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Spectroscopic and structural studies of nickel ferrite doped with rare earth ions

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Abstract : The Nickel Ferrite of composition $Ni_{(x)}Fe_{(3-x)}O_4$ with $x = 0.3, 0.5, 0.7, 0.9$ doped with neodymium and gadolinium were studied by infrared absorption spectroscopy. The IR spectrum showed two main absorption bands ν_1 and ν_2 in the range 400cm^{-1} - 600cm^{-1} arising from the octahedral and tetrahedral complexes. The positions of absorption bands are compositional dependent whose dependence could be attributed to the variation in cation – oxygen bond distances. The force constant of tetrahedral and octahedral sites supports cation distribution. Addition on gadolinium the absorption band ν_1 & ν_2 were found to be broadened and the peaks are not sharp. The lattice constants were found to decrease by the addition neodymium and gadolinium. The samples confirm cubic spinel structure and also it was observed that nickel ferrite doped with Nd^{3+} and Gd^{3+} show a linear increase in lattice constant.

Key words : ferrite, rare earth ions, IR, XRD.

Introduction:

Nanophase ferrites are a class of magnetic materials that have been the most attractive area of the research . Nickel ferrite has inverse spinel structure. The crystal structure is fcc with the unit cell containing $32O^{2-}$, $8Ni^{2+}$ and $16Fe^{3+}$ ions. The oxygen ions form 64 tetrahedral site and 32 octahedral site, where 24 cations are distributed. The eight Ni^{2+} and eight Fe^{3+} cat ions occupy half of the octahedral site and the other eight Fe^{3+} ions occupy eight tetrahedral sites^{1,2}. Ferrites nanoparticles are usually prepared by various physical and chemical methods like mechanical milling, iner gas condensation, hydrothermal reaction, ceramic method, sol gel and co precipitation technique etc³⁻⁵. Influence of rare earth ions on spinel ferrite causes structural disorder and lattice strain, thereby increasing the electrical and magnetic properties⁶. The effect of rare earth ion substitution on curie temperature was reported in⁷⁻⁸. Different studies shows⁹⁻¹⁰ the concentration of rare earth doping in the ferrites is important in describing the properties of ferrites. The unique characteristics of rare earth doped systems are 4fn electronic states¹¹.

The infrared spectroscopy is an important and non destructive characterising tool which provides qualitative information regarding structural details of crystalline material¹². This technique is based upon the fact that a chemical substance shows marked selective absorption in the infrared region. The results from IR absorption study can be used to interpret the electrical and magnetic properties of the ferrites¹³. The various

absorption bands present in the spectrum represents the details regarding functional groups and their linkages can be explored. They are found to be dependent on atomic mass, cationic radius, cation – anion bond distances, cation distribution etc. Infrared spectral analysis have been carried out for several ferrites and reported two absorption bands within the wave numbers $(800-200)\text{cm}^{-1}$, which are respectively attributed to the tetrahedral and octahedral group complexes of the spinel structure.

Experimental:

The starting materials for preparing nickel ferrite having general chemical formula $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ (where $x = 0.3, 0.5, 0.7$ & 0.9) by taking the necessary amount of nickel chloride and iron powder according to the stoichiometric ratio $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ to obtain single phase spinel structure. The weighed chemicals were dissolved in dilute HNO_3 and to ease the reaction it was heated slowly to evaporate the solvent. The remaining mire was transferred into a porcelain crucible and was kept in a furnace and heated in air for four hrs at 500°C . Then it was allowed to cool slowly, till to reach the room temperature. The fired sample was grinded to fine powder and was again heated to 950°C for two hrs. After cooling it was grinded to a fine powder. To confirm the completion of molecular state reaction the samples were subjected to characterization by X ray diffraction & Infra red absorption spectroscopy. The IR absorption spectra of finely crushed powder of the sample were obtained in the range from 1000 cm^{-1} to 200 cm^{-1} by using FITR– SHIMADZU Spectrophotometer model 8700 where in KBr is used as the medium. The spectrum, transmittance (%) against wave number (cm^{-1}), is used for interpretation of the results. X–ray diffractograms were taken using Rigaku-mini flex system with $\text{Cu-}\alpha$ radiation of wavelength 1.5418 \AA Ni filter was used. The sample was scanned between 80° and 2° .

Result & Discussion :

X-ray diffraction

A phase analysis was performed to confirm the formation of single-phase which spinel ferrites and all the samples demonstrate the high crystalline structure. The X-ray diffraction pattern of nickel ferrite doped with Nd^{3+} and Gd^{3+} are presented in fig (1&2). The samples show all the characteristics peaks of ferrite material with most intense peak (311), which confirms the formation of cubic spinel structure. It was observed that nickel ferrite doped with Nd^{3+} and Gd^{3+} show an linear increase in lattice constant from 8.34 to 8.35 \AA for Nd^{3+} , 8.32 to 8.34 \AA for Gd^{3+} . Both Nd^{3+} and Gd^{3+} ions prefer octahedral B-site and replace Fe^{3+} ion in the spinel structure as shown in table(1). Since Fe^{3+} ions are being replaced by the bigger ions Nd^{3+} and Gd^{3+} Similar results have been reported for La^{3+} doped¹⁵ and Gd substituted $\text{Mg} - \text{Cd}$ ferrite¹⁶ The reduction lattice constant in rare earth substituted ferrite was reported by Rezlecu and Rezlescu suggesting the occupancy of rare earth ion on B site¹⁷. It is found that a decreases with increasing RE doping concentration for all RE addition samples. These results confirm that La, Nd and Gd can enter the lattice while keeping the spinel structure unchanged. The decrease in lattice constant may be due to the iron vacancies in these samples, as described in¹⁸.

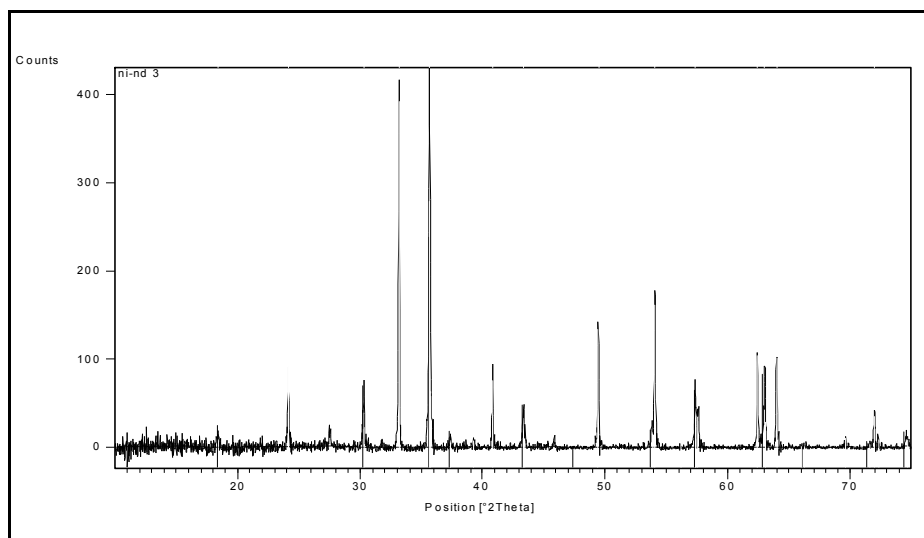


Fig (1) X-Ray diffraction pattern for $\text{Ni}_{0.3}\text{Fe}_{2.7}\text{O}_4$ (Nd doped)

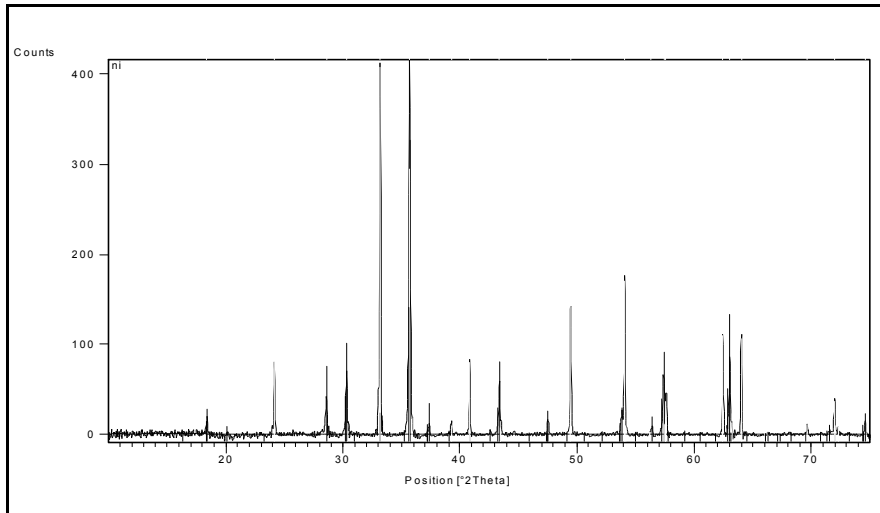


Fig (2) X-Ray diffraction pattern for $\text{Ni}_{0.3}\text{Fe}_{2.7}\text{O}_4$ (Gd doped)

Table(1) Lattice constant for Nd and Gd doped nickel ferrite

$\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ Where x	Lattice constant Nd ³⁺ doped A ⁰	Lattice constant Gd ³⁺ doped A ⁰
0.3	8.3405	8.3293
0.5	8.3408	8.3348
0.7	8.3479	8.3388
0.9	8.3524	8.3422

Spectroscopic studies

FTIR absorption spectra for all samples are obtained from IR spectrophotometer as shown in Fig (3 and 4). It is found that spectra consists of two significant absorption bands, one around 550cm^{-1} and second around 460cm^{-1} . Absorption bands observed in this range are characteristics of spinel structure having two sublattices, tetrahedral (A) site and octahedral (B) site¹⁹. The absorption band ν_1 , observed at around 550cm^{-1} are due to metal oxygen stretching vibrational modes and it is attributed to $\text{Fe}^{3+}\text{-O}^{2-}$ vibrations at the tetrahedral site, whereas ν_2 observed at 460cm^{-1} is assigned to octahedral $\text{Fe}^{2+}\text{-O}^{2-}$ group complexes²⁰.

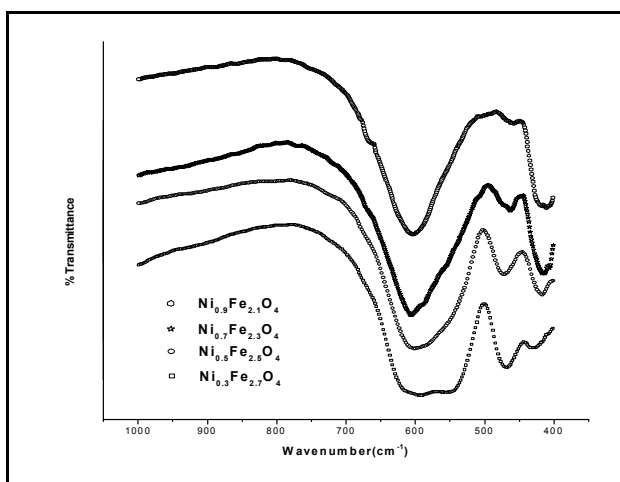


Fig (3) IR spectra for nickel ferrite doped with neodymium

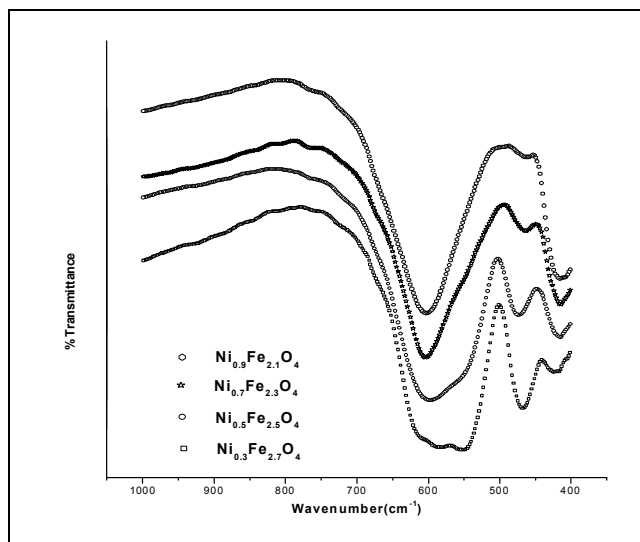


Fig (4) IR spectra for nickel ferrite doped with gadolinium

It was observed that for nickel ferrites doped rare earth ions the absorption bands were found to decrease. The peaks observed around 550cm^{-1} and 460cm^{-1} are not sharp for the impure samples. The broadening of the bands is due to addition of gadolinium in the samples of Ni ferrites of concentration ($x= 0.7$ & 0.9). This fact is also supported by²¹.

On substitution of Nd^{3+} and Gd^{3+} the position of ν_2 band shift towards lower side, which suggests the occupancy of Nd^{3+} & Gd^{3+} Octahedral (B) site. However on substitution of impurities as said before broadening of ν_2 band take place which may be due to occupancy of cations of different character on the same site.

By this relation $\nu = 1 / 2\pi (K/M)^{1/2}$
 ν = Vibrational frequency of the ion.
 K = force constant of the ion.
 M = reduced mass of the ion

The decrease in vibrational frequencies indicates that the bond length decreases. It is found to decrease the octahedral force constant and which supports the occupancy of neodymium and gadolinium on B site. The compositional dependent behaviour of force constant are attributed to the cation oxygen bond distances²².

Conclusions :

The results obtained from IR absorption spectra of the samples under investigation reveal cubic spinel structure showing two significant absorption bands.

- I. The absorption bands ν_1 and ν_2 are found in the expected range and the difference in band position is due to the difference in the $\text{Fe}^{3+} - \text{O}^{2-}$ for the octahedral and tetrahedral complexes.
- II. The Positions absorption bands are compositional dependent whose dependence could be attributed to the variation in cation – oxygen bond distances.
- III. Variations in the force constant of tetrahedral and octahedral sites support predicted cation distribution. Where in adding gadolinium the absorption band ν_1 & ν_2 were found to be broadened and the peaks are not sharp.

The lattice constants were found to decrease by the addition neodymium & galodinium.

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