Characterization of Magnesium Substituted Nickel Ferrites Nano-Particles Synthesized Using Combustion Technique

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Abstract: **Pure nickel ferrite ($NiFe_2O_4$) and magnesium substituted nickel ferrite ($Ni_{1-x}Mg_xFe_2O_4$) with particles size in nano-meter range were synthesized by using auto combustion technique. In this study, it has been observed that with increase in sintering temperature, the estimated bulk density of the materials increases. The XRD patterns of the samples show the formation of single phase materials and the lattice parameters estimated using XRD patterns. FT-IR spectra shows two small peaks in the band region 400-1000 cm^{-1} (vibrational) and another peaks in the band range 1000- 4000 cm^{-1} in all the samples, characteristics of spinel structure. From Raman spectra, the Raman shift of pure $NiFe_2O_4$ and $Mg_xNi_{1-x}Fe_2O_4$ are comparable with the experimental values reported in literature. The Raman spectra gives five Raman active modes ($A_{1g} + E_g + 3F_{2g}$) which are expected in the spinel structure.**

Keywords: **Combustion Method, Spinel structure, XRD, FTIR, Raman Spectroscopy.**

1. INTRODUCTION

In the past few decades, magnetic nanoparticles (MNPs) have attracted lots of interests. A considerable amount of researches have been carried out on Ni-ferrites and substituted ferrites owing to their large magnetic permeability, relatively low magnetic loss, high cut-off frequency, high saturation magnetization, high Curie temperature, chemical stability, low coercivity and biodegradability [1,2], as well as their wide applications in areas of biology, medicine, environment, machine, military affairs, etc**.** Spinel ferrites are complex transition metal oxides having general formula $M^{2+}Fe_2^{3+}O_4$, (M^{2+} is transition metal ions, like Ni^{2+}, Co^{2+}, Zn^{2+} etc) possess special magnetic and electrical properties with high chemical stability and mechanical hardness, are important magnetic materials, suitable for operating at higher frequency region, extensively used in electromagnetic devices such as memories, sensors and microwaves, as well as in our modern information technology applications [4, 5

Nickel ferrite, $NiFe_2O_4$ is a well-known ferromagnetic material with an inverse spinel structure [4]. This compound is represented by the formula (Fe^{+3}) $(Ni^{+2}Fe^{+3})$ O_4; half the atoms of iron occupy the tetrahedral (A) sites, and the other half plus magnetic atoms occupy the octahedral (B) sites. In this structure the tetrahedral site (A site) is fully occupied by Fe 3þ while the octahedral site (B site) is occupied by Ni 2þ and Fe 3þ ions. It shows ferri-magnetism originating from anti-parallel spins between Fe 3þ at the tetrahedral site and Ni 2þ at the octahedral site. The surface effect becomes progressively dominant as the particle size reduces. Modification of the structural and electronic properties near and at the surface of the particle results in disorder in lattice symmetry that introduces anisotropy. Many of the properties originate from the single domain nature of the particles such as superparamagnetism. Super-paramagnetism is a very useful and unique property of nano-particles [6].]. Looking to the importance of this category of material, we thought it pertinent to explore the properties of magnesium substituted nickel ferrites (Ni-Mg ferrites) through its synthesis using auto combustion technique.

2. EXPERIMENTAL DETAILS

Combustion method is one of the most popular, cheap and efficient low temperature techniques that allow control over the chemical composition as well as densification of material synthesized. Based on the property of matched oxidation and

reduction between the fuel and the oxidizer, the extremely safe combustion synthesis can be controlled through initial parameters. Depending upon the fuel and the oxidizer the temperature rises rapidly and as a result of auto combustion, highly pure and crystalline nano size materials are formed. Reaction between the mixture of nitrates and highly pure glycine results a self-sustained exothermic process. This technique has associated advantages of getting soft and fine crystalline materials with high surface area and high purity at very low temperature ($<300^0$C).

The calculation of molar ratio (stoichiometric fuel to oxidant ratio) has a significant role in redox based combustion synthesis. In the present work, to prepare the spinel ferrite materials ($NiFe_2O_4$ and $MgFe_2O_4$ and also Mg doped $NiFe_2O_4$ ($Ni_{1-x}Mg_xFe_2O_4$)), we choose the auto-combustion method. In this technique, nitrate salts (Ni $(NO_3)_2$, $6H_2O$ [99%], Mg $(NO_3)_2$, $6H_2O$ [99%] and $Fe(NO_3)_2$, $9H_2O$) [99%] are taken as reactants and citric acid($C_6H_8O_7$) [99%] is taken as fuel. The nickel, magnesium and ferric nitrate salts are taken in a stoichiometric amount in a beaker, then this mixture of these salts are heated above their melting point (~70°C) for10-15 minutes with citric acid as a fuel. All these salts are melted to form homogeneous solution. Then this solution is heated at temperature 90°C~100°C (depending upon composition) for 15- 20 minutes. As a result the combustion take place inside the beaker and it converted into brownish color powder. After grinding the samples, cylindrical pellets are formed by using KBr press pelletizer and sintered at two different temperatures 700^0C and 900^0C for 6 hours. The XRD of sintered samples were taken by Rigaku Smart Lab (Japan) X-ray diffracto-meter (with Cu-Kα radiation). FTIR of the sintered product in powder form was taken by Shimadzu 8400.S (Japan) and Raman spectra were taken by STR-500 Micro-Raman Spectrometer (Japan) at room temperature. In FT-IR, spectra were recorded using KBr as reference in a wave number region of 350 to 4000 cm^{-1}. The ratio of KBr and samples were taken as 95:05 in a cylindrical die and measured at room temperature.

3.   RESULTS AND DISCUSSION

1. *Density measurement:*

The geometrical density of the samples sintered at different sintering temperatures (i. e. 700 °C and 900 °C) are measured by measuring the geometrical dimensions. M is the mass and V is the volume of the pellets, the density of the pellets calculated using the following formula

$$D = \frac{M}{V} = \frac{M}{T \times \pi r^2}$$

The variation of density with concentration of magnesium (Mol%) at two sintering temperatures is shown in figure 1 which reveals that as the sintering temperature increases, the geometrical density of the sintered samples increases. A higher sintering temperature increases the rate of diffusion of ions which increase of density and reduces amount of pores present in the samples.
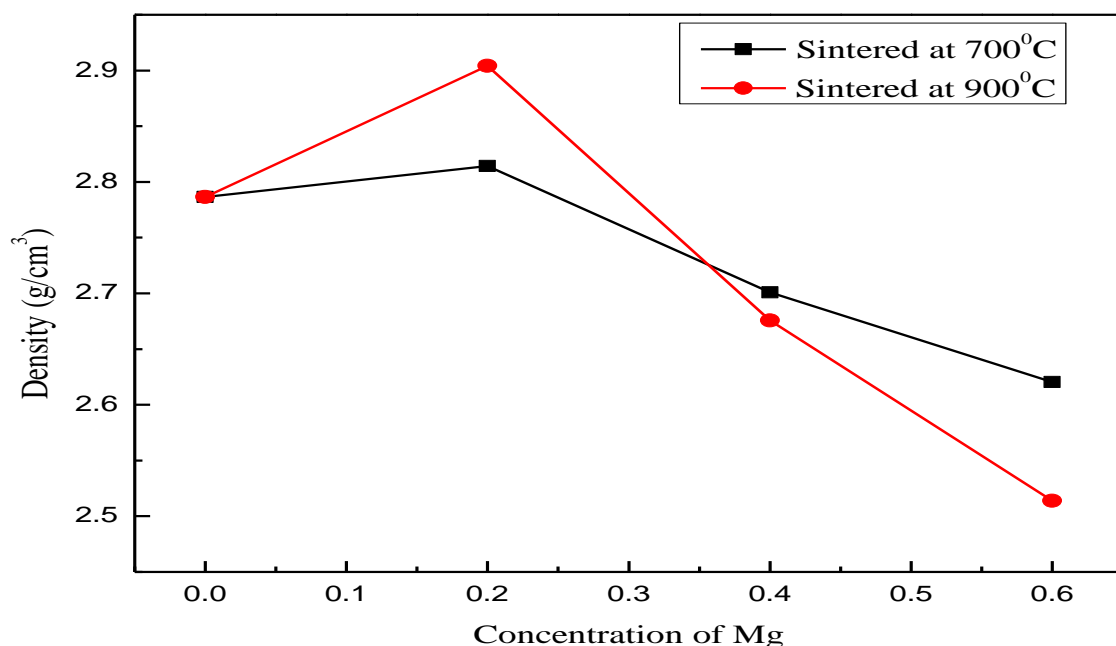

Fig.1: Density versus composition plot at two different sintering temperatures.

2. XRD ANALYSIS:

The XRD patterns of powdered samples of $Ni_{1-x}Mg_xFe_2O_4$ (x = 0.2, 0.4, 0.6) ferrite system were obtained at room temperature using Rigaku SmartLab diffractometer (Cu Kα radiation, 2θ = 20^0-80^0) are shown in Figure 2. The analysis of XRD patterns show the formation of single phase compound of cubic structure for all compositions sintered at both 700^0C and 900^0C. The lattice parameters 'a_{exp}' for all the samples have been determined for the most prominent peak (311) of the XRD pattern. From the diffraction pattern, it is observed that with increase of Mg content the peak position for (311) is displaced continuously towards higher angle. It is indicating a linear increase in the lattice parameter upon increasing magnesium content in nickel ferrite. The larger ionic radii of Mg^{2+} to that of Ni^{2+} and Fe^{3+} results an increase in the lattice parameter. The average crystalline size (D in nm) was calculated from the XRD peak broadening of (311) peak by using Debye-Scherrer's relation

$$D_{hkl} \text{ (nm)} = \frac{k\lambda}{\beta \, Cos \, \theta} \qquad (1)$$

where, k= 0.9 is the Scherrer's constant, λ = 1.540562 Å and β (in radian) is the full width of half maxima (FWHM) of the diffraction peak at an angle θ. The (311) peak has been chosen for calculation as the most intense peak. The variation of lattice parameters and average crystalline sizes with concentration of magnesium are given in Table-1.
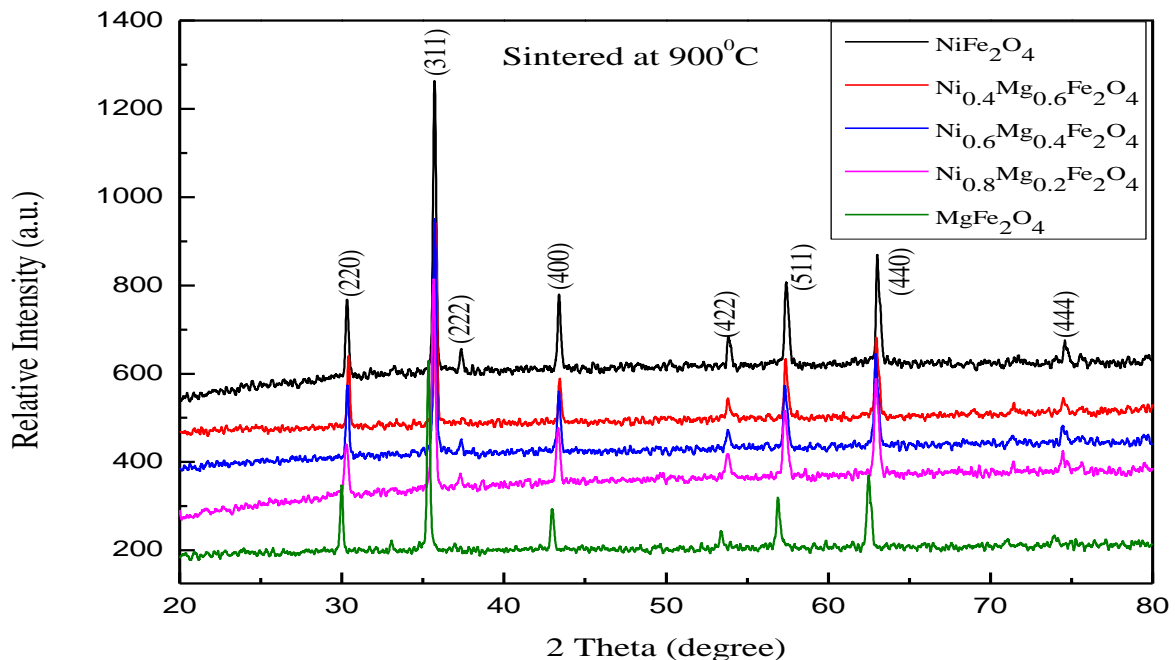

Fig. 2: XRD pattern of Mg substituted $NiFe_2O_4$ sintered at 900^0C

TABLE-1: VARIATION OF LATTICE PARAMETER, DENSITY AND CRYSTALLITE SIZE WITH CONCENTRATION MAGNESIUM (MOL%).

Composition (mol %)	Lattice Parameter (Å)	Experimental Density (gm/cm^3)		Crystallite Size (nm)
		900^0C	700^0C	
$NiFe_2O_4$	8.3297	2.79	---	36.9
$Ni_{0.4}Mg_{0.6}Fe_2O_4$	8.3161	2.51	2.62	40.3
$Ni_{0.6}Mg_{0.4}Fe_2O_4$	8.3270	2.68	2.70	40.1
$Ni_{0.8}Mg_{0.2}Fe_2O_4$	8.3433	2.90	2.62	32.7
$MgFe_2O_4$	8.4147	2.46	---	39.7

3. RAMAN ANALYSIS:

The Raman spectra were recorded by STR-500 Micro-Raman spectrometer equipment at the room temperature for different sintering temperature of the pellets. The recorded Raman spectrums are given in the figure 3 shows Raman spectra for pure $NiFe_2O_4$ and $MgFe_2O_4$ and its solid solutions i.e. Mg substituted $NiFe_2O_4$ of the type $Ni_{1-x}Mg_xFe_2O_4$ (x = 0.2, 0.4, 0.6) prepared by the auto-combustion method. The spinel ferrites have cubic structure belonging to space

group Fd3m (No.227, Z=8). In this structure the tetrahedral A-sites (8A) are occupied by half of the Fe^{3+} cations, whereas the rest of the Fe^{3+} and Ni^{2+} cations are distributed over the octahedral B-sites (16B). As a result, the factor group analysis predicts the following modes for the inverse spinel structure

$$A_{1g}(R) + E_g(R) + F_{1g} + 3F_{2g}(R) + 2A_{2u} + 2E_u +\ldots\ldots.$$

There are five Raman active modes ($A_{1g} + E_g + 3F_{2g}$) which are expected in the spinel structure. The five Raman modes are observed also which are shown in the following table for pure $NiFe_2O_4$ and $MgFe_2O_4$ along with $Mg_xNi_{1-x}Fe_2O_4$ (x = 0.2, 0.4, 0.6).
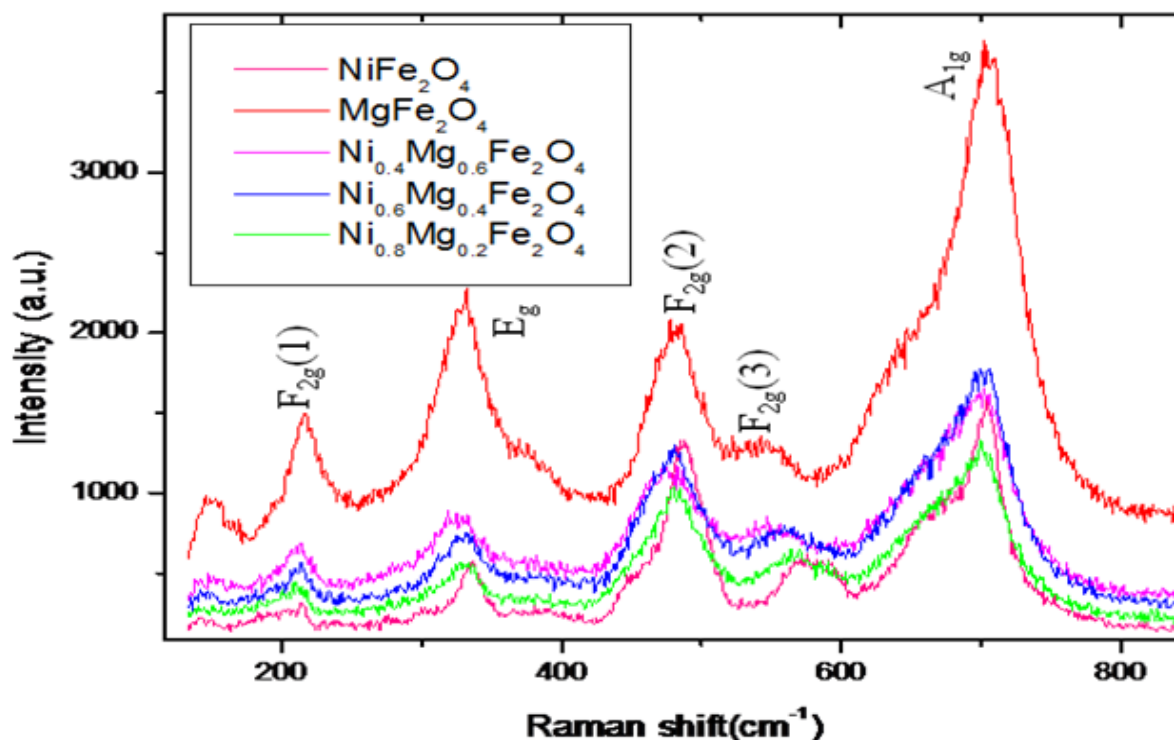

Fig. 3 Room temperature Raman spectra of Mg substituted Ni-ferrite

In $NiFe_2O_4$, due to differences in ionic radii of Ni and Fe ions, the Fe/Ni–O bond distance shows a considerable distribution. This means that the local structure in the two cases is different and the Raman spectrum, being a local structure-sensitive tool, detects these changes very effectively. This distribution in bond distances probably results in the doublet-like structure in $NiFe_2O_4$. The A_{1g} mode is due to symmetric stretching of oxygen atoms along Fe-O (and Ni-O) bonds in the tetrahedral coordination. E_g is due to symmetric bending of oxygen with respect to the metal ion and $F_{2g}(3)$ is caused by asymmetric bending of oxygen. $F_{2g}(2)$ is due to asymmetric stretching of Fe (Ni) and O. $F_{2g}(2)$ and $F_{2g}(3)$ correspond to the vibrations of octahedral group. $F_{2g}(1)$ is due to translational movement of the tetrahedron (metal ion at tetrahedral site together with four oxygen atoms). There is a negligible displacement of metal atoms in modes A_{1g}, E_g and $F_{2g}(3)$ [8]. Since the Raman peaks over the region 620 – 720 cm^{-1} reflect the nature of the tetrahedral in ferrites, while those in the 450 – 620 cm^{-1} region reflect the octahedral; this clearly indicates a high degree of disorder in cations distribution in the octahedral sites in $NiFe_2O_4$ and $MgFe_2O_4$ [9,10].

4. FTIR ANALYSIS:

The IR spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. FT-IR analysis was used to identify unknown materials as well as to determine the quality or consistency of a sample and the amount of components in a mixture. Figure -4 shows the recorded spectra in 400 to 800 cm^{-1} range for Ni-Mg ferrite system. The inspection of the spectra shows a narrow absorption band and it is due to the fact for these classes of compound, the absorption in that range is not restricted but occurs in spectra of most metallic oxide [11]. The reasons for origin of these bands are due to lattice vibrations of the oxygen ions against the cations. A gradual increase in absorption at higher frequency is observed due to electronic transitions.
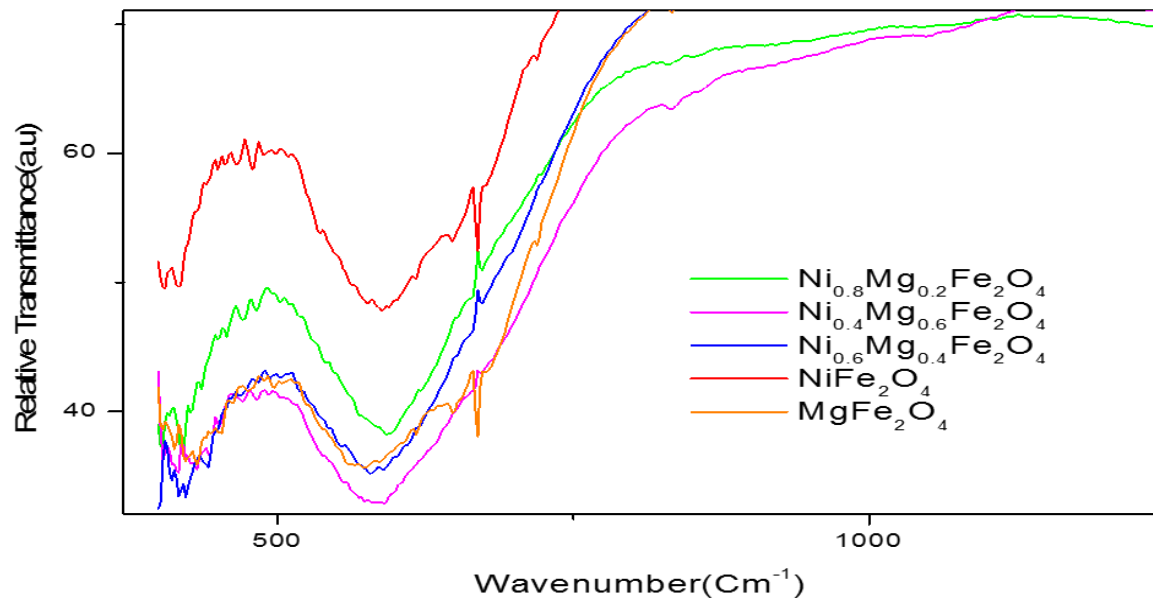
Fig.4 FTIR spectra of Mg doped NiFe$_2$O$_4$

The spectrum elucidates the position of the ions in the crystal structure and their vibrational modes which represents the various ordering position on the structural properties of the synthesized compound.

In order to explain the spectra we consider two ranges of the absorption bands 400 to 1000 cm^{-1} and 1000 to 4000 cm^{-1}. In the range 400 to 1000 cm^{-1}, two strong prominent absorption bands ν_1 and ν_2 around 417 and 590 cm^{-1} are observed. The high frequency band ν_1 around 590 cm^{-1} is attributed to that of tetrahedral (A) site and the low frequency band ν_2 around 417 cm^{-1} corresponding to octahedral (B) site which are indicative of the formation of spinel ferrites structure. The bonds are attributed to the stretching vibration due to interaction between oxygen and the cations in tetrahedral and octahedral sites.

The difference between ν_1 and ν_2 is due to the changes in Fe^{3+}- O^{2-} bond length at the octahedral and tetrahedral sites. It is seen that the normal mode of vibration of the tetrahedral cluster is higher than of octahedral cluster. This may be due to the shorter bond length of tetrahedral cluster than the octahedral cluster.

From the FT-IR spectra, it is observed that the peak shifting in ν_1 band is higher than that of the ν_2 band with increasing doping concentration. So, only the ν_1 is perturbed with the incorporation of Mg ions in Ni-ferrite. Significant changes were observed in the ν_1 band (tetrahedral site). The behaviour is attributed to the stretching of Fe-O bonds on substitution of Mg ions. FT-IR results clearly indicate that Mg ions occupy the tetrahedral site in the NiFe$_2$O$_4$ nano particles.

In the range of 1000 – 4000 cm^{-1}, vibration of NO$_3^-$ and moisture were observed. The broad band between about 2350 and 3350 cm^{-1} in the spectrum of the Ni-Mg ferrite is caused by O-H and C-H stretching vibration for water and starch molecules. The intensive band at 1605 cm^{-1} is due to O-H stretching vibration interacting through H bonds. Anti-symmetric and symmetric N-O vibration from NO$_3^-$ ions appears at 1385 cm^{-1}.

4.   CONCLUSIONS

The present work reports synthesis of single phase Ni & Mg ferrites and its solid solutions i.e. Mg doped NiFe$_2$O$_4$ of the type Ni$_{1-x}$Mg$_x$Fe$_2$O$_4$ prepared by the auto-combustion method. The synthesized Ni-Mg ferrite at different magnesium concentration is characterization through XRD, Raman and FTIR. In the study, it has been observed that due to continuous shrinkage and densification of material, during sintering estimated bulk densities of the materials increases from 2.62 to 2.81 gm/cm^3 (for 700^{0}C) and from 2.51 to 2.90 gm/cm^3(for 900^{0}C). The crystalline size varies from 50.5 nm to51.6 nm. The Raman spectra shows five Raman active modes (A$_{1g}$ + E$_g$ + 3F$_{2g}$) which are expected in the spinel structure and Raman spectra has a very good agreement with reported data. In the range 400 to 1000 cm^{-1}, two strong prominent absorption bands ν_1 and ν_2 around 417 and 590 cm^{-1} are observed. The high frequency band ν_1 around 590 cm^{-1} is attributed to that of tetrahedral (A) site and the low frequency band ν_2 around 417 cm^{-1} corresponding to octahedral (B) site which indicative the formation of spinel ferrites structure. FTIR spectra have a good agreement with the earlier reported literature.

ACKNOWLEDGEMENTS

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