

EFFECT OF SAMARIUM SUBSTITUTION ON THE STRUCTURAL, MORPHOLOGICAL AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE NICKEL FERRITES

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ABSTRACT

The compositions of samarium substituted nickel ferrites having a general formula $NiSmFe_2O_4$ ($Sm = 0.0, 0.025, 0.050, 0.075, 0.1$) were synthesized by the sol-gel route. The samples thus obtained were analysed for their structural, morphological magnetic properties as a function of increasing Sm content. Nickel ferrite being one of the most important inverse spinel ferrite has a wide range of applications especially as microwave devices. Samarium, a rare earth metal, having an electronic configuration $4f^6 6s^2$ is used as a dopant along with nickel ferrite and the consequent modifications in the properties are characterized accordingly. The structural analysis of all the as prepared samples was done using the XRD and FTIR studies which confirmed the formation of the single phase inverse spinel cubic structure. The crystallinity and the crystal size were found to decrease with increasing samarium content. The surface morphology of all the samples were determined using the SEM analysis. Substituting samarium has a remarkable influence on the magnetic properties, which is confirmed from the magnetic measurements recorded at room temperature.

Keywords: Sol-gel, Samarium, FTIR, XRD, SEM

I. INTRODUCTION

Spinel ferrites nano crystallites attract special attention due to their wide range of applications and play a predominant role in the microwave components like isolators, phase shifters and circulators. Nickel ferrite has been widely investigated due to its extreme chemical stability, reasonable saturation magnetisation, and very high mechanical hardness. These characteristics make it potentially applicable in magnetic drug targeting, magnetic data storage, magnetic refrigeration and bio-sensors [1-7]. The unit cell of the inverse spinel ferrites comprises of 32 oxygen atoms located in a cubic closed-packed structure, distributed in the tetrahedral (A) sites and octahedral (B) sites

Ferrite nanoparticles possess good dielectric and magnetic properties. These properties are influenced by the choice of the cations and also the manner in which they are spread among the tetrahedral and octahedral sites in the inverse spinel lattice. The sintering temperature, doping additives, preparation conditions, chemical composition and the method of preparation are found to affect the properties of the nanoferrites [8]. There are several physical and chemical methods available such as combustion technique, co-precipitation, sol-gel, spray

pyrolysis, high energy milling for fabricating chemically and stoichiometrically pure nanoferrites [9]. Among the existing synthesis techniques, the sol-gel method has drawn much attraction owing to its inherent advantages such as homogeneity in the reactant distribution and low processing temperature. The end products of the method exhibit a very narrow size distribution and also have a uniform shape [10].

The substitution of the rare earth ions into the inverse spinal lattice induces a strain due to which the electrical and magnetic properties are significantly modified [11,12]. Rashad et al [13] reported a change in the magnetic properties of samarium doped cobalt ferrite nanoparticles synthesized by the citrate precursor route. The results reported a decrease in the value of the saturation magnetization and coercivity upon the addition of Sm^{3+} ions. Pay et al [14] indicated that the substitution of gadolinium into CoFe_2O_4 nanoparticles showed an increasing trend with respect to the crystallite size. The results reported by Guo et al [15] suggested that the substitution of samarium into nickel ferrite tends to increase the lattice parameter and decrease the crystallite size of the material. Tahar et al [16] investigated the effect of gadolinium and samarium doping on the magnetic properties of cobalt ferrite nanoparticles synthesized using forced hydrolysis in polyol and concluded that there was a slight increase in the crystallite size during the rare earth substitution. In this paper we report the effects of Sm^{3+} substitution on the structural and magnetic properties of nickel ferrite nanoparticles synthesized by the sol-gel route.

II. EXPERIMENTAL

Samarium substituted nickel ferrite nanoparticles ($\text{Sm}=0.0, 0.025, 0.050, 0.075, 0.1$) were synthesized using the sol-gel technique. Stoichiometric ratio of nickel nitrate hexahydrate, ferric nitrate hexahydrate, samarium nitrate hexahydrate (AR grade MERCK) were dissolved in a medium of ethylene glycol using a magnetic stirrer. The solution thus obtained was then subjected to heating at 60°C for 3 hours. The solution, which is now transformed into a wet gel comprising of all the metal nitrates is further dried in a furnace at 120°C where auto combustion occurs and a highly voluminous fluffy end product is obtained. The powder so obtained is ground well and then sintered for 4 hours in a muffle furnace maintained at 800°C .

III. RESULTS AND DISCUSSION

3.1 Structural analysis

The X-ray diffraction (XRD) pattern of the as prepared samples of samarium substituted nickel ferrite ($\text{Sm}=0.0, 0.025, 0.050, 0.075, 0.1$) are as shown in the Fig: 1. The presence of the (220), (311), (222), (400), (511) and (440) major lattice planes in the XRD spectra of the synthesized samples shows the formation of the inverse spinal cubic structure and belongs to the $\text{Fd}3\text{m}$ space group. The spectrum is found to possess well defined intense and sharp peaks. The peaks so obtained are found to be in good agreement with the standard data (JCPDS card number 074-2081). The absence of any extra peaks indicates the fact that the samples have acquired the single phase inverse cubic spinal structure thereby indicating the fact that the samarium ions have completely dissolved into the spinal lattice of nickel ferrite. As seen from the spectrum, the intensity of the prominent peak increased with an increase in Sm concentration, which indicated that solid solubility of

samarium was very small. The calculated values of the lattice constant tabulated in Table:1 show that there has been no structural distortion for the various dopant ratios. The fact that samarium goes as a substitution into the spinal lattice is evident from the absence of any extra peaks in the XRD spectrum. The presence of broad peaks in the spectrum of the synthesized nano particles can be associated with the small crystallite size. Nickel ferrite belongs to the inverse spinal class of ferrites possessing a formula represented as $[\text{Fe}^{3+}]_{\text{tet}} [\text{A}^{2+}, \text{Fe}^{3+}]_{\text{oct}} \text{O}_4^{2-}$ ($\text{A} = \text{Ni}$), where tet and oct represent the tetrahedral (A site) octahedral (B site) ions respectively. The nickel ions (Ni^{2+}) and half of the iron ions (Fe^{3+}) occupy the B site and the A site is occupied by the remaining (Fe^{3+}) ions. Thus it can be inferred that the presence of electrons and holes in the B site is due to the existence of Ni and Fe ions. As seen from Table 1, the invariance of the lattice constant values for the various dopant ratios, establishes the fact that the Sm^{3+} ions in general have a tendency of replacing the Fe^{3+} ions in the octahedral sites. The average grain size of the particles, calculated using the Scherer's equation using the full width half maximum (FWHM) values of the (311) reflection indicates a decrease in the crystallite size as the samarium content increases.

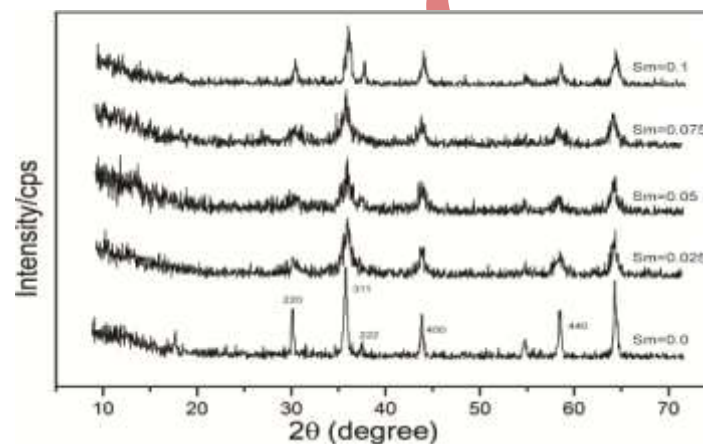


Fig:1 XRD pattern of nickel samarium ferrite for various concentration of Sm

Table:1 Structural parameters of samarium doped nickel ferrite for various ratios of Sm

Concentration of Sm (m mol)	Crystallite size (nm)	Lattice Constant (Å)	Measured density (ρ_x) (gm/cm^3)
0.00	17.02	8.306	2.450
0.025	15.10	8.309	2.483
0.050	14.41	8.309	2.485
0.075	13.00	8.319	2.488
0.1	12.20	8.309	2.490

3.2 Morphological study: (SEM)

The SEM images of nickel samarium ferrite for ($\text{Sm}=0.0, 0.025, 0.050, 0.075, \text{ and } 0.1$) are as shown in the Fig: 2a. The specimens exhibit a homogenous grain distribution. It is difficult to calculate the accurate grain size as the exact grain boundaries cannot be distinctly focused. The agglomeration of the particles is usually what leads to the constituent structure which is of the order of few nanometres. The particles are found to be spherical and the cohesion of the grains is mainly because of the magnetic attraction. The composition of the sample was

verified using the EDS spectrum and is as indicated in Fig: 2b. The spectrum shows the presence of Sm, Ni, Fe and O in the sample and no other appreciable impurities were detected, which indicated the purity of the sample. Moreover the ratio of the detected elements matched the chemical formula for the respective compositions. Hence the sol-gel method has indeed produced fairly good ferrites.

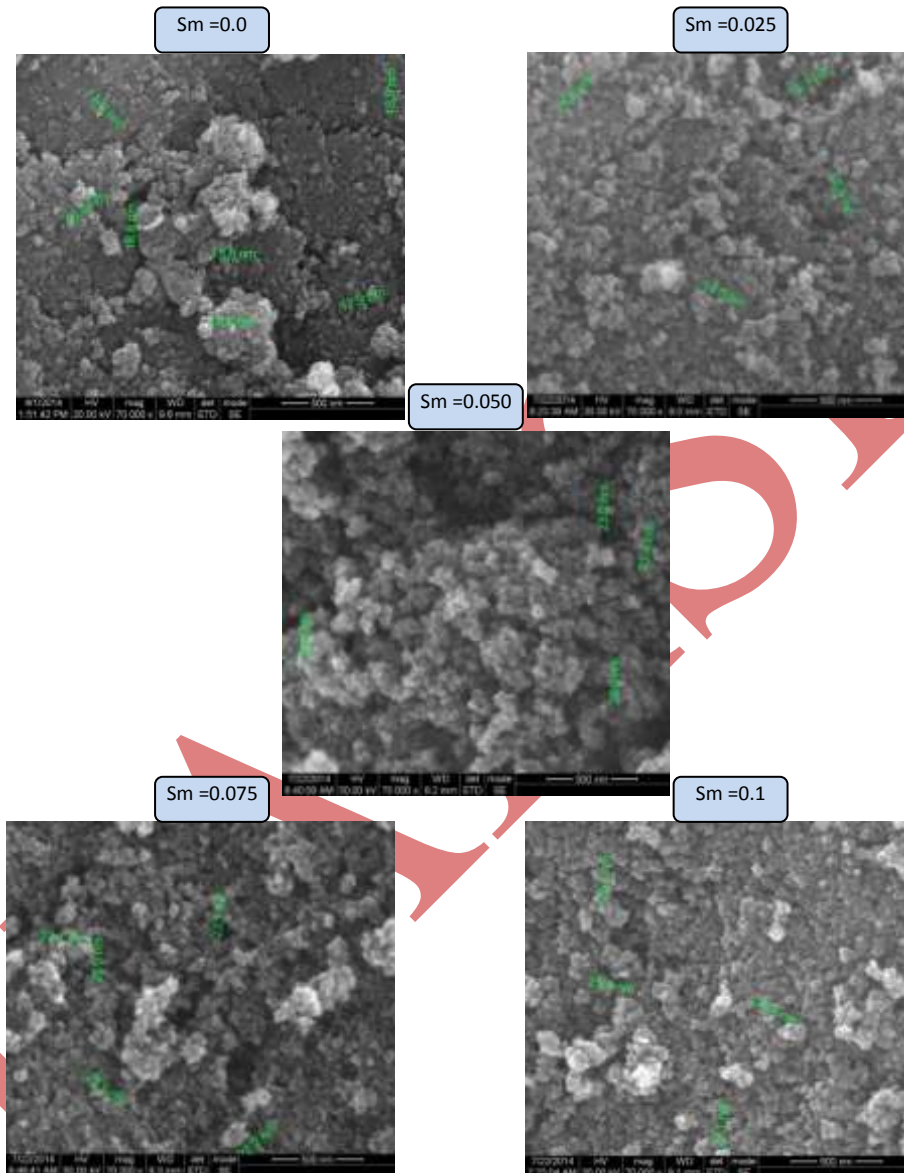
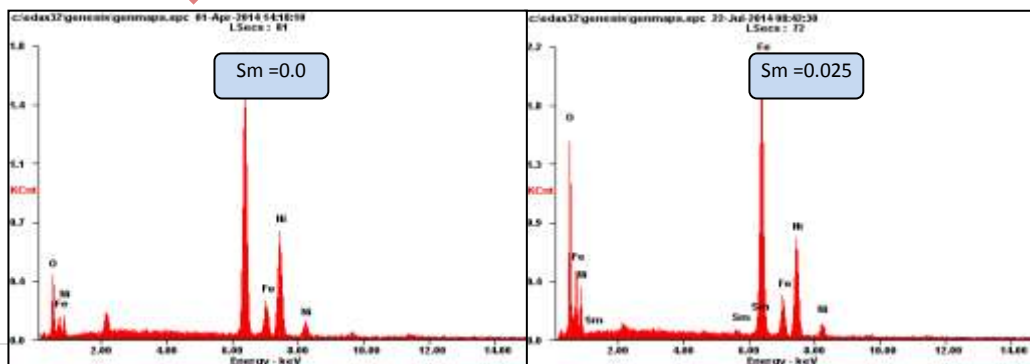


Fig: 2a SEM images of nickel ferrite nanocrystals for various concentrations of samarium.



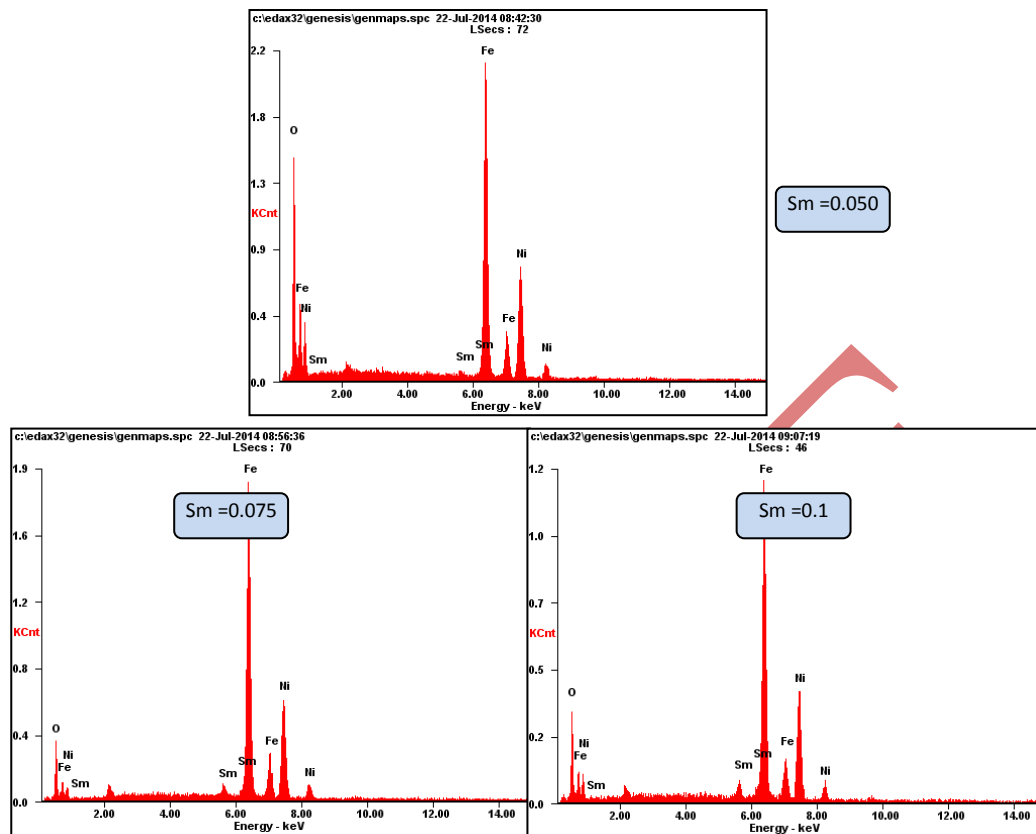


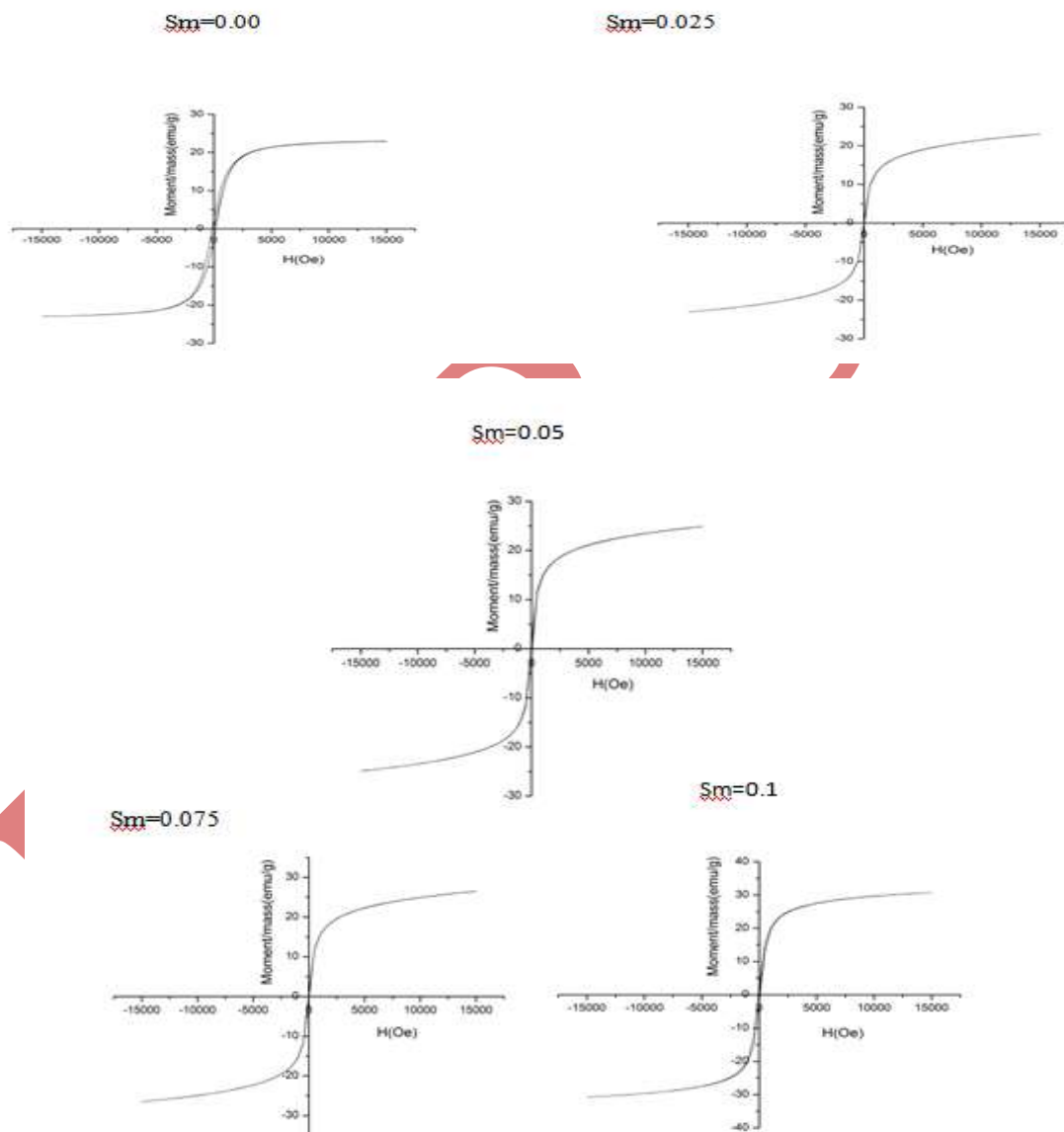
Fig: 2b EDAX spectrum of Sm doped Nickel Ferrite

3.3 Magnetic study

The various magnetic parameters such as saturation magnetization, coercivity and retentivity was measured using a vibrating sample magnetometer and are as tabulated in Table2. The values were all recorded at room temperature up to a maximum field of 20 KOe. The magnetic hysteresis loops for the samarium substituted nickel ferrites are as shown in the Fig:3. The value of the saturation magnetization for pure nickel ferrite is 22.98 emu/g at room temperature. This value is very much less compared to the bulk value (56emu/gm). This low value can be explained based on the core shell model which clarifies that, it is the finite size effects of the nano crystallites that lead to the canting or non collinearity of the spins present on their surface which may be due to the broken super exchange bonds and hence reduce the magnetization [24, 25]. These effects are predominant in ferrites owing to the presence of the super exchange ion interactions. These effects are found to be more pronounced in the case of smaller ferrites having a larger surface to volume ratio.

According to Neel's theory of ferromagnetism, the cations present on different sub lattices in spinal structure, have magnetic moments that are oppositely aligned. The net magnetic moment of the inverse spinal ferrites mainly depends on the number of magnetic ions that occupy the tetrahedral and octahedral sites. In general the magnetic moments of the rare earth ions are usually influenced by the 4f electrons which are in turn characterized by lower temperature, usually less than 40 K [26]. The magnetization in general, is expected to be proportional to the effective magnetic moment of the samarium ions. The replacement of Fe^{3+} ions by Sm^{3+} ions in the octahedral site increases the $Fe^{3+} - Fe^{3+}$ interactions. Hence the magnetization is increased due to the

strong Fe^{3+} - Fe^{3+} interactions. As seen from values listed in the Table 2, the substitution of samarium can be considered to be a magnetic substitution which in turn increases the exchange interaction involved between the octahedral and tetrahedral sites. This results in the increase in magnetization. Substitution of Sm^{3+} ions has a direct bearing on the coercivity. Recent researches suggest that coercivity was found to be affected by factors such as micro strain, size distribution, magneto crystallinity, magnetic domain size and anisotropy [27, 28]. In the multi domain regime, the coercivity was found to be inversely proportional to the particle size [27]. A decrease in the particle size induces a strain in the motion of the domain walls and thereby increases the coercivity.



This fact can be verified from the particle size and coercivity values listed in Table 1. These results suggest that the properties of samarium can be fine tuned for specific applications. The remnant ratio, calculated using the formula $R=Mr/Ms$ gives an indication regarding the ease with which the direction of magnetization reorients itself in the direction of the nearest possible axis of magnetization, once the magnetic field is removed. The

values of remnant ratio of the synthesized samples are in the range 0.01 to 0.09, thereby indicating a decrease in the anisotropy of the crystal lattice [30].

Table:2 Magnetic parameters of samarium doped nickel ferrite for various ratios of Sm

Concentration of Sm	Saturation magnetization(Ms) (emu/gm)	Coercivity (G)	Retentivity (emu/gm)	Remnant ratio (R)
0.00	22.98	20.849	0.4232	0.0184
0.025	23.07	43.294	0.4916	0.0213
0.050	24.88	52.516	1.33	0.0534
0.075	26.41	65.741	2.346	0.0888
0.1	30.73	76.191	2.80	0.0911

3.4 FTIR studies

The FTIR analysis is considered to be a very important tool which is used to investigate the inverse spinel phase formation in addition to the XRD analysis. The FTIR spectra of all the investigated nickel samarium samples are as shown the Fig: 4. In the 1000-300 cm^{-1} wave number range usually two main metal-oxygen broad bands are visible in the IR spectra of all the spinel in particular the ferrites. The higher band (γ_1), usually seen between 600-400 cm^{-1} is due to the stretching vibrations in the tetrahedral metal oxygen bond. The IR vibrational frequencies are found to be in good agreement with the values reported (Montemayor et al 2007; Priyadharsini et al 2009). The prominent peaks in the range 3400-1600 cm^{-1} can be associated with the H-O-H bending vibrations and the stretching modes of the free or absorbed water. The presence of traces of CO_2 is indicated by the occurrence of the band around 2300 cm^{-1} . The band around 1400 cm^{-1} can be attributed to the antisymmetric NO-stretching vibrations arising from the residual nitrates present in the sample (Priyadharsini et al 2009). As seen from the spectra of the samples, this band appears to be a bit weak; thereby indicating the purity of the sample synthesized using the sol-gel technique.

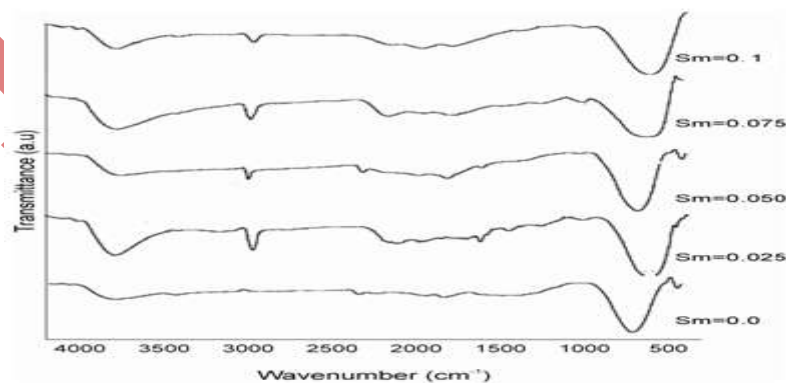


Fig:4 FTIR images of Sm doped Nickel Ferrite

IV CONCLUSION

The present study was initiated to produce samarium doped nickel nano crystallites for the purpose of microwave applications. Nickel Samarium Ferrites were successfully prepared by the sol-gel process and they were sintered at 800°C for 4 hours. The X-ray diffraction analysis showed the formation of single phase inverse spinel structure for NiSmFe₂O₄. The gradual increase in the Sm content brought about a decrease in the crystallite size followed by a corresponding increase in the saturation magnetisation, retentivity and coercivity. Materials with high coercivity are usually called magnetically hard materials, and they are used to make permanent magnets which find their application in electric motors, magnetic recording media and magnetic separation. Thus the samarium substituted nickel nano ferrites have a high potential as compared to normal ferrites for various applications like inductor cores, transformers, recording heads, magnetic shielding and microwave devices. The sintering temperature and sintering time plays a vital role in determining the particle size. It is also worthy to note that there has been no structural distortion for the different compositions reported in the present study.

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