CHAPTER III

Electrical properties

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ELECTRICAL PROPERTIES

Composite materials show sum properties. Ferrites and ferroelectrics show semiconducting properties [1, 2]. But the conduction mechanism in them is quite different from that of in the semiconductors because in ferrite carrier concentration is almost constant but mobility of carriers is affected by temperature. The electrons are localized and not free to move. Hence free electron theory is not applicable to the ferrites. The conduction in ferrite and ferroelectric can be explained in terms of polaron hopping process [3, 4]. The electron coupled with the strain field is called a polaron. There are mainly two types of polarons viz. large polaron and small polaron. If the polaron or its strain field spreads beyond lattice constant, it is called as large polaron and if strain field extends over a distance less than lattice constant is called as small polaron. There is the interaction between the conduction electron or hole with nearby ions so that polarization of surrounding region takes place. It can be referred as the polarization well, at the centre of which the carrier is situated may be trapped at the centre of site. Hence to move it from one lattice site to another one , thermal activation is required. Thus the carrier jumps from one lattice site to another lattice site. This process is called as electron hopping. Many references [5, 6] have reported that the conduction in ferrites is mainly due to small polaron hopping.

SECTION A: DC RESISTIVITY

3A.1 Introduction

Ferrites are very useful tool in industry due to their high resistivity. In case of ferrites the electrical conductivity is dependent on the iron ions. The conduction process takes place due to the presence of Fe ions having different valence states present in crystallographically similar positions in the lattice. Under the influence of electrical field and thermal energy, these electrons jump from one iron ion to next produce the conduction current. Thus in ferrites, the conduction is due to the hopping electrons [1]. The relation between temperature and resistivity is given by the following equation

$$\rho = \rho_0 \exp(-\Delta E / kT) \qquad \dots (1)$$

where,

ρ_0 = constant

ΔE = the energy required to jump the electron called activation energy

k = Boltzmann constant and T = absolute temperature

3A.2 Experimental

The experimental set up for the resistivity measurement is shown in Fig. 3.1The Dc resistivity measurement of the samples was taken by two probe method [7]. For good ohmic constant the samples were coated with silver paste. The resistivity of the sample was calculated using the relation,

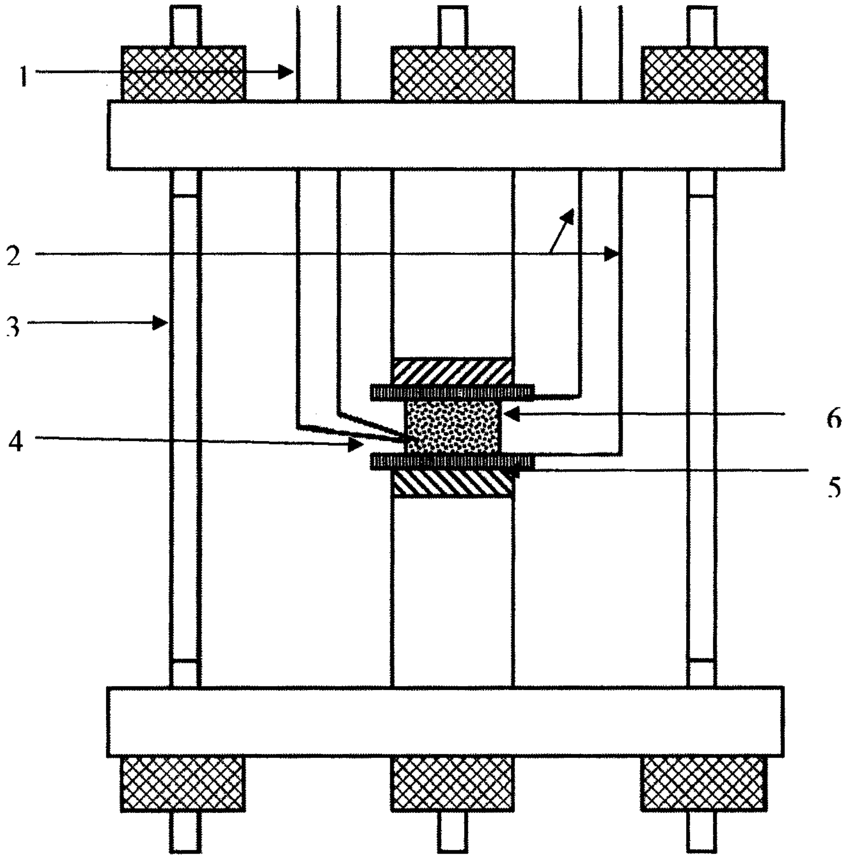
$$\rho_{dc} = R\pi r^2 / t \qquad \dots (2)$$

where,

R = ohmic resistance of the pellet

r = radius of the pellet

t = thickness of the pellet



1 Thermocouple, 2 Silver wires
3 Sample holder, 4 Silver disc
5 Mica sheet , 6 pelletized sample

Fig.3.1 Experimental set up for resistivity measurement

3A.3 Results and discussion

Fig. 3.2 show the variation of resistivity with temperature for $Co_{1-x}Cd_xFe_2O_4$ ferrites where x = 0.1, 0.3.and PZT. There are two regions in the plots. The linear decrease in resistivity with increasing temperature reflects the semiconducting nature of ferrites. According to the Verway model of the electron exchange between ions of the same elements present in different valence states takes place leading to a random distribution of electrons over the crystallographic equivalent sites [8]. In the present system of ferrites the conduction is consider to be due to the exchange of 3d electrons between Fe^{2+} and Fe^{3+} ions. The control of resistivity in ferrites is a serious problem. There are two general approaches to this;

1. Controlling sintering temperature and
2. Addition of minor constituents to increase or decrease in conductivity [9].

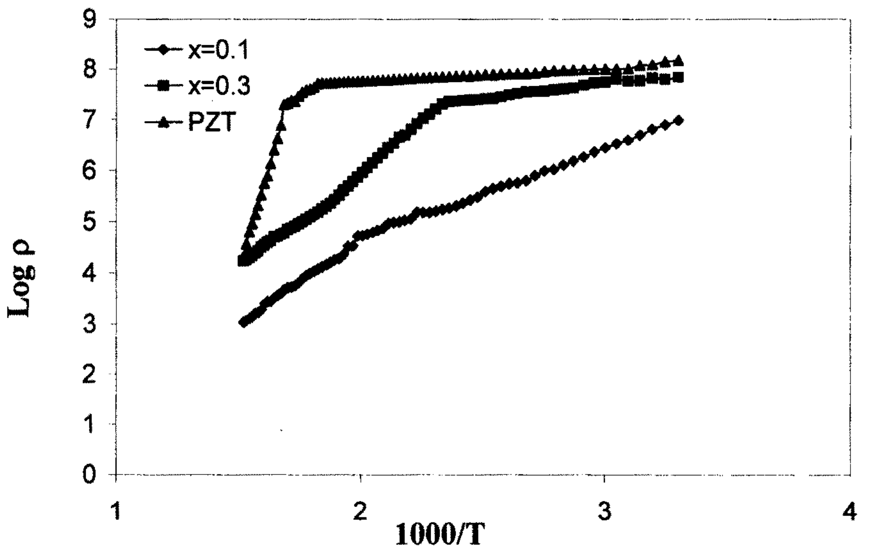


Fig.3.2 Variation of dc resistivity with temperature for $Co_{1-x}Cd_xFe_2O_4$ ferrites and PZT

In present case the Cd content in ferrite phase affects the resistivity of it. As the Cd content increases the resistivity of ferrite goes on decrease. This decrease in resistivity can be explained as follows.

Since the Cd ions occupy tetrahedral position (A site only) [10]. The substitution of Co^{2+} by Cd $^{2+}$ causes the migration of Fe^{3+} ion to octahedral site increases the hopping rate of electrons which causes to minimize the resistivity. Also as Cd^{2+} ions enter the tetrahedral sites, instead of Fe^{3+}, the lattice vacancies are created [11]. Since valency of Cd is less than Fe ions the lattice vacancies play a fundamental role in the conduction mechanism between Fe^{2+} and Fe^{3+}. So the resistivity decreases as the diffusion coefficient of lattice vacancies increases.

Fig.3.3 shows the temperature dependence resistivity for (y) $Co_{0.9}Cd_{0.1}Fe_2O_4$ + (1-y) PZT ME composites where y = 0.15, 0.30, 0.45. The plots show two regions. The first region at low temperature is attributed to the ordered state of ferroelectric phase of the composites, while the second region is due to the paraelectric state of the composites [12].

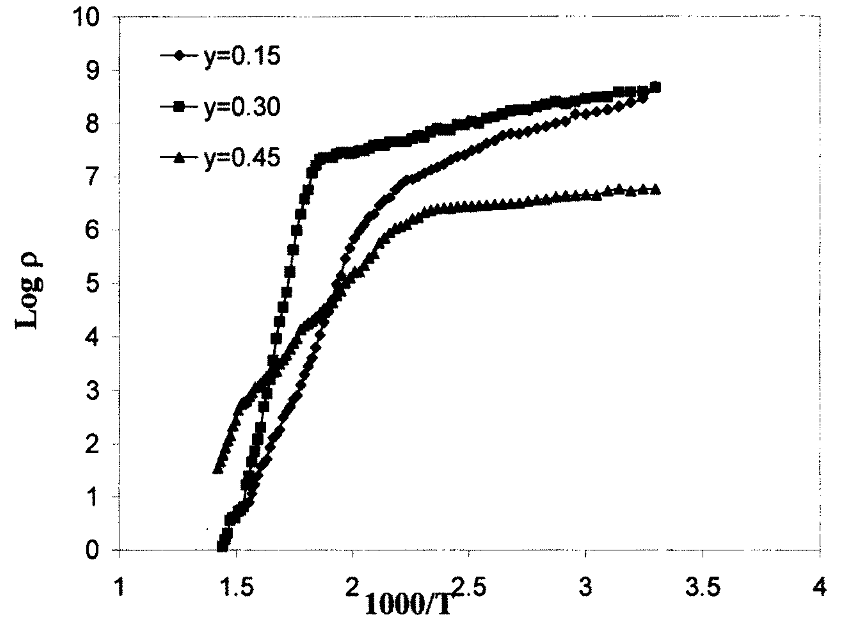


Fig.3.3 Variation of resistivity with temperature for (y) $Co_{0.9}Cd_{0.1}Fe_2O_4$ + (1-y) PZT ME copmposites

Resistivity of composites is a 'sum property' may be attributed to the parallel arrangement of ferrite and ferroelectric grains in composites. Also the resistivity of phases varies with sintering conditions, constituents, average grain size and in turn with porosity. Connectivity of phases is also a significant factor which affects the resistivity [13].

The temperature dependent variation of resistivity for (y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT ME composites where y= 0.15, 0.30, 0.45 is shown in the Fig.3.4 The large drop in resistivity was observed due to the addition of ferrite phase to the composite was observed. Resistivity is the basic requirement for good ME output. Hence to avoid the leakage of charges during electric poling, all composite samples were prepared in ferroelectric rich regions. In the present case the resistivity of the composite with y = 0.15 is maximum than that for composites with y = 0.30 and 0.45.

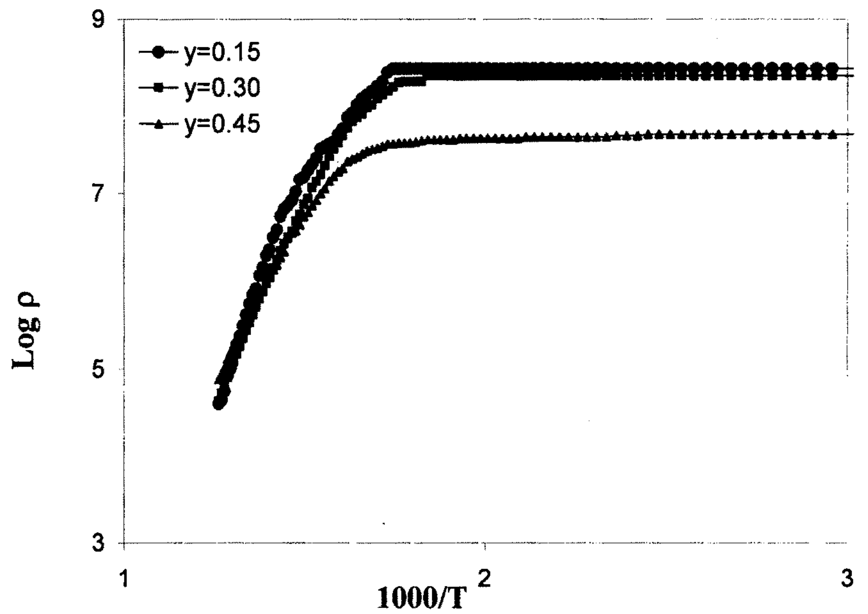


Fig.3.4 Variation of resistivity with temperature for (y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT ME copmposites

The activation energies for all the compositions of the composites are listed in the Table.3.1 In the present case the activation energy for ferro region is smaller than that for the para region. For all the compositions the activation energy of para region is greater than 0.2eV, indicating that the electron hopping between Fe^{2+}/Fe^{3+}, Ti^{3+}/Ti^{4+}, and hole hopping between Co^{2+}/Co^{3+} are responsible for electrical conduction in the composites. The activation energy value suggesting the temperature dependent of charge mobility [14]

Table3.1 Activation energies corresponding to para and ferro regions

Composition (y)	**Activation energy (eV)**	
	Ferro region	**Para region**
(y) $Co_{0.9}Cd_{0.1}Fe_2O_4$+ (1-y) PZT ME composites		
0.00	0.15	1.36
0.15	0.08	0.74
0.30	0.08	0.52
0.45	0.03	0.29
1.00	0.02	0.31
(y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT ME composites		
0.15	-	0.42
0.30	-	0.44
0.45	-	0.46
1.00	-	0.26

SECTION B: DIELECTRIC PROPERTIES

3B.1 Introduction

Ceramics are electrical insulators and can be used for number of applications such as in capacitor, microelectronic circuit in high voltage insulator applications etc. In so called dielectric materials the constituent atoms are considered to be ionized to a certain degree and are either positively or negatively charged. In such ionic crystals, when an electric field is applied, the electron cloud deforms causing electron dipoles. This phenomenon is known as "electric polarization" of the dielectric and polarization is the sum of electric dipoles per unit volume (c/m^2) [15]. The parameters such as dielectric strength, dielectric constant and loss tangent, electrical resistivity and operating frequency are important factors. Dielectric strength Dielectric strength is the maximum voltage field that the material like ceramic can withstand before electrical breakdown occurs. The dielectric constant is the relative permittivity of a material compared to a vacuum or free space. In dielectric materials the loss tangent or a loss coefficient is the ratio of the imaginary or loss permittivity to the real permittivity of a material. Resistivity is the longitudinal electrical resistance (Ω.cm) of a uniform rod of unit length and unit cross sectional area. Operating frequency is the frequency range that the material is capable of operating within while providing acceptable performance and/or without excessive power losses. There are mainly three primary contributions to polarization as electronic, ionic, and dipole reorientation. The degree to which each mechanism contributes to the overall polarization of the material depends on the frequency of the applied field.

1. Electronic polarization (10^{12} to 10^{15} cycles/s)
2. Ionic polarization (10^{9} to 10^{12} cycles/s)
3. Dipole reorientation (10^{6} to 10^{9} cycles/s)

Below microwave frequency, the polarization is due to the microstructure of polycrystalline materials followed by the migration of free charges. This polarization is referred as space charge polarization or interfacial polarization [16].

3B.2 Frequency dependent Dielectric constant

Koops [17] gave the phenomenological theory of dispersion based on Maxwell [18] and Wagner [19] interfacial polarization model for inhomogeneous dielectric structure. This model explains the dispersion of dielectric constant and dielectric loss at low frequencies, which suggest the grains of different sizes contribute to the value of dielectric constant and relaxation frequency. The dielectric displacement (D) is found to an alternating field (E) is,

$$D = \varepsilon^* E \qquad \ldots (3)$$

where ε^* = dielectric constant which is a complex quantity;

$$\varepsilon^* = \varepsilon' - i\,\varepsilon'' \qquad \ldots (4)$$

ε' = real part of dielectric constant

ε'' = imaginary part called as dielectric loss or tan δ

$$\tan\delta = \varepsilon''/\varepsilon' \qquad \ldots (5)$$

The frequency dependence of ε^* can be written as;

$$\varepsilon^* = [\varepsilon'_{inf} + \varepsilon/1+\omega^2T^2] + j[\varepsilon'_0 - \varepsilon'_{inf}/\ 1+\omega^2T^2]\omega T \qquad \ldots (6)$$

where ε'_0 and ε'_{inf} are dielectric constants at low and high frequencies respectively.

T = relaxation time and ω = angular frequency

The dielectric loss is;

$$\tan\delta = \text{loss current/charging current}$$

Thus dielectric constant depends on the alternating electric field. At high frequency only electronic polarizability contributes to the polarization. Hence dielectric constant attains a constant but small value.

3B.3 Experimental

The pelletized samples were coated by silver foils for good ohmic contact. The parameters such as capacitance (c) and dielectric loss (D) were measured by two probe method in the frequency range 20Hz to 1MHz using LCR meter (HP 4284A). The real dielectric constant was calculated using the formula [20],

$$\acute{\varepsilon} = C\, d \,/\, \varepsilon_0 A \qquad \dots (7)$$

where,

C = capacitance

d = thickness of pellet

A=area of the surface of pellet

ε0 = permittivity of free space=8.85x 10-12 F/m

The ac conductivity was calculated from the dielectric constant and dielectric loss using the following relation [21],

$$\sigma_{ac} = \acute{\varepsilon}\, \varepsilon_0\, \omega \tan\delta \qquad \dots (8)$$

where,

$\acute{\varepsilon}$ = dielectric constant

ε_0 = permittivity of free space

ω = angular frequency = $2\pi f$

$\tan\delta$ = dielectric loss.

The frequency response of the dielectric behaviour and ac conductivity is known as relaxation spectra or dispersion curve which gives the information about the conduction mechanism present in the ceramic composites.

3B.4 Results and discussion

Figs. 3.5 and 3.6 show the variation of dielectric constant (ε') with frequency for the composites (y) $Co_{0.9}Cd_{0.1}Fe_2O_4$ + (1-y) PZT and (y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT respectively. From the figures it is observed that for all the composites the dielectric constant decreases with increase in frequency showing dispersion in a certain lower frequency range and reaches a constant value at higher frequencies. It is also seen that at the same frequency there are different values of dielectric constant for (y) $Co_{0.9}Cd_{0.1}Fe_2O_4$ is 242 and (y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ is 520 which is greater than that of the first. This may be due to the two possible regions as follows,

i. Space charge polarization

ii. Migration of ferric ion

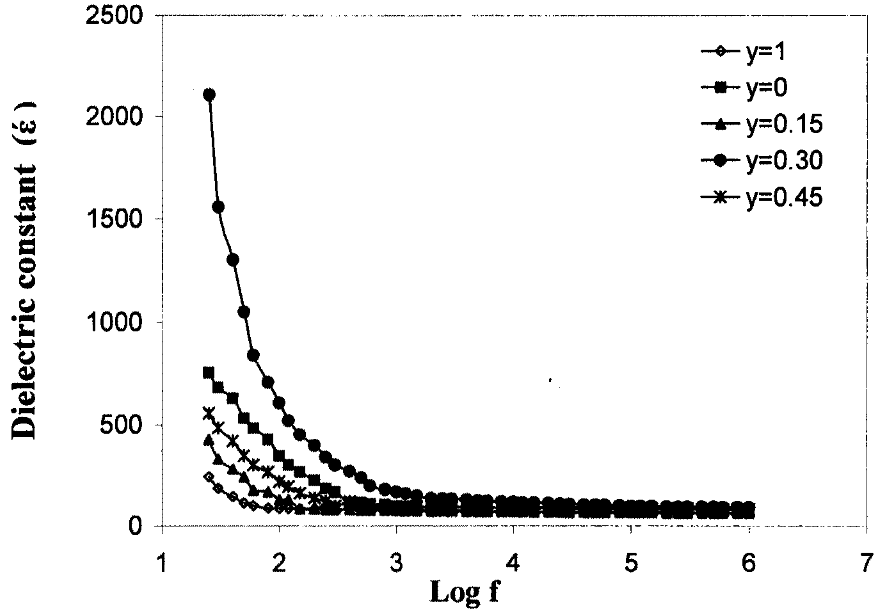


Fig.3.5 Variation of Dielectric constant with frequency for (y) $Co_{0.9}Cd_{0.1}Fe_2O_4$ + (1-y) PZT ME composites

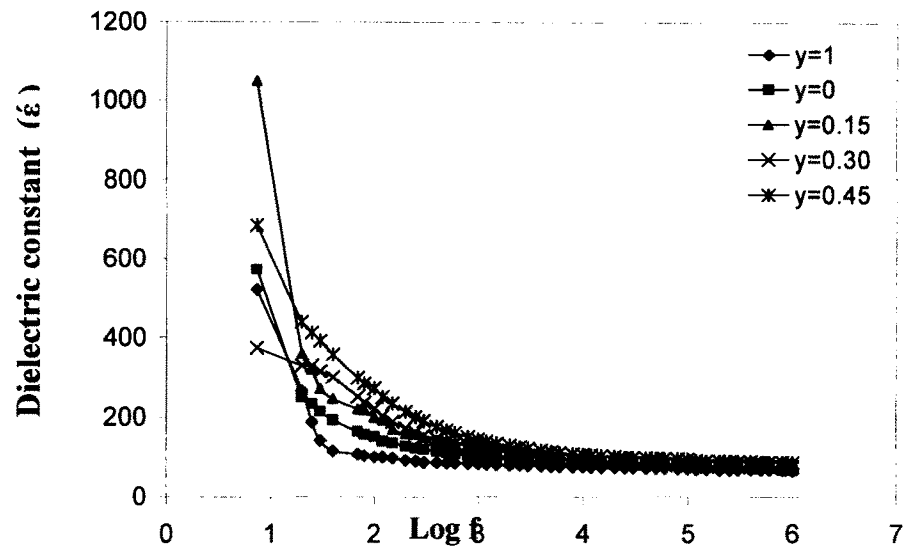


Fig. 3.6 Variation of Dielectric constant with frequency for (y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT ME composites

i. Space charge polarization

In the ferrites the grains are separated by grain boundaries. Grains are conducting while grain boundaries are nonconducting. Therefore as in general capacitor in which two conducting plates are separated by the dielectric material in the present case the neighboring grains are analogous to two conducting plates while grain boundaries act as the insulating material.

When an electric field is applied to it the charges orient in the direction of field and moves towards the grain boundaries. But as the grain boundaries are non conducting they are unable to flow through it and get accumulated at the grain boundary, at the same time the oppositely charged ions get accumulated to the opposite side. Thus the charge gets stored. This process is called as space charge polarization.

ii. Migration of ferric ions

The dielectric constant of $Co_{0.7}Cd_{0.3}Fe_2O_4$ is larger than that of for $Co_{0.9}Cd_{0.1}Fe_2O_4$. As Co^{2+} ions, the migration of ferric ion from A site to B site occur. This decreases AA interaction and increases BB interaction leading to the decrease of jump length. The hopping electrons at B site were directed under the applied field leading to the increase in polarization and gets high dielectric constant [20]. All the samples show the dispersion in lower frequency range due to the Maxwell - Wagner [18, 19] type interfacial polarization. For all the composites the high value of dielectric constant observed at lower frequencies are explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The inhomogeneities present are grain structure, porosity etc. [7, 22].

Figs.3.7 and 3.8 show the variation of loss tangent with frequency for all the composites show the similar behaviour as that of the dielectric constant with frequency. The similar reports have been reported by various workers for other composites [23, 24].

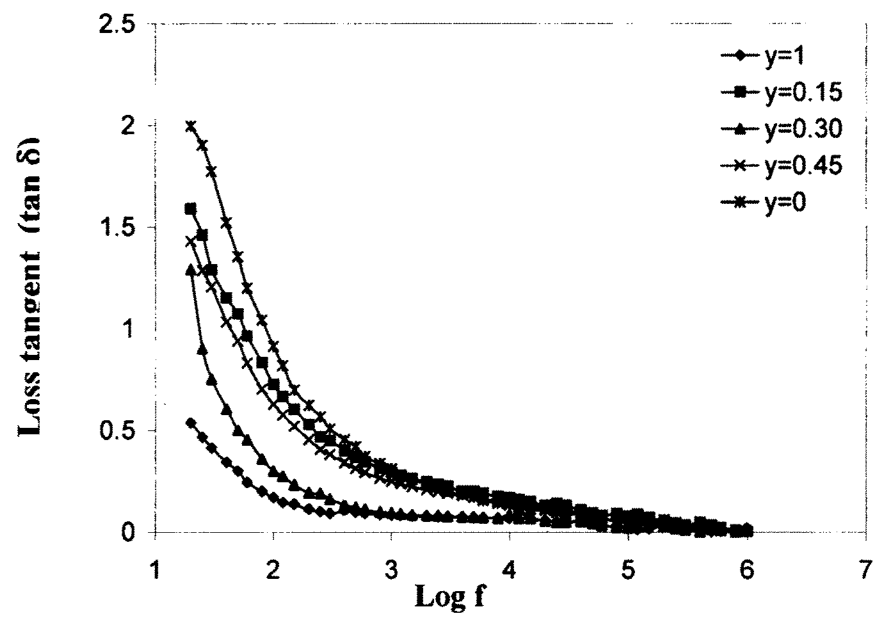


Fig.3.7 Variation of loss tangent with frequency for (y) $Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT ME composites

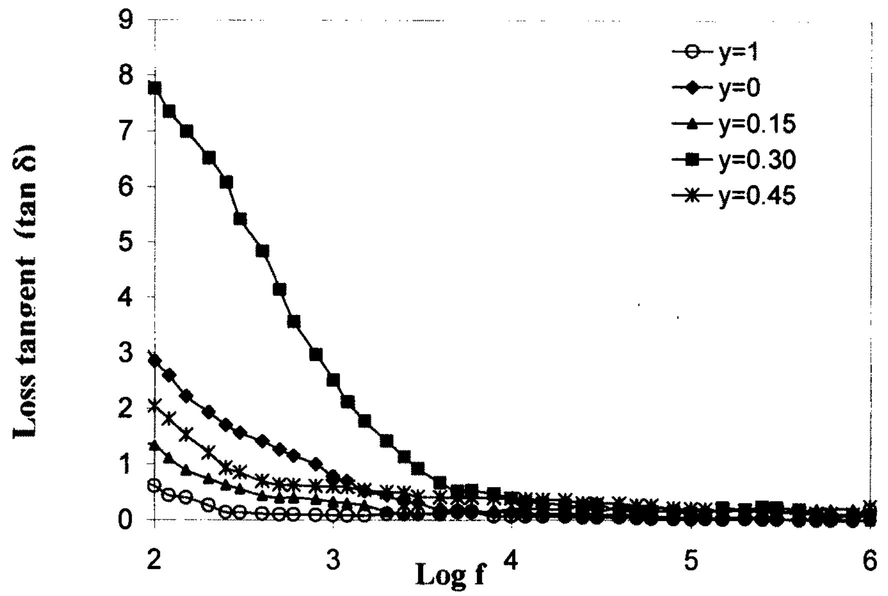


Fig.3.8 Variation of loss tangent with frequency for (y) $Co_{0.9}Cd_{0.1}Fe_2O_4$ + (1-y) PZT ME composites

Figs. 3.9 and 3.10 show the frequency dependent nature of ac conductivity for all the composites. The plots are linear showing that the conductivity increases with frequency. The results are similar to those observed those observed by the other workers for different composites [25, 26, 27]. Adler and Feinleib [28] have shown that for conduction by small polarons, the conductivity increases with increasing frequency which supports the present results. The electrical conduction mechanism in terms of electron and polaron hopping model has also discussed earlier by Austin and Mott [29] and Appel et al. [30]. As reported by S. L. Kadam et al. [31] the slight decrease in conductivity at certain frequency is attributed to mixed polaron.

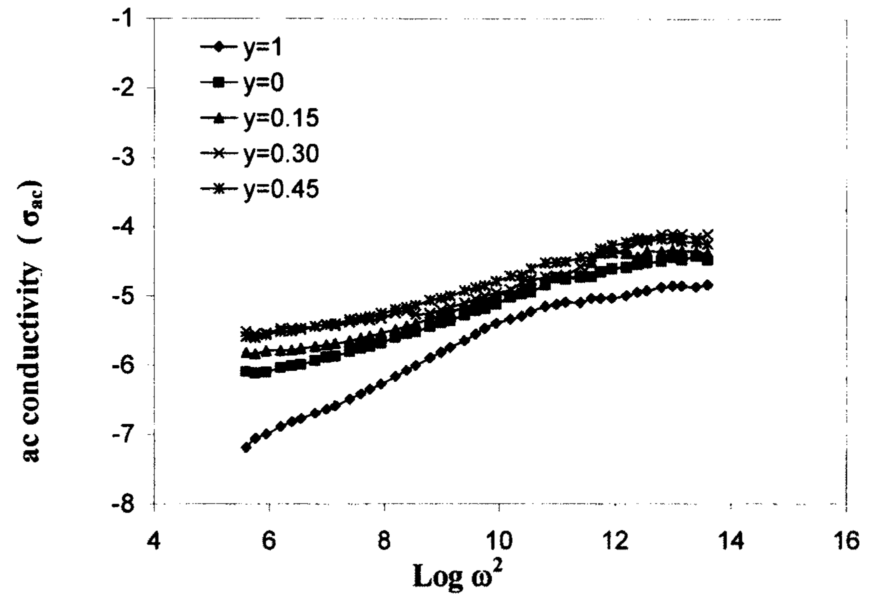


Fig.3.9 Variation of ac conductivity with frequency for (y)$Co_{0.7}Cd_{0.3}Fe_2O_4$ + (1-y) PZT ME composites

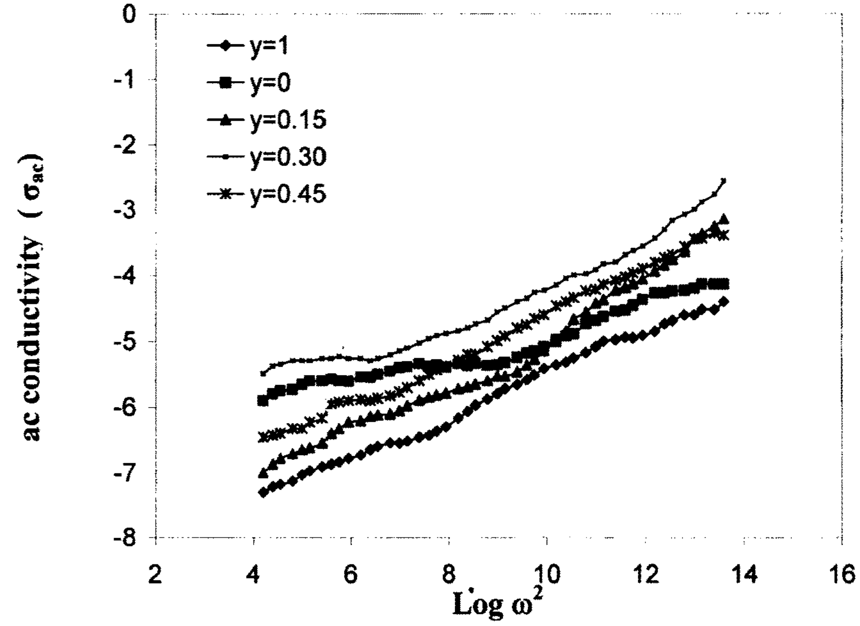


Fig.3.10 Variation of ac conductivity with frequency for (y)$Co_{0.9}Cd_{0.1}Fe_2O_4$ + (1-y) PZT ME composites

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