Influence of Mo⁶⁺ on Dielectric properties of Copper Ferrites

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Abstract: Two series of copper ferrites are prepared using the chemical compositional formula $Cu_{1.0-3y}Fe_{2.0-2x}Mo_{x+y}O_{4.0}$. They are calcinated at 750 C and sintered at 950C. When x =y = 0.0, the ε' of the basic copper ferrite is probably due to electronic exchange interactions of copper and iron ions as $Cu^{2+} \leftrightarrow Cu^{1+}$ and $Fe^{3+} \leftrightarrow Fe^{2+}$. The observed value of dielectric constant (ϵ') decreases as a function of substituent concentration (x) up to x = 0.20 and for further values of 'x' it found to increase. In the case of 'C' (x = 0) series ferrites ϵ' decreases with substituent concentration (y) up to y = 0.04, later it found to increase. The dispersion of ac resistivity with frequency is observed indicating their strong dependence on frequency as in the case of dielectric behaviour. These results are explained with different possible mechanisms.

Keywords: Copper ferrite, Substituent concentration, Dielectric constant, Frequency, Electronic exchange, Polarization

1. INTRODUCTION

Copper ferrite has specific behaviour among spinel ferrites because of structural phase transition that observed due to the Jahn-Teller distortion effect under certain condition(s) [1]. Consequently, electrical properties also expected to be significant due to the above mentioned distortion. No systematic studies of high valence cation(s) impact on copper ferrite dielectric constant are available. Contrary to conventional dielectric loss mechanism, the unusual behaviour called 'dimensional resonance' which is also a loss mechanism arises due to change in the pattern of lines of force occurs inside the core. This was reported [2] in Cu-Zn ferrite way back in 1952. Recently similar type results have also been reported [3, 4] for Ni-Zn and Zn-Mn ferrites. Contrary to this, no such

Rao, BV
Narayana, PVL
Rao, ADP

behaviour was observed in Ti/Nb substituted copper ferrite [5]. Therefore, the present investigation is motivated to verify, whether dimensional resonance present similar to Zn substitution in copper ferrite that mentioned above is existing or not, along with its influence on dielectric property of copper ferrite in the present materials.

2. PREPARATION OF SAMPLES

Two series of copper ferrites are developed using the chemical compositional formula $Cu_{1.0-3y}Fe_{2.0-2x}Mo_{x+y}O_{4.0}$. They are

(I)   Substitution of Mo^{6+} at the expense of Fe^{3+} varying 'x' from 0.00 to 0.40 (x is varied in steps of 0.02 up to x=0.10; further in steps of 0.10 up to x=0.40 terming as F series materials, y=0.00) is performed.

(II)   On the other hand Mo^{6+} substituted ferrites at the expense of Cu^{2+} have been prepared. 'y' varies in steps of 0.02 from y=0.00 to y=0.10 and then in steps of 0.10 from y = 0.00 to y = 0.20 (C series) in which x is kept at 0.00. These materials are prepared following standard ceramic technique [5], thus calcinations at 750Cis carried out, after calcinations these are subjected for fine grinding, later pellets are prepared and sintered at 950C.

(III) The obtained pellet form samples are silver coated on both the surfaces of the pellets to act as electrodes for the experimental measurements. At room temperature capacitance of the present materials is measured as a function of substituent concentration and frequency by using spring loaded cooper electrodes connected to a HP 4192 impedance analyzer. From these measurements dielectric constant (ε') and dielectric loss (tan δ) values as a function of substituent concentration (x/y) and frequency (f) are evaluated.

3. DIELECTRIC PROPERTIES

During preparation of ferrite materials, formation of highly conductive grains and their separation by thin layers that show poor conduction (grain boundaries) results due to heterogeneous dielectric nature. Morphological studies of the present materials namely grain size etc are already published elsewhere [6]. On the other hand, formation of ferrous ions from ferric ions takes place. Usually, at low frequencies, value of dielectric constant (ε') of ferrites ranges on the order of $10^4 - 10^6$, so these are considered as good dielectric materials and inexpensive one. In general, with the increase of applied frequency, ferrites ε' exhibit dispersion and reach to a constant value at higher frequencies.

## 3.1 Variation of dielectric property with substituent concentration

The variation of obtained log ε′ at fixed frequency (f) i.e. 100 Hz for 'F' and 'C' series ferrites (at lower values of x or y) is shown in Fig.1. The observed value of ε′ decreases with the increase of 'x' up to x=0.20. For further values of 'x' it found to increase, in the case of 'C' series ferrites log ε′ decreases with substituent concentration (y) up to y=0.04, beyond which it found to increase. Nevertheless, values of all the specimens log ε′ is found to have lower relative to the un-substituted copper ferrite (ε′). Iwauchi [6] reported a strong correlation between conduction mechanism due to electronic exchange of ferrous and ferric ions and dielectric polarization process. It is well known [7] that the real part of ε′ is directly proportional to the root mean square value of the dc conductivity. Hence one can interpret the dielectric behaviour of ferrites in terms of conductivity mechanisms too based on electronic exchange interactions that allow the flow of charge carriers to build up polarization. The basic copper ferrite has tetragonal structure and it attributed to the Jahn – Teller effect of Cu^{2+} [1] that causes for partial inverse of CuFe$_2$O$_4$. Depending upon the copper ions distribution, Jahn – Teller effect becomes responsible for crystal distortion [9]. 0.25 is the critical value of copper ions occupancy at 'A' sites causing crystal distortion [1]. The divalent copper ions i.e. Cu^{2+} have strong tendency to occupy octahedral (B) sites [10] while Cu^{1+} prefer to occupy 'A' sites [11]. The cation distribution of the basic ferrite can be written as (Fe$_{1-x}$Cu$_x$)$_A$ [Cu$_{1-x}$Fe$^{3+}_{1+x}$]$_B$O$_4^{2-}$ [10]. As reported earlier [12, 13] the substituent i.e.Mo^{6+} is expected to enter into tetrahedral sites at lower concentration and at higher concentration it occupies 'B' sites,. Therefore the cation distribution for the present 'F' series ferrite materials can be assumed with the following generalized formula

$$\left(Cu^{2+}_{q}Mo^{6+}_{x-p}Fe^{3+}_{1-q-(x-p)}\right)_A \left[Fe^{3+}_{1+q-p}Mo^{6+}_{p}Cu^{2+}_{1-q}\right]_B O_4^{2-}$$
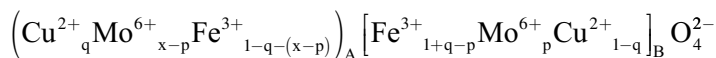
and for 'C' series the assumed cation distribution formula

$$\left(Cu^{2+}_{q-(y-p)}Mo^{6+}_{y-p}Fe^{3+}_{1-q}\right)_A \left[Fe^{3+}_{1+q}Mo^{6+}_{p}Cu^{2+}_{1-q-p}\right] O_4^{2-}$$
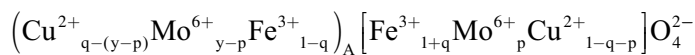
Initially the following process can be expected for the present ferrite materials with Mo^{6+} substitution
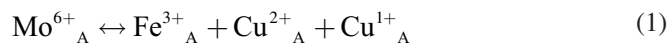
$$Mo^{6+}_{A} \leftrightarrow Fe^{3+}_{A} + Cu^{2+}_{A} + Cu^{1+}_{A} \qquad (1)$$

When x = 0.0, the ε′ of the basic copper ferrite is probably due to electronic exchange interactions of copper and iron ions as Cu^{2+} ↔ Cu^{1+} and Fe^{3+} ↔

Rao, BV
Narayana, PVL
Rao, ADP

Fe^{2+}. With the rise of 'x', the fall of ε' might be understood with the following reasons. If Mo^{6+} occupies 'A' sites at the expense of 'A' site iron ions, then the contribution from 'B' sites for decrease of ε' can be ruled out since no change of ionic distribution in 'B' sites taking place. Formation of stable bonds as depicted in the equation (1) is expected in 'A' sites since it is known [14] that high valence cation(s) form stable bonds that impede electronic exchange interaction process resulting decrease of the ε' besides the contribution that arises due to hindering of Verwey mechanism among ions of the same metal. Due to substitution of foreign cation, cation distribution might have modified resulting obstruction for the flow of charge carriers leading to poor in building up the space charge polarization causing to decrease dielectric parameters. The increase of (log ε') at higher concentrations of Mo^{6+} is probable due to its entry into 'B' sites. At x = 0.30, the increase of dielectric parameters can be attributed to the significance of electronic exchange interaction than the impact of other mechanisms since the quantity of substituted molybdenum concentration is high, it can increase number of ions with different charge states. Though Mo is capable of forming stable bonds with ferrous, ferric and copper ions as described above which hinder the conduction process resulting impede local displacements of charge carries that show impact on polarization; multiple valence states of molybdenum and ions inter site exchange interaction contribute for displacement of ions resulting polarization
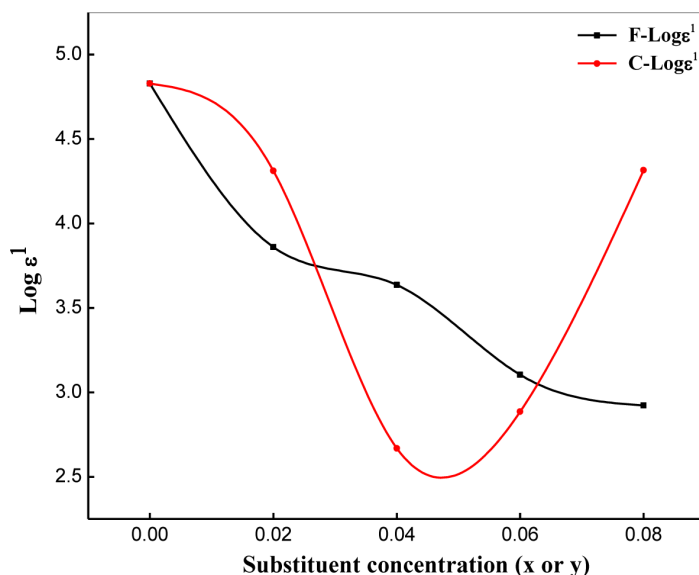

Figure 1: Variation of dielectric constant as a function of Mo^{6+} concentration.

along with the vacancies formed due to high valence cation substitution. In the case of 'C' series ferrite materials, Mo^{6+} is substituted at the expense of copper ions that present in 'B' sites, consequently molybdenum ions are expected to enter into 'B' sites forming stable bonds which causes decrease of log ε'. In 'C' series beyond y = 0.04 the increase of dielectric constant can be attributed to inter site exchange contribution that described above probably due to significant contribution from iron ions as there is no change in iron ions concentration. The decrease of log ε' at higher values of 'y' can be attributed to modified microstructure of the material due to substituted Mo^{6+} ions since the dielectric structure depends on grains (charge carriers) and grain boundaries. On the other hand, copper content becomes very low leading to negligible exchange interactions between copper ions as $Cu^{2+} \leftrightarrow Cu^{1+}$, consequently the ε' decreases.

3.2 Variation of dielectric constant with frequency

The variation of log ε' with the increase of frequency (f) is depicted in Figs 2 (a) & (b) to the 'F' and 'C' series materials for lower and higher values of Mo^{6+} respectively. These illustrate the rapid fall of log ε' with 'f' indicating its strong dependence on 'f'. But on reaching to higher frequencies, this type of dependence found to decrease slowly and a minimum value is attained at certain 'f', which can be designated as f_{rlx}. The f_{rlx} is found to occur around 100 kHz for all the specimens except at x = 0.40 of 'F' series ferrites which occurred this at 10 kHz. From this f_{rlx} onwards no considerable change of
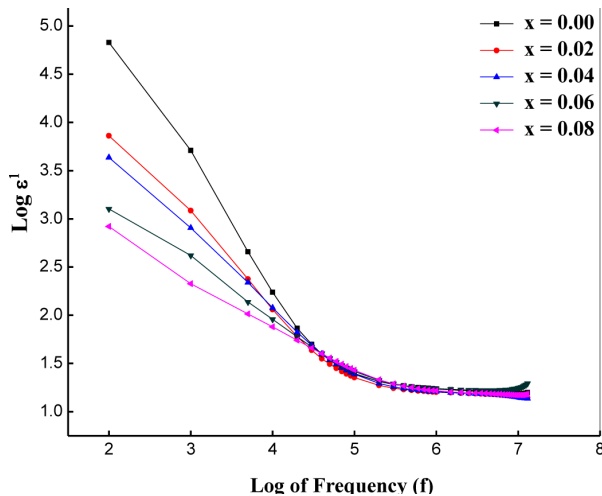

Figure 2(a): Variation of dielectric constant as a function of frequency (F-series).
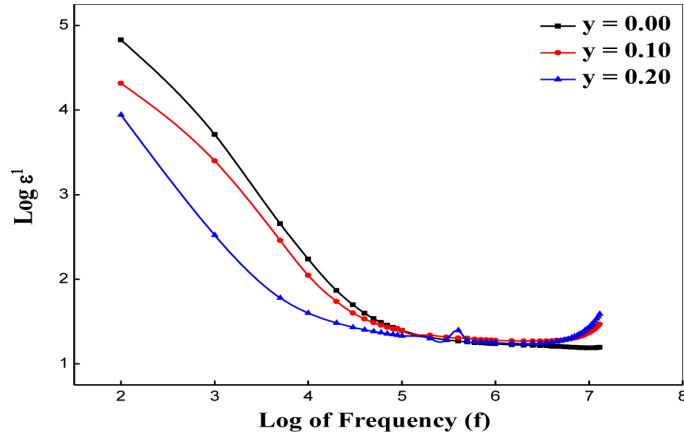
Rao, BV
Narayana, PVL
Rao, ADP

Figure 2(b): Variation of dielectric constant as a function of frequency (C-series).

ε′ is observed and thus it could be considered as relaxation frequency. This kind of dispersion usually exhibit by all soft spinel ferrites that termed as low frequency dispersion (LFD). This bears close resemblance of the classical Maxwell-Wagner [15] effect that arises due to the interaction of capacitive barriers with bulk resistance.

The dispersion of log ε′ can be understood with the similar type of dispersion that showed earlier in other ferrites viz. Li-Zn ferrites studied by Prankishan et al [16], Reddy et al. [17] in Li-Ti ferrites and Ravinder [18] in Li ferrites. He observed the relaxation for dielectric constant at 10 kHz and for tan δ from 100 kHz onwards. Rezlescu and Rezlescu [19] explained about this type of behaviour that occurs in the case of dielectric constantof spinel ferrites. The variation of dielectric constant depends on number of ions available with different valence states that are responsible for hopping among them. The presence of relaxation occurs due to the fact that the electronic hopping 'f' between these ions cannot follow the applied alternating field. At x = 0.30, 0.40 and for 'C' series materials the small increase of log ε′ is observed beyond the frequency 5MHz. This sort of behaviour might be due to either ferrimagnetic resonance property or dimensional resonance [4]. Now this 'f' should be corroborated with the theoretically evaluated ferrimagnetic resonance frequency (f_{res}). It is well connected [20] to the permeability and the saturation magnetization (Ms) as given below

$$f_{res}(\mu - 1) = (4\gamma Ms)/3 \qquad (2)$$
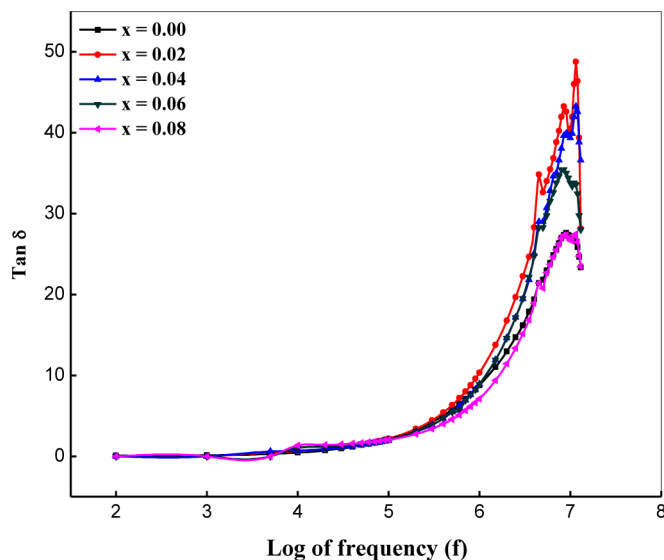
Figure 3: Variation of dielectric loss with the increase of applied frequency

where γ is a constant and called as gyromagentic ratio. Using the above equation, theoretically f_{res} values are computed to the specimens for whom increase of log ε' at high 'f' is found. Probably it might be related to the loss mechanism by changing the lines of force pattern inside the core of the material contrary to the conventional loss mechanism or change in conduction mechanism due to some sort of structural/phase transition. This is expected to reflect in other parameters too such as imaginary part of dielectric constant and dielectric loss.

The above mentioned LFD is characterized by the imaginary component of dielectric property. To understand the impact of dielectric imaginary part (ε'') on the variation of log ε' as a function of applied frequency, imaginary component of ε' values are computed (product of dielectric real component and dielectric loss tangent). These also shown dispersion approximately similar to the variation that exhibited by log ε', however from the frequency 'f_{rlx}' where specimen begin to exhibit relaxation of log ε' as mentioned above, imaginary component shows an increase with the rise of frequency (f) except for x=0.30 and 0.40 of 'F' series.

For higher values of Mo^{6+} substitution, up to 3 kHz, values of dielectric imaginary component could not be computed because of dielectric loss (tan δ) was absence up to 3 kHz for which product of ε' and tan δ need to be evaluated to obtain imaginary part of ε'. Up to dielectric relaxation frequency (f_{rlx}), the observed log ε' is relatively higher than the imaginary part while the

Rao, BV
Narayana, PVL
Rao, ADP

latter is dominant from 'f_{rlx}' onwards. This observation indicates the existence of one or more relaxation process with super imposition of dielectric loss contribution to the imaginary part over the observed log ε' in the studied 'f' range, particularly from 'f_{rlx}' onwards. The variation of dielectric loss (tan δ) for one of the series (F) is depicted in Fig 3. Specimens of 'F' series and few specimens of 'C' are showing a peak at close to 10 MHz. The other specimens of 'C' series show continue increase of tan δ without having any peak. This indicates that the ferrites which are not exhibiting tan θ peak might fall outside 'f' range of the present study. The observed maximum of tan δ close to 10 MHz is the jump 'f' that coincides with the applied external 'f', which usually takes place in spinel ferrites. It can be understood on the lines as described earlier for several other ferrite materials [20, 21].

4. VARIATION OF AC RESISTIVITY WITH SUBSTITUENT CONCENTRATION

Probing the materials from different directions is required to understand their behaviour. Therefore, study of ac resistivity (ρ_{ac})is also undertaken for the present ferrite systems. At 50 KHz the observed values of 'ρ_{ac}' at room temperature with the rise of x or y (for higher values of Mo) is depicted in Fig. 4. The ρ_{ac} is found to exhibit smaller value relative to basic ferrite ρ_{ac} except at x = 0.02. Though 'ρ_{ac}' for all the specimens is lower than the basic ferrite 'ρ_{ac}'
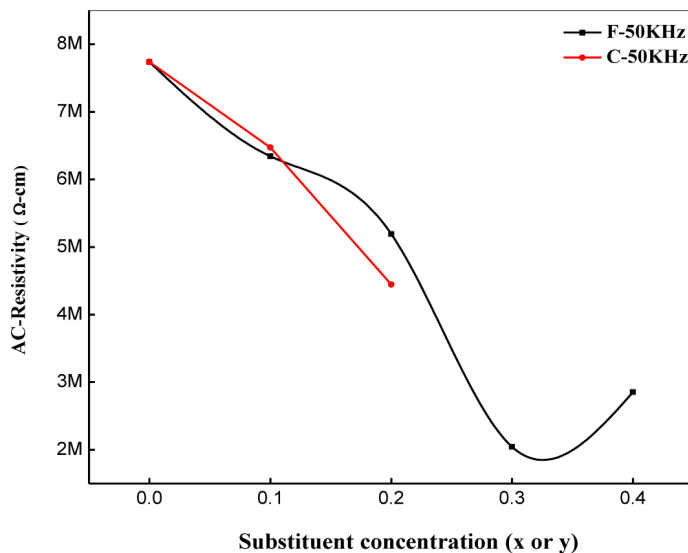

Figure 4: Variation of resistivity with the increases concentration of molybdenum.

in C-series, it found to increase for y = 0.02 to 0.06. The present 'ρ$_{ac}$' values are on the order of MHz, as obtained earlierby Ahmed et al [22] on MHz order, but the present basic ferrite 'ρ$_{ac}$' seems to be very high. Significantly the Mo^{6+} substituted materials could not yield 'ρ$_{ac}$' values at lower 'f'; this may be probably due to fluctuation of vacancies, which might have stabilized at higher 'f'. The increase of 'ρ$_{ac}$' at x = 0.02 and y = 0.04 to 0.06 can be attributed to the stable bonds formation by the substituted Mo^{6+} with other metallic ions in the crystal lattice as described above, which promote resistivity due to hindrance of electronic exchange of the ions. This corroborates the results of dielectric studies discussed in the previous section. The decrease of 'ρ$_{ac}$'probably because of valence fluctuation since 'Mo' has multiple valence states and the increasing concentration of 'Mo' is also expected to influence largely by generating multiple valance state ions. The decrease of 'ρ$_{ac}$' at y = 0.02 might be significance of modified microstructure because of Mo^{6+} substitution.

4.1 Variation of ac resistivity with frequency

The variation of ρ$_{ac}$ in response to the applied frequency (f) is depicted for one of the series (lower F) of ferrites in Fig. 5. These found to exhibit dispersion of 'ρ$_{ac}$' with 'f' indicating their strong dependence on 'f' as in the case of dielectric behaviour. But all the materials are displaying relaxation from certain 'f'; 5.2X10^5 Hz. Beyond this 'f' the value of 'ρ$_{ac}$' seems to be practically almost constant showing independent of 'f'. In spinel ferrites, generally, dispersion arises as a consequence of resonance or relaxation. Considering the real part of resistivity, results are explained. The real part of complex conductivity (σ$_{ac}$) is expressed as [23],

$$\sigma_{ac} = \sigma_1(T) + \sigma_2(\omega) \tag{3}$$

$$\sigma_1(T) = \sigma_0 \exp(-E/kT) \tag{4}$$

The σ$_0$ is a constant and other symbols of the above equation have their usual meaning. The 2nd termσ$_2$(ω) contributes from dielectric relaxation process and is due to bound cations. The conductivity depends on frequency as studied on Sn/Nb substituted Mn-Zn ferrite [24]

$$\sigma_2(\omega) = B'\omega \tag{5}$$

where B' is a proportionality constant. Resistive grain boundaries in low 'f' region and conductive grains in the high 'f' region contribute to the ac
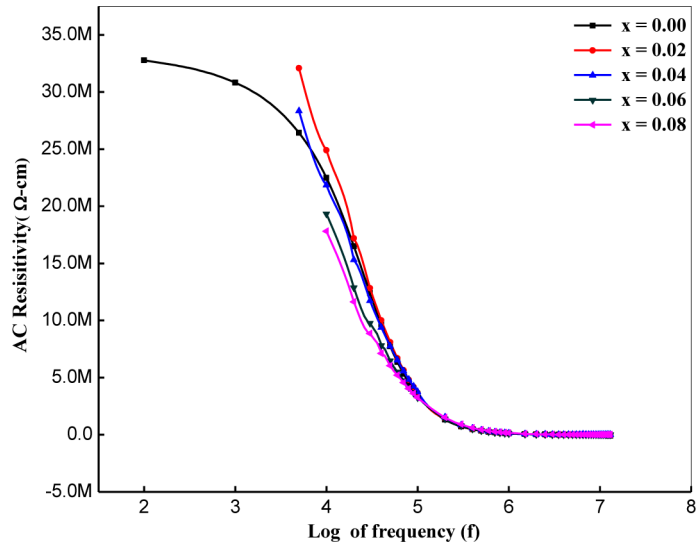
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Figure 5: Variation of A.C Resistivity with the increase of applied frequency for x = 0.00 to 0.08 (F-series).

conductivity/resistivity [25]. So, the dispersion in lower 'f' region is believed to be due to modified microstructure, which changes behaviour of grain boundaries that affect the hopping process. Maxwell-Wagner two-layer theory or the heterogeneity model for soft ferrites [26, 27] explains the dispersion of ρ_{ac}. The dielectric structure of the heterogeneous material consists of two layered capacitors with well conducting grains separated by grain boundaries that have low conductivity. Earlier, σ_{ac} studies with 'f' were investigated for Co substituted SbNi ferrite [28] and the results were discussed based on the heterogeneity. The observed relaxation of 'ρ_{ac}' without showing any change in its value beyond certain value of applied 'f' (MHz) can be ascribed to the 'f' that not rapid enough to affect grains where conductivity/resistivity at higher 'f' is understood due to conductive grains.

CONCLUSIONS

1. Values of all the specimens dielectric constant (ϵ') is found to have lower relative to the basic (un-substituted) copper ferrite (ϵ').
2. The rapid fall of dielectric constant with frequency is observed indicating its dispersion followed by relaxation from a certain frequency.
3. The ρ_{ac} is found to show smaller value relative to basic ferrite ρ_{ac} except at x = 0.02 and the present 'ρ_{ac}' values are on the order of MHz.

4. The dispersion of ac resistivity with frequency is observed indicating their strong dependence on frequency as in the case of dielectric behaviour. But all the materials are displaying relaxation from certain frequency i.e. 5.2×10^5 Hz from which its behaviour shows independent of frequency.

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