



INFLUENCE OF CR³⁺ ION SUBSTITUTION ON STRUCTURAL AND ELECTRICAL PROPERTIES OF NICKEL FERRITE NANOPARTICLES

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Abstract

Chromium substituted Nickel Ferrite nano particles with general formula NiFe_{2-x}Cr_xO₄ (x=0.0, 0.1, 0.2, .3, 0.4, 0.5) have been synthesized using sol gel auto combustion method. Rietveld refinement analysis of XRD pattern indicates the formation of single phase cubic spinal structure. The lattice constant as well as particle size (crystalline size) was found to be decrease with increase in Chromium concentration up to X=0.2. But for X=0.3 slight increase is observed and further increase of X gives decrease in lattice parameter. The investigation on dielectric const (ϵ), dielectric loss factor ($\tan \delta$) and A.C. resistivity was carried out in the frequency range 100HZ to 1MHZ from room temp to 523K. The A.C. resistivity is found to be decreases with increase in frequency which suggest conduction due to small Polaron hopping. Frequency dependence of dielectric constant shows normal behavior and agrees with Koops phenomenological theory of dielectric dispersion.

Keywords: Spinal Ferrites, Sol gel auto-combustion, small polaron hopping.

Introduction

Oxides having general formula MFe₂O₄ where M and Fe are transition metal ions are known as Ferrites. These material crystallizing in spinal structure have been gaining attention of scientist and technologist because they posses high electrical resistivity and good magnetic properties. The interest in these materials emerges due to their versatile applicability in radio to microwave frequency regions. The

interesting physical, chemical, electrical, magnetic and dielectric properties of Ferrites arises from their ability to distribute the cation among available tetrahedral (A) and octahedral (B) sites (1)

Nickel Ferrites are the important class of spinal ferrites. According to crystal structure Nickel Ferrites are inverse spinal and posses high electrical resistivity and low eddy current losses. They are useful in microwave application, high quality filters, antenna rods, transformer cores etc. (2, 3, and 4). The structural, electrical and magnetic properties of Ni-Zn spinal ferrites have been reported in the literature (5, 6, 7)

Verway and Heilmann (8) in Netherland studied the distribution of metal ions over the tetrahedral and octahedral sites. Neel (9) presented the theory about magnetic properties of Ferrites. The influence of minor addition of Magnesium and Cobalt in high resistivity Nickel Ferrite prepared by solid state reaction method was reported by Uiter (10). Nam et al (11) reported the effect of Aluminium substitutions on the physical properties of NiZn ferrite prepared by solid state reaction method. It was found that D.C. resistivity increased up to $x \leq 0.2$ and then decreased with substitution level x. The D. C. resistivity on two series of Ni_{0.65} Zn_{0.35} Fe_{2-x} Sc_x O₄ and Ni_{0.65-x} Zn_{0.35+x} Fe_{2-x} Sc_x O₄ were reported by Rao et. al (12). The resistivity has been found to increase with increases of Sc and Zn content in both series.

Many researchers achieved remarkable result both in basic research as well as in the applied study of ferrites. Each ferrite product has its own advantages and disadvantages it is not easy

to make novel Ferrite material. However the search for quality material is going on to prepare new materials which have optimum parameters of Ferrite like high resistivity, high permeability low eddy current losses, low FMR line width, high saturation magnetization and good homogeneity.

In the present investigation we have decided to study effect of trivalent substitution of Cr^{3+} in Nickel-Ferrites. Especially we report structural and electrical properties of Cr substituted Nickel-Ferrites.

Experimental

Nano crystalline Ferrite materials are distinguished from the conventional Ferrites by the size of crystallites. Nanostructure materials are single phase or multi-phase polycrystals, the crystal size of material is of the order of 1 to 100nm. These materials are different in the sense that atomic arrangement in the grain boundaries deviates from crystalline structures. Because of extremely small dimensions a large fraction of the atoms are located at grain boundaries or within one or two nearest neighbor planes of the boundaries. Such grain boundaries play an important role in dielectric, electric and mechanical properties of Ferrites. The properties of nanocrystalline material are often superior to these of conventionally prepared Ferrites. The synthesis of material by consolidation of small clusters was first suggested in 1980 by Herbert Gleiter and was applied initially to metals. (13)

The last decade has seen a tremendous increase in industrial and academic interest in nanostructure material scientist has acquired the ability to produce different types of nanostructure material and control their properties. These materials might be influencing the day to day life of man in many ways in future. Various methods have been reported for the preparation of nano Ferrites like Co precipitation method, micro emulsion method, spray pyrolysis, microwave decomposition, Gas evaporation technique, and Laser ablation. Sol gel combustion technique is used for the production of Ferrite system which is used by several investigators for production of Ceramic material exhibiting nm- size structure (14, 15, 16, and 17). In combustion synthesis, the exothermicity of Redox chemical reaction is used to produce useful materials. Depending on nature of reactant, elements or compound and exothermicity it is described as, self

propagating high temperature synthesis, low temperature combustion synthesis, solution combustion synthesis, sol-gel, combustion or emulsion combustion etc. (18)

Following features of this method make it an attractive method for manufacture of technologically useful material at lower cost compared to conventionally ceramic process.

- 1) Use of relatively simple equipment
- 2) Formation of high purity product
- 3) Stabilization of meta stable phases
- 4) Ultrafine dimension of product

The Ferrites powder with general formula $\text{Ni Fe}_{2-x}\text{Cr}_x\text{O}_4$

Where $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$. were synthesis by Sol gel auto combustion method using AR grade Citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), Nickel Nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Chromium Nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Iron Nitrate($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$).

The desired quantities of Nickel and Iron nitrates salts were dissolved in double distilled water and required amount of citric acid were added as a chelating agent .AR grade dilute aqueous ammonia was poured slowly into nitrate-citrate mixture to adjust ph 7.00. The mixed solution was heated at about 100°C for 4 to 6 hours heating with uniform stirring and evaporated on hot plate magnetic stirrer to obtain highly viscous gel denoted as precursor. The obtained gel was placed in hot plate for further heating, the gel swelled and ignited with an evolution of large amount of gaseous product, resulting the desired ferrite in the form of foamy powder.

For the substitution of Chromium trivalent ion Chromium nitrate is added as per stichometric ratio. The powder then pressed at pressure of 5 tons per inch into 1 to 2 cm diameter pellets in KBr press machine. The pellets were sintered at 500°C in air for 4 hours. Sintered pellets were subjected to X ray diffractometer in Rigaku Geiger 3 kW with wavelength 1.5404 \AA to study structural properties. Citric acid is a weak acid and has there carboxylic and one hydroxyl group for coordinating metal ions and therefore enhances the homogeneous mixing. The aqueous ammonia is used to adjust the PH for improving the complexation, gel formation and also to improve solubility of metal ions.

Result and discussion

1) Structural measurement –

The X ray diffraction pattern of all sample of were recorded on Philips X ray diffract meter at room temp. The single phase cubic spinal structure formation was confirmed from X ray diffraction pattern. All the peaks were sharp and do not contain any impurity phase. All the peaks of XRD pattern were indexed using Bragg’s law. XRD data was used to determine structural parameter of all samples. The lattice constant ‘a’ was determined using following relation. $a=d\sqrt{h^2+k^2+l^2}$

Where (h,k,l) are miller indices

d is inter planer spacing

The values of lattice constant obtained from XRD data are given in the table. Generally, in a solid solution series linear increase or decrease

of lattice constant within the miscibility range with composition is observed. (19)

The X-ray density and Bulk density (d_x) was calculated according to following relation $d_x=8M/Na^3$

Where M is molecular weight

N is Avogadro’s number

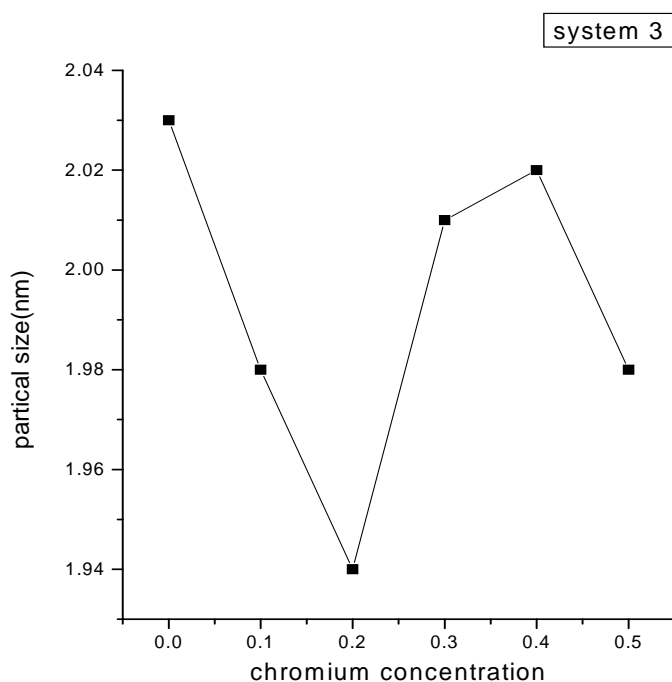
a is lattice constant.

The variation of X ray density with x exhibits exactly reverse behavior compared to the variation of lattice constant with X. This is because, X ray density is inversely proportional to the lattice constant (a). The average particle size for each sample was estimated using Scherrer relation

The theoretical lattice parameter ‘a_{th}’ was calculated using the values of tetrahedral radii (r_A) and (r_B) respectively.

Table -1 Representing theoretical and calculated values of d with Cr content

Cr content	d(theo)	d (cal)
0.0	2.020	2.036
0.1	1.988	1.988
0.2	1.950	1.940
0.3	2.055	2.014
0.4	2.017	2.023
0.5	1.961	1.988



Graph (B)- Variation in Lattice constant with Cr content.

Table -2 Representing theoretical and calculated values of lattice constant (a) with Cr content

Cr content	a (theo) in \AA	a (cal) in \AA
0.0	7.599	7.658
0.1	7.477	7.479
0.2	7.301	7.299
0.3	7.732	7.578
0.4	7.587	7.609
0.5	7.378	7.478

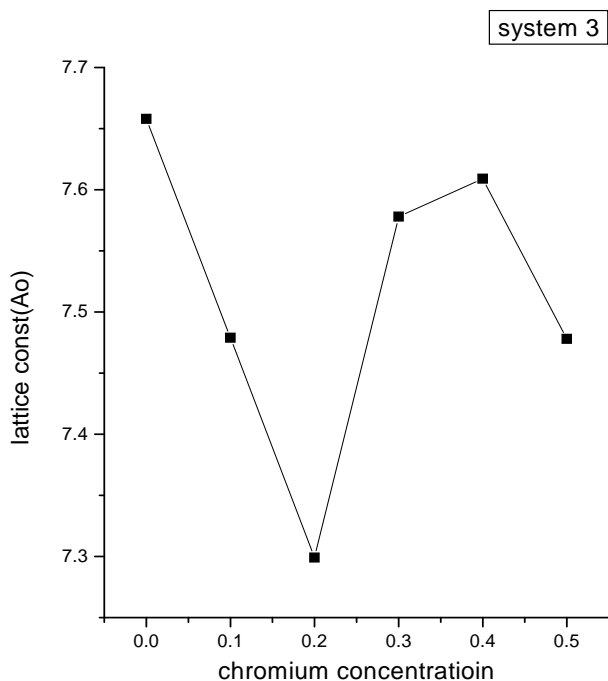
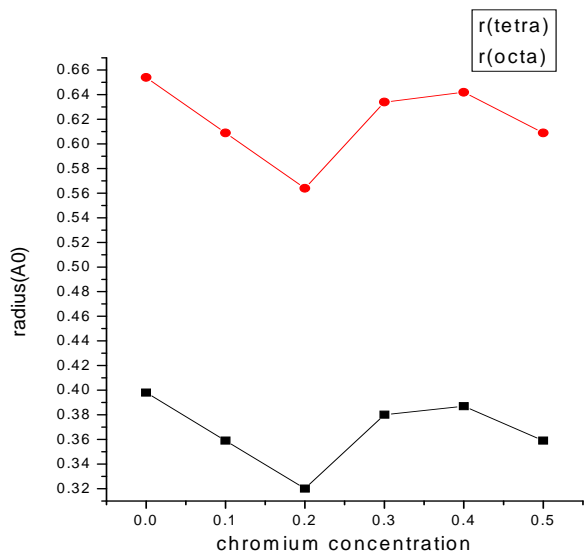


Table-3 Representing radii of tetra and octahedral site with Cr content

Cr content	Tetrahedral A site (in \AA)	Octahedral B site (in \AA)
0.0	0.398	0.654
0.1	0.359	0.609
0.2	0.320	0.564
0.3	0.380	0.634
0.4	0.387	0.642
0.5	0.359	0.609

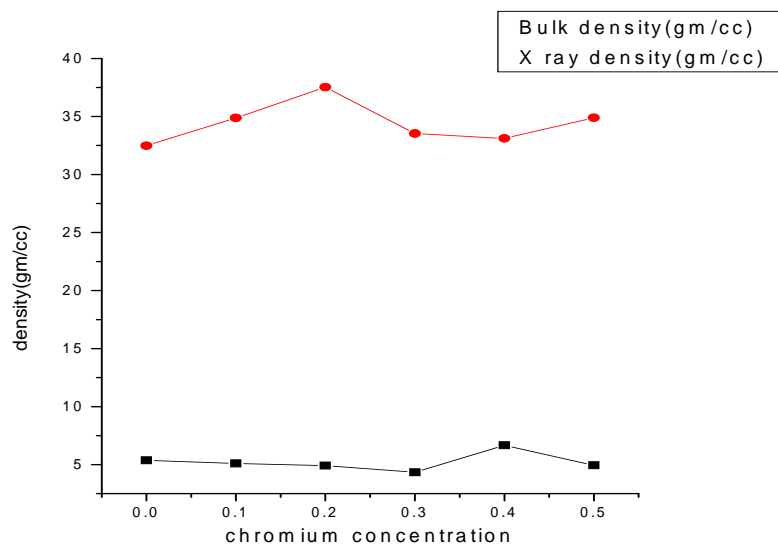


Graph (C)- Variation in radii of A site and B site with Cr content

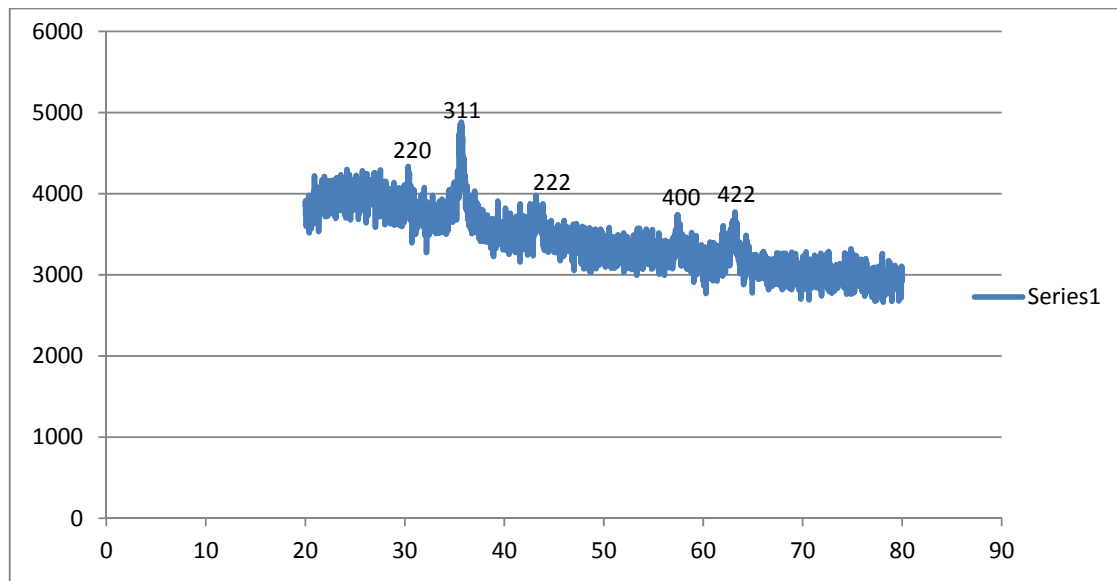
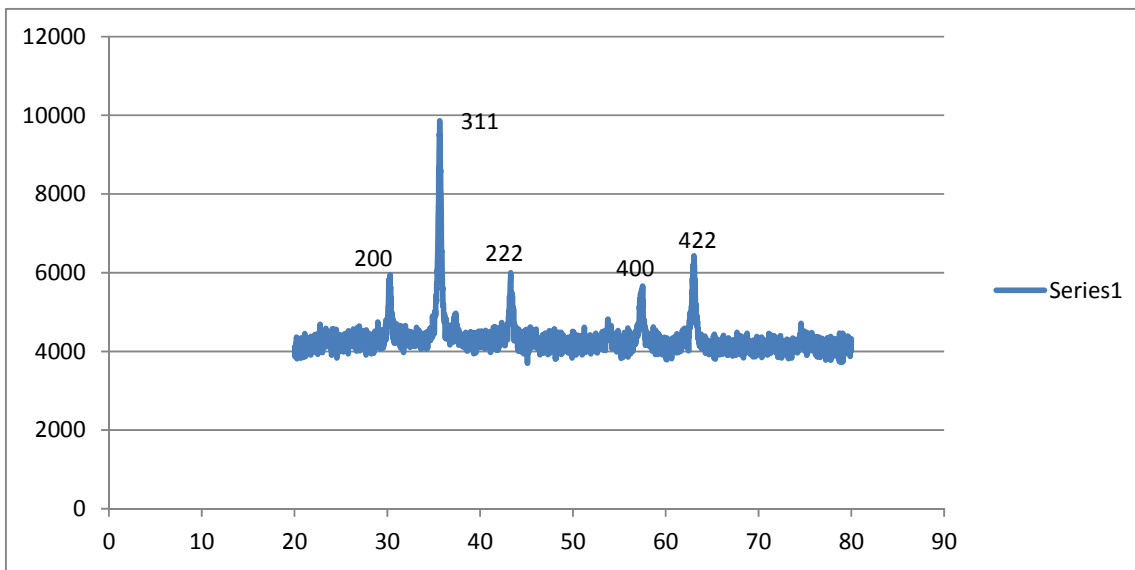
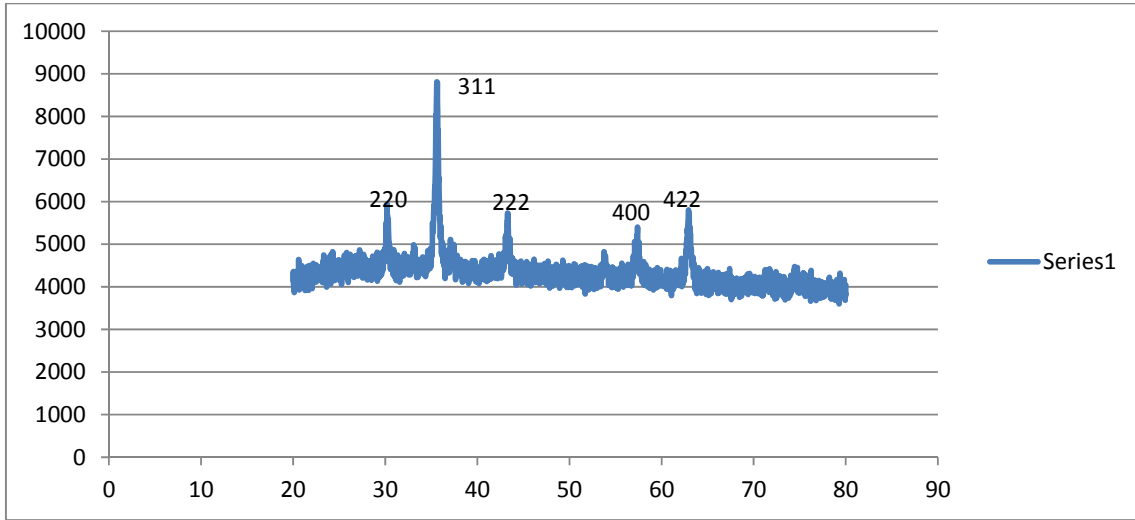
Table-4 Representing bulk density, X-ray density and porosity with Cr content

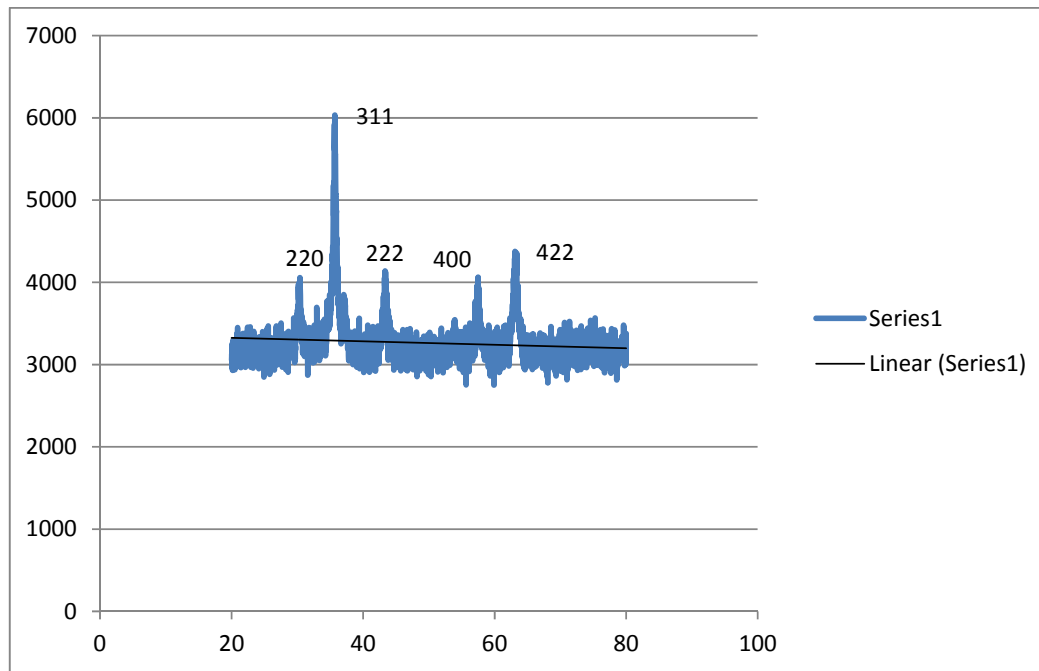
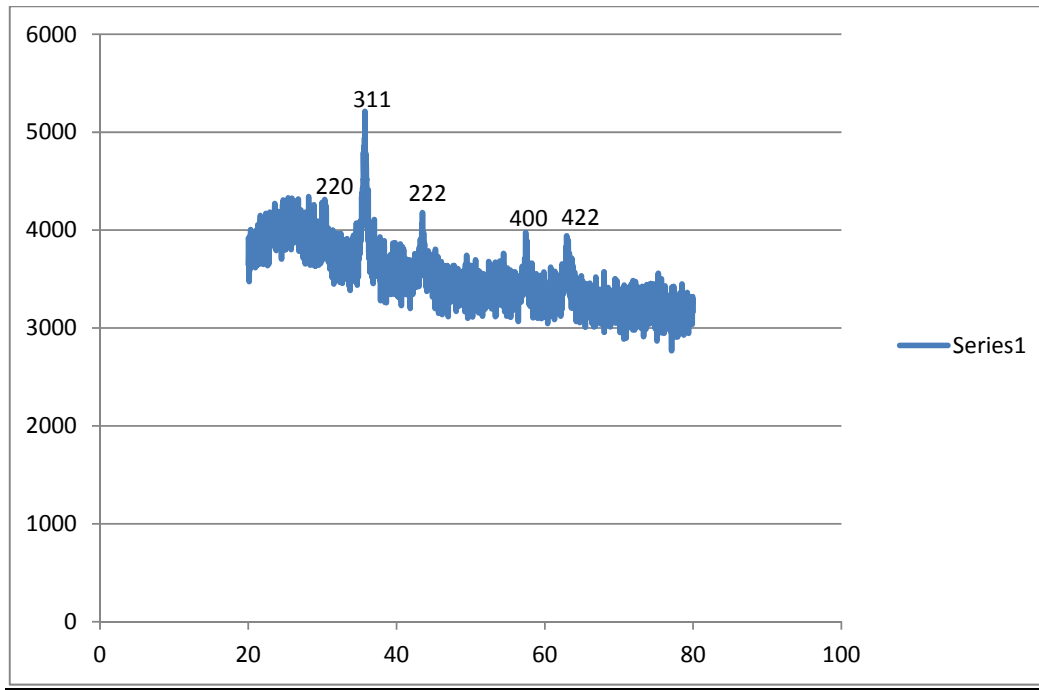
Cr content	Bulk density	X ray density	porosity
0.0	5.376	32.48	83.45
0.1	5.109	34.88	85.36
0.2	4.928	37.53	86.87
0.3	4.343	33.53	87.05
0.4	6.678	33.11	79.84
0.5	4.941	34.89	85.84

Graph (D) - Variation in densities with Cr content



Graph (E) - XRD pattern of all samples of the prepared system.





Measurement of Dielectric Constant

The parameters such as dielectric constant (ϵ'), dielectric loss (ϵ'') and dielectric loss tangent ($\tan \delta$) and A. C. resistivity depend on frequency. The measurement of resistance (R) and capacitance (C) were made with the help of LCR-Q meter (model HP 4192) in the frequency range 100HZ to 1MHZ. The dielectric const (ϵ') are found to decrease and increase with increase in frequency which is normal behavior of spinal ferrites. The dielectric behavior and dispersion phenomenon of spinal ferrites can be explained on the basis

of polarization process. The dielectric constant is the function of degree of polarization. As the frequency increases beyond the certain frequency, the electronic exchange $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$, does not follow the applied attempting filed, resulting in reduction of dielectric constant.

All the samples revealed dispersion due to Maxwell- Wagner interfacial polarization (20, 21) in the agreement with Koops phenomenological theory (22). Variation in dielectric constant and tangent loss with log of frequency is given in graph(f)

The variation of dielectric const (ϵ), dielectric loss tangent ($\tan \delta$) as a function of temperature is observed and found that it appreciably increases with temperature. This can be explained on the basis of polarization effect. The number of space charge carriers governs the space charge polarization. As temp increases electrical conductivity increases due to increases in thermally activated drift mobility of electric charge carriers according to hopping conduction mechanism. Hence dielectric polarization increases with causes increases in dielectric const (ϵ) and tangent loss ($\tan \delta$) as observed in graph (g). This behavior is in good agreement with other worker.

Measurement of Resistivity – It is observed that resistivity of samples decrease with increase in log of frequency as shown in graph(h). The

variation of resistivity with temperature obeys exponential relation.

$$\rho = \rho_0 \exp [\Delta E / KT]$$

Where ρ_0 is temperature dependent factor

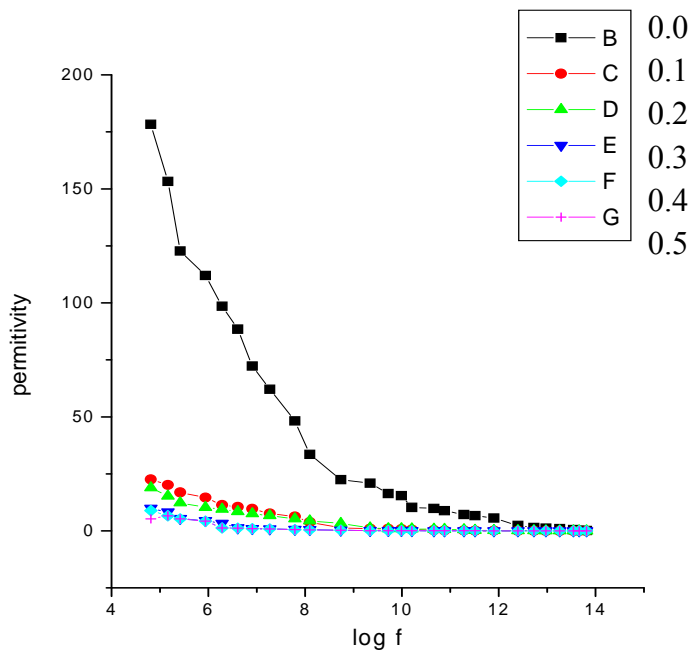
ΔE activation energy

K is Boltzmann constant

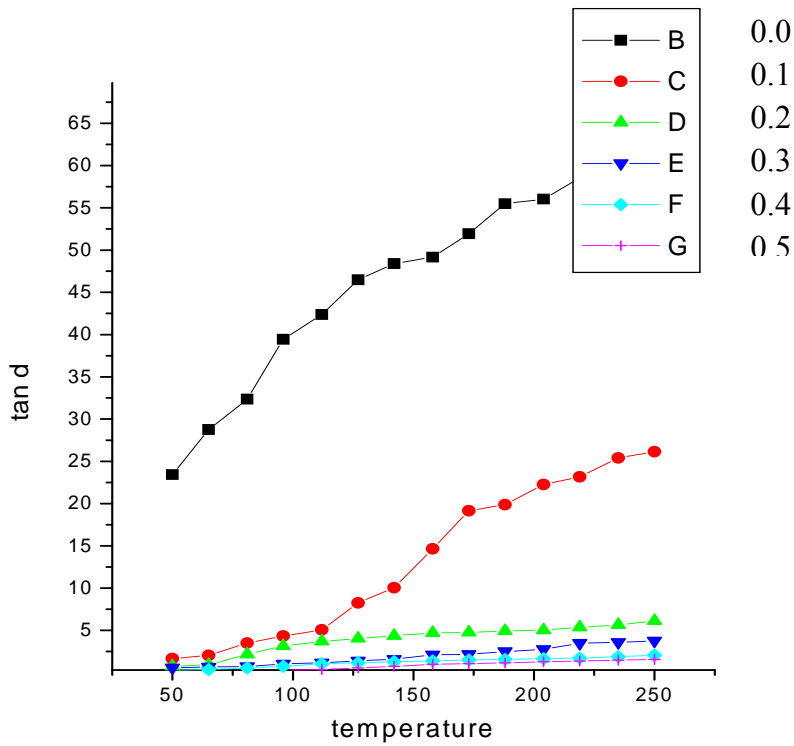
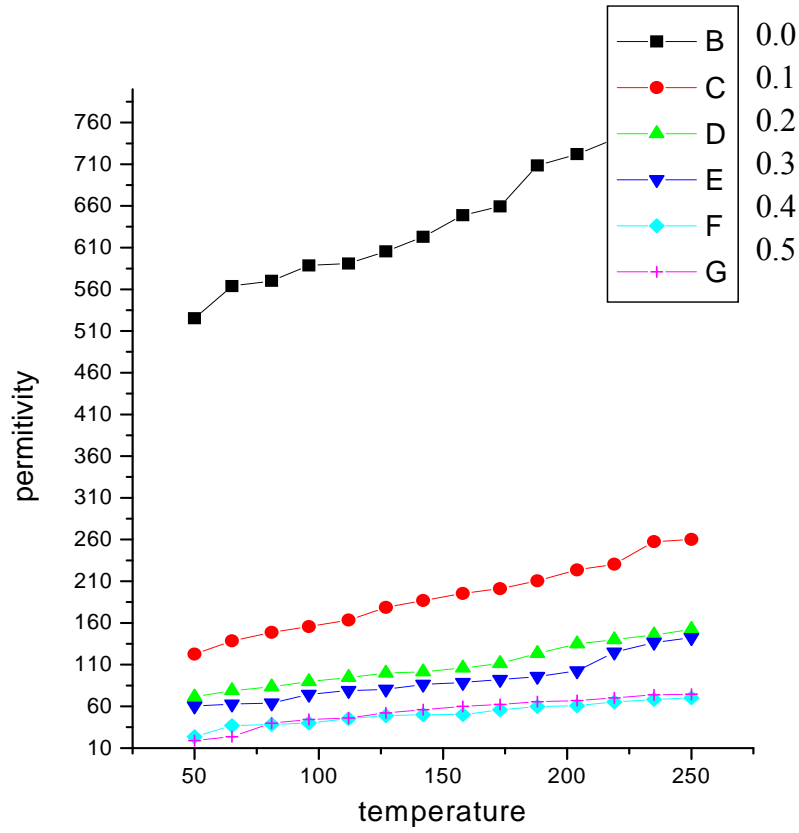
The conductivity in ferrites can be explained on the basis of Verwey and De Boer mechanism

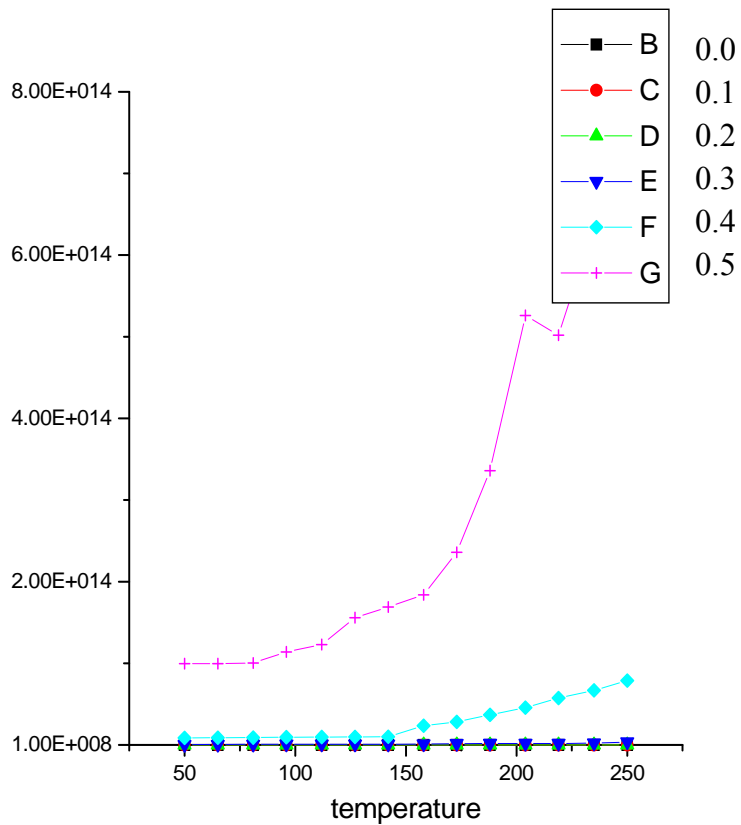
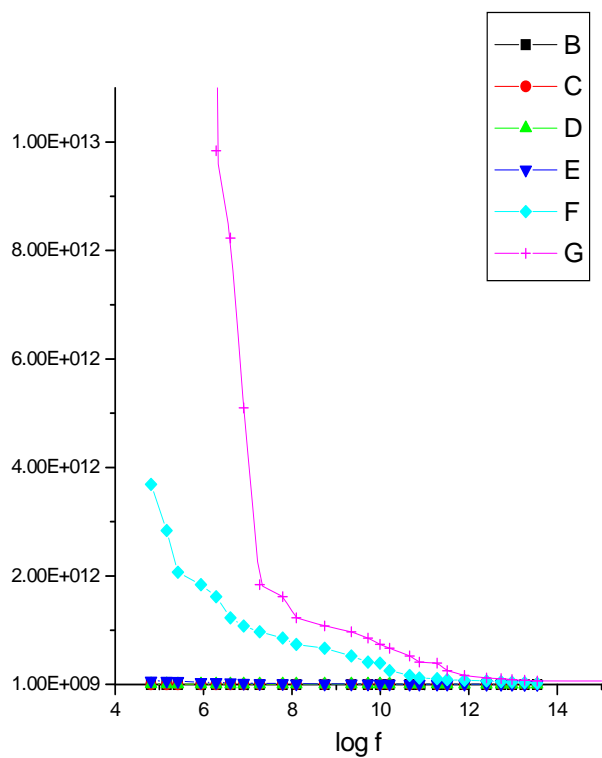
(23) i e exchange of electron between ions of same element that are present in more than one valence state distributed randomly over equivalent crystallographic sites. The electron can have a transition from Fe^{2+} to Fe^{3+} within the octahedral position without causing much change in the energy of system.

permittivity vs log f for different concentration of Cr at 50°C



Plot of permittivity vs temperature for different concentration of Cr at 1000HZ





Conclusion

The lattice constant is calculated by Rietveld method and values are listed in the table. The lattice constant initially decreases and then again increases for $x=0.3$ and further decrease for $x=0.4, 0.5$. It may be due to fact that substitution of chromium ion related to difference in ionic radii of Fe^{3+} and Cr^{3+} . In the present system Fe^{3+} ion ($0.67A^0$) are replaced by relatively small Cr^{3+} ($0.64A^0$). The average crystalline size (d) was determine by using line broadening of most intense (311) diffraction peak using Debye Scherrer formula which found to be of the order of 20 nm. The radii of tetrahedral and octahedral sites in A^0 are calculated for each samples listed in the table. Porosity of all samples is found to be about 80% on an average. The resistivity is found to increasing with substitution of Cr concentration. The highest recorded resistivity in our investigation is of the order of 10^{12} to $10^{13} \Omega.m$

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