been great interest in studying the properties of nanoferrites by irradiating them with a suitable ion beam [11-13]. Two models, Coulomb explosion model and thermal spike model were proposed to explain how electronic excitation causes displacement of lattice atoms [14]

Thus both irradiation and doping of rare earth ion affect the properties of ferrites, which motivated present work for studying structural and optical properties of oxygen irradiated cerium doped nickel ferrite nanoparticles.

2. Experimental Details

Nanoparticles of nickel ferrite doped with cerium were prepared by chemical route which is a bottom up approach. Nitrates of iron, nickel and cerium along with citric acid were dissolved in distilled water in stoichiometric proportion corresponding to NiCe$_{0.04}$Fe$_{1.96}$O$_4$. Cation to citric acid ratio was taken as 1:2. The solution was magnetically stirred at 85°C, till it became viscous. Overnight heat treatment at 100°C was given to dry the obtained viscous solution. The precursor thus obtained was sintered for 2 hours at 500°C to get nanoparticles of 4% Ce doped nickel ferrite. For the confirmation of pure spinel phase XRD pattern of nanoparticles was recorded by Rigaku X-ray Diffractometer using Cu-Kα X-rays of wavelength 1.54 Å. The nanoparticles were irradiated by 100 MeV O$^{7+}$ beam at fluences of 1×10$^{12}$, 5×10$^{12}$, 1×10$^{13}$ and 2×10$^{13}$ ions/cm$^2$ at IUAC Delhi. All samples (pristine and irradiated) were characterized by XRD, FTIR and Raman spectroscopy for the study of irradiation induced structural changes. FTIR spectra was recorded by making pellets of sample with KBr. Optical behavior was studied by UV-Vis spectroscopy in reflectance mode by Perkin Elmer Model Lambda 365 UV-Vis Spectrophotometer in the wavelength range 200-800 nm. SRIM calculation was done to get the values of $S_e$ and $S_n$ which comes out to be as 8.4×10$^7$ keV/nm and 1.48 keV/nm for 100 MeV Oxygen beam.

3. Results and Discussion

3.1 XRD

XRD pattern of pristine and irradiated samples of NiCe$_{0.04}$Fe$_{1.96}$O$_4$ nanoparticles are shown in figure 1. All diffraction peaks are matched and indexed with JCPDS, PDF number 742081. The single phase cubic spinel structure is clearly reflected from XRD pattern. All the peaks are well resolved indicating polycrystalline nature of the samples. Basic crystal structure remains invariant even after irradiation up to fluence of 2×10$^{13}$ ions/cm$^2$. The crystallite size (D), lattice parameter (a), and X-ray density ($d_s$) are determined using following formulae from the most intense peak (311):

\[
D = \frac{0.9λ}{h\cosθ} \\
a = \frac{λ}{2Sinθ}\sqrt{h^2+k^2+l^2} \\
d_s = \frac{8M}{N_A a^3}
\]

\[h^2 + k^2 + l^2 = 9\]
Where \( \lambda \) is wavelength of X-ray, \( \theta \) is Bragg position of the peak, \( \beta \) is full width at half maximum and \( h, k, l \) are Miller indices. \( M \) is molecular weight of the sample, \( N_A \) is Avogadro’s number. Lattice strain in irradiated samples is estimated with respect to the pristine sample by using the relation

\[
\text{Strain} = \frac{a_i - a_o}{a_o}
\]

where \( a_o \) is lattice parameter for pristine sample and \( a_i \) is for irradiated sample. Negative strain shows decrease and positive strain shows increase of lattice parameter. All the estimated parameters are shown in table 1.

![XRD pattern for pristine and irradiated samples of NiCe0.04Fe1.96O4](image)

**Table 1. XRD parameters for pristine and irradiated NiCe0.04Fe1.96O4 particles**

| Sample         | Crystallite Size D (nm) | Lattice parameter±0.0001 (Å) | Strain \((10^{-3})\) | X-ray density (g/cm³) |
|----------------|-------------------------|------------------------------|-----------------------|-----------------------|
| Pristine       | 15.2 ±0.2               | 8.3261                       | -                     | 5.47                  |
| \(1 \times 10^{12}\) ions/cm² | 15.2 ±0.8               | 8.3258                       | -0.04                 | 5.47                  |
| \(5 \times 10^{12}\) ions/cm² | 14.7±0.2               | 8.2798                       | -5.50                 | 5.56                  |
| \(1 \times 10^{13}\) ions/cm² | 15.2±0.2               | 8.3355                       | 1.13                  | 5.45                  |
| \(2 \times 10^{13}\) ions/cm² | 15.0 ±0.6               | 8.3259                       | -0.06                 | 5.47                  |

The crystallite size was found to be about 15 nm, which is almost constant for pristine as well as irradiated samples. From figure 2, it seems that lattice parameter also remains unaffected after irradiation at all fluences except that at \(5\times10^{12}\) ions/cm². However, strain calculation shows that lattice parameter first decreases then increases and again slightly decreases with irradiation, though significant changes are observed only for \(5\times10^{12}\) ions/cm² fluence. Random variation of lattice parameter may be due to change in distribution of cations between A and B sites. It has been reported in literature [15] that irradiation with swift heavy ion can affect cation distribution and since in spinel ferrite many A and B sites are vacant, redistribution of cations can be random when ions get displaced due to the electronic energy given by incoming ion. Presently 100 MeV oxygen beam is used, for which electronic stopping (1.4 keV/nm) is less than the threshold (13 keV/nm) for creating columnar...
defects, therefore point defects are expected to occur. Change in lattice parameter affects the hopping lengths of A and B sites as well as X-ray density of the sample as can be seen from figures 3, 4 and 5 respectively. Hopping lengths at A and B sites were calculated by the relations $L_A = \frac{a\sqrt{3}}{4}$ and $L_A = \frac{a\sqrt{2}}{4}$ respectively. Because of small hopping length for sample irradiated at $5 \times 10^{12}$ ions/cm$^2$, smooth conduction or relatively small band gap can be expected. Higher X-ray density shows higher packing of ions in lattice.

**Figure 2.** Variation of lattice parameter with fluence of irradiation

**Figure 3.** Variation of X-ray density with fluence of irradiation

**Figure 4.** Variation hopping length $L_A$ with fluence of irradiation

**Figure 5.** Variation hopping length $L_B$ with fluence of irradiation

### 3.2 FTIR

IR spectra play a significant role to extract information regarding structure and functional groups present in a compound. FTIR spectra of pristine and irradiated samples are displayed in figure 6. Literature [16] shows that two primary absorption bands are generally observed in the vibrational spectra of spinel ferrites in the range 300 to 700 cm$^{-1}$, one high frequency band due to intrinsic vibrations at tetrahedral sites and other low frequency band because of intrinsic vibrations at octahedral sites. The peak marked with * around 590 cm$^{-1}$ in figure 6, is due to the intrinsic vibrations of ions at tetrahedral sites of crystal lattice and is in good agreement with the peaks reported at 597.5 cm$^{-1}$ for nickel ferrite [17]. The peaks which appear at wavenumber less than 400 cm$^{-1}$ are not observed owing to the range 400-4000 cm$^{-1}$ of available spectrometer and therefore the bands corresponding to octahedral sites are not visible in the present spectra. The broad hump observed in
the range 1600-3400 cm\(^{-1}\) is due to the H-O-H stretching and bending vibrations of the water. The band around 1300 cm\(^{-1}\) is due to –CH\(_3\) bending [18]. Position and area of the peak corresponding to vibrations at tetrahedral site is tabulated in table 2 for pristine and irradiated samples. In comparison to pristine sample the irradiated samples show shifting of peak towards lower wavenumber side. Area of the peak is also reduced after irradiation as can be seen from figure 7. However the change in position and area of the peak don’t follow any regular trend with fluence. Decrease in area of peak after irradiation indicates partial amorphisation of the sample.

![Figure 6. IR spectra of pristine and irradiated samples of NiCe\(_{0.04}\)Fe\(_{1.96}\)O\(_4\).](image)

**Table 2.** IR peak position and area for pristine and irradiated samples

| Sample       | Peak Position(cm\(^{-1}\)) | Area (cm\(^2\)) |
|--------------|-----------------------------|------------------|
| Pristine     | 590.03±0.22                 | 108±15           |
| 1 \times 10^{12} ions/cm\(^2\) | 572.95±0.46                 | 45±3             |
| 5 \times 10^{12} ions/cm\(^2\) | 579.86±0.57                 | 27±1             |
| 1 \times 10^{13} ions/cm\(^2\) | 582.88±0.34                 | 41±1             |
| 2 \times 10^{13} ions/cm\(^2\) | 577.68±0.57                 | 30±1             |

3.3 RAMAN

For detailed microstructural changes induced by irradiation, Raman spectra of all the samples were recorded and are shown in figure 8. According to Group theory there are five first order Raman active modes (A\(_{1g}\) + E\(_g\) + 3T\(_{2g}\)) for spinel ferrites [19]. All the modes with their position are shown in table 3. Similar to IR spectra, Raman modes are also shifted towards lower wavenumber side after irradiation. Here it is clearly visible that the intensity of Raman peaks is decreased after irradiation. Since sensitivity of all the modes towards irradiation is not same [20], hence some peaks show significant shifting in position and decrease in intensity while some does not. There is one shoulder at 666 cm\(^{-1}\) in pristine sample which gradually disappear as the fluence of irradiation is increased. In comparison to IR, Raman spectra clearly show degradation of crystallinity of the sample after irradiation. Though,
the rate of degradation cannot be said to follow an increasing trend with increasing fluence of irradiation.

![Figure 8](image-url)  
**Figure 8.** Raman spectra for pristine and irradiated NiCe$_{0.04}$Fe$_{1.96}$O$_4$ nanoparticles

![Figure 9](image-url)  
**Figure 9.** UV-Vis spectra for pristine and irradiated NiCe$_{0.04}$Fe$_{1.96}$O$_4$ nanoparticles

### 3.4 UV-Vis spectroscopy

UV-Vis spectra for pristine and irradiated samples in reflectance mode are shown in figure 9. Since the spectrum is recorded in reflectance mode, hence for analysis Kubelka Munk function $F(R) = \frac{(1 - R)^2}{2R}$ is calculated where $R$ is reflectance [21]. To determine the band gap, $(F(R)h\nu)^2$ vs $h\nu$ is plotted and straight line is fitted in linear portion of the graph. Intercept of straight line on x-axis gives the value of band gap. Representative graph for pristine sample is shown in figure 10. It is clear that two straight
lines can be fitted corresponding to two band gaps. Two direct band gaps for NiFeO$_4$ are reported in literature also and are attributed to transitions from 2p orbitals of O to 3d ($t_{2g}$, $e_g$) orbitals of Ni and Fe.

Table 3. Raman band positions (cm$^{-1}$) for pristine and irradiated NiCe$_{0.04}$Fe$_{1.96}$O$_4$ nanoparticles

| Raman Mode | Fluence (ions/cm$^2$) | 1×10$^{12}$ | 5×10$^{12}$ | 1×10$^{13}$ | 2×10$^{13}$ |
|------------|-----------------------|------------|------------|------------|------------|
| T$_{2g}$   | pristine              | 213        | 206        | 208        | 205        | 198        |
| E$_g$      |                       | 333        | 328        | 332        | 327        | 311        |
| T$_{2g}$   |                       | 482        | 480        | 482        | 482        | 471        |
| T$_{2g}$   |                       | 572        | 567        | 566        | 564        | 554        |
| A$_{1g}$   |                       | 697        | 696        | 694        | 693        | 683        |

Figure 10. Linear fit for pristine sample

Figure 11. Variation of band gaps with fluences

Table 4. Energy band gap values at different fluences of irradiation

| Fluence (ions/cm$^2$) | Band Gap 1 (eV) | Band Gap 2 (eV) |
|-----------------------|-----------------|-----------------|
| pristine              | 1.68±0.02       | 1.99±0.03       |
| 1×10$^{12}$           | 1.72±0.02       | 2.05±0.02       |
| 1×10$^{13}$           | 1.75±0.02       | 2.17±0.03       |
| 2×10$^{13}$           | 1.79±0.02       | 2.28±0.07       |

The existence of both high and low spin states in nickel ferrite is responsible for two band gaps [22]. Calculated band gap energy values $E_{g1}$ and $E_{g2}$ for pristine and irradiated samples are shown in table 4 and their variation with fluence is shown in figure 11. In comparison to pristine sample both the band gaps are increased after irradiation at 2×10$^{13}$ ions/cm$^2$. Point/cluster type of defects produced by irradiation may be the possible reason for this.

4. Conclusion

NiCe$_{0.04}$Fe$_{1.96}$O$_4$ nanocrystals synthesized by chemical route show pure spinel phase with no impurity. As observed from XRD pattern, irradiation with 100 MeV oxygen beam doesn’t affect much the
The crystalline structure of the samples. However, Raman spectra show a clearly partial amorphisation with irradiation. Decrease of areal intensity of IR peak also supports this. Two band gaps corresponding to low and high spin states were observed in all the samples by UV-Vis spectroscopy. Increase in band gap after irradiation is due to the point/cluster type of defects produced by heavy ion irradiation. No regular trend between the observed effect and fluence of irradiation was observed. Therefore, more data corresponding to intermediate fluences is required so that dose of irradiation can be optimized to have desired modifications in structural and optical properties for application point of view.

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