CHAPTER -1

BASIC CONCEPTS
CHAPTER-1
BASIC CONCEPTS

1.1 INTRODUCTION

One of the most important groups of advanced materials belongs to the groups of ceramic ferroelectrics - a special class of dielectrics. Dielectrics are the materials in which electrostatic field can persist for a long time. These materials offer very high resistance to the passage of direct current and therefore, sharply differ from metal, semiconductor and superconductors. It is well known that dielectric properties of ceramic materials depend on their composition, structure and experimental conditions. All crystalline dielectrics in which polarization or electric dipole moment can be induced by the application of external electric field, are divided into two classes:

- Polar (dipole) dielectrics.
- Non-polar (neutral) dielectrics.

In polar dielectrics, a permanent polarization \( P_s \) exists even in the absence of applied electric field. In the case of non-polar dielectrics, there is no such permanent polarization [1].

1.2 DIELECTRIC MATERIALS

Dielectrics are a group of materials that possess electric polarization when applied with external electric field and have the capacity of storing the charges. Most of these materials have low electrical conductivity and thus are insulators. A broad range of non-metals are referred to as dielectrics, when we consider their interaction with electric, magnetic, or electromagnetic fields. The various dielectric properties are the storage and dissipation of electric and magnetic energies.
polarization, magnetization and conduction. Polarization and magnetization measures the electric and magnetic dipole moment per unit volume. These microscopic moments are composed of elementary molecular moments. Induced electric dipole moments result from the displacement of electrons of nuclei (electronic and atomic polarization); the permanent dipole moment of molecules may be oriented (orientational polarization). Orientation polarization in liquids and solids causes relaxation spectra whereas the spontaneous alignment of electric dipoles by mutual interaction causes (ferroelectricity). The permanent dipole moments anchored in the structure without a centre of symmetry; under mechanical distortion creating a voltage generates piezoelectric effect. On the basis of temperature dependence of dielectric constant, and the value of the Curie constant, it is observed that ferroelectrics are classified into two groups:

- Compounds having the Curie constant in the order of $10^3$ belong to the order-disorder type [2] and,
- For those which undergo displasive type of transition, with Curie constant in the order of $10^5$ [3].

1.2.1 MICROSCOPIC DIELECTRIC PARAMETERS

The electrical properties of dielectric materials are expressed in terms of certain parameters which are termed as microscopic dielectric parameters. These parameters are as follows:

(1) DIELECTRIC CONSTANT: - The dielectric constant ($\varepsilon_r$) of a material is defined as the ratio of the permittivity of the medium ($\varepsilon_r$) to the permittivity of the free space $\varepsilon_0$. 
\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \] ........................(1.1)\\

Where \( \varepsilon_r \) is the dielectric constant, which is a dimensionless quantity. The measurement of the relative dielectric constant or the relative permittivity gives the properties of the dielectric material. The dielectric constant of air is one [4].

(2) **DISPLACEMENT VECTOR:** The displacement Vector (\( \mathbf{D} \)) is defined as the vector, whose magnitude is equal to the surface density of free charges and whose direction is from positive charges to the negative charges unit vector (\( \hat{n} \)). If charge \( Q \) is given to the parallel plates of a condenser, and \( A \) be the area of the each plate, then

\[ \mathbf{D} = \frac{Q}{A} \hat{n} \] .................................. (1.2)\\

We know that electric field between the plates \( \mathbf{E} = \frac{Q}{\varepsilon_0 A} \hat{n} \), hence

\[ \mathbf{D} = \varepsilon_0 \mathbf{E}_0 \] ...........................................(1.3)\\

(3) **POLIRIZATION VECTOR:** Polarization is defined as a vector (\( \mathbf{P} \)) whose magnitude is equal to the surface charge density of bound charges, (whose direction is from negative induced charge) for the plate area \( A \), it can be written as:-

\[ \mathbf{P} = \frac{Q_d}{A \cdot d} \hat{n} \] .................................(1.4)\\

“\( \mathbf{P} \)” is a polarization vector, “\( A \)” is an area of the plate, “\( Q_d \)”is a charge and “\( d \)” is a distance between plates.

1.2.2 **DIFFERENT TYPES OF POLARIZATION**

The application of an electric field to dielectric materials creates or realigns the dipoles resulting in to polarization. There are four different types of polarizations.

\[
\begin{align*}
\text{Electronic or Induced Polarization (Pe)} \quad \text{which occurs due to distortion of the electron density.}
\end{align*}
\]
- Atomic or Ionic polarization \((P_i)\) which is due to elastic deformation of ionic charges.
- Orientation Polarization \((P_o)\) which is due to the changes in orientation of permanent dipole moments.
- Interfacial or Space charge polarization due to spatial separation of charges within the material.

Different types of polarizations are schematically shown in figure 1.1

![Figure 1.1 Schematic representations of different types of polarizations](image-url)

1.2.3 DIELECTRIC LOSS

When an a.c. field is applied to a dielectric material, some amount of electrical energy is absorbed by the dielectric material and is dissipated in the form of heat. This loss of energy is known as dielectric loss.
The dielectric loss is major engineering problem. In an ideal dielectric, the current leads the voltage by an angle of $90^0$ as shown in the Figure 1.2 (a). But in the case of commercial dielectrics, the current does not exactly lead the voltage by $90^0$. It leads by some other angle $\Theta$ that is less than $90^0$. The angle $\phi = 90 - \Theta$ is known as dielectric loss angle [5] as shown in figure 1.2 (b).

![Figure-1.2](image)

The dielectric loss is increased by following factors:

- High frequency of the applied voltage, the frequency variation s shown in fig. 1.3
- High value of the applied voltage, as shown in fig.1.2 ( c)
- High temperature, and
- Humidity.

A subgroup of the dielectric materials shows the property of spontaneous polarization [6]. For these materials the centre of positive and negative charges does not coincide even without an applied electric field. When the spontaneous polarization of a dielectric can be reversed by an electric field of magnitude less than the dielectric breakdown of the material, it is called a ferroelectric material [7].
1.2.4 DIELECTRIC BREAKDOWN

When a voltage is applied to a dielectric material and thereby the electric field is increased, it can withstand up to a certain maximum voltage before it permits large current to pass through it. This phenomenon in which the dielectric material fails to offer insulation resistance for large applied voltage is known as dielectric breakdown [8].

The different types of dielectric breakdowns are:

- Intrinsic breakdown
- Thermal breakdown
- Electrochemical breakdown
- Defect breakdown, and
- Discharge breakdown.

1.3 FERROELECTRIC MATERIALS

Ferroelectric materials are those highly polar dielectric materials which have a very high value of relative permittivity or dielectric constant [9]. The characteristics of ferroelectrics are represented in terms of the dynamics of the phase transition. Though a large number of theories have been proposed, Cochran [10] suggested the most general
theory of ferroelectric phase transitions based on Lyddane-Sachs-Teller (LST) relation [11]. Ferroelectric crystals have been known for almost a century. The discovery was preceded by the occurrence of two related phenomena viz. piezoelectricity and pyroelectricity which are known since ancient time because of ability of such materials, to attract object when they are heated. In 1880, Jacques and Pierre Curie discovered the piezoelectric effect [12]. In 1894, Pockets [13] reported the large piezoelectric constants of Rochelle salt (NaKC4H4O6.4H2O) [14]. The ferroelectricity in this salt was discovered in 1917 by A.M. Nicholson, J. A. Anderson, and W.G. Cady [15]. In 1920, Valasek [16] observed the ferroelectric hysteresis loop in Rochelle salt crystal [17], later on, Busch and Scheerer [18] discovered ferroelectricity in KH2PO4 and its sister crystals [19]. Now, it was realized that Ferroelectricity was not a property of some isolated materials, but rather a more common phenomenon [20]. With the discovery of ferroelectricity in BaTiO3, a number of “firsts” were established: first ferroelectric without hydrogen bonds, first ferroelectric with more than one ferroelectric phase [21]. In addition, the ceramic materials were found very stable and hard with a simple perovskite crystal structure, which facilitated the theoretical progress at microscopic level. By 1960s, many new ferroelectric materials were discovered, and research was focused on the most promising materials, such as the perovskite and tungsten bronze structure oxides and ferroelectric polymers [22], with the improved thin film deposition techniques, attention was partly moved from ceramics and single crystals to ferroelectric thin films [23].

The name ferroelectricity originates from the similarity of the fundamental concept to those in ferromagnetic materials, such as magnetization, magnetic domains, and magnetic hysteresis loop. However, the physics behind this phenomenon is
completely different from those in ferroelectric materials. While magnetism can be understood as an intrinsically quantum mechanical phenomenon, ferroelectricity in general may be described by means of classical physics [24].

1.4 BASIC FEATURES OF FERROELECTRICS

There are certain dielectric substances called ferroelectrics, having the following typical properties:-

1. Curie- Weiss law and Curie temperature.

2. Spontaneous polarization.

3. Hysteresis loop

1. CURIE WEISS LAW AND CURIE TEMPERATURE (T_c):- In ferroelectric materials, dielectric constant changes with temperature according to the following relation:-

\[ \varepsilon_r = B + C/(T - T_c) \] ..........................(1.5)

for , T > T_c where B and C are temperature independent constant. This relation is called Curie – Weiss law [25].Constant ‘C’ is called Curie constant and T_c, the Curie temperature. Relation (1.5) is shown by a plot in \( \varepsilon_r \) vs. T in Fig.1.4

For T< T_c the above behavior does not hold well.
2. SPONTANEOUS POLARIZATION: - In the temperature below $T_c$ ($T<T_c$), the materials become spontaneously polarized, (i.e., an electric polarization develops in it without the application of an external field). Thus at $T_c$, a phase transition occurs. Above $T_c$ the substance is in paraelectric phase in which elementary dipoles are randomly oriented and below $T_c$, the dipoles interact with each other. Their interaction gives rise to an internal field, which lines up the dipoles. Thus the process of spontaneous polarization ($P_s$) arises. This polarization increases gradually as the temperature is lowered [26] as shown in figure 1.5.
3. HYSTERESIS LOOP: - Characteristic of a ferroelectric substance is that the polarization is not fixed in a certain definite direction of the crystal, when a sufficiently strong electric field is applied, the polarization direction can be reversed. Then, crystal polarization shows hysteresis loop in alternating fields. In Fig.1.6, a polarization versus electric field curve is obtained. Ferroelectric hysteresis loop is quite similar to B-H curve of the ferromagnetic materials [27].

Figure 1.6 Typical Hysteresis Loop of Ferroelectrics

When electric field is zero, the polarization of the whole material is zero. When electric field is applied, electric polarization grows in the field direction. At a very high electric field, the polarization attains maximum value and becomes saturated. This value of polarization is called saturated polarization [28]. At this stage if we decrease the field, the polarization curve does not retrace its growth curve but retains larger values. This value is remnant polarization (Pr). when direction of field is changed, it increased. Then polarization decrease and goes to zero at field $E_c$ (coercive field). If the field is increased in opposite direction, the polarization becomes saturated in reversed direction. If now field is again reversed the polarization follows the path as shown in
figure gets a close curve called hysteresis loop [29]. For a ferroelectric material, the essential feature observed hysteresis curve is below $T_c$.

1.5 FERROELECTRIC DOMAINS

In general, uniform alignment of electric dipoles occurs in a certain region of a ferroelectric crystal. These regions are called the ferroelectric domains and the boundary between two domains is called the domain walls. Domain walls are characterized by the angle between the directions of polarization on either side of the wall. Generally domains are formed to reduce the energy of the wall, which changes with direction.

When applying the weak electric field on the ferroelectric crystal, rotation of electric dipoles will change in the direction, leading to the rotation of the ferroelectric domains. When a strong electric field is applied the rotation of electric dipole is occurred in the first step, and the domain which are aligned in the direction of electric field has the maximum area and the domain which has the direction opposite to the electric field gets minimized. [30].

1.6 PROPERTIES OF FERROELECTRICS

(a) PIEZOELECTRICITY : - The word piezo is a Greek word meaning pressure; piezo- electricity means pressure electricity [31]. The production of electric polarization by the application of mechanical stresses can take place in some dielectric materials. This effect is called piezoelectricity. All ferroelectric materials are piezoelectric but all piezoelectric materials are not ferroelectric. The best known piezoelectric material is quartz which is non-ferroelectric.

(b) PYROELECTRICITY :- The production of electric polarization by the application of thermal stresses can take place in some dielectric materials such as quartz, tourmaline
etc. Heating or cooling develop bound charges such that one end becomes positively charged and other negatively. The pyroelectric property like piezoelectricity is solely determined by the symmetry properties of crystals. All pyroelectric crystals are piezoelectric but converse is not true [32].

1.7 PHASE TRANSITION

Phase transition is the transformation of a material from one thermodynamic phase to another, which is accompanied by an abrupt/slow change of certain physical properties of the substance on continuous change of external parameters. The value of temperature, pressure, or some other physical quantities, at which the phase transition occurs, is referred to as the transition point.

The crystal structure of many dielectric materials change with temperature (i.e., they undergo a phase transition). The phase transitions in crystals are due to the change in the forces of interaction between atoms in crystals. This change may produce various new properties in the crystal. The phase transition that produces or alters the spontaneous polarization is called ferroelectric phase transition. By changing temperature or pressure, the atomic arrangements in the crystals may be changed without any change in chemical composition. The difference in crystal structure on either side of $T_c$ may be large or small. The higher temperature phase with higher symmetry generally transforms to lower temperature phase with loss of some symmetry elements. Usually phase transition can be classified into two categories, first and second order. In first order phase transition, entropy, volume, polarization and structural parameters of a crystal (i.e., atomic position, thermal vibration and lattice constants etc.) change discontinuously at the transition point. In the second order transition, these parameters do not change
continuously at the transition point, whereas the temperatures derivatives of the above parameters show discontinuity. Ehrenfest [33] first defined the kind (order) of transition \( (T_1) \) and according to his definition an \( n^{th} \) order transition is a transition where the \( (n-1)^{th} \) derivative of Gibbs free energy \( (G) \) is continuous while the \( n^{th} \) derivative shows discontinuity at the transition temperature. Landau explained the ferroelectric phase transition by means of thermodynamical theory. This theory is known as Landau theory of phase transition [34]. A thermodynamical theory explaining the behavior of a ferroelectric crystal can be obtained by considering the expansion of the free energy as a function of the polarization \( P \). Accordingly the Landau free energy \( F \) can be written as

\[
F (P, T) = \frac{1}{2} \alpha P_s^2 + \frac{1}{4} \beta P_s^4 + \frac{1}{6} \gamma P_s^6 + \ldots \ldots (1.6)
\]

\[
\frac{\partial F}{\partial T} = \alpha P_s + \beta P_s^3 + \gamma P_s^5 + \ldots \ldots (1.7)
\]

The coefficients \( \alpha, \beta, \gamma \) depend, in general, on the temperature. The series does not contain terms in odd powers of \( P_s \) because the free energy of the crystal will not change with polarization reversal \( (P_s \rightarrow -P_s) \). The phenomenological formulation should be applied for the whole temperature range over which the material is in the paraelectric and ferroelectric states.

The equilibrium polarization in an electric field \( E \) satisfies the condition,

\[
\frac{\partial F}{\partial P_s} = E = \alpha P_s + \beta P_s^3 + \gamma P_s^5 + \ldots \ldots (1.8)
\]

To obtain the ferroelectric state, the coefficient of \( P_s^2 \) term must be negative for the polarized state to be stable, while in the paraelectric state it must be positive passing through zero at some temperature \( T_0 \) (usually called as Curie-Weiss temperature), leading to,

\[
a = \frac{(T-T_0)}{\varepsilon_0 C} \ldots \ldots (1.9)
\]
Where \( C \) is taken as a positive constant called the Curie-Weiss constant. The value of \( T_0 \) may be equal to or lower than the actual transition temperature \( T_c \) (Curie temperature).

The first or second order phase transition can also be explained with the help of the order parameter \( \eta \). In first order phase change, \( \eta \) changes from a finite value to zero abruptly at the transition temperature whereas in 2\textsuperscript{nd} order it changes continuously as shown in figure 1.7(a). Spontaneous polarization (\( P_s \)) and dielectric permittivity (\( \varepsilon_r \)) show anomalies at phase transition. The typical changes are depicted in figure 1.7(b) in 2\textsuperscript{nd} order phase change and in Figure 1.7(c) for first order phase transition.

If \( \eta \) approaches to zero from some finite value over a small range of temperature around \( T_c \), the transition is of second order. The schematic representation of temperature dependence of order parameter (spontaneous polarization process), physical properties (Permittivity) for the first and second order phase transitions are shown in Fig.1.7.

Depending on the temperature variation of dielectric constant or the Curie constant \( C \), ferroelectric materials are broadly divided into two groups:

- Soft ferroelectrics (KDP-type).
- Hard ferroelectrics (BaTiO\(_3\)-type).
The phase transition in soft (H-bounded) ferroelectrics is of order-disorder type while for hard ones (i.e., BaTiO$_3$) it is of displasive type. The ferroelectric phase transition of barium titanate was discovered 1946 [35]. In the earlier literatures, the phase transition was considered to be displasive for most of the ferroelectric materials that were microscopically non-polar in the paraelectric phase. However, materials in macroscopic or thermally arranged sense as non-polar were considered to undergo order-disorder type of phase transition [36]. This classification is practically equivalent to that based on the existence of permanent or induced dipoles in the non-polar phases of the crystal. The nature of phase change (i.e., order, disorder/displasive can be understood on the basis of the structural investigations. In some cases, however, this information is already available from the results of dielectric investigations [37].

On the basis of temperature dependence of dielectric constant, and the value of the Curie constant, it is observed that ferroelectrics are classified into two groups; (i) compounds having the Curie constant $\approx 10^3$ belong to the order-disorder type and, (ii) those which undergo displasive type of transition, with Curie constant $\approx 10^5$.

The phase transition in soft ferroelectrics involves not only the ordering of the disordered hydrogen atoms, but also the deformation of the atomic groups like SO$_4^{2-}$, ScO$_4^{2-}$ and PO$_4^{-3}$ [38]. In case of displacive type of transition, a small atomic displacement of some of the atoms is mainly responsible for the phase transition, which has been observed in some of the perovskites [39]. However, the difference between displacive and order –disorder type of transition becomes uncertain when the separation of relevant disorder become comparable to the mean thermal amplitude of those atoms [40].
The characteristics of ferroelectrics are represented in terms of the dynamics of the phase transition. Cochran [41] suggested the most general theory of ferroelectric phase transitions based on Lyddane-Sachs-Teller (LST) relation [42].

\[ \frac{\omega_{1,o}^2}{\omega_{TO}^2} = \frac{\varepsilon(0)/\varepsilon(x)}{\varepsilon(\infty)/\varepsilon(0)} \] ..........................(1.10)

Where \( \omega_{TO} \) and \( \omega_{1,o} \) are the frequencies of transverse and longitudinal optic modes respectively and \( \varepsilon(x) \) and \( \varepsilon(0) \) are the high frequency and static dielectric constant respectively. This LST relation predicts an anomaly in the lattice vibration spectrum of ferroelectrics at the transition temperature [43]. In a ferroelectrics crystal, if the value of \( \varepsilon(0) \) is high corresponding \( \omega_{TO} \) become very low. In case of second order phase transition, \( \varepsilon(0) \) follows the Curie-Weiss law (i.e., \( \omega_{TO}^2 \propto (T-T_0) \)). As the phase transition temperature approaches from above or below, \( \varepsilon(0) \) diverges and \( \omega_{TO} \) becomes zero. The ferroelectric phase transition could be regarded as instability of the crystals for a particular normal mode of vibration, often referred to as soft mode. But in case of first order phase transition, \( \omega_{TO} \) is not zero at the transition temperature.

1.8 DIFFUSE PHASE TRANSITION: - The transition temperature in many macroscopic homogeneous materials is not quite sharply defined. The transition is smeared over certain temperature interval known as Curie range, resulting in the gradual change of physical properties. The width of the Curie region depends on compositional fluctuation and sensitivity of the Curie temperature to composition change. This type of phase transition is generally known as” Diffuse Phase Transition” (DPT). Though this phenomenon is observed in several types of materials [44] the most remarkable example of DPT was found in ferroelectric materials [45]. Ferroelectricity with diffuse phase transitions (DPTT) was first reported [46] and their extensive studies were carried out in
different systems [47]. Some of the characteristics of ferroelectric diffuse phase transitions are:

- Broadened maxima in the permittivity – temperature curve.
- Gradual decrease of spontaneous polarization with rise in temperature.
- No Curie-Weiss behavior in a certain temperature interval above the transition temperature.
- Relaxation behavior of dielectric properties in transition region and,
- Transition temperature obtained by different techniques does not coincide.

The diffuseness of the phase transition is assumed to be due to the occurrence of fluctuation in a relatively large temperature interval around the transition. Usually, two kinds of fluctuation are considered:

(a) Compositional fluctuation and, (b) Polarization (structural) fluctuation.

From the thermodynamic point of view, it is clear that the compositional fluctuation is present in ferroelectric solid-solutions, and polarization fluctuation is due to the small energy difference between high and low temperature phase around the transition. Kanzig [48] observed from X-ray diffraction that in a narrow temperature range (around the transition) BaTiO₃ single crystal splits up into ferroelectric (FE) and paraelectric (PE) micro-regions. According to Fritsberg [49], substances of less stability are expected to have a more diffuse phase transition. For relaxer as well as other FDPT the width of the transition region is mainly important for practical applications. Smolenkii [50] and Rolov [51] introduced a model based on Gaussian distribution to calculate diffusivity of DPT (due to compositional and polarization fluctuations). Diffuse phase transition was also
studied by Smolenskii- Isupov theory [52] and the results are compared with those of experimental findings.

1.9 FERROELECTRICS WITH OXYGEN OCTAHEDRAL

One of the most important group of ferroelectrics is the family of oxygen octahedral consisting of one or more component oxides. A common feature of all these materials is BO₆ octahedral building blocks [53] although the materials may have different crystal structures, electrical and mechanical properties. The family of oxygen octahedral ferroelectrics has four basic structures, namely

- Perovskite type ferroelectric
- Tungsten-Bronze type ferroelectrics
- Layer structure oxides and complex compounds
- Pyrochlore-type ferroelectrics

1.10 APPLICATION OF FERROELECTRIC MATERIALS

1. The dielectric constant of ferroelectrics is very high and so they are used in manufacture of small size high capacity capacitors.

2. Piezoelectric acoustic transducers and pyroelectric infrared detectors are the devices based on ferroelectrics.

3. The electrooptic characteristics of ferroelectrics such as BaTiO₄ and KDP have been used for modulating and deflecting laser beams inside and outside the optical cavity.

4. Ferroelectric films are used in non-volatile memories, integrated optics, electro optic displays, micro transducers and capacitors fabricated in a film from [54].
5. Ferroelectric crystal exhibit the property of piezoelectricity. Hence they are used as transducer (i.e., in devices used to convert electrical energy into mechanical energy). They are used in the construction of crystal microphones.

6. Ferroelectric crystals, also exhibit application of temperature. Using this property these are used as IR sensors and detectors.

7. The property of hysterersis makes it possible to use them as memory devices for computer, actuators micro transducer and capacitors fabricated in a film form. Other applications of ferroelectrics are exploiting the electrostrictive effect, positive temperature coefficient of resistively, and stress-induced dipoling.
REFERENCES


[33] Ehrenfest, Phase Transition in Ferroelectrics (1950).


