Chapter 1
Introduction

Abstract

The foundation and strength of an effort depend on the history of its evolution. To make the effort success, it is imperative to review its history and make out the suitable future course of action............

With this vision, we have presented a brief description on the phenomenon on Ferroelectric materials has been presented. The different mechanisms responsible for their occurrences and their corresponding properties are described in detail. The application domains of the systems are also presented. At last, we have addressed to the motivation for different experiments performed on the ferroelectric materials and the choice of materials for the current research progress.
1. Introduction to Ferroelectric materials and its applications

The discovery of ferroelectricity in single-crystal materials (Rochelle salt) in 1921 and its subsequent extension into the realm of polycrystalline ceramics (barium titanate, $\text{BaTiO}_3$) during the early to mid-1940s has been a continuous succession of new materials and technology developments that have led to a significant number of industrial and commercial applications that can be directly credited to this most unusual phenomenon [1-3]. Among them, some of the applications are high dielectric-constant capacitors, piezoelectric sonar and ultrasonic transducers, radio and communication filters, pyroelectric security surveillance devices, medical diagnostic transducers, stereo tweeters, buzzers, gas ignitors, positive temperature coefficient (PTC) sensors and switches, ultrasonic motors, electro-optic light valves, thin-film capacitors and ferroelectric thin-film memories[4-7].

In classical literature on ferroelectrics, a ferroelectric material was usually defined by enumerating a number of features such as the existence of spontaneous polarization, the Curie point, behaving under Curie-Weiss law dependence and hysteretic $P(E)$ dependence. This standard has already pointed out that the definition of spontaneous polarization is impossible, when no unpolarized reference system is defined. Discoveries of new single-crystalline materials and non-single-crystalline systems as well as problems concerning magnitudes of lifetime materials have shown that, not all of the above enumerated features are the necessary conditions to define a material as ferroelectric. It appears reasonable from the point of view of both physical and engineering approaches to consider a material as a possible ferroelectric, if it contains a phase in which, there are regions of one or more kinds which can be assigned to one of 213 ferroelectric species.

1.1.1. Definition and characteristics of a Ferroelectric Material

Ferroelectrics are substances in which a built-in spontaneous polarization, $P_s$ (in units of electrical dipole moments per unit volume) exists in a certain range of temperatures and isotropic pressures in the absence of an external electric field. This
spontaneous polarization has two or more orientational states and can be switched from one state to the other by an external electric field, or in some cases, by a mechanical stress. As noted by Lines and Glass, [8] this definition is not very strict since the ability to switch the polarization depends on the experimental conditions and the sample properties such as the crystalline perfection and the electrical conductivity. For example, distinguishing ferroelectric hysteresis loops from nonlinear dielectric losses in some materials with large dielectric losses is difficult. However, ferroelectric switching is an important feature in distinguishing it from pyroelectric crystals. A pyroelectric material shows a flow of charge to- and from- its surfaces on changing the temperature, which changes its spontaneous polarization.

**Hysteresis curve**

The plot of polarization ‘P’ versus the applied field ‘E’ in which the material is polarized in one direction and then in opposite direction is called the hysteresis curve of the specimen. When a piece of ferroelectric material is initially unpolarized, is subjected to a gradually increasing electric field, the polarization ‘P’ varies with ‘E’. However ‘P’ does not vary linearly with electric field ‘E’ but varies with ‘E’ as shown in Fig.1.1.

**Remnant polarization or retentivity or remanance**

When the applied electric field ‘E’ reduces to zero, the material still remained polarized and ‘P’ has a certain value. The polarization remaining in the material when the polarizing field is reduced to zero is called the remanent polarization ($P_r$). The power of a material of retaining this polarization is called the retentivity or remanence of the material. Therefore, the retentivity or remanence of a material is a measure of the polarization remaining (residual polarization) in the material when the electric field is totally removed.

**Spontaneous Polarization**

A material is said to be spontaneously polarized when electric field ‘E’ is zero but polarization ‘P’ is not zero. This phenomenon is called spontaneous (by its own) polarization.

**Coercivity**

The coercivity of a material is a measure of the strength of the reverse polarising field ‘E’ required to wipe out the remnant polarization ($P_r$) of the specimen.
1. Introduction

The simplest ferroelectric materials turn out to provide a 'text-book' example of quantum criticality in the solid state. Ferroelectrics are materials that when cooled below their phase transition temperature $T_c$, undergo breaking of lattice inversion symmetry and spontaneously develop a macroscopic polarization. Pressure can be used as a 'quantum tuning parameter', as shown in the Fig.1.2, to suppress $T_c$ towards absolute zero. In the region where the temperature scale is much less than the Debye temperature of the lowest transverse-optic soft mode, quantum rather than classical statistical mechanics are required to understand the observed behaviour. In this (yellow) region, order-parameter fluctuations are typically found to exist in a four-dimensional space and the lattice is observed to fluctuate in a wildly unconventional form.

Ferroelectrics are spontaneously polarised, but are also piezoelectric, in that their polarisation changes under the influence of stress. The Venn diagram for the representation of ferro, pyro and piezoelectric materials is shown in Fig.1.3

Fig.1.1. Hysteresis curve for a standard ferroelectric sample
1. Introduction

Pyroelectrics are materials which typically experience a decrease in polarisation when their temperature is increased. The piezoelectric effect in ferroelectrics is very dependent on its atomic structure. Depending on the orientation of a crystal, applying a compressive stress can increase or decrease the polarisation, or sometimes, have no effect at all.

Fig. 1.2 Schematic of ferroelectric quantum critical point with typical perovskite crystal structure shown in the top right inset

Fig. 1.3 Venn diagram for the representation of ferro, pyro and piezoelectric materials
1. Introduction

1.1.2 Classification based on Crystal Classes

Out of a total of 32 crystal point groups, 21 are non-centrosymmetric i.e. crystals not having a center of symmetry. The term centrosymmetric refers to a space group which contains an inversion center as one of its symmetry elements i.e. for every point (x, y, z) in the unit cell, there is an indistinguishable point at (-x, -y, -z).

Table 1.1 Detailed crystal system with space groups for the classification of materials.

<table>
<thead>
<tr>
<th>Crystal class</th>
<th>Centro symmetric Point groups</th>
<th>Non-Centrosymmetric Point groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Polar</td>
</tr>
<tr>
<td>Cubic</td>
<td>m3</td>
<td>m3m</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4 or m</td>
<td>4 or mmm</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>mmm</td>
<td>mm2</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6 or m</td>
<td>6 or mmm</td>
</tr>
<tr>
<td>Trigonal</td>
<td>(\bar{3})</td>
<td>(\bar{3})m</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2 or m</td>
<td>2</td>
</tr>
<tr>
<td>Triclinic</td>
<td>(\bar{1})</td>
<td>1</td>
</tr>
<tr>
<td>Total Number</td>
<td>11 groups</td>
<td>10 groups</td>
</tr>
</tbody>
</table>

From 21 point groups, except the group 432, crystals containing all other point groups exhibit piezoelectric effect i.e. upon the application of an electric field, they exhibit strain or upon application of an external stress, charges develop on the faces of crystal resulting in an induced electric field.

It is interesting to note that among, non-centrosymmetric point groups, 10 belong to polar crystals i.e. crystals which possess a unique polar axis, an axis showing different
properties at the two ends. The detailed crystal system for the above class of materials is listed in Table 1.1. These crystals can be spontaneously polarized and polarization can be compensated through external or internal conductivity or twinning or domain formation [9]. Spontaneous polarization depends upon the temperature. Consequently, if a change in temperature is imposed, an electric charge is developed on the faces of the crystal perpendicular to the polar axis. This is called pyroelectric effect. All 10 classes of polar crystals are pyroelectric. In some of these polar non-centrosymmetric crystals, the polarization along the polar axis can be reversed by reversing the polarity of electric field. Such crystals are called ferroelectric (i.e.) these are spontaneously polarized materials with reversible polarization.

Hence by default, all ferroelectric materials are simultaneously pyroelectric and piezoelectric. Similarly, all pyroelectric materials are by default piezoelectric but not all of them are ferroelectric.

1.2 Concepts of Ferroelectrics
1.2.1 Dipole Moment, Polarization, Dielectric Permittivity, and Nonlinear Behavior

The polarization, ‘P’, is the key concept of ferroelectricity. In many texts, the macroscopic polarization is given as the dipole moment per unit volume. This is strictly correct for a system composed of elementary dipoles. However, in most dielectric crystals exhibiting a pyroelectric effect, such elementary dipoles cannot be individually distinguished and the material is better represented by an assembly of point charges. In a perfect insulator composed of a system of bound electric charges of charge density ρ(r), ‘P’ given by

\[ P = \frac{1}{V} \int V r \rho(r) dV \]  

where ‘V’ is a representative volume containing all of the species of interest and \( r \) is position. It can be shown that ‘P’ is independent of the spatial reference frame if the volume considered is electrically neutral. This is automatically ensured for a system of elementary dipoles when ‘P’ is simply the dipole moment averaged over a unit volume and in this case, the definition of ‘P’ is analogous to that of magnetization, ‘M’, in magnetic materials. It can be shown that even if the assembly is neutral as a whole, the
polarization defined by (1.1) depends on the shape of the sample, while a small change in the polarization does not. This Standard is concerned with both the value of ‘$P$’ and in changes, $\Delta P$, induced by variations of temperature or by external forces acting on the system [10,11].

A polarization can be induced in a dielectric material of any symmetry by an applied electric field ‘$E$’. In a linear dielectric, the induced polarization is linearly related to the applied field by $\partial P$:

$$\partial E = \varepsilon_0 \chi$$

This defines the dielectric susceptibility $\chi$, and $\varepsilon_0 \sim 8.854 \times 10^{-12}$ Fm$^{-1}$ is the permittivity of free space given in MKS units. This relation can be written in tensorial form as $\partial P_i$:

$$\partial E_j = \varepsilon_0 \chi_{ij}$$

where the Einstein convention for summation of repeated indices is used. The differential dielectric displacement, $\partial D$, is defined as

$$\partial D/\partial E = \varepsilon_0 + \partial P/\partial E$$

so that the change induced by the electric field is given by

$$\partial D_i/\partial E_j = (1+\chi_{ij}) \varepsilon_0 = \varepsilon_{ij}$$

The response of the dielectric described by (1.2) and (1.4) relates to equilibrium states. It can be shown that the susceptibility, $\chi$, is a real and symmetric tensor, $\chi_{ij} = \chi_{ji}$ and that $\chi_{ij} > 0$ for any $i, j$ and thus there are 6 permittivity components $\varepsilon_{ij} = \varepsilon_{ji}$, represented by real numbers. Depending on the symmetry of the dielectric medium, some of the components may be zero and some may be mutually related. For an isotropic medium, there is only a single permittivity value.

This basic dielectric response must be generalized in two ways. First, when an alternating sinusoidal field $E(\omega)$ of angular frequency $\omega$ is applied to a lossy dielectric, the polarization response can be delayed. This is described by introducing the complex susceptibility given as,

$$\chi_{ij} = \chi'_{ij} - j\chi''_{ij}$$

where

both the real $\chi'_{ij}$ and the imaginary $\chi''_{ij}$ components are symmetric and $\omega$-dependent. The complex permittivity is defined in a similar manner ($\varepsilon_{ij} = \varepsilon'_{ij} - j\varepsilon''_{ij}$). The second
generalization accounts for the fact that the response of the dielectric can be nonlinear. The static response can be described by
\[
\frac{\partial P_i}{\partial E_j} = \varepsilon_0 \left[ \chi_{ij}^{(2)} \varepsilon_k E_k + \chi_{ijk}^{(3)} E_k E_l + \ldots \right] \quad (1.6)
\]
where \( \chi^{(k)} \) are nonlinear susceptibilities represented by polar tensors of corresponding ranks. To treat the dynamic frequency-dependent response, Fourier components of nonlinear susceptibilities have to be introduced [12,13]. For easier understanding, it is also useful to consider a capacitor (i.e., a plate-like sample of a dielectric material provided with parallel conducting electrodes on which potentials are imposed by external circuitry) as the standard experimental configuration. The dielectric is assumed to be a perfect insulator. Fig.1.4 shows the arrangement for an idealized situation with an anisotropic dielectric with a right handed coordinate system.

![Fig.1.4. The experimental arrangement for dielectric measurement.](image)

On the left, the sample has none of the three crystallographic axes either perpendicular or parallel to the plane of the plate; on the right, the pyroelectric axis is assumed to be normal to the plate. The lateral dimensions should be much larger than the thickness dimension.
1.2.2 Piezoelectricity

Piezoelectricity is the linear relationship between an applied electric field and an induced strain, or an applied stress and an induced polarization. Non-zero components of the tensor $d$ can exist only in 21 point groups. Now, considering the above mentioned equations together describe the linear electric response of the material for the simultaneous applied electric field and mechanical stress.

Experimentally, the free permittivity can be determined by applying static or low frequency electric fields while the clamped permittivity manifests itself at high frequencies, when the sample deformation due to piezoelectricity is no longer significant due to inertia. It must be noted that the low and high frequency measurements can also differ due to the differences in adiabatic and isothermal permittivities, especially when measured near the Curie temperature [14 - 16].

1.3 Ceramic Systems

1.3.1 Ferroelectric Ceramics

A ferroelectric ceramic is a polycrystalline material in which individual grains are single crystals of a ferroelectric phase. Such grains are generally separated by well-defined grain boundaries. Conventionally in ceramic, the grains are randomly oriented, although with special processing, it is possible to orient the grains to produce textured specimens. The ceramic microstructure can have a strong impact on the observed ferroelectric domain structure and all of them associated with ferroelectric properties.

Grain Boundaries

A grain boundary is a junction between grains. The thickness and composition of the grain boundaries control the interaction between grains. In a polycrystalline ceramic, each of the grains has a local symmetry which is similar to that of a single crystal of the same composition. The material properties of each grain may be the same as that of a large single crystal, if the grains are large enough.

For small grain systems, properties may be modified due to “size effects.” There are many causes for the so called “size effects;” one of them is the increase of surface to volume ratio, so that the grain boundaries play a substantial role in determining the
material properties. A second result from the elastic and electrical constraints at the boundary of the grain. The grain boundaries break the continuity of the ordering of the single grain, which in turn forces the material properties to vary with grain size. For thin grain boundaries, as in some highly densified ceramics, significant correlation of the order parameter may be established across the grain boundaries. Domain walls relate twins such that the structure is coherent across the wall; in contrast a grain boundary demarcates incoherent crystallographic regions. For a ferroelectric ceramic, the cross-grain coupling includes both the long range electric and elastic interactions.

The difference in material properties between the ferroelectric grains and the grain boundaries could be large; therefore, grain boundaries are also an important constituent to form a composite with the polycrystalline systems in determining the macroscopic material properties. Even, when the grain boundaries are quite thin, significant changes in the macroscopic properties can be observed in fine-grained materials. Grain boundaries typically dilute the dielectric constant and can result in large apparent differences between the Curie-Weiss temperature and the peak permittivity.

It should also be noted that grain boundaries can have appreciable different electrical resistivities than the grains themselves. This can result in large space charge contributions to the dielectric response.

Depending on the processing techniques, the grain sizes of ferroelectric ceramics typically range from 0.01 μm to >10 μm. Under some conditions, grain boundaries can be made atomically sharp; however, the lack of atomic coherency still makes them behave differently from the domain boundaries in responding to applied electrical and mechanical fields. Domain walls allow the atoms to cross back and forth over the walls.

1.3.2 Poling and Switching of the Spontaneous Polarization

All ferroelectrics are a subset of the family of pyroelectric materials in which the direction of the spontaneous polarization can be changed between two or more orientational states by a realizable applied electric field. The orientational states have the same crystal structure, but differ in the direction of the spontaneous polarization at zero applied electric field. These are called ferroelectric domains.
Poling of a ferroelectric material is the process by which a unipolar electric field is applied to a multidomain ferroelectric to produce a net remnant polarization. By the application of a high electric field to the ceramic system, domain switching may occur, resulting in a global polarization. This is referred to as poling, and is essential in developing a net piezoelectric or pyroelectric response in a ceramics. Since the coercive field is generally minimum near \( T_C \), common poling practice is to cool through \( T_C \) with a field applied. Due to the random alignment of the grains, in most ceramics, the maximum achievable polarization is smaller in a ceramic system than in a properly oriented single crystal [17].

Switching is the process by which the domain polarizations are reversed (or reoriented) to give a new value (or direction) of \( P_r \). As grown, ferroelectric crystals usually contain multiple domains. As a result, they may exhibit little or no net macroscopic polarization. In a single crystal, a net polarization is imparted, and in the limit, a single-domain state is achieved by poling. To pole a crystal, an electric field is usually applied along one of the possible polar axes.

As the electric field is increased in magnitude, domains with the polarization direction favorably oriented with respect to the field direction grow at the expense of other domains. This process continues with increasing electric field until the least favorably oriented domains switch to the polar direction most nearly coinciding with the electric field direction. When no further domain reorientation can occur, the saturation arm of the \( P \) versus \( E \) response usually becomes anhysteretic. The polarization achieved at the highest applied fields is the maximum polarization \( P_{\text{max}} \). The field at which \( P_{\text{max}} \) is measured should be specified.

The switching process (typically from \( \pm P_r \) to \( +P_r \)) occurs through nucleation and growth of domains that are favorably oriented with respect to the applied electric field. When the electric field is removed, the mechanical boundary conditions may nucleate new reverse domains. The resulting polarization state where \( 'E' = 0 \) is defined as the remnant polarization, \( P_r \). Due to the existence of domains, \( P_r \) is always \( \leq P_s \). Thus, when \( P_s \) is determined from a square hysteresis loop, it is important that its magnitude be checked by other means, since full poling is not always achieved. The poling process is illustrated in Fig.1.5 by the \( 'P' \) versus \( 'E' \) curve from a depoled state (\( P = 0 \)) to the \( P_{\text{max}} \).
In a ferroelectric single crystal initially poled to $P_r$, it is possible to switch the polarization to the opposite sign by applying an electric field (equal in magnitude but of opposite polarity to the initial poling field). Similarly, if an alternating electric field of sufficient magnitude is applied to the crystal, preferably along one of the alternative polar axes, the polarization ‘P’ will vary through a hysteresis loop similar to the one shown in Figure 1.5, although many virgin samples will show constricted loops before expanding to show a normal hysteresis. Even though each domain of a crystal can have only a single polarization state, the average of many domains allows the macroscopic polarization of the same crystal to possess intermediate remanence values designated $P_{r(i)}$.

![Hysteresis Loop Diagram](image)

**Fig.1.5.** (a) Polarization versus Electric Field Hysteresis Loop. The solid line is for normal ac measurements. The measured quantity is $D$ rather than $P$, but the two numbers are nearly identical for the large permittivities associated with most ferroelectrics. (b) One possible example of corresponding domain structures. The electrodes are not shown.

The switching process generally occurs through nucleation and growth of domains that are favorably oriented with respect to the applied electric field. The domains
propagate through the crystal with a direction and velocity determined by and related to the direction and magnitude respectively of the applied electric switching field. Elastic interactions may result in back-switching of some domains over time. This is one of the main reasons for aging. A highly oriented ceramic should, in principle, produce higher net polarization with less aging. Rapid cooling of a poled ceramic will pyroelectrically induce electric fields that can sometimes depole the ceramic through the creation of antiparallel domains. Polishing or mechanical perturbation after poling can also change the original domain structure in ferroelastic ferroelectrics.

The global symmetry of a macroscopic sample of a ceramic is usually higher than the local symmetry and can to some extent, be controlled by processing. Poling is one of the ways to change the global symmetry from $\infty\infty m$ to $\infty m$. From a statistical viewpoint, the global symmetry of the sample has significance only when the number of grains is very large; it gradually loses its meaning as the number of grains is reduced either by the growth of grains or by a reduction in system size.

1.3.3 Ferroelectric Thin Films

Thin films are layers which are usually under ~10 μm in thickness which are deposited on substrates. In most cases, it is not possible to remove the film from the substrate, so that the composite film/electrode/substrate system is measured rather than the free-standing film. As a result, the dielectric, piezoelectric and pyroelectric, etc. coefficients reported for films are generally effective coefficients (i.e.) for the case of a film rigidly clamped to a substrate. In addition, many thin films are under hundreds of MPa to GPa of in-plane stress as a consequence of intrinsic growth stresses, lattice misfits in unrelaxed films and/or the thermal expansion coefficient mismatch between the film and the substrate. These stresses can shift the transition temperature even alter the equilibrium domain structure, change the order of the phase transition, and may shift the phase transition sequence as a function of temperature [18-20].

To augment the definitions given above, there is additional terminology which is becoming widespread in the ferroelectric film community. Several of these terms are defined in this section.
**Fatigue:** Fatigue is the loss of switchable polarization as a function of the number of times the polarization has been re-oriented.

**Imprint:** Imprint refers to a shift of the hysteresis loop along the voltage axis (see Fig.1.6). If the voltage shift is large enough, this can lead to both remnant polarization states having the same sign at zero applied electric field.

**Retention:** Retention refers to the magnitude of the measured remnant polarization of a ferroelectric as a function of time after the poling operation. These measurements are often made by characterization of the non-switched current.

![Hysteresis Loops](image)

Fig.1.6. Normal (solid line) and imprinted (dashed line) hysteresis loops.

A **Write** event refers to the application of an electric field to a ferroelectric non-volatile memory element in order to define the polarization direction. A **Read** event describes an attempt to determine the sign of the remnant polarization.

In terms of piezoelectric properties, it is important to remember that the properties of films are often measured with the film still elastically clamped to a substrate, or at least a thin supporting structure. As a result, the measured piezoelectric coefficients differ from those widely in use for bulk materials. A good review of this has been given elsewhere [21]. If the substrate plane is defined as the 1-2 plane, with 3 corresponding to the substrate normal, then the in-plane strains of the film and the underlying support...
structure must be identical in 1 and 2 directions. In contrast, the film is free to deform in
direction 3, so that $T_{33} = 0$. For a thin film rigidly attached to a much thicker substrate,
when a field is applied, $S_{11} = S_{22} = 0$; in-plane stresses and an out-of-plane strain are
developed. The equation of state (in contracted notation) using the compliance tensor and
d coefficients (for the average polar directions parallel to E-field no shear components)
shall be represented as,

$$S_1 = (s^{E}_{11} + s^{E}_{12})T_1 + d_{31}E_3 = 0$$

$$S_3 = 2s^{E}_{13}T_1 + d_{33}E_3$$  (1.7)

From (1.7), it is possible to define effective piezoelectric coefficients

$$e_{31,f} = -(T_{1}/E_{3}) \text{ and } d_{33,f} = S_{3}/E_{3}:$$

$$e_{31,f} = \frac{d_{31}}{s^{E}_{11} + s^{E}_{12}}$$

$$d_{33,f} = \frac{d_{33} - d_{31}}{s^{E}_{11} + s^{E}_{12} d_{31}}$$  (1.8)

The effective coefficients can be measured in different ways [22-26]. It is extremely
important that in these measurements the applied stress, the electrode geometry, and
sample deformation be known in detail as many measurement techniques are prone to
substantial errors associated with unintentional flexure of the substrate [27].

1.4 Applications of Ferroelectric Materials

Much interest in ferroelectric materials arises because they possess properties that
are of use in a number of applications. In some cases ferroelectrics are already among the
leading materials for a particular application; in others the possibilities that are presented
by novel materials and geometries are starting to be realized. Here we present a brief
overview of both established applications and those that may still to come.
1. Introduction

1.4.1 Pyroelectric and Piezoelectric Devices

Many applications for ferroelectric materials do not make use of the ferroelectricity itself but of the related properties of pyroelectricity and piezoelectricity. Pyroelectrics are useful in a variety of imaging and detection applications. Piezoelectrics find a host of uses in electromechanical devices. More particular in micro-electromechanical systems (MEMS), the large piezoelectric coefficients of ferroelectric solid solutions such as PZT allow for novel miniature electromechanical devices [28].

1.4.2 Ferroelectric Memory Technology

The desirability of nonvolatile memory technology in computing applications, in particular in mobile devices has long been evident, as demonstrated by the current success of FLASH-based technology, in digital cameras, mobile phones, MP3 players and a host of other portable devices. FLASH is not, however, the long-term nonvolatile memory of choice, because of limitations regarding endurance, scalability and voltage requirements. Ferroelectrics have been considered for almost twenty years [29] to be a leading candidate for the next generation of nonvolatile memories. Commercially available devices do exist, but seem to be more common in niche applications or as part of an integrated memory device involving several different memory technologies, rather than as a standalone high-capacity nonvolatile memory. Other competing technologies also exist, most notably MRAMs and phase-change memory.

One of the issues that has hindered widespread implementation of ferroelectrics as memory elements is that to determine the polarization state of a ferroelectric, it is usually necessary to attempt to switch the polarization; the data stored is then erased and must be rewritten, i.e., the read-out operation is destructive. As ferroelectrics can suffer from fatigue with repetitive cycling, this destructive read-out places a limitation on the reliability, though over the years fatigue resistance has been improved by the use of oxide electrodes. Many applications of ferroelectric compounds for memory devices has been discussed earlier [30]. There is still also considerable interest in nondestructive read-out devices including ferroelectric field-effect transistors or through the use of materials or composite structures where ferroelectric and ferromagnetic orderings are coupled and the
electrical polarization direction can be measured from the magnetization. More information on multiferroics was also outlined elsewhere [78].

1.4.3 Potential Future Applications

Here, we like to take a look at a number of interesting possible applications of ferroelectrics that are in the earlier stages of development. This section is intended to be inspiring rather than comprehensive.

1.4.3.1 Ferroelectric Nanostructures

In recent years ferroelectrics have been fabricated in a number of novel geometries, which in turn have suggested some new applications. Ferroelectric materials appear to retain their properties on reduction of size remarkably well with ferroelectric nanoparticles remaining ferroelectric to sizes at least as small as 20nm [32,33].

The critical thickness in ferroelectric thin films is on the order of a few unit cells (being highly dependent on boundary conditions) [34]. High-density arrays of ferroelectric nanocapacitors are thus feasible as the basis for extremely high capacity memory devices. Focused-ion-beam (FIB) milling [35] and e-beam direct writing [36] can be used effectively to make capacitors with nanoscale dimensions. A key problem that remains is to produce these high-density arrays in a time- and cost-effective manner, while maintaining good registry and material properties, which has led to interest in the idea of self-patterning of ferroelectric nanocapacitors [37].

Ferroelectric nanoshell tubes (polycrystalline ceramic tubes with walls of nanoscale thickness) have been fabricated by a number of group and show significant applications, ranging from high aspect ratio memories to microfluidic delivery systems. The tubes are made by growth in a porous matrix which gives them a high degree of regularity and good registry. Another approach for fabricating ferroelectrics with novel nanoscale geometries i.e. yielding interesting results is the FIB technique used by the group in Belfast to cut single crystals into thin films, rings and a variety of other interesting shapes.
1.4.3.2 Field-Effect Devices

Ferroelectric field-effect transistors in which the gate dielectric on a conventional FET is replaced by a ferroelectric material. The conductivity of the semiconductor channel is modified by the screening charge of the ferroelectric. The key obstacle to overcome is that the poor retention time is typical in these devices. The ferroelectric field effect can also be used to modify the properties of more exotic systems, particularly superconducting or magnetic oxides [38-43].

1.4.3.3 Ferroelectric Device Fabrication Using Atomic Force Microscopy

Ferroelectricity can be controlled on the nanoscale using an atomic force microscope (AFM) tip as a mobile top electrode. With this approach, one can envisage using an AFM tip to write extremely dense arrays of ferroelectric domains for use as a memory device [44]. Another idea is to make a surface acoustic wave device (commonly used as a frequency filter in mobile phones) with reduced feature size by using the AFM tip to write a nanoscale ferroelectric domain structure in place of the conventional interdigital electrodes, thereby achieving a much higher operating frequency [45]. Combining the nanoscale control of ferroelectric domain structure achievable with the AFM with the modulation of electrical conductivity allowed by the ferroelectric field effect allows one to locally define in the same material regions of differing electronic properties [46]. Using this approach on highly correlated electronic materials, such as high-temperature superconductors, one could potentially design one-dimensional superconducting wires, superconducting rings and junctions, superconducting quantum interference devices (SQUIDs) or arrays of pinning centers.

1.4.3.4 Ferroelectric Cooling Devices

The idea of using the thermoelectric effect associated with a ferroelectric phase transition for cooling has some history [47,48], but has recently received a revived attention through the demonstration that with moderate voltages applied to thin films [49], significant cooling can conceivably be achieved. This approach is of interest in computing applications where the problem of heat production is a key challenge. In this section we have only just scratched the surface of what can conceivably be achieved with
ferroelectrics. Several other proposals already exist and an interesting overview of some other novel device ideas has recently been written by Scott [50], beyond this, new ideas are sure to continually emerge as we push the boundaries of material design in ferroelectric systems.

1.5 Materials and Structures

Important optical ferroelectric materials can be classified into oxygen-octahedra ferroelectrics and phosphate/arsenate/sulphate/selenate-type ferroelectrics. These materials are either used as single crystals or thin films. These are briefly described below.

Fig.1.7. (a) LiNbO$_3$ - type structure, where grey circles are Li, black circles are Nb, and open circles are oxygen. (b) Tungsten Bronze structure with the general formulae (A1)$_x$(A2)$_{5-x}$Nb$_{10}$O$_{30}$. The black circles are Nb, placed inside oxygen octahedras (squares), open circles are A1 atoms, and grey circles are A2 atoms.

Structure of lithium niobate is shown in above Fig.1.7(a). There are Nb$^{5+}$ und Li$^+$ ions on non-centrosymmetric lattice sites. Thus the material has a preferred direction and a spontaneous polarization. An external electrical field can be used to move the ions and to invert the preferred crystal direction.

The tetragonal tungsten bronze (TTB) structure arrangement is shown in Fig.1.7(b). The arrangement of NbO$_6$ octahedra in the form of five-members rings provides three types of interstitial sites: trigonal sites are vacant, tetragonal (A1) and
pentagonal (A2) sites are partially occupied (5/6) by the divalent Sr and Ba atoms, and partially vacant (1/6) for reasons of electroneutrality. In this structure NbO$_6$ octahedra are not equivalent and two types must be distinguished. For both types the octahedral axes are not perfectly perpendicular to the (a, b) plane but slightly tilted from the polar c-axis (about 8°). Above Tc the displacement of metallic atoms from their mean oxygen planes along the c-axis becomes zero except for one of the two types of Nb atoms (80% of them), which are distributed above and below oxygen planes with equal probability. The symmetry point group of the crystal transforms from 4mm to 42m, which is a non polar but also a non-centrosymmetric class. Birefringence and second harmonic generation exist above Tc.

1.5.1 Oxygen Octahedra Ferroelectrics

Classification of oxygen octahedra ferroelectrics based on structure leads to perovskite type, Aurivillius-type, LiNbO$_3$-type, and tungsten-bronze type ferroelectric structures as shown in Fig.1.7. All these ferroelectrics have a common motif structure of BO$_6$ composed of six oxygen’s (O) surrounding a central tertravalent or pentavalent transition metal ion, labeled generally as B here. The oxygen cage has 8 faces, hence called an octahedron. The highest symmetry phase (typically the highest temperature phase) is called the paraelectric phase, where the time-averaged mean position of the cation B occupies the geometric center of the oxygen octahedron. At lower temperature, a Jahn-Teller distortion of the octahedron results in the creation of ferroelectricity. This is accompanied by a displacement of the B ion from the geometric center of the cage which occurs during a ferroelectric phase transition and contributes in large part to the ferroelectricity in these structures.

1.5.2 Perovskite-type ferroelectrics have the general formulae ABO$_3$ are the most common type of optical ferroelectrics (see Fig.1.8(a)), where A are monovalent or divalent metal ions that occupy the corners of the pervoskite cube, the oxygens that form the octahedra occupy the six face centers and the transition element B occupies the center of the cube. The perovskite structures form a larger lattice by stacking of the cubes, leading to a network of vertices sharing octahedra. The most common optical
ferroelectrics of this type are BaTiO$_3$, KNbO$_3$, KTa$_{1-x}$Nb$_x$O$_3$ (also called KTN:$x$), PbTiO$_3$, and Pb$_{1-x}$La$_x$(Zr$_y$Ti$_{1-y}$)$_{1-0.25}$VB$_{0.25}$O$_3$, (also called PLZT:$x/y/1-y$), all of which are primarily useful for electro-optic applications and Ba$_{1-x}$Sr$_x$TiO$_3$ which is used in pyroelectric detectors. It is to be noted that multiple ferroelectric phases can exist with a single material in different temperature ranges. For example, BaTiO$_3$ and KNbO$_3$ both show a high temperature cubic paraelectric phase, which on cooling results successively in tetragonal, orthorhombic and rhombohedral ferroelectric phases. These are respectively accompanied by displacement of the cation $B$ from the geometric center of the perovskite unit cell in the directions of $<100>$, $<110>$ and $<111>$. These displacements are typically small (of the order $\sim 0.1 \Delta$). KTN and PLZT are examples where multiple cations occupy the $A$ and the $B$ sites.

Fig.1.8:Schematic diagrams of units cells of (a) Perovskite ABO3: Open circles are oxygen, light grey circles are $A$ atoms, and dark grey circle (center) is the transition element $B$. (b) Aurivillius phase of the general formulae $(\text{Bi}_2\text{O}_2)^{2+}(\text{Me}_{x+1}\text{R}_x\text{O}_{3x+1})^{2-}$, where in this example of Bi$_4$Ti$_3$O$_{12}$, Me is a Bi-atom (half black-half white circles), R is a Ti-atom (black circles), and open circles are oxygen.
For example, KTN can be considered to be a solid solution (on atomic scale) of $(1-x)\text{KTaO}_3 + x\text{KNbO}_3$, where $\text{KNbO}_3$ is a ferroelectric with a cubic-to-tetragonal $T_c$ of $435^\circ\text{C}$ ($708\text{ K}$) and $\text{KTaO}_3$ is paraelectric down to $1.6\text{ K}$. By varying the relative composition, $x$ from 0 to 1, a continuous gradation of ferroelectric properties such as Curie temperature, polarization, electro-optic, nonlinear-optical coefficients and dielectric response can be achieved [51]. $\text{PbTiO}_3$ is a tetragonal ferroelectric below the $T_c = 493^\circ\text{C}$, and $\text{PbZrO}_3$ is orthorhombic and antiferroelectric below the Neel temperature, $T_N = 230^\circ\text{C}$. Their solid solution, $\text{PbZr}_{x}\text{Ti}_{1-x}\text{O}_3$, also called PZT:$x$ is the most commonly used piezoelectric material today, though its application in optics is limited. However, the addition of $\text{La}$- to the $\text{Pb}$- site helps in sintering these materials into highly transparent ceramics, $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{y}\text{Ti}_{1-y})_{0.25}\text{VB}_{0.25}\text{O}_3$, (VB stands for vacancies in the $B$ site) which are useful for electro-optic modulators due to their large electro-optic coefficients [52].

**Aurivilli** phases are closely related to the perovskite type structures, but contain a layered approach to building each unit cell, which can be very large. They are composed of perovskite-like layers of $(\text{Me}_{n-1}\text{RnO}_{3n+1})^{2-}$ slabs regularly interleaved with $(\text{Bi}_2\text{O}_2)^{2+}$ layers, where $\text{Me}$ is a monovalent or divalent element such as $\text{Bi}^{2+}$, $\text{Ba}^{2+}$, $\text{Sr}^{2+}$, $\text{Ca}^{2+}$, $\text{Na}^{+}$, $\text{Pb}^{2+}$ etc, and $\text{R}$ can be $\text{Ti}^{4+}$, $\text{Nb}^{5+}$, $\text{Ta}^{5+}$, $\text{Mo}^{6+}$, $\text{W}^{6+}$, $\text{Ga}^{3+}$, $\text{Fe}^{3+}$, $\text{Cr}^{3+}$, and $n$ can be 1 to 8. Their overall general formulae is therefore $\text{Me}_{n-1}\text{RnO}_{3n+3}$. Examples of ferroelectrics in this class are $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{SrBi}_2\text{Nb}_2\text{O}_9$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, $\text{BaBi}_2\text{Nb}_2\text{O}_9$, $\text{BaBi}_2\text{Ta}_2\text{O}_9$, $\text{PbBi}_2\text{Nb}_2\text{O}_9$, $\text{PbBi}_2\text{Ta}_2\text{O}_9$, and other more complex multi-cation compounds such as $\text{BaBi}_3\text{Ti}_2\text{NbO}_{12}$ etc. Of these, the only one to receive some attention for optical applications is bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with $n=3$. [53,54] Strontium bismuth niobate and tantalate have received considerable attention for non-volatile ferroelectric memory, but their optical properties have not been investigated.

**Lithium Niobate type ferroelectrics**, particularly $\text{LiNbO}_3$ and $\text{LiTaO}_3$ (Fig.1.7(a)), are widely used optical ferroelectrics today, with applications in high speed electro-optic and acousto-optic modulators, domain engineered devices for optical frequency conversion, beam steering, dynamic focusing and beam shaping and pyroelectric detectors. Unlike perovskites, the oxygen octahedra units O6 are joined not by connecting vertices, but by connecting the octahedral faces. [55,56] This results in a stack of distorted oxygen octahedra on top of each other joined by their faces along the
polar c-axis. Unlike perovskites, not all of these stacked octahedra are filled by B cations. Along the c-axis of the trigonal structure, the octahedral are filled in the sequence “Li, Nb (or Ta), vacancy, Li, Nb(or Ta), vacancy,….” etc. Two formulae units of LiNbO$_3$ form one unit cell, because of staggered oxygens that repeat after two consequentive operations of the c-glide symmetry. The high temperature paraelectric phase is trigonal 3m, which transforms to the ferroelectric, trigonal 3m phase below the $T_c$ of ~1200°C for LiNbO$_3$ and ~620°C for LiTaO$_3$. This transition is accompanied by a small displacement of the Nb(Ta) from the center of its octahedron to an asymmetric position along the c-axis within the same octahedron and a corresponding motion of the Li from one octahedron to the adjacent vacant octahedron through the intermediate close-packed oxygen plane. The direction of motion of these cations defines the positive end of the spontaneous polarization, $P_s$.

**Tungsten Bronze (TB) ferroelectric structures** are so called because they are closely related to the tetragonal tungsten bronzes K$_x$WO$_3$ and Na$_x$WO$_3$. The general TB compositions are considered to be close to one of the following: (A1)$_x$(A2)$_{5-x}$Nb$_{10}$O$_{30}$ (when A1 and A2 are alkaline earth ions), (A1)$_{4+x}$(A2)$_{2-2x}$Nb$_{10}$O$_{30}$ (when A1 is alkaline and A2 is alkali), and (A1)$_{6-x}$(A2)$_{4+x}$Nb$_{10}$O$_{30}$ (when A1 and A2 are both alkali ions). The well-known optical ferroelectrics of this type are strontium barium niobate (Sr$_{5.5}$Ba$_x$Nb$_{10}$O$_{30}$, also called SBN), barium sodium niobate (Ba$_{4+x}$Na$_{2-2x}$Nb$_{10}$O$_{30}$, also called BNN), and potassium lithium niobate (K$_{6-xy}$Li$_{4+x}$Nb$_{10+y}$O$_{30}$, also called KLN), which are useful for electro-optics and holography. They also have a frame of BO$_6$ octahedron in an ABO$_6$ lattice. The tetragonal unit cell consists of 10BO$_6$ octahedra linked by their corners to form three different types of channels (labeled as A1, A2 and C) running through the structure parallel to the c-axis (Figure 7(b)). [57,58] In addition there are two different B-cation sites, B1 and B2. In SBN, for example, the unit cell contains 5 formulae units (10NbO$_6$ octahedra) (Fig.1.7(b)). The A (Sr, Ba) atoms take ~ 5 interstitial sites out of 6 available sites (2 A1+4 A2) among the octahedron. A1 site has four-fold symmetry and contains the smaller Sr ion, while A2 is pentagonal and larger in size preferred by the Ba and also the remaining Sr. The interstitial sites (C) are empty in SBN and BNN because the A1 and A2 site ions are too big to enter the C sites. This is not the case in KLN where
the small Li atoms fill the C sites, along with some of the excess Nb. The B1 and B2 sites are occupied by Nb in all three materials. The O-Nb-O octahedral axes in the octahedra are not precisely parallel to the c axis. They are tilted through about 8° from the polar axis (c axis) in SBN. The small displacements of Sr/Ba and Nb atoms in SBN along the c axis from their adjacent oxygen planes at room temperature create the permanent dipole inside the crystal and make them ferroelectric at room temperature. The ferroelectric properties reflect the disorder in the structure. For example, a diffuse phase transition occurs, where the transition temperature shifts from ~330 K for \( x = 1.25 \) to ~469 K for \( x = 3.75 \).

1.5.3 StrontiumBarium Niobate SBN structure

The interest in tungsten bronze ferroelectrics renewed in 1969’s because of its large optical non-linearities. Attention further centered on solid solutions of alkali and alkaline earth niobates from which transparent crystals could be grown with a variety of ferroelectric properties depending on the specific cations introduced into the structure. The composition may be considered to be close to one of the following formulae:

(a) \((A1)_x (A2)_{5-x} \text{Nb}_{10} \text{O}_{30}\), (A1 and A2 are alkaline earth ions)

(b) \((A1)_{4+x} (A2)_{2-2x} \text{Nb}_{10} \text{O}_{30}\), (A1 is alkaline earth ion and A2 is alkali ions)

(c) \((A1)_{6-x} (A2)_{4+x} \text{Nb}_{10} \text{O}_{30}\) (A1 and A2 are alkali ions).

Probably the best-known and most widely studied examples of each of the three categories above are Sr\(_5\cdot \text{Ba}_{x} \text{Nb}_{10} \text{O}_{30}\) (SBN), Ba\(_{4+x} \text{Na}_{2-2x} \text{Nb}_{10} \text{O}_{30}\) (BNN) and K\(_{6-x-y} \text{Li}_{4+x} \text{Nb}_{10+y} \text{O}_{30}\) (KLN) respectively. Ferroelectricity was found and studied in these systems by Francombe (1960) [59], Rubin, Van Uitterat, and Levenstein (1967) and Van Uitterat et.al. (1967) respectively.

The existence of strontium barium niobate crystals (Sr\(_x\cdot \text{Ba}_{1-x} \text{Nb}_2 \text{O}_6\), noted SBN:100x) was first reported in 1960 (Francombe, 1960) and first large SBN single crystals were grown by Ballman and Brown [59] over the range \( 0.25 < x < 0.75 \) (Ballman & Brown, 1966). In 1970, the Bell Telephone Laboratories had published successive thorough investigations of the optical, electrical and structural properties of SBN crystals. The high values of the electro-optic and pyroelectric coefficients oriented further work mainly towards holographic and pyroelectric applications.
The development of SBN films started at the USSR Academy of Science in Novosibirsk (Baginsky et al. [60], 1978) using a RF sputtering technique. Different deposition techniques have been then investigated: mainly sol-gel process, metal-organic chemical vapour deposition (MOCVD), and pulsed laser deposition (PLD).

Strontium Barium Niobate (SBN) crystals belong to the tetragonal unfilled tungsten-bronze (TB) structure with the space group $P4bm$. Tungsten bronze materials have a general chemical formula, $(A1)_4(A2)_2C_4(B1)_2(B2)_8O_{30}$. Its structure is built up of two types of crystallographically independent NbO$_6$ octahedra linked by their corners in such a way that three different types of channels are formed along the tetragonal c axis [61-64]. Firstly a triangle channel shown as C in the figure 8 is always empty secondly, a tetragonal channel is partially filled only by Sr atoms (A2) and thirdly a pentagonal channel is also partially occupied by Sr and with Ba (A1).

![Detailed view of the structural channels in SBN crystal and tungsten-bronze type structure projected to the (001) plane.](image)

Strontium barium niobate, $\text{Sr}_{x}\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (congruent composition with $x=0.61$) was synthesized and identified as a ferroelectric crystal at room temperature in the 1960’s [65]. Due to the outstanding photorefractive, electro-optic, nonlinear optical, and
dielectric properties, SBN is a very attractive material for technological applications and basic research. SBN is employed in pyroelectric detectors [66,67], holographic data storage systems [68-71] phase conjugation devices [72], Generation of photorefractive solitons [73], quasi-phase-matched second-harmonic generators [74] and also for electro-optic modulators [75]. The exceptional properties of the SBN ceramics have drawn the attention of scientists and a number of studies have been carried out. In the literature, there are several articles concerning the SBN ceramics, especially on the congruent composition. It is worthwhile to mention here that the existence of stable tetragonal tungsten-bronze structure of strontium barium niobate lies in the composition range 0.26 - 0.87 [76].

**Origin of ferroelectricity in SBN**

The SBN unit cell contains five formula units (of 10NbO$_6$ octahedra linked by their corners) with only five alkaline earth cations to fill six interstitial A1 and A2 sites. Both these ions are too large to enter the small C sites. The structure is thus incompletely filled and a certain degree of randomness is expected. The O-Nb-O octahedral axes in the octahedral are not precisely parallel to the c axis. They are tilted about 8° from the polar axis (c axis) in SBN. The small displacements of Sr/Ba and Nb atoms in SBN along c axis from their adjacent oxygen planes at room temperature create a permanent dipole inside the system and make them ferroelectric at room temperature.

New strategies for materials fabrication are of fundamental importance in the advancement of science and technology. All particle synthesis fall into one of the three categories: vapor-phase, solution precipitation, and solid-state process. There are a handful of processes that combine aspects of one or more of these broad categories of processes.
1.6. Scope of the thesis

The need for ferroelectric strontium barium niobate (SBN) is of much industrial importance. New strategies for materials fabrication are of fundamental importance in the advancement of science and technology.

The present investigation is aimed

(i) to synthesis of pure $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ and Ce doped $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ ceramic powder samples

(ii) to prepare thin films of both $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ and Ce doped $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$ sample

(iii) to study the structural, optical and surface properties of SBN and Ce doped SBN ceramics and thin films.

(iv) to investigate electrical properties of SBN and Ce:SBN.

(v) to study the silver ion irradiation effects on the SBN and Ce:SBN thin films

(vi) to understand its feasibility on the device fabrication from the above mentioned results were discussed.
References

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[58] M. H. Francombe, Acta Crystallographica, 13 (1960)131


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[61] P. B. Jamieson, S. C. Abrahams and J. L. Bernstein, “Ferroelectric Tungsten Bronze-Type Crystal Structures Barium Strontium Niobate Ba$_{0.27}$Sr$_{0.75}$Nb$_2$O$_{5.78}$”, Journal of Chemical Physics, 48 (1968) 5048.


[63] T. S. Chernaya, Maksimov, B. A.; Verin, I. V.; Ivleva, L. I.; Simonov, V. I. “Crystal structure of Ba$_{0.39}$Sr$_{0.61}$Nb$_2$O$_6$ single crystals Crystallography Reports”, 42 (1997) 375-380.


1. Introduction


