Chapter I: 
Introduction to 
Ferroelectrics and their classification
1.1 Introduction.

About 80 years ago, Rochelle salt (Sodium Potassium Tartarate tetra hydrate Na KC₄H₄O₆ 4H₂O) showed a peculiar phenomenon of 'Ferro electricity'. Also Joseph Valesek [1] observed the phenomenon of Ferro electricity in Rochelle salt from the measurement of its dielectric properties. The concept was later generalized [2,3] and the term 'ferric' was used to describe all materials that exhibited one or more phases showing a twin or a domain structure in which the individual domain states would be re-oriented by an applied magnetic field, electric field or electric stress field or combinations of such fields. The nomenclature, 'Ferroelectricity' is the consequence of phenomenological similarity with ferromagnetism. At first, the complicated structure of Rochelle salt was thought to be the reason for this; but this impression gradually vanished with the discovery of similar phenomenon in a series of Phosphates and Arsenates among which the best example is potassium Dihydrogen phosphate (KH₂PO₄) generally abbreviated as KDP [4,5].

Research activity in theoretical and experimental aspects increased with the inclusion of BaTiO₃ in the list of ferroelectric materials [6]. First systematic attempt to compile the list of ferroelectrics was carried out by Jona and Shirane [2]. Which includes 76 ferroelectric materials known up to 1961. The comprehensive compilation of ferroelectrics and antiferroelectrics with the inclusion of solid solutions known up to 1968 in London-Bornstein Table was
given by Mitsu et al [7]. Galasso [8] provided with the details regarding structural and property data on a large number of perovskite type compounds. The compilation provides an excellent source of data on the spontaneous polarization at the specified temperature and the Curie temperature of ferroelectric and antiferroelectric materials. A list of known ferroelectric and antiferroelectric materials was given by Subba Rao [9] with the updating program in 1977 and it consists of total of 368 ferroelectrics [10].

1.2 Characteristic Properties of Ferroelectrics

When an electric field, \( E \) is applied to an insulator, polarization is induced into it, which forms an important parameter in the theory of insulators and hence when polarization is being investigated, dielectrics are included into this category [11]. Classification of these materials based on their response in a realizable range of an electric field gives two types of dielectrics, linear and nonlinear. From the theory of linear dielectrics, as the nomenclature shows, the electric polarization \( P \) varies linearly with the applied electric field \( E \), whereas it varies inversely in the case of nonlinear dielectrics and the ferroelectric materials fall into the later category which can exhibit spontaneous polarization \( P_s \). Spontaneously polarized regions in ferroelectrics are known as domains. A suitably directed external electric field can be used to bring about a transformation from one state to another, which is a characteristic of ferroelectrics. Pyroelectric materials, which are very closely related to
FIG. 1.1 SCHEMATIC CIRCUIT FOR THE OBSERVATION OF FERRO-ELECTRIC HYSTERESIS LOOPS (Jona and Shirane, 1962)

FIG. 1.2 SCHEMATIC CIRCUIT FOR THE OBSERVATION OF FERRO-ELECTRIC HYSTERESIS LOOPS (Jona and Shirane, 1962)
ferroelectrics, result from the interaction between thermal and electrical forces and form a suitable source of research, as the re-orientation of domain structure with an applied electric field as in the case of ferroelectrics is not feasible in pyroelectrics. Thus, spontaneous polarization $P_s$ and its reversibility are the most fundamental properties of the ferroelectric crystals. It is measured in terms of displacement per unit volume. The Sawyer and Tower circuit [12] as shown in Fig. 1.1 proved to be the best method for observing the hysteresis loop on the cathode ray oscilloscope screen and measuring the spontaneous polarization experimentally. The usual hysteresis loop is schematically shown in Fig. 1.2. In this figure spontaneous polarization $P_s$ (OE) is given by the extrapolation from saturation region to the zero field. The intercepts made by the hysteresis loop on the $P$-axis and the $E$-axis indicate the remnant polarization, $P_r$ (OD) and coercive field, $E_c$ (OF) respectively. The intercept OG represents the total polarization of the ferroelectric material in the saturation field, $P_{sat}$. Other methods, which are used, commonly for measuring the magnitude of spontaneous polarization, $P_s$, are charge integration technique and pyroelectric measurement using calibration for scaling [13].

The spontaneous polarization, $P_s$, in ferroelectric materials generally vanishes at a certain temperature termed as transition temperature or Curie temperature ($T_c$). As a rule, the low temperature phase is polar and possesses a lower symmetry as compared to non polar phase above $T_c$. Generally all
materials are characterized by only one transition temperature above which \( P_s \) is zero. Exception to this general rule is Rochelle Salt, which has two transition temperatures, upper = 24°C and lower = -18°C and its polar phase is only stable in the temperature range between 24°C to -18°C. From this example, one may conclude that the experimental limitations could be the main hurdles for finding the lower \( T_e \) for majority of materials and its existence cannot be ruled out. Almost all the properties of ferroelectric materials such as dielectric, thermo-optical, etc.; exhibit pronounced variation in the neighborhood of \( T_c \).

The properties exhibited by most of the ferroelectric materials are enlisted below:

1. They exhibit dielectric hysteresis loop between polarization and the applied electric field, below Curie temperature \( T_c \).
2. They have ferroelectric domain structure, which may be visible in polarized light.
3. They have a high relative permittivity along the polar axis, which is a function of temperature. Above the Curie temperature, \( T_c \), it falls off obeying Curie-Weiss Law, which is given by

\[
\varepsilon = \frac{C}{T - T_0}
\]

Here \( T_0 \) is the Curie-Weiss temperature, which is equal to \( T_c \), only for the cases of continuous transition, and \( C \) is the Curie constant.
4. They possess a pseudo-symmetric structure belonging to polar class.

5. They undergo a transition at the Curie temperature to form a structure of higher symmetry.

6. The Curie temperature is generally raised by the application of biasing field or the hydrostatic pressure.

7. They exhibit piezoelectric and pyroelectric properties below $T_c$.

8. There is a sudden appearance of surface charges at the transition.

1.3 Classification of Ferroelectrics.

The fundamental property of a ferroelectric crystal is that it exhibits one or more ferroelectric phases in a realizable range of temperature and pressure. The crystal in ferroelectric phase is spontaneously polarized and the polarization has more than one possible equilibrium orientation. To establish ferroelectricity, it must be demonstrated that the polarization can be re-oriented between orientation states by a realizable electric field. Ferroelectrics, classified on symmetric grounds [14], defined a prototype symmetry from which the spontaneous deformation parameters of the domain states could be unequivocally deduced. In ferroelectric crystals, a similar definition of the prototype is applicable since spontaneous strain has no meaning without reference to the prototype form.
As far as the ferroelectric crystals are concerned, electric polarization \( P \) is the fundamental parameter that characterizes the phase transition into the ferroelectric form; whereas elastic, piezo-electric, optical and thermal changes that occur may be regarded as essentially secondary consequences of the appearance of the nonzero vector \( "P" \). For example; \((\text{Gd}_2\text{MoO}_4)\), \([\text{Gd}_2(\text{NH}_4)_2\text{SO}_4]_3\). These are useful for pyroelectric imaging applications as the spontaneous polarization in these types of crystals is not a function of temperature and is not accompanied by high dielectric permittivity.

i) Perovskites

Barium Titanate was the first perovskite type compound shown as ferroelectric and is till todate the most thoroughly investigated ferroelectric material. \( \text{TiO}_6 \) Octahedra , forms the basic cell of Barium Titanate, which determines its dielectric properties because of its high polarizability. The small \( \text{Ti}^{4+} \) ions, having more space with oxygen octahedra are the cause for this high polarizability. For example; materials belonging to this group include solid solutions of \( \text{PbZrO}_3 - \text{PbTiO}_3 \) and \( \text{Pb} (\text{Mg}_{1/3}\text{Nb}_{2/3})_3 \text{O}_3 \).

ii) Tungsten-Bronze Family

The ferroelectric materials include bronze compounds like lead meta niobate \( (\text{PbNb}_2\text{O}_6) \) and lead meta tantalate \( (\text{PbTa}_2\text{O}_6) \) in which, the bronze form has a meta stable structure at room temperature. The stabilization of
the bronze structure seems to be possible with a certain degree of disorder, as the bronzes usually appear as solid solutions of at least two components. Apart from $\text{PbNb}_2\text{O}_6$ and $\text{PbTa}_2\text{O}_6$, other compounds of interest are $\text{Ba}_x\text{Sr}_{1-x}\text{Nb}_2\text{O}_6$ and $\text{Ba}_2\text{NaNb}_3\text{O}_{15}$. Meta niobate is still widely used in poled ceramic form as a low Q piezo-electric transducer; $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Nb}_2\text{O}_6$ composition in single crystal form, in pyroelectric detectors and $\text{Ba}_2\text{NaNb}_3\text{O}_{15}$ and similar derivative compositions for their very high non-linear optical properties.

iii) Tungsten-Bronze Structure.

Hagg and Magneli [18] determined the structure of Tungsten-Bronze by using X-ray technique and found that it had a tetragonal symmetry as shown in Fig 1.3. The ferroelectric tungsten-bronzes were also found to be transparent falling in the visible range having tetragonal symmetry and hence the name tetragonal tungsten-bronzes. These tungsten-bronze structure ferroelectrics show metallic luster contrary to the cubic tungsten-bronzes and are related to the non-stochiometric phases $\text{Na}_x\text{WO}_3$ and $\text{K}_x\text{WO}_3$ [15,16,17].

The general chemical formula is $[(\text{A}_1)^{\text{VI}}]_2 [(\text{A}_2)^{\text{VII}}]_4 [(\text{C})^{\text{VI}}]_4 [(\text{B}_1)^{\text{IV}}]_2 [(\text{B}_2)^{\text{VI}}]_8 [(\text{O})^{\text{VII}}]_{30}$ in which $\text{A}_1,\text{A}_2$ and $\text{C}$ are 12-,15- and 9- fold coordinated interstitial sites in the crystal structure surrounded by oxygen.
Fig. 1.3. Tungsten Bronze type structure projected on (001) plane.
anions. The B1 and B2 sites are 6-fold co-coordinated interstitial sites inside oxygen octahedra with the only difference being that the B2 oxygen octahedra has larger distortion in shape. In fact there are five different oxygen sites, distinguishable by the number and variety of surrounding cations [18]. In the prototype symmetry, the unit cell is only one octahedron high (~0.4 nm) in the C-direction with \( a = b \) dimension of typically 1.25 nm \([(10 C)^{1/2}]\).

The chemical formula can be treated as \([Al_{1.5} A2_{2.5} C_{2.5} BO_3]_0\) as this is the composition of a primitive unit cell in which ten BO6 octahedra are linked by their corners in such a fashion as to form three (A1:square, A2: pentagonal and C: triangular) different types of tunnels running through the structure parallel to the C-axis (Lines and Glass)[10]. These three types of interstitial sites can accommodate a large variety of metal atoms. A1 and A2 sites can be occupied by large monovalent, divalent or trivalent ions; the small c-site may be vacant or occupied by very small ions eg. lithium; two different B-sites (B1, B2) are usually occupied by smaller, highly charged cat ions such as Nb, Ta, W or Ti [19,20,21]. The distinction between the structure of Perovskites and the long chains of oxygen octahedra along the c-axis is that the structure consists of puckered sheets of oxygen atoms in planes perpendicular to the (001) direction.
Among the numerous individual ferroelectric complex compounds of the Tungsten-bronze structure and a large number of possible solid solutions between those and members, only two ferroelectric forms are reported [22], namely; orthorhombic (point group 2 mm) and tetragonal form (point group 4 mm). From the above known ones, the popular one is tungsten-bronze and lead meta niobate \((\text{PbNb}_2\text{O}_6)\) and lead meta tantalate \((\text{PbTa}_2\text{O}_6)\) [23,24], form the simple compounds with tungsten bronze structures. The ferroelectrics discussed so far have the bronze structure in the meta stable structure at room temperature [25]. Ferroelectrics with tungsten bronze structure are stable at room temperature and are solid solutions of at least two components in which case neither of the component material itself has a stable tungsten-bronze structure at room temperature [10]. Hence it can be said that, in ferroelectric tungsten-bronzes, charge compensation takes place by ionic rearrangement.

Three different formulae have been deduced for the classification of ferroelectric tungsten-bronzes depending on the occupancies of \(A1\), \(A2\) and \(C\) sites [10].

i) \((A1)_x(A2)_{5-x}\text{Nb}_10\text{O}_{30}\) where \(A1\) and \(A2\) are alkaline earth ions. This is referred to as an incompletely filled structure and a certain degree of randomness is expected as only five out of six \(A1\) and \(A2\) sites are filled and \(C\) sites are empty. ex. \(\text{Sr}_{5,x}\text{Ba}_x\text{Nb}_{10}\text{O}_{30}\).
ii) \((A1)_{4-x}(A2)_{2-2x} Nb_{10} O_{30}\) where \(A1\) and \(A2\) are alkaline earth and alkali ions respectively. Here both \(A1\) and \(A2\) sites are completely filled and the \(C\) sites are completely empty. ex. \(Ba_{2-x}Na_{2+4x}Nb_{10}O_{30}\).

iii) \((A1)_{6-x}(A2)_{4+x} Nb_{10} O_{30}\) where \(A1\) and \(A2\) are alkali ions.

iv) Ex. \(K_{6-x}Li_{4+x}Nb_{10} O_{30}\) here all the \(A1,A2\) and \(C\) sites are expected to be filled with small Li ions in the \(C\) sites and this is called the completely filled structure.

1.4 Morphotropic Phase Boundary (MPB)

Morphotropic Phase Boundary (MPB) is used to denote an abrupt structural change in a solid solution with variation in the composition but nearly independent of temperature Jaffe Cook and Jaffe 1971 [11]. MPB composition usually refers to a specific composition that is a two-phase zone, where the two phases are considered to be in equal quality.

A critical variation in the composition between ferroelectric phases may lead to the instability of the ferroelectric phases, which can be linked to the occurrence of MPB. Expectations are that even though the phases that are separated differ slightly in composition, they are energetically very similar. The mechanical restraints to preserve one phase against another may very well be relaxed, i.e.; softened because of the structural instability.
Therefore, many properties will be either greatly enhanced or suppressed near the MPB compositions. As an example, the remnant polarization $P_r$ may increase either due to the increase in magnitude of displacement or in number of possible displaced directions. The crystallographic structure may get softened due to the impending phase change, which may result in the decrease of $C_{ijkl}$ in the case of elastic stiffness. Although the individual magnitude of physical properties will depend on the symmetry and chemical compositions of each phase next to MPB, the basic behavior mentioned above will be similar. The phase transition in morphotropic can occur at a temperature much lower than the Curie–Weiss temperature and hence preserve high dielectric constant through phase transitions which is in contrast to the case of ferroelectric to paraelectric phase transition, where the phase transition is a function of temperature and the physical properties such as dielectric constant and polarization change drastically with temperature. This feature is of utmost importance, particularly in electro-optic applications.

MPB separating ferroelectric tetragonal (4 mm) and rhombohedral (3 mm) phases, in different lead compositions for, ex.; 1. Pb (Zr, Ti) O$_3$ (PZT) [27,28], 2. Pb (Sn, Ti) O$_3$ [29], 3. Pb (Zr, Sn, Ti) O$_3$ [29], 4. (Pb, Ba)(Ti, Sn) O$_3$ [30], and 5. Pb (Hf, Ti) O$_3$ [29] revealed several properties as given below [11].
Dielectric Constant \((k)\), Piezoelectric Coefficient \((d)\), Electro-mechanical planar coupling factor \((k_p)\), Electrical constant \(Q\) and Mechanical constant \(Q_m\) achieve their highest values just on the tetragonal side of the MPB, whereas, on the other hand, coefficient ‘\(g\)’ \(\left[ g = \frac{d}{k \varepsilon_0} \right]\) \(\text{Vm / N}\) and the remnant polarization \(P_r\), maintain their high values onto the rhombohedral phase. Also, the elastic modulii \(\left( \frac{1}{S_{i,j}} \right)\) have minimum values at the MPB. Applicationswise, these compositions prove their candidature because of anomalous high dielectric and piezoelectric properties observed for these compositions near the MPB. Tungsten-bronze solid solution families show a peculiar property which is slightly different from the MPB discussed above wherein the MPB separates two ferroelectric phases with mutually orthogonal polarization directions. Most probably \(\text{Pb}_{1-x} \text{Ba}_x \text{Nb}_2\text{O}_6\) has been the first recognized MPB composition. Later numerous such possibilities for the MPB systems within the TB ferroelectric family have been found because of the inherent flexibility of the Tungsten-Bronze crystal structure in comparison to the more limited flexibility found in other crystal structures. Oliver et al [31] in 1989 exploited the possibility of the MPB in a number of binary, ternary or quaternary solid solutions of Tungsten-Bronze ferroelectrics.

Advantage of MPB composition TB family over perovskite family may be due to lower prototype point of TB \((4/mmm)\) compared with the
cubic prototype point symmetry of perovskite (m3m). Several other advantages that arise are:

(i) There are only two independent modes of polarization confined to either parallel or perpendicular to the uniaxial direction (001) hence the domain patterns are markedly simplified and there are no 90° domain walls in ferroelectric tetragonal phase[32].

(ii) Larger family of electro-optic coefficient can be chosen for different applications, e.g. the utilization of quadratic electro-optic coefficient in the high temperature paraelectric phase [31] and the larger $d_{15}$ for shear mode piezoelectric transducer applications [33].

The open structure of tungsten bronze that can make for a large variety of ion substitution for tailoring the crystal properties to meet different applications, stands for the remaining advantages [15,16]. One of the unique advantage of the existence of the MPB in tungsten bronze is the mutually perpendicular polarization vector, which could be of various potential device applications.

1.5 Dielectric properties of ferroelectrics

Dielectrics have been primarily used in capacitors and as electrical insulators. The polarization effect, which occurs due to displacement of charges within the material through the progressive orientation of permanent
of induced dipoles when subjected to electric field, is important in dielectric. Relative permittivity \( (\varepsilon_r) \), which is referred to as a quantitative measure of displacement or charge effect of the material has a characteristic value for each material. The permittivity is a measure of ease with which polarization is produced in a material and is defined as the ratio of the permittivity \( \varepsilon \) of the dielectric to the permittivity of empty space \( \varepsilon_0 \).

\[
\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{\varepsilon}{1.2}
\]

The relative permittivity \( \varepsilon_r \) of the dielectric material depends on several factors such as temperature, frequency bonding crystal structure phase constitution and defects. All these factors influence the response of the induced or permanent electric dipoles in the dielectric to a static or alternating electric field. The dielectric loss is another parameter of great concern in dielectrics which occurs due to lagging with applied as well as electron and ion migration. A good dielectric material exhibits high relative permittivity and dielectric loss.

The dielectric constant in the ferroelectric phase consists of two components. Firstly, the component in the dielectric constant due to individual domains, which is independent of the frequency of the electric field, generally up to far infrared frequencies. The second component is due
to the domain wall motions that is to partial reversal of the spontaneous polarisation. The process can give rise to dielectric losses and is dependent strongly on the frequency the electric field strength the domain structure and temperature.

In ferroelectrics the permittivity is raised to very high value at Curie point $T_c$ (Curie transition temperature) and the above $T_c$ the dielectric behavior is governed by the simple law as Curie–Weiss law (Ref. Eq 1.1)

The following are some important points regarding the ferroelectric ceramics based on the thermodynamical model suggested by Yurkevich and Rolov [34].

1. The ferroelectric Curie temperature $T_c$ or the temperature for $\varepsilon_{\text{max}}$ of ceramic material strongly depends upon the grains in it the presence of pores and the micro volume in homogeneity it.
2. The Curie–Weiss constant has a value higher than that of the single crystal and depends on the dimension and density of pores in ceramics.
3. The temperature for maximum $\tan \delta$ does not coincide with the temperature correspond to $\varepsilon_{\text{max}}$ in some ceramic materials.
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