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### Dielectric properties of Chromium substituted Nickel nano ferrites

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#### ABSTRACT

**Background** The powders of Ni-Cr Nano ferrites were synthesized with the chemical formula,  $\text{NiCrXFe}_2\text{-XO}_4$  (Where  $X = 0.1, 0.3, 0.5, 0.7, 0.9$  and  $1.0$ ) by using citrate-gel auto combustion technique. The structural characterization was investigated by X-Ray Diffractometer (XRD). X-ray analysis shows that the samples are cubic spinel structure (single phase) without any impurity peak and average crystallite size was in the range of 8.5-10.5nm. The dielectric measurements were carried out as a function of frequency and composition (X) at room temperature in the range of 20Hz-2MHz. The real part of dielectric constant ( $\epsilon'$ ) and dielectric loss factor ( $\tan \delta$ ) showed a decreasing trend with increasing field frequency. The ac conductivity ( $\sigma_{ac}$ ) is calculated from the dielectric measurements and it is increased with the increase of frequency. The composition dependent dielectric parameters are reported.

**Keywords:** Ni-Cr nano-ferrites: Citrate-gel technique: XRD: Dielectric parameters:

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## Introduction

Among the spinel ferrites, nickel ferrite a typical inverse spinel ferrite has been generally used in electronic devices such as telecommunication equipments, excellent core materials for power transformers and microwave devices for the reason that of their remarkably high electrical resistivity, mechanical hardness, chemical stability and low cost value [1]. Many investigators have been focused on substituted nickel ferrites as they have high frequency applications [2]. The properties of ferrites are also dependent on preparation method, chemical composition and type of substituent [3]. Divalent or trivalent substituted nickel ferrites are important materials, extensively used as magnetic materials in a wide range of technological applications because of their high electrical resistivity, low eddy current, low dielectric and magnetic losses [4-5].

For the synthesis of nanostructured materials offer some advantages by the chemical techniques in comparison with the physical techniques concerning simplicity, energy saving and product homogeneity. Several chemical methods were developed for preparing nano ferrites, the citrate-gel auto combustion technique has been used for the synthesis of nanosize spinel ferrites because of the low cost, simplicity, time period is very less and homogeneity of final product are included among its advantages. .

$\text{Fe}^{3+}$  ion replace with trivalent cations like  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$  etc in divalent ion is involved to achieve definite objectives [6]. Antiferromagnetic nature  $\text{Cr}^{3+}$  ions are known for achieving good control over magnetic and dielectric parameters in build up particular significant materials. Many researchers had been reported the influence of trivalent substitutions to improve their structural and dielectric properties in nickel ferrite system [7-8]. Best of my knowledge, there are no such incorporated study has been reported in the literature on the preparation and dielectric properties of  $\text{Cr}^{3+}$  substituted nickel nano ferrites through the citrate-gel auto combustion

technique. Therefore, the aim of the present investigation is to synthesis of the compositions  $\text{NiCr}_x\text{Fe}_{2-x}\text{O}_4$  (Where  $X=0.1, 0.3, 0.5, 0.7, 0.9$  and  $1.0$ ) by citrate-gel auto combustion method and dielectric properties as a function of frequency and composition at the room temperature of nickel nano ferrite have been investigated and hereby reported.

## Experimental procedures

The mixed Ni-Cr nano ferrite system having the compositional formula  $\text{NiCr}_x\text{Fe}_{2-x}\text{O}_4$  (Where  $X=0.1, 0.3, 0.5, 0.7, 0.9$  and  $1.0$ ) were synthesized by citrate-gel auto combustion method. Analytical grade raw materials (Nickel Nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Chromium Nitrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Ferric Nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Citric Acid-Citrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) and Ammonia ( $\text{NH}_3$ )) were used as starting materials for the synthesis. The required quantities of metal nitrates with aqueous solution of citric acid (1:3 molar ratio of nitrate to citric acid) were dissolved in deionized water. Ammonia solution was then added with a constant stirring to maintain the pH of the solution at 7. The resulting solution was continuously heated first on hot plate at  $80^\circ\text{C}$  to transform into gel and then ignited in a self-propagating combustion manner to form a fluffy loose powder. The as-burnt ferrite powders were grained by agate motor to get ferrite powder. Then, the ferrite powder calcined in air at  $700^\circ\text{C}$  for 5hrs and the calcined ferrite powders were again grained by agate motor to get a fine ferrite powder. As this technique is a chemical route, it requires no ball milling hence little scope of contamination, better homogeneity, low sintering temperature, less preparation time and it has the capacity to yield a homogeneous mixture of the constituent ions. The calcinations powder samples were thoroughly mixed with 3wt% PVA binder (poly vinyl alcohol) drying at  $50^\circ\text{C}$ . The samples were pressed into a circular disc shaped pellets into  $\approx 1\text{cm}$  diameter and  $\approx 0.5\text{cm}$  thickness with KBr Press Model No. M-15 by applied 4.5-5.5 tones for 2-3minutes, these pellets are sintered at  $400^\circ\text{C}$  for 4 hours. The prepared pellets are

silver coated on both sides and air dried to have good ohmic contact.

The structural characterization was carried out using X-ray Diffractometer (Bruker (Karlsruhe, Germany) D8 advanced system) with a monochromatic diffracted beam Cu K $\alpha$  radiation ( $\lambda=1.5405 \text{ \AA}$ ) source between the Bragg angles  $20^\circ$  to  $80^\circ$  in steps of  $0.04^\circ/\text{Sec}$ . The crystallite size was calculated for all prepared samples using the high intensity 311 peak and Scherer Formula [9]

$$\text{Crystallite size } D_{hkl} = \frac{0.91\lambda}{\beta \cos\theta}$$

The dielectric constant values of the prepared samples were measured in the frequency range of 20Hz-2MHz at the room temperature using a PRECISION LCR METER-E4980A. The dielectric constant ( $\epsilon'$ ) was calculated by using the relation [10].

$$\epsilon' = \frac{Cd}{\epsilon_0 A}$$

The dielectric loss factor ( $\tan \delta$ ) was measured by using the following relation [11]

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

The ac conductivity was determined using the following relation [11]

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta$$

## Results and Discussion:

### XRD analysis

**Figure 1** shows the X-ray diffraction pattern of mixed Ni-Cr nano ferrite system. It shows the crystalline phases were identified with standard reference data PDF# 862267 for Nickel ferrites ( $\text{NiFe}_2\text{O}_4$ ) from the international centre for diffraction data (ICDD). It was observed that XRD pattern imply spinel phase and all the samples show cubic spinel structure in single phase without showing any other impurity phases [12].

The average crystallite size was in the range 8.55 -10.36 nm and the values are reported in **table 1**. Best of my knowledge the small size mixed Ni-Cr nano ferrite samples are possible

only with the citrate-gel auto combustion method and the no other method has resulted the such a small size nano ferrites. By this method, phase of the prepared ferrite samples can produce very fast at low temperature but conventional methods need to high temperatures and prolonged heating time [13-14].

### Dielectric properties

#### Frequency Dependence of the Dielectric Constants ( $\epsilon'$ )

**Figure 2** shows the frequency dependence of the dielectric constant ( $\epsilon'$ ) of mixed Ni-Cr nano ferrite system in the frequency range of 20Hz to 2MHz at the room temperature. It is clear that dielectric constant decreases with increasing frequency, it is a normal behavior of ferrites. In the low frequency region, the dielectric constant decreases sharply where as in the mid-range frequency region it decreases slowly and in the high frequency range, the dielectric constant is independent of frequency [15].

The variation of dielectric constant with frequency may be explained on the basis of space-charge polarization phenomenon [16]. According to this, dielectric material has well conducting grains separated by highly resistive grain boundaries. On the application of electric field, space charge accumulates at the grain boundaries and voltage drops mainly at grain boundaries [17]. Koop's proposed that grain boundary effect is more at low frequencies [18], as the frequency is increased beyond a certain limit, the electron exchange between  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  ions does not follow the variations in applied field. Thus, the value of dielectric constant becomes constant. Rabinkin and Novikova [19] pointed out that polarization in ferrites is similar to that of conduction.

#### Frequency Dependence of the Dielectric Loss Factor ( $\tan \delta$ )

The dielectric loss factor ( $\tan \delta$ ) is a strong correlation between the conduction mechanism and the polarization mechanism in ferrites. **Figure 3** shows the variation of the dielectric

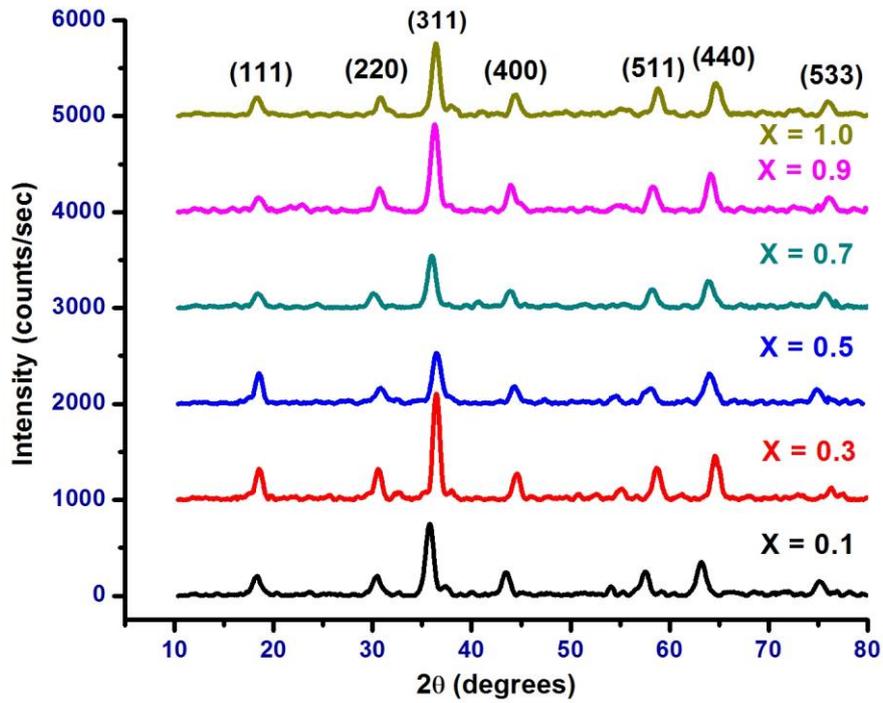


Figure 1: XRD pattern of mixed  $\text{NiCr}_x\text{Fe}_{2-x}\text{O}_4$  nano ferrite system

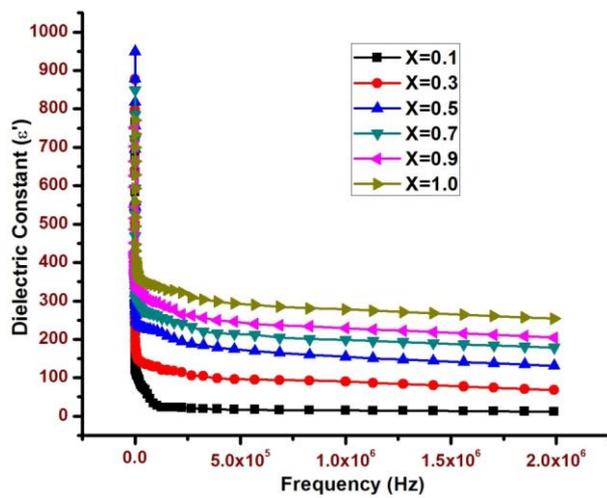


Figure 2: Frequency dependence dielectric constant

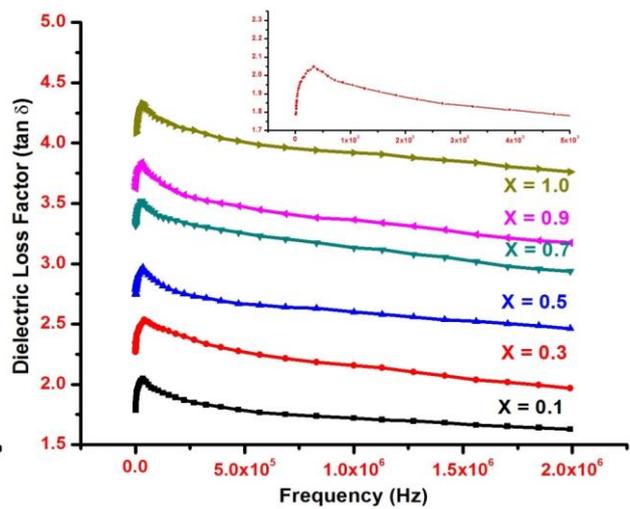


Figure 3: Frequency dependence dielectric loss tangent

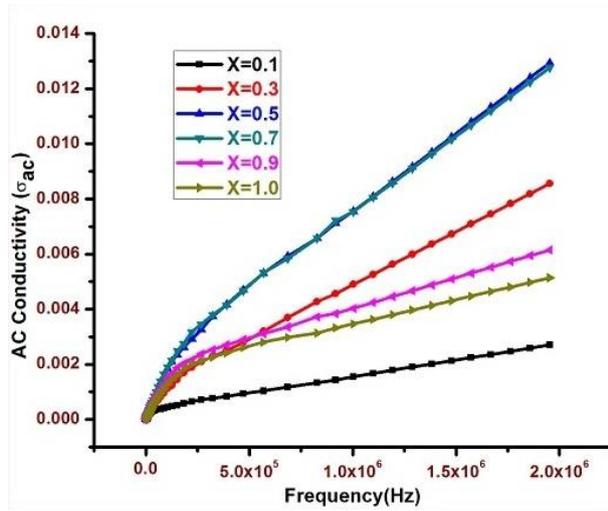


Figure 4 : Frequency dependence of ac conductivity

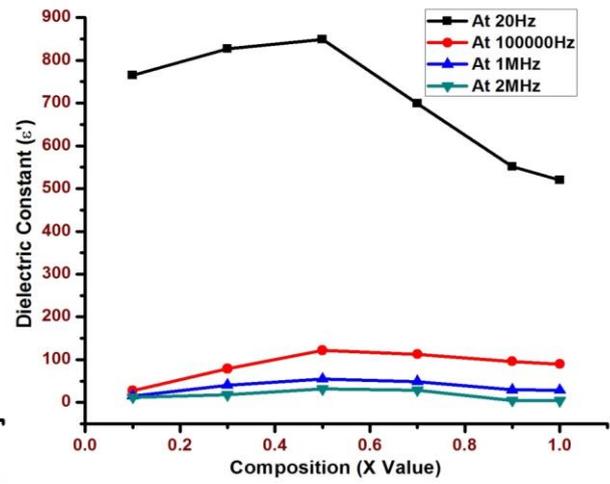


Figure 5 : Dielectric constant ( $\epsilon'$ ) variation with composition at various frequencies

Table -1: XRD pattern & Dielectric constant analysis of Ni-Cr nano ferrite system

Sl.No.	Composition	Crystallite size (nm)	Dielectric constant ( $\epsilon'$ )			
			AT 20Hz	AT 10 <sup>5</sup> Hz	AT 1MHz	AT 2MHz
1	NiCr <sub>0.1</sub> Fe <sub>1.9</sub> O <sub>4</sub>	8.96	765.32	27.45	15.04	11.85
2	NiCr <sub>0.3</sub> Fe <sub>1.7</sub> O <sub>4</sub>	10.36	827.12	78.74	40.54	17.86
3	NiCr <sub>0.5</sub> Fe <sub>1.5</sub> O <sub>4</sub>	7.95	848.84	121.89	54.57	31.24
4	NiCr <sub>0.7</sub> Fe <sub>1.3</sub> O <sub>4</sub>	8.55	699.14	112.62	48.88	28.65
5	NiCr <sub>0.9</sub> Fe <sub>1.1</sub> O <sub>4</sub>	8.84	551.56	96.08	29.18	4.643
6	NiCrFe <sub>2</sub> O <sub>4</sub>	9.26	520.26	89.59	28.29	4.166

loss factor ( $\tan \delta$ ) of mixed Ni-Cr nano ferrite system as a function of frequency (20Hz to 2MHz) at the room temperature. In the present system, the value of  $\tan \delta$  increases initially in all compositions and exhibits the loss factor which becomes maximum between  $1 \times 10^3$  Hz and  $4 \times 10^4$  Hz and further it has been decreased by increasing the frequency. It shows the Debye-type relaxation and this type of peaking behavior is observed when the jumping frequency between  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  ions is exactly equal to the frequency of the applied field [17]. Similar type of maxima in dielectric loss factor ( $\tan \delta$ ) with the frequency has been reported by other researchers [20-21].

It is clear that dielectric loss decreases sharp at low frequency region and the rate of decrease is slow at high frequency region, it shows an almost frequency independent behavior. All the compositions are exhibited in dispersion due to the Maxwell-Wagner [22-23] interfacial type polarization in good agreement with Koop's phenomenological theory [24].

According to Koop's theory, the effect of grain boundaries is more at low frequencies which corresponds to a high resistivity. This fact indicates that more energy is required for electron exchange between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, as a result the loss is high at low frequency region. It corresponds to a low resistivity due to the presence of grains in the high frequency region and hence a small energy is required for electron transfer between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at the octahedral site resulting in a low loss. It is clear that the energy loss is decreased when Cr concentration is increased at high frequencies. The low loss at higher frequencies shows the potential applications of these materials in high frequency microwave devices. The dielectric loss tangent also depends on number of factors such as stoichiometry,  $\text{Fe}^{2+}$  content and structural homogeneity which in turn it depends upon the composition and sintering temperature of the samples [25].

### Frequency Dependence of the AC Conductivity ( $\sigma_{ac}$ )

**Figure 4** shows the variation of the ac conductivity ( $\sigma_{ac}$ ) of mixed Ni- Cr nano ferrite system as a function of frequency in the range of 20 Hz to 2 MHz at the room temperature. It is clear that ac conductivity increases at low frequency region and it is almost independent behavior at higher frequency region for all the compositions. This behavior is similar to Maxwell-Wagner type which is in good agreement with Koop's phenomenological theory [23-24].

According to Koop's phenomenological theory, the conductivity was found low at lower frequency region due to the hopping electrons between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is less as the grain boundaries are more active which acts as barrier for mobility of charge carriers. The conductive grains become more active and promote the hopping electrons between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at higher frequency region, hence the conductivity is more and they are taken apart for creating charge carriers, these charge carriers are responsible for increasing the ac conductivity. It is in good agreement with Zn-Cr ferrite system by R. M. Sebastian et al [26].

### Compositional Dependence of Dielectric Constant ( $\epsilon'$ )

The variation of dielectric constant ( $\epsilon'$ ) as a function of  $\text{Cr}^{3+}$  concentration in Nickel nano ferrite system at the selected frequencies (20Hz, 10000Hz, 1MHz and 2MHz) are tabulated in **table 1** as the evident shown in **figure 5**. It is clear that dielectric constant ( $\epsilon'$ ) increase with the composition (X), reaches maximum at  $X=0.5$  and thereafter they decrease with the further Cr concentration. This behavior can be explained by the dielectric polarization mechanism and it is similar to that of the conduction in ferrites, initial Cr ions prefer to occupy the octahedral site until the Cr concentration becomes greater than 50%, thereafter Cr ions may increase in tetrahedral sites causing migration of equal number of ions to the octahedral sites [27].

According to Robinkin and Novikova observation, polarization takes place in the

ferrites with local displacement of electrons in the applied field direction due to the electron exchange interaction between  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  ions. In Ni-Cr nano ferrite system, Cr ions occupy octahedral (B) site and Fe ions are distributed equally into both tetrahedral (A) and octahedral (B) sites. For the initial addition of Cr concentration in the place of Fe ion, some of the  $\text{Fe}^{3+}$  ions are converted to  $\text{Fe}^{2+}$  ions to maintain the charge neutrality. Therefore, electronic exchange interaction between  $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$  ions increases, hence the resistance of grains decreases. This increases the probability of electrons to reach the grain boundary, as a result, polarization and dielectric parameters are increased [28]. For the further addition of Cr ion concentration,  $\text{Fe}^{3+}$  ions decrease and there will be the least possibility of electronic exchange interaction between  $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$  ions, hence it is decreased in dielectric parameters with increasing in Cr concentration in the present system. Similar trend is reported in Mg-Cr ferrite system by Raghasudha et al [29].

It can be seen from the table that the composition with  $X=0.5$  exhibits high dielectric constant 848.84 at 20Hz among mixed Ni-Cr ferrite system under investigation, due to the fact that it has maximum number of ferrous ions whose exchange  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  gives rise to maximum dielectric polarization.

## Conclusions

The Citrate-gel auto combustion technique is to be a convenient and versatile method for obtaining homogeneous nanostructured mixed Ni-Cr ferrites. The XRD pattern shows the

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single phase cubic spinel structure with the average crystallite size in the range of 8.55 nm to 10.36 nm. The dielectric constant decreases with increase in frequency which is a normal behavior of ferrites due to hopping electrons between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at localized sites. Dielectric loss factor ( $\tan \delta$ ) increases initially in all compositions and exhibits the loss factor which becomes maximum between  $1 \times 10^3 \text{ Hz}$  and  $4 \times 10^4 \text{ Hz}$  further it has been decreased by increasing the frequency. It shows the Debye-type relaxation and this type of peaking behavior is observed when the jumping frequency between  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  ions is exactly equal to the frequency of the applied field. The ac conductivity increases with increasing in frequency at low frequency region and it is almost independent behavior at higher frequency region with the frequency. This behavior is similar to Maxwell-Wagner type in good agreement with Koop's phenomenological theory. The dielectric constant ( $\epsilon'$ ) becomes maximum at  $X=0.5$  thereafter decreases with increasing in Cr ion concentration.

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