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## Synthesis, characterization, study of electrical properties and survey of applications of nanoferrites-an approach by chemical method

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### ABSTRACT

Nano ferrites with general chemical formula  $Cu_xCo_{1-x}Fe_2O_4$  ( $x < 1$ ) were synthesized by sucrose method and characterized by X-ray diffraction and IR studies. DC resistivity shows break near Curie temperature indicating the change in conduction mechanism. AC resistivity exhibits large dispersion at low frequency which is in agreement with Koops theory. Dispersion in dielectric constant ( $\epsilon'$ ) is attributed to Maxwell-Wagner type interfacial polarization. While dispersion in loss angle  $\tan \delta$  is due to variation in AC resistivity with frequency.

### INTRODUCTION

Taniguchi of Tokyo University coined the word Nanotechnology in 1950. Nanophase and nanostructure are found to have potential application<sup>1</sup> in the field of nanocomposites, optics and electronics. The unique properties of nanomaterials are determined by their size, surface structure and interparticle interactions.

In view of the above survey [1,2], chemical method has been selected to prepare nanosized uniform particles of high purity. So an attempt has been made to synthesize and characterize Co-Cu ferrites by chemical method in the present work, which in future will be extended for the preparation of Ni-Cu, Ni-Co, Ni-Cu-Co etc ferrites.

The chemical method has been preferred over ceramic method as the former being more efficient to produce fine grained powders having better physical properties and improved purity and homogeneity.

### MATERIALS AND METHODS

About 20g of polyvinylalcohol (PVA) was dissolved in 200 mL distilled water using magnetic stirrer. 10 mL of this PVA solution was added to the hot sucrose solution obtained by dissolving ~ 30g of sucrose in 50 mL distilled water. It is then heated, stirred to get clear solution.

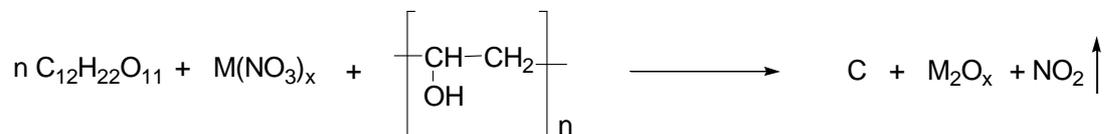
Metal nitrates viz.,  $Co(NO_3)_2$ ,  $Cu(NO_3)_2$  and  $Fe(NO_3)_2$  (A.R. Grade) in required molar proportion i.e.,  $Co_xCu_{(1-x)}Fe_2O_4$  ( $Co_{0.5} + Cu_{0.5} + Fe_2O_4$ ) were dissolved in 50 mL distilled water to get homogenous solution. To this was added mixture of PVA and sucrose solution prepared above and heated on a magnetic stirrer at suitable temperature till  $NO_2$  fumes disappear to form a viscous mixture. This viscous mixture was then heated on an electric or gas heater till the powder began to burn like live charcoal undergoing oxidation to form nanoferrites in powder form. The ferrite powder was pre-sintered at 800 °C for 8 h. in air medium. This powder was pressed into pellets which were subjected to final sintering at 1000 °C for 10 h. to complete the solid state reaction. These samples were furnace cooled for homogenization of the composition of the raw materials, densification and grain growth simultaneously.

## RESULTS AND DISCUSSION

**3.1 Role of sucrose**

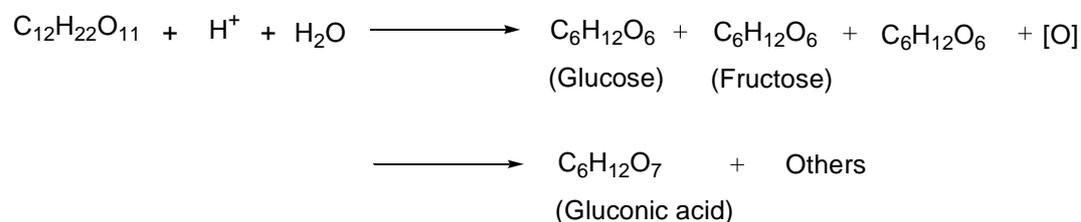
Sucrose in the solution form provides wrapping through co-ordination for the cations in solution and works as chelating agent and ensures atomistical distribution of the cations throughout the polymeric network structure.

The overall reaction is:



Sucrose serves also as an efficient fuel for the combustion reaction by oxidation of nitrate ions. The polymeric stability is due to the formation of chemical bonding of the cations on the polymeric chain and formation of extremely high viscosity polymeric solution. Though the chemical bonding is destroyed during pyrolysis, the high viscosity favours low cation mobility and helps for the crystallite (agglomerate) morphology.

The aqueous solution of sucrose, in presence of dilute nitric acid hydrolyzes to fructose and glucose. They get further oxidized to gluconic acid or polyhydroxy acid.



The gluconic acid, having carboxylic acid groups and five linear hydroxy groups at one end, takes part in the complexation of metal ions to form branched polymer with PVA. The presence of small quantity of PVA in sucrose leads to the formation of crushable fluffy powder of the oxide system. Higher the fluffiness of the powder, smaller will be the particle size.

**3.2 Role of PVA [3]**

PVA provides polymeric matrix structure for the cations. Also it helps in the polycondensation reaction in presence of oxidized disaccharides and gives rise to branched chain polymeric network structure where metal ions ( $\text{M}^{+2}$ ) are held in the hydroxylic pockets of the branch chain through complex formation. During the pyrolysis various gases are evolved from the pockets and make the structure highly porous and fluffy.

**3.3 Characterization****3.3.1. X-ray studies**

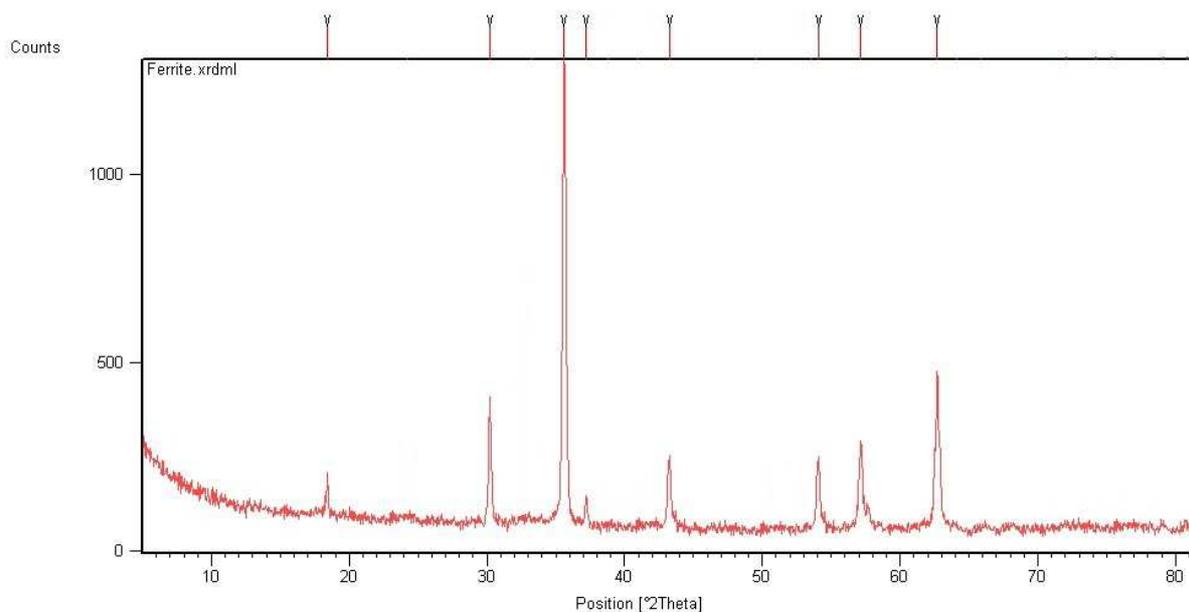
X-ray diffraction pattern of the samples were obtained (I.I.Sc. Bangalore) using filtered CuK- $\alpha$ -radiation of wavelength 1.5418 Å. The interplanar distance were calculated.

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad \text{and} \quad a = \frac{\lambda}{2 \sin \theta} (h^2 + k^2 + l^2)^{1/2}$$

Where  $\theta$  = glancing angle

$\lambda$  = wavelength of radiation.

The prominent line in the X-ray pattern corresponds to (311) plane (Fig. 1). Knowing the value of  $\theta$  for (311) plane and  $\lambda$ , lattice constant 'a' is calculated. Then values of interplanar distances for other planes were calculated in the light of natural spinel structure  $\text{MgAl}_2\text{O}_4$  [4].



**Figure 1.** X-ray diffraction pattern of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$

X-ray pattern exhibits face centered cubic structure and confirms the formation of single phase ferrites. The indexing of other prominent lines is achieved on the basis of A.S.T.M. data, that are in good agreement with those expected for spinel structure. The calculated and observed values of 'd' for sample ( $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ,  $a = 8.3720 \text{ \AA}$ ,  $\lambda = 1.5418 \text{ \AA}$ ) are given in the table 1.

The prominent peak corresponding to plane (311) is very narrow which is expected for nanoferrites.

The size of the grains is calculated by the relation,

$$D = 0.9 \lambda / \beta \cos \theta$$

and is found to be  $\sim 10 \text{ nm}$ .

Where  $\lambda$  = wavelength,  $\theta$  = diffraction angle,

$\beta$  = angle corresponding to F.W.H.M of (311) plane.

**Table 1.** The calculated and observed values of 'd' Sample:  $\text{Cu}_{0.5} \text{Co}_{0.5} \text{Fe}_2\text{O}_4$ ,  $a = 8.3720 \text{ \AA}$ ,  $\lambda = 1.5418 \text{ \AA}$

2 $\theta$ deg.	$\theta$ deg.	Sin $\theta$	$d_{\text{obs.}}$ $\text{\AA}$	$D_{\text{cal.}}$ $\text{\AA}$	hkl
18.3988	9.1994	0.1599	4.8223	4.8334	111
30.2260	15.1130	0.2607	2.9569	2.9599	220
35.5651	17.7825	0.3054	2.5243	2.5242	311
37.2148	18.6074	0.3191	2.4161	2.4168	222
43.2396	21.6198	0.3685	2.0924	2.0930	400
53.5711	26.7855	0.4507	1.7107	1.7089	422
57.1384	28.5692	0.4782	1.6121	1.6112	511
62.7115	31.3557	0.5204	1.4816	1.4800	440

There is a good agreement between calculated and observed values of 'd'. For 'fcc' structure, the cyclic sum of miller indices (h+k), (k+l) and (l+h) is even number. This has been observed in case of present sample.

### 3.3.2. IR Spectra

The IR spectra of the samples (obtained from I.I.Sc. Bangalore) were obtained in the range of  $200 \text{ cm}^{-1}$  to  $800 \text{ cm}^{-1}$  (Fig. 2).

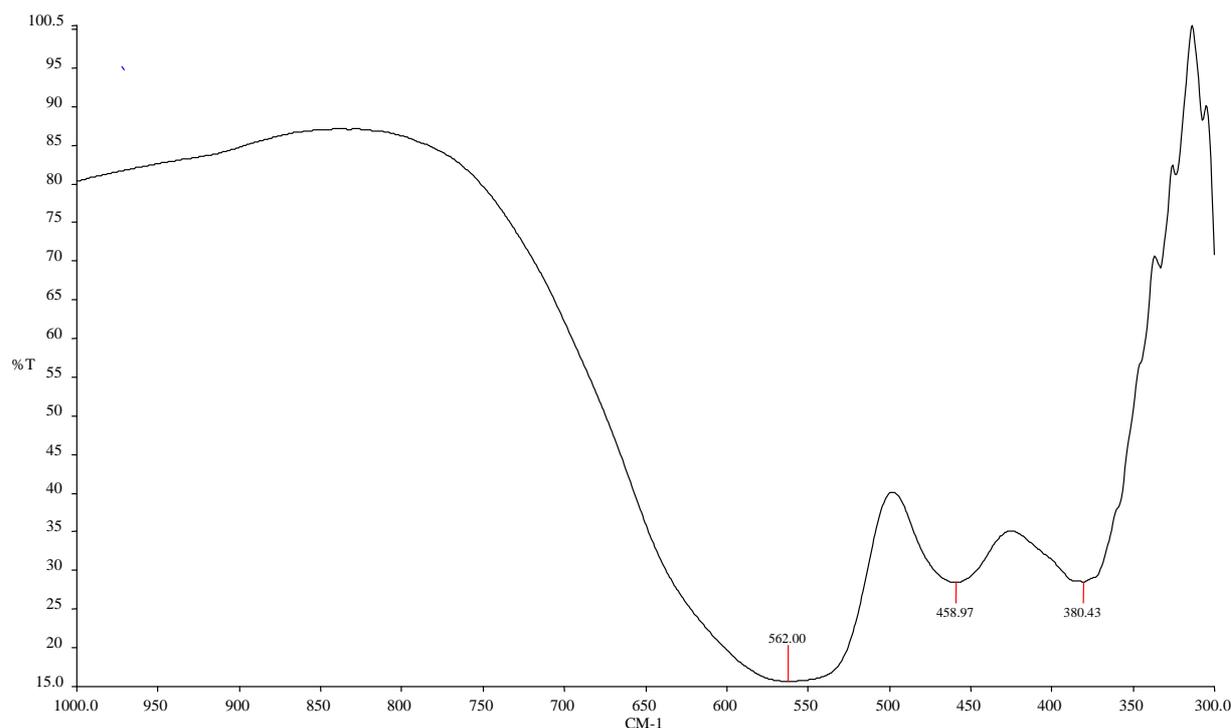


Figure 2. The IR spectrum of  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$

The spinel ferrites crystallize in 'fcc' with the space group  $\text{Fd}_{3m}-\text{O}_h^7$  and show four IR active fundamentals in the vibrational spectra of normal and inverse structure. The vibrational frequency depends upon the cation mass, cation-oxygen bonding force, distance and parameters of the unit cell. The IR spectra reveals two prominent bands near  $562\text{ cm}^{-1}$  and  $458\text{ cm}^{-1}$  which are assigned to tetrahedral and octahedral complexes respectively. There is no sign of splitting of band  $\nu_1$  near  $562\text{ cm}^{-1}$  which suggests that  $\text{Fe}^{+2}$  ions cannot occupy A sites (Tetrahedral site). The splitting of  $\nu_2$  band near  $458\text{ cm}^{-1}$  giving rise to  $\nu_3$  band near  $380\text{ cm}^{-1}$  indicates the presence of  $\text{Fe}^{+2}$  ions at B site (octahedral site) due to John-Teller effect in  $\text{Fe}^{+2}$  ions. The absence of splitting of  $\nu_1$  band is attributed to occupancy of A site by  $\text{Fe}^{+3}$  ions which do not undergo John-Teller effect.

### 3.3.3. Electrical Properties

#### 3.3.3.1. DC Conductivity

The DC conductivity was measured by two probe method on pellets from room temperature to  $700\text{ }^\circ\text{C}$ . The variation of  $\log \rho$  Vs.  $1/T$  is depicted in the figure 3. The change in the slope is either due to Curie temperature or change in conduction mechanism. From the figure 3, the activation energy is calculated by the relation

$$\rho = \rho_0 \cdot e^{\Delta E/KT}$$

Where  $\rho_0$  = constant depending on temperature

$\Delta E$  = activation energy

T = absolute temperature

K = Boltzmann constant.

Activation energies for para and ferri-region are found to be  $0.86\text{ eV}$  and  $0.30\text{ eV}$  respectively.

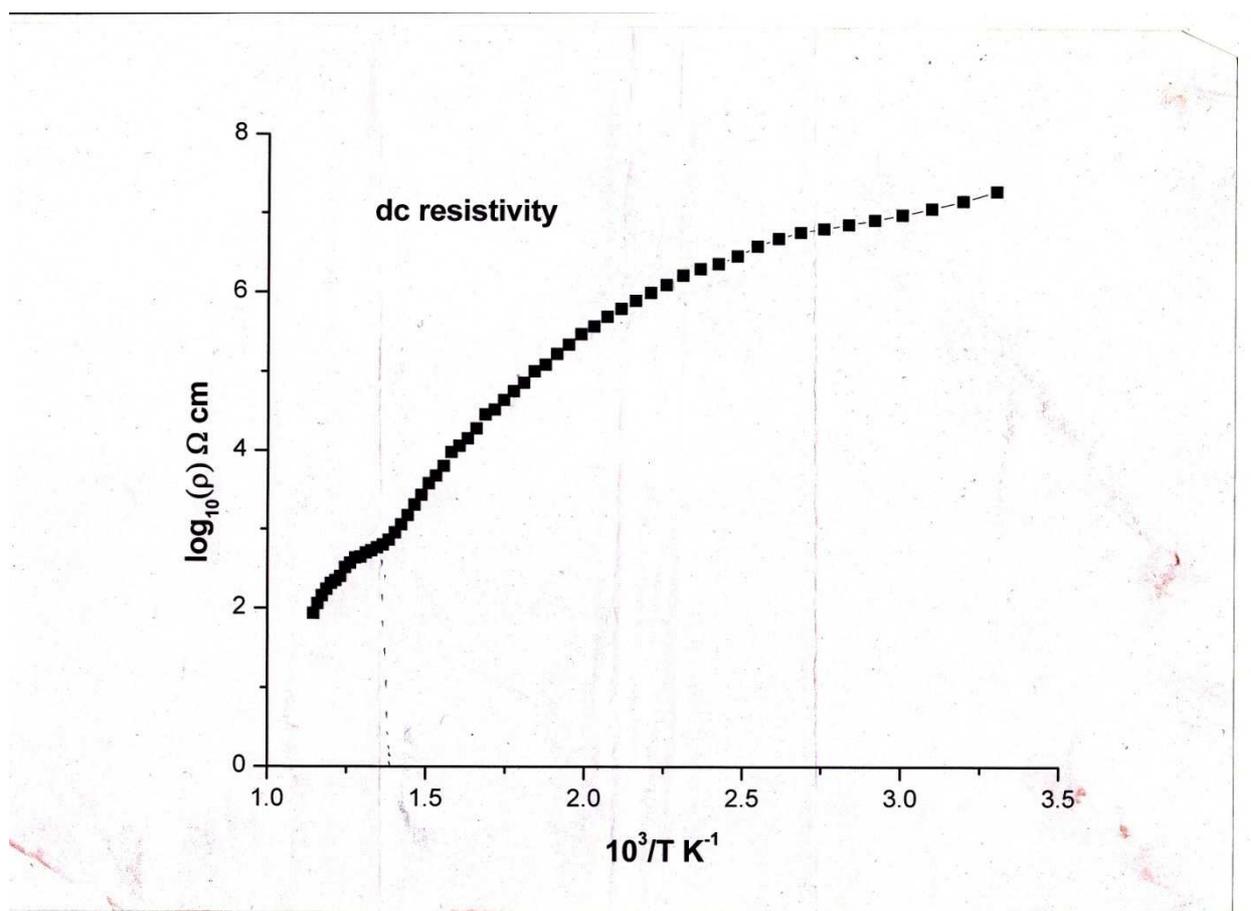


Figure 3. The variation of  $\log \rho$  Vs.  $1/T$

The lower activation energy in ferromagnetic region is due to magnetic ordering caused by the decrease in the concentration of current carriers. The change in slope at Curie temperature (534 °C from the figure 3) is due to the spin ordering of electrons from  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  ions. Therefore it can be concluded that there is a predominant change in the conduction mechanism due to magnetic phase transition.

### 3.3.3.2. AC Conductivity:

The capacitance, resistance and loss angle ( $\text{Tan } \delta$ ) were recorded directly in the range of frequency 10 Hz to 1MHz on LCR meter [at Karnatak University, Dharwad]. The dielectric constant was calculated using the relation

$$\epsilon' = c.d / \epsilon_0 A$$

Where  $c$  = capacitance of a pallet

$d$  = thickness of a pallet

$A$  = area of cross-section of a pellet

$\epsilon_0$  = Permittivity of free space.

'AC' resistivity was calculated by the relation

$$\rho_{ac} = \pi r^2 R / d$$

Where  $R$  = resistance of a pallet

$r$  = radius of a pallet

$d$  = thickness of a pallet.

The variation of dielectric constant with frequency is shown in the figure 4.

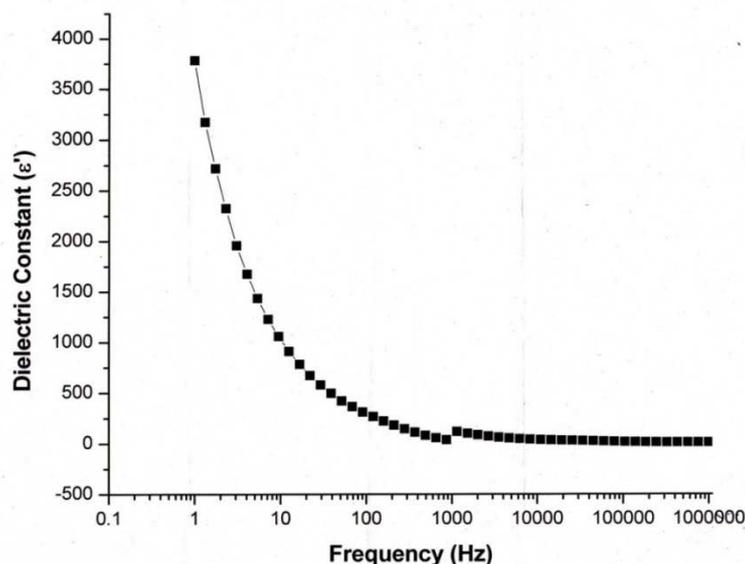


Figure 4. The variation of dielectric constant with frequency

The large value of  $\epsilon'$  at low frequency is due to the predominance of  $\text{Fe}^{+3}$  ions, oxygen vacancies, grain boundary defects etc., while the decrease in  $\epsilon'$  with frequency is due to the lagging of species contributing to polarizability behind the applied electric field. At higher frequencies  $\epsilon'$  remains constant which is attributed to the contribution of electronic polarizability only.

The variation of  $\text{Tan } \delta$  with frequency (Fig. 5) is attributed to the variation of AC resistivity according to the relation

$$\text{Tan } \delta = 1 / \omega \epsilon_0 \epsilon' \rho_{ac}$$

Where  $\omega$  = angular frequency corresponding to maximum value of  $\text{Tan } \delta$ .

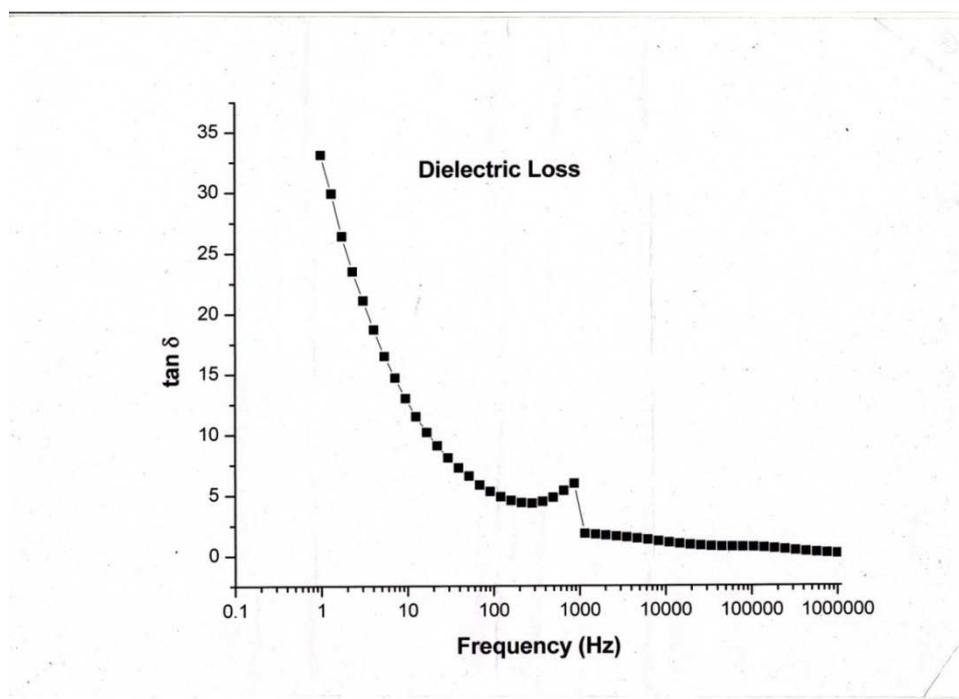


Figure 5. The variation of  $\text{Tan } \delta$  with frequency

The physical properties like 'dc' resistivity, 'ac' conductivity, dielectric constant, Tan  $\delta$  etc., are very sensitive to method of preparation, sintering temperature, sintering atmosphere etc. Sintering at reduced conditions results in the formation of divalent ions which form high conductivity grains, separated by low conductivity layers and makes the material in homogeneous.

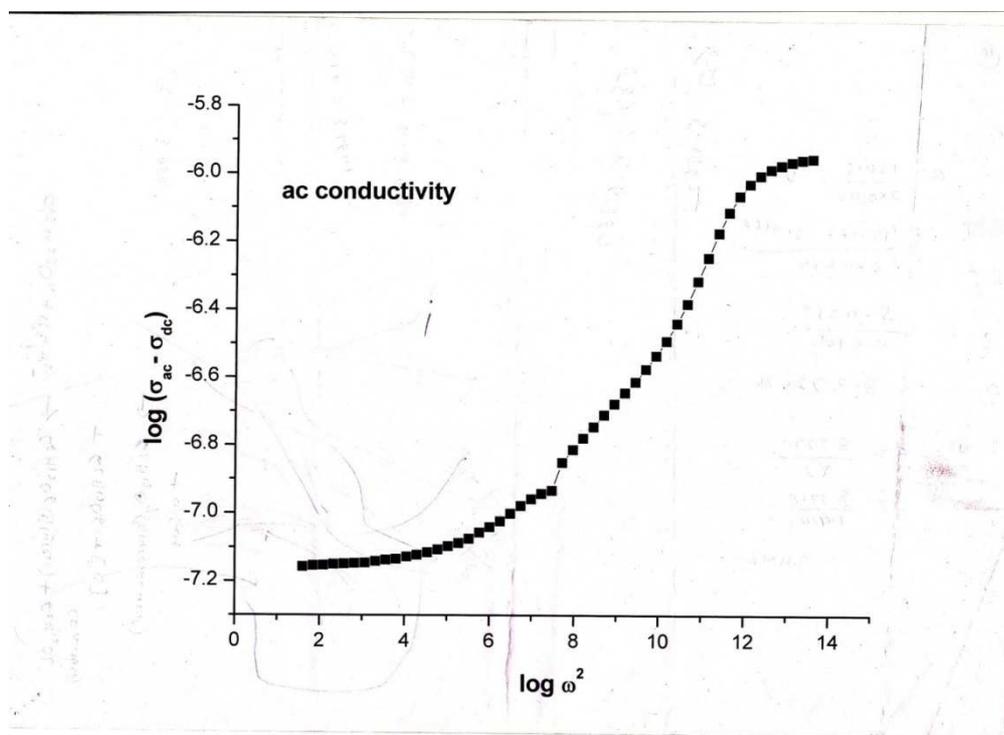


Figure 6. Variation of AC conductivity with frequency

From the figure 6, it is observed that ac conductivity exhibits large dispersion on the low frequency side and tends to level off at higher frequencies. This is in agreement with Koops theory [5].

#### Scope for applications

1. The largest use of ferrites is in flyback transformer core for television picture tube and digital computers.
2. Ferrites are used to suppress gyromagnetic and dielectric losses.
3. Recent utility of ferrites is in ultrasonic and radiofrequency electronics [6].

Copper ferrite is partially inverse. Hence Cu-Co ferrites show different physical properties at different temperatures. Hence Copper-Cobalt ferrites are found to be superior to other ferrites in the following aspects.

- i) Manufacture of multilayer chip inductor and LC filters.
- ii) High resolution display monitor.
- iii) Video cameras, L.C.D., hard discs for computer, cellular phone etc.
- iv) Manufacture of magnetic shielding to prevent cross talk with near by devices.

We are planning to proceed for synthesis and characterization of some more Co-Cu, Ni-Cu, Ni-Co, Ni-Cu-Co ferrites by chemical methods. The ferrites thus prepared would be screened for their highly applied parameters.

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