4.1 Introduction of transport properties

4.1.1 Percolation Theory

Percolation theory deals with the effects of varying, in a random system, the richness of interconnections present [1]. It can be used to model many things including flow of liquid through a porous medium, spread of disease in a population, polymer gelation, and conductor-insulator composites. From the perspective of condensed-matter physicists (who have been the main ones to adopt this mathematical subject for use in their own discipline), the single most seductive aspect of the percolation model is the presence of a sharp phase transition at which long-range connectivity suddenly appears. This percolation transition, which occurs with increasing connectedness or density or occupation or concentration, makes percolation a natural model for a diversity of phenomena.

The classic example of a percolation theory problem is an array of wires connecting one communication station with another. The communication network, represented by a large square-lattice network of interconnections, is attacked by a crazed saboteur who, armed with wire cutters, proceeds to cut the connecting links at random. Thus, what fraction of the wires must be cut to sabotage the communications array. This fraction, which is 0.5, is the percolation threshold. When half of the bonds are broken, the communications array fails to work.

There are three major categories of percolation – bond, site, and continuum. Bond and site are used when talking about arrays. Site percolation occurs when there is a connected path of sites from one side of the array to the other. Bond percolation is
utilized when there is a connected path of bonds across the array. Continuum percolation is used for system where an array model is inappropriate.

Arrays of squares of geometrical figures are shown in (Figure 4.1) with randomly shaded in one square at a time. A group of touching shaded squares is called a cluster. When enough squares are shaded to make a path across the array, the cluster to which the path belongs is called the spanning cluster [2]. Now, as this cluster grows, the path across the array becomes less tortuous. At the same time, other paths may be forming – parallel paths. This concept of parallel paths explains the increase in conductivity of a system even after the percolation threshold has been passed. The same thinking exercise above can be done by throwing random circles on a sheet of paper (Figure 4.2). These circles can overlap. This is an example of continuum percolation.

Figure 4.1  Square array percolation problem. (a) First is the empty array (b) Then, squares are randomly filled in (c) The cluster of squares that creates a complete path across the lattice is called the spanning or infinite cluster (d) Parallel paths are created.
Figure 4.2: Random circle problem – demonstrate continuum percolation

4.2 DC Conductivity

In DC conductivity, the resistance data is also geometry dependent. Therefore the resistivity ($\rho$) was calculated using the formula, $\rho = RA/l$ where, $R$, $A$ and $l$ are respectively the resistance, area of cross section ($\pi d^2/4$) and the thickness of the pellet used. The DC conductivity ($\sigma_{dc}$) can be estimated using the following equation

$$\sigma_{dc} = \frac{1}{\rho} = \frac{1}{R} \left( \frac{4l}{\pi d^2} \right)$$

The variation of DC resistivity for the ceramic composites with temperature in the range $300^0C – 800^0C$ may be expressed as $\rho = \rho_0 \exp(\Delta E/KT)$

Where $\rho$ is resistivity at temperature $T$, $\Delta E$ the activation energy for electrical process. It is observed that all the samples shows three regions with changing slope at different temperatures. It is suggested that the conduction mechanism changes from one region to another region. The variation of resistivity was explained on the basis of actual
location of cation in the spinel structure. Conduction in ferrite is due to electron transfer between divalent and trivalent ions. The conduction at low temperature (i.e. $< 450$ K) is due to impurities, whereas at higher temperature (i.e. $> 400$ K) due to charge hopping. The calculated activation energies ($\Delta E$) are greater than 0.4 eV which clearly suggest that the conduction is due to charge hopping [3]. The result of conduction by hopping process is large effective mass and low mobility to current carriers. The temperature dependence of electrical conductivity in such a case involves less of temperature dependent concentration of carriers and mostly associated with temperature dependent mobility.

4.2.1 Experimental Technique

The specific electrical conductivity of a solid `$\sigma$' $\Omega^{-1} \text{cm}^{-1}$, is defined as the current, in amps, flowing through a centimeter cube of the material under unit electrical potential. A typical experiment setup used for the measurement of dc conductivity consists of following components as shown in figure 4.3:

1. A sample holder consisting of sample, electrodes, leads and a means of securely locating the sample.
2. A means of controlling the ambient atmosphere
3. A heater capable of giving a variable but linear rate of temperature increase over a broad range of temperatures.
4. A current detector capable of measuring currents from as small as $10^{-10}$ A to as high as $10^{-4}$ A and a source of controlled, low-rippled dc potential.
DC conductivities are measured by using the above mentioned two probe setup for the following samples:

i) Nickel ferrites

ii) Barium hexaferrites

iii) Calcium ferrites


Figure 4.4  DC conductivity of nickel ferrites as a function of temperature

The temperature dependence of the dc conductivity of nickel ferrites is shown in figure 4.4. The deviation of the conductivity as a function of temperature due to increase in oxidations and this deviation from a straight line for polycrystals are frequently attributed to grain boundary conductivity, as discussed by Koops [4] and Volger [5]. However, Sigmsa and Zaveta [6] found that it is possible to arrive at the same results from a model based on band concepts. This model requires that the energy levels of the Fe$^{2+}$ ions be distributed in the forbidden gap around certain mean values. The dc conductivity of different weight percentages of nickel ferrites were
measured from 40°C to 450°C. For all ferrites, the conductivity increases with increase in temperature. It is observed from the graphs that conductivity is in two steps. Initially the temperature from 400°C to 250°C, conductivity is remains constant afterwards increases with increase in temperature from 250°C to 450°C. Among all nickel ferrites compositions, 20 wt% of nickel ferrite show 2.5 x10^{-8} S/cm of higher conductivity.

4.2.4 DC conductivity of barium hexaferrites as a function of temperature

![Figure 4.5](image)

**Figure 4.5** DC conductivity of barium hexaferrites as a function of temperature
The variation of DC resistivity for the composites with temperature in the range 500–450°C is shown in figure 4.5. From these plots it is observed that all the samples show three regions with changing slope at different temperatures. It is suggested that the conduction mechanism changes from one region to another region. The variation of resistivity was explained on the basis of actual location of cation in the hexagonal structure. Conduction in ferrite is due to electron transfer between divalent and trivalent ions. The conductivity of all composition of barium hexaferrites increases with increase in temperature. In first step, from the temperature of 40 to 250°C, conductivity is slowly increase after that in second step conductivity is gradually increase from 250 to 320°C. In third step from the temperature of 320 to 450°C the conductivity suddenly increases. Among all composition of ferrites, 20 wt % of barium hexaferrites shows high conductivity of $7.0 \times 10^{-8}$ S/cm.
4.2.5 DC conductivity of calcium ferrites as a function of temperature

Figure 4.6 DC conductivity of calcium ferrites as a function of temperature

Figure 4.6 shows the temperature dependence of the dc conductivity of calcium ferrites at different weight percentages of calcium doped in ferrites (x = 0.1, 0.2 and 0.3). The deviations in the conductivity graphs as a function of temperature may be due to increase in oxidations. The dc conductivity of different weight percentages of calcium ferrites were measured from 40°C to 450°C. For all ferrites,
the conductivity increases with increase in temperature. It is observed from the graphs that conductivity is in two steps. Initially the temperature from 400°C to 250°C, conductivity is remains constant afterwards increases with increase in temperature from 250°C to 450°C. Among all compositions 30 wt% of calcium ferrites show $2.5 \times 10^{-4}$ S/cm of higher conductivity.

4.3. AC Conductivity

4.3.1. Introduction

Electrical conductivity measurements are known to be very sensitive for the study of electronic properties of materials. In ceramic systems, DC conductivity measurements are used to study the localization of ionic states, while AC conductivity measurements provide useful information concerning various relaxation phenomenons related to the electrical polarization process. In high frequency measurements, the characteristic hopping lengths and hopping rates of carriers between localized states can be determined. The low frequency data are however, more sensitive to slower relaxation process like the reorientation of dipoles etc. In the latter case most relaxation process can be explained in the Debye theory of energy loss for dipole relaxations [7 - 9].

It is well known fact that frequency dependent complex conductivity in case of disordered materials such as ceramic composites can arise from interfacial or atomic polarization at contacts, grain boundaries and other inhomogeneities present in the sample [10, 11]. Hence in the following sub-section a brief theoretical approach regarding how the direct current induces polarization effects, in these materials is discussed.
4.3.2 Polarization

The total electric dipole moment per unit volume of the dielectric material is called polarization. It is a measure of the contribution to the total dielectric displacement by a dielectric material. When field is applied to a dielectric, the polarization of the dielectric takes place.

There are four primary mechanisms of polarization in ceramics. Each mechanism involves a short-range motion of charge and contributes to the total polarization of the material. The polarization mechanisms include:

a) Electronic polarization ($P_e$);

b) Atomic polarization ($P_a$);

c) Dipole polarization ($P_d$) and

d) Interfacial polarization ($P_i$).

4.3.2.1 Electronic Polarization:

This is due to the shift of the valence electron cloud of the ions within the material with respect to the positive nucleus. This mechanism of polarization occurs at very high frequencies ($10^{15}$Hz), which are in the ultra-violet optical range. The mechanism of polarization gives rise to a resonance absorption peak in the optical range as shown in figure 3.1. The index of refraction of the material depends on the electronic polarization.

4.3.2.2 Atomic polarization:

Atomic polarization is observed when the nucleus of the atom reorients in response to the electric field. This is a resonant process. Atomic polarization is
intrinsic to the nature of the atom and is a consequence of an applied field. This is also called ionic polarization and occurs at frequencies in the IR range, \(10^{12} - 10^{13}\) Hz. Electronic polarization refers to the electron density and is a consequence of an applied field. Atomic polarization is usually small compared to electronic polarization.

### 4.3.2.3 Dipolar polarization:

This type of polarization is also sometimes called orientational polarization. It occurs in the sub infrared range of frequencies, and contributes to the dielectric properties. This involves perturbation of the thermal motion of ionic or molecular dipoles, producing a net dipolar orientation in the direction of applied field.

Mechanism of dipolar polarization is generally divided into two categories. One is called Stevles’ deformation polarization, which occurs in the frequency range \(10^{11} - 10^{12}\) Hz at room temperature. Here, the molecules containing a permanent dipole moment may be rotated against an elastic restoring force about an equilibrium position and the other type occurs in the frequency range of \(10^{3} - 10^{6}\) Hz at room temperature. Here, the rotation of dipoles between two equivalent equilibrium positions is involved. It is the spontaneous alignment of dipoles in one of the equilibrium positions that give rise to the non-linear polarization behaviour of ferroelectric materials. It is responsible for dielectric constant of values \(10^{4}\) or more in some materials.

### 4.3.2.4 Interfacial polarization:

This is also called space-charge polarization. It occurs when a physical barrier that inhibits charge migration impedes mobile charge carriers. The charges pile up at
the barrier producing a localized polarization of the material. When an ac field is of sufficiently low frequency, less than $10^{-3}$ Hz, a net oscillation of charge can be produced between barriers as far apart as 1cm, producing a very large capacitance and dielectric constant (Fig. 4.7) If the barriers are an internal structural feature, or the density of charges contributing to the interfacial polarization is sufficiently large, the frequency range of sensitivity for interfacial polarization may extend into Kilocycle ($10^3$ Hz) range. In such a case it may be impossible to distinguish the frequency response of a dipole polarization mechanism, such as $P_{dl}$ and an interfacial polarization mechanism such as $P_{i2}$ as shown in figure. 4.7.

Figure 4.7  
Frequency dependence of the polarization mechanisms in dielectrics contribution to the charging constant

( representative values of $\varepsilon_r$)
4.4 Loss tangent

Loss tangent is also called loss angle ($\tan\delta$) or dissipation factor (D). This represents the relative expenditure of energy to obtain a given amount of charge storage as shown in figure 4.8.

![Figure 4.8 Frequency dependence of the polarization mechanisms in dielectrics contribution to the loss angle (representative values of $\tan\delta$)](image)

4.4.1 Dipole relaxation

This originates from permanent and induced dipoles aligning to an electric field. Their orientation polarisation is disturbed by thermal noise (which mis-aligns the dipole vectors from the direction of the field), and the time needed for dipoles to relax is
determined by the local viscosity. These two facts make dipole relaxation heavily dependent on temperature, pressure and chemical surrounding.

4.4.2 Ionic relaxation

Ionic relaxation comprises ionic conductivity and interfacial and space charge relaxation. Ionic conductivity predominates at low frequencies and introduces only losses to the system. Interfacial relaxation occurs when charge carriers are trapped at interfaces of heterogeneous systems. A related effect is Maxwell-Wagner-Sillars polarization, where charge carriers blocked at inner dielectric boundary layers (on the mesoscopic scale) or external electrodes (on a macroscopic scale) lead to a separation of charges. The charges may be separated by a considerable distance and therefore make contributions to the dielectric loss that are orders of magnitude larger than the response due to molecular fluctuations.

4.4.3 Principle and Theory for evaluation of \( \sigma_{ac} \) from Dielectric measurements:

A capacitor when charged under an a.c. voltage will have some loss current due to ohmic resistance or impedance by heat absorption. If \( Q \) be the charge in Coulomb due to a potential difference of \( V \) volts between two plates of a condenser of area, \( a \), and interpolate distance, \( d \), then a.c., conductivity (\( \sigma_{a.c.} \)) due to a.c. voltage \( v(ve^{j\omega t}) \) is given by the relation.

\[
\sigma_{a.c.} = \frac{J}{E} \quad \text{(4.1)}
\]

where \( J \) is the current density and \( E \) the electric field strength vector.

But the electric field vector, \( E = D/\varepsilon \). \( D \) is the displacement vector of the dipole charges. \( \varepsilon \) is the complex permittivity of the material. For a parallel plate
capacitor, the electric field intensity ($\vec{E}$) is the ratio of potential difference between the plates of the capacitor to the inter-plate distance i.e.,

$$E = \frac{V}{d} \quad \text{---------------------- (4.2)}$$

Since the current density $\vec{J} = dq/dt$, but $q$ is given by

$$\frac{Q}{A} = \frac{V \varepsilon}{d}$$

$$\vec{J} = \frac{d}{d} \left( \frac{V \varepsilon}{d} \right) = \frac{\varepsilon}{d} \frac{dV}{dt} \quad \text{------------------------- (4.3)}$$

$$\vec{J} = \frac{\varepsilon}{d} Vjw \quad \text{---------------------------(4.4)}$$

Substituting for $\vec{E}$ and $\vec{J}$ in (3.3.1)

$$\sigma_{a.c} = \frac{\vec{J}}{\vec{E}} = \varepsilon j\omega$$

Since $\varepsilon$ being a complex quantity

$$= (\varepsilon' - j\varepsilon'') j\omega = \varepsilon' j\omega + \omega \varepsilon'' \quad \text{-------- (4.5)}$$

in order that a.c. conductivity may be a real quantity, the term containing $j$ has to be neglected hence

$$\sigma_{a.c} = \omega \varepsilon'' \quad \text{---------- (4.6)}$$

In any dielectric material, there will be some power loss because of the work done to overcome the frictional rotation. If an a.c. field is considered, then in an ideal case the charging current $I_C$ will be $90^0$ out of phase with the voltage. But in most of the capacitors due to the absorption of electrical energy some loss current, $I_L$ will also be produced, which will be in phase with the voltage. Charging current, $I_C$, and loss current, $I_L$, will make angle $\delta$ and $\theta$, respectively with the total current, $I$, passing
through the capacitor. The loss current is represented by \( \sin \delta \) of the total current, \( I \), generally \( \sin \delta \) is called the loss factor but when \( \delta \) is small then \( \sin \delta = \delta = \tan \delta \). But the two components \( \varepsilon' \) and \( \varepsilon'' \) of the complex dielectric constant \( \varepsilon \), will be frequency dependent and is given by

\[
\varepsilon'(\omega) = D_0 \cos \frac{\delta}{E_0} \tag{4.7}
\]

\[
\varepsilon''(\omega) = D_0 \sin \frac{\delta}{E_0} \tag{4.8}
\]

Since the displacement vector in a time varying field will not be in phase with \( \vec{E} \) and hence there will be a phase difference \( \delta \) between them. From (4.7) and (4.8) we have,

\[
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \tag{4.9}
\]

Substituting the value of \( \varepsilon''(\omega) \) from (4.6) in (4.5) then we have

\[
\sigma_{\text{a.c}} = \omega \tan \delta \varepsilon'(\omega) \tag{4.10}
\]

where \( \omega = 2\pi f \) and \( \varepsilon' = \varepsilon_0 \varepsilon_r \), here \( \varepsilon_r \) is the relative permittivity of the material and \( \varepsilon_0 \) the permittivity of free space. So

\[
\sigma_{\text{a.c}} = 2 \pi f \tan \delta \varepsilon_0 \varepsilon_r \tag{4.11}
\]

This equation is used to calculate the a.c. conductivity using dielectric constant and \( \tan \delta \) at a given frequency.

### 4.4.4 Maxwell-Wagner- Sillars [M-W-S] Theory:

Heterogeneities are another source of polarization in polycrystalline ceramics. Wagner (1914) was the first to extend Maxwell’s multilayer dielectric analysis to include dispersed spherical phases. Sillars (1937) later generalized heterogeneous
dielectrics to include dispersed ellipsoidal phases. An important consequent of the final Maxwell-Wagner-Sillars (M-W-S) theory is that the dielectric parameters of an insulator may be interpreted in terms of a distribution of ellipsoidal particles of a given volume fraction and size, instead of atomistic dipoles as Debye theory requires. Since the frequency location of loss peaks and the frequency and temperature dependence $\varepsilon'$ and $\varepsilon''$ can be equivalent in both the M-W-S and Debye theories, independent confirmation of a model for the dielectric behaviour of a particular material must be obtained.

![Figure 4.9](image)

**Figure 4.9**  Schematic of a dielectric containing high conductivity ellipsoidal heterogeneity of ratio $= a/b$ with $\sigma_2 \gg \sigma_1$

A schematic of the M-W-S heterogeneous dielectric model is shown in figure 4.9. This diagram shows isolated ellipsoidal particles of conductivity $\sigma_2$ in a matrix of conductivity $\sigma_1$. When $\sigma_2 > \sigma_1$, the phase boundary between the particles and the matrix will serve as a barrier to charge migration, and ac charge oscillation and interfacial polarization will occur. Sillars (1937) has shown that for a volume fraction of spheroids, $q$, of conductivity $\sigma_2$ and permittivity $\varepsilon_2$ and axial ratio of $a/b$, embedded
in a perfect dielectric matrix of conductivity $\sigma_1$ and permittivity $\varepsilon_1$, the dielectric parameters of the composite material are

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_1 N}{1 + \omega^2 \tau^2} \quad \text{----------------------------------------} \quad (4.12)$$

$$\varepsilon'' = \frac{\varepsilon_1 N \omega \tau}{1 + \omega^2 \tau^2} \quad \text{----------------------------------------} \quad (4.13)$$

$$\tan\delta = \frac{\varepsilon_1 N \omega \tau}{\varepsilon_\infty (1 + \omega^2 \tau^2) + \varepsilon_1 N} \quad \text{----------------------------------------} \quad (4.14)$$

Where

$$\tau = \frac{(\varepsilon_1 \lambda - 1 + \varepsilon_2) \varepsilon_0}{\sigma_2} \quad \text{----------------} \quad (4.15)$$

and

$$N = q \frac{\lambda^2 \varepsilon_1}{\varepsilon_1 (\lambda - 1) + \varepsilon_2} \quad \text{----------------------------------------} \quad (4.16)$$

and

$$\varepsilon = \varepsilon' \left(1 + q \frac{\lambda (\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 (\lambda - 1) + \varepsilon_2}\right) \quad \text{----------------} \quad (4.17)$$

The location of the M-W-S dielectric relaxation is primarily a function of the axial ratio of the ellipsoidal particles and the conductivity of the dispersed phase. The M-W-S model also shows that the magnitude of both $\varepsilon'$ or $\varepsilon''$ are dependent on the volume fraction of the dispersed particles and their axial ratio. Consequently, a change in magnitude of $\varepsilon'$ or $\varepsilon''$ cannot be unambiguously interpreted unless other evidence is available to estimate independently the axial ratios or the volume fraction [12].
4.5 Complex Impedance Spectroscopy:

Complex impedance spectroscopy is a well-known and powerful technique, used for investigating dielectric materials. The contribution of various processes such as the electrode effects, and their interfaces can be resolved in the frequency domain. In general, one or more of four representations are used to represent data in the complex plane. These are complex impedance $Z^*$, complex admittance $Y^*$, complex permittivity $\varepsilon^*$, and complex modulus $M^*$. All these four admittance functions are interrelated [13] by,

$$
M^* = j\omega C_0 Z^* \quad \text{(4.18)}
$$

$$
\varepsilon^* = (M^*)^{-1} \quad \text{(4.19)}
$$

$$
Y^* = (Z^*)^{-1} \quad \text{(4.20)}
$$

and

$$
Y^* = j\omega C_0 \varepsilon^* \quad \text{(4.21)}
$$

Where $\omega$ the angular frequency and $C_0$ is the vacuum capacitance of the measuring cell and electrodes with an air gap in place of the sample.

In order to analyze and interpret experimental data, it is essential to have a model equivalent circuit that provides a realistic representation of the electrical properties. This is chosen based on

(i) Intuition as to what and whether they are connected in series or in parallel,

(ii) Examination of the experimental data to see whether the response is consistent with the proposed circuit, and

(iii) Inspection of the resistance and capacitance values that are obtained in order to check that they are realistic and that their temperature dependence, if any, is reasonable.
In practice, it is usually possible to find more than one equivalent circuit that
fits, numerically, a given data set, but only one of these is likely to provide a realistic
representation of the electric makeup of the sample. In the ceramic materials, both
inter and intra granular impedances are present and the electrical properties are
determined in general by a series combination of such impedances. Each of these
components may be represented by a parallel RC element, and the simplest
appropriate equivalent circuit is a series array of parallel RC elements (Fig.4.10).

![Figure 4.10](image)

**Figure 4.10 Equivalent circuit used to represent the electrical properties of
bulk and grain-boundary effects**

It is not necessary to include an impedance element representing the ceramic
electrode interface in cases where the contact resistance is small. The circuit in Fig.
3.8 is widely used to represent bulk and grain boundary phenomena in polycrystalline
materials, especially in cases, where the grain boundary impedance is the dominant
impedance in the sample.

With a series circuit such as given in Fig. 4.10 it is desired to separate each of
the parallel RC elements and measure their component R and C values. This is best
achieved using a combination of the impedance and modulus formalisms since each
parallel RC element gives rise to a semicircle in the complex plane (Z” vs. Z”; M” vs.
M’) or a Debye peak in the spectroscopic plots of the imaginary component (Z’ M” vs. log f). This is seen from the equation for the impedance of this circuit:

\[ Z^* = (1/R_1 + J\omega C_1)^{-1} + (1/R_2 + j\omega C_2)^{-1} \]  

\[ = Z' - jZ'' \]  

\[ (4.22) \]

where

\[ Z' = \frac{R_1}{1 + (\omega R_1 C_1)^2} + \frac{R_2}{1 + (\omega R_2 C_2)^2} \]  

\[ (4.24) \]

and

\[ Z'' = \frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2} + \frac{\omega R_2 C_2}{1 + (\omega R_2 C_2)^2} \]  

\[ (4.25) \]

The corresponding equations for M’ and M” are obtained by substituting into Eq. (4.20), these are

\[ M' = \frac{C_0}{C_1} \left( \frac{\omega R_1 C_1^2}{1 + (\omega R_1 C_1)^2} \right) + \frac{C_0}{C_2} \left( \frac{\omega R_2 C_2^2}{1 + (\omega R_2 C_2)^2} \right) \]  

\[ (4.26) \]

and

\[ M'' = \frac{C_0}{C_1} \left( \frac{\omega R_1 C_1^2}{1 + (\omega R_1 C_1)^2} \right) + \frac{C_0}{C_2} \left( \frac{\omega R_2 C_2^2}{1 + (\omega R_2 C_2)^2} \right) \]  

\[ (4.27) \]

**4.5.1 Vogel-Fulcher behavior**

The Vogel-Fulcher relationship may be interpreted as a normal Debye relaxation with temperature-dependent activation energy. The activation energy increases as the temperature decreases becoming undefined as the freezing temperature is approached. A more realistic interpretation of this relationship in reference to relaxors, is that E_a represents the activation energy for polarization
fluctuations of an isolated cluster with temperature dependence arising from the development of short-range order between neighbouring clusters with kTf where k = Boltzmann constant and Tf = static freezing temperature being a measure of the interaction energy. It is certainly possible that the ferroelectric clusters interact via dipole and dipole-induced dipole exchanges. The possibility also exists that the clusters could interact elastically through local rhombohedral distortions, implying that the clusters may freeze into an orientational glassy state and are super para electric above the freezing temperature.

The super para electric model, the Vogel-Fulcher dipole glass and dipolar dielectric model are all based on the assumption that the mechanism of the response is related to the thermally activated reorientation of the local spontaneous polarization in small (about 100 a diameter) polar regions distributed in non-polar matrix. As has been perceived till now it appears that disorder in the B-site to be a necessary condition for the observed dielectric relaxation. However, there are still questions concerning the fundamental physical origin of the dispersion behaviour.

Furthermore two different models with very different implications have described the structure of the chemically ordered domains. In the first model, the ordered domain contains a space charge and would therefore have its growth limited by the electrostatic interactions. The second model describes the ordered structure as being possessing an intrinsic B-site disorder even in ‘fully’ ordered crystals. According to this model, there should be no limitation on the ordered domain growth and one should be able to obtain full order of the crystal. Davies et al [14] has shown that the ordered structure can be made to spread in the entire crystal in Pb(Mg1/3Ta2/3)O3 (PMT), a similar relaxor even for fully ordered of the B-site as described above. In
the case of Pb(Sc\textsubscript{1/3}Ta\textsubscript{2/3})O\textsubscript{3} (PST) when the structure is fully ordered, the relaxor behaviour disappears, as there is no more B-site disorder [15].

4.5.2 Koops model:

Many polycrystalline materials show a decrease of electrical resistivity and dielectric constant over the frequency range d. c. to the microwave frequency region. This anomaly is thought to be due to the inhomogeneous nature of these materials and may be explained theoretically by consideration of the Maxwell-Wagner two-layer model. The specimen is considered to contain low-resistivity crystallites \((R_g, C_g)\), which are separated by high-resistivity grain boundaries \((R_b, C_b)\), where \(R_g, C_g, R_b, C_b\) are constants where \(R\) and \(C\) are functions of \(R_g, C_g, R_b, C_b\) and are not constants with respect to frequency.[16].

4.5.3 Phenomenological theories

The study of ferroelectrics has been greatly assisted by so-called ‘phenomenological’ theories that use thermodynamic principles to describe observed behaviour in terms of changes in free-energy functions with temperature. Such theories have nothing to say about mechanisms but they provide an invaluable framework around which mechanistic theories can be constructed. A.F. Devonshire was responsible for much of this development between 1949 and 1954 at Bristol University.

The theories clarify relationships between observed facts and to reveal problems to be treated in molecular theories. Since the interaction between electric polarizations and lattices of crystals is much stronger than between magnetizations
and lattices, phenomenological theories have an especially important significance in ferroelectricity.

4.5.4 Devonshire theory

Devonshire calculated the temperature dependence of dielectric constants. He showed that the Gibb’s free energy can take minimum values as temperature decreases making the phase more stable. The theoretical equations were derived and obtained results were in good agreement with experiments [17] e.g., the single crystal of BaTiO$_3$ grown, has a Curie point around 120$^0$C. The temperature dependences of spontaneous polarization ($P_s$) spontaneous deformation and dielectric constant change discontinuously at about 0$^0$C and -80$^0$C in addition to the changes at about 120$^0$C. These changes correspond to a discontinuous change of the direction of spontaneous polarization. $P_s$ is oriented at <100> between 120$^0$ and 0$^0$C, and <110> between 0$^0$C and -80$^0$C, and <111> below -80$^0$C. These three phase transitions are all first order. Merz [18] showed that $P_s$ changes discontinuously at Curie point.

4.5.5 Cochran theory

Cochran’s theory [19] is based on the assumption that the ferroelectric phase transition is the result of instability of crystal lattice with respect to one of the homogeneous (wave vector $g=0$) transverse optical mode ($\omega_T$). Essentially the theory is based on the assumption that if the crystal is wholly or partially ionic, lattice vibrations are accompanied by polarization oscillations of equal frequency, which create a local field interacting with the ions through long-range coulomb forces. If for one particular mode of vibration these long-range forces have the magnitude equal
and opposite in sign to the short-range forces, the crystal becomes unstable for this mode. The $\varepsilon_c$, which is connected to the frequency of the critical mode, becomes large as it happens at the Curie temperature.

Ferroelectric phase transitions are a special case of structural phase transitions, and can thus be interpreted in terms of stability of the crystal lattice dynamics. In a structural phase transition, the order parameter (polarization in case of ferroelectric phase transition) is associated with a lattice vibrational mode that exhibits instability at the transition temperature. For a second order transition, for example, the frequency spectrum of the lattice vibrations related to the order parameter is proportional to $T - T_c$, so that this mode ‘softens’ (its frequency goes to zero) as the material is cooled towards $T_c$. Freezing of the vibrations at $T_c$ gives rise to non-zero order parameter and the corresponding reduction in symmetry. A soft mode is an optic mode and can be studied experimentally by infrared spectroscopy and neutron scattering. The lattice dynamics approach and its recent extension [20] have been very successful in describing qualitatively ferroelectric phase transitions.

4.6 Experimental Technique

The capacitances of ferrites in the form of pressed pellets, coated with silver paste are measured as a function of applied frequency using Hioki impedance analyzer 3532-50 (JAPAN) in the frequency range 50 Hz to 5 MHz at room temperature. In this experiment three different samples of each ferrites varying in their weight percentage are investigated for their frequency dependent dielectric parameters. During this course of study, silver electrodes are painted on the sample surface and then placed under dynamic vacuum during measurement.
4.7 Results and discussion

Using the values of equivalent parallel capacitance (Cp), dissipation factor (D), phase angle (δ) and parallel equivalent resistance (Rp) that are recorded by the LCR meter at selected frequency range (f), the ac conductivity (σac), dielectric constant (ε’) and dielectric loss (tan δ) parameters have been calculated.
4.7.1 Nickel ferrites

Figure 4.12 Variation real permittivity ($\varepsilon'$) of nickel ferrite of various composition as a function of frequency.

Figure 4.12 shows the variation real permittivity ($\varepsilon'$) of nickel ferrite of various composition as a function of frequency. It is found that in all these nickel ferrite compositions, as frequency increases, dielectric constant decreases up to the frequency range of $10^4$ Hz and after that it remains constant for further increasing in frequency. The strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior above 10 kHz.
It is observed that Debye type relaxation mechanism is responsible for higher value of \( \text{Ni}_{X}\text{Fe}_{X-1}\text{O}_4 \) (\( X=0.1, \) and \( 0.3 \)) compositions [21].

![Graph showing variation of \( \tan\delta \) as a function of frequency for \( \text{Ni}_{X}\text{Fe}_{X-1}\text{O}_4 \) (\( X=0.1, 0.2 \) and \( 0.3 \)).]

**Figure 4.13** Variation of \( \tan\delta \) as a function of frequency for \( \text{Ni}_{X}\text{Fe}_{X-1}\text{O}_4 \) (\( X=0.1, 0.2 \) and \( 0.3 \)).

Figure 4.13 shows the variation of \( \tan\delta \) as a function of frequency for \( \text{Ni}_{X}\text{Fe}_{X-1}\text{O}_4 \) (\( X=0.1, 0.2 \) and \( 0.3 \)). The high value of dielectric constant of the sample \( \text{Ni}_{X}\text{Fe}_{X-1}\text{O}_4 \) (\( X=0.1, 0.2 \) and \( 0.3 \)) may be explained on the basis of the structural changes associated with the nickel ferrite when the grain size is reduced to nanometer order. Nickel ferrite crystallizes into a cubic close-packed arrangement of oxygen ions. It belongs to the class of ferrites with an inverse spinel structure having structural
formula, Fe$^{3+}$[Ni$^{2+}$Fe$^{3+}$]O$_4$. The metal ions given in the square bracket are called octahedral (B site) ions and that outside the square bracket are called tetrahedral (A site) ions. The nickel ions (Ni$^{2+}$) together with half of the iron ions (Fe$^{3+}$) occupy the B site and the remaining half of the iron ions reside in A site. The presence of Ni$^{2+}$ and Ni$^{3+}$ ions gives rise to p-type carriers (holes) whereas Fe$^{2+}$ and Fe$^{3+}$ ions produce n-type carriers (electrons). Therefore, both electrons and holes that are present in the B sites are due to the presence of Ni and Fe ions. Since only iron ions are present in A sites, electrons are the carriers in A sites. The distance between the ions in A sites (0.357 nm) is larger than the distance between the ions in B site (0.292 nm). Also, the degree of covalency for the A site ions is higher than that of the B site ions. All the above factors result in a high activation energy for the A sites compared to the B sites. Hence, in ordinary nickel ferrite with an inverse spinel structure the electron movement in B sites dominates compared to that in A sites.
Figure 4.14 Variation of real part of impedance as a function of frequency for different weight percentages of Ni$_X$Fe$_{X^{-1}}$O$_4$ (X=0.1, 0.2 and 0.3).

The variation of real part impedance as a function of frequency for different composition of Ni$^{+2}$ in ferrites is shown in figure 4.14. It is observed that 20 wt% of nickel ferrites show low impedance value compare to 0.1 and 0.3 wt % this is may be the grain capacitance ($C_b$) which are comparable with the grain boundary capacitance ($C_{gb}$) for the investigated samples. However, the resistance due to interfacial grain boundary is much larger in compare to the grain resistance. This implies that the grain boundary contribution dominates over the grain contribution.
Figure 4.15 Variation of $\sigma_{ac}$ of Ni$_X$Fe$_{X-1}$O$_4$ (X=0.1, 0.2, 0.3) as a function of logarithmic frequency.

Figure 4.15 shows the variation of $\sigma_{ac}$ of Ni$_X$Fe$_{X-1}$O$_4$, (X=0.1, 0.2, 0.3) as a function of frequency. The conductivity of nickel ferrites for various weight percentages is increases with increase in frequency. Among all nickel ferrite (Ni$_X$Fe$_{X-1}$O$_4$, X=0.2) percentage shows high $\sigma_{ac}$ conductivity compared to other composition of nickel ferrite (X=0.1 and 0.3). This is may be attributed to the dipole polarization i.e., the rotation of dipoles between two equivalent equilibrium positions is involved. It is the spontaneous alignment of dipoles in one of the equilibrium positions that give rise to the nonlinear polarization behaviour of this composition.
This behavior of Ni$_X$Fe$_{X-1}$O$_4$ (X=0.1, 0.2 and 0.3) obeys the universal power law, $\sigma(\omega)=\sigma_0+A(\omega)^n$ (the solid line is the fit to the expression), where $\sigma_0$ is the dc conductivity (frequency independent plateau in the low frequency region), A is the pre-exponential factor, and n is the fractional exponent between 0 and 1. On crystallization, the conductivity spectrum remains similar as that of the nickel ferrite except dispersion in the low frequency region, where the deviation from $\sigma_{dc}$ (plateau region) is more prominent. The deviation from $\sigma_{dc}$ (plateau region) value in the conductivity spectrum (in the low frequency region) is due to the electrode polarization effect. The values of $\sigma_0$, A, and n were obtained by fitting the $\sigma(\omega)$ to $\sigma(\omega)=\sigma_0+A(\omega)^n$. The overall behavior of $\sigma_{ac}$ follows the universal dynamic response, [22] which has widely been observed in disordered materials like ionically conducting glasses, [23] conducting polymers, and also doped crystalline solids, [24, 25] and is generally believed to be reflected in the mechanism of charge transport behaviour of charge carriers.
4.7.2 Barium Hexaferrites

Figure 4.16 Variation of real permittivity of barium hexaferrites as a function of frequency.

The real part of permittivity in Barium Hexaferrite (figure 4.16) on space charge polarization and charge formation at grain boundary and additional interface, introduced by dielectric matrix. Barium hexaferrites materials, in which magnetic particles are coated with dielectric layers, introduce additional interfaces leading to interfacial polarization and this forms more polarization charges on the surface of the particles. This causes dielectric relaxation behavior more complex. It has been reported in literature [26, 27] that the properties of interfaces could have a dominant
role in determining dielectric performance. The dielectric constant (Figure 4.16) of all samples exhibits nonmonotonic variation with substitution of Ba$^{+2}$ ions. The non-linear variation of resistivity with substitution reflects two maxima at lower (sample 30 wt %) and lower substitution (sample 10 & 20 wt %) and high resistivity discourages polarization and conductivity. Thus real permittivity values are low in doped samples 30 wt% while comparatively higher in other doped samples. All samples exhibit large value of permittivity in spite of only 30 % volume fraction of ferrite. . It has been reported elsewhere that electron hopping between Fe$^{2+}$ ions and Fe$^{3+}$ ions leads to conductivity and dielectric polarization in ferrites [28].

![Graph showing variation in tanδ with frequency for different weight percentages of barium ferrites at room temperature.](image)

**Figure 4.17** Variation tanδ as a function of frequency for different weight percentages of barium ferrites at room temperature.
The variation $\tan\delta$ as a function of frequency for different weight percentages of barium ferrites at room temperature as shown in figure 4.17. It is observed that the $\tan\delta$ value increases with increase in frequency up to $10^4$ Hz and further increase in frequency decreases the $\tan\delta$ value. The initial increase in loss may be due to the electrode polarization between the ferrites and electrode surface. All the barium ferrites shows similar behavior and among all the composites, 30 wt% have low loss because of less grain boundary distance between the ions in A sites than the distance between the ions in B site [29].

![Figure 4.18](image-url)

*Figure 4.18  Variation of real part impedance as a function of frequency for different composition of barium hexaferrites*
The variation of real part impedance as a function of frequency for different composition of Ba$^{+2}$ in ferrites is shown in figure 4.18. It is observed that 30 and 20 wt% of nickel ferrites show low impedance value compare to 0.1 wt % this is may be the grain capacitance ($C_b$) which are comparable with the grain boundary capacitance ($C_{gb}$) for the investigated samples. However, the resistance due to interfacial grain boundary is much larger in compare to the grain resistance. This implies that the grain boundary contribution dominates over the grain contribution [30, 31].

Figure 4.19  Variation of ac conductivity as function of frequency of barium ferrites
The plots of a.c. conductivity with frequency are shown in figures 4.19 for compositions $x = 10, 20$ and $30$ wt%. It is clear from the figures that the conductivity is found to be high for higher frequency at room temperature, thus confirming small charge hopping in the present samples (Adler 1968 [32]; Appel 1968 [33]; Austin and Mott 1969 [34]). It is also observed that $\sigma_{ac}$. It has been reported that frequency dependence of $\sigma_{ac}$ is large in ferrimagnetic or in lower temperature region (El Hitti 1996 [35]). This is also true in $x = 0\times6$ sample, but an abrupt jump in $\sigma_{ac}$ around 430 K is observed for 100 kHz, 500 kHz and 1 MHz frequency [36].

4.7.3 Calcium ferrites

The real part of permivity ($\varepsilon'$) of calcium ferrites at different weight percentages in room temperature shown in figure 4.20. The $\varepsilon'$ value of all composition of decreases with increase in frequencies. The large dispersion throughout the frequency range is observed may be due to the Maxwell-Wagner-Sillars polarization and interfacial polarization in ferrites. The real permittivity values are low in doped samples $30$ wt% while comparatively higher in other doped samples. All samples exhibit large value of permittivity in spite of only $30$ % volume fraction of ferrite.
Figure 4.20  Real part of permivity ($\varepsilon'$) of calcium ferrites at different weight percentages in room temperature.
Figure 4.21 shows the variation of $\tan\delta$ as a function of frequency for different weight percentages of calcium ferrites at room temperature. It is observed that the $\tan\delta$ value increases with increase in frequency up to $10^4$ Hz and further increase in frequency decreases the $\tan\delta$ value. The initial increase in loss may be due to the electrode polarization between the ferrites and electrode surface. All the barium ferrites show similar behaviour and among all the composites, 30 wt% have low loss because of less grain boundary distance between the ions in A sites than the distance between the ions in B site.
The variation of real part impedance as a function of frequency for different composition of Ca\(^{+2}\) in ferrites is shown in figure 4.22. The \(Z'\) value decreases with increase in applied frequency throughout the range. It is observed that 30 wt% of calcium ferrites show lowest impedance value compare other compositions. This is may be due to the the grain capacitance \((Cb)\) which are comparable with the grain boundary capacitance \((Cgb)\) for the investigated samples. However, the resistance due to interfacial grain boundary is much larger in compare to the grain resistance. This implies that the grain boundary contribution dominates over the grain contribution.
The variation of $\sigma_{\text{ac}}$ conductivity as a function of frequency of various weight percentage of calcium ferrites at room temperature is shown in figure 4.23. The ac conductivity of all compositions of calcium ferrites increases with increase in frequency. For all compositions, initially the conductivity is constant up to 103Hz and further increase in frequency gradually increase the conductivity. 30 wt % of calcium ferrites shows high conductivity may be due to the dominance in interfacial polymerization in samples.
4.8 Reference


