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Synthesis, Characterization and Dielectric properties of Nanoparticles of Cobalt Doped Ferrite ($Co_x Fe_{1-x} Fe_2 O_4$)

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Abstract— *Ferrites, a recently uncovered category of materials, have found extensive application in various critical domains. Among them, cobalt ferrites stand out as hard magnetic materials with exceptional coercivity.. We successfully prepared cobalt ferrites by using nanocrystalline powers by Sol gel method. In our study Crystalline, Magnetic nanoparticles of Cobalt ferrites ($Co_x Fe_{1-x} Fe_2 O_4$) (x = 0.4, 0.5, 0.6, 0.8) were synthesized by Sol Gel Method using ferric chloride and cobalt nitrate with NaOH as a reactant. Structural characteristics of samples were determined by X-Ray diffraction and TEM. Particle size found between 8.8 nm to 14.26 nm using Debye Scherrer method. Lattice constant decreases as the value of 'x' increases. Dielectric properties were investigated using impedance analyser. The relative dielectric constant and loss tangents of ferrites a function of frequency (1kHz-30MHz) was investigated at room temperature, both parameter decreases as frequency increases.*

Keywords— ***Cobalt ferrites, Dielectric constant, Impedance analyser, Nanoparticles, XRD***

I. INTRODUCTION

Nanotechnology is a field of research and innovation which use nanoparticles for building things, materials and devices. Particles with size less than 100nm are known as Nanoparticle. First ferrite compounds were synthesized by Yogoro kato and Takeshi Takei in 1930 at Tokyo institute of technology. Now a days their wide application not only in military, but also being used with the civil perspective, along with the development of science and technology, and now became a hot area of interest in the context of developing function materials [1-3]. Spinel ferrites are a complex oxide crystal which has face-centered cubic structure with formula MFe_2O4, where M is metallic cation. Spinel ferrite contains 16 octahedral positions and eight tetrahedral positions. The spinel ferrites are important ferromagnetic materials due to their combined electrical and magnetic properties. Cobalt ferrites ($Co_x Fe_{1-x} Fe_2 O_4$) having spinel structure is great topic of interest. Cobalt ferrite is a familiar hard magnetic material with great physical and chemical stabilities. Among all the ferrite family they have properties like high coercivity, moderate magnetization and good magnetostriction. Due to these property Cobalt ferrites have a great importance from the application point of view, where these materials are widely used in many ferrite devices and production of magnetic and electronic components, high frequency devices, memory cores, high density information storage devices and also in biomedical field [4-5]. The crystalline structure and particle size of spinel nanoparticles are greatly affected by the synthesis route. A number of research reports are available concerning the preparation techniques like sol-gel [6], chemical coprecipitation [7], Sono chemical [8], micro emulsion [9], combustion [10], hydrothermal [11], etc. Among the various methods we used sol gel method [6]. Sol gel method is very easy and efficient method. The presented work is about cobalt ferrite nanoparticles synthesis, characterization and Dielectric properties. One of the most important property of ferrites is Dielectric behavior that depends on the preparation conditions, composition, grain size and sintering temperature [12-13]. There are many reports available on the electrical conductivity and dielectric properties of bulk cobalt ferrite [14-17]. Characterization of cobalt nanoparticles is done by XRD, FESEM and TEM. Particle size using XRD characterization was calculated by debye Scherrer method [18].

II. METHODOLOGY

2.1 Synthesis: Magnetic nanoparticles were prepared by the sol-gel method. We used $FeCl_3.6H_2O$, $FeSO_4.7H_2O$, Co $(NO_3)_2.6H_2O$ and NaOH as reactant to make cobalt doped ferrites. We made four types of cobalt doped ferrites using reactants in different concentrations. We made solutions of stoichiometric amount of $FeCl_3.6H_2O$, Co $(NO_3)_2.6H_2O$ and $FeSO_4.7H_2O$ in 100ml distilled water and a solution by using 6.4g NaOH dissolved in 200 ml distilled water.

All solutions were continuously stirred using a magnetic stirrer for 20 minutes individually. Subsequently, a 100 ml solution of NaOH was taken in a 500 ml beaker, and cobalt nitrate, ferric chloride, and ferrous sulfate solutions were added to it while stirring. The pH of this mixture was maintained between 8-9, and then NaOH was slowly added to achieve a pH between 11-12 under continuous stirring for 15 minutes. The mixed solution was then transferred to a hot plate and heated up to a temperature of 80°C. After 10 minutes, 5 ml of oleic acid was added to the mixture, which was kept at 80°C for an additional 20 minutes. The hot plate was then turned off and left for one hour while the stirrer remained active. After one hour, the hot plate was switched on again, and the temperature was raised to 90°C. The hot plate was turned off once more, and the solution was allowed to cool to room temperature while the stirrer continued running. Then, 6 to 7 drops of HNO3 were added to the solution, resulting in the separation of precipitate and dirty water. The dirty water was discarded, and the precipitate was washed with distilled water. The washed precipitate was then placed in distilled water and left overnight. The following day, the precipitate was washed multiple times with boiled water and acetone. To dry the sample, the precipitate was placed on filter paper for some time, followed by exposure to sunlight in a petri dish until it reached a powdered form.

2.2 Characterization: Different techniques for the characterization of nanomaterials was done. A complex analytical system is necessary which is capable to determine the composition and the properties of the substances. We used Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) to study Structural morphology**.** These methods aim at determining the crystal structure, chemical analysis, phase identification, crystal or grain size. Dielectric behavior is one of the most important property of ferrites. Impedance Analyzer was used to study dielectric properties.

III. RESULT AND DISCUSSION

3.1 X Ray diffraction analysis: Its composition, phase structure and morphology are characterized by X-ray diffraction (Cu target, Wavelength 1.54184 Å). XRD patterns of different cobalt doped ferrites are shown in figures (1.a -1.d). In these patterns one peak (h k l) value (3 1 1) is presented intensively. Crystalline size of every sample was calculated by debye scherrer formula [18] –

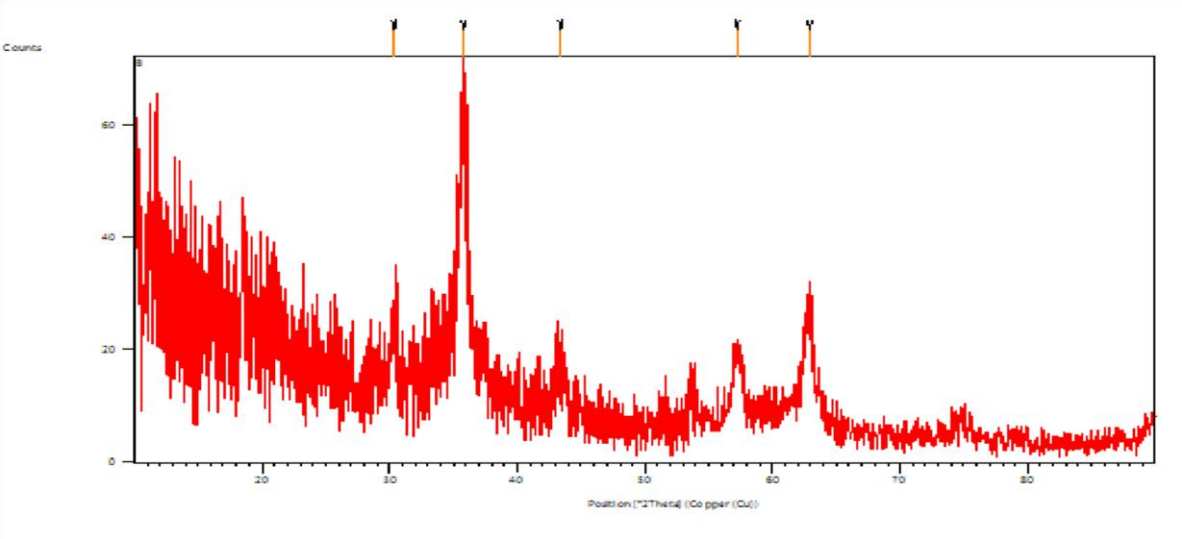
$$t=k\lambda/\beta\cos\theta,$$

Where k is shape factor. In this the value of k is 0.9. λ is wavelength of X Ray used, θ is Bragg's angle. β is the full width at half maximum (FWHM) (in radian). From the above formula it was found that values of particle size 't' between 8.8nm-14.26nm. One can obtain lattice constant by Bragg's equation. Particle size, D spacing and lattice constant of different cobalt ferrites are shown in Table 1.

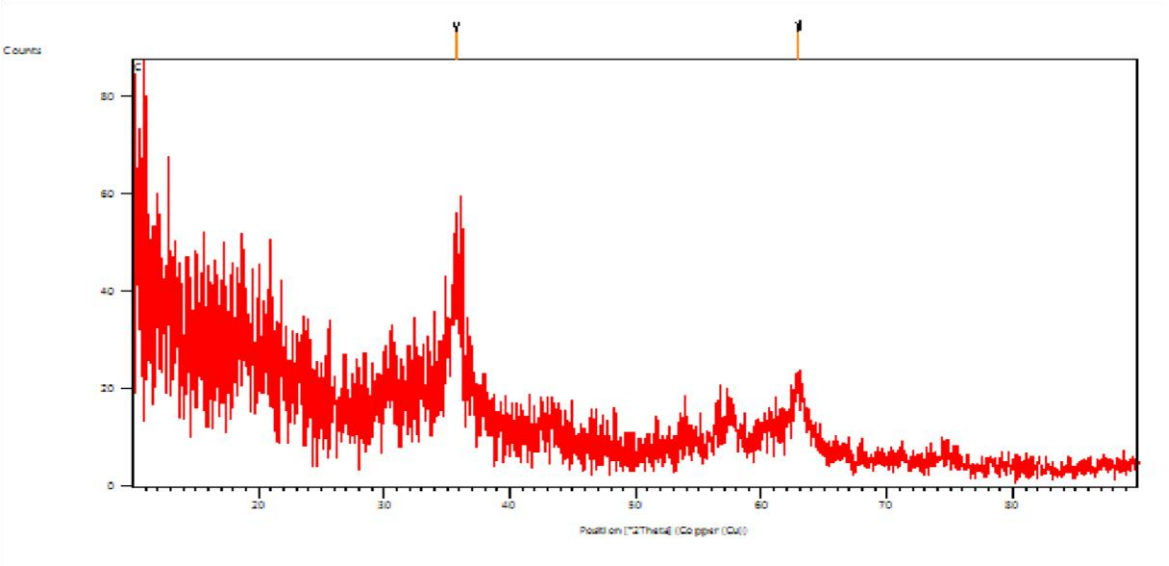
Table 1: Particle size, D spacing, Lattice constant of cobalt ferrite

Cox Fe1-x Fe2 O4	x =0.8	x =0.6	x =0.5	x =0.4
Particle size	14.26nm	8.81nm	9.60nm	9.64nm
D spacing	2.50Å	2.51 Å	2.52 Å	2.525 Å
Lattice constant	8.31Å	8.33 Å	8.35 Å	8.36 Å

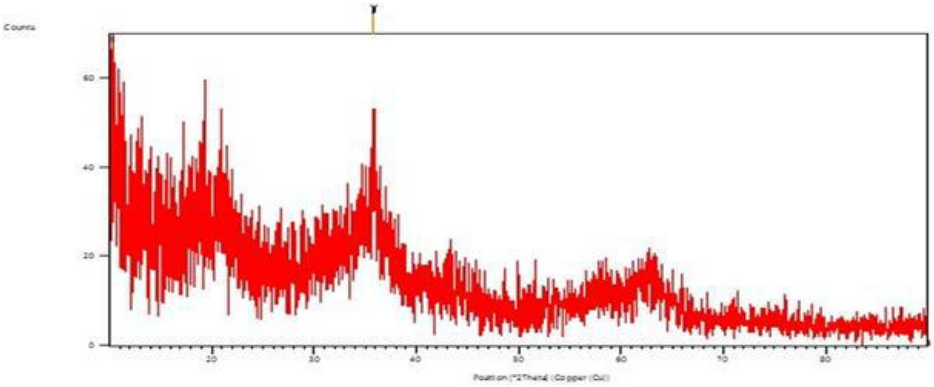
Particle size does not follow any symmetric pattern with the value of 'x' [table 1]. D spacing and lattice constant both are decreasing as the value of 'x' increasing. Similar results were found by Babukutty et al [19]. and soleimani et al. [20].



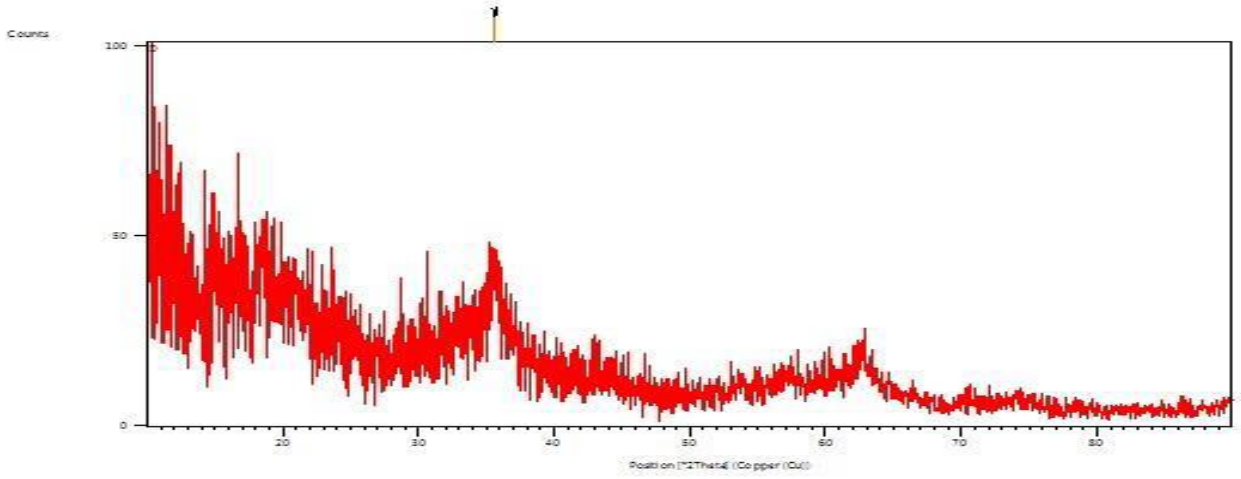
1.a: XRD pattern of $Co_{0.8}\ Fe_{2.2}\ O_4$



1.b: XRD pattern of $Co_{0.6}Fe_{2.4}O_4$



1.c: XRD pattern of $Co_{0.5}Fe_{2.5}\ O_4$



1.d: XRD pattern of $Co_{0.4}Fe_{2.6}O_4$

3.2 TEM analysis: transmission electron microscopy is done for cobalt ferrite. The images of TEM are shown in figure 2. SEAD pattern of this ferrite is also shown in last image. Plane (3 1 1) shows in this pattern intensively. Other planes are also shown in this pattern [21].

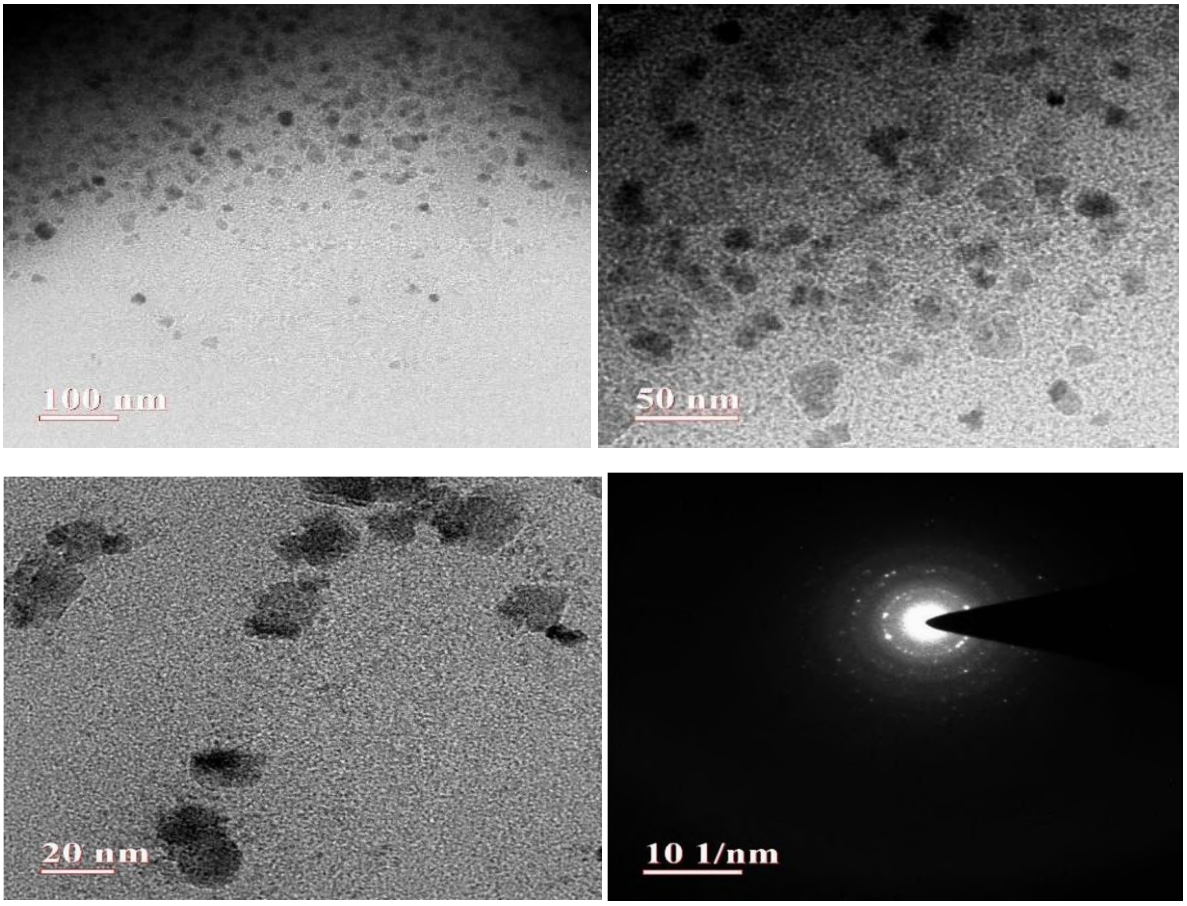
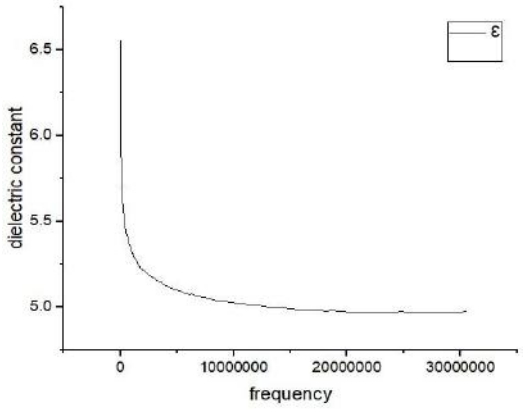


Fig.2: TEM images and SEAD pattern of Co $_{0.8}Fe_{2.2}O_4$

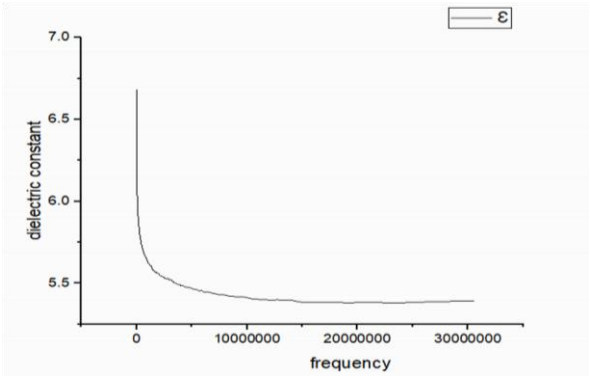
3.3 ***Dielectric constant***: Dielectric measurement was performed by using 6500 series of precision Impedance Analyzer. For dielectric measurements, the sample powder was dried and compressed into disc shaped pellet of diameter 13 mm and thickness about 2 mm by applying the pressure of 5,6 tons. After that silver electrodes were deposited on both sides of the samples. Dielectric constant was calculated using the following formula-

$$\varepsilon = cd/\varepsilon_0 A$$

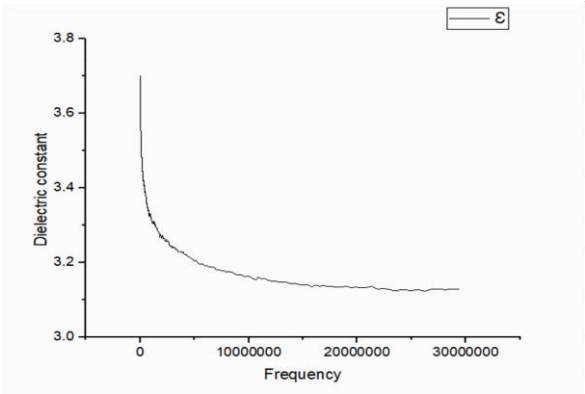
where C- capacitance of the pellets, d - thickness of the pellets; A- cross-sectional area of the flat surface of the pellets (m^2) and □□ − permittivity of free space. The dielectric constants measurement was done in the range 1kHz to 30MHz using Impedance Analyzer. The graphs of dielectric constant against frequency are depicted in Fig.3 (a-d). Dielectric constant is highest at the frequency of 1kHz and it decreases as frequency increase. The presence of interfacial polarization, as predicted by Maxwell-Wagner [22], leads to a decrease in polarization with increasing frequency across all samples. According to their model, ferrite materials consist of two layers: a conductive layer composed of large ferrite grains and a second layer consisting of grain boundaries with poor conductivity. Rabinkin and Novikova [23] proposed a similar conduction mechanism that induces polarization in ferrites. This polarization occurs due to the local displacement of electrons in the direction of the applied electric field, resulting from the exchange between Fe^{+2} and Fe^{+3} ions. The dielectric constant decreases with increasing frequency because any polarization-contributing effect lags behind the applied field at higher frequencies. Beyond a certain limit, the electron hopping cannot keep up with the electric field fluctuations, causing a decrease in the dielectric constant. Koop [24] suggested that the low-frequency dielectric constant arises from the grain boundaries, which exhibit high resistivity and thus have a high dielectric constant. On the other hand, the high-frequency dielectric constant comes from the grains, which have low resistivity and a lower dielectric constant. Therefore, it can be concluded that the exchange of electrons between Fe^{+2} and Fe^{+3} ions, resulting in the alignment with the electric field, is responsible for the electrical polarization of ferrites. At lower frequencies, the higher dielectric constant may be attributed to factors such as dislocations, voids, and defects.



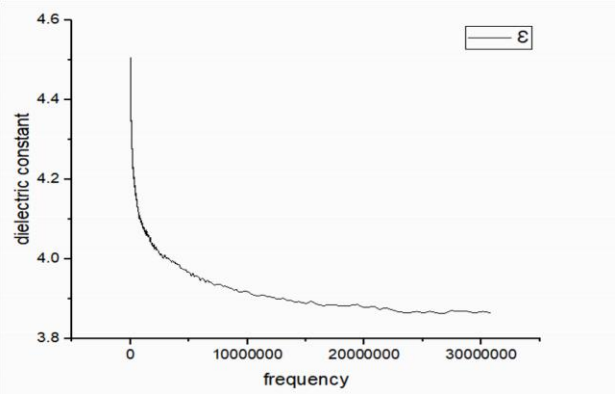
3.a $Co_{0.8}Fe_{2.2}O_4$



3.b $Co_{0.6}Fe_{2.4}O_4$



3c $Co_{0.5}Fe_{2.5}O_4$



3.d $Co_{0.4}Fe_{2.6}O_4$

Dielectric constant values at 1kHz for all samples were found 6.5, 6.7, 3.7, 4.5 as the value of x = 0.8, 0.6, 0.5, 0.4 respectively. These results are similar as Yadav et al.[25]. Dielectric constant for cobalt ferrites with different concentration at 1kHz is shown in figure 4. Dielectric constant varies as concentration changes.

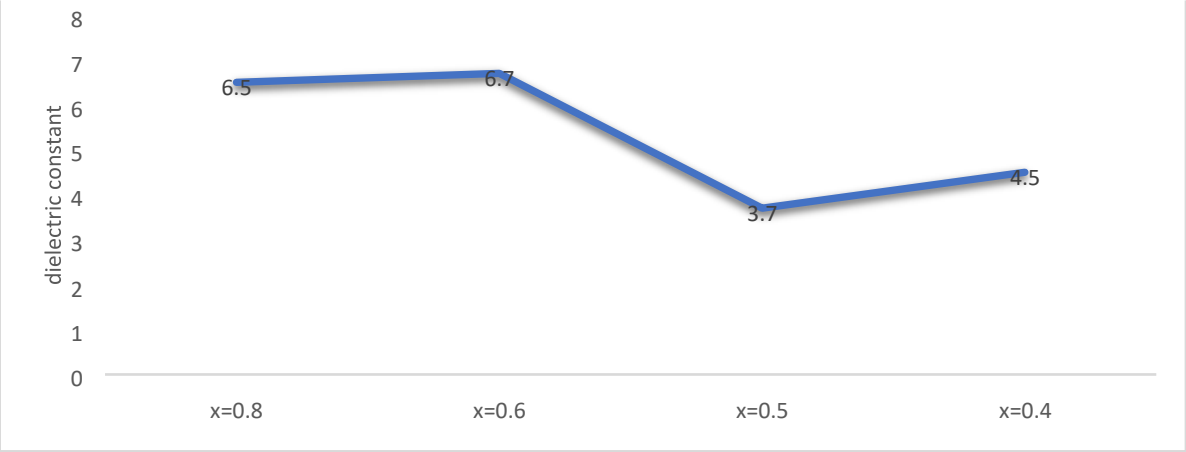
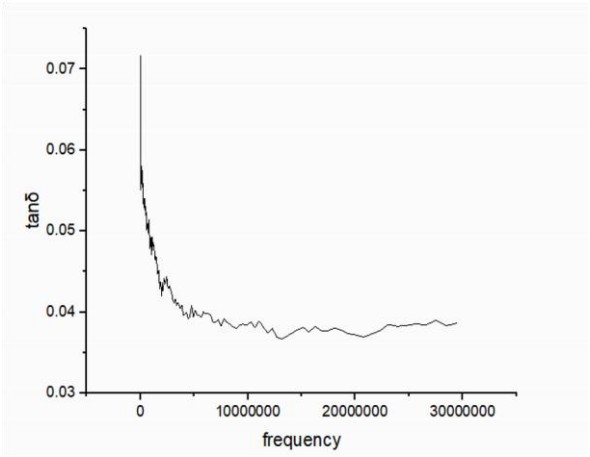
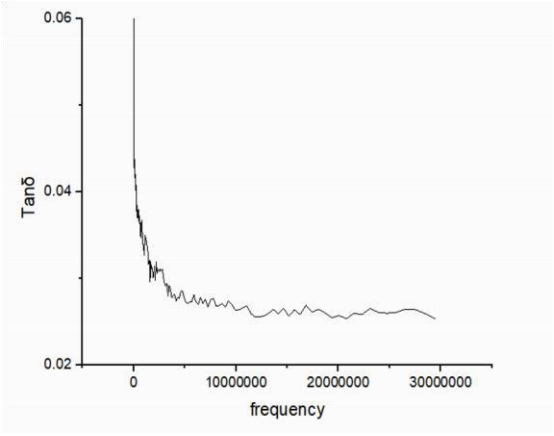


Figure 4

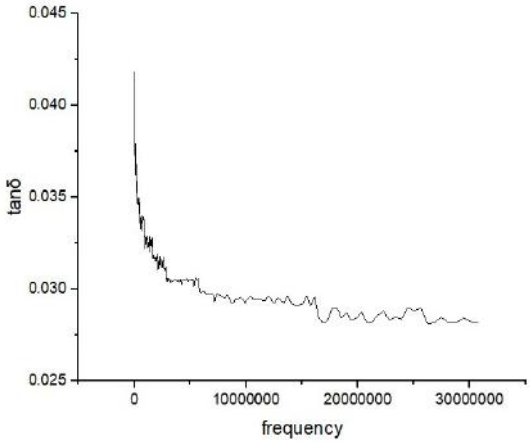
3.4 Dielectric loss factor: Dielectric loss factor (tan δ) was measured by using Impedance analyzer in the range 1kHz to 30MHz. The graph between tan δ and frequency are shown in figures 5(a-d). With the increase of frequency dielectric tangent loss (tan δ) decreases and then became almost constant at higher frequencies for all samples. The value of dielectric tangent loss (tan δ) depends on a number of factors, such as stoichiometry, Fe^{+2} content and structural homogeneity, which in turn depends on the composition and synthesis methods.



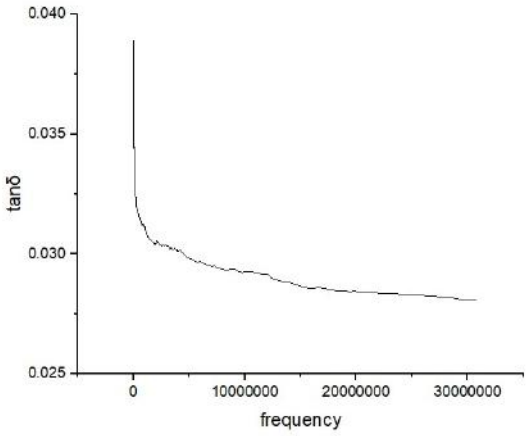
5.a $Co_{0.8}Fe_{2.2}O_4$



5.b $Co_{0.6}Fe_{2.4}O_4$



5.c $Co_{0.5}Fe_{2.5}O_4$



5.d $Co_{0.4}Fe_{2.6}O_4$

IV. CONCLUSION

In this paper we presented method of preparing cobalt ferrite ($Co_x Fe_{1-x} Fe_2 O_4$) (x = 0.4, 0.5, 0.6, 0.8) nanoparticles by Sol Gel method. Their structural morphology was studied using XRD, FESEM and TEM. Debye Scherrer method was used to find out particle size from X-Ray diffraction pattern and using this method we got particle size between 9 -15nm. Lattice constant is decreases as the value of 'x' increases. After analyzing the images of TEM we found that particle shape is not perfectly spherical but follow symmetrical pattern. TEM images showed that the similar particle size. The dielectric constant and the loss tangent decrease rapidly with increase in frequency initially and later reaches to a constant value. Materials with low dielectric constant are useful for high frequency applications in electrical circuits.

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