Original Research Article

Composition and Frequency dependent Dielectric properties of Cr-Co Nano ferrites

ABSTRACT

- Chromium substituted Co-ferrite nanoparticles with general formula $Cr_xCoFe_{2-x}O_4$ ($0\leq x \leq 0.5$) have been synthesized by using sol-gel technique. The samples were sintered at 900°C for 3hours. The effect of chromium substitution on dielectric properties of Co-ferrites is reported in this paper. The X-ray diffraction patterns indicate the formation of single phase spinel structure for all the samples. The particle size of all samples was calculated using Debye- Scherer's formula and it is in the range of 56-75 nm. The investigation on dielectric constant (ε'), dissipation factor(D) and AC conductivity(σ_{ac}) was carried out at a fixed frequency 1kHz and in the frequency range of 100Hz to 1MHz at room temperature using LCR meter. The frequency dependence of the dielectric constant (ε') and AC conductivity (σ_{ac}) show a normal dielectric behaviour. The frequency dependence of dissipation factor (D) of the chromium substituted cobalt ferrite samples displays a relaxation peak at certain frequency. This peak suggests the presence of relaxing dipoles in the Cr-Co nano ferrite samples. It is also observed that the broadening of the relaxation peak with chromium-content(x) in dissipation factor versus frequency curve is due to the strengthening of dipole-dipole interactions. The dielectric behaviour of the Cr-doped cobalt nano ferrites is explained based on Koop's two layer model and Maxwell- Wagner interfacial polarization theory and Debye-relaxation theory.

Keywords: Co-Cr ferrites, nanoparticles, dielectric properties, dipole - dipole interaction.

1. INTRODUCTION

Now a day’s material science research is focused on the invention of new materials with enhanced properties and novel synthesis techniques. Nano crystalline materials attract several researchers due to their tremendous applications and interesting properties.

In early days, Garnets were used in microwave devices, where they have high value of electrical resistivity and low dielectric loss. But because of low Curie temperature and high cost of garnets, they are rarely used.

In recent technology, chromium nano ferrites and substituted chromium nano ferrites replace the garnets because of its high resistivity, low dielectric loss and high Curie temperature and low cost. So Lithium ferrites are widely used in micro wave devices like isolators, regulators and phase shift oscillators.

When transition metal cations are incorporated in the chromium lattice then we can observe subsequent change in their structural, electrical, magnetic and optical properties [1-2]. The properties of Chromium substituted Cobalt nano ferrite are strongly depends on method of preparation technique, sintering time, sintering temperature, pH value, etc,

Several methods are used for synthesizing nano structured Chromium substituted Cobalt nano ferrite such as co precipitation, sol-gel, micro emulsion, hydrothermal, citrate gel, and reverse micelle methods [3–5] but the citrate gel method is used to speed up the synthesis of complex materials. It is a simple process, which offers a significant saving in time and energy consumption over the traditional methods.

In this communication, we report the synthesis of Chromium substituted Cobalt nano ferrite dielectric properties of these ferrites at room temperature at various selected frequencies up to in the frequency range 1 MHz have been studied

$CoFe_2O_4$ possess an inverse spinel stricture in which Co^{2+} ions present in the octahedral (B) sites and Fe^{3+} ions distributed almost equally between the tetrahedral (A) and octahedral (B) sites [3]. Cobalt ferrite is a familiar hard magnetic material with great physical and chemical stabilities, high coercivity, moderate magnetization and good magnetostrictive properties among all the ferrite family. Due to these properties Co-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 [7-8].

In earlier communication, we reported the detailed synthesis and characterization of Chromium substituted Co-ferrite nano particles [9], so in this communication, we focused dielectric properties. The variations of dielectric constant, dissipation factor, ac conductivity, have been analyzed as a function of frequency at room temperature.

2. EXPERIMENTAL

2.1 Synthesis Technique

Nanocrystalline $Cr_xCoFe_{2-x}O_4$ ($0.0 \leq x \leq 0.5$) samples were prepared by sol-gel route using high purity (Analytical grade) $Co(NO_3)_2$ $.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Cr(NO_3)_3.9H_2O$ and $C_6H_8O_7.H_2O$(Hydrated citric acid) respectively in stoichiometric proportions. The sol was prepared by taking 1:3 ratio of citric acid and metal nitrates and the pH was adjusted to 7 by adding small quantity of ammonia to the sol. Then the sol was heated on a hot plate at 100°C under constant and intensive stirring to transform it into a gel. The gel was then heated at 150°C for auto-combustion to take place. Then the dried gel burnt in a self-propagating combustion lead to form loose powder .The powder is crushed in an agate mortar. After that the powder was pre-sintered at 900°C for 3 hrs and cooled slowly to room temperature to obtain the nano ferrite particles. The step by step procedure of synthesis of Cr-Co ferrite nanoparticles is shown in the Fig. 1.

The pre-sintered ferrite samples were mixed with an organic binder (small quantity of polyvinyl alcohol (PVA)) for granulation. Then the granulated powder was dried and compressed into disc shaped pellet of diameter 10 mm and thickness about 2 mm by applying the pressure of 3 tons. The samples were finally sintered at 950°C for 5hrs and slowly allowed to cool to room temperature. For dielectric measurements both sides of the pellets were coated with a thin layer of silver paste and air dried for making a good electrical contact.

2.2 Dielectric measurements

The dielectric parameters of the Co-Cr ferrite samples were measured at room temperature in the frequency range of 100Hz to 1MHz by using LCR Meter (Waynekerr Model: 43100). The values of capacitance (C) and dissipation factor (D) were noted directly by this LCR meter at different frequencies.

The dielectric constant (ε') was calculated by using the following formula [10]

$$\varepsilon' = C\,t / \varepsilon_o A \qquad \ldots..(1)$$

Where C is the capacitance of the sample, A is the surface area, t is the thickness of the pellet, and ε_o is the permittivity of free space.

From dielectric constant and dissipation factor (D), the ac conductivity (σ_{ac}) of the ferrite samples can be calculated by using the following equation [11]

$$\sigma_{ac} = 2\Pi f\, \varepsilon'\, \varepsilon_o\, D \qquad \ldots..(2)$$

Where $\omega = 2\Pi f$ is the angular frequency.

3. RESULTS AND DISCUSSION

3.1. Dielectric Properties

The dielectric properties of Cr-Co ferrites have been investigated as a function of composition and frequency. Dielectric studies of these samples may be useful for widening its range of applications.

3.1.1. Dielectric constant (ε')

The polarization phenomenon in ferrites is quite consistent with the conduction process. The transferring of electrons between the Fe^{2+} and Fe^{3+}ions in octahedral sites results in the local displacement of electrons in the direction of the external applied electric field and these electrons induce the polarization in the ferrite materials. The frequency dependence of the dielectric constant (ε') for $Cr_xCoFe_{2-x}O_4$ ($0.0 \leq x \leq 0.5$) spinel ferrite system was studied at room temperature in the frequency range of 100Hz to 1MHz. Fig.2 shows the variation of the dielectric constant of Cr-Co nano ferrite samples as a function of frequency at room temperature. It can be observed that all the compositions exhibit dielectric dispersion where the dielectric constant decreases rapidly with increasing frequency in low frequency region and the rate of decrease is slow in the high frequency region, the dielectric behaviour approaches almost frequency independent in high frequency region. The dielectric dispersion with increasing frequency is a normal behaviour observed in most of the ferrimagnetic materials [12, 13]. The dielectric dispersion in Cr-Co ferrites is due to the Maxwell-Wagner type interfacial polarization which is in agreement with Koop's theory [14, 15]. According to this theory, a ferrite material has been assumed to be composed of fairly well conducting grains which are separated by highly resistive grain boundaries. It has been noticed that in ferrite materials the relative permittivity or dielectric constant is directly proportional to the square root of electrical conductivity. At lower frequencies the grain boundaries are more predominant in electrical conduction hence they have high values of relative permittivity, while the grains are highly effective at high frequency region thus they have smaller values of relative permittivity. However, in case of nano ferrite material, both grains and grain boundaries are large in number as compared with the bulk ferrite material case, which makes the dielectric polarization mechanism more complex. In case of nano ferrite materials, there is a chance of having a high relative permittivity because of large surface polarization due to the high surface area of individual grains. In the low frequency region, surface polarization plays a predominant role than ionic or electronic polarization in determining the dielectric behaviour of nano-ferrite materials [15]. The higher value of dielectric constant (ε') at lower frequency is due to the inhomogeneous dielectric structure in ferrite material. The inhomogeneities present in the material can be oxygen vacancies, grain boundary defects, interfacial dislocation pile ups, high concentration of Fe^{2+} ions and porosity, etc., while the decrease in dielectric constant value with increase in frequency is due the fact that the lagging of the species which are contributing to the polarization behind the applied ac electric field at very high frequencies [16-17]. The independent behaviour of the dielectric constant (ε') on frequency in the high frequency region (5.1KHz-1MHz) can be understood on the basis of Debye relaxation theory [18]. This independent behaviour of the dielectric constant (ε') is due to the impact of a large relaxation time; since the space charge carriers in a dielectric material require a finite time to align their axes in the direction of an applied ac field. If the frequency of the field reversal increases, at some stage, the space charge carriers cannot line up with the applied field and unable to follow the field variation, as a result dielectric constant of the material decreases and becomes frequency independent.

To investigate the influence of composition on the dielectric properties of Cr-Co ferrite system, the dielectric parameters of Cr-Co ferrite system were measured at a fixed frequency of 1 kHz. The values are recorded in Table 1. In the present investigation the dielectric behaviour of $CoFe_2O_4$ was drastically affected by Cr doping. From Table 1 one can conclude that, the dielectric constant of $CoFe_2O_4$ linearly increases up to x=0.3, suddenly decreases at x=0.4 and again it increases for x=0.5. The variation of dielectric constant as a function composition is shown in Fig.5. The increase in dielectric constant with increasing Cr-content may be attributed to the formation of Fe^{2+} ions in octahedral site. The formation of Fe^{2+} ions in octahedral site increases the electron exchange between Fe^{2+} and Fe^{3+} ions which in turn enhances the polarization. However, the decrement in dielectric constant value for $Cr_{0.4}CoFe_{1.6}O_4$ sample may be due to the migration of Fe^{3+} ions from octahedral site to tetrahedral site which decreases the hopping and dielectric polarization.

3.1.2. Dissipation factor (D)

The dielectric loss in ferrites mainly originates due to the exchange of electrons between ferrous ions (Fe^{2+}) and ferric ions (Fe^{3+}) on the octahedral site and defect dipoles. The variation of dissipation factor (D) against frequency at room temperature for $Cr_xCoFe_{2-x}O_4$ (where x = 0.0 to x = 0.5) ferrites is depicted in Fig.3. It can be observed that all the Cr doped cobalt nano ferrite samples exhibit the loss peak nearly at 5kHz frequency except $Cr_{0.0}CoFe_2O_4$ (x=0.0) and $Cr_{0.5}CoFe_{1.5}O_4$ (x=0.5) ferrite samples. In the case of $Cr_{0.0}CoFe_2O_4$ and $Cr_{0.5}CoFe_{1.5}O_4$ ferrite samples, the dissipation factor (D) exhibits an inverse dependence on frequency which is a normal behaviour of any ferrite materials. The appearance of the relaxation peak in Co-Cr mixed ferrites ($Cr_{0.1}CoFe_{1.9}O_4$ $Cr_{0.2}CoFe_{1.8}O_4$, $Cr_{0.3}CoFe_{1.7}O_4$, and $Cr_{0.4}CoFe_{1.6}O_4$) can be explained according to Debye relaxation theory [18]. The loss peak in dissipation factor versus frequency curves can be found when the hopping frequency of electrons is approximately matching with the frequency of the applied electric field [19,20]. The condition for observing a maximum in dielectric loss of dielectric material is given by

$$\omega\tau = 1 \qquad \ldots..(3)$$

Where $\omega=2\Pi f$, f is the frequency of the applied electric field and τ is the relaxation time.

From Fig. 3, it is important to notice that the relaxation peaks become broad, and the height of the peak also increases with increasing chromium concentration(x) up to x=0.3 after that decreases for x=0.4 composition. The increase in peak height with the increase of Cr^{3+} ion substitution is due to the increase of conductivity of the sample arising due to the increase of the Fe^{3+}/Fe^{2+} ions available for the conduction process. The increase in the peak width is due to strengthening of the dipole-dipole interactions which causes hindrance to the dipole rotation. The strength and frequency of the relaxation depend on characteristic property of dipolar relaxation.

The relation between dissipation factor (D) and angular frequency of applied electric field (ω) is shown in the following equation.

$$D = 1/\omega \varepsilon' \varepsilon_0 \rho \qquad \ldots..(4)$$

From above relation, it can be concluded that the dissipation factor (D) is approximately inversely proportional to the frequency of applied electric field. Thus the dielectric loss of ferrites is expected to decrease with increase in frequency.

3.1.3. AC conductivity

Fig.4 shows the frequency dependence of ac conductivity for the Cr-Co ferrite system sintered at 950°C. All the curves exhibit the significant dispersion with frequency, which is an important behaviour of ferrites. It can be seen that the ac conductivity (σ_{ac}) seems to be nearly frequency independent for all the compositions upto 0.1 MHz but above this frequency range, σ_{ac} rapidly increases until it reaches a maximum value. The electrical conductivity in ferrites is mainly due to the hopping of electrons between the ions of the same element presented in more than one valence state and distributed randomly over crystallography equivalent lattice sites .On the application of ac electrical field, the frequency of electrons gets boosted up. The increase in the frequency of the applied electric field increases the hopping phenomenon which in turn enhances the ac conductivity of the ferrite ceramics. From Fig. 4 and table 1 it can also noticed that Cr-doped Co-ferrites have higher conductivity than undoped ones. The number of ferrous (Fe^{2+}) ions at octahedral (B) sites plays a dominant role in the process of conduction in these ferrite materials. The highest conductivity for composition x=0.3, may be attributed due to the presence of a large number of Fe^{2+} ions in the $Cr_{0.3}CoFe_{1.7}O_4$ ferrite sample.

4. CONCLUSIONS

We have successfully synthesized $Cr_xCoFe_{2-x}O_4$($0.0 \leq x \leq 0.5$) nano ferrites with single phase spinel structure by sol-gel method. The dielectric properties have been investigated as a function of composition and frequency. The room temperature dielectric constant decreases rapidly with increasing frequency indicates the normal dielectric behaviour for all the samples, and this has been elucidated on the basis of interfacial polarization phenomena as discussed in Maxwell-Wagner theory. All the Cr^{3+}substituted samples have high dielectric constant than the basic cobalt composition without chromium. The ac conductivity was found to increase with an increase in frequency and Cr concentration. Relaxation peaks were observed for the Cr-substituted Cobalt ferrite samples in dissipation versus frequency curves. It is also found that the height and width of the relaxation peak increased for the Cr-Co ferrite system when Cr-content is between x=0.0 and x= 0.3 and after that, decreased with the further addition of chromium and this has been explained based on the Debye relaxation theory. The substitution of Cr^{3+} for Fe^{3+} ions results in a significant impact on the dielectric behaviour of the Cr-Co ferrite system. The low-temperature sintered Cr–Co ferrites exhibit good dielectric properties, as well as fine-grained nanostructures, making them become good materials for high-frequency applications with high-performance and low-cost.

REFERENCES

[1]. P. V. Reddy and T. S. Rao, “X-ray studies on lithium-nickel and manganese-magnesium Mixed ferrites,” Journal of the Less-Common Metals, vol. 75, no. 2, pp. 255–260, 1980

[2] R. S. Devan, Y. D. Kolekar, and B. K. Chougule, “Transition metal-doped rare earth vanadates: a regenerable catalytic material for SO FC anodes,” Journal of Physics: Condensed Matter, vol.18, no. 43, pp. 9809–9821, 2006.

[3] E.VeenaGopalan, I. A. Al-Omari, K. A.Malini et al., “Impact of zinc substitution on the

Structural and magnetic properties of chemically derived nano sized manganese zinc mixed Ferrites," Journal of Magnetism and Magnetic Materials, vol. 321, no. 8, pp.1092–1099, 2009.

[4] E. Veena Gopalan, K. A.Malini, S. Saravanan, D. Sakthi Kumar,Y. Yoshida, and M. R. Anantharaman, "Evidence for polaron conduction in nano structured manganese ferrite," Journal of Physics D: Applied Physics, vol. 41, no. 18, Article ID 185005, 2008.

[5] M. Srivastava, S.Chaubey, andA.K.Ojha, "Investigation on size dependent structural and Magnetic behavior of nickel ferrite nano particles prepared by sol-gel and hydrothermal Methods, "Materials Chemistry and Physics, vol. 118, no. 1, pp. 174–180,2009

[6] Sharma, R.K., et al. Materials Letters, 59 (2005) 3402-3405.

[7] Moya, C., del Puerto Morales, M., Batlle, X. and Labarta, A. Physical Chemistry Chemical Physics, 17 (2015) 13143-13149.

[8] Keluskar, S.H., Tangsali, R.B., Naik, G.K. and Budkuley, J.S. J. Magn. Magn. Mater., 305(2006) 296-303.

[9] M. Lakshmi, K. Vijaya Kumar, and K. Thyagarajan. Advances in Nanoparticles, 5 (2016) 103-113.

[10] Pandya, Rutvi J., U. S. Joshi, and O. F. Caltun, Procedia Materials Science, 10 (2015) 168-175.

[11] M. Farid, I. Ahmad, S. Aman, M. Kanwal, G. Murtaza, I. Alia, and M. Ishfaq, J. Ovon Res, 11 (2015) 1-10.

[12] D. Ravinder and K. Vijaya kumar, Bull. Mater. Sci., 24(2001) 505–509.

[13] Wahba, Adel Maher, and Mohamed Bakr Mohamed, Ceram. Int., 40 (2014) 6127-6135.

[14] K.W. Wagner, Ann. Phys., 345 (1913)817–855.

[15] C.G. Koops, Phys. Rev., 83 (1951) 121–124.

[16] M.A. El Hiti, J. Magn. Magn. Mater., 192 (1999) 305–313.

[17] N. Rezlescu, C. Prakash, G.Prasad: J.Phys. D: Appl. Phys., 39(2006) 1635.

[18] C. Venkataraju, G. Sathishkumar, and K. Sivakumar. J. Alloys Compd.,498 (2010) 203-206.

[19] A.M. Abdeen, O.M. Hemeda, E.E. Assem, M.M. El-Sehly, J. Magn. Magn. Mater., 238 (2002) 75–83.

[20] M.A. Dar, K.M. Batoo, V. Verma, W.A. Siddiqui, R.K. Kotnala, J. Alloys Comp., 493 (2010) 553–560.

[21] Azadmanjiri, J., H. K. Salehani, M. R. Barati, and F. Farzan. Materials Letters, 61 (2007) 84-87.

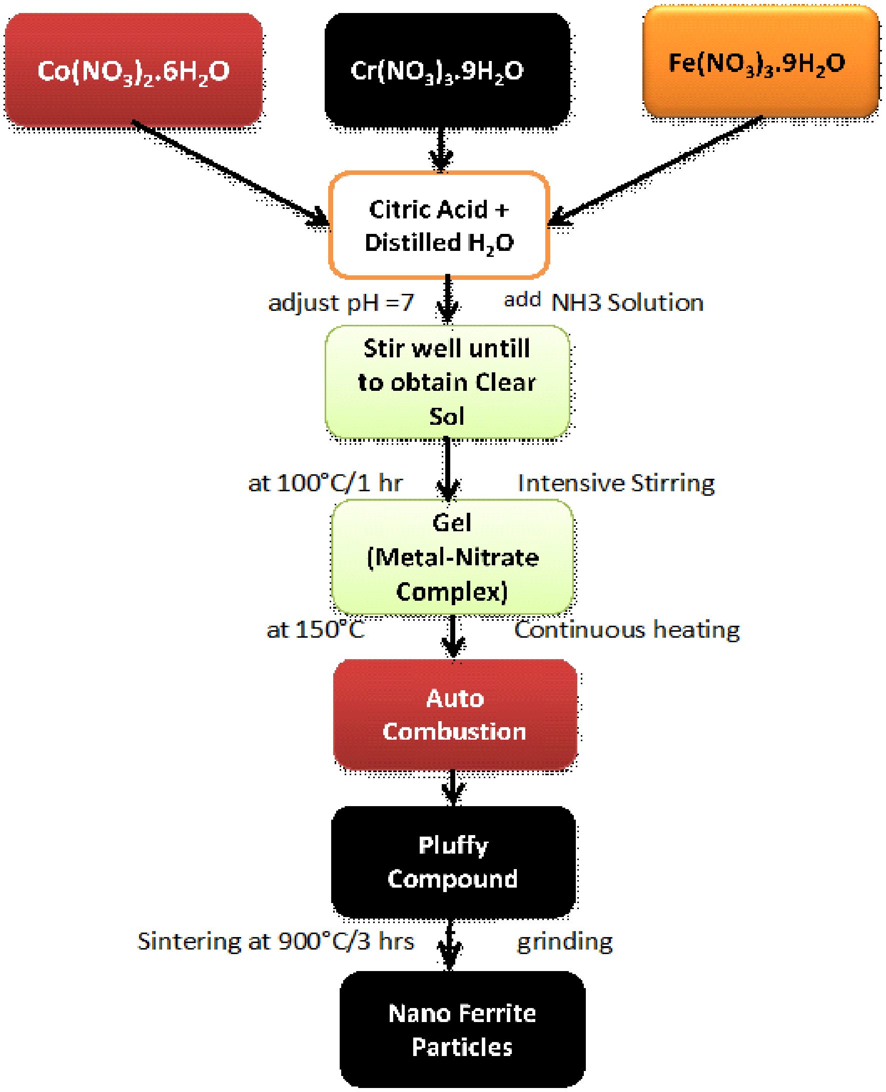

Fig.1: Flow chart for the synthesis of $Cr_xCoFe_{2-x}O_4$ nanoparticles by Sol-Gel method

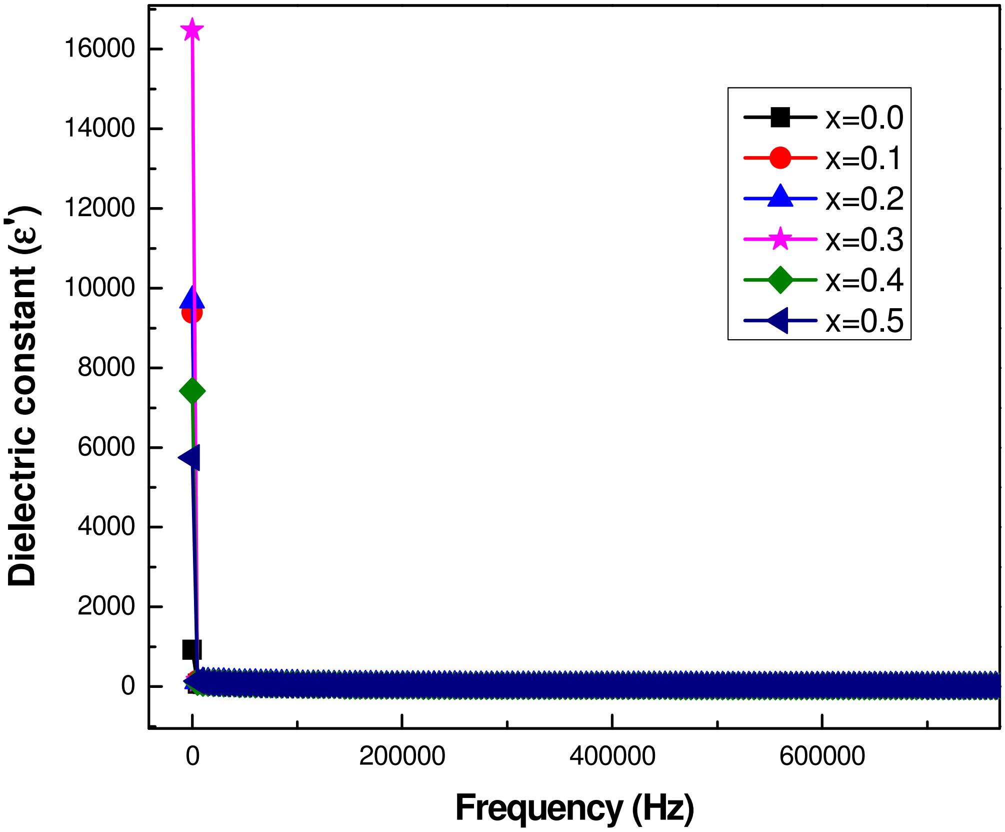

Fig. 2: Variation of dielectric constant with frequency for $Cr_xCoFe_{2-x}O_4$ ($x = 0.0$ to 0.5)

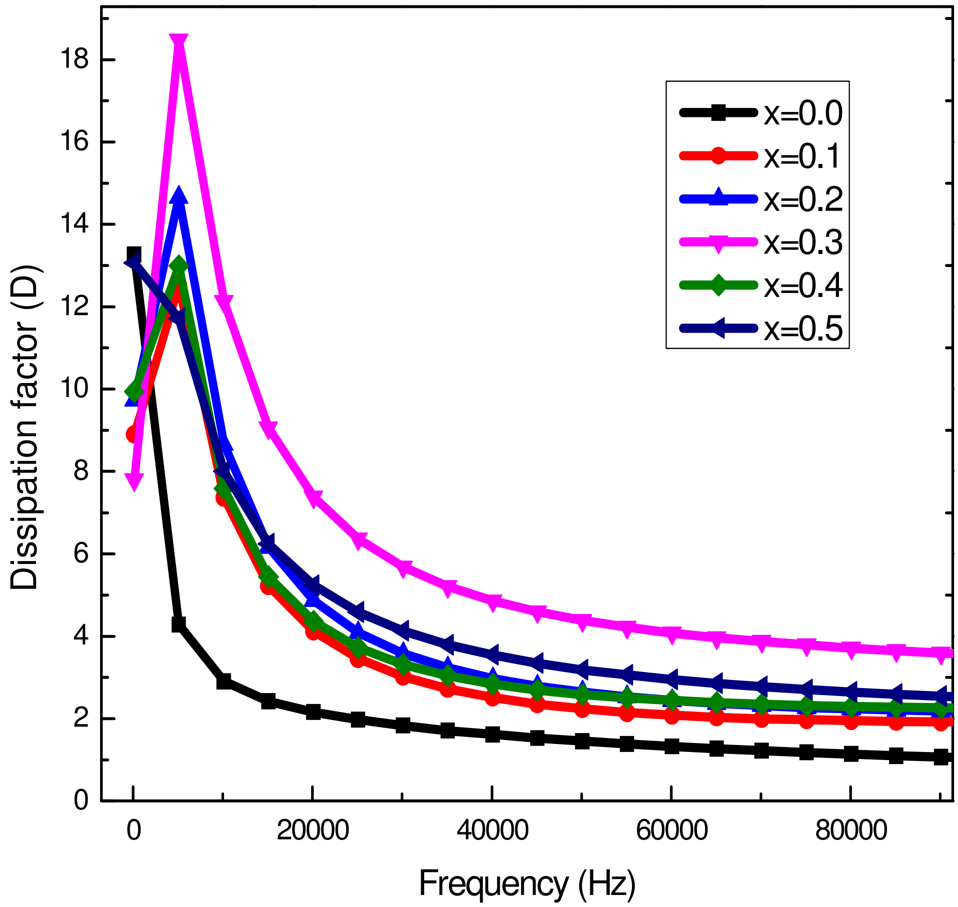

Fig. 3: Variation of dissipation factor (D) with frequency for $Cr_xCoFe_{2-x}O_4$ ($0.0 \leq x \leq 0.5$)

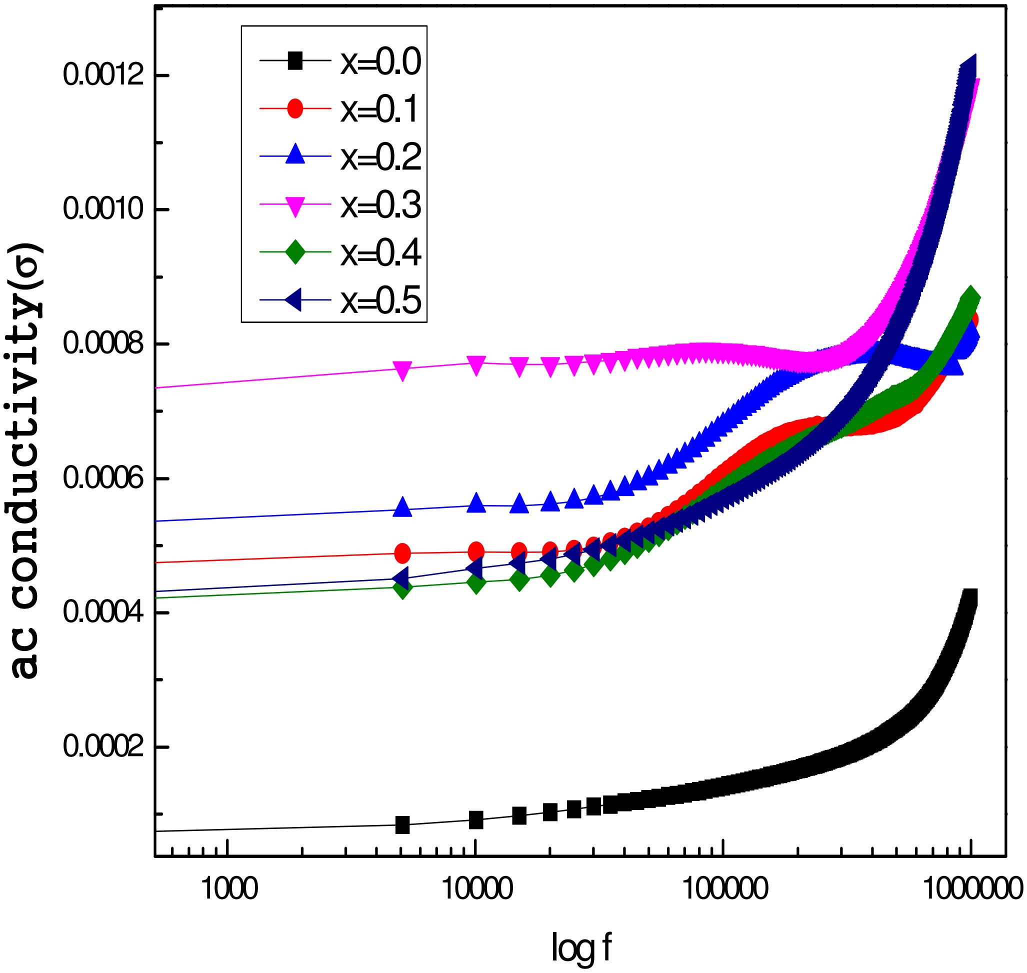

Fig. 4: Variation of Ac conductivity with frequency for $Cr_xCoFe_{2-x}O_4$ ($0.0 \leq x \leq 0.5$)

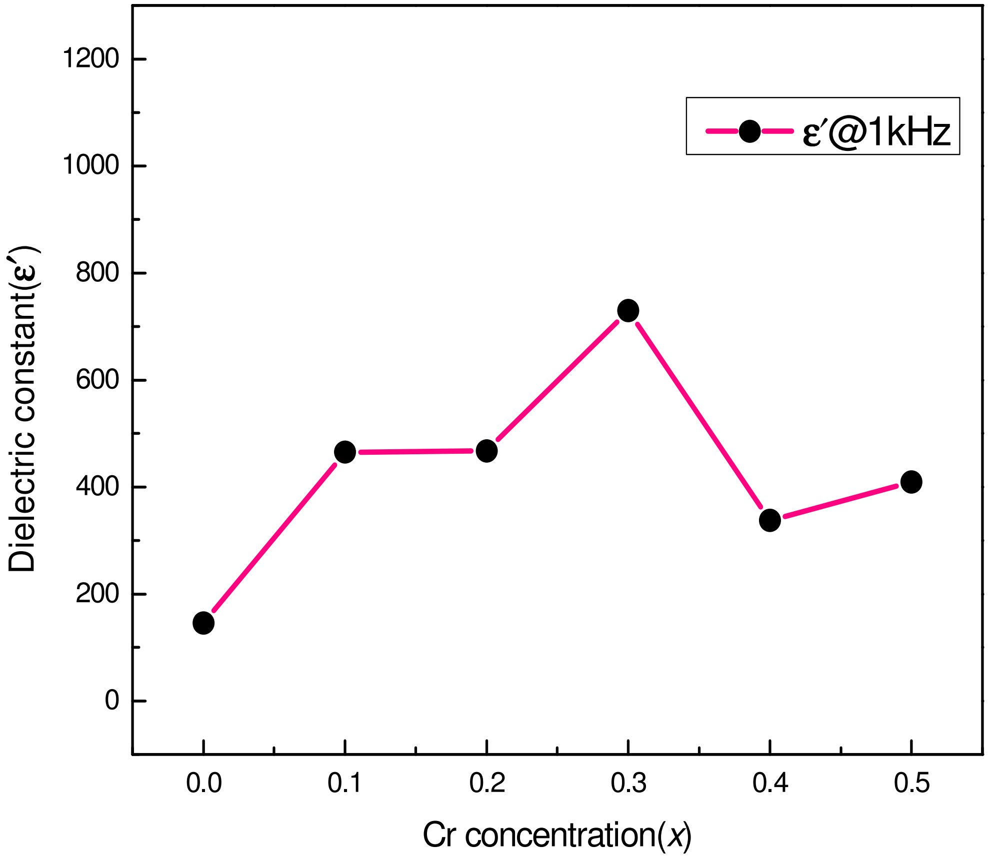

Fig. 5: Variation of dielectric Constant (ε') as a function of Cr content (x) for $Cr_xCoFe_{2-x}O_4$ ($0.0 \leq x \leq 0.5$) samples at 1 kHz frequency

Table 1: Dielectric parameters of $Cr_xCoFe_{2-x}O_4$ ($0.0 \leq x \leq 0.5$) at 1kHz

S.No	**Ferrite Composition**	**Dielectric constant(ε')**	**Dissipation factor(D)**	**ac conductivity (σ_{ac} x10^{-6})**
1	$CoFe_2O_4$	145.76	9.28	1.32
2	$Cr_{0.1}CoFe_{1.9}O_4$	465.36	20.85	9.85
3	$Cr_{0.2}CoFe_{1.8}O_4$	467.08	24.14	11.63
4	$Cr_{0.3}CoFe_{1.7}O_4$	729.56	20.33	15.04
5	$Cr_{0.4}CoFe_{1.6}O_4$	337.60	24.49	8.55
6	$Cr_{0.5}CoFe_{1.5}O_4$	409.45	19.53	8.07