1. INTRODUCTION

A brief introduction to the classification of dielectrics phenomena of ferroelectricity, piezoelectricity, classification of crystal systems, interrelationship between the piezoelectric and subgroups with respect to symmetry of crystal structure are presented in this chapter.

1.1 DIELECTRICS

Dielectrics are a class of materials which are insulators in which polarization plays a significant role. The polarization can occur by four different mechanisms. The first one is the electronic polarization, $P_e$, which arises from a displacement of the centre of the negatively charged electron cloud relative to the positive nucleus of an atom by the electric field. It can be investigated through optical methods. This effect occurs in materials, but the magnitude is very small. The second one is ionic polarization, $P_s$, which originates from the relative displacement or separation of cations and anions from each other in an ionic solid. The third contribution is the orientation polarization, $P_o$, which is found only in materials with permanent dipole moments. This mechanism is generally uncommon in ceramics because most of the permanent dipoles cannot be reoriented without destroying their crystal structure. But it is observed in several hundreds of perovskite ferroelectric ceramics with non-cubic or distorted structures. The last one, $P_s$, is the space charge polarization. This type of polarization results from the build-up of charges at interfaces of heterogeneous systems. Depending on the local
conductivity, the space charge polarization might be occurring over a wide frequency range from mHz up to MHz. The summation of four possible components of polarizability is given by the following equation:

\[ \psi = \psi_{\text{electronic}} + \psi_{\text{ionic}} + \psi_{\text{orientation}} + \psi_{\text{space charge}} \]

The relationship between polarisation (P) and electric field (E) is given by:

\[ P = (\varepsilon_r - 1)\varepsilon_0 E, \quad \text{Where} \quad \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \]

Dielectric loss is the energy loss that goes into heating a dielectric material in a varying electric field. In an ideal capacitor of an ac circuit, the current leads the voltage by 90°. In a real capacitor, there are always some losses, resulting in a phase shift of, δ, where the current leads the voltage by a smaller angle of 90-δ degrees. The phase shift is commonly called the loss angle (δ) and the dielectric loss is defined as the tangent of the loss angle (tanδ).

Generally on the base of the magnitude of dielectric constant and loss dielectrics can be broadly classified as follows [1]:

1.2. FERROELECTRICITY

Some crystals by virtue of their symmetry possess a built-in spontaneous polarization that can be reversed by an applied electric field. By analogy with ferromagnetics such crystals are called ferroelectric even though iron is seldom a constituent. The most outstanding feature of a ferroelectric material is its hysteresis loop which describes the behavior of non-linear polarization (P) as a function of field (E). Fig.1.1 (a) illustrates a typical hysteresis loop. For small field applied to an initially un polarized specimen the P-E relation is linear, but as the field strength increase, the field influences some domains
to align their direction of polarization eventually leading to saturation. When the field is reversed the material still exhibits a remnant polarization \( P_r \) even at zero field. A reverse field is required to reduce \( P_r \) to zero and the field necessary to bring the remnant polarization to zero is called the coercive field. For a given ferroelectric material ferroelectricity is exhibited only below a specific temperature, \( T_C \), called the Curie temperature, characteristic of the material. Above this temperature, thermal agitation is sufficient to destroy the cooperative ordering of the dipoles that gives rise to spontaneous polarization and the material becomes paraelectrics. Near the Curie point the material exhibits highest dielectric constant when measured as function of temperature which is shown in the Fig.1.1(b). Above Curie temperature, \( T_C \), the curve usually follows a Curie-Weiss law. The corresponding variation of polarization as a function of temperature is depicted in Fig.1.1(c). The transition from ferroelectric to paraelectric change is essentially an order-disorder change and such a transition is always accompanied by a change of crystal symmetry unlike in ferromagnetic. For example, Barium titanate undergoes a tetragonal to cubic phase transition at the Curie temperature 120°C. Proper history of ferroelectrics has been documented in reports [2-3]. Several hundred ferroelectrics have been reported since the discovery of the first ferroelectric almost ninety years ago [4]. Based on the magnitude of Curie constant, ferroelectrics can be classified in to three groups [5].
Figure 1.1 Variation of (a) polarization as a function of applied field (b) relative permittivity versus temperature (c) polarization versus temperature for a typical ferroelectric material with exception of LiNbO₃ which is monoclinic, with $T_c$ increases in the following order perovskite $<$ Tangsten Bronze $<$ Layered perovskite.

In the first group, the Curie-Weiss constant is about $10^5$ and most of the compounds in this family are mixed metal oxides. The second group comprises of materials whose $C$ values are near $10^3$. Ordering of rotatable permanent dipoles in this group takes place at
the transition temperatures. Such dipoles are associated with hydrogen bonds as in KH$_2$PO$_4$ or with molecular groups such as NO$_2^-$ in NaNO$_2$. Most water soluble ferroelectrics are in this category. The third group possesses C values near one and is termed improper ferroelectrics. The best example in this category is Gadolinium Molybdate. Ceramics capacitors of BaTiO$_3$ with dielectric constants in excess of 2000 are made commercially. Apart from oxides of perovskite structure, some oxides belonging to tungsten bronze [6] and layered perovskite [7-8] structures are also found to be ferroelectric with useful properties. Examples of these categories are Barium sodium niobate and lanthanum dititanate respectively. Tungsten bronze type sodium niobate is useful for frequency doubling applications. Layered perovskites which are effective ferroelectric substances with higher Curie temperature and coercive fields, and low dielectric loss are good candidate materials for high frequency applications.

Relaxor ferroelectrics [5,6] are a relatively new class of Pb based complex perovskites, with general formula Pb(B$_1$,B$_2$)O$_3$ where B$_1$ is a low valent cation such as Mg$^{2+}$,Zn$^{2+}$,Ni$^{2+}$,Fe$^{3+}$ etc and B$_2$ is a higher valent cation, eg.Nb$^{5+}$,Ta$^{5+}$,W$^{5+}$ etc. They have been attracting considerable attention in view of their unique physical Properties [9]. A key feature of relaxors is the appearance of a broad temperature and frequency dependent maximum of the dielectric permittivity as well as the absence of long range ferroelectric order in zero fields at any temperature [10]. The high value of the dielectric constant ($\varepsilon$) in a broad temperature range around the peak temperature,$T_{pc}$, make relaxors attractive for various technological applications, [11-12]. Therefore, relaxor ferroelectrics show a
larger working temperature range than normal ferroelectrics in capacitor applications.

The diffuse nature of relaxor ferroelectric transition is believed to be due to the compositional heterogeneity on a microscopic scale.

1.3 PIEZOELECTRICITY

All materials undergo small changes in dimension when subjected to an electric field. If the resultant strain is proportional to the square of the field, it is known as the electrostrictive effect. The polarization, $P$, and stress, $\sigma$, are related to the piezoelectric coefficient, $d$, by $P = d \sigma$. Some materials show the reverse effect. They develop electric polarization when they are strained through an applied stress, i.e. $S = d E$, where $S$ is strain and $E$ is electric field. The most common piezoelectric material is single crystal quartz, which is widely utilized in watches and phonograph pickups.

The symmetry of a given crystal structure determines the existence of piezoelectricity. Among 32 classes of single crystal materials, 11 possess a centre of symmetry and are non-polar materials. For these systems when stress is applied, it leads to symmetric ionic displacements so that there is no net change in dipole moment, consequently they do not exhibit piezoelectric behavior. The other 21 crystal classes are non centro symmetric and 20 of these exhibit piezoelectric effect. Of these only 10 systems show variation of $P$ as a function of temperature, i.e. pyroelectric and the remaining are non-pyroelectric. Among the 10 pyroelectric crystals, only some shows variation of $P$ as a formation of applied electric field i.e. ferroelectric, while the remaining are non-ferroelectric. These all ferroelectrics exhibit piezoelectricity but the converse is not true.
Polycrystalline materials normally do not display a macroscopic piezoelectric effect because the piezoelectric axis of the crystallites are randomly distributed and macroscopically averaged. However, when these oxides powders are compressed and sintered at high temperature they form a compact polycrystalline mass. Such a material would be intrinsically isotropic because its properties would be averaged over all the crystal directions. A polar direction can be developed in a ferroelectric ceramic by means of a strong electric field. A polar direction can be developed in a ferroelectric ceramic preferentially at elevated temperatures by a process called polling. The axis of crystallites is reoriented along that field. A polar axis is thus effectively formulated in the crystal resulting in macroscopic piezoelectricity. Since 1947, when this poling process was first described by (Roberts 1974)[13], a large variety of piezoelectric ceramics have been developed. Comprehensive review of piezoelectric ceramics is given by (Jaffrey et al., 1971) [14]. The suitability of a particular piezoelectric ceramic material for a given application is based on various physical and electrical characteristics. Since piezoelectricity is a tensor property there are several different piezoelectric coefficients that relate the polarization change developed in one dimension of the ceramic to the stress applied in a different direction. A poled ferroelectric ceramic has three non-zero piezoelectric coefficients ($d_{33}$, $d_{31}$ and $d_{15}$ the longitudinal, the transverse and the shear piezoelectric coefficient respectively). By convention the first subscript refers to the measured direction strain. Another important parameter associated with piezoelectric materials for device applications as transducers is effective electromechanical coupling coefficient $K$ defined as follows:
The coupling factors are also tensor quantities, a specific \( K_{ij} \) is associated with each piezoelectric coefficient \( d_{ij} \). The magnitude of the piezoelectric coupling in non-ferroelectric piezoelectric crystal typically is less than 0.1. However, the piezoelectric coupling achieved in ferroelectric ceramics is much higher and it is of the order of 0.4 to 0.9.

The piezoelectric effect of ferroelectric ceramics has vast potential for the development of electrochemical transducers. The piezoelectric transducers are limited to devices involving only very small mechanical displacements and small amounts of electrical charge per cycle. Effective use of piezoelectric ceramics depends on matching the electrical and mechanical impedances of the energy source and the driven load. Application based on piezoelectric effect are given by Burfoot and Taylor [15]. Some important applications of piezoelectric materials with examples are listed in table 1.1.

<table>
<thead>
<tr>
<th>Application of Piezoelectric materials</th>
<th>Examples</th>
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<tr>
<td>a) Gramophone pickup elements</td>
<td>Rochelle Salt, BaTiO$_3$</td>
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<tr>
<td>b) Delay line transducers and sonar application</td>
<td>Quartz, PZT</td>
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c) Wave length modulators, where the electro optic effect is used | BariumSodium Niobates (BNN)
d) Piezoelectric accelerometers | PZT, Lead metaniobates
e) Underwater acoustics | PZT
f) Air transducers (Ear Phones, Hearing aids, Microphones) | Pb(Ti,Zr)O₃
g) High voltage generation (Gas lighters) | BaTiO₃
h) Resonators (for frequency control) | Quartz

1.4. STRUCTURAL DESCRIPTION OF PEROVSKITE TYPE COMPOUNDS

Most of the mixed metal oxides with the general formula ABO₃ have the perovskite structure. Pervoskite is the mineral name for CaTiO₃. The crystal structure of this is which in such the unit cell contains Ti⁴⁺ ions at the body centre and oxygen ions at the centre of faces as shown in Fig 1.2. This cubic structure has retained the name perovskite, even though CaTiO₃ was later determined to be orthorhombic. In the perovskite structure, with general formula ABO₃ the A cation is coordinated with 12 oxygen ions and the B cation with 6. The cation A is therefore larger than the B cation. A perfectly spherical cation in contact with all its coordinating oxygen ions, would give rise to a regular coordination polyhedron with a volume expressed in terms of the relevant centre to vertex distance \((R_A + R_O)\) or \((R_B + R_O)\). For a regular cub octahedron, \(V_A = 10(3x2^{1/2})(R_O + R_A)^2\) and for a regular octahedron, \(V_B = 4/3((R_B + R_O)^3\). Thus the ratio \(V_A/V_B\) in the idealized case is equal to \(5/(2x2^{1/2})\left\{\frac{(R_A + R_O)}{(R_B + R_O)}\right\}^3\), and the
observed values of the $V_A/V_B$ in cubic m3m perovskites requires that $R_A + R_O = 2^{1/2} (R_B + R_O)$. This is the equality which has commonly been used as a stability criterion, for perovskites. The Goldschmidt tolerance factor, $t$, is given by $(R_A + R_O)/2^{1/2} (R_B + R_O)$. For the ideal perovskite structures, $t$ is unity. The perovskite structure is, however found for lower values of $t$ ($0.75 < t \leq 1.0$) also. In such case, the structure distorts to tetragonal, rhombohedral or orthorhombic symmetry. This distortion arises from the smaller size of the A ion which causes a tilting of the BX$_6$ octahedra in order to optimize A-X bonding. (Katz and Ward 1964) have given an alternative description of perovskite structure in terms of close packing of A & O ions [16]. In this model of the ABO$_3$ perovskite structure, close-packed AO$_3$ layers are stacked one over the other with B cation occupying octahedral holes surrounded by oxygen.

Figure 1.2 Cubic perovskite of ABO$_3$ unit cell.
1.5 EFFECT OF SUBSTITUTION IN PEROVSKITE A OR B SITES

Dielectric properties of perovskite type compounds can be modified by suitable dopants at A-sit or B- site in the crystal lattice. For instance in BaTiO$_3$ (BT) one can dope Sr, Pb, Ca etc in the place of A – site as $(\text{Ba}_{1-x}\text{M}_x)\text{TiO}_3$ or also can dope Zr, Sn, Mg etc in the place of Ti giving $\text{Ba}(\text{Ti}_{1-x}\text{M}_x)\text{O}_3$ [17]. By this representation one can effectively change the Curie temperature as well as dielectric constant. The doping effect and thermal treatment in these ceramics lead to changes in physical properties and give wider opportunities for their practical use [18, 19]. A number of reports are taken on the effects of doping on BT that improve their dielectric permittivity, Curie temperature and influence the diffuse phase transitions of ceramic materials. The room temperature resistivity of BaTiO$_3$, can also be reduced to a much lower value by introducing small amounts of trivalent ions (such as Bi$^{3+}$, La$^{3+}$, Y$^{3+}$, etc.) in the place of Ba or pentavalent ions (such as Nb$^{5+}$, Ta$^{5+}$ etc.) in the Ti-site to produce n-type semiconductor[21,22].

Many commercial BT-based multilayer capacitors contain a certain amount of bismuth because of its significant effect on lowering the sintering temperatures [22]. Bismuth is also found to be able to enhance the magnitude of positive coefficients of resistance and dielectric properties [23]. The additives for BaTiO$_3$ transducers, Sr$^{2+}$, lower Tc downward from 130°C, Pb$^{2+}$ used for varying the Tc upward, Ca$^{2+}$ for increasing the temperature range of stability of the tetragonal phase, and Co$^{2+}$ for decreasing the high-electric-field losses without affecting the piezoelectric constants. Depressors, such as $\text{Bi}_2(\text{SnO}_2)_3$, MgZrO$_3$, CaTiO$_3$, NiSnO$_3$, as well as Curie point shifters are added in small (1-
8 wt%) quantities to the base BaTiO$_3$ composition to lower or depress the sharpness of the dielectric constant peak at the Tc, thus giving a flat dielectric constant-temperature profile [19]. In some cases suitable solid solutions leads to the formation of morphotropic phase boundary (MPB) which exhibits enhanced properties compared to the separate components on either side of the compositions. The Morphotropic Phase Boundary (MPB) is considered as the region where the two phases co-exist in the compositions. Thus for instance, PbTiO$_3$ and PbZrO$_3$ show morphotropic phase boundary around Pb(Ti$_{0.48}$Zr$_{0.52}$)O$_3$ which shows a Tc of 230°C, compared to 495°C for PbTiO$_3$. Any ferroelectric material is therefore amendable to changes with proper doping. Even in the case of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$, a morphotropic phase boundary has been reported as a solid solution of BNT with 6 mol % BT, as (Na$_{0.5}$Bi$_{0.5}$)$_{0.94}$Ba$_{0.06}$TiO$_3$ (BNBT). The ferroelectric and piezoelectric properties can be further altered by suitable dopants which forms the basis of this present study.