A study of the structural and electrical properties of $Ni_{1-x} Co_x Fe_2O_4$ ferrites

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Abstract

Ferrite with general formula $Ni_{1-x} Co_x Fe_2O_4$ (where x=0.0.1,0.3,0.5,0.7, and 0.9), were prepared by standard ceramic technique. The main cubic spinel structure phase for all samples was confirmed by x-ray diffraction patterns. The lattice parameter results were (8.256-8.299 $°A$). Generally, x -ray density increased with the addition of Cobalt and showed value between (5.452-5.538gm/cm^3). Atomic Force Microscopy (AFM) showed that the average grain size and surface roughness was decreasing with the increasing cobalt concentration. Scanning Electron Microscopy images show that grains had an irregular distribution and irregular shape. The A.C conductivity was found to increase with the frequency and the addition of Cobalt, D.C conductivity was found to increase with temperature due to decreases in resistivity. Dielectric constants were noticed to decrease with frequency and Co addition. The Hall coefficient was found to be positive. This demonstrates that the majority of charge carriers are p-type, suggesting that the mechanism of conduction is predominantly caused by hopping of holes.

دراسة الخواص التركيبية والكهربائية لفرايت $Ni_{1-x} Co_x Fe_2O_4$

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الخلاصة

تم تحضير أحد انواع الفيرايت ذو الصيغة التركيبية العامة ($Ni_{1-x} Co_x Fe_2O_4$) حيث أن x=0.0.1,0.3,0.5,0.7, (0.9), استخدمت بالتحضير الطريقة القياسية في معالجه المساحيق. طور التركيب الرئيسي لكل العينات السبينل المكعب الذي أكد بأنماط انحراف الأشعة السينية. ثابت الشبيكة الذي يتراوح قيمته بين ($°A$8.256-8.299). بصوره عامه الكثافة المقاسة بالأشعة السينية تزداد مع زيادة تركيز Co حيث تتراوح قيمتها بين (5.452-5.538gm/cm^3). أن استعمال مجهر القوة الذري AFM يبين بأن معدل الحجم الحبيبي ومسامية السطح تقل كلما زاد تركيزCo. صورة المجهر الالكتروني بينت بأن الحبيبات غير منتظمة في التوزيع والشكل. التوصيلية الكهربائية تزداد بزيادة تركيزCo وبزيادة التردد. التوصيلية المعتمدة على درجه الحرارة وجد بأنها تزداد بزيادة درجة الحرارة. ثوابت العزل الكهربائية $\varepsilon_1, \varepsilon_2$ تنخفض مع أضافه Co والتردد. معامل هول بين بأن حاملات الشحنة الأغلبية تكون من نوع p, تم الاقتراح بأن أمكانية التوصيل بالدرجة الأولى سببها قفز الفجوات.

Introduction

Ferrites form a very good class of electrical materials due to their high resistivity and low loss behavior, and thus have vast technological applications over a wide range of frequencies. Ferrites are preferred in the field of electronics and telecommunication industry because of their novel electrical properties which makes them useful in radiofrequency circuits, high quality filters, rod antennas, transformer cores, read/ write

heads for high digital tapes and other devices[1].

One of the most important members of spinel Ferrite systems is the nickel ferrite ($NiFe_2O_4$), which is a soft magnetic material with an inverse spinel structure[2]. $NiFe_2O_4$ is a suitable material for microwave applications. It is noted for its high Curie temperature and good temperature stability of saturation magnetization[3].

The crystal structure is face center cubic with the unit cell containing $32O^{2-}$, $8Ni^{2+}$ and $16 Fe^{3+}$ ions. The oxygen ions form 64 tetrahedral sites and 32 octahedral sites, where 24 cations are distributed. The eight Ni^{2+} and eight Fe^{3+} cations occupy half of the octahedral sites and the other eight Fe^{3+} ions occupy eight tetrahedral sites. Ferrimagnetic property of the material arises from magnetic moments ofanti-parallel spins between Fe^{3+} ions at tetrahedral sitesand Ni^{2+} and Fe^{3+} ions at octahedral sites[4].

Several investigations on structure and electrical properties of Ni- modified ferrites have been reported in literature. Most reports, however, describe the obtaining and characterization of bulks through several processing routes[2]. This paper investigates the structural and electrical properties of Ni-ferrites bulk ceramics doped with Co.

 Experiment

Ferrites with general formula Ni_{1-x} Co_x Fe_2O_4 (where x=0.0.1,0.3,0.5,0.7, and 0.9), were prepared by standard ceramic technique. Powders of Fe_2O_3, NiO and Co_2O_3 were weighed and mixed according to the general composition formula by moles ratio. The powders were mixed and blended homogenously through dry mixing using a ball mill. After powder mixture, they were pressed using a die with diameter (1.8 cm) to produce specimens in a pellet shape. The pressing load used was (3 ton) and the specimen held for 1min under pressure using a hydraulic press (of a

maximum load 15 ton). The specimens were then sintered at 900C° for two hours and then left to cool down to room temperature. The spinel structure was characterized by x-ray diffraction carried out using Shimadzu XRD-6000 diffractometer with Cu kα radiation (λ=1.5405 °A) at scanning speed 5 deg/min. The Atomic Force Microscopy(AFM) studies were performed on Angstrom Advanced Inc, 2008,USA. Scanning Electron Microscopy (SEM) studies were performed using (JOEI JSM-6400) with magnification 589 and 477. The AC measurements were performed using Agilent impendence analyzer 4294 A. D.C conductivity measurements were done using sensitive digital electrometer type keithley (616) and electrical oven. The Hall Effect measurements were performed using four-point probe on Ecopia HMS-3000.

Result and discussion
1. X-ray Diffraction
 Figure 1shows XRD patterns of $Ni_{1-x} Co_x$ Fe_2O_4 where (x=0,0.1,0.3,0.5,0.7 and0.9) doped Co prepared by standard ceramic technique. The patterns were compared with standard data (96-230-0296) and the formation of single phase cubic spinel structure in all specimens was confirmed with the appearance of secondary phases. The component $Ni_{1-x} Co_x$ Fe_2O_4 were multi phases. The correspond miller indices (311) referred to the nickel ferrite while the other one (311) referred to the ferric oxide.
 The lattice parameter (a) of individual composition for cubic structure was calculated. The calculated lattice constant (a) is seen to increase with an increase in cobalt content. A small change in lattice parameter may be related to the oxidation states and distribution of cations among tetrahedral (A) and octahedral (B) sites of the spinel structure, the probability that the Co^{+3} ions occupy the (A) sites of Fe^{+3} ions must be excluded, since the

tetrahedral sites too small to be occupied by the large Co^{+3} ions which have large ionic radius. However the probability of occupancy of the octahedral (B) sites by the cobalt ions increases with decreasing of the R ionic radius [2,5]. X-ray densities generally increase with Co addition as shown in Table1. The x-ray density (d_x)

determined as follows:-

$$dx = (ZM/Na^3) \qquad (1)$$

Where Z is the number of molecules per unit cell(Z=8), M is the molecular weight, the value of M varies with x concentrations and ($N=6.022*10^{23}$ /mol^{-1}) is avagadro's number[6].

Table 1: Effect of Co content on lattice parameter(a), density of unit cell (dx), molecular weight(M) and unit cell volume(V).

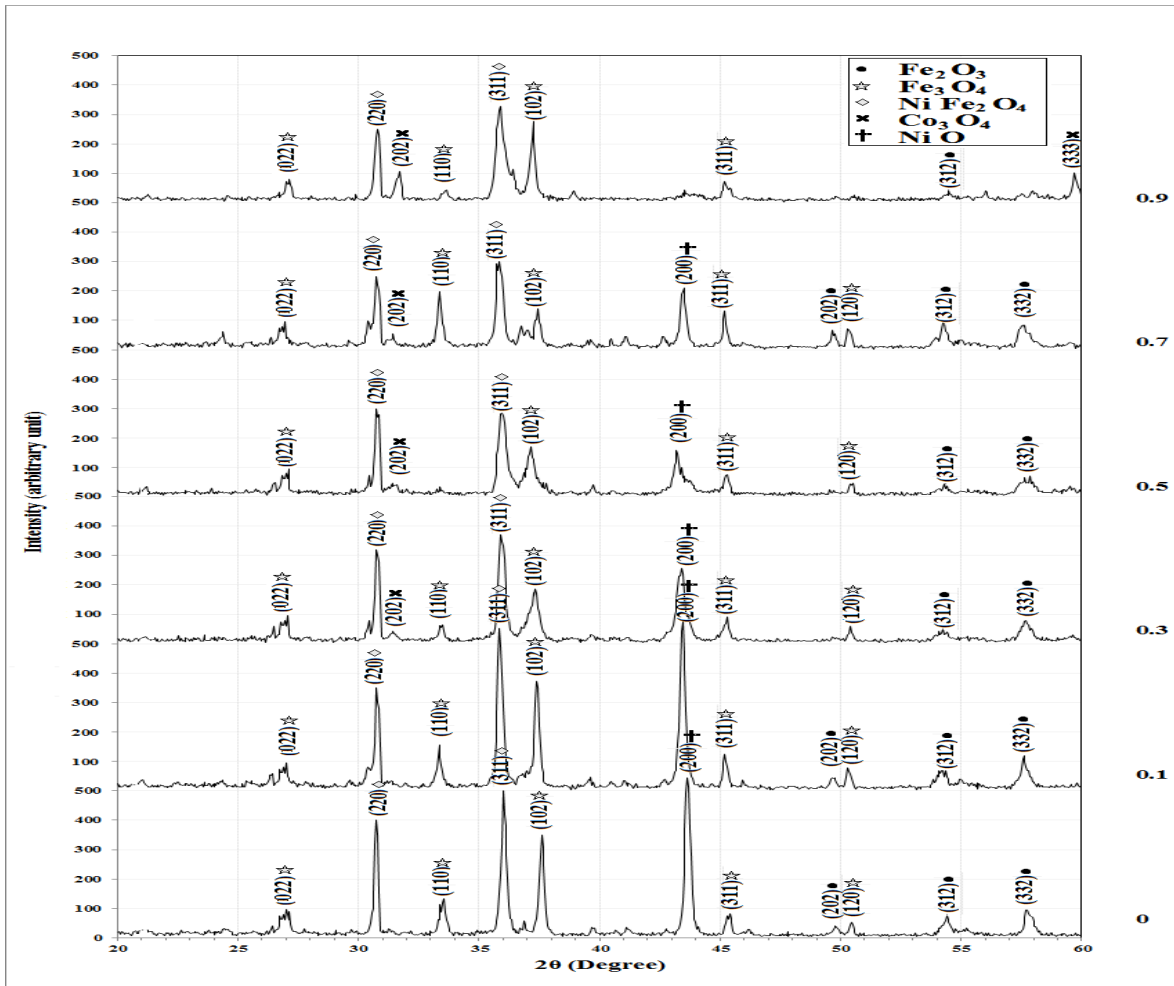| Co content	d_{hkl} (A)	(hkl)	M (gm/mol)	a (A°)	V(cm³)	d_x(gm/cm³)
0	2.493	311	234.379	8.266	5.647*10⁻²²	5.513
0.1	2.502	311	234.402	8.296	5.709*10⁻²²	5.454
0.3	2.501	311	234.450	8.293	5.703*10⁻²²	5.461
0.5	2.496	311	234.498	8.276	5.668*10⁻²²	5.496
0.7	2.503	311	234.546	8.299	5.715*10⁻²²	5.452
0.9	2.490	311	234.594	8.256	5.627*10⁻²²	5.538

Fig.1: XRD spectra of bulk Ni$_{1-x}$ Co$_x$ Fe$_2$O$_4$ with different content of Co.

2. Atomic force microscopy (AFM)

Figs. 2 and 3 shows the AFM images for bulk $Ni_{1-x}Co_xFe_2O_4$ ferrites where (x=0.3 and 0.7) respectively. AFM pictures show that the all specimens have granular nature. The grain size and roughness as determined from AFM are given in Table 2. Both The grain size and surface roughness decreased with the increase in Co substitution, though the average grain size of x=0.3 and 0.7 from 113.87nm to 91.08nm, respectively as shown in Figs 2 and 3. On the other hand the average roughness decreases from 1.96 to 1.22nm for x=0.3and 0.7 respectively.
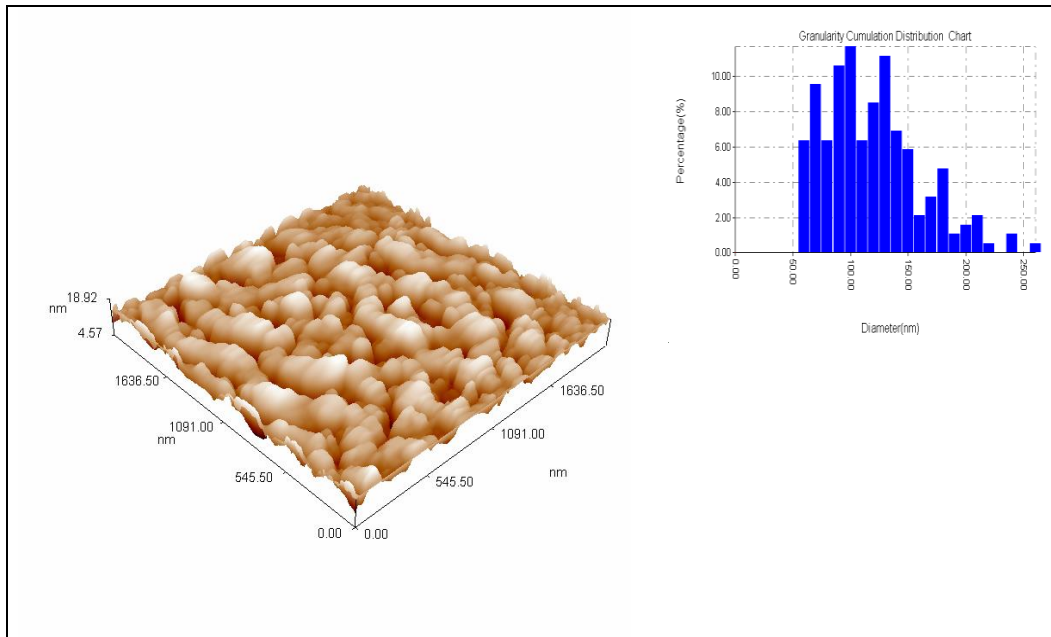

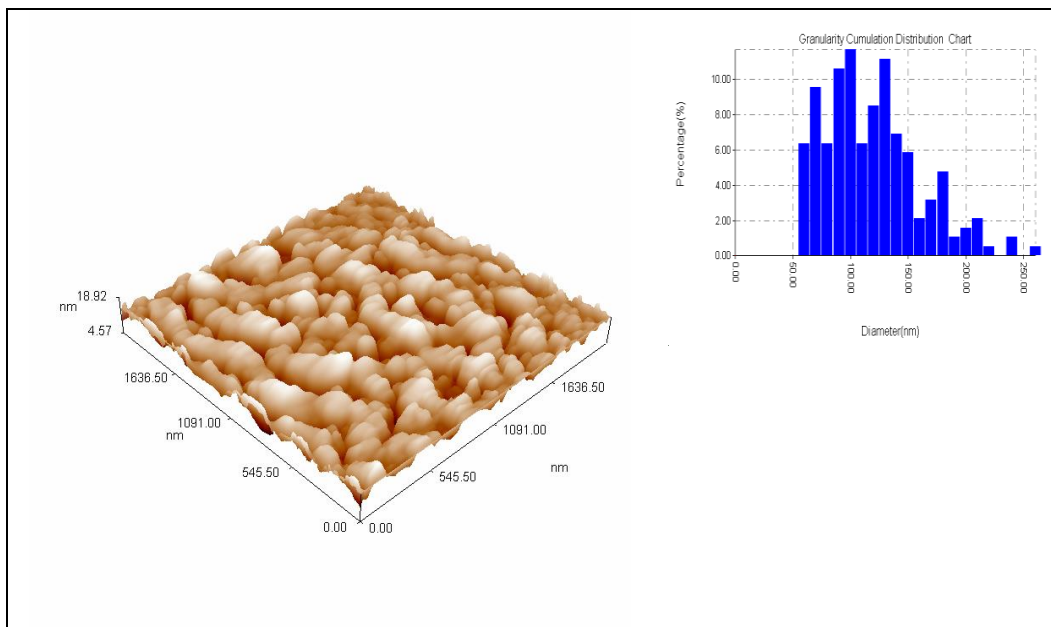*Fig.2 : AFM micrographs for the composition ($Ni_{0.7}Co_{0.3}Fe_2O_4$).*

Fig .3: AFM micrographs for the composition ($Ni_{o.3}Co_{0.7}Fe_2O_4$).

Table 2: Average grain size and average roughness for bulk $Ni_{1-x}Co_xFe_2O_4$ where x=0.3 and 0.7.

Co content	Ave. grain size (nm)	Ave. Roughness (nm)
0.3	113.87	1.96
0.7	91.08	1.22

3. Scanning electron microscopy(SEM)

In addition to atomic force microscopy, scanning electron microscopy was carried out to further characterize the topographical properties of the material. Fig. (4a and b) represents the SEM micrographs for bulk $Ni_{1-x}Co_xFe_2O_4$ where (x=0.3 and 0.7) respectively. The grains were observed as irregular distribution and irregular shape.

The images showed that the specimens were not closely packed and consist of several grains. It is obvious from Fig.(4a and b) that the cobalt addition increase had no major effect on the surface morphology of the ferrite.
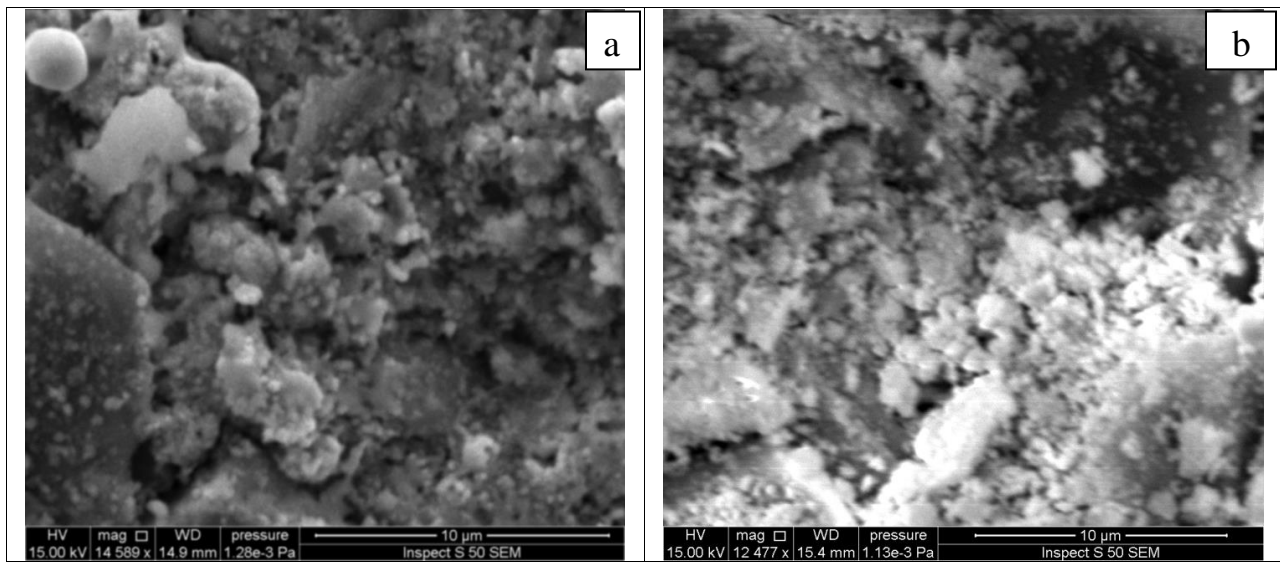

Fig.4: SEM images for a) $Ni_{0.7}Co_{0.3}Fe_2O_4$, b)$Ni_{0.3}Co_{0.7}Fe_2O_4$.

4. AC measurement

In this study, we report the A.C conductivity for bulk cobalt addition nickel ferrite ($Ni_{1-x}Co_xFe_2O_4$) where (x=0, 0.1, 0.3, 0.5, 0.7 and 0.9) of cobalt additions. The $\sigma_{a.c}(\omega)$ for all specimens was found to increases with increasing the frequency as shown in Fig. 5. In this case, $\sigma_{a.c}(\omega)$ is proportional to (ω^s) which means that $\sigma_{a.c}(\omega)$ dominates at higher frequency in the range (50kHz to 5MHz), for lower frequency in the range (50Hz to 50kHz) $\sigma_{a.c}(\omega)$ becomes independent of the frequency because D.C conductivity dominate in this frequency range.

The values of exponent (S) for bulk ($Ni_{1-x}Co_xFe_2O_4$) where (x=0,0.1,0.3,0.5,0.7 and (0.9) were estimated from the slope of the curves plotted between Ln $\sigma_{a.c}(\omega)$ versus Ln(ω) as shown in Fig.5 which found to be less than unity for all prepared specimens which corresponding to correlated barrier model. Fig. 6 shows the value of exponent (S) with different content of Co.
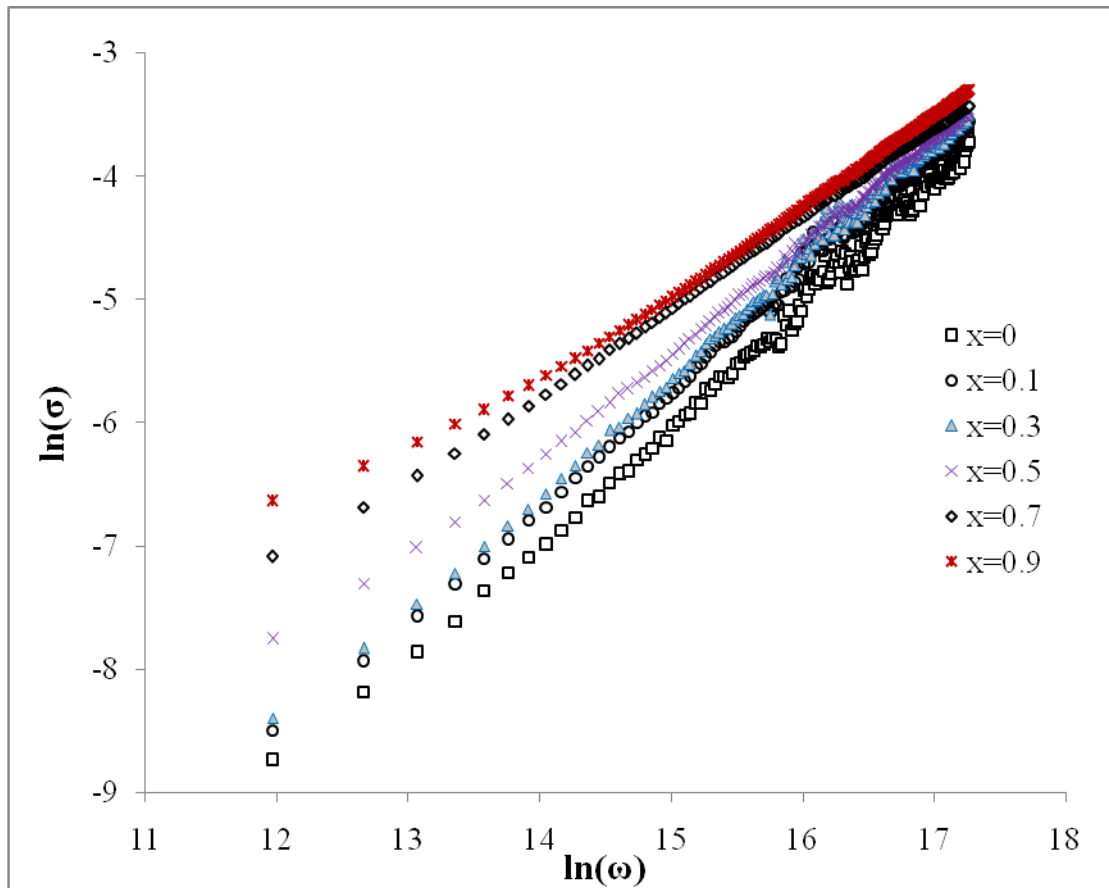
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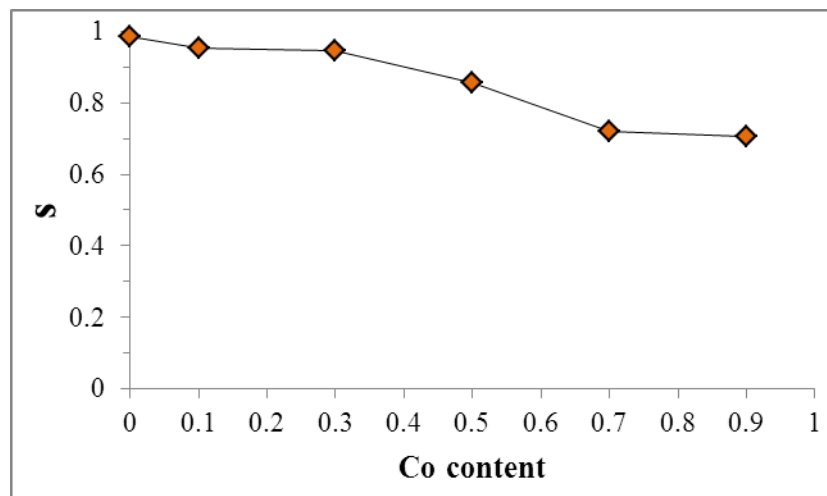*Fig.5: Effect of conductivity as a function of frequency.*

Fig .6: S- value as a function of different content of Co for bulk (Ni$_{1-x}$Co$_x$Fe$_2$O$_4$).

The electrical conduction is a thermally activated process and follows the Arrhenious law :-

$$\sigma_{ac} = \sigma_\circ \exp[-E_a /KT] \qquad (2)$$

Where σ_{ac} conductivity, $\sigma_\circ$ is pre exponential factor, E_a is the activation energy and K is Boltzman constant.

When a field is applied to a dielectric, the polarization of the dielectric takes place. The dielectric displacement found in a dielectric material when subjected to an alternating field (E) is not in phase. Hence the dielectric constant is a complex quantity and is expressed as:-

$$\varepsilon^* = \varepsilon_1 + i\varepsilon_2 \qquad (3)$$

where ε_1 is the real part of dielectric constant which can be calculated by the equation

$$\varepsilon_1 = C/C_o \qquad (4)$$

Where C is the capacitance and C_o is the free space capacitance

The dielectric constant (ε_1) is found to decrease sharply with increasing frequency for all samples as shown in Fig7. This is may be attributed to the dipole polarization i.e, the rotation of dipoles between two equivalent equilibrium positions is involved. It is the spontaneous alignment of dipoles in one of the equilibrium positions that give rise to nonlinear polarization behavior of this composition[7].
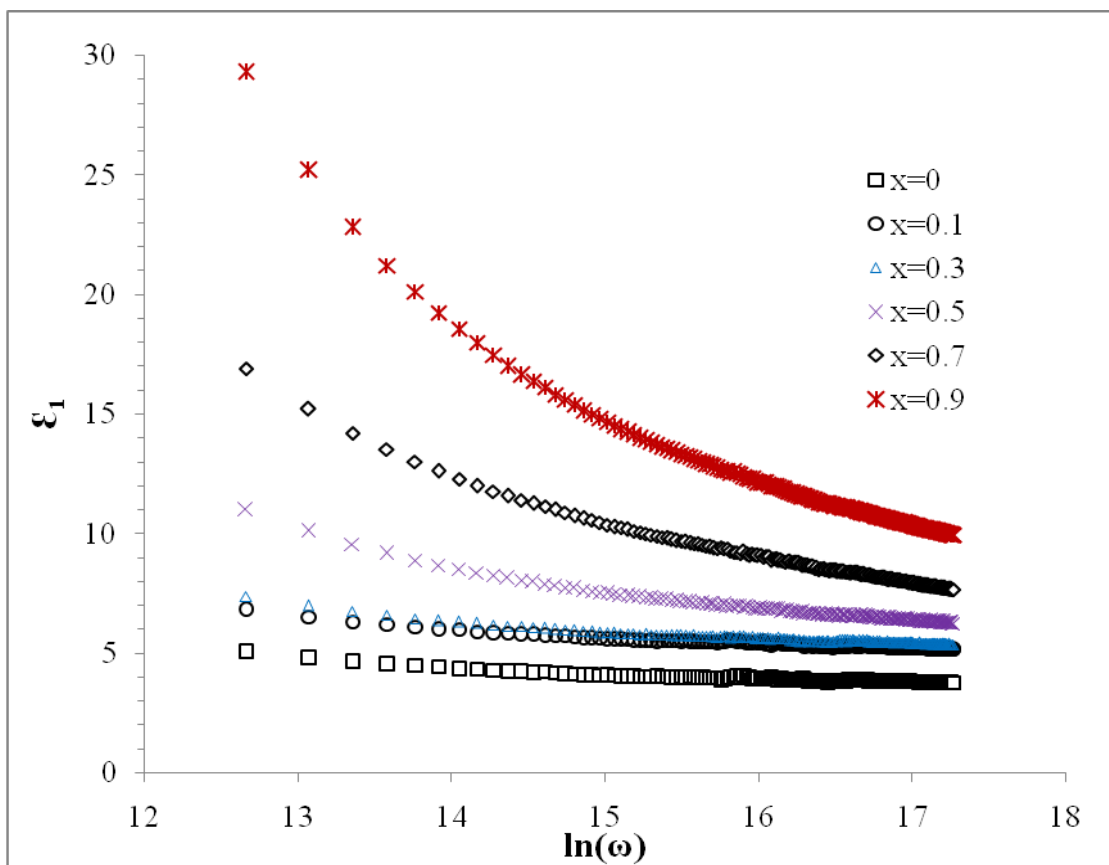

Fig.7: Effect of dielectric constant with frequency and with Co addition.

ε_2 is imaginary part of dielectric constant (dielectric loss factor) which can be calculated by the equation

$$\varepsilon_2 = \varepsilon_1 D \qquad (5)$$

Where D is the loss factor $\tan \delta$

The imaginary part of dielectric constant (ε_2) versus frequency is shown in Fig.8. The

decrease in (ε_2) with increasing frequency agrees well with Deby's type relaxation process[5]. The dielectric loss factor (ε_2) was noticed to decrease with Co content because Cobalt oxide (Co_2O_3) is known as low dielectric loss materials.
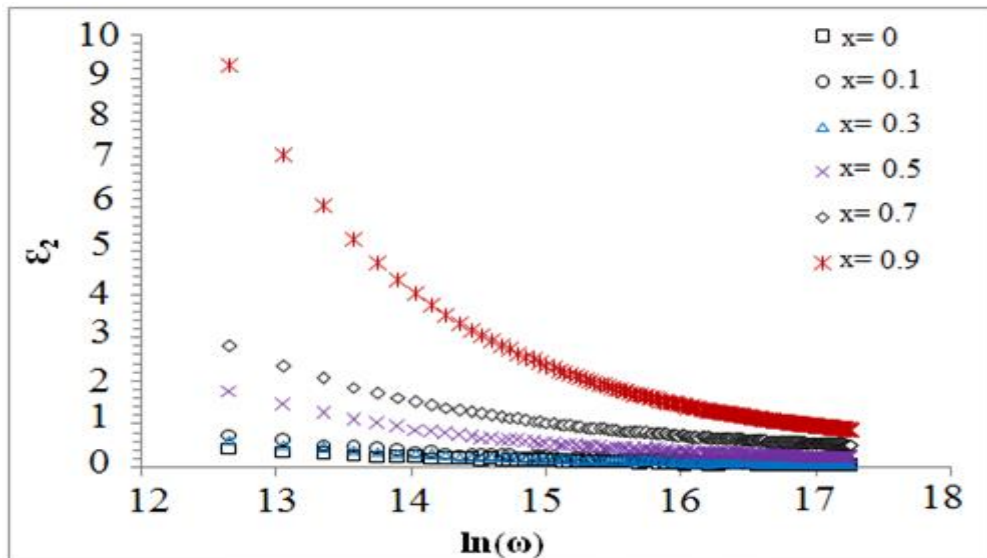
Fig.8: Effect of dielectric loss with frequency and with Co addition.

5. D.C Conductivity

In order to study conductivity mechanisms, it is convenient to plot the logarithm of the conductivity (Lnσ) as a function of 1000/T for bulk cobalt addition nickel ferrite $Ni_{1-x}Co_xFe_2O_4$ with different content of Co (x=0,0.1,0.3,0.5,0.7 and 0.9) as shown in Fig.9. It is clear that all specimens have two transport mechanisms, giving rise to two activation energies E_{a1} and E_{a2} respectively. At higher temperature range (373-473) K, the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperature range (293-373) K; the conduction mechanism is due to carries excited into localized states at the edge of the band.
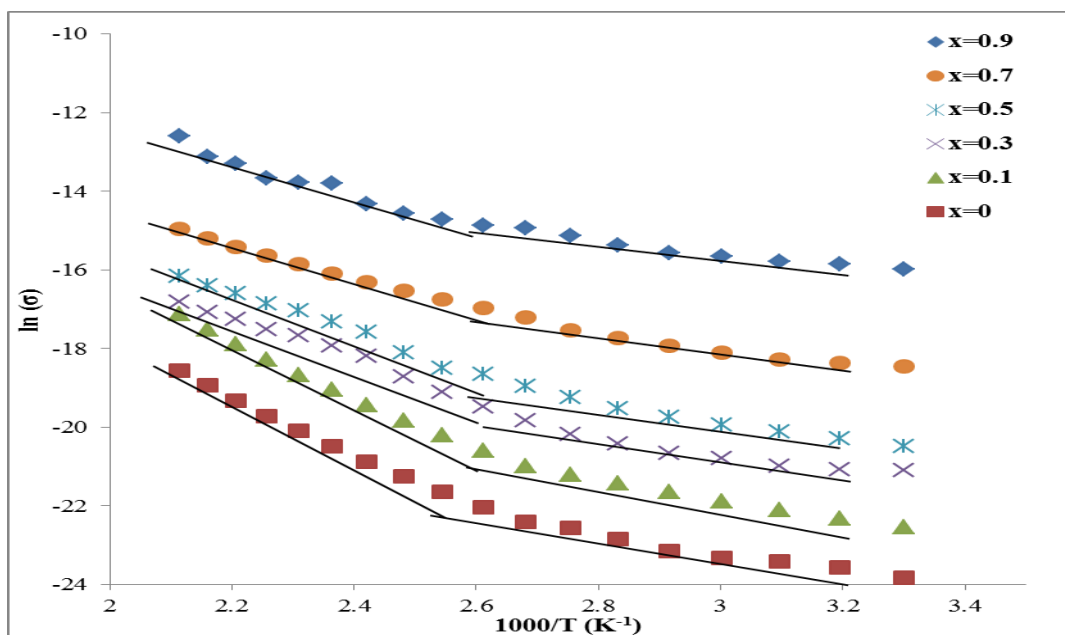

Fig.9: Ln(σ) as a function of $10^3/T$ for bulk $Ni_{1-x}Co_xFe_2O_4$ with different content of Co.

Table 3 : Activation energies E_{a1} and E_{a2} for bulk $Ni_{1-x}Co_xFe_2O_4$ with different content of Co.

Co content	E_{a1} (eV)	Range (K)	E_{a2} (eV)	Range (K)	σ_{RT} ($\Omega^{-1}.cm^{-1}$)
0	0.192	293-373	0.587	373-473	4.51E-11
0.1	0.217	293-373	0.587	373-473	1.62E-10
0.3	0.173	293-373	0.464	373-473	6.93E-10
0.5	0.206	293-373	0.441	373-473	1.27E-09
0.7	0.168	293-373	0.339	373-473	9.78E-09
0.9	0.140	293-373	0.348	373-473	1.15E-07

Fig.10 show the relation between D.C conductivity at room temperature with different concentration of Co for bulk $Ni_{1-x}Co_xFe_2O_4$. It is clear that there is an increasing in the value of conductivity ($\sigma_{d.c}$) when increases in Co contents(x), and these values increase to reach to the maximum ($1.15x10^{-7}\Omega^{-1}.cm^{-1}$) at x=0.9.
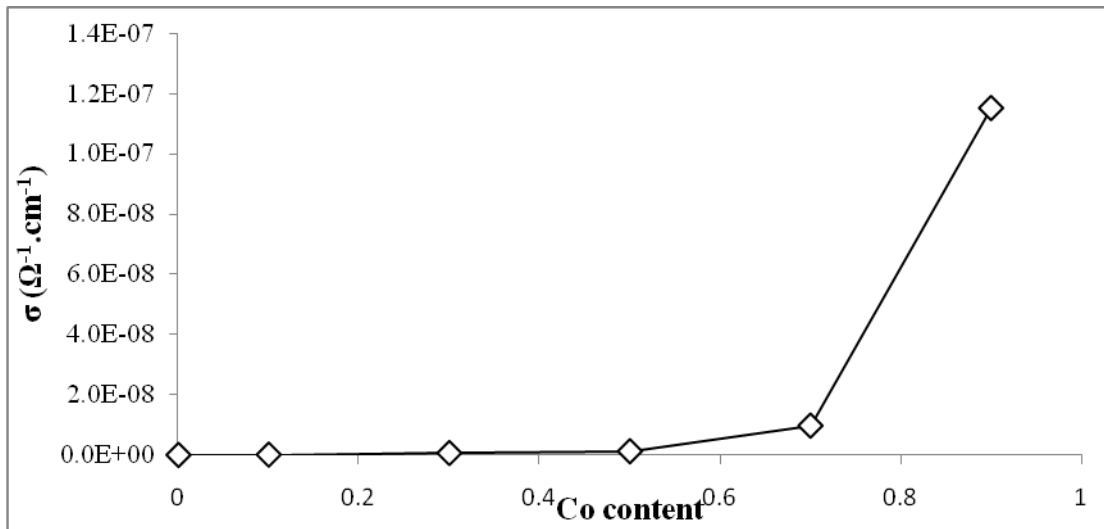

Fig.10 : Variation of $\sigma_{d.c}$ versus concentration(x) for bulk $Ni_{1-x}Co_xFe_2O_4$.

6. Hall Effect

The type of charge carries, carrier concentration (n_H) and hall mobility (μ_H) for bulk $Ni_{1-x}Co_xFe_2O_4$ where (x=0,0.1,0.3,0.5,0.7 and 0.9) have been estimated from Hall measurement.

The results of Hall coefficient listed in Table4 shows a p- type semiconductors behavior. Fig.11 shows the variation of carrier concentration for bulk $Ni_{1-x}Co_xFe_2O_4$ with different content of Co. We see that the carrier concentration increases with increasing Co content, therefore the conduction mechanism in this ferrite is hopping of electrons between Fe^{3+} and Fe^{2+}ions and hopping of holes between Ni^{+2} and Ni^{+3}which is the dominant one. The number of hopping of holes between Ni^{+2} and Ni^{+3} ions increases with Co^{+3}doping. This is because of Fe^{3+} ions migration from the octahedral to the tetrahedral sites[8]. Fig.12 show the variation of Hall mobility with different content of Co. The decrease in Hall mobility with Co addition can be attributed to the increase in the carrier concentration.
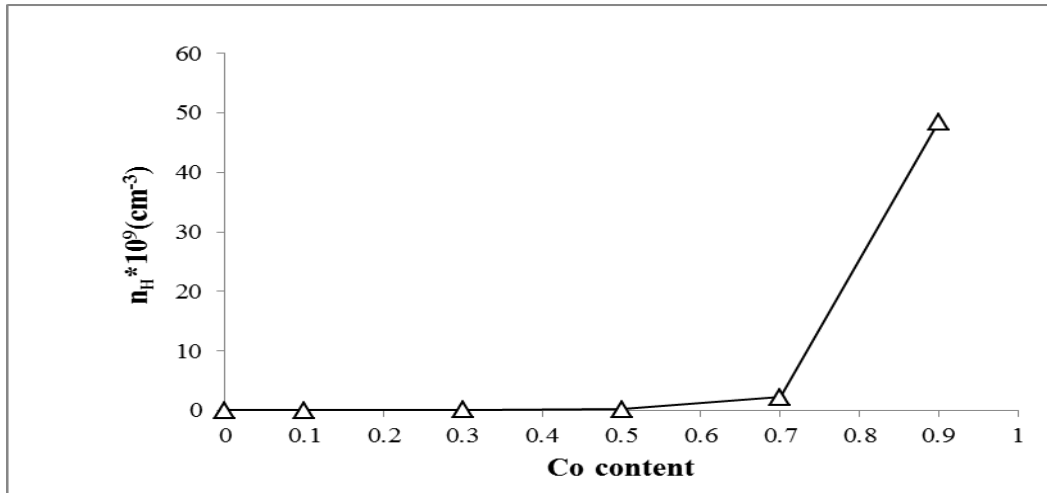
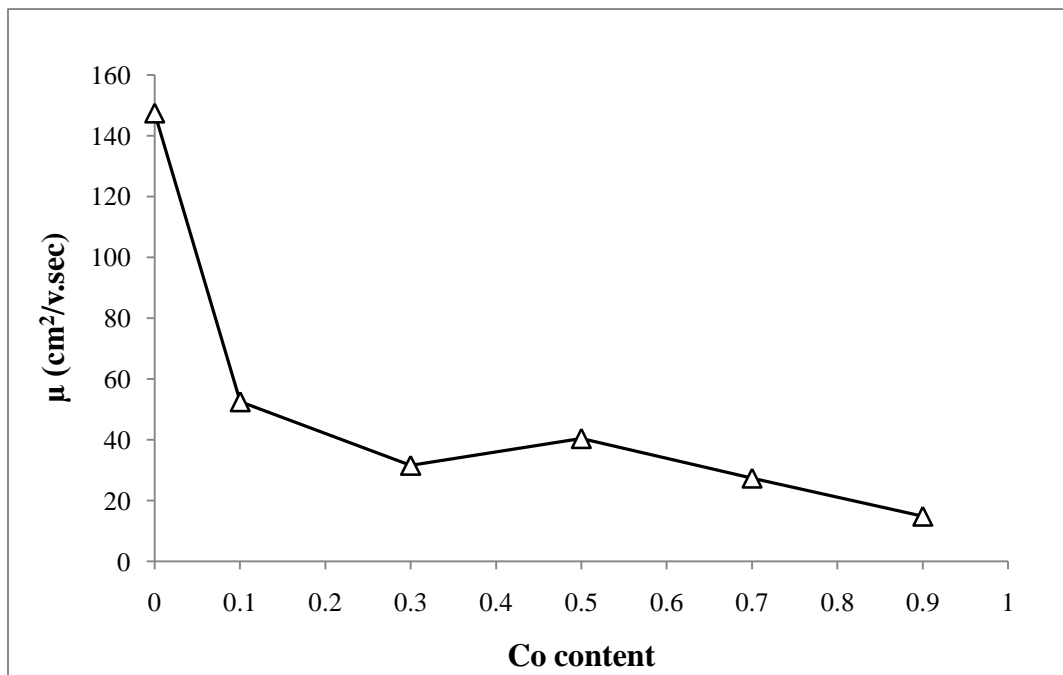*Fig. 11: Variation of carrier concentration for bulk $Ni_{1-x}Co_xFe_2O_4$ with different content of Co.*

Fig. 12: Variation of Hall mobility for bulk $Ni_{1-x}Co_xFe_2O_4$ with different content of Co.

Table 4 : Hall parameters for bulk $Ni_{1-x}Co_xFe_2O_4$ with different content of Co.

Co content	R_H (cm³/c)	n_H (cm⁻³)	μ_H (cm²/v.sec)	type	$\sigma(\Omega.cm)^{-1}$
0	3.27E+12	19113149.850	147.5	p	4.51E-11
0.1	3.24E+11	19290123.46	52.5	p	1.62E-10
0.3	4.56E+10	137061403.5	31.6	p	6.93E-10
0.5	3.18E+10	196540880.5	40.4	p	1.27E-09
0.7	2.80E+09	2232142857	27.4	p	9.78E-09
0.9	1.29E+08	48449612403	14.8	p	1.15E-07

Conclusion

Standard ceramic technique was employed to prepare the cobalt nickel ferrites were at 900C°sintering temperature. From the x-ray diffraction results the samples are polycrystalline because the appearance more than one phases. X-ray density generally increases with the addition of Cobalt. Atomic Force Microscopy (AFM) showed that the average grain size and surface roughness was decreasing with the increasing Cobalt concentration.. Scanning Electron Microscopy (SEM) images show that grains had an irregular distribution and irregular shape. AC conductivity was found to increase with frequency and Co addition, D.C conductivity was found to increase with temperature due to decreases in resistivity. Dielectric constants were noticed to decrease with frequency and Co addition. The Hall coefficient was found to be positive. It demonstrates that the majority of charge carriers of p-type, suggesting that the mechanism of conduction is predominantly caused by hopping of holes.

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