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DIELECTRIC BEHAVIOUR OF COBALT FERRITE NANOPARTICLES

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ABSTRACT

The cobalt ferrite ($CoFe_2O_4$) samples of different particle size were successfully prepared by nitrate route. The X-ray diffraction (XRD) patterns of all the samples show the single phase spinel structure of nanoparticles. The dielectric constant and loss tangent for the samples were determined as a function of frequency, and the frequency range was used from 75 kHz to 5 MHz. The dielectric constant and the loss tangent decreases rapidly with increasing frequency, and then reaches a constant value. Low dielectric constants materials are required for high –frequency application in electrical circuits, to reduce dielectric losses and skin effect. The high value of electrical resistivity in ferrite is suitable for the high frequency application where eddy current losses are appreciable. The resistivity is decreased with increase in temperature and the material behaves like a semiconductor.

KEYWORDS: XRD, Dielectric Constant, Dielectric Loss and Electrical Resistivity

INTRODUCTION

Ferrite nanoparticles are important magnetic materials due to their specific magnetic and electric properties. They are widely used in high density magnetic recording, microwave devices and magnetic ferro-fluids [1]. Cobalt ferrite crystallizes in partially inverse spinel structure represented as $(Co_x^{2+}Fe_{1-x}^{3+})$ $(Co_{1-x}^{2+}Fe_{1+X}^{3+})O_4$, where x depends on thermal treatment and preparation conditions [2]. It is ferrimagnetic with a Cruie temperature (Tc) around 520 ^{0}C and shows a relatively large magnetic hysteresis with distinguishes it from the rest of spinel ferrite [3]. Spinel ferrite nanoparticles have high electrical resistivity and low eddy current and dielectric losses. Cobalt ferrite is one of the potential candidates for magnetic and magneto-optical recording media [4-5]. Dielectric behaviour is one of the most significant properties of ferrites which depend on the preparation conditions, sintering temperature, composition and the grain size [6-7]. Giri et. al. [8] have observed structural disorder, enhanced optical absorption and high coerctivity with the reduction of grain size in nanocrystalline cobalt ferrite.

Several reports are available on the electrical conductivity and dielectric properties of bulk cobalt ferrite [9-12]. Jonker [10] has studied the electrical properties of a series of bulk $Co_{3-X}Fe_XO4$ ferrites and observed two region of conductivity. The hole hoping between Co^{2+} and Co^{3+} ions contributes to the low-conductivity regions and the electron hopping between Fe^{2+} and Fe^{3+} ions is found to be responsible for the high –conductivity region. Na et al. [11, 12] have reported the mechanism for electrical conduction for bulk $CoFe_2O_4$ under various heat treatment conditions. They have also observed a decrease in the electrical resistivity with quenching temperature, which is mainly because of the decrease in grain boundary resistance in Fe-excess cobalt ferrites.

EXPERIMENTAL

In the present work we have synthesized nanoparticles of $CoFe_2O_4$ using the chemical route. The stoichiometric amounts of $Fe(NO_3)_3.9H_2O$, and $Co(NO_3)_2.6H_2O$ were dissolved in distilled water. In the aqueous salt solution, citric acid solution was added with the cations to citric acid molar ratio of 1:2. The solution was heated at 85^{o}C under constant magnetic stirring until the solution got converted into a viscous gel, and was allowed to cool at room temperature. The cooled gel was dried in an oven at 100^{o}C for overnight to form the precursor material. The precursor material was sintered at 300,500,700 and 900^{o}C for 2 hrs to get the nanoparticles of cobalt ferrite of different particle sizes.

The ferrite powder was pressed into pellets of 10mm diameter at a presser of 5 tons after mixing with about 2% by weight of polyvinyl alcohol binder. These pellets were heated in a furnace at 1200 ^{0}C for 10hrs.The pellets were then polished and coated with silver on both surfaces for dielectric measurements. The dielectric properties of the samples were measured with an Agilent 4285A precision LCR meter in the frequency range 75 kHz to 5MHz. The synthesized samples were coded as CFT, where CF denotes the cobalt ferrite and T denotes the sintering temperature in degree Celsius.

RESULTS AND DISCUSSIONS

X-Ray Diffraction Analysis

The XRD patterns of the cobalt ferrite nanoparticles after final sintering at 1200 deg C are shown in the figure1. It shows the pure phase of the cobalt ferrite nanoparticles. The crystallite size was determined by using the Scherrer formula [13] form the most instance peak (311)

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where λ is the wavelength of X-ray used, θ is the Bragg's angle, β is the full width at half maximum (FWHM) in radian. Specific surface area (surface area per unit mass) can be calculated by the following relation

$$S = \frac{6000}{D\rho_x} \tag{2}$$

where D is the crystallite size, ρ_x is the X-ray density.

The X-ray density ρ_x was calculated by using the formula

$$\rho_x = \frac{8M}{Na^3} \tag{3}$$

where M is the molecular weight of the samples, N is the Avogadro number, a is the lattice constant and 8 stands for the number of formula units in a unit cell.

The measured density ρ_m was determined using the standard formula [14]

$$\rho_m = \frac{m}{\pi r^2 h} \tag{4}$$

where m is the mass, r is the radius and h is the thickness of the samples.

The porosity for all the samples was calculted using the following formula [15]

$$P = 1 - \frac{\rho_m}{\rho_x} \tag{5}$$

The diffraction peaks are broad because of the nanometer size of the crystallite. The crystallite sizes are 45, 40, 53 and 42nm of the samples CF300, CF500, CF700 and CF900 respectively and listed Table 1. The lattice parameter is ~8.36 Å while the X-ray density is ~5.33 (gm/cm^3) for all the samples (Table1). It was observed that X-ray density of each sample is greater than its corresponding measured density.

This was due to the pores present in the prepared materials. The values of porosity are 0.23, 0.27, 0.11 and 0.28 for these samples (Table1). The number of pores is reduced due to increase of grain size. Smaller grains coalesce to form larger grains and resultantly grain to grain contact area increases and porosity decreases.

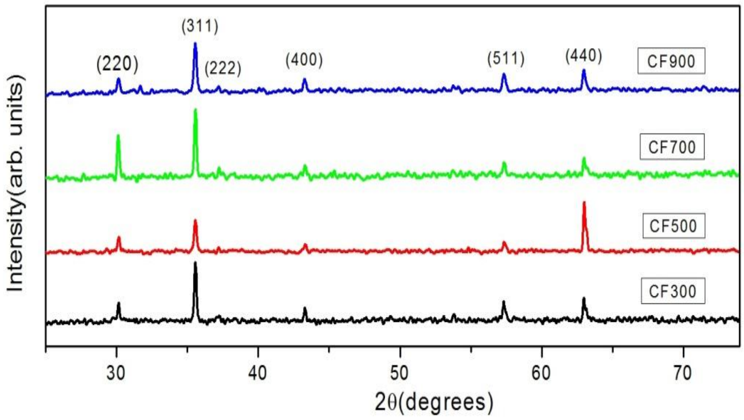


Figure1: XRD Patterens of the Samples

Table1: Calculated XRD Parameters and Porosity of the Samples

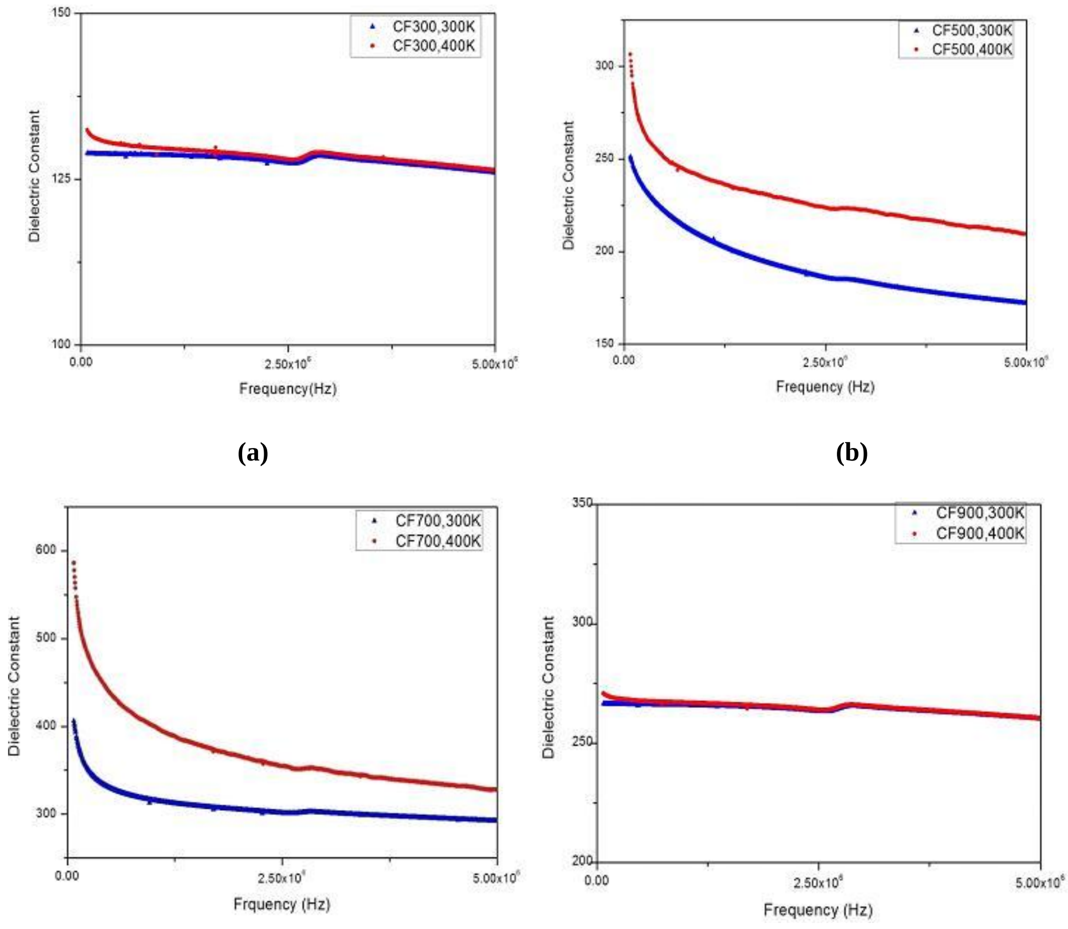
Sample	**Crystallite Size D (nm)**	**Lattice Parameter a (Å)**	**X-Ray Density ρ_x (gm/cm^3)**	**Specific Surface Area S (m^2/gm)**	**Measured Density ρ_m(gm/cm^3)**	**Porosity (P)**
CF300	45±1	8.36±0.01	5.33±0.02	25±1	4.05	0.23
CF500	40±1	8.37±0.01	5.33±0.02	28±1	3.87	0.27
CF700	53±1	8.36±0.01	5.34±0.02	21±1	4.74	0.11
CF900	42±1	8.36±0.01	5.33±0.02	27±1	3.83	0.28

Dielectric Constant Behaviour

The dielectric constant ε' of cobalt ferrite was determined using the formula [16]

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \tag{6}$$

where C is the capacitance of the pellets, d is the thickness of the pellets; A is the cross-sectional area of the flat surface of the pellets in m^2 and ε_0 is the permittivity of free space. The dielectric constants measurement was done in the range 75 kHz to 5MHz using Agilent 4285A precision LCR meter. The values for dielectric constant at different frequency and temperature are listed in the Table2. The graphs of dielectric constant against frequency are depicted in Fig.2 (a-d). Dielectric constant is highest at the frequency of 75 kHz and it decreases with the increase of frequency in all the samples. This dependence upon frequency is because of the interfacial polarization as predicted by Maxwell-Wagner [17]. According to this model, the dielectric structure of a ferrite material is assumed to be made up of two layers; the first layer being a conductive layer that consists of large ferrite grains and the other being the grain boundaries that are poor conductors. Rabinkin and Novikova [18] showed that the polarization in ferrites is through a mechanism similar to the conduction process. Due to the electron exchange between Fe^{+2} and Fe^{+3} the local displacement of the electrons in the direction of the applied field occurs and these electrons determine the polarization. The large value of dielectric constant at lower frequency may be due to the predominance of species like Fe^{+2} ions, oxygen vacancies, grain boundary defects, etc. The decrease in dielectric constant with frequency is obvious because of the fact that any effect contributing to polarization is found to show lagging behind the applied field at higher and higher frequencies. By increasing the frequency beyond a certain frequency limit, the electron hopping cannot follow the electric field fluctuations causing a decrease in the dielectric constant. Koop [19] argued that the dielectric constant at low frequency comes from the grain boundaries which have a high dielectric constant due high resistivity at the grain boundary region. The dielectric constant at high frequency comes from the grains which have a small value of dielectric constant due to low resistivity. It may be concluded that the electrons exchange between Fe^{+2} and Fe^{+3} ions results in the direction of an electric field, which is responsible for electrical polarization in ferrites. The higher value of dielectric constant at low frequency may be due to voids, dislocations and defects etc.



(a) (b)

(c) (d)

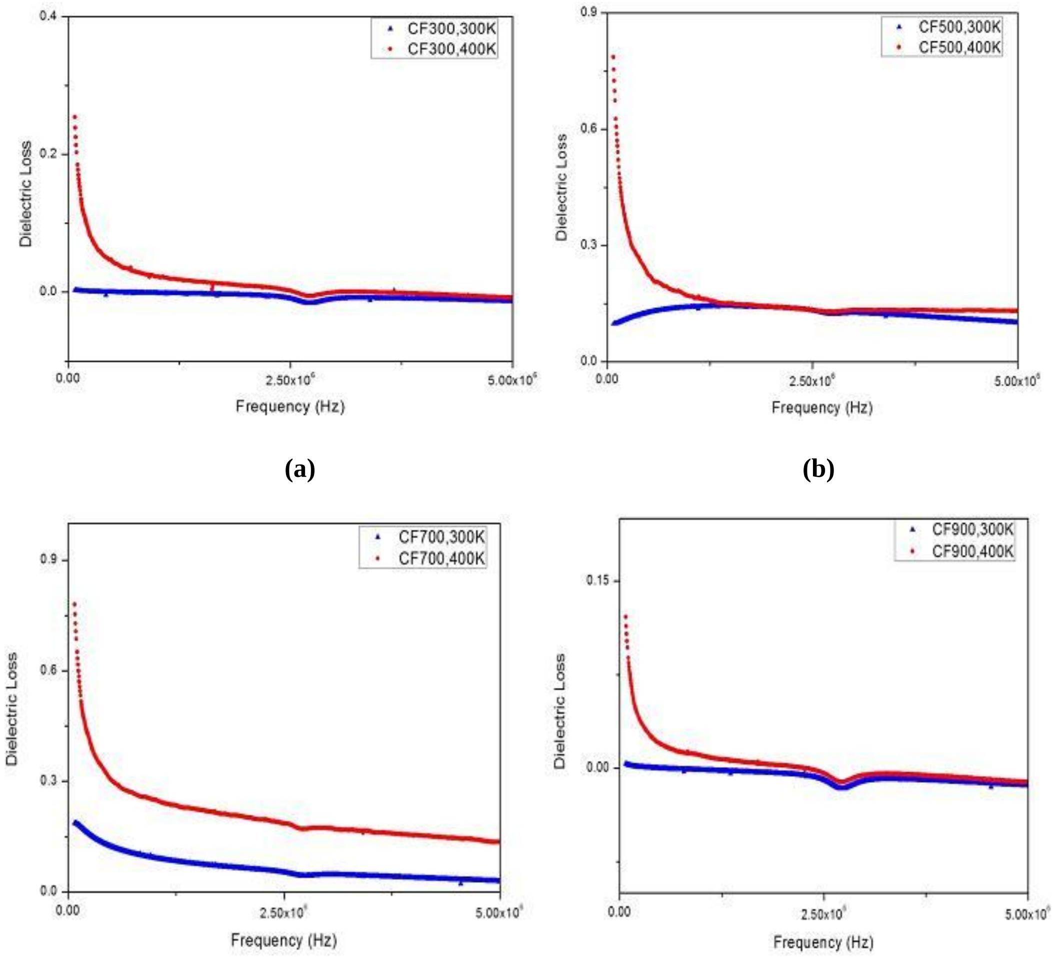
Figure 2: (a-d) Dielectric Constant (ε') Behaviour of the Samples in the Frequency Range 75 kHz to 5MHz

Dielectric Loss Behaviour

Dielectric tangent loss (tanδ) was calculated using the relation [20]

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{7}$$

where ε'' is the imaginary part of the dielectric constant and is a measure of the absorption of energy by the dielectric from the alternating field, ε' is the real part of the dielectric constant and δ is the loss angle. The value of the dielectric tangent loss (tanδ) at different frequencies is tabulated in the Table3. The graph of dielectric loss tangent versus frequency is depicted in figure 3(a-d). The dielectric tangent loss (tanδ) decreases with the increase of frequency and then becomes almost constant at higher frequencies for all the samples. The value of dielectric tangent loss (tanδ) depend on a number of factors, such as stoichiometry, Fe^{+2} content and structural homogeneity, which in turn depends on the composition and synthesis methods. The decrease in loss tangent with frequency may be attributed to the Maxwell-Wagner polarization and conduction mechanism in ferrites [17].



(a) **(b)**

(c) **(d)**

Figure 3: (a-d) Dielectric Loss Tangent (tanδ) Behaviour of the Samples in the Frequency Range 75 kHz to 5MHz

Table 2: Dielectric Constant ε' at Different Frequencies

Samples	**ε' (300K)**			**ε' (400K)**		
	75kHz	**1MHz**	**5MHz**	**75kHz**	**1MHz**	**5MHz**
CF300	128	128	126	132	129	126
CF500	251	207	172	306	239	209
CF700	406	315	292	586	400	327
CF900	266	265	260	270	267	260

Table 3: Dielectric Loss Tangent (tanδ) at Different Frequencies and the Electrical Resistivity (ρ) of the Samples

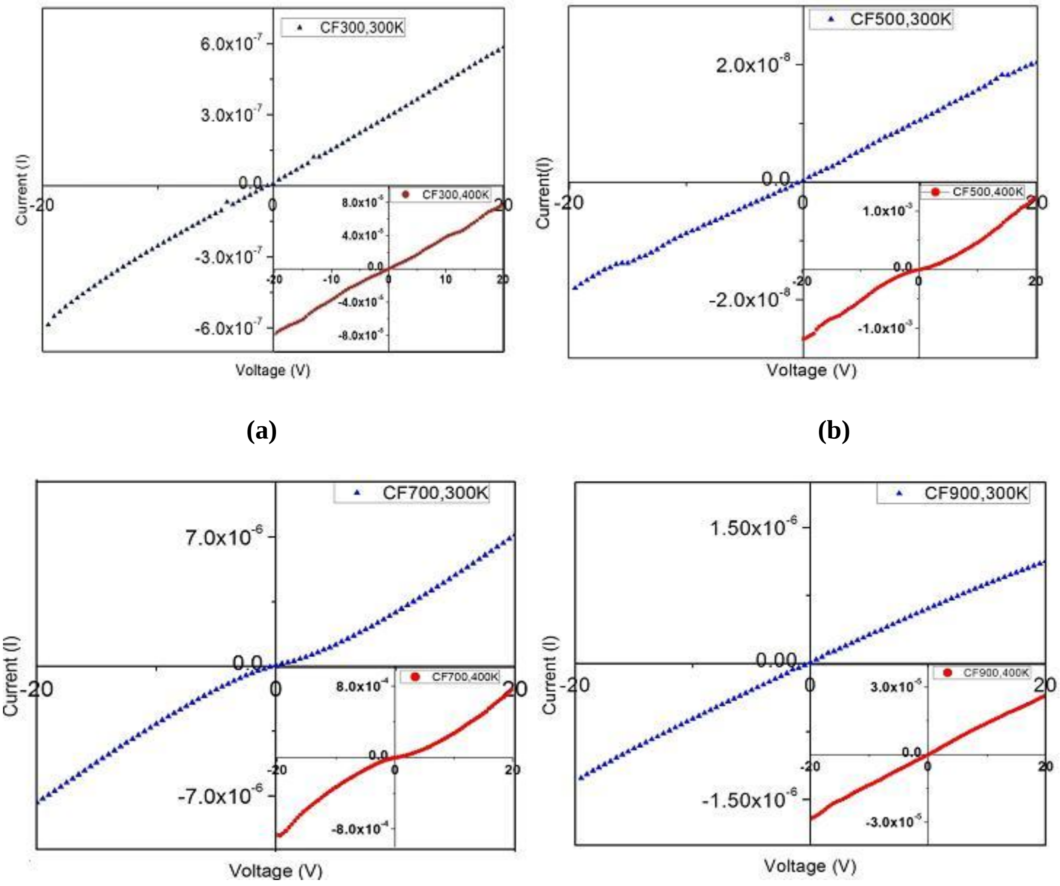
Samples	**(tanδ)(300K)**			**(tanδ)(400K)**			**ρ (ohm-cm)×10^6**	
	75kHz	**1MHz**	**5MHz**	**75kHz**	**1MHz**	**5MHz**	**300K**	**400K**
CF300	0.003	0.001	0.0001	0.25	0.02	0.007	33	2.492
CF 500	0.098	0.140	0.100	0.78	0.169	0.131	78	0.1393
CF 700	0.186	0.091	0.029	0.77	0.25	0.13	15	0.1385
CF 900	0 .003	0.001	0.001	0.120	0.010	0.001	75	3.331

Electrical Resistivity

The electrical resistivity was calculated using this formula

$$\rho = R\frac{A}{L} \tag{8}$$

where L is the width, R is the resistance and A is the area of the pellet. The value of electrical resistivity at 300K and 400K is tabulated in the Table3. The graph of current versus voltage is depicted in figure 4(a-d). The value of electrical resistivity is high at room temperature and it decreases with increase in temperature. Since the resistivity is decreased with temperature the material behaves as a semiconductor. The electrical resistivity depends upon the crystal structure and composition of the materials.



(a) (b)

(c) (d)

Figure 4: (a-d) Current versus Voltage Relationship for the Samples

CONCLUSIONS

The cobalt ferrite ($CoFe_2O_4$) samples of different particle size were successfully prepared by nitrate route. The X-ray diffraction (XRD) patterns of all the samples show the single phase spinel structure of nanoparticles. The dielectric constant and the loss decreases rapidly with increasing frequency, and then reaches a constant value. Low dielectric constants materials are required for high –frequency application in electrical circuits, to reduce dielectric losses and skin effect. The high value of electrical resistivity in ferrite is suitable for the high frequency application where eddy current losses are appreciable. The resistivity is decreased with increase in temperature and the material behaves like a semiconductor.

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