

CHAPTER - IV

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DIELECTRIC PROPERTIES

4.1 INTRODUCTION: -

So far, we have been largely concerned with the properties of charge carriers in metals and semiconductors. However there are, many other materials with very few electrons to take part in normal electric conductivity such materials have dielectric properties and therefore it is possible to conceive the ideal insulators which would have no free electrons. A dielectric material has interesting electrical properties because of the ability of an electric field to polarize material to create electric dipoles. A dipole is an entity in which a small distance separates equal positive and negative charges, and the electric dipole moment μ is given by

$$\mu = q dl \quad (4.1)$$

The electric dipole is a vector that is conventionally directed from negative to positive charge. The unit of electric dipole is the Debye

$$(1 \text{ Debye} = 3.3 \times 10^{-30} \text{ coulomb-metre}).$$

Though dielectrics are poor conductors of electricity, they are most interesting and useful electrical engineering materials. They found extensive applications in insulators, capacitors and their properties can predetermine the electrical performance and quality of such devices.

It is the experimental result, first discovered by Faraday that the capacitance of a condenser is increased if the space between the conductors is filled with a dielectric materials. The capacity of condenser with dielectric medium is given as

$$C = \epsilon_r C_0 \quad (4.2)$$

where C_0 is capacitance of condenser with the region between the conductors evacuated and C is capacitance of condenser when region is filled with a dielectric.

Here $\epsilon_r = C / C_0$ is found to be independent of the shape or the dimensions of the conductor and is solely a characteristics of the particular dielectric medium used. ϵ_r is called the relative permittivity or the dielectric constant of the medium. In the S.I. system of units the permittivity of the medium is defined as

$$\epsilon = \epsilon_0 \epsilon_r \quad (4.3)$$

where $\epsilon_0 = 8.8 \times 10^{-12}$ F/m is a permittivity of free space (or vacuum).

Here ϵ_r is relative permittivity of the material. The term dielectric constant is sometimes used for both ϵ and ϵ_r . In order to avoid the confusion of the terms, permittivity and relative permittivity are to be preferred. The dielectric constant of a material is a macroscopic quantity that measures how effective an electric field is in polarizing the material.

Insulators or dielectrics are substances, which do not possess free electric charges under ordinary circumstances. This does not mean that they can not modify the electric field into which they are introduced. In fact the most important property of dielectrics is their ability to become polarized under the action of an external electric field (1,9). An external electric field influences the atoms and molecules of dielectrics and hence the positive charged particles are pushed in the direction of the electric field, while the negative charged

particles are pushed in the opposite direction from their equilibrium position. Hence dipoles are developed and they produce a field of their own. The process of producing electric dipoles out of neutral atoms and molecules is referred to as polarization. In case of polycrystalline materials, dielectric constant is frequency dependent. Dielectric constant of polycrystalline materials exhibits dispersion with respect to frequency. Koop's has explained this dispersion by considering the oxides, compact as multi-layer capacitor in which their grains and grain-boundaries have different properties. A strong correlation between conduction mechanism and dielectric behavior for mixed oxides has reported by many workers (2,3,4). It is observed that dielectric constant decreases with increase of frequency and remains constant at higher frequencies. At very high frequencies dielectric loss occur due to the relaxation processes in the electronic polarization with the crystal lattice.

In oxides three principles of polarization can be distinguished within a frequency range from 0 to ultra-violet frequency region. In optical frequency region the polarization due to the movement of cations and anions. Below the microwave frequency, the polarization arises due to microstructure of polycrystalline material and also from the migration of free charge carriers.

4.2 DIPOLE MOMENT AND POLARIZATION: -

Dielectrics may be broadly divided into non-polar and polar materials. In non-polar material the molecules, are usually diatomic which are composed of two atoms of the same type may be represented as positive nuclei of charge q surrounded by symmetrically distributed negative electron cloud of charge $-q$. In the absence of an applied field the center of gravity of the positive and

negative charge distributions coincide. When molecules are placed in an external electrical field, the positive and negative charges experiences electric forces tending to move them apart in the direction of the external field. The distance moved is very small (10^{-10} m). Since the displacement is limited by restoring force that increases with increasing displacement, the center of positive and negative charges no longer coincide. Therefore they are polarized. Each molecule forms a dipole whose moment is defined as

$$\mu = q \cdot dl$$

where dl distance between two centers of charge and is a vector pointing from the negative to positive charge. Dipoles so formed are known as induced dipoles since when the field is removed, the charges resume their normal distribution and the dipoles disappear.

In considering dielectric material from the microscopic point of view (5), we restrict our attention to average values over volume which are sufficiently small in comparison with the dimensions of the material specimen, but large enough to contain a sufficient no of molecules for the purpose of averaging. Thus the sum of the dipole moments of volume Δv is

$$\sum_{i=1}^{N\Delta v} \mu_i = N\Delta v \mu = P \cdot \Delta v \quad (4.4)$$

where μ is average dipole moment of each molecule, N be the no of molecules per unit volume and P is the dipole moment per unit volume which is called the electrical polarization.

In polar dielectrics the molecules, which are normally composed of two or more different atoms have dipole moments even in the absence of an electric

field, that is the centers of their positive and negative charges do not coincide. Normally these molecular dipoles are randomly oriented through out the material owing to thermal agitation, so that average moment over any macroscopic volume element is zero. In the presence of an externally applied field, the molecules tend to orient themselves in the direction of the field in such a manner that the elementary volume has a net dipole moment given by

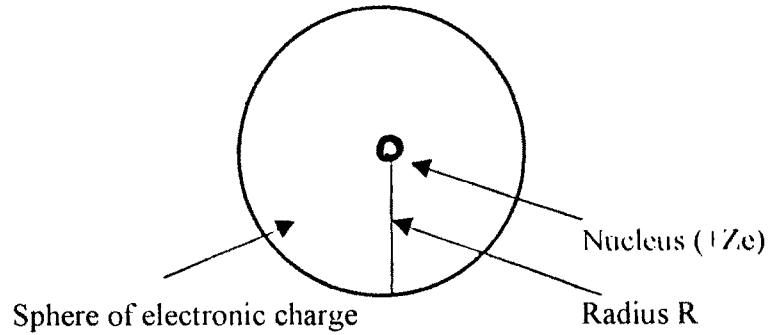
$$\sum_{i=1}^{N\Delta v} \mu_i = N\Delta v \mu = P \cdot \Delta v \quad (4.5)$$

In some polar materials a spontaneous dielectric polarization can exist even in the absence of an applied electric field. Such materials are known as ferroelectrics.

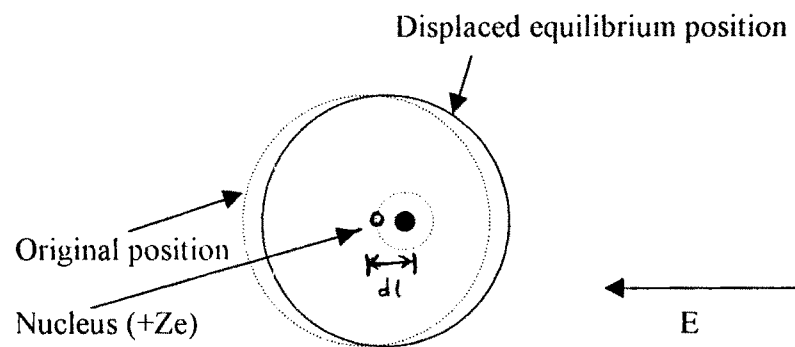
4.3 THE MICROSCOPIC CONCEPT OF POLARIZATION: -

Dielectric polarization is nothing but the displacement of charged particles under the action of the dielectric field to which they are subjected. Devices based on this manifestation are numerous. They range from condenser and switchgear equipment in power and distribution installations to rectifiers, resonators, amplifiers and transducers converters of electrical energy to other form of energy in communication technology. They include memory devices used for storage of information in modern computers.

The above said displacement of electric charge results in the formation of electric dipole moment in atoms, ions or molecules of the material. The dielectric polarization may be classified under four basic types as electronic polarization, ionic polarization, dipole polarization and migrational polarization.



(a) An atom without any field



(b) Electronic polarization

Fig.4.1 Model of an atom showing electronic polarization

4.3.1 ELECTRONIC POLARIZATION: -

Electronic polarization represents the displacement of electron orbits about the nuclei in an electric field. As seen from following fig 4.1, the electric field shifts the orbit to a new position (dashed circle is new position). This polarization arises in the atoms of any substance (including dielectrics), regardless of whether or not other type of polarization affects the substance. Electronic polarization sets in over a very short period of time is about 10^{-14} to 10^{-15} second, which is comparable to the light oscillation period. That is why electronic polarization shows up in a very wide frequency range, up to the optical band (1). The larger the size of an atom, the greater the effect of electronic polarization since the band between the outer shell electronic and the nucleus gets weaker, the shell displaces for a longer distance l and moreover the nucleus has a stronger charge q .

4.3.2 IONIC POLARIZATION: -

When atoms form molecules, electronic polarization is still possible but there may be additional polarization due to a relative displacement of the atomic components of the molecule in the presence of an electric field. Ionic polarization arises from the displacement of ions of unlike charges relative to one another in substance displaying ionic bonding. The ionic polarization takes a short time to set in, about 10^{-13} to 10^{-14} second, which is just a little larger than the set up time of electronic polarization. Ionic polarizability is higher in substances where the ionic bond strength is weak and ions carry large charges. Examples of such ions are Ti^{4+} , Pb^{2+} and O^{2-} .

4.3. 3 DIPOLE POLARIZATION: -

It is the characteristics of polar dielectrics. It arises due to the orientation of dipole molecules in the field direction. Strictly speaking, the field does not directly orient (rotate) polar molecules, but affects a certain order lines in the positions of these molecules, which execute permanent thermal motion in random fashion. It follows that dipole polarization is inherently associated with the thermal motion of molecules and is rather dependent on temperature. This type of polarization occurs in gases, liquids and amorphous viscous substances. In crystal the molecules are generally fixed in their positions and are incapable of orientation of temperature that lies below the melting point. Yet this polarization mechanism is observed in certain loosely packed crystalline substances such as water ice and some other crystal with hydrogen bonds, where the dipole reorientation shows up as a jump over of a proton from one position to the other. In polymers an electric field can force a proton of the molecule to turn or shift in the field direction.

In contrast to inertialess processes of electronic and ionic polarization, dipole polarization sets in for a lengthy period after field application and persists so after field removal. The dipole polarization P_d decreases during a time period t in an exponential manner.

$$P_d(t) = P_d(o) \text{ Exp}(t/\tau) \quad (4.6)$$

where τ is called relaxation time. If the period of the applied field is below τ , the dipoles have no time to line up parallel to the field as it reverses its direction and the dipole polarization doesn't affect the dielectric. Since τ generally ranges between 10^{-6} to 10^{-10} second, dipole polarization makes itself felt with in a

frequency band of 10^{16} to 10^{10} Hz. The time constant grows rapidly as temperature decreases.

4.3.4 MIGRATIONAL POLARIZATION: -

This type of polarization exists in certain dielectrics and insulation systems, particularly in heterogeneous materials containing semiconducting impurities, where the charges that migrate within impurity regions store up at the interface. The process during which the migration of polarization sets in or decay can last seconds, minutes and even hours. Therefore migrational polarization commonly occurs at very low frequencies.

4.4 PROPERTIES OF DIELECTRICS IN ALTERNATING FIELDS: -

The behavior of dielectrics in alternating electric fields reveals that dielectric constant under these conditions is a complex quantity. The imaginary part of this complex dielectric constant determines the dielectric losses of the material.

In the macroscopic theory of isotropic dielectrics under the static field, the electric flux density D is proportional to the electric field intensity E , so that $D = \epsilon E$, where ϵ is a constant defined as the electric permittivity and is a property of dielectric.

When a dielectric material is subjected to an alternating field, the orientation of the dipoles and hence the polarization will tend to reverse every time the polarity of the field changes. As long as frequency remains low (10^6 Hz), the polarization follows the alternations of the field without any significance lag and the permittivity is independent of the frequency, even if the frequency is increased.

The dipole will no longer be able to rotate sufficiently rapidly so that their oscillations will begin to lag behind those of the field. As the frequency is further raised the permanent dipoles, if present in the medium, will be completely unable to follow the field and the contribution to the static permittivity from this molecular process, the orientation polarization ceases. (This usually occurs at radio frequency range 10^6 - 10^{10} Hz of the electromagnetic spectrum). At still higher frequencies, usually in the infrared (10^{11} - 10^{14} Hz) the relatively heavy positive and regular ions can not follow the field variations so that the contribution to the permittivity from the atomic or ionic polarization ceases and only the electronic polarization remains.

The above effect leads to fall in the permittivity of a dielectric material with increasing frequency, which is referred as anomalous dielectric dispersion. Dispersion arising during the transition from full orientation polarization of zero (or low) frequency to negligible orientation of polarization at high radio frequencies is referred to a dielectric relaxation.

4.5 KOOP'S MODEL: -

The resistivity, dielectric constant and relative permittivity all vary with frequency. Koop's (6) explained the dielectric dispersion based on a model and gave a phenomenological theory.

According to Koop's model the heterogeneous dielectric materials consisting of conducting grains separated by the regions of low conductivity grain boundaries. The grain can be represented as double layered dielectric as shown in fig 4.2 In Fig 4.2, subscript 2 refer to grains and 1 to boundary layer. Resistance R_2 and possibly R_1 may contribute to dielectric losses. This is

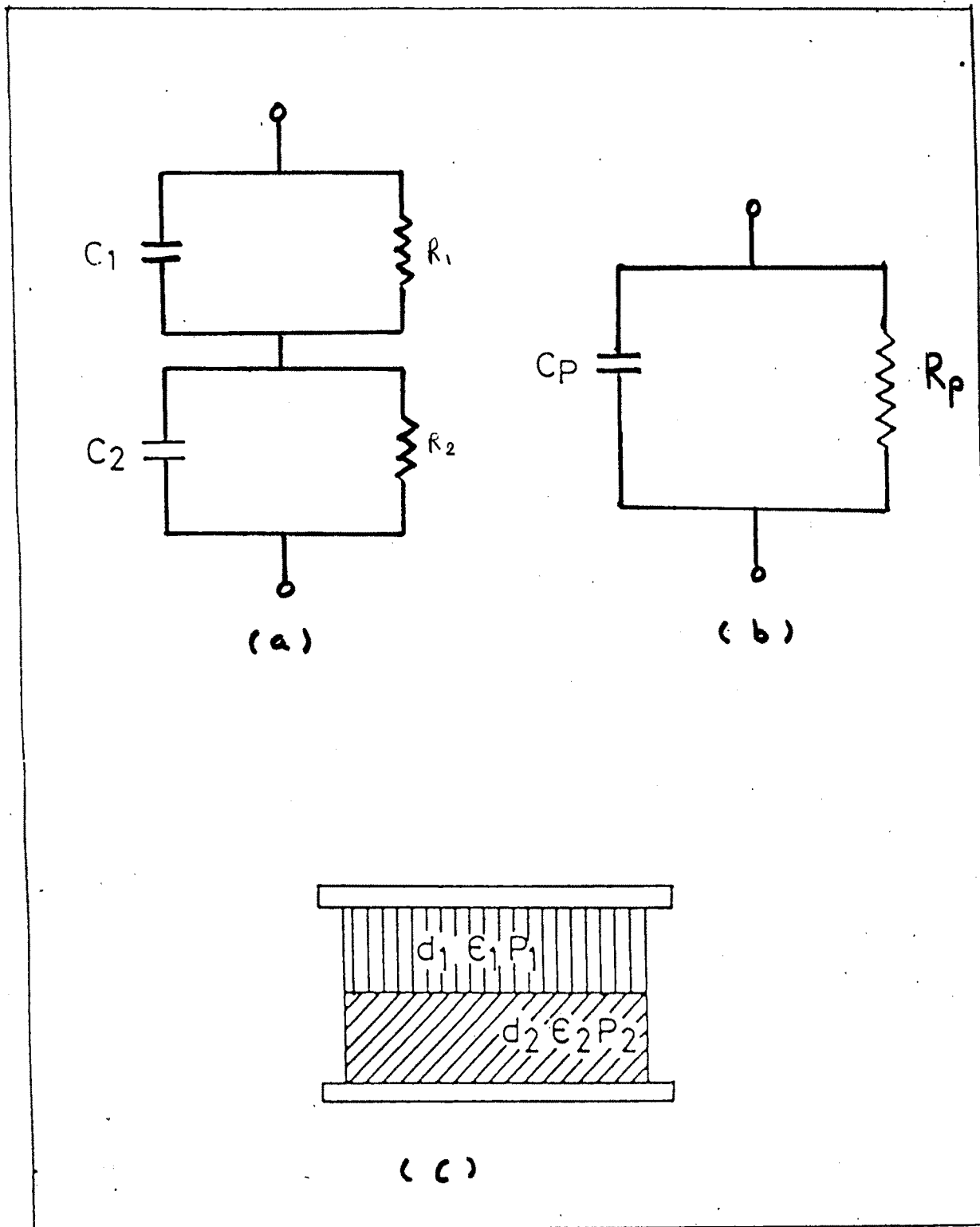


Fig. 4.2: — DOUBLE LAYER CAPACITOR

equivalent to network consisting of resistances and capacitance connected parallel as shown in fig 4.2 a and 4.2b.

Besides inhomogeneous structure, the dielectric material consists of inter-grain contacts and pores, which are highly resistive regions and this resembles the structure as described by Maxwell and Wagner.

As shown in network of fig 4.2a the values of C_1 , C_2 , R_1 and R_2 remain constant and do not depend on frequency. However as shown in the network of fig 4.2b, the values of C_p and R_p are not constant but depend on frequency. If specimen is assumed to be parallel plate capacitor of area A then it is possible to write the following relations.

$$C_1 = \epsilon_0 \epsilon_1 A/d_1 \qquad C_2 = \epsilon_0 \epsilon_2 A/d_2 \qquad (4.7a)$$

$$R_1 = \rho_1 A/d_1 \qquad R_2 = \rho_2 A/d_2 \qquad (4.7b)$$

where $\epsilon_0 \epsilon_1$ is permittivity and ρ is resistivity.

4.6 ENERGY LOSS IN DIELECTRICS OR DIELECTRIC LOSSES:-

When electric field acts on any matter, the later dissipates a certain quantity of electric energy that transform into heat energy. This phenomenon is commonly known as the expense or loss of power. As a rule the loss of power in specimen of material is directly proportion to square of the applied a.c. voltage to specimen.

Most of the dielectrics display a characteristic feature, under a given voltage, the dissipation of power in these dielectrics depends on the voltage and frequency. The loss of power at an a.c. voltage is markedly higher than at a d.c. voltage and rapidly grows with an increase in frequency, voltage and capacitance, and also depends on the material of dielectric. The amount of

power losses in a dielectric under the action of a.c. applied voltage is commonly known as dielectric losses. This is the general term determining the loss of power in an electrical insulation both of direct and an alternating voltage. Dielectric losses at direct voltage can easily be found from equation,

$$P = V^2/R \quad (4.8)$$

where V is applied d.c. voltage to insulating specimen of resistance R .

The tangent of dielectric loss angle of ($\delta = 90^\circ - \phi$, where ϕ is phase angle) is equal to the ratio between the active current (I_a) and reactive current (I_r).

$$\text{Tan}\delta = I_a / I_r \quad (4.9)$$

This is also called as tangent loss.

The tangent loss also can be defined as “the ratio of active power (P_a) to reactive Power (P_r)”.

$$\text{Tan}\delta = P_a / P_r \quad (4.10)$$

Hence the dielectric loss angle is an important parameter both for the material of a dielectric and an insulated portion. All other conditions being equal, the dielectric losses grow with this angle. The so-called loss tangent $\text{Tan}\delta$ usually describes this parameter. Some time the quality factor of an insulation portion is determined i.e. the value reciprocal of the loss tangent.

$$\text{Quality factor (Q)} = 1/\text{Tan}\delta \quad (4.11)$$

The values of $\text{Tan}\delta$ for the best electrical insulating material employed in high frequency and high voltage engineering practice are of the order of

thousands and even tenth of thousands of fractions. In case of materials with a lower quality used in less critical cases and may come to hundred of fractions.

4.7 DEPENDENCE OF TAN δ WITH FREQUENCY: -

The values of Tan δ as well as the other parameters of dielectric are not strictly constant and depend on various external factors i.e frequency and temperature. The nature of this graph (Tan δ Vs frequency) can be discussed as follows.

when limit ω tends to zero then tan δ becomes infinity and when limit ω tends to infinity then tan δ becomes zero.

This means that the value of tan δ is inversely proportional to frequency. The condition for the maximum of defect losses in a polar dielectric at a given temp is

$$\omega\tau = 1 \quad (4.12)$$

where ω is angular frequency and τ is relaxation time.

As ϵ depends on frequency and time, the real and imaginary parts of dielectric constant depends on frequency and time given by

$$\epsilon = [\epsilon + (\epsilon_s - \epsilon) / (1 + \epsilon^2 \tau^2)] + i[(\epsilon_s - \epsilon) / (1 + \epsilon^2 \tau^2)] \omega \tau \quad (4.13)$$

where ϵ_s and ϵ represents low and high frequency dielectric constant respectively. ω is angular frequency and τ is relaxation time.

Considering equation

$$\text{Tan}\delta = \epsilon'' / \epsilon' \quad (4.14) \text{ with equation (4.13) we have}$$

$$\text{Tan}\delta = \epsilon'' / \epsilon' = (\epsilon_s - \epsilon) \omega \tau / (\epsilon_s + \epsilon) / \omega \tau \quad (4.15)$$

The plots of $\tan\delta$, ϵ'' and ϵ' as a function of frequency explore the dielectric properties of the material.

4.8 DEPENDENCE OF TAN δ WITH TEMPERATURE: -

As a general rule, $\tan\delta$ appreciably increases when temperature rises. Hence increase in $\tan\delta$ as in the case of a decrease in ρ , the insulation will operate under more strenuous conditions at high temperature. This growth in $\tan\delta$ is brought about by an increase, both in the conduction of residuals current and condition of absorption current.

The dielectric losses caused by the dipole mechanism reach their maximum at a certain frequency and a definite temperature (T_k). In actual fact, the rise in temperature and the resulting drop in viscosity exert a double effect on the amount of losses due to the friction of the rotating dipoles. The degree of dipole orientation increases and at the same time there is reduction in the energy required to overcome the resistance of viscous medium, when, the dipole rotate through a unit angle. The increase in degree of dipole orientation increases polarizability P and reduction in energy reduces the polarizability, hence $\tan\delta$ increases due increase of degree of dipole orientation and $\tan\delta$ decreases due to reduction in energy.

4.9 EXPERIMENTAL: -

Using two-probe method in our laboratory carried out the dielectric measurements. The measurements were carried using Hewlett Packard, precision LCR meter (Model 4284A) in the range 20Hz to 1MHz at room temperature and also with temperature ranging from room temp to 1070K. The

pallets were coated with silver paste to ensure good ohmic contact. The pallets were then sandwiched between the silver foils in sample holder for measurements.

The dielectric constant ϵ' was calculated from the measured capacitance C_p using the formula.

$$\epsilon' = 11.29 C_p t / A \quad (4.16)$$

where t is thickness of pellet, C_p is capacitance in pF and A is cross section area of flat surface of pellet ($A = \pi r^2$).

Imaginary part (ϵ'') of dielectric constant was calculated using equation

$$\text{Tan}\delta = \epsilon'' / \epsilon' \quad (4.17)$$

4.10 RESULTS AND DISCUSSION: -

4.10.1 VARIATION OF ϵ' , ϵ'' AND $\text{TAN}\delta$ WITH FREQUENCY:-

Variation of dielectric constants ϵ' , ϵ'' and loss tangent ($\text{Tan}\delta$) with frequency ($\log F$) at room temperature is shown in Fig 4.3 to fig 4.5 for different compositions. From these figures it is clear that all the samples show the usual dielectric dispersion. The dielectric constant (ϵ') decreases rapidly with increase in frequency at the beginning and with further increase in frequency rate of decrease in ϵ' decreases. At high frequency (above 100 KHz) ϵ' reaches to a constant value. A comparative study of dispersion curves of these samples show that, there is large dispersion for high values of dielectric constant than that of at low. It is further noticed that at very high frequency, dielectric constant is almost independent of frequency. The real value of dielectric constant (ϵ') of present

selected series ($\text{Ce}_{2-x}\text{Nd}_x\text{Ti}_2\text{O}_7$) are found to lie between 20-40. These values are in good agreement with the previously reported value(7).

The high values of dielectric constant (ϵ') at low frequencies have been ascribed to the effect of heterogeneity of the sample like pores, surfaces and layers on grains. Some electronic polarization effect is supposed to be connected with the conduction hopping mechanism itself and it could be contribute to the low frequency dispersion of ϵ' .

At higher frequency the measured values may be regarded as insensitive to both the contributions as already discussed (4) and they are usually taken as actual intrinsic dielectric constant ϵ' corresponding to normal, ionic and electronic polarization. The dielectric constants reaches to a constant value due to fact that, beyond certain frequency of alternating field, the electron exchange does not follow the alternating field.

According to the reaction



where all species are written according to Kroger-Vink notation of defects. Electrons released in equation (4.18) make the materials semiconducting. During cooling of these samples after sintering, reoxidation takes place. Due to decrease in temperature and insufficient time available for diffusion of oxygen to the bulk of material, reoxidation is limited to the surface and grain boundaries. This makes grain boundaries insulating as compared to the grains which still remain semiconducting. This difference in conductivity of the grains and grain boundaries gives raise to barrier at their interfaces importing very high value of dielectric constant to the resulting ceramic (8).

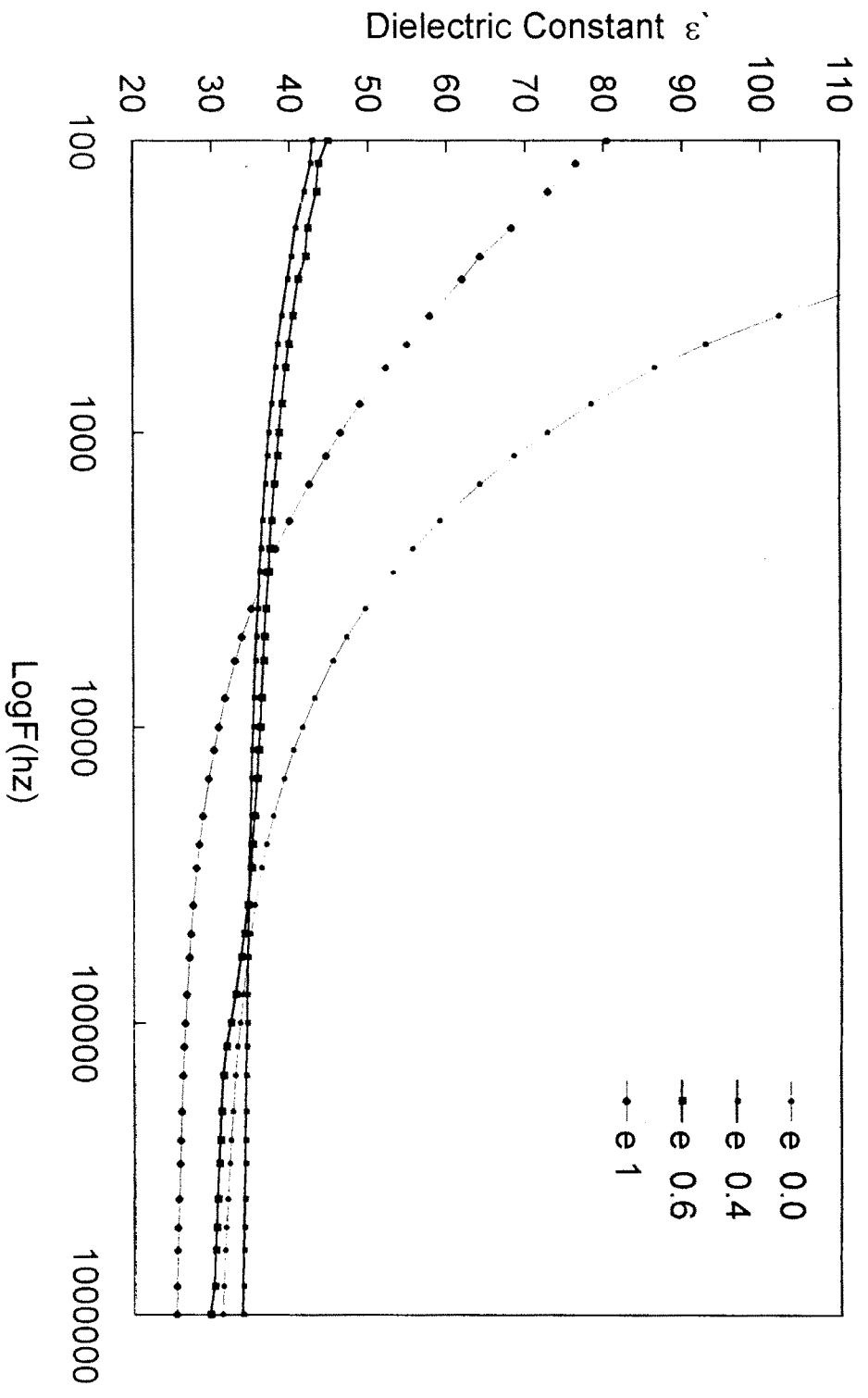


Fig4.3:- Variation of dielectric Constant with frequency for all compositions

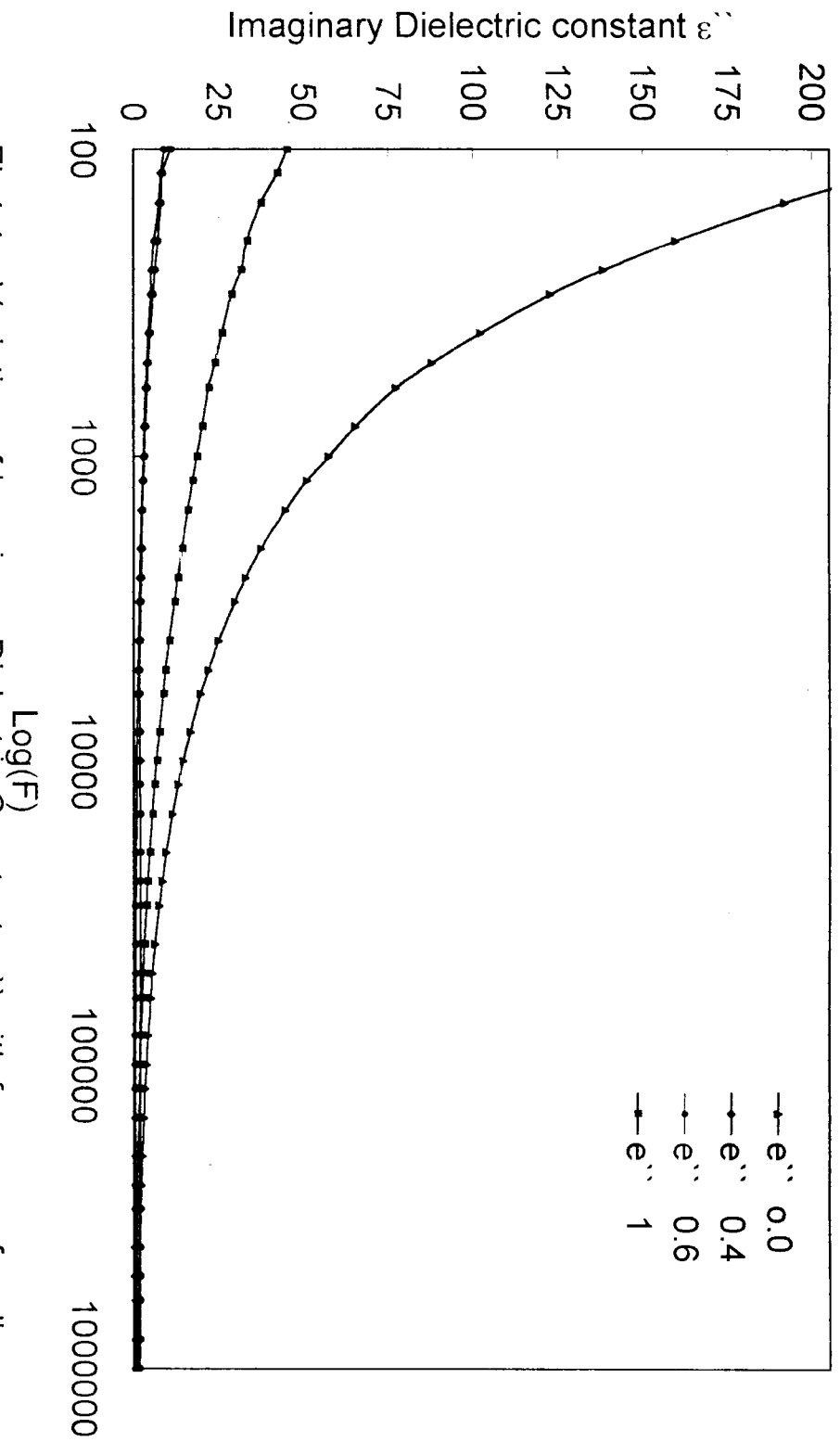


Fig4.4:- Variation of Imaginary Dielectric Constants ϵ'' with frequency for all compositions

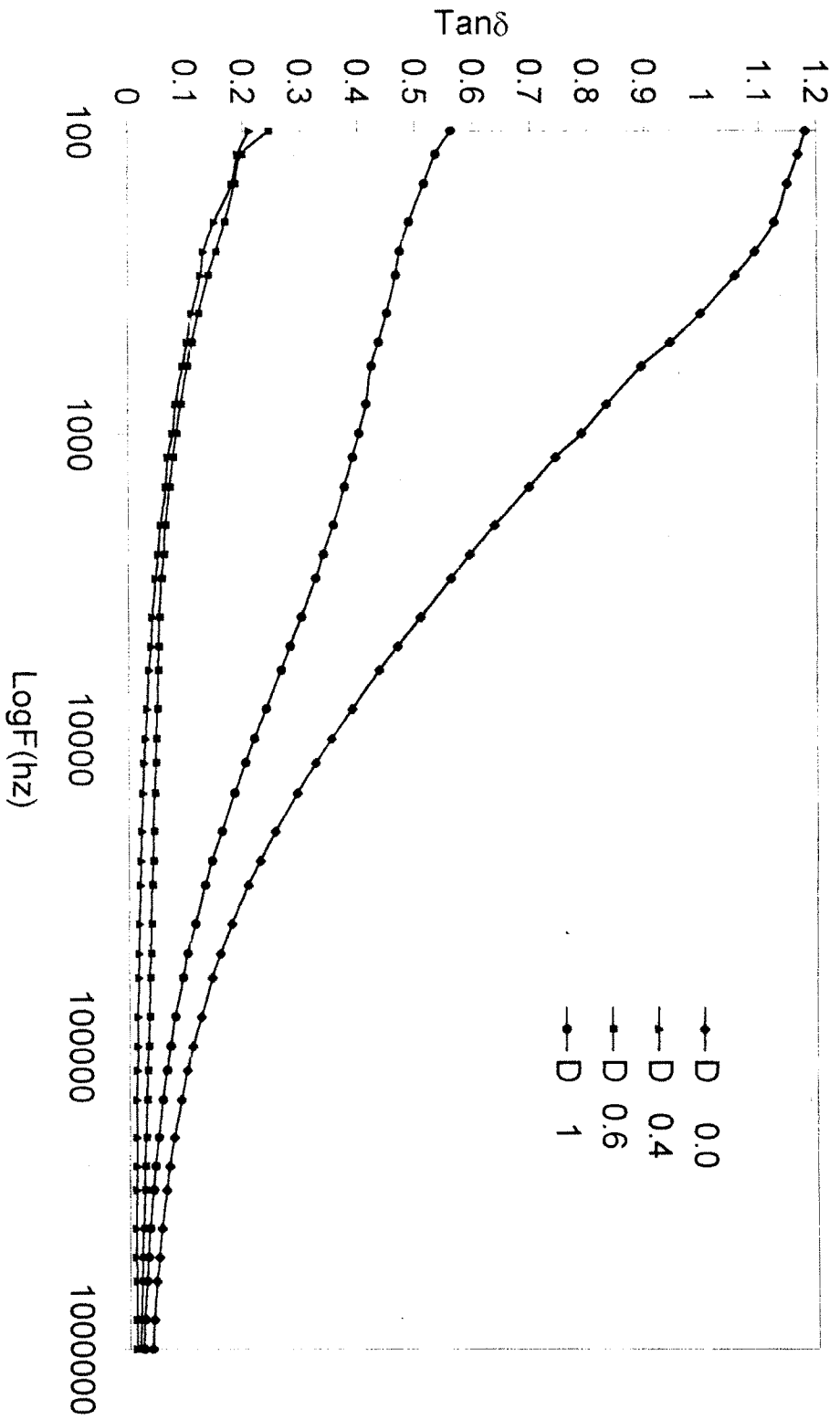


Fig4.5:-Variation of $\tan \delta$ with frequency for all samples

Fig 4.3 to 4.5 shows variation of loss tangent with frequency for all compositions. From these figures, it is seen that loss tangent is very small at high frequency. This type loss is known as leakage loss because these losses may be due to the leakage current. Leakage loss is fairly, large only in low frequency range from 100 Hz to 1KHz. Similar behavior in ϵ'' with f for all the compositions is observed.

4.10.2 VARIATION OF ϵ' AND ϵ'' AND $\tan\delta$ WITH TEMPERATURE:-

The variation of ϵ' and $\tan\delta$ with temperature at 10KHz frequency for all compositions ($x = 0.0, 0.2, 0.4$ and 0.8) is shown in fig 4.6 to 4.7. These figures shows that real dielectric constant ϵ' and $\tan\delta$ (loss tangent) remain constant (increases slowly) with increase in temperature up to 600 K. But above 600 K both increases with increase in temperature. This property is not due to ferroelectric behavior but it is due to the exponential decreases of electric resistivity (9). This increase in loss tangent ($\tan\delta$) with increasing temperature is due to increase in the conductivity. The loss tangent may be very large at high frequency and at high temperature. From these graphs it is seen that dielectric constant increases with increase in Nd content. It is also seen that loss tangent decreases with increase in Nd content. This can be explained as Nd content causes to increase in dielectric constant as it helps to increase the conduction. The replacement of Ce by Nd causes increases in dielectric constant may be due to exponential decrease in resistivity.

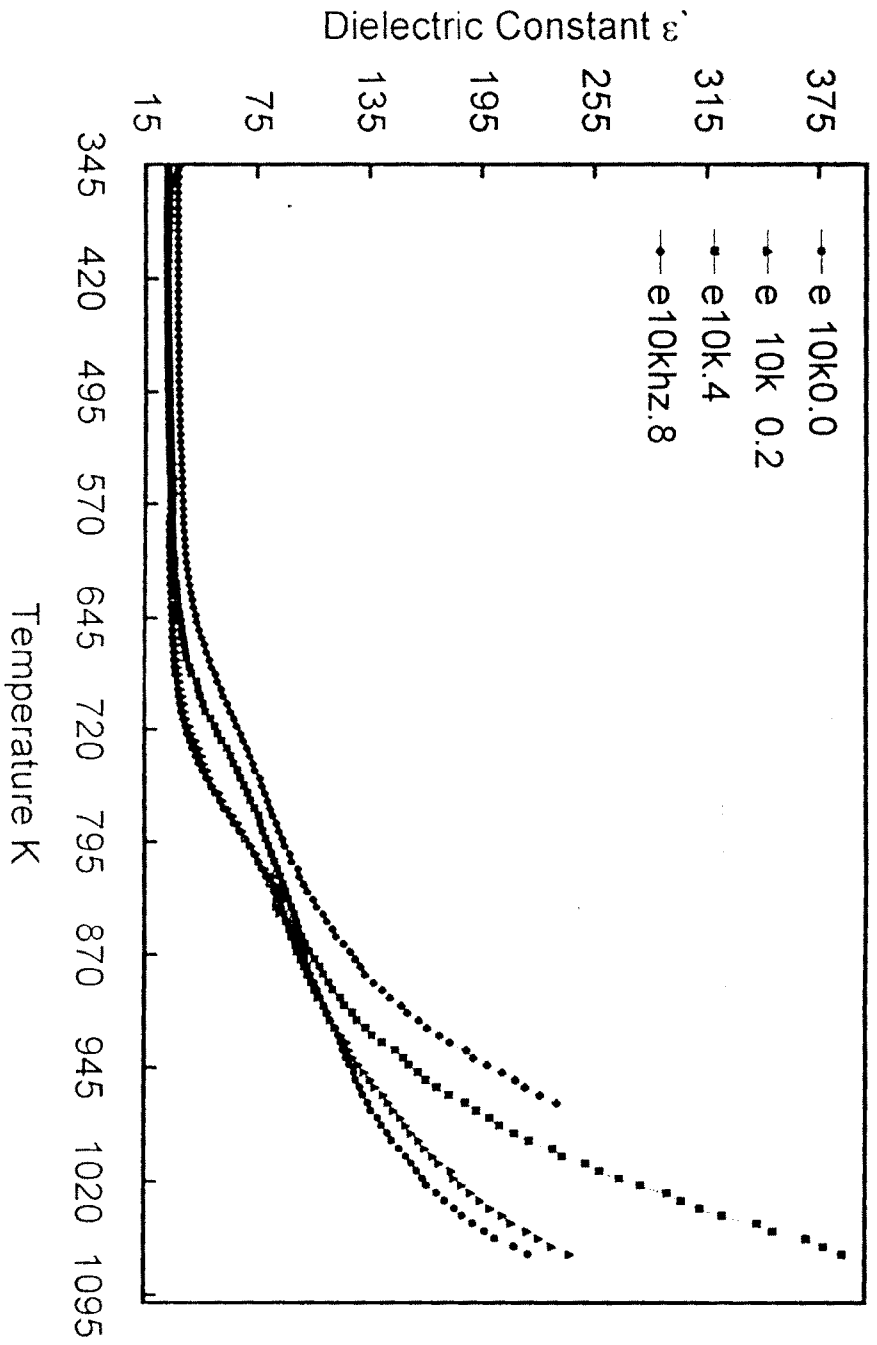


Fig4. 6:- Variation of dielectric Constant with temperature for all Compositions at 10 khz

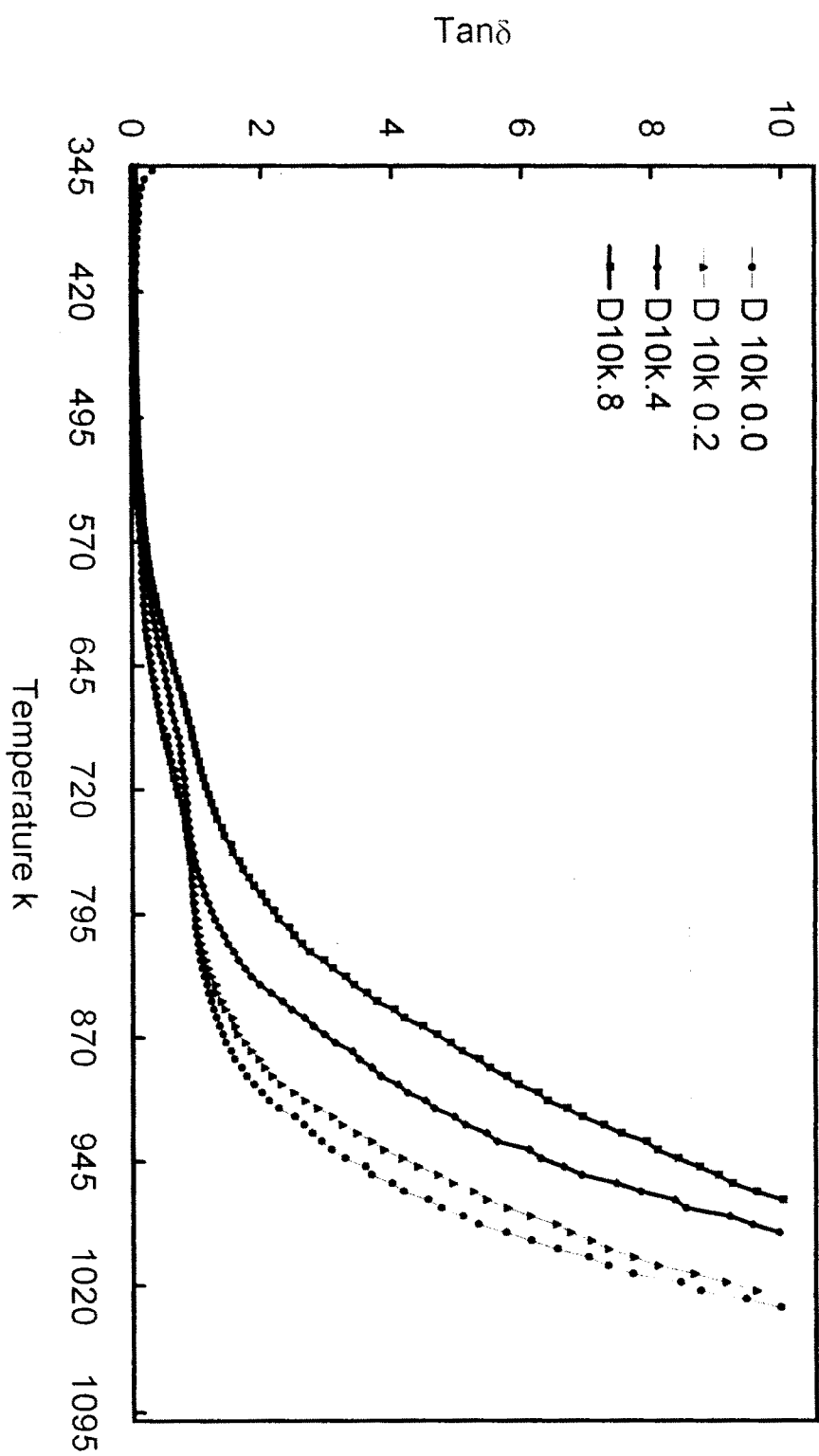


Fig4.7:- Variation of $\text{Tan } \delta$ with temperature for all Compositions at 10khz

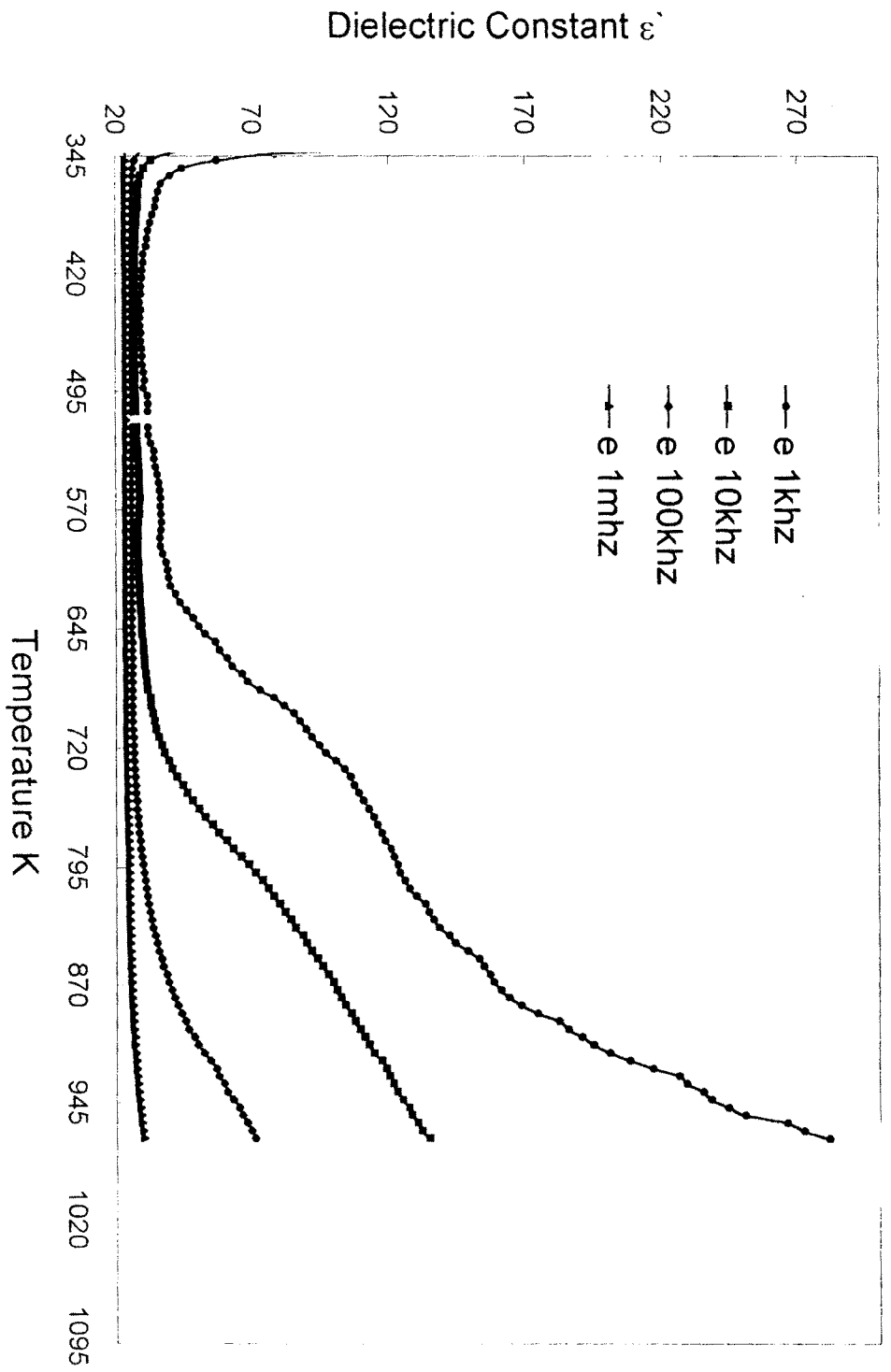


Fig 4.8:-Variation of dielectric Constant ϵ' with temperature for $x = 0.0$

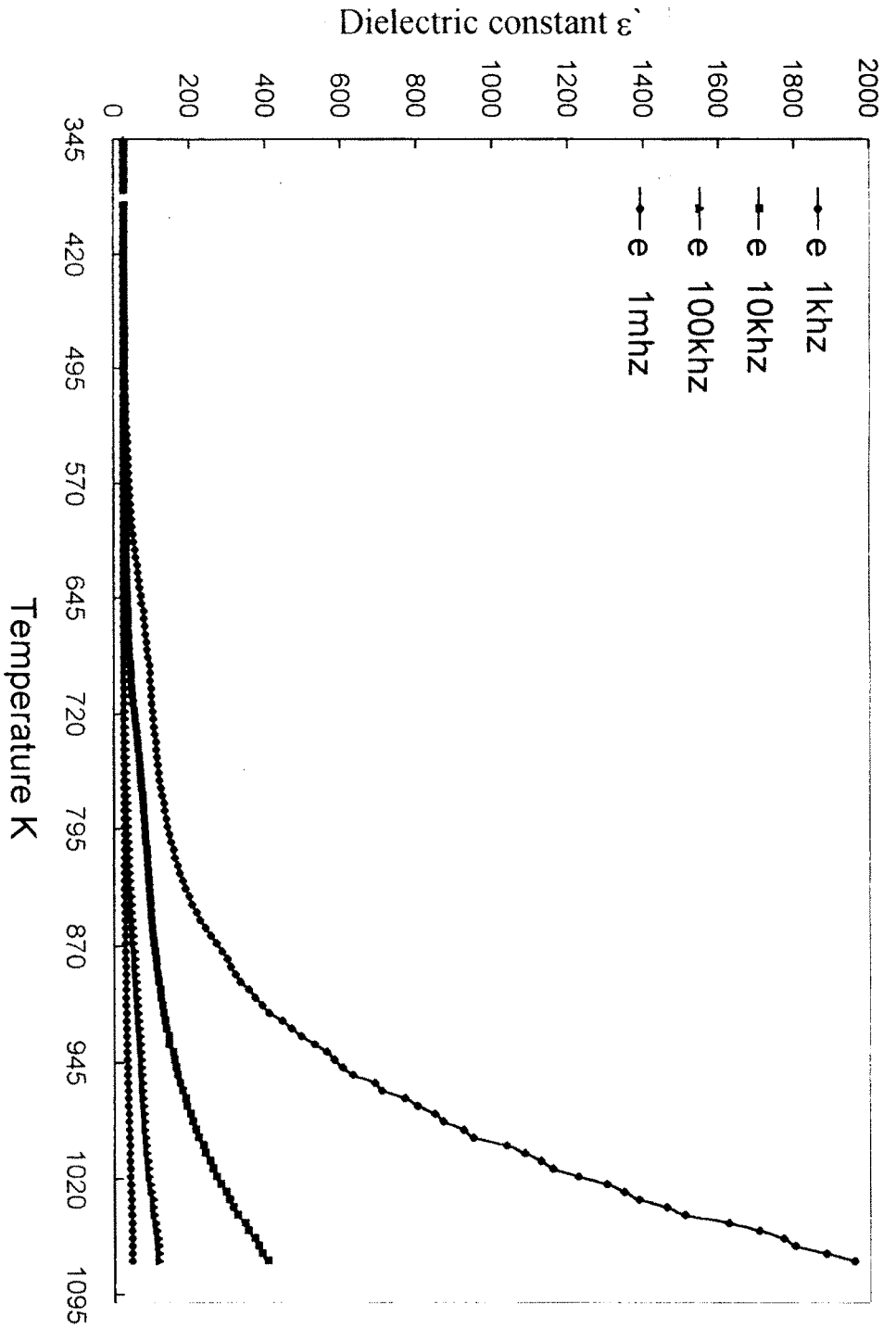


Fig4.9 Variation of ϵ' with temperature for x= 0.4

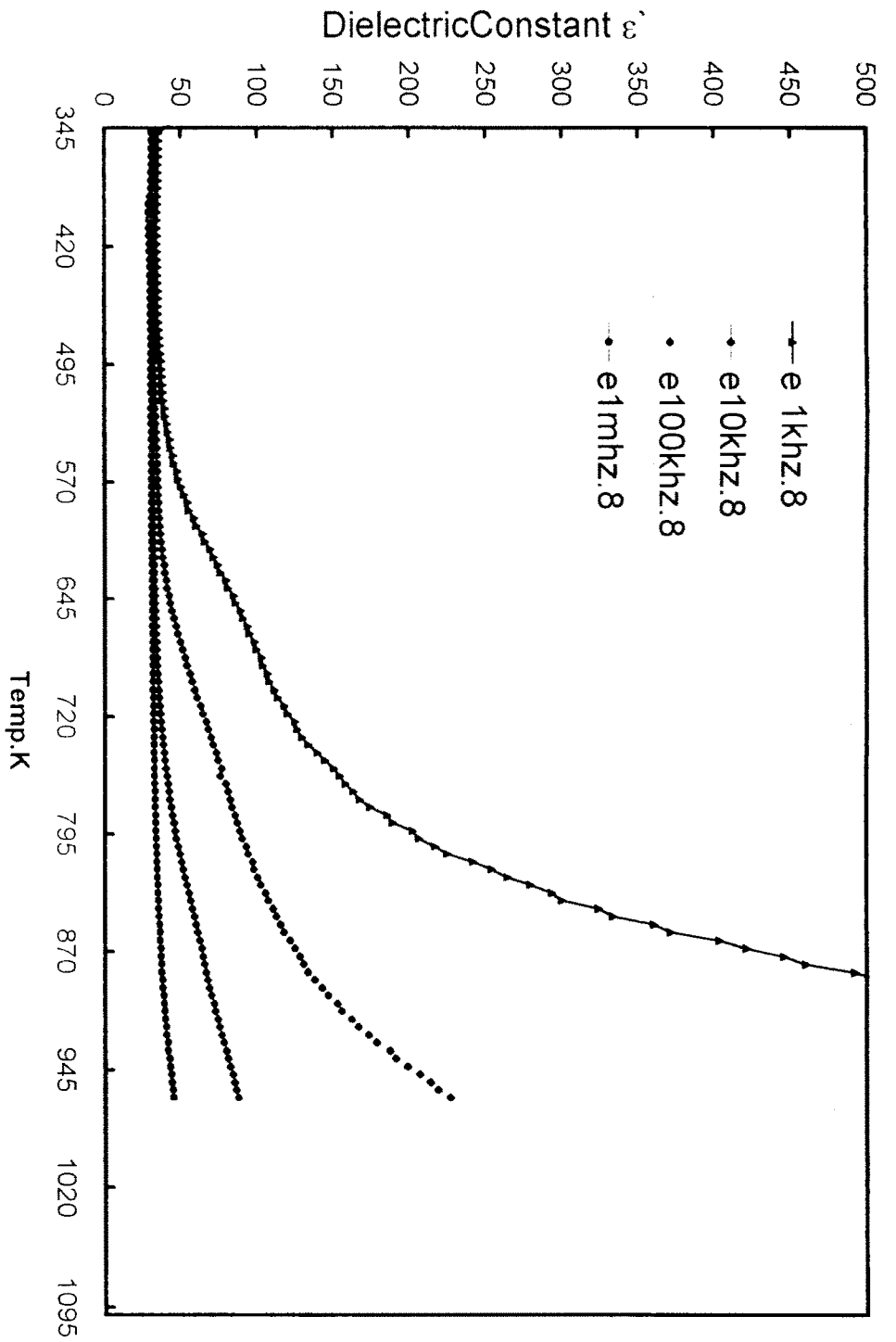


Fig 4.10:-Dielectric Constant Vs Temp.K for x = 0.8

The power loss (loss tangent) due to electric conduction is negligible in such high resistivity insulating material, which is similarly observed for the present samples.

Fig. 4.8 to fig. 4.10 shows the variation of ϵ' with temperature at different frequencies, for the compositions $x = 0.0, 0.4$ and 0.8 . From these plots it is observed that the dielectric constant increases with increase in frequency at different temperature for particular compositions. It is noted that the temperature (at which ϵ'' increases) increase with increase in frequency. This can be related with the relaxation process of the type of charge carriers.

REFE R E N C E S

- (1) B. Tareev, physics of dielectric materials,
mir publishers Moscow, 155, (1979).
- (2) I Wanch K. Jap. J.
Appl. Phys 10, 1520 (1971)
- (3) Ram Murthy S.
J. Mat. Sc. Lit. 3, 1049 (1984)
- (4) Krotzsech M,
Phys. Stat. Sol, 6, 479 (1964)
- (5) S.O. Pilai,
Solid State Physics, New Age international publishers, 583,1997.
- (6) T.C. Jain,
properties of Electrical Engineering materials, New York Harper and Row
(1967)
- (7) J.Jona,J Shirane and R. Piepinsky,
Phys.,Rev.,98,903(1955)
- (8) Shail Upadhyay, Devendrakumar and Om Prakash
Bull. Mat Sc. 19, 3, 519 (1996).
- (9) S.K. Hajra Choudhary;
Materials Science and processes,334, (1982).