

PbTiO₃ based FERROELECTRICS

Introduction Background

Throughout history, technology has widely facilitated human development. Each technological innovation has marked an approach to change in human behavior and physical capabilities, which in turn, has allowed for further technological innovations. Materials technology too has exercised an intense impact on the evolution of human civilization. Historians have defined the various time periods in the human history distinctly as the Stone Age, Bronze Age, the Iron Age and Silicon or the Synthetic materials Age. Each era followed by another has been brought about by the invention of even better products. The beginning of the 21st century has already witnessed the emergence of the ‘Smart Materials Age’. It has been categorized by a technological revolution that will exploit several emerging technologies such as materials science, biotechnology, biomimetic, nanotechnology, molecular electronics, and artificial intelligence. By developing state-of-the-art technologies in diverse fields of sciences, today’s engineers, chemists, physicists and materials scientists are devising innovative inter-disciplinary techniques for synthesizing, analyzing, and manufacturing new generations of engineered materials.

Smart materials systems are non-living systems that incorporate the utilities of actuation, sensing, logic, and monitor to respond adaptively to changes in their environment to which they are exposed, in a useful and usually repetitive manner. Smart materials are part of the smart systems-functional materials for a variety of engineering applications. They possess both sensing and actuating functions. Many existing engineering materials can be engaged as sensor and actuator materials if they can be correctly designed. They include piezoelectric ceramics and polymers, shape memory alloys, optical fibers and conductive, etc. Each system can suit specific potential requirements of future smart materials systems. In this chapter, the general features of piezoelectric and ferroelectric materials are discussed. The chapter covers a brief historical introduction which includes the macroscopic and microscopic aspects of ferroelectricity/piezoelectricity.

Lead Titanate (PbTiO₃)

Pure PbTiO₃ belongs to a perovskite ABO₃ type family. At room-temperature, PbTiO₃ is a ferroelectric material with tetragonal structure $\overline{4}2m - P4mm$ space group as shown in **Figure 1.1a**. Pure PbTiO₃ is not commercially used as a piezoelectric material due to practical problems of making a sintered pellet or single crystal. However, it can be modified to form solid solutions with other elements for obtaining materials with excellent piezoelectric properties. PbTiO₃ undergoes structural first order phase transition at 763 K into cubic $\overline{2}3m - Pm3m$ paraelectric structure as shown in **Figure 1.1 (a-b)**. The phase transition behaviour is of displacive nature as the central Ti atom and the oxygen atoms are displaced from their centro-symmetric position of the cubic form [1]. One of the perovskite, BaTiO₃ is widely studied among ferroelectric materials. Although PbTiO₃ is isomorphous at room temperature with BaTiO₃ ceramic, there are important differences between these ferroelectric materials. The lattice constant of PbTiO₃ at room-temperature are $a = b = 3.902 \text{ \AA}$ and $c = 4.156 \text{ \AA}$. This gives a c/a ratio of 1.06 whereas for BaTiO₃, c/a ratio is 1.01. Hence, PbTiO₃ has more tetragonal distortion than BaTiO₃. In tetragonal PbTiO₃ phase, the position of the ions may be described by keeping the *Pb* ion at the origin (0, 0, 0), *Ti* ions (0.5, 0.5, 0.5+dz1), *O1*(0.5, 0.5, dz2), and *O2*(0.5, 0, 0.5+dz3) for Rietveld refinement. Displacement of Ti and O atoms from the ideal cubic position is denoted by dz. The shifting of *Ti* and *O* in the PbTiO₃ system is in the same direction whereas BaTiO₃ is in the opposite direction from the cubic system.

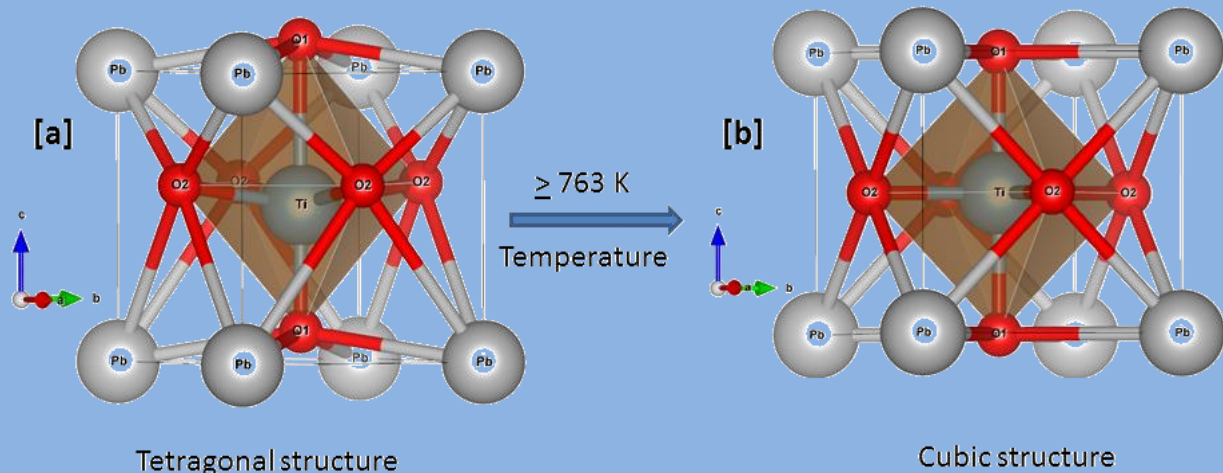


Figure 1.1: Schematic diagram of PbTiO₃ structures where (a) Tetragonal, and (b) Cubic structures are shown after phase transition at 763 K temperature.

The covalent character of *Pb* and its significant feature in ferroelectric/piezoelectric properties have been widely discussed in literature of PbTiO_3 and based compounds. Cohen [2] has elaborated the difference in PbTiO_3 and lead-free perovskites (BaTiO_3 , KNbO_3) properties. It has been shown that in PbTiO_3 , the hybridization between Ti-O and Pb-O are important contributions towards ferroelectricity by weakening short-range repulsions. A weakening of this hybridization reduces the ferroelectricity in the PbTiO_3 . $\text{Pb}(6s^2)$ states hybridize with the O(2p) and Ti(3d) to O(2p) states. This hybridization makes PbTiO_3 -based materials important as ferroelectrics. Since it is difficult to grow single crystals of PbTiO_3 of a size suitable for measurements; there have been relatively few attempts to systematically study dielectric, elastic, and piezoelectric properties of this crystal. A few complicated, experimental studies exhibit large conductivity, possibly related to a high concentrations of *Pb* vacancies. The most relevant difference between PbTiO_3 and other perovskite ferroelectrics is a low anisotropy of permittivity and relatively low shear piezoelectric coefficients in PbTiO_3 . PbTiO_3 has many important technological applications in electronics and microelectronics due to its high spontaneous polarization, Curie temperature, and pyroelectric coefficient [3, 4]. Ferroelectric PbTiO_3 films deposited onto various substrates has proven advantageous in memory applications, field effect devices and pyroelectric detectors which have hence stimulated technological interest in this field of study.

Literature survey

Lead titanate (PbTiO_3) is widely known as a classical ferroelectric ceramic material which possesses excellent useful dielectric, pyroelectric, piezoelectric properties and belongs to the ABO_3 perovskite group. Perovskite oxides, with chemical formula ABO_3 , are a wide range of compounds. It has a larger twelve-coordinated *A* cation and a smaller six-coordinated *B* cation. The structure is commonly represented by a cuboid unit cell with *A* cations at the corners, and *B* cations at the centre, while the *O* anions are located around the central point of each face. Lattice distortions in perovskite crystals arise out of off-centred ionic displacements and order-disorder transitions which generate reversible spontaneous polarization [5]. Ferroelectric/piezoelectric materials are recognized as excellent sensors and actuators due to their cost-effectiveness and design flexibility with excellent functionalities [6, 7]. Industrial applications of piezoelectric are

found in ultrasonic nondestructive devices, fuel injection valves, and piezoelectric motors, etc. Hence, they are essential components of civil, aerospace, mining, automotive industries, etc., [8]. Usage has increased exponentially in the last decade. With switchable spontaneous polarization, ferroelectrics are the soul of piezoelectric transducers and sensors. Ferroelectrics are also core parts of many energy conversion devices, such as ultrasonic medical diagnostic apparatus, ultrasonic nondestructive detectors, pyroelectric infrared sensors and magnetoelectric sensors. Amongst the various ferroelectrics, perovskites are technologically the most prominent due to their strong polarization, good response and multiple phases [2]. At room-temperature, PbTiO_3 has tetragonal structure. The PbTiO_3 perovskite structure when combined with other perovskites, forms many crystalline solutions such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{PbTiO}_3$, $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{PbTiO}_3$, $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{PbTiO}_3$, $\text{Ba}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $x\text{PbTiO}_3$, $\text{Ba}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $x\text{PbTiO}_3$, BaSnO_3 – $x\text{PbTiO}_3$, $(1-x)\text{PbTiO}_3$ – $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$, $(1-x)\text{PbTiO}_3$ – $x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 , PbHfO_3 – $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 , $\text{Pb}(\text{Sn}, \text{Ti})\text{O}_3$ – $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{PbTiO}_3$, $\text{Pb}(\text{Ho}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 , $\text{Pb}(\text{Y}_{1/2}\text{Nb}_{1/2})\text{O}_3$ – $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 and $(1-x)\text{PbTiO}_3$ – $x\text{BiFeO}_3$ etc., [9-16]. These PbTiO_3 -based materials are families of ferroelectric, paraelectric, anti-ferroelectric, and several other properties, etc. and have applications as capacitors, actuators, energy harvesting and sensors among several others. The physical properties of PbTiO_3 can be significantly modified with the help of substitution on the sites of *Pb* as well as *Ti* with suitable ionic radii and valency. The perovskite oxides have attracted significant attention due to their diverse physical properties and related practical applications in electronics. In the present time, a significant interest has emerged in the area of the ferroelectric/piezoelectric field due to dynamic random access memories (DRAMs), capacitors, non-volatile random access memories (RAMs), infrared sensors, piezoelectric actuators, shutters, optical modulators, colossal magneto-resistance, uncooled infrared detectors, microwave, magneto-optic and electro-optic devices, etc. PbTiO_3 perovskite structure has structural phase transition from ferroelectric to paraelectric phase at 763 K temperature. Suitable substitution at *Pb* or *Ti* site may shift the structural phase transition and consequently makes the materials necessary for device application at the desired temperature.

A.P. Barranco suggested [17] that A-site doping of PbTiO_3 reduces its remarkable tetragonality but yet can maintain ferroelectric properties for practical applications. It was found that rare earth doping of PbTiO_3 conserve electromechanical anisotropy and restores ferroelectric

properties [18, 19]. The impressive range of structures and property interaction of perovskites endows them with outstanding potential for research in the fields of physics, materials science, and solid state chemistry, etc. Owing to the flexibility of the bond length and angles, myriad types of lattice distortion can occur in the different perovskite structure. A wide range of novel functional materials and device perceptions can be imagined through the fundamental understanding of the relationship between the structural, chemical, thermal, solid solubility, and lattice strain, etc. More explorations in these exciting fields also may not exhaust the different aspects of perovskite materials. Ikegami *et al.* reported [20] that PbTiO_3 developed excellent piezoelectric properties by the combination of La and Mn substitution, and that ceramics are very good for resonator applications. Hiroshi *et al.* investigated electromechanical properties of modified PbTiO_3 ceramics with formula $(\text{Pb/R})(\text{Ti/Mn})\text{O}_3$ where $R = \text{La}, \text{Pr}, \text{Nd}, \text{Sm},$ or Gd , were rare-earth elements [18]. In these systems, Mn^{3+} substituted Ti^{4+} (investigated with ESR studies), while R^{3+} substituted Pb^{2+} . These substitutions were intentionally prescribed to maintain electrical neutrality of the lattice. An electromechanical coupling factor was discussed between a thickness dilatational mode and planar extensional mode in this system. It was found that *Sm* substitution for *Pb* dramatically increases this electromechanical coupling factor. In the same group of samples some work was reported on surface acoustic-wave delay time [21-23]. Gurgel *et al.* [24] reported that *Sm* modified PbTiO_3 could be used to improve mechanical and electromechanical properties and also improve sintering capabilities. Structural characteristics are changed, due to incorporation of *Sm* in PbTiO_3 and depend on *Sm* content. This also modifies lattice tetragonality and induces tetragonal to cubic phase transition and coercive field values. Paris *et al.* [25] correlated the *O2p* and *Ti3d* orbital behavior from density of states (DOS) calculations with the vibrational properties of $(\text{Pb}/ \text{Sm})\text{TiO}_3$. Sun *et al.* have suggested [26] that, usually the spontaneous polarization decreases with doping *Fe, Zr, Hf*, etc. at *Ti-site* in PbTiO_3 . On the other hand, the effect of aliovalent Al^{3+} at the same *Ti-site* increases the spontaneous polarization [27]. In Al-doped PbTiO_3 samples, the strong *Pb6s-O2p* hybridization was strengthened. Intensification of both the A_1 transverse optical Raman modes and the stretching and bending vibration FTIR modes further signifies the increase of spontaneous polarization in the A and B-sites. Yilin Wang *et al.* has reported [27] $\text{NdFeO}_3\text{-PbTiO}_3$ for $x = 0.10$ thin films prepared by sol-gel route. Thin films oriented along (100) direction show defect-dipoles induced *c*-domains at 150 °C, which is lesser than 345 °C (phase transition temperature from tetragonal

to cubic phase). Such a phenomenon was ascertained by constant absence of (001) XRD peak at any temperature, hinting that *c*-domains are not triggered by lattice reorientation.

Solid solutions $AB'_{1-x}B''_xO_3$ with perovskite structure represent a well-studied class of materials. Multiferroic properties were first observed within this class in the 1950s. A great number of ferroelectrics and substances with magnetic ordering have perovskite-like structure. Perovskite-like compounds (ABO_3) typically have a large internal field which is necessary for appearance of ferroelectric state. At the same time, "cation B-oxygen-cation B" angle $\simeq 180^\circ$. This is an optimal condition for appearance of magnetic ordering in the B sub-lattice, owing to an indirect exchange interaction. Therefore in compounds of perovskite structures, one may expect coexistence of electric and magnetic ordering [28]. Stoupin *et al.* reported [29] substitution of Ti by Mn up to 20 mol % in $PbTiO_3$ without additional charge-compensation of A-site substituent. With the help of XANES spectra, a mixed phase of Mn^{3+} and Mn^{4+} charge states was observed. These samples were found to be weakly ferromagnetic below 50 K.

In the past, it was considered that the electrical properties are dependent on the particle size of the samples [30-32]. However, due to requirement of miniaturization of measurement devices, individual elements are required to be smaller and smaller. This is particularly important in electrical measurement systems related to ferroelectric properties. Particularly, when the grain size is on the nanometer scale, the ferroelectric properties can be affected in many ways. As a result, the effect of grain size on the ferroelectric properties has attracted considerable attention. Particle size effects on the ferroelectric phase transition behaviour were extensively investigated by theoretical as well as experimental studies. It is well known that small ferroelectric properties or thin film show different dielectric properties from those of the bulk samples because the long-range Coulomb force plays an important role [33]. Chattopadhyay *et al.* [34] suggested the particle size dependence on the phase transition behavior in $PbTiO_3$ ceramics. The effects of size become essential below ~ 100 nm in $PbTiO_3$ samples. The $PbTiO_3$ tetragonal distortion of the unit cell, which is related to the spontaneous polarization, decreases exponentially with the particle size at 7 nm. With the reducing size of the particle, transition temperature gradually reduces and becomes diffuse type phase transition from 80 to 30 nm particle size, and there is no dielectric or DSC (Differential scanning calorimetry) anomaly below this particle size. Tetragonal distortion (*c/a* ratio) decreases exponentially with particle size and diminishes at 7 nm, which is the critical size for ferroelectricity in the samples. Similar other perovskite-related

materials are also studied to explore the nature of phase transition behavior and ferroelectric properties [35, 36].

Motivation behind PbTiO₃ based system

The PbTiO₃-based perovskite materials have many technological applications such as in capacitors, dielectric resonator, piezoelectric transducers, thin film resistor, hydrogen sensors, switch magnetic bubble memory, and electrostrictive actuators, etc. These types of properties in different environments are required for the current generation. So for these applications, the property of PbTiO₃-based materials can be enhanced by the substitution of the alkali, rare-earth, and transition materials in the perovskite PbTiO₃. At present, much attention has been paid to the lead-based complex perovskites compounds and their solid solutions due to a variety of physical properties and a wide range of industrial applications. Depending on the ionic radii and charges, ordering of cations may occur which gives rise to different structural and physical properties. A comprehensive literature survey reveals that a considerable amount of work has been carried out on the A-site, B-site, and A/B-site in ABO₃ type PbTiO₃ perovskite with different substituents. However, an annealing process is often accompanied with the undesirable secondary phases such as substituents oxides or pyrochlore phase, which is non-ferroelectric material. Therefore, in the recent years, the substitution of suitable ions either A, B, and A/B-site in the perovskite lattice has garnered much attention.

There are no systematic reports on the PbTi_{1-x}Fe_xO₃ ($x = 0, 0.03, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.37, 0.43, \text{ and } 0.50$) compositions with the detailed study of XANES/EXAFS, ferroelectric and ferromagnetic properties. Although some reports are available on the same compounds, they have secondary phases of pyrochlore, which is one of the big questions of magnetic properties. In our present study, we have used sol-gel combustion method, and there is no secondary phase in any of the samples. These samples are multiferroics at room temperature. Also, there was no detailed study of A-site modified with the (Na_{0.5}Sm_{0.5}) and (K_{0.5}Sm_{0.5}) at the *Pb*-site with approximately the same ionic size and equal charge. Pb_(1-x)(K_{0.5}Sm_{0.5})_xTiO₃ ($x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.37, \text{ and } 0.50$) and Pb_(1-x)(Na_{0.5}Sm_{0.5})_xTiO₃ ($x = 0, 0.10, 0.20, 0.30, 0.40, \text{ and } 0.50$) samples were prepared with the sol-gel combustion assisted method. Crystal structure and lattice dynamics were confirmed with synchrotron-based powder x-ray diffraction in rotating capillary mode. Rietveld refinement was performed on all the samples to

study the change in crystal structure keeping in mind the purity of the samples with an increase in substitution. There were no secondary phases observed in any of the samples. Also, Raman spectroscopic studies were carried out to see the vibrational study in the samples with the increase in composition. A dielectric study was performed for all the samples to see the variations in the phase transition temperature with the increase in composition. Substitution enhances the dielectric constant with the increase in substitution. A detailed study of increases in dielectric constant was elaborated in the corresponding chapters. Ferroelectric properties were measured for all the substituted samples to see the variations in the remnant polarisation and coercive fields. Impedance analysis was carried out to see the conduction mechanism due to substitution effect in the samples and also the effect of grain and grain-boundary contributions in the samples. We have also played, both side substitution effect in the PbTiO_3 ceramics. The main objective is to study the crystal structure and ferroelectric properties of the $(\text{Pb}_{(1-x)}\text{La}_x)(\text{Ti}_{(1-x)}\text{Al}_x)\text{O}_3$ ($x = 0, 0.03, 0.06, 0.09, 0.12, 0.18, \text{ and } 0.25$) ceramics. The detailed crystal structure was performed with the Rietveld refinement of the synchrotron powder XRD and Raman spectroscopy data. A temperature-dependent dielectric study was carried out to see the variation in phase transition with the compositions. Phase transition temperature shifted towards lower temperature with the increase in substitution. To confirm the exact phase transition temperature and lattice dynamics, we have carried out the temperature-dependent x-ray diffraction using the synchrotron-based source. There are many reports on *La* modified PbTiO_3 ceramics but there is rarely any reports on *La*, and *Al* substituted in PbTiO_3 ceramics. These atoms have compatible size effect with the parent elements. These compositions were studied in detail with the crystal structure and ferroelectric/piezoelectric point of view. One more A/B-site substitutions with Bi/Mn such as $(\text{Pb}_{(1-x)}\text{Bi}_x)(\text{Ti}_{(1-x)}\text{Mn}_x)\text{O}_3$ ($x = 0, 0.06, 0.09, 0.12, 0.18, 0.25, 0.31, 0.34, 0.37, \text{ and } 0.50$) were similarly prepared as previous sol-gel method. Crystal structure study was carried out with Rietveld refinement of synchrotron-based x-ray diffraction data. Also, some selected samples were performed with temperature-dependent x-ray diffraction data to confirm the phase transition temperature and lattice dynamics. Significant observations included high phase transition temperature up to certain substitution and negative thermal expansion behavior to phase transition temperature. After phase transition temperature, we observed the positive thermal expansion behavior. Detailed studies related to these series are provided in the corresponding chapters.

Perovskites

The CaTiO_3 mineral was discovered in 1939 by Gustav Rose from the Ural Mountains and the structure possessed by this mineral is named as perovskite after Russian mineralogist Lev Perovski.

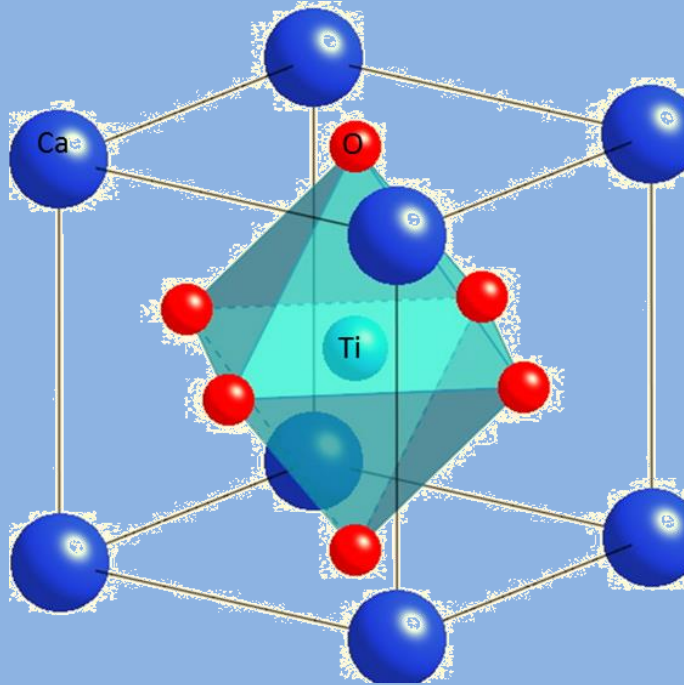


Figure 1.2: A schematic unit cell structure of CaTiO_3 where Ca, Ti, and O representative is shown in the schematic figure.

The structure of perovskite is an ABO_3 type a primitive cube. In an ideal case of ABO_3 type perovskite structure, A-site cations occupied the corner of the cube; B-site cations placed the centre and the oxygen anions at the face centre of the primitive cube. A-site cations can be monovalent (K, Na, Li, etc.), divalent (Pb, Ba, Sr, Ca, ..etc.), or trivalent (Bi, La, Sa, etc.) and the B-site can be trivalent (Fe, Mn, etc.), tetravalent (Ti, Ce, etc.), and pentavalent (V, W, Ta, Nb etc). The coordination number of A-site cation is 8 to 12 whereas B-site cations coordination number is six. Ideal perovskite is known as cubic structure while most of the structure is different from the cubic structure. The deviation from the ideal cubic structure is estimated from the Goldschmidt tolerance factor [37, 38] (t):

$$t = \frac{(R_A + R_B)}{\sqrt{2}(R_A + R_B)} \dots \dots \dots (1.1)$$

where, R_A , R_B , and R_O are the ionic radii of A-site, B-site, and O ions respectively. For ideally closed cubic perovskite structure, tolerance factor is one. Mostly there are three main factors to deviate the ideal cubic structure to other: tilting of octahedra (BO_6), displacement of A/B-site cations from the centres of polyhedra, and displacement of anion octahedra. The displacement of the cations and distortions of the octahedra are correlated and driven by the electronic instability of the cations. As tolerance factor decreases, the A-site becomes too small for the cuboctahedral site. When octahedron tilting occurs, it has the effect of reducing the volume and improving the stability of the structure. The room-temperature perovskite structure with $0.985 < t < 1.06$ are expected to have untilted perovskite. Perovskites with $0.964 < t < 0.985$ are usually tilted in anti-phase type and perovskites with $t < 0.964$ are predicted to show in-phase and anti-phase tilting. Tolerance factor continues to decrease, the stability of the perovskite phase decreases and eventually, perovskites get formed [39]. Perovskite structure also has its different expression such as: (a) double perovskite ($AA'B_2O_6$) or ($A_2BB'O_6$) and (b) layered perovskite which is of three types (i) Dion Jacobson ($A[A'_nB_nO_{3n+1}]$), (ii) Ruddlesden Popper ($A_2[A_{n-1}B_nO_{3n+1}][AO][ABO_3]_n$) & (iii) Aurivillius ($[BiO_2][A_{n-1}MnO_{3n+1}]$). Practical benefits of the perovskite structure are that different cations can be substituted for both A and B sites in ABO_3 perovskite structure without changing the complete structure. The complete solid solutions are simply formed between many cations. Hence, it is very useful to manipulate the materials properties such as ferroelectric properties, Curie point and thin film substrate application, and the tailoring of lattice constants with the substitution.

Ferroelectricity

The term ferroelectrics rose to prominence because of its similarity with ferromagnetic under magnetic fields for the ferromagnetic and electric field for ferroelectric phenomena. The word *Ferro* is derived from the word *Ferum*, which means iron in Latin. This term is highly suitable for the ferromagnetic phenomena because all ferromagnetic occurrences are associated with the special type of spin arrangement of the iron atoms. In ferroelectric term, there is no significance of iron atoms, so, no meaning of iron here. Rather, similarities like ferromagnetic and ferroelectric materials exhibit a spontaneous polarization under the applied electric field

below the phase transition temperature. It also forms the hysteresis loop and mechanical strain with the applied electric field. Nevertheless, ferroelectrics are different from ferromagnetic in their fundamental mechanism and also in some of their applications. For many researchers in Europe, the nomination of ferroelectric is called Seignette electrics. This name is highly confusing because Seignette did not discover these ferroelectric phenomena. During the 17th century Pierre Seignette, of La Rochelle, France discovered Rochelle salt (potassium-sodium tartrate tetra hydrate), a colorless crystalline compound with an orthorhombic structure. This material was used as a laxative at that time. After 200 years later, in 1921 Valasek [40], obtained the hysteresis curves for the Rochelle salt; same as the *B-H* curves of ferromagnetism, and also studied the piezoelectric response of the crystal. For about 15 years, ferroelectricity was accepted as a very important property of Rochelle salt. After that, Busch and Scherrer discovered ferroelectricity in KH_2PO_4 and its sister crystals in 1935. During World War II, abnormal dielectric properties were discovered in ceramic by Wainer and Solomon in the USA in 1942; by Ogawa in Japan in 1944; and by Wul and Goldman in Russia in 1946. After that, many ferroelectrics have been investigated, and research has rapidly increased in this field. There are more than 1000 solid materials recognized at present that possess ferroelectric properties. Ferroelectric materials are the sub-group of the pyroelectric materials. In this, spontaneous polarization can be switched upon the application of an applied electric field (by changing the vector orientation of the electric dipole). We cannot determine whether a material will exhibit ferroelectric ordering by the knowledge of the crystal class alone. Switching off electrical polarization of the materials can be determined and plotted within a changing field to yield hysteresis, and a loop is observed. After the application of an electric field to the material, the individual dipoles align with the electric field lines with spontaneous polarization in the direction of the electric field. One important characteristic of this type of materials is that, after removal of the electric field, the spontaneous polarization does not disappear; it remains. This phenomenon is called remnant polarization. This will start to reduce, only when the electric field will apply in reverse direction. Application of certain strength of electric field will reverse, to give net polarization.

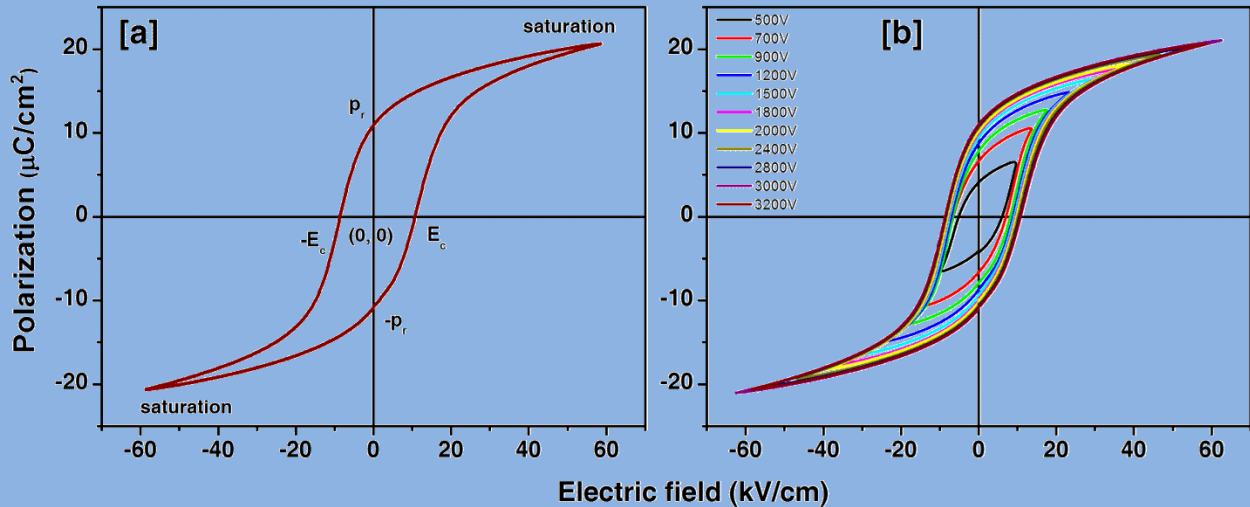


Figure 1.3: (a) Ferroelectric polarization is shown in hysteresis loop, (b) Ferroelectric polarization hysteresis shape at different voltages.

Experimentally, we can examine the ferroelectric properties in the samples, with the help of applied *ac* electric fields that corresponds to polarization in the materials, and takes a form of hysteresis loop as shown in **Figure 1.3 (a-b)**. Starting at the origin (0, 0) such as electric field ($E = 0$), polarization is zero. This is because, macroscopically, samples have multiple domains canceling resultant to each other. As the applied electric field increases, the polarization also increases simultaneously and reaches a saturation value. Hence, all the ferroelectric domains are oriented in the applied electric field. On further increasing the electric field, a small increment in polarization happens due to the dielectric charging effect. Now, the electric field starts to decrease, and the curve does not follow the same path. The total polarization decreases with the decrease of electric field is little at the zero electric field. The value of polarization at zero electric field is called the remnant polarization (P_r). The further increase of electric field in a negative direction up to zero remnant polarization is called the coercive field ($-E_c$). With continuous increase of negative direction electric field, saturation of polarization and dielectric response occur. Again, the same behavior observed when the electric field is reversed and the repeated cycling results in a symmetric hysteresis loop. Ideally, saturation polarization should be equal to remnant polarization. But, saturation polarization is often higher than remnant polarization in polycrystalline materials because of the formation of reverse domains during the ramping of the electric field to zero. But in the single crystal, it is very close value [41, 42]. **Figure 1.3b** shows

how the ferroelectric hysteresis loops will look like at different voltages. Here, the proper ferroelectric hysteresis loop is obtained at an optimum voltage at which all the domains will switch in the same direction, as J F Scott has discussed in '*Ferroelectrics go bananas*' about the proper ferroelectric loop and misleading ferroelectric loop in the sample [43]. A proper ferroelectric loop of the sample looks like pinch type at the saturation point of the maximum applied field. Ferroelectric property is significant for the application to be exploited to create a 1/0 binary state, where each direction of spontaneous polarization represent either an on or off state, and the application of an alternating electric field can be used to switch between them.

Piezoelectricity

In piezoelectric, the prefix piezo- is derived from the Greek word piezein, meaning pressure. Piezoelectrics are the materials in which electricity can be generated by an application of mechanical stress. Mechanical stress can also be produced by an applied electric field. This convertible behavior (electric to mechanical stress vice versa) was first discovered by Pierre and Jacques Curie in 1880 in some special crystal, such as quartz, tourmaline, and Rochelle salt. The word piezoelectricity has been used by the scientists since 1881 to discriminate the piezoelectric phenomena from electrostriction. The direct piezoelectric effect is known as the ability to convert mechanical to electrical energy also known as generator or transducer effect while the converse piezoelectric effect describes the ability to transform electrical to mechanical energy known as motor/actuator effect [44]. According to the description of 'direct piezoelectric effect', when a mechanical strain is applied to piezoelectric material by an external stress, an electric charge occurs on the surface(s) of the piezoelectric material and the polarity of this observed electric charge on the surface(s) can be reversed by reversing the direction of the mechanical strain applied as shown in **Figure 1.4 (a-c)**. On the other hand, according to the explanation of 'converse piezoelectric effect,' when an electric field is applied to a piezoelectric material subjected to an electric field, a mechanical deformation on the surface is observed which is seen as a change in dimensions of the piezoelectric material. The direction of mechanical strain can also be changed by changing the applied electric field and vice-versa.

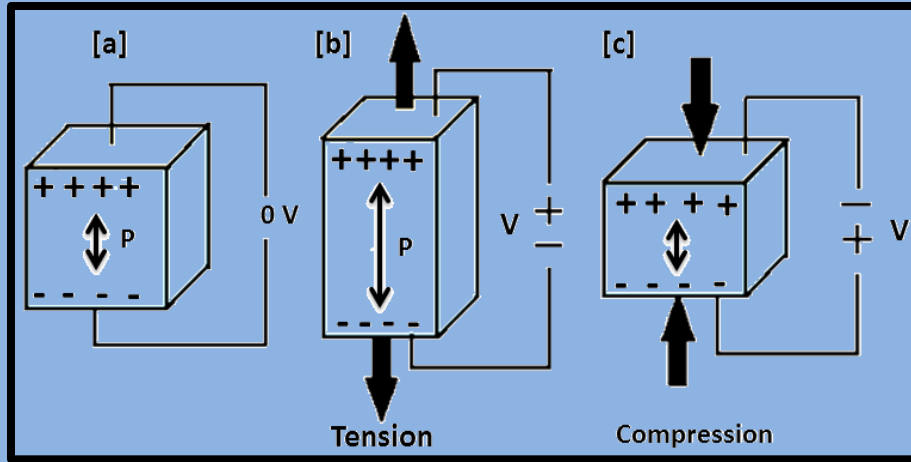


Figure 1.4: A schematic diagram of piezoelectric effect where (a) piezoelectric material, (b) energy generation under tensile stress, and (c) energy generation under compressive strain.

The phenomenon of piezoelectricity can also be described as the motion of ions inside certain crystalline structures, leading to a variation of the dipolar moment. In the presence of a centre of symmetry, no dipoles are present, and thus no piezoelectricity can be found. Applying stress to a polar crystal, the piezoelectric polarization will contribute to already existing spontaneous polarization. In polar-neutral crystals, with the exception of 432 group, the effect of external mechanical stress is to generate a single polar direction. A graphical example is given in **Figure 1.5**.

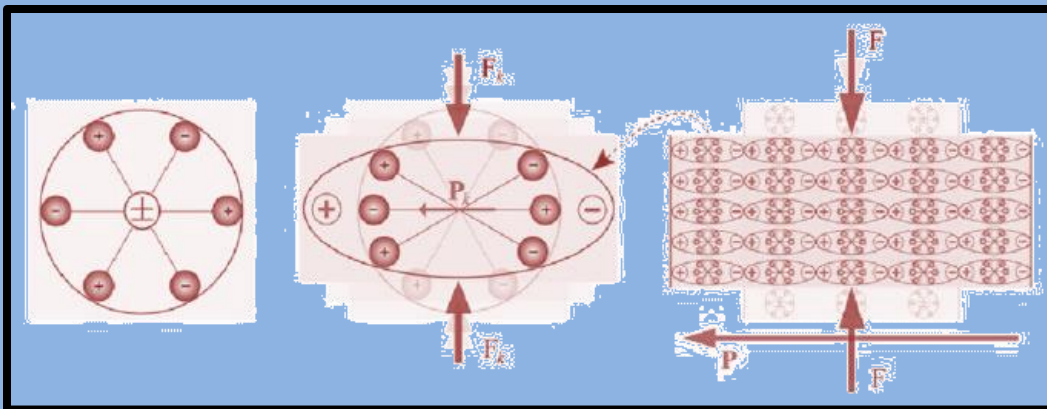


Figure 1.5 Piezoelectric effect in polar-neutral symmetries explained with a simple molecular mode.

According to the converse piezoelectric effect, the strain is linearly proportional to the applied electric field when the piezoelectric coefficient is constant. When the electric field is parallel to the polarization, the strain increases with the increase of the electric field and the maximum strain occurs at the maximum electric field. However, polarization switching in a ferroelectric subjected to an electric field leads to electromechanical hysteresis, as shown in **Figure 1.6**. The loop shows piezoelectric response as well as polarization switching under a bipolar electric field. The sign of strain depends on the relative directions of the polarization and the electric field. When the field and polarization are in parallel, the lattice expands, and the strain is positive. When the field and polarization directions are antiparallel, the lattice contracts and the strain is negative. An abrupt change in the strain axis occurs due to polarization switching. The electromechanical response is, in general reversible. The piezoelectric coefficients can be calculated from the slope of linear regions in the loop.

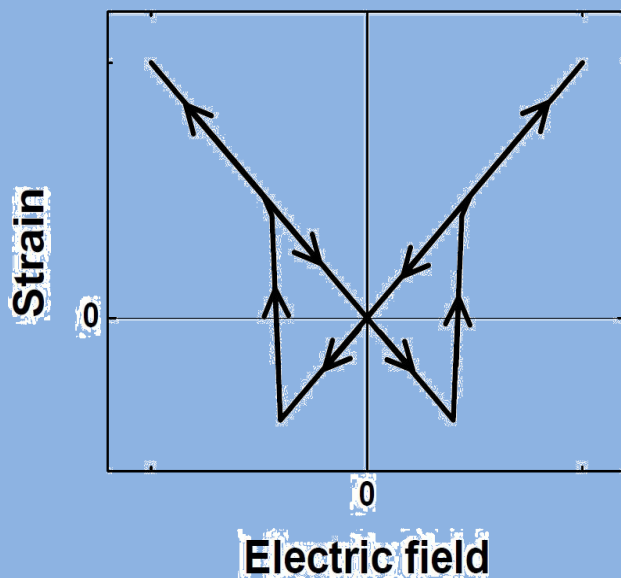


Figure 1.6: A schematic electromechanical hysteresis loop. The piezoelectric coefficient is determined from the slope of the straight lines.

Human beings have been in extended contact with piezoelectricity phenomena for the longest time. It is understood that human beings used the flint, a variety of quartz to produce the fire by applying a mechanical stress. In reality, flint was the core material during the Stone-age because of its worthy cutting properties that were useful to construct the tools and arms. The

lighter was an accidental discovery during the processes of the manufacturing tools. Later on, and before the invention of the matches, the materials continued to be used like a lighter knocking it against the iron. A piezoelectric material reveals in a type of lattice where the central cation exhibit the center of the lattice (called centrosymmetry of the lattice) as it would be in a cubic lattice; whereas small offset from the center of symmetry of the central cation is called the non-centrosymmetry of the lattice. This small offset of the center cation will form an electric dipole. This electric dipole moment can switch between two available symmetric positions. The piezoelectric material can also be polarizing on the application of externally applied mechanical force since it is a reversible process. The magnitude of the polarization is directly connected to the magnitude of the applied mechanical force since non-centrosymmetric materials are categorized as piezoelectric materials. **Figure 1.7** shows how electrical properties depend on the symmetry of the lattice. Since there is a direct relationship between polarization and mechanical stress, that effect can be achieved in two different ways. The mechanical stress on the piezoelectric material can cause the physical change to the material and polarization state of the material. This is called the direct piezoelectric effect. Similarly, the application of electric field will produce the mechanical strain on the piezoelectric sample. This is called the indirect/converse piezoelectric effect. This property was mathematically constructed from fundamental thermodynamic principles by Lippmann in 1881[45]. It was confirmed experimentally by the Curies who foregrounded the existence of the converse effect and also found the quantitative proofs of the reversibility of electro-elastomechanical deformation in piezoelectric materials. The first use of the piezoelectric material was in ultrasonic submarine detector during World War-I. This was the beginning of the development of Sonar (Sound Navigation and Ranging). This type of investigation also opens up many areas of investigations on the application of piezoelectric devices such as microphones, ultrasonic transducers, and signal filters. The continued development of piezoelectric materials has directed to more extensive market products extending from the everyday products to scientific and military applications. Also, during Second World War in the United States, Japan, and the Soviet Union, research groups working on the capacitor materials explored that some polycrystalline anisotropic showed a high dielectric constant (Roughly 100 times higher than cut crystals) and it was the case of barium titanate polycrystalline ceramic. Before 1946, the scientists thought that polycrystalline materials are only ferroelectric not piezoelectric. It was followed by the

investigation on the effect of an electric field (a process called poling) to understand that polycrystalline ferroelectric ceramics could be converted into piezoelectric materials. This investigation enhances the development of the piezoelectric devices.

Crystal structure for ferroelectricity

The crystal structure is the primary governing point for the ferroelectric/piezoelectric properties.

The lattice structure designated by the Bravais unit cell governs the crystal symmetry. There are many crystal structures in nature; they all can be coupled in 230 space groups based on the symmetry elements [46], with most of the crystal structure symmetry elements in addition to the repetitions expressed by the crystal lattice. In analysing the physical properties of crystals; only the orientations of the symmetry elements are considered as important and not their relative positions. Hence, If only the orientations of the symmetry elements are taken into account, then the macroscopic symmetry elements in crystals reduce to a centre of symmetry, mirror plane- 1, 2, 3, 4 or 6 fold rotation axes and 1, 2, 3, 4 or 6 fold inversion axes. A combination of these symmetry elements gives us the macroscopic symmetry also known as point groups. It can be shown by the inspection of the 230 space groups that there are only 32 point groups as shown in **Figure 1.7**. The seven crystal systems can be divided into these point groups according to the point group symmetry it possesses. There are 32 point groups [47], and in that 21 are non-centrosymmetric, i.e., they do not show an inversion of the symmetry with respect to the centre of the unit cell. In the 21 non-centrosymmetric; 20 are piezoelectric, i.e., they exhibit accumulation of charge when mechanical stress is applied and one non-piezoelectric material. Among these 20 piezoelectrics, 10 carry a unique polar axis and possess spontaneous polarization. They are called pyroelectric. Similar to pyroelectric materials, ferroelectrics possess spontaneous polarization, but the magnitude and direction of the polarization can be reversed by an external electric field.

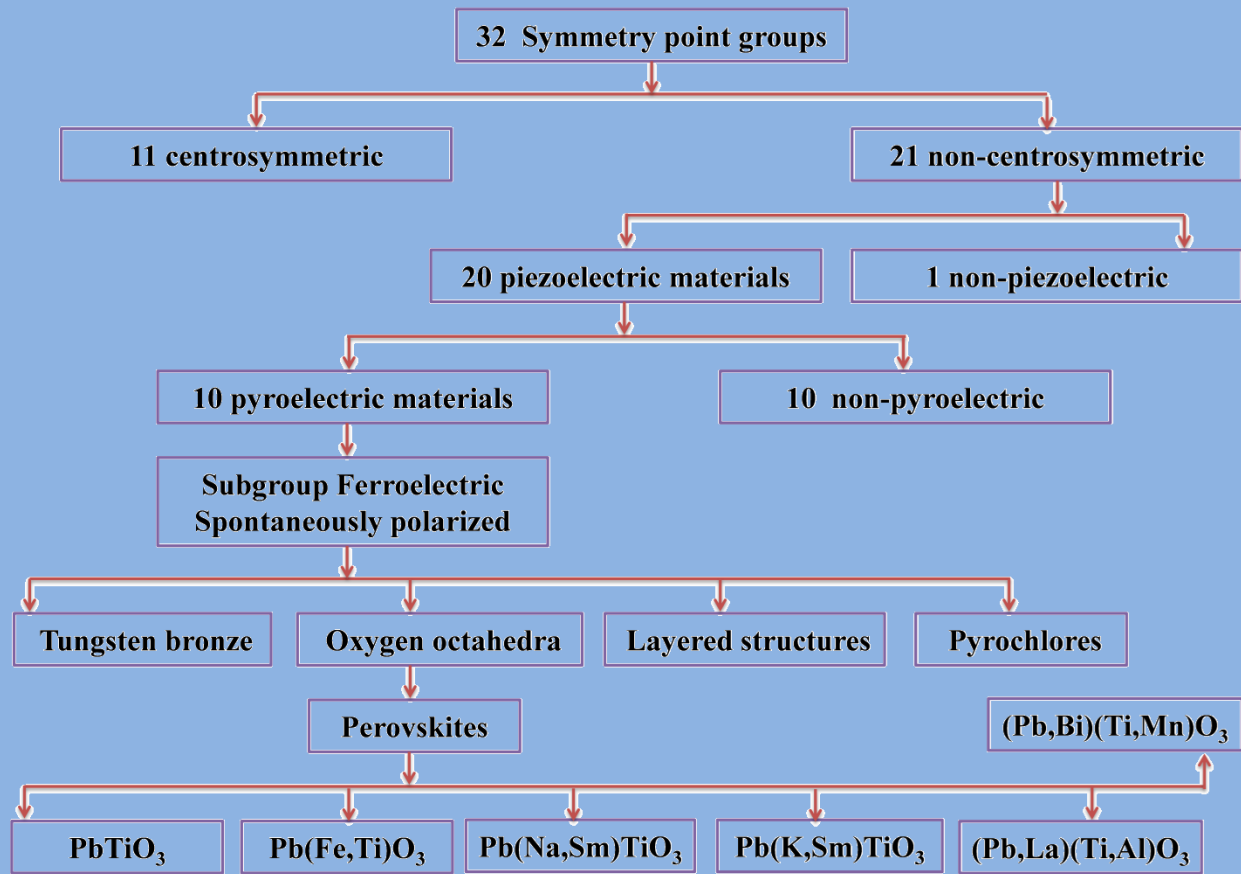


Figure 1.7 Symmetry relationships of piezoelectricity, pyroelectricity and ferroelectricity and some ferroelectric materials.

Crystalline materials are distinguished into seven different crystal structures as shown in **Table 1.1**. These crystal structures are easily identified by the constraint on the unit cell parameters.

Table: 1.1 Seven crystal systems with their crystal constraints, centrosymmetric and non-centrosymmetric point groups in crystals with different symmetries.

Crystal system	Cell parameters		Centro-symmetric	Non-centro-symmetric
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	$m\bar{3}, m\bar{3}m$	23, $\bar{4}3m$, 432
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$4/m, 4/mmm$	4, $\bar{4}$, 442 , $4mm$, $\bar{4}2m$

Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$6/m, 6/mmm$	6, $\underline{6}$, $622, 6mm, \underline{6}m2$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	mmm	$222, mm2$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	$\underline{3}, \underline{3}m$	$3, 32, 3m$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	$2/m$	$2, m$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\underline{1}$	1

With the help of these crystal systems, we can construct a three-dimensional lattice. At the corner, the lattices with lattice points are called primitive lattices. All other lattices are known as non-primitive. The structure and symmetries of the materials, whether it is amorphous or crystalline, entirely affect its overall physical properties. According to the Neumann's principles [48], "if the structure of a material is invariant with respect to certain in symmetry elements, any of its physical properties is also invariant with respect to the same symmetry elements." Hence, if the materials do not change, the structure also exhibits the same physical properties.

Ferroelectric materials are the subgroup of dielectric materials with a crystalline structure. A crystalline exhibits a periodic arrangement of its atoms, ions, or molecules in the three-dimensional space, being a unit cell the smallest and simplest pattern recognizable in such a structure. **Figure 1.8** graphically indicates the family of ferroelectric as groups of pyroelectric, piezoelectric and dielectric crystals, hence exhibiting physical properties such as pyroelectric, piezoelectricity, and dielectric permittivity which are briefly discussed below.

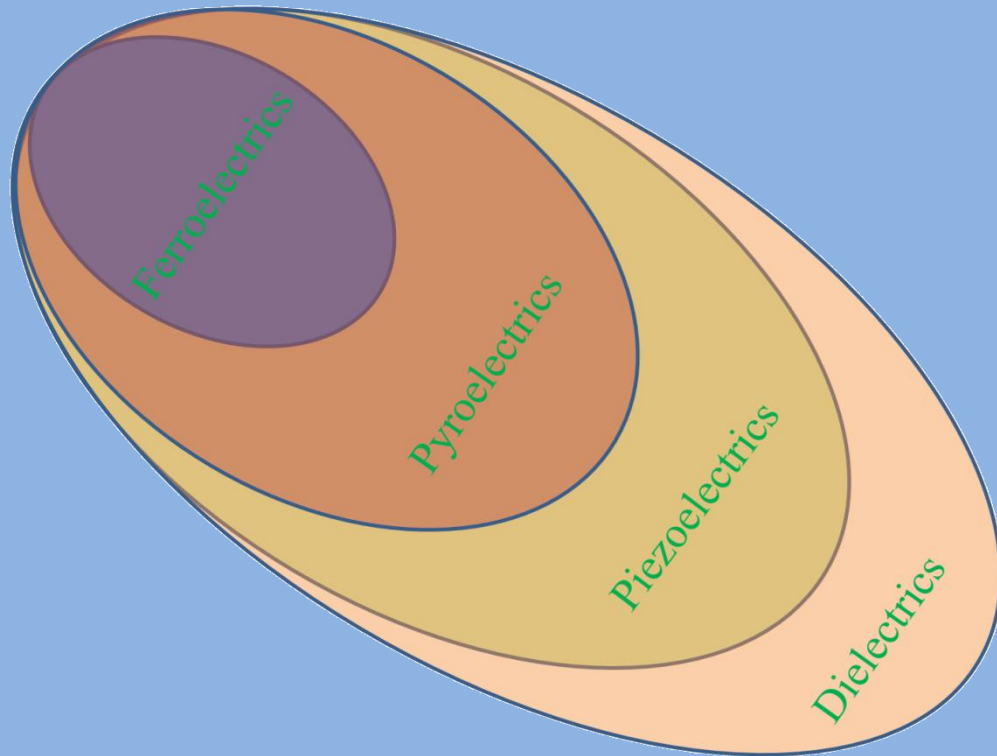


Figure 1.8: A schematic Venn diagram demonstrating the four classes of the polar dielectric.

All piezoelectric materials are non-centrosymmetric. Hence, mechanical stress can induce dielectric dipole moments. Additionally, because all piezoelectrics are dielectrics, they are electrical insulators. In some piezoelectrics and pyroelectric materials, dipoles can be created when they are heated or cooled, even in the absence of an external field. Additionally, some pyroelectrics exhibit spontaneous electric polarization that can be switched by an electric field or stress. Accordingly, all ferroelectric materials are pyroelectric and can be considered as piezoelectric materials. Piezoelectric, pyroelectric and ferroelectric behaviors are related to the crystalline structure of the materials.

Ferroelectric to paraelectric phase transition

The spontaneous origin of polarization in ferroelectric materials is understood in the concept of structural phase transition temperatures which are accompanied by a reduction of macroscopic symmetry. The point groups of the complete (high) symmetry non-polar phase and

the low-symmetry polar phase fulfill the group-subgroup relation. All equivalent orientations of the polar axis concerning the parent phase, thus define the number of ferroelectric axes and reversible polarization orientations (states) which can occur during the phase transition. This is allowed to behave polarization as an order parameter which is zero in the paraelectric phase and non-zero in ferroelectric phase. The complete understanding in ferroelectrics was attained by the phenomena of logical Landau theory of ferroelectric phase transitions which merges macroscopic symmetry breaking and thermodynamic phenomenological concepts [49]. Properties of the materials can be enhanced when they undergo a structural phase transition from one space group to others. This is mostly true for ferroelectric/piezoelectric ceramic materials. All ferroelectric materials have a structural phase transition temperature called the Curie point (T_c) as shown in **Figure 1.7**. At a temperature $T < T_c$, the crystal exhibits ferroelectricity, while for $T > T_c$ the crystal does not have a ferroelectric ordering. Decreasing the temperature from the non-ferroelectric phase (here paraelectric state) to ferroelectric phase, crystal undergoes a structural phase transition. At or near the structural phase transition temperatures, the thermodynamic properties including the dielectric constant, elastic, optical, etc. show anomalous behavior. This is due to a distortion in the crystal during the change in the phase structure. The net spontaneous polarization (ferroelectric characteristic) disappears after the Curie point. Sharp phase transition behavior follows the Curie-Weiss law [50, 51]:

$$\chi = \frac{C}{T - \theta}, \quad T \geq \theta$$

.....(1.2)

where C is the Curie constant and the Curie-Weiss temperature. Usually, T_c and θ differ only a few degrees. Hence, the dielectric constant shows high values and tends to infinity as shown in **Figure 1.9**. This type of phase transition characteristic is called the first order phase transition behavior.

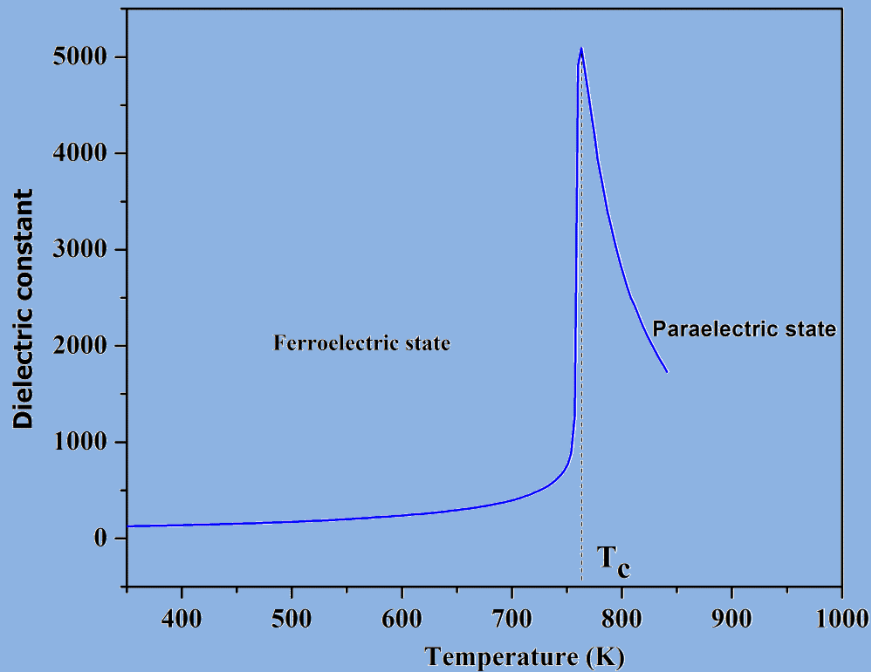


Figure 1.9: Dielectric constant versus temperature of a PbTiO_3 -based ferroelectric material.

Thus we can observe that dielectric constant has a maximum value at the point of transition temperature. Some factors which directly affect the dielectric constants are porosity in the sample, secondary phase in the sample, inhomogeneity defects, grain size and material conductivity, etc.

Diffuse phase transition

The exploration of ferroelectric possessing diffuse type phase transition is one of the significant areas of research interests because they have unique physical properties and wide practical applications. In respect of normal ferroelectric materials, they do not possess a sharp change of structure and properties at the Curie point. However, the transition temperature is smeared over a large temperature range. There are numerous attempts to understand the reasons behind this smearing. The most widely accepted model takes into account the fact that the structure of crystals with diffuse ferroelectric phase transition is characterized by a different type of ions randomly occupying the equivalent lattice sites. Diffuse type phase transition behavior is considered to result from composition fluctuations on a microscopic scale caused by disordering of the ions. If the Curie point temperature depends on composition, the phase transition temperature in different micro-regions takes place at different temperatures [52]. The shape

observed for the diffuse type of phase transition temperature is shown in **Figure 1.10**, where we can observe that in dielectric constant versus temperature, the curve is showing the broad peak, this dielectric behavior is called diffuse type of phase transition temperature. This is also called second-order phase transition behavior.

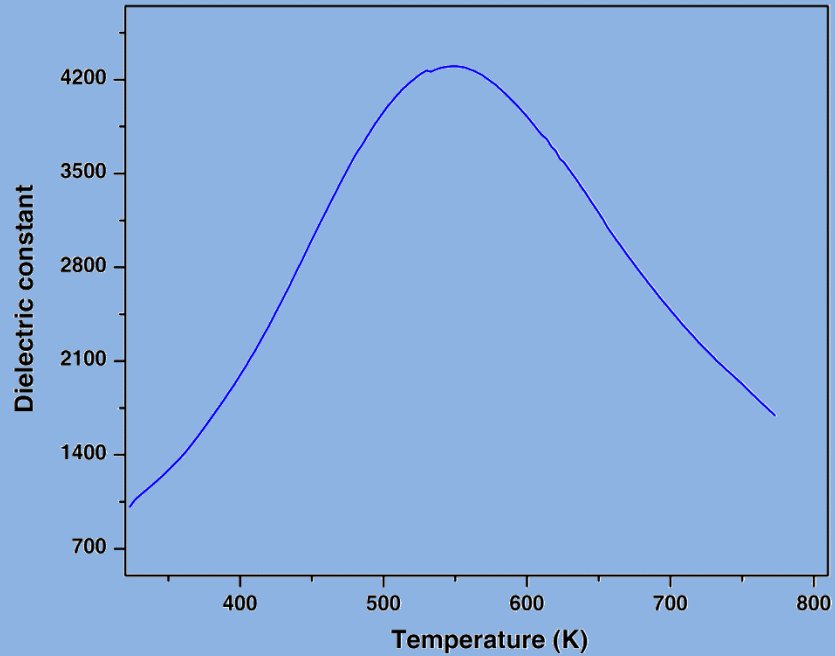


Figure 1.10: Diffuse type of phase transition behavior of sodium bismuth titanate sample.

Diffuse type of phase transition behavior does not follow the Curie –Weiss law. It follows the modified Curie –Weiss law [53]:

$$\frac{1}{\epsilon} - \frac{1}{\epsilon_0} = C^{-1} (T - T_m)^\gamma \dots\dots\dots(1.3)$$

where, C is Curie-Weiss constant, and γ ($1 \leq \gamma \leq 2$) gives the degree of diffuseness. A sharp transition is achieved for $\gamma = 1$, while $\gamma = 2$ is an ideal diffuse phase transition. The degree of diffuseness was calculated by the least square linear fitting of $\ln(\frac{1}{\epsilon} - \frac{1}{\epsilon_0})$ versus $\ln(T-T_m)$ curves. In ferroelectrics, diffuse type of phase transitions was first discovered in the literature in the early 1950’s. Some significant characteristics of the diffuse phase transitions include: broadened

maxima in the dielectric constant versus temperature curve; gradual decrease of spontaneous and remanent polarizations with increase in temperature; relaxation character of the dielectric properties in transition region; transition temperatures obtained by different techniques which do not coincide, and no Curie-Weiss behavior in certain temperature that intervals above the transition temperature. The diffuseness of the phase transition is supposed to be due to the occurrence of the fluctuations in a relatively large temperature range around the transition. Two kinds of fluctuations are considered- compositional fluctuation, and polarization (structural) fluctuation. From the thermodynamic point of view, it is confirmed that the compositional fluctuation is present in ferroelectric solid-solutions and that polarization fluctuation is due to the small energy difference as ferroelectric and paraelectric phase will cause a large probability of fluctuation.

1.11 Domain structures

Ferroelectric materials are considered by a finite electric polarisation in the absence of an electric field. This polarisation must exist in at least two stable states. These stable states must have the capability to be reversibly switched by the application of an applied electric field to one state to other. Thus, regions with the different orientations of the polarisations vector may coexist within a ferroelectric sample and are called ferroelectric domains [54].

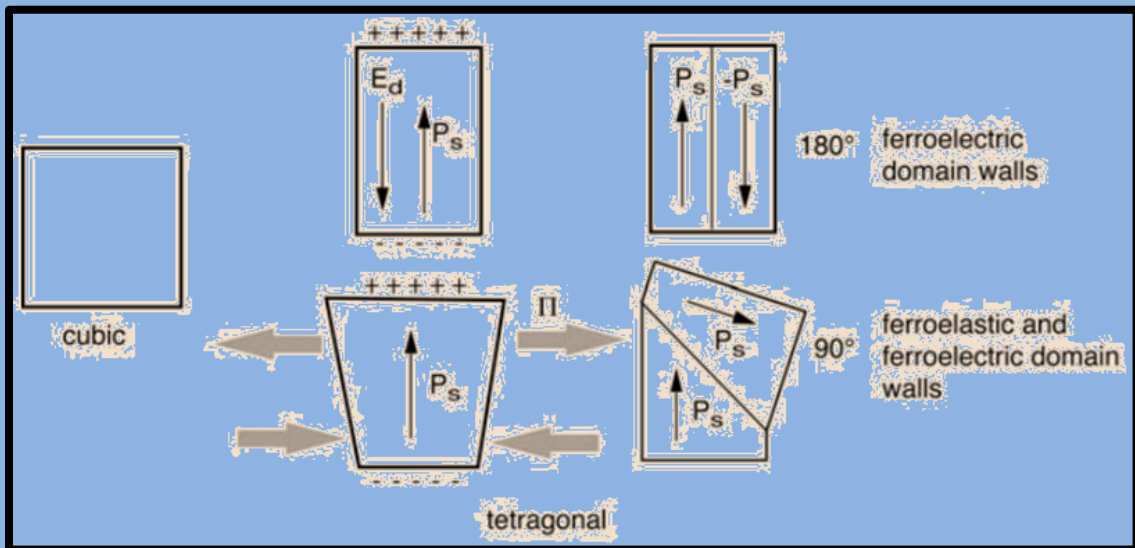


Figure 1.11: Formation of 90 and 180 domain wall in a tetragonal perovskite [55].

In the case of ferroelectric material, the spontaneous polarisation does not mean that all the domains are aligned uniformly through all the volume in the same direction. In PbTiO_3 -based compounds of mostly tetragonal structure, by cooling a perovskite structure through Curie temperature, the ion in the centre of the octahedra shifts towards one of the oxygen. There are six possible directions and are all equal. Hence, the spontaneous polarisation in all the possible direction will give the same result. Overall, the volume of the ferroelectric material showing the single polarisation orientation is called domains. The region between different domains is called the domain wall. There are two kinds of domain wall that can be found in the tetragonal perovskite: 90° domain wall (The polarisations of the neighbor regions are perpendicular), and 180° domain wall (The polarizations of the neighbour regions are opposite). Across the domain walls, the polarisation changes continuously but sharply. Generally, it has been found as a width of about 2-3 crystal unit cells; much smaller than the respective ferromagnetic domain wall. These ferroelectric domains allow for the minimising of the electrostatic energy of the depolarization field and the elastic energy accumulated during the structural phase transition from the centrosymmetric paraelectric to non-centrosymmetric ferroelectric phase. The polarisation of the material creates the accumulation of the charge at the surface of the material. This charge generates electric fields which are oriented oppositely to the polarisation. The opposite electric fields can be strong of the order of MV/m. To minimize these electric fields in the ferroelectric samples, different domains with opposite polarisation will form. Let us assume that the cubic cell of a perovskite above the Curie temperature is compressed along the [100] direction. To minimize the elastic energy, the long axis of the tetragonal cell will develop perpendicularly to the stress direction, while other unstressed areas remain parallel to the stress. The combination of electrical and elastic boundary conditions acting during the ferroelectric phase transition determines the domain structure as shown in **Figure 1.11**. Only 90° domains minimize the elastic energy. Both 180° and 90° domain walls contribute to the reduction of electrostatic energy. They are called ferroelectric domain wall because they differ in orientation concerning the spontaneous polarisation. Only the 90° minimize the elastic energy. This kind of wall is also called ferroelastic because the orientation differs from the spontaneous strain tensor [55].

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