CHAPTER - IV

CHAPTER – IV

SUM PROPERTIES OF COMPOSITES

ELECTRICAL PROPERTIES

4.1 INTRODUCTION

Any physical property of a material can be considered as the action of physical quantity X from an external agency in the material, resulting in a physical quantity Y as measured by a measurement system. This property can be defined as an X-Y effect. (X = input parameter, Y = output parameter) In a composite material the submaterials have their own sets of X-Y effects for all possible physical quantities. The combination of these effects determines the properties of composite materials. The X-Y effect in a submaterial I and an X-Y effect in submaterial II (with a proportionality factor different from that in I), together will give an X-Y effect of the composite. These properties are named as sum properties [1].

Sum properties are very common. For instance, the resistivity tensor of a composite (diagonalised form) is made up of essentially series and parallel resistances of the two submaterials with some geometrical factor. The other example is the Siemens "Feldplatte"[2], which consists of conductive needles (metallic) with a small Hall angle and diameter of about 1μm, dispersed in a semiconductor matrix of large Hall angle.

This eutectic composite exhibits a strong magnetoresistive effect, in a mutually perpendicular direction with respect to the needles and the magnetic field.

In short the combination of two or more submaterials having their own X-Y effect can be used to design a composite for combining their properties suitably to give more effective sum property.

4.2 DIELECTRIC DISPERSION

As in case of ferrites the study of their dielectric behaviour is important, the composite containing both phases i.e. ferrite and ferroelectric, has been studied from the point of view of the dielectric dispersion[3].

When field is applied to a dielectric, the polarization of the dielectric takes place. The polarization can be distinguished as electronic, ionic interfacial and orientational. It is electronic in the spectral frequency region below infrared frequencies it is ionic. Below microwave frequency the polarization is due to microstructure of polycrystalline material and from the migration of free charge carriers.

The dielectric constant shows dispersion with respect to frequency. Koops explained this considering the ferrite compact as a multilayer capacitor in which ferrite grain and grain boundary have different properties [4].

When alternating electric field E is applied to a dielectric material, there is dielectric displacement which is given by D = εE where ε = dielectric constant. The dielectric response to AC field shows complex dielectric constant involving real as well as imaginary components related by

$$\tan \delta = \varepsilon'' / \varepsilon'$$

As ε' depends on frequency and time, the real and imaginary parts of dielectric constant also depend on frequency and time which is given by

$$\varepsilon = [\varepsilon_\infty + \varepsilon_0 - \varepsilon_\infty / 1 + \omega^2 \tau^2] + i [\varepsilon_0 - \varepsilon \infty / (1 + \omega^2 \tau^2) \omega \tau]$$

where ε_0 – low frequency dielectric constant

ε_0 – high frequency dielectric constant

$\varepsilon\infty$ – high frequency dielectric constant

ω – Angular frequency

τ – Relaxation time

$$\text{Tan}\delta = \varepsilon'' / \varepsilon' = (\varepsilon_0 - \varepsilon_{00}) \omega / (\varepsilon_0 + \varepsilon_{00})$$

4.2.1 DIELECTRIC CONSTANT MEASUREMENT

The dielectric constant measured along a ferroelectric axis increases in the paraelectric phase when the curie temperature is approached. In many ferroelectrics this increase is given by Curie-Weiss law[5].

$$\varepsilon = C/(T - Tc)$$

where,

T – temperature of the sample

Tc – Curie temperature temperature

C – is called Curie constant.

4.2.2 AC CONDUCTIVITY

The electrical conductivity and dielectric behaviour of ferrites, ferroelectrics and their composites depend on sintering treatment, chemical composition, preparation conditions and the quantity and the type of additives. The study of the effect of composition and frequency on AC electrical conductivity offers much valuable information on the behaviour of the localized electric charge carriers which can be helpful in understanding the mechanism of electric conduction and dielectric polarization in ferrite ferroelectric systems[6]. Studies on AC conductivity in a wide range of frequencies combined with DC conductivity and TEP measurements would help to suggest the conduction mechanism.[7] Moreover AC conductivity as sum property in ferrite ferroelectric composites has not been hitherto reported.

4.2.3 EXPERIMENTAL

The experimental set up used for the measurement of dielectric constant at various temperatures is shown in fig. 4.1. The experimental set up consists of an electrically heated furnace with temperature controller arrangement and (HP Make – 4284A Model) LCR meter. Pellet of the composite is placed in a sample holder which was heated in a furnace.

The dielectric constant is calculated using the formula

$$\varepsilon' = Cd/\varepsilon_0 A$$

where,

C = capacitance in Pf

d = thickness of the pellet in cm

AC conductivity data was derived from dielectric constant and loss tangent measured using the relation

$\sigma ac = \varepsilon \, \varepsilon_0 \omega \tan\delta$ [7]. Hence dielectric constant and loss tangent (tan δ) at various frequencies and their variation with temperature were measured using HP Model 4284A - LCR meter, laboratory designed sample holder and furnace for heating as shown in fig. 4.1
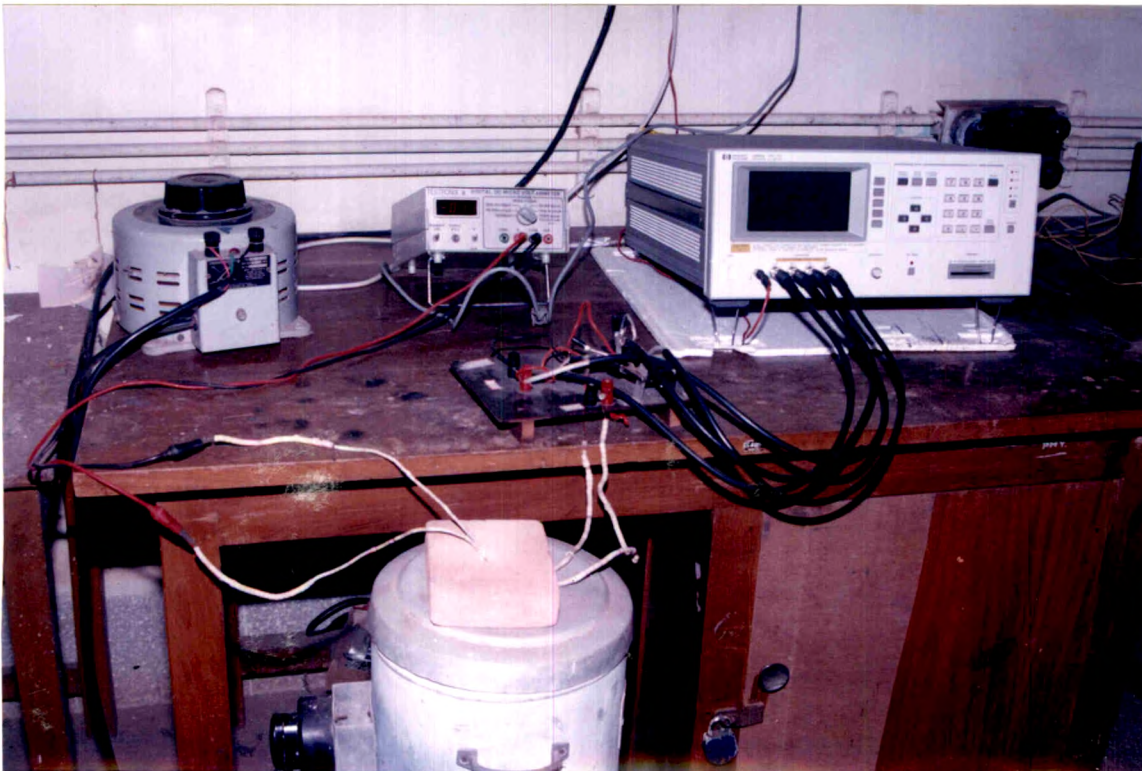
Fig. 4.1   HP MAKE - 4284 A MODEL

4.2.4 RESULTS AND DISCUSSION

The variation of dielectric constant (Σ') and loss tangent $(\tan\delta)$ with frequency for the composites $xBaTiO_3$ + $(1-x)$ $MnFe_{1.8}Cr_{0.2}$ O_4 in which X varies from 1, 0.85, 0.70, 0.55 and 0 in mol. percent is shown in figs. 4.2(a) and 4.2(b).

An examination of the figure shows that some of the samples reveal dielectric dispersion. Σ' and $\tan\delta$ decrease rapidly at low frequencies and remains fairly constant beyond 10 kHz. It is also clear from the figure that at low frequency like 100 Hz, Σ' is maximum for the composition x = 1 and minimum for x = 0.85 composite. For the other compositions the value of ε' lies in between these maximum and minimum values. The dispersion is large for compositions with high value of ε' at 100 Hz frequency. The composites with composition x = 0.85, x = 0.55 and x = 0, ε' remains almost independent of frequency. The frequency independent value is called as static value of dielectric constant. For the present ceramics this constant value lies in the range 100 to 500. In case at x = 1 composite this large value of ε' has been attributed to the effect of heterogeneity of the samples like pours and layered structure. However, for x = 0.70 composite the dielectric dispersion is ascribed to the fact that ferroelectric regions $(BaTiO_3)$ are surrounded by non ferroelectric regions $(MnFe_{1.8}Cr_{0.2}O_4)$, similar to that reported in the case of relaxor ferroelectrics. [8,9]. This gives rise to interfacial polarization. This is reflected in sharp fall of dielectric constant for x = 0.70 composite in

the frequency range 100 Hz to 10 kHz. Sometimes polaron hopping mechanism resulting in electronic polarization also contributes to low frequency dispersion[8]. The fig 4.2 (a) shows the low values of dielectric constant for the composite x = 0.85 and x = 0.55. The structure of the composite x = 0.85 shows virtually no tetragonal splitting indicating a very low c/a ratio. Hence although 85% of the composite is constitutionally barium titanate it naturally shows low value of dielectric constant. However the case of the composite x = 0.55 is different. In this case increase in conductivity does not allow build up of space charge there by keeps the value of dielectric constant low.

The variation of tanδ with frequency for various compositions is shown in the fig. 4.2(b). All the samples show dispersion in tanδ with frequency. Careful observation of the figure also reveals that the loss is minimum for x = 1, and maximum for x = 0.55 composite. It is obvious as ε' is highest for x = 1 composite and ε' is low for x = 0.55 composite.

The electrical conduction in magnetoelectric composites is hitherto not reported. However, attempts have been made by several workers to explain AC conductivity in the magnetoelectric composite [8]. Fig. 4.3 shows the variation of log(σ_{ac} – σ_{dc}) with log ω^2 for x = 0.85, 0.70 and 0.55 the plots are almost linear indicating that the conductivity increases with increase in frequency. The results are similar to that observed by other workers [1]. Adler and Feinleib [4] have shown that for conduction by small
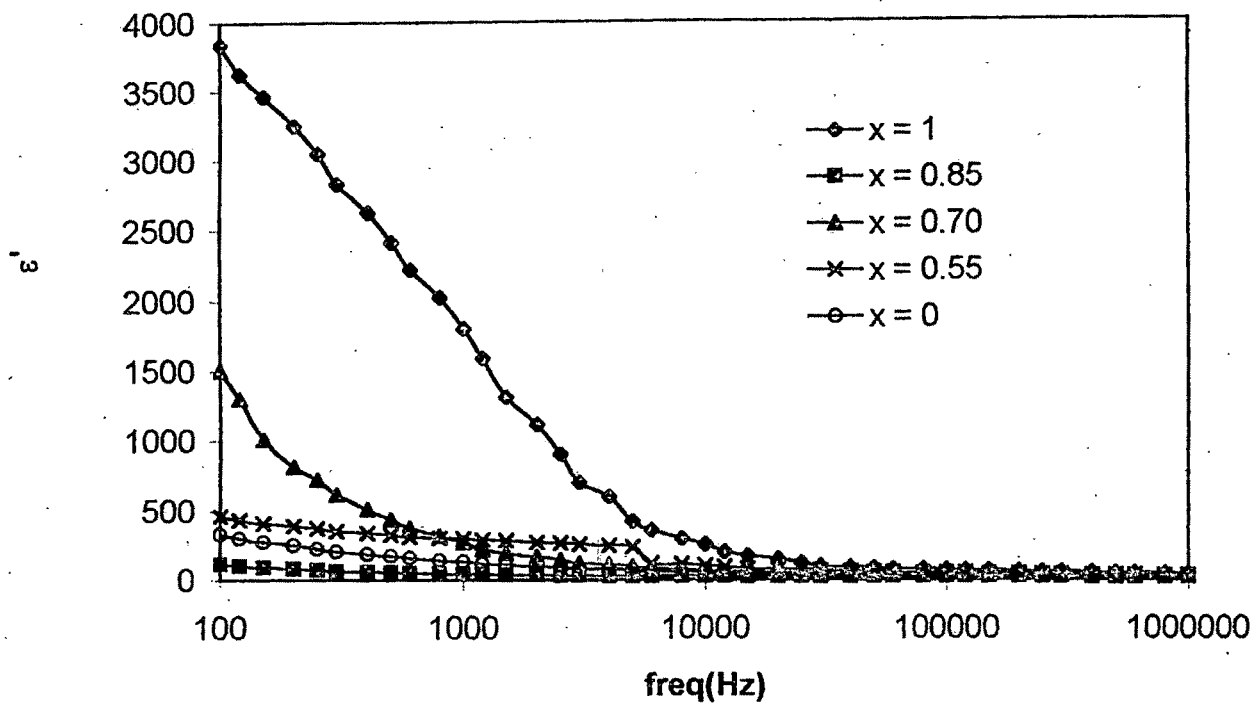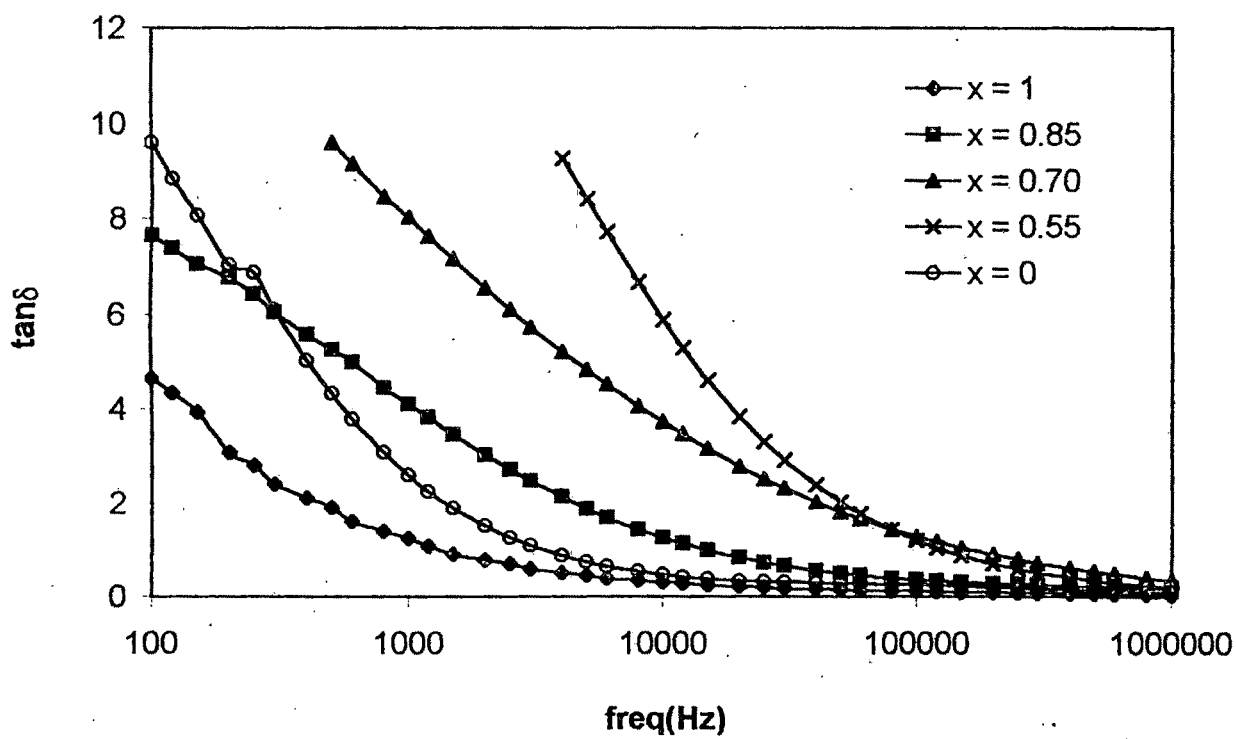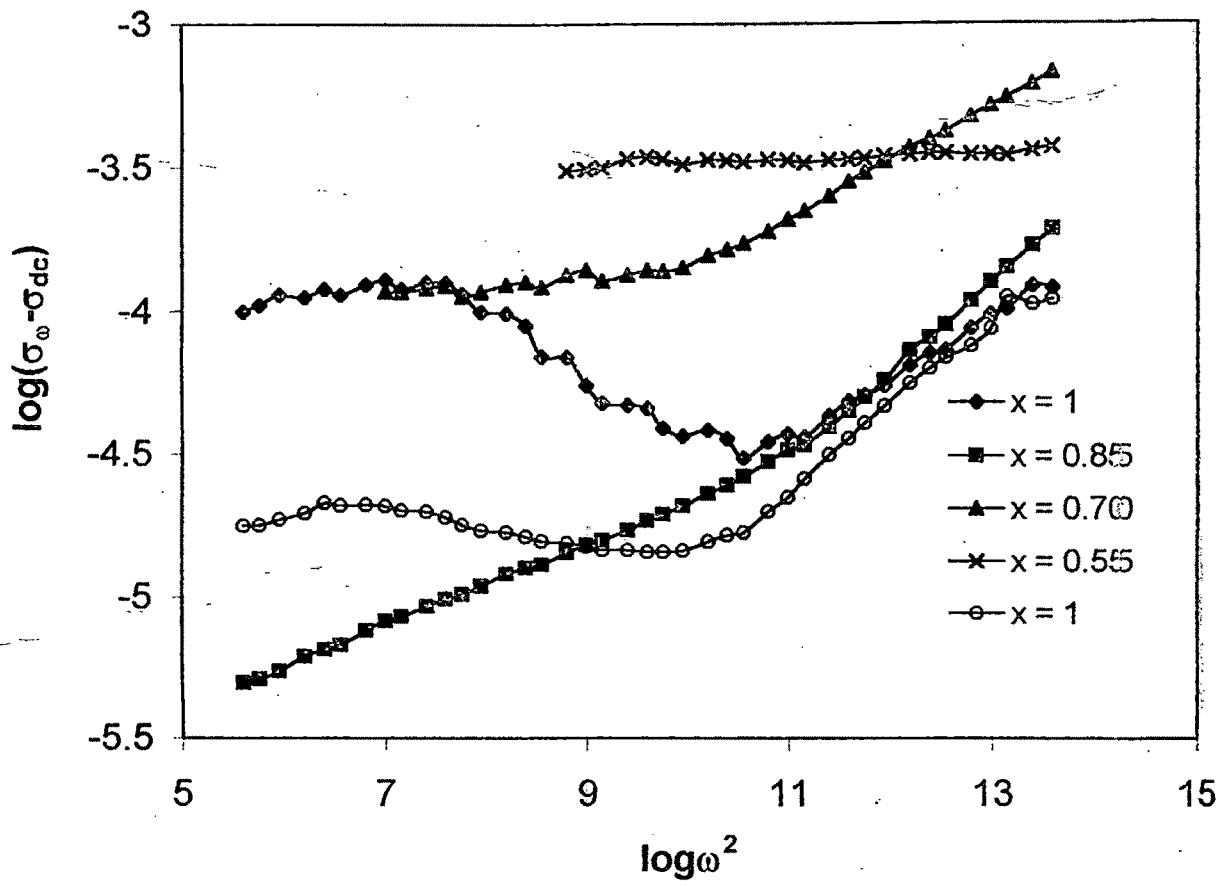
Fig.4.2 a

Fig. 4.2 b

Fig.4.3

Fig.4.3

polarons, the conduction increases with frequency and the following relation holds good.

$$\sigma_{ac} - \sigma_{dc} = \omega^2\tau^2 \, / \, (1 + \omega^2\tau^2 \,)$$

where,

ω – angular frequency

τ – staying time (10^{-10} sec.)

Therefore $\omega^2\tau^2 < 1$. Hence plot of log ($\sigma_{ac} - \sigma_{dc}$) Vs log ω^2 should be a straight line. For the present ceramics as already mentioned, the plots are linear for x = 0.85, 0.70 and 0.55 confirming small polarons type of conduction in these composites. However in case of end members barium titanate and $MnFe_2O_4$, i.e. for x = 1 and x = 0, the variation is of different type. At low frequency the AC conductivity gradually decreases and reaches a minimum at about 50 kHz and there after increases linearly with increase in frequency. This type of variation suggests that at low frequency conduction is due to large ploarons and beyond 50 kHz it is rather small polaron type of conduction [5]. Hence it can be concluded that the conduction in the pure components is mixed polaron type. The conductivity at low frequency is maximum for x = 0.55 composite whereas, minimum for x = 0.85 composite. For the other composites the conductivity lies in between these maximum and minimum values. It is also worth noting that the maximum ME sensitivity was observed in x = 0.85 and no

magnetoelectric effect was detected in x = 0.55 composite. This can be attributed to the build up of polarization changes due to maximum resistivity leading to maximum M.E. effect while leakage and dissipation of charges forestalling any M.E. effect due to maximum conductivity in X = 0.55 composite.

4.3   DIELECTRIC CONSTANT VARIATION WITH TEMPERATURE

The term "dielectric properties" in its broad usage refers to electric responses developed in a medium on application of an electric/ magnetic field. In order to characterize these responses, the permitivity (ε_r of the material is of interest. In vaccum the permitivity (ε_0) is 8.854 $\times 10^{-12}$ F/m. Hence the relative permitivity or dielectric constant (ε^r) of the medium, defined as ratio of $\varepsilon/\varepsilon_0$ is always greater than 1.

A dielectric constant (ε') is a function of temperature. In case of alternating field this quantity also depends on frequency (ω), Practically, a parallel plate capacitor is pla ced with a dielectric medium. This system is exposed to the field of known frequency and its macroscopic characteristics such as capacitance (c) & loss factor (tanδ) are measured as a function of temperature and frequency. The scientist have unravelled the molecular phenomenon behind these parameters. This has enabled dielectric synthesis of materials where the properties of materials are tailored by combining proper atoms and molecules into specific arrangements.

This approach provides a quantitative basis for important parameters namely, complex dielectric constant.

Complex dielectric constant :

Consider a parallel plate condenser filled with some dielectric material. If it is connected to sinusoidal signal of applied frequency (ω), then in addition to charging current there exists a loss current[11]. The loss is responsible for conduction which is energy consuming process.

In a dielectric material the power dissipation or the conduction need not be necessarily ohmic/electric. The dielectric constant is a complex quantity denoted by ε *.

$$\varepsilon\ ^* = \varepsilon' - j\ \varepsilon"$$

where ε' is the real part of relative dielectric constant and $\varepsilon"$ is the imaginary part of the complex relative dielectric constant. The corresponding loss $\tan\delta$ is defined as the ratio of the loss current to the charging current which is also written as

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

Practically, $\varepsilon' = C/C_0$ where C is capacitance due to dielectric material and Co is the capacitance in the vaccum when the dielectric substance is removed. Also, the loss is a function of frequency, hence the dielectric conductivity (σ_{ac}) is defined as

$$\sigma_{ac} = \omega \, \varepsilon_0 \, \varepsilon' \, \tan\delta$$

The frequency response of these parameters (ε', ε'', σ) are generally known as "relaxation spectra or dispersion curves", which characterize the materials[11].

4.3.1 EXPERIMENTAL

The measurement of dielectric constant and dielectric loss is done with the help of laboratory designed sample holder and LCR meter HP 4284 A model. The variations of capacitance and losses with temperature at four different frequencies namely 1kHz, 10 kHz, 100 kHz and 1 MHz were studied.

4.3.2 RESULTS AND DISCUSSION

Variation of dielectric constant with temperature at 1kHz,, 10 kHz, 100 kHz and 1 MHz for x = 1, 0.85, 0.70, 0.55 and 0 are shown in the figs. 4.4 to 4.8. The variation of ε' for $BaTiO_3$ i.e. x = 1 sample is shown in fig 4.4. Normally in ferroelectrics, the dielectric constant initially increases with increase in temperature, reaches a maximum value at transition temp. (Tc) and thereafter suddenly decreases obeying Curie-Weiss law. In the present case the Tc obtained is 120^0C which compares very well with the value reported in literature. Tc does not show any frequency dependence but the dielectric constant exhibits decreasing values for higher frequencies.

Fig. 4.5. shows the variation of dielectric constant with temperature for pure

$MnFe_{1.8}Cr_{0.2}O_4$ i.e. x = 0 composition. The ε' for ferrite is very less when

compared to that of ferroelectric, which is obviously due to Verwey type

of electron exchange mechanism in ferrite on one hand and polarization

being an inherent property of ferroelectrics on the other. The polarization

in ferrite can be explained by applying Koops model [12]. Koop has

explained the dispersion in dielectric by considering ferrite compact

as multilayer capacitor having different properties. The grain boundaries act

as an insulating medium between two conducting grains. The variation

of dielectric constant with temperature in ferrites was studied by many

workers [13,14]. The electron hopping between $Fe+^2$ (ferrous) and Fe^{+3}

(ferric) ions and also in the present ferrite between $3Mn^{+2} \rightarrow 2\ Mn+^3$ on the

octahedral sites are responsible for conduction mechanisms. The electron

hopping is thermally activated by increasing temperature. This electron

hopping causes local displacements in the direction of external applied

electric field. This includes dielectric polarization in ferrites. Hence

an increase in temperature results in increase of dielectric polarization

causing an increase in ε' and $\tan\delta$ for all the frequencies. The transition

temperature for the present ferrite is 210^0C as reported earlier [14']. In the

present study we also observe an anomaly at this temperature. The ε' which

was increasing with temperature starts to decrease after passing through the

transition temperature (Tc). The decrease is not gradual. Beyond 230^0C, ε'

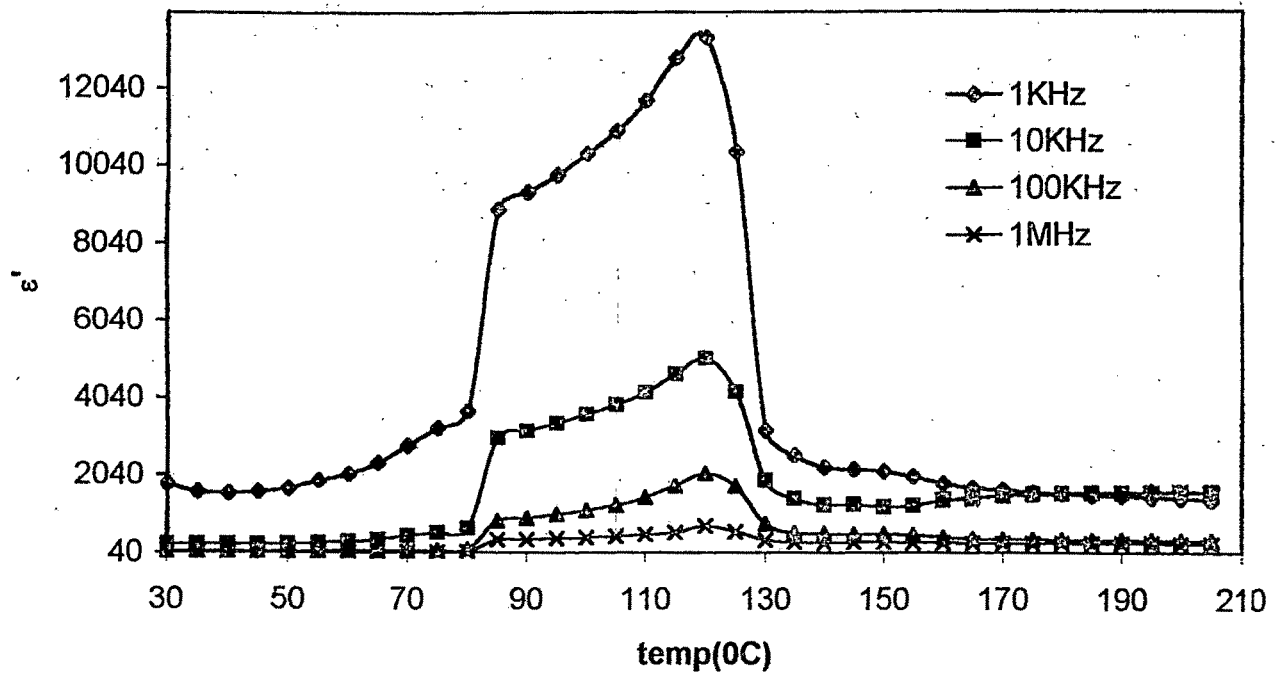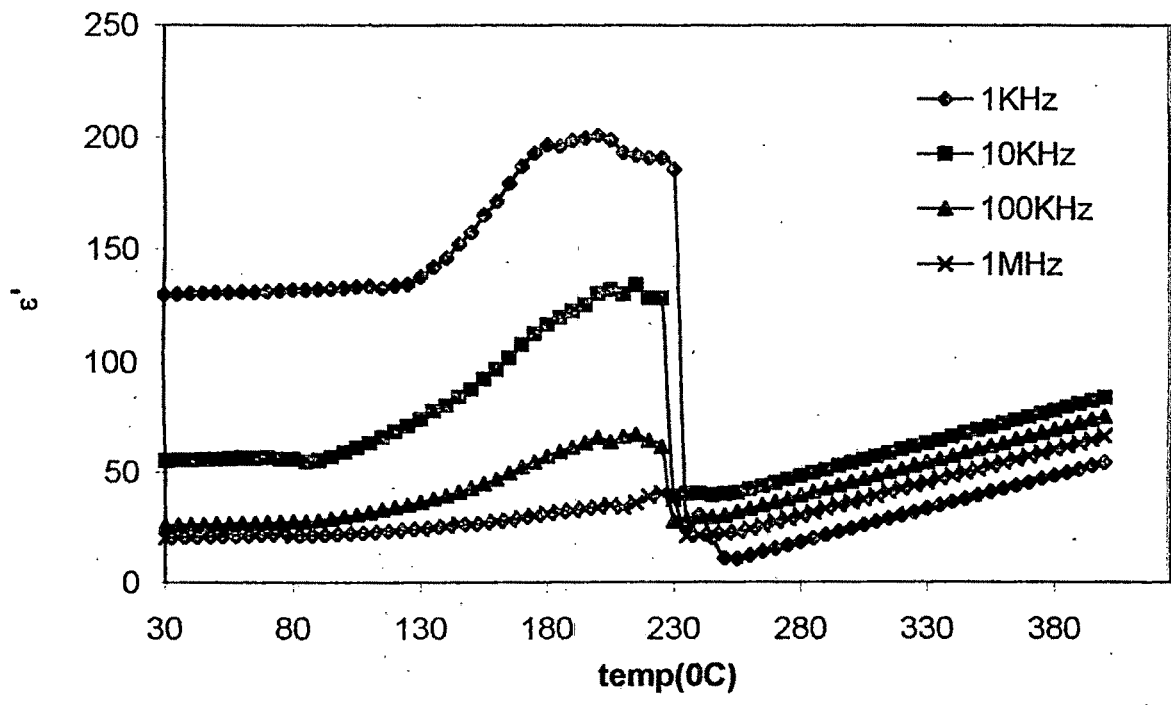again increases with increase in temperature as normally observed in any
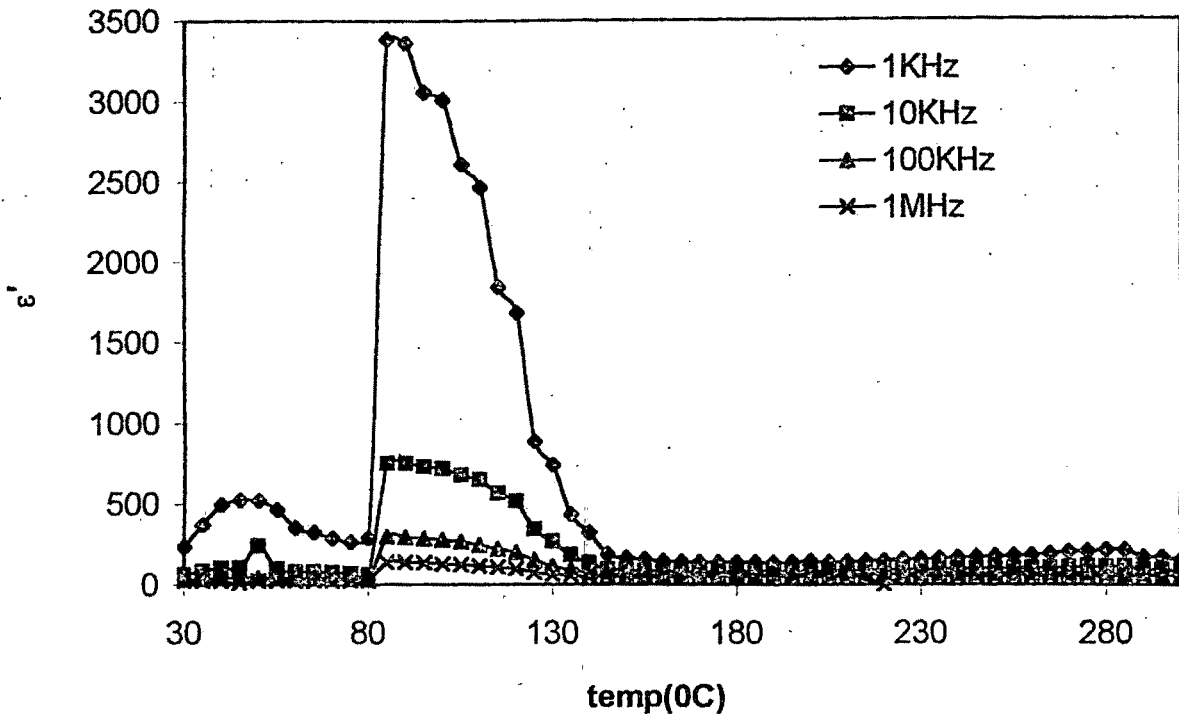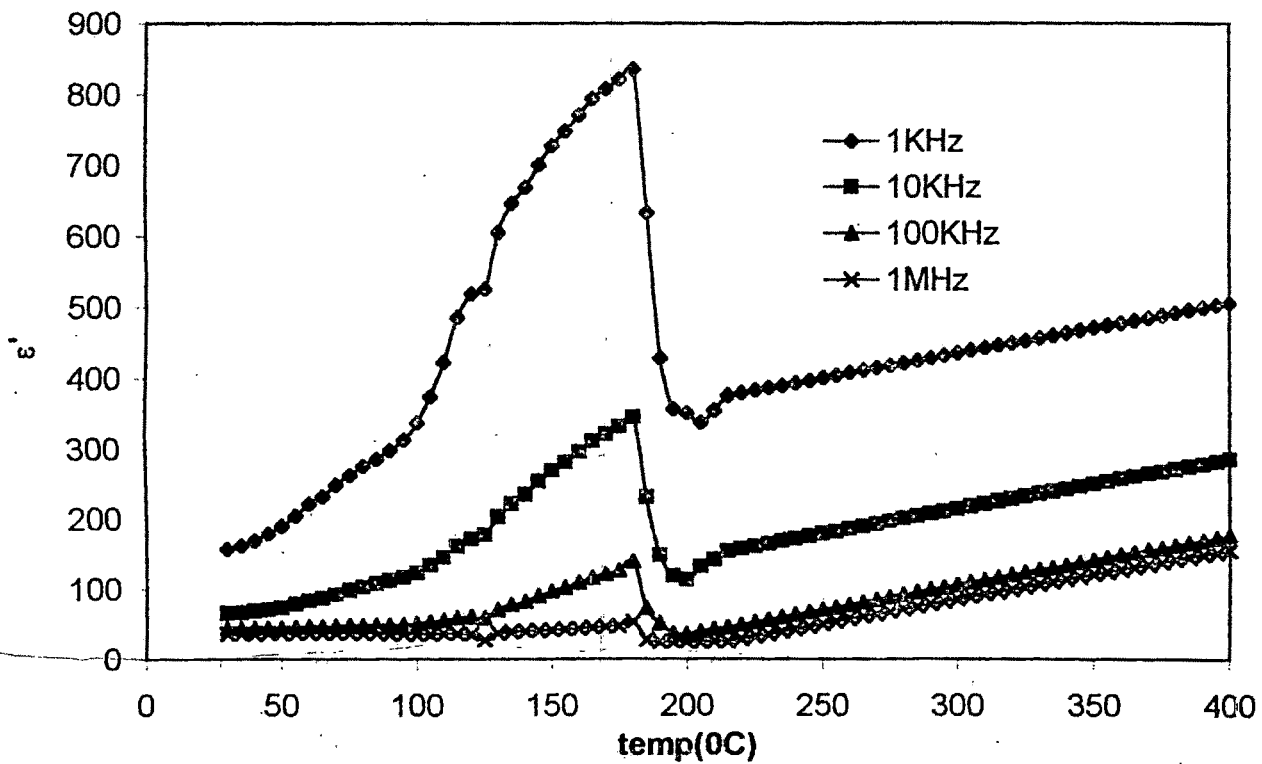
Fig.4.4
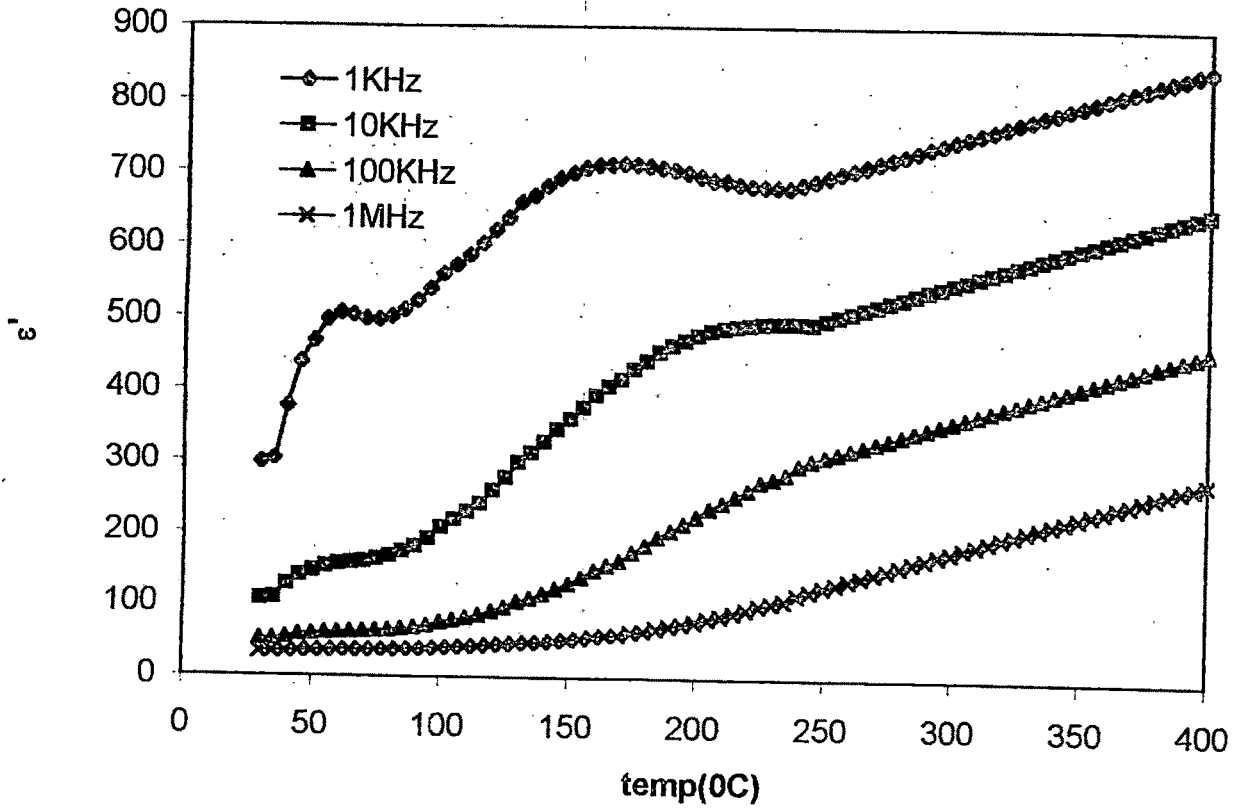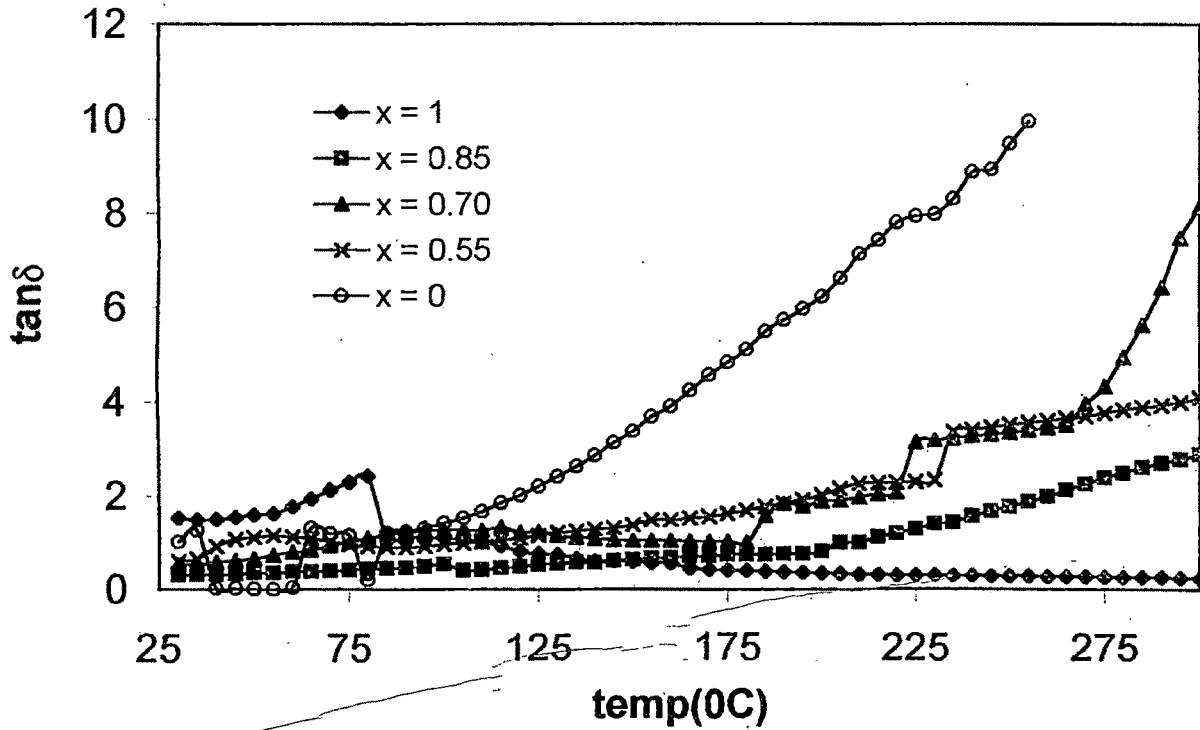

Fig.4.5

Fig.4.6

Fig.4.7

Fig.4.8

Fig.4.8A

dielectric at higher temperatures [15,16]. It was reported that on passing through the curie point a change in dielectric behaviour takes place depending on the exchange interaction between the outer and inner electrons which change at transition temperature.

In case of composites of $MnFe_{1.8}Cr_{0.2}O_4$ and $BaTiO_3$ the ε' versus temperature variation is shown in figs. 4.6. to 4.8. For x = 0.85 composite the dielectric behaviour is similar to that observed for pure $BaTiO_3$. However the dielectric maximum and Tc are very much reduced when compared to that of pure $BaTiO_3$. The transition in the present sample is at 85^0C and is accompanied by a change in ferroelectric to paradectric state. The decrease in temperature Tc is independent of the mole ratio of constituent phases incomposites. Such a decrease in Tc is already observed and reported by earlier workers. The decrease in dielectric constant is attributed to the dopping effect of ferrite addition in this composite. It is reported that different behaviour of permivitity as a function of composition is a result of superposition of two effects; modification of the piezoelectric material with ferrite components and change in grain size of piezoelectric materials [16]. In addition to that increase in ferrite concentration results in decrease in polarization efficiency as a result of increased conductivity. The DC resistivity study carried out by us has confirmed this fact. Similarly for x = 0.70 composite and x = 0.55 composite the transitions occur at 180^0C and 170^0C as shown in fig. 4.7. and 4.8. The transitions for this composites are ascribed to ferromagnetic to

paramagnetic phase transition rather than to ferroelectric to paraelectric phase transition. The reasons are :

1) The ferromagnetic to paramagnetic phase transition at Tc = 210°C is already observed and mentioned for $MnFe_{1.8}Cr_{2.0}O_4$ ferrite.

2) The Tc = 180°C and 190°C as observed for x = 0.70 and 0.55 composite are close to ferrimagnetic transition temperature rather than ferroelectric phase transition temperature.

3) Earlier workers who have investigated $CuFe_2O_4$ BPT composites have reported that in case of composites two dielectric maxima are obtained corresponding to ferroelectric phase transition and the other diffused tetragonal to cubic phase transition common to $CuFe_2O_4$. Higher content of ferrites in composites resulted in only one maximum corresponding to that of ferrite phase [17].

The variation of losses with temperature at 100 kHz frequency is shown in fig. 4.8.A. The variation is similar to that observed for other ferrites [16]. The increase in tanδ with increase in temperature at all the frequencies is accounted by following the same discussion applied to increase in ε with temperature. Thus polaron hopping mechanism also holds good for this type of variation.

DC ELECTRICAL RESISTIVITY

Electrical conductivity is an intrinsic or inherent property of the polar materials. The conduction can not occur unless charge carriers are able to cross the potential well and for this purpose they need to be activated by some external agency. Activation can be affected by thermal and electrical energies. The variation of conductivity with temperature T can be expressed by the general exponential law

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

where, ΔE - Activation energy

σ_0 – constant

k – Boltzman constant

Most polar dielectric materials show only a gradual increase in conductivity with increase in temperature. However, sudden changes have been observed in certain ferroelectric materials near their curie point. The conduction mechanism in ferroelectric can be ionic and/or electronic in nature and it is the first step in understanding of electrical transport in ferroelectrics. Type of conduction strongly depends on the temperature and the purity of material.

4.3.3 EXPERIMENTAL

The experimental set up used for the measurement of D.C. electrical resistivity of the samples is shown in fig. 4.9. It consists of an electrical furnace, a digital d. c. microvoltmeter, a transistorized power supply unit [TPSU TYPE LVA 30/1] to provide the d. c. electric filed and a temperature controller arrangement. Roberts has reported that the electrodes play an important role in the measurement of conductivity and thermoelectric power and suggested that ohmic contact is essential for such measurements. The conductivity cell in fig. 4.9a and a circuit diagram for the measurement of resistivity is shown in fig. 4.9b.

The pellet is mounted in a special sample holder by sandwiching it tightly between the two brass rods of holder. Silver foils are introduced in it over the two surfaces of pellet, before sandwiching it, to ensure good ohmic contact. A calibrated chromel alumel thermocouple is used to measure the temperature of the furnace. Resistivity measurements are carried out by measuring the current at constant voltage of about 0.5 to 10 volts from room temperature to 200^0C.

4.3.4 RESULTS AND DISCUSSION

The variation $\log\rho$ Vs 1000/T (temperature is given in Kelvin scale) for all the samples is shown in Fig.4.10. In pure $BaTiO_3$ i.e. x = 1, the plot is similar to that obtained by earlier workers [18]. The resistivity for $BaTiO_3$
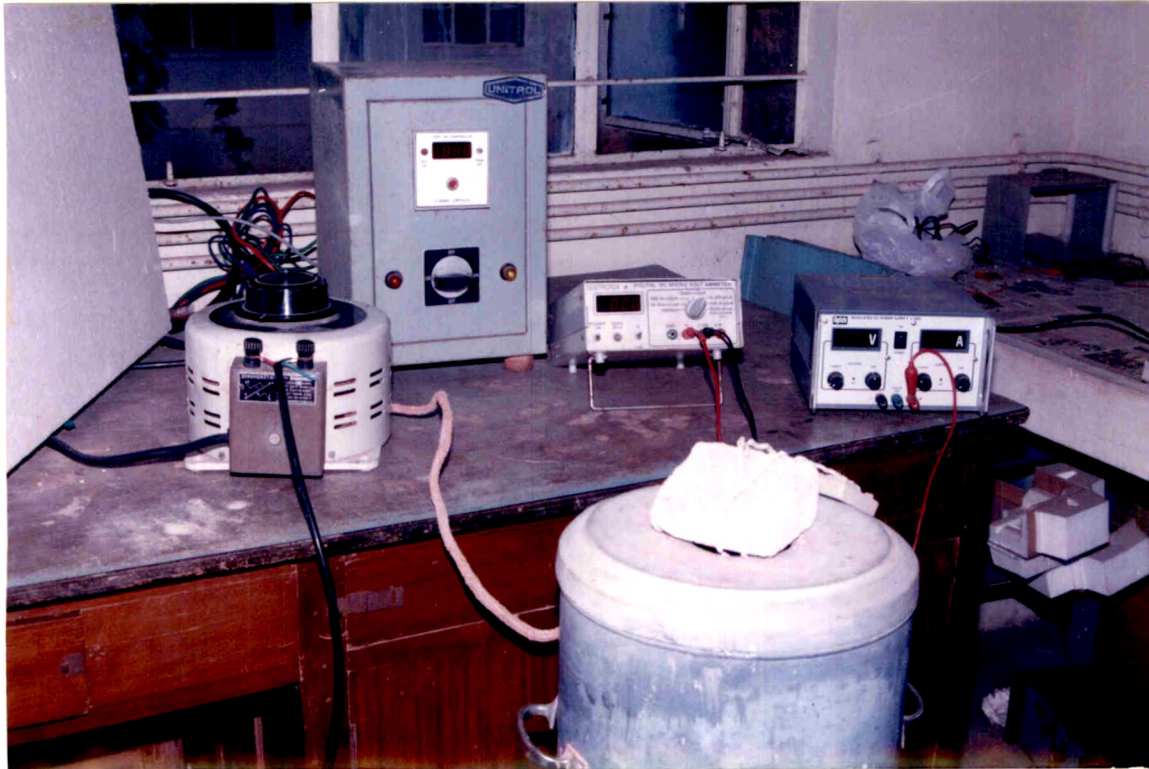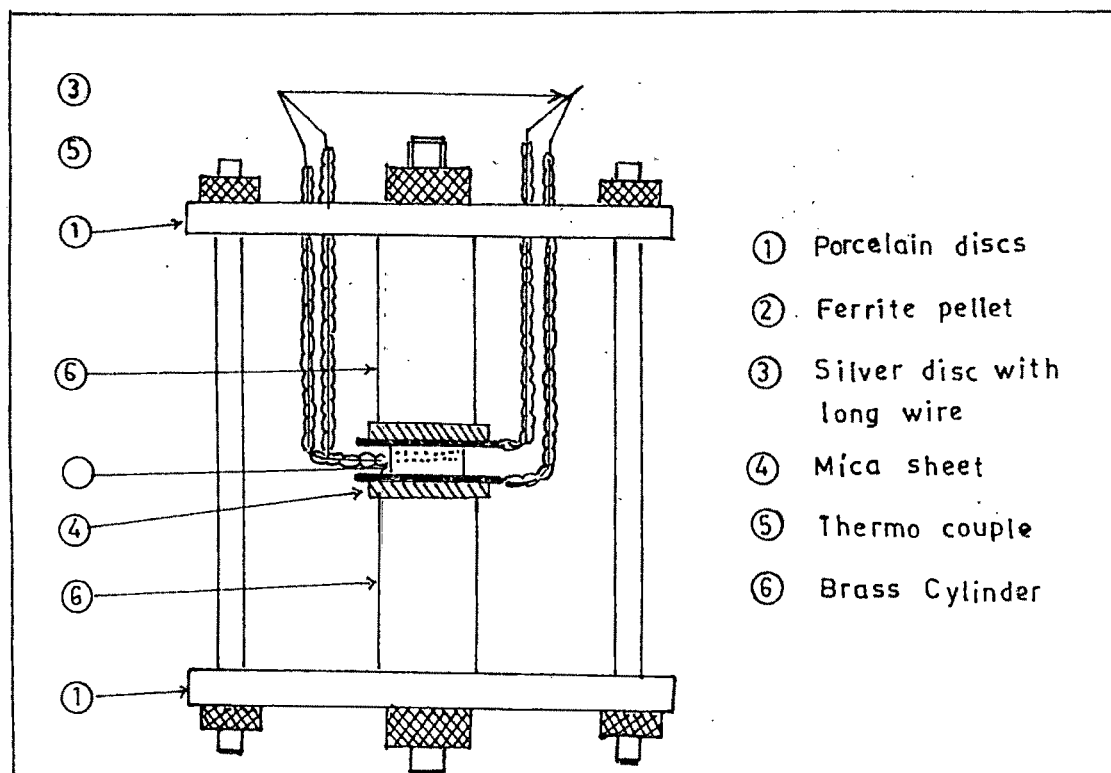
Fig. 4.9   Measurement of DC electrical resistivity

③
⑤
①

⑥

○

④

⑥

①

① Porcelain discs

② Ferrite pellet

③ Silver disc with
long wire

④ Mica sheet

⑤ Thermo couple

⑥ Brass Cylinder

FIG. 4·9(a) _THE CONDUCTIVITY CELL .

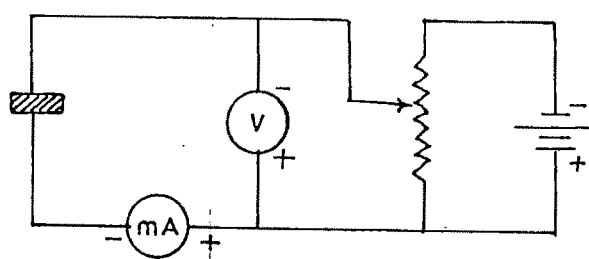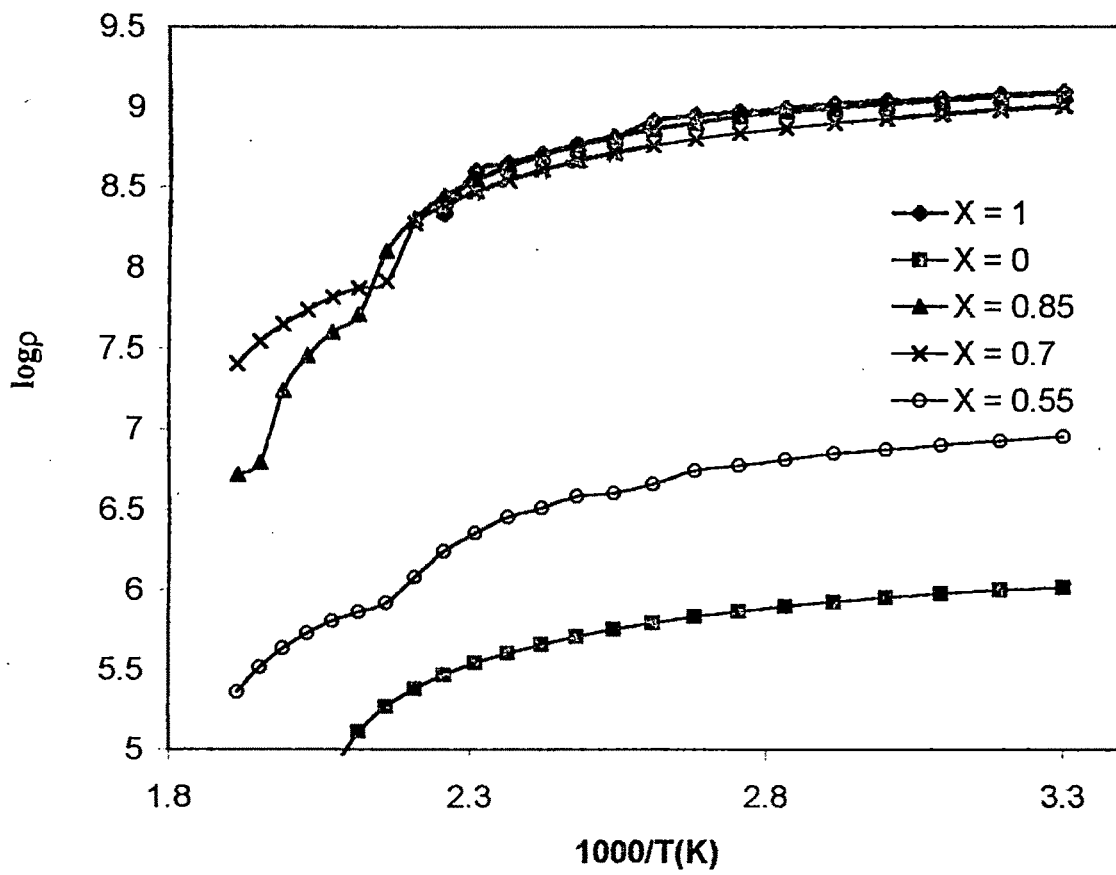FIG. 4·9(b)-CIRCUIT DIAGRAM FOR ELECTRICAL
RESISTIVITY .

Fig.4.10

is maximum and minimum for pure $MnFe_{1.8}Cr_{0.2}O_4$ for the ferrite the is similar to that studied by earlier workers [19] i.e. $x = 1$ composition. Compositions for the composited i.e. $x = 0.85$, 0.70 and 0.55 the resistivity decreases with increase in $MnFe_{1.8}Cr_{0.2}O_4$ content. It can be evinced from the fig. 4.10 that there is a very large drop in resistivity for $x = 0.59$ composite in which mole ratio of constituent is vary equal. It has been reported earlier that the resistivity of composites is sum or parallel of the resistances of their constituent phases [20]. In the present case it seems that parallel mode is valid. In $MnFe_{1.8}Cr_{0.2}O_4$ ferrite, the conductivity is explained on the basis of polaron hopping model [21]. Moreover, in the ferroelectrics the polaron hopping mechanism is valid [22]. Hence in composites containing both the ferrite and holds good. The hopping in pure $MnFe_{1.8}Cr_{0.2}O_4$ and its phase in composite is between Fe^{+2} and Fe^{+3} ions or $3Mn^{=2}$ $2Mn^{=3}$ ion at octahedral site. It is also clear from the figure that there is a change in the slope at log p Vs log T plots beyond ferroelectric and ferrite phase transition temperature. The Tc obtained from there plots matches well with these obtained from dielectric studies. The change in slope the Tc is explained on change in magnetic ordering case of ferrites on that is the ferrite transforms from ferromagnetic to paramagnetic state [23]. n case of ferroelectric the change in slope is also passed on the same reason that thee is a phase change from ferroelectric to paralectric state [24]. Hence the same cause holds good in case of composites. The trend obtained in present composites is similar to

the obtained for $CaFe_{1.8}Cr_{0.2}O_4$ – PBZT composites. $Ni(COMn)$ Fe_2O_4 – $BaTiO_3$ and $Nife_2O_4$ – PZT composites[26].

4.4   THERMOELECTRIC POWER

Seebeck coefficient for two dissimilar metals, their junction being maintained at different temperatures can be determined by ratio $\Delta V/\Delta T$ where ΔV represents emf developed across the junction and ΔT is the temperature difference. The seebeck effect may be thought of as a diffusion process. The electrons or holes from hot end have higher kinetic energy as compared to those from the cold and hence the electric current is produced.

According to quantum theory for semi-conductor with both types of carriers α is given by

$$\alpha = (\alpha_n \sigma_n + \alpha_p \sigma_p)/(\sigma_n + \sigma_p)$$

where, $\sigma_n = ne\mu_n$

$$\sigma_p = Pe\mu_{p+}$$

$$\alpha_n = (k/e) (A_n - E_f/kT)$$

$$\alpha_p = (k/e) [A_p + (E_g + E_f)/kT]$$

where n and p are the electron and hole densities. E_f is the fermi energy and E_g is the band gap energy μ_n and μ_p are the electron and hole mobilities.

For a partially filled band, the seeback coefficient varies linearly with the temperature.

$\alpha_n = \pi^2 k^2/3eT$ [d log σ (E)/dT] at E = E_f for a specimen in which the fermi level is at E_f.

The term d(log σ)/dT can be approximated according to whether the fermi level is temperature dependent or not. The temperature dependence of the thermoelectric power for ferrite materials having one type of charge carriers can be expressed as

$$\alpha = (k/e)[\log \{No/n-1\} + e/kT] \, a$$

where k and e are Boltzman constant and electronic charge respectively. 'No' is the concentration of trivalent ions on the octahedral sites, n is the concentration of Fe^{2+} ions, the term 'a' is a part of activation energy transported by the electrons and T is the absolute temperature.

4.4.1 THERMOELECTRIC POWER MEASURMENET

The experimental set up for measurement of thermoelectric power is as shown in fig. 4.11. It consists of an electrical furnace, a temperature controller, a digital multimeter. For the measurement of the thermoelectric power the samples in the form of pellet are used. The pellets are coated with a thin layer of silver paste for ensuring good ohmic contact. A pellet is sandwiched between the silver plates and over the silver plates thick mica sheets are placed.

Fig.4.11
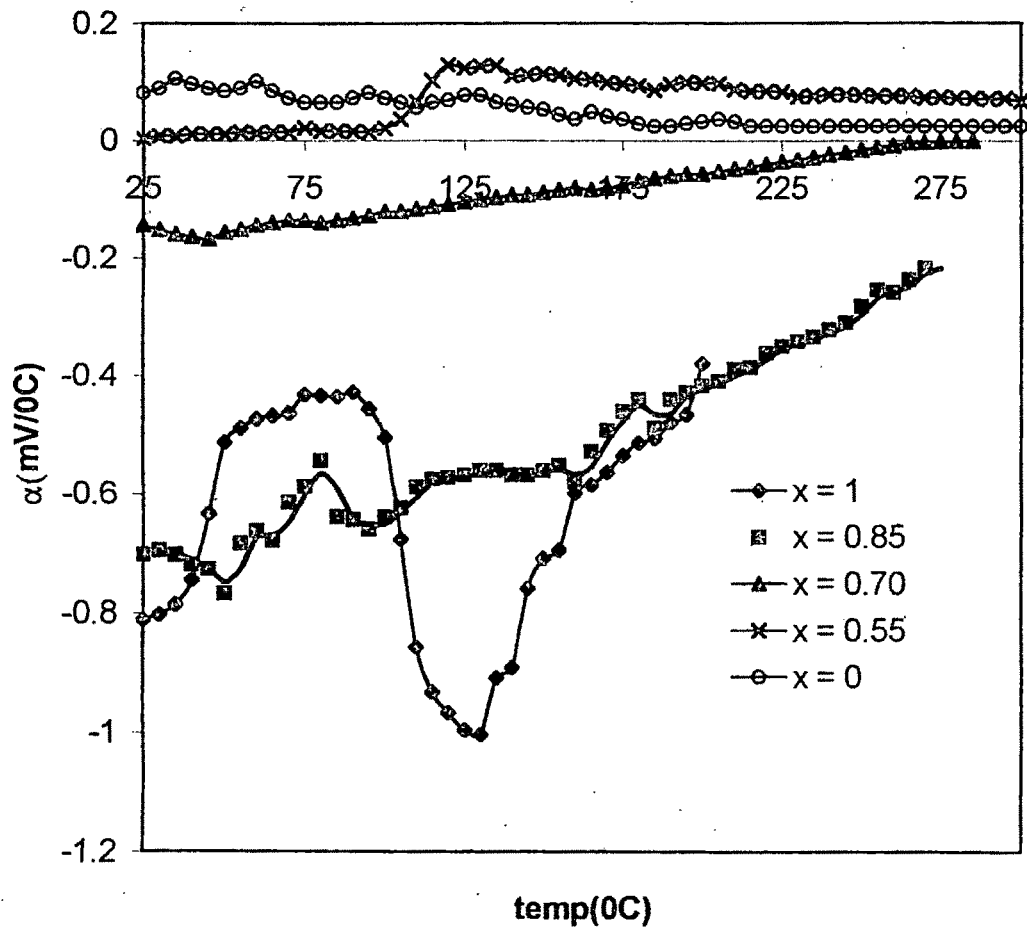
A thermal gradient across the sample is produced with the help of a small heater attached to one of the electrodes of the sample holder. Thermal gradient T is measured by using chromel alumel thermocouple. The thermo-emf E developed across the pellet is measured on a digital d. c. voltmeter. Sufficient time is allowed for applying the thermal gradient to obtain stability before recording. The samples are heated by establishing a constant thermal gradient and the developed thermo emf is measured at different temperatures of the sample. The thermoelectric power is determined using the relation

$$\alpha = \Delta E / \Delta T$$

The sign convention used for the thermoelectrical power measurement α is derived from

$$\alpha = (E_H - E_c)/(T_H - T_c)$$

where E_H and T_H are the electrical potential and temperature at hot end. Ec and Tc are electrical potential and temperature at cooled end. If in measuring E, the voltmeter gives a +ve terminal to the hot end of the sample, n type of charge carriers are present. The situation reverses when the charge carriers are p type. (Voltmeter show –ve deflection on connecting its +ve terminal to the hot end if charge carriers are holes). Thus hot end is +ve for n type carriers and –ve for type carriers.
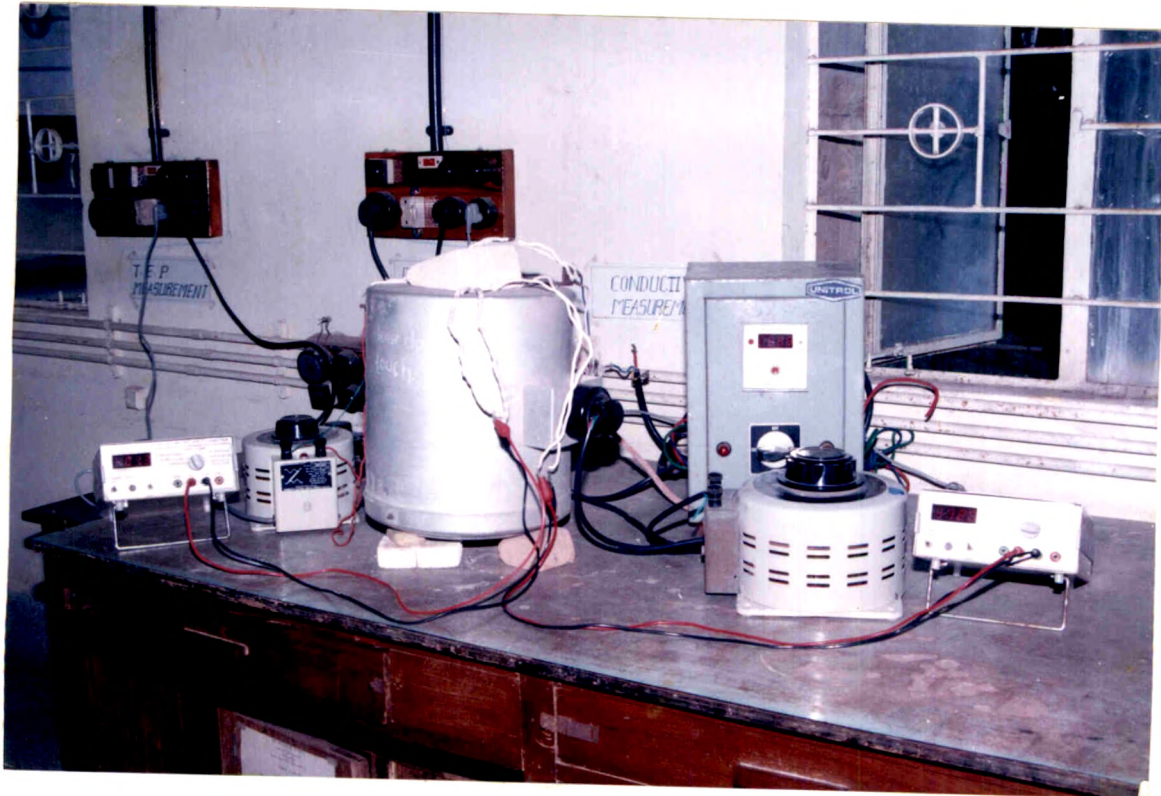
Fig. 4.11   Measurement of thermoelectric power

4.4.2 RESULTS AND DISCUSSION

The variation of the power with temperature for x =1, 0.85, 0.70, 0.55 and 0 is shown in fig. 4.12. From the figure. it is clear that, the majority charge carriers are electrons in x = 1, 0.85, 0.70 samples whereas majority charge carriers are holes in case of x = 0.55 and 0 samples. It has been pointed out earlier that oxidoreduction process appears during sintering in air atmosphere.

$$3Fe^{2+} \rightarrow 2\ Fe^{3+} + (0)\ \text{total reaction (100 to 250}^0\text{C)}$$

$$(0) + 3Mn^{4+} \rightarrow 4\ Mn^{3+}\ \text{total reaction (400 to 450}^0\text{C)}$$

$$4\ Mn^{3+} \rightarrow 3Mn^{4+} + (0)\ \text{total reaction (250 to 300}^0\text{C)}$$

Here (0) represents a cation vacancy [27]. The cation vacancies act as p type carriers[28]. Hence the observed p type conduction in pure $MnFe_{1.8}Cr_{0.2}O_4$ and composite containing 55% $MnFe_{1.8}Cr_{0.2}O_4$ depends on the above referred cation vacancies. However the n type conduction observed in x = 0.70 and 0.85 samples is accounted on the fact that hopping takes place between fe^{2+} and Fe^{3+} ions of the ferrite phase of the composite and moreover the majority charge carriers are of n type in $BaTiO_3$.

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