Chapter I
Introduction
General

Materials are the working substance of the society and they are so intimately related to our culture and our very existence that the ages of mankind are defined in terms of materials. The measure of mankind’s progress has been given names like stone, bronze and iron ages. Not only naturally occurring materials, but manmade ones have become such an integral part of our lives that we often tend to take them for granted. In the words of Morris Cohen “materials science and engineering is concerned with the generation and application of knowledge relating the compounds, structure, and processing of materials to their properties and uses”. Correlations between the structures and properties of materials have made rapid advances in the past few decades.

Materials now-a-days have been come to be regarded as substances which find use in structures, machines, devices or products. The plethora of materials useful in the categories mentioned includes metals, ceramics, semi conductors, polymers, glasses, dielectrics, magnetic materials etc.

The following sections give an introduction to dielectrics in general, ferroelectrics in particular.

1.1 Dielectrics

These are insulating materials which offer a high resistance path to the flow of an electric current under the action of a ‘direct current’ voltage. The most important property of dielectrics is their ability to be polarized under the action of an externally applied field. The concept of polarization of dielectrics was put forward for the first time by Faraday.

In most cases of ‘linear dielectrics’, the magnitude of polarization $P$ is directly proportional to the intensity of the electric field $E$. For a dielectric
\[ P = \varepsilon_0 \chi_e E \]  \hspace{1cm} (1.1)

provided the field is not too strong. The constant of proportionality \( \chi_e \) is the electric susceptibility and is a dimensionless quantity. The term \( E \) in the above equation represents the total field and may have contributions due to free charges and the polarization etc.

In a linear dielectric, the electric displacement \( (D) \) is given in terms of \( E \) and \( P \) as

\[
D = \varepsilon_0 E + P \hspace{1cm} (1.2)
\]

\[ D = \varepsilon_0 E + \varepsilon_0 \chi_e E \hspace{1cm} (1.3) \]

\[ D = \varepsilon_0 (1 + \chi_e) E \hspace{1cm} (1.4) \]

Hence it can be seen that \( P \) and \( D \) are proportional to \( E \) and

\[
D = \varepsilon E \hspace{1cm} (1.5)
\]

Where

\[ \varepsilon = \varepsilon_0 (1 + \chi_e) \hspace{1cm} (1.6) \]

And \( \varepsilon \) is called the ‘permittivity’ of the material. In vacuum, on account of there being no matter to polarize, the susceptibility is zero and the permittivity is equal to \( \varepsilon_0 \) itself and in such a case, is referred to as the permittivity of free space. The term in brackets can be written as

\[ \varepsilon_r = (1 + \chi_e) \hspace{1cm} (1.7) \]

Substituting the value of \( \varepsilon_r \) from equation (1.7) in (1.6) we get

\[ \varepsilon_r = \varepsilon / \varepsilon_0 \]

The term \( \varepsilon_r \) is called the dielectric constant or the relative permittivity of a material and is a dimensionless quantity.
1.2 Ferroelectrics

In ferroelectrics, there is no linear correlation between polarization and the external electric field. Ferroelectricity is defined as the reversibility of the direction of the electric field in a polar crystal. A ferroelectric crystal has a permanent electric polarization as dictated by the electric displacement. A ferroelectric crystal is also pyroelectric i.e. temperature changes bring about a charge release. As a result of changes in temperature or stress, the permanent polarization in the lattice is altered. The changes in polarization caused by temperature are characteristic of ferroelectrics.

Some of the salient features of this class of materials are listed below.

- Analogous to the hysteresis loop observed in ferromagnetic materials, it is possible to trace a loop of ‘electric hysteresis’ in ferroelectrics, between polarization and electric field.
- They have very high values of permittivity.
- Their dielectric properties show marked temperature dependence and exhibit an anomalous dielectric peak. The presences of ferroelectric properties are observable only within a definite range of temperature. The dielectric constant obeys the Curie-Weiss law \( \varepsilon = \frac{C}{(T-T_c)} \) where \( C \) is the Curie constant and \( T_c \) the Curie temperature.
- They are spontaneously polarized.

In the ensuring paragraphs, some of these and other features will be elucidated.

The seven crystal systems are subdivided into 32 point groups (crystal classes) according to their symmetry. Of the 21 non-Centro symmetric classes, all but one exhibit electrical polarity when subjected to a stress. The effect is termed as the piezoelectric effect. Of these 20 piezoelectric classes, 10 are characterized by the fact that they have a unique polar axis. Crystals belonging to these classes are called polar
because they possess a spontaneous polarization. Ferroelectricity is the presence of a spontaneous electric moment which can be changed in its orientation between two or more distinct crystallographic directions by applying an external field. Thus ferroelectrics are characterized by the fact that their polarizations can be reversed by the application of a suitable field. The term ‘Ferroelectricity’ was coined to indicate the close analogy to ferromagnetism.

Prior to 1940 only two types of ferroelectrics were known. Rochelle salt (KNaC$_2$H$_4$O$_6$.4H$_2$O) and some closely related tartarates and potassium di hydrogen phosphate (KDP) and its isomorphs. The first inkling of unusual dielectric properties in refractory oxides amenable to ceramic preparation came out of the work on a series of barium oxide-titanium oxide compositions in 1941. Such materials showed very high values of dielectric constant.

In the last four and half decades, ferroelectricity has been detected in hundreds of crystals. Ferroelectric oxides in general, may be classified into two groups:

(a) Ferroelectrics in which spontaneous polarization may exist along one crystallographic axis in the non polarized state, this group comprise potassium, dia hydrogen phosphate and related compounds, tartarates etc. (b) Ferroelectrics having more than one polar axis and may further be subdivided into 4 structure types (Subba Rao, 1962(a)) viz.

1. Perovskites (e.g. BaTiO$_3$)
2. Pyrochlores (e.g.Cd$_2$Nb$_2$O$_7$)
3. Tungsten bronze materials (e.g. PbNb$_2$O$_9$)
4. Layer type bismuth compounds (e.g.PbBi$_2$Nb$_2$O$_9$)

A feature common to all the above structures is the presence of ions of small size and large charge (e.g. Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$ etc) in the oxygen octahedra, which
are linked through corners forming continuous chains of oxygen-metal-oxygen. Mathias (1951), Smolenskii and Kozhevnikova (1951) have pointed out that such a structural arrangement is favorable for the occurrence of Ferroelectricity in oxides.

A brief description of some of the salient features of materials belonging to these structure types is given below.

1.2.1. Perovskites

Compounds belonging to this group are represented by an ABO$_3$ structure where A ions (Ba, Sr, Pb, Ca etc.) are large and have a 12 fold co-ordination with oxygen ions, B ions have a smaller radius (e.g. Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$ etc) and are surrounded by oxygen in an octahedral environment (TiO$_6$ octahedra).

Barium titanate can be taken to be the prototype of perovskite structured materials and is the most thoroughly investigated. All such perovskites are characterized by structures in which one type of cation is present, e.g. Ti$^{4+}$ in BaTiO$_3$ can undergo a significant displacement relative to its anionic neighbors. These charge displacements give rise to dipoles and the high dielectric constants characteristic of ferroelectrics. When compared to older ferroelectrics such as Rochelle salt, KDP etc., Barium titanate is stable over a wide range of temperatures, humidity etc. it can be produced both in single crystal as well as in the ceramic form in many shapes. Intensive research on this compound has led to a wide variety of applications (Jona and Shirane, 1962: Jaffe, 1971). The piezoelectricity and dielectric constant of BaTiO$_3$ show strong temperature dependence. The addition of La, Sb, Nb etc. to BaTiO$_3$ have produced the PTCR effect, which has resulted in its utility in thermistor preparation.

After BaTiO$_3$ was found to be useful as a piezoelectric transducer, a number of compounds like PbTiO$_3$, PbZrO$_3$, PbSnO$_3$, have been studied. The solid solution of
PbTiO$_3$ - PbZrO$_3$ modified PZTs have become important materials for piezoelectric applications. The additives causing O-position vacancies in lead titanates has resulted in materials with low dielectric constants, low losses, low resistivity’s, but high coercive field. The A-vacancy additives have resulted in dielectrics with high dielectric constant, high dielectric loss, high piezoelectric coupling factor, low coercive field, increased resistivity etc.

SrTiO$_3$ is yet another material which has a perovskite structure similar to BaTiO$_3$. In the primitive cubic unit cell, titanium ions occupy corner positions, oxygen ions occupy the cubic edge centers and strontium is at the cube body centre. Alternately, the unit cell may displace so that its origin is at strontium. In this case, titanium is at the body centre and oxygen ions occupy the face centre positions. Either way, the structure is composed of (TiO$_6$) octahedra. Such an ideal, cubic, perovskite structure, which is stable above a particular temperature ($T_c$) does not possess a net dipole moment since the charges are symmetrically positioned. The material thus behaves as a normal dielectric, albeit with a very high dielectric constant. Below the $T_c$, a structural distortion occurs. The TiO$_6$ octahedra are no longer regular because titanium is displaced off central position and in the direction of one of the oxygen’s. This gives rise to a spontaneous polarization. At high temperatures the dielectric response of SrTiO$_3$ follows a Curie-Weiss law suggesting a ferroelectric phase transition at 35-40K (Lines & Glass, 1977).

Today all these perovskite materials find applications in piezoelectric devices like phonograph pickups, underwater sound detectors and transducers, delay line transducers, high voltage sources and wave filters etc.(Jaffe, 1971; Randersat, 1968).
1.2.2 Pyrochlores

These compounds have a general formula $A_2B_2X_7$. Can be oxygen or partially occupied by a halogen (Aleshin and Roy, 1962).

1.2.3 Tungsten Bronze structured compounds ($A_xB_2O_6$ compounds)

A number of ferroelectrics of present and potential commercial importance have the potassium tungsten bronze structure. These are characterized by oxygen octahedra linked together at the corners in a complex way to yield three types of openings two of which normally contain A ions. The B ions are niobium or tantalum and are inside the oxygen octahedra. PbNb$_2$O$_6$ is the most well known material in this group having a Curie temperature of 570°C and a large $d_{33}/d_{31}$ ratio. It has a polymorphic form and is difficult to synthesize the compound through standard techniques. All the compounds of this group exhibit high $d_{33}$ values and are increasingly finding their utility in devices and in electro-optic applications.

1.2.4 Layer Structured Bismuth Compounds

The structure of such compounds consists of layer of perovskite; infinite in two dimensions separated from each other by $(Bi_2O_2)^{2+}$ layers. The perovskite layers can be one, two, three or more units thick. Each of these thickness results in a separate structure type, but has the perovskite oxide layer alteration. The crystal chemistry of such perovskite-like layer-type ferroelectrics has been considerably developed by many workers. Hence, it would be in order to look into some of the fundamental aspects related to the structure and chemistry of these materials and these form the concepts of the ensuring paragraphs.

It was in 1949 that Aurivillius (1949) reported the synthesis of several compounds and examined the crystal structure of these phases. This was nearly a decade prior to the interest evinced in these ferroelectric oxides. These materials, now
grouped under the Aurivillius family of compounds are represented by the general formula.

\[(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}\]

In the above formula, A can be a mono, dia, trivalent ion, or a mixture of these for e.g. A= Bi, Sr, Ba, K, Ca, Na, Pb and several rare earth ions, while the smaller but highly charged ions like Ti, Nb, Ta, Fe, W, Mo and Cr can go into the B sites. The number of layers is denoted by ‘n’ (n refers to the number of perovskite layers in between the Bi-O layer). These structures basically consist of Bi$_2$O$_2$ layers interleaved with perovskite – like (A$_{n-1}$B$_n$O$_{3n+1}$) layers. The schematic representation of BLSF compounds are shown in figure 1.1.

There are several empirical rules that have resulted as a result of extensive studies concerning the crystal chemistry of such materials and some of them outlined by Newnham et al., (1971) are listed below.

- The bismuth oxide layer is almost inviolate, so much so that even isoelectronic Pb$^{2+}$ can hardly substitute for Bi$^{3+}$ whilst, on the other hand, the bismuth ions in the perovskite are readily replaced by a large number of univalent, divalent and trivalent cations.

- The size requirements are in fact no more stringent than those of the perovskite structure itself. Ions ranging from sizes as small as Na, Ca and Gd to as large as Ba and K can substitute for Bi$^{3+}$; although ions about the size of Sr and La form the most extensive solid solutions. Subba Rao (1962) found that the tolerance factors for the perovskite layer lie in the range 0.81~0.93, whereas, Ismailzade et al., (1967) calculated the tolerance factors and concluded that a layered structure could be found if the tolerance factor was between 0.86 and 0.97.
The octahedral site in the bismuth titanate structure lacks the flexibility found in perovskite. Ti$^{4+}$ can be replaced by cations of valence 3, 4, 5 and 6 but only for those in a limited size range.

It is interesting to note that even in so far as the number of layers is concerned, there are differences in the properties of materials.

Ordinarily ferroelectrics obey the Curie-Weiss law. In such ferroelectrics, the transition is sharp. However, there are also other materials in which broad or diffuse phase transitions occur. Such a phenomenon generally observed in tungsten bronze ferroelectrics, was discovered in solid solutions of the perovskite BaTiO$_3$ – BaSnO$_3$ by Smolenskii et al. (1954). Early studies on diffuse phase transitions (DPT) were reviewed by Smolenskii (1970). It is however, now evident that broadening of the phase transition is a very common occurrence in solid solutions of disordered structures. The ferroelectric – Para electric transition in these systems is characterized
not by an abrupt structural transition, but rather by a gradual diffuse transition which occurs over a range of temperatures-usually referred to as the Curie range. At temperatures well below this range the materials belong to a pyroelectric class and from most points of view, behave as normal ferroelectrics, and while at temperatures well above the Curie range the crystals exhibit unusual dielectric and ferroelectric properties. The temperature at which the dielectric constant shows a peak value depends on the frequency of measurement, and this does not generally coincide with the peak of the dielectric loss, as in normal ferroelectrics, nor with the peak of the pyroelectric coefficient. The spontaneous polarization and other ferroelectric properties such as the specific heat anomaly, the optical observation edge, the refractive index and the electro–optic properties, vary slowly through the Curie range rather than exhibit the abrupt changes normally expected at a ferroelectric transition.

Ferroelectric oxide ceramics are used in a very broad range of functional ceramics and form the materials base for the majority of electronic applications. These electronic applications in fact account for more than 60% of the total high technology ceramics (High Technology News, 1990). The majority of applications can be divided into distinct areas based on the different combinations of properties some of which are listed below.

Dielectric applications make use of the very high dielectric permittivity, low dispersion and wide frequency response for compact multilayer capacitors, in the thick and thin film form. Piezoelectric and electrostrictive responses in poled and unpoled ferroelectric and relaxor ferroelectric (ferroelectrics which show a dielectric relaxation) compositions are of importance in transducers (Levinson, 1988) for converting electrical to mechanical response (Rosen, 1959) and vice versa (Herbert, 1985).
Pyroelectric systems rely upon the strong sensitivity of electric polarization \(\frac{dP}{dT}\) (Porter, 1981). Simple point detectors are widely used these days in domestic and industrial applications and there is now a strong focus on imaging systems which may be used for night vision and thermal medical diagnostics. A PTC semiconductor is a specialized area of applications and is exhibited by materials such as, specially processed barium titanate based ceramics. Electro-optic applications, in which ferroelectric properties of materials can be made use of in modulation, switches etc.

1.3 Piezoelectric Ceramics

All materials undergo a small change in dimensions when subjected to an electric field. If the resultant strain is proportional to the square of the field, it is known as the electrostrictive effect. Some materials show the reverse effect – the development of electric polarization when they are strained through an applied stress. These are believed to be piezoelectric. If the polarization is proportional to the stress, then the effect is said to be direct. If a piezoelectric plate, shown in Figure 1.2 is polarized in the direction indicated by P, carries electrodes over its two flat faces, then a compressive stress causes a transient current to flow in the external circuit, a tensile stress produces current in the opposite sense Figure 1.2(a) Conversely, the application of an electric field produces strain in the crystal, the reversal of the field causes a tensile strain Figure1.2(b) the changes in polarization, which accompany the direct piezoelectric manifest themselves in the appearance of charges on the crystal surface [Moulson and Herbert (1992)]

In a piezoelectric crystal, dipoles are arranged in several compensating directions such that there is no crystal dipole. When the pressure is applied, one of the directions is favored and a net crystal dipole is created. For example, quartz is a non-polar piezoelectric crystal. The principal direction along which a pressure will
generate a charge is the a-axis. However there are three such axes symmetrically spaced at 120° apart in a plane. Thus a uniform hydrostatic stress will affect each axis equally and the net charge will be zero. A pressure applied to an individual a-axis compresses one dipole at the expense of the other two and a charge is thus created. [Jaffe et al.,(1971)].

The equations of state of the piezoelectric effect relate the elastic variables, stress and strain to the electric variables field and displacement. Dielectric displacement (D) is the electric flux density per unit area, having the properties of vector. Strain (S) and stress (T) are tensor quantities.

Figure 1.2. (a) Direct effect (b) Indirect effect (c) The strain changes the direction (d) A piezoelectric crystal with no applied field, the dashed rectangle is the original sample size.

The equation of state relating the electric and elastic variables can be written in the following form:

\[ D = dT + \varepsilon^T E \] \hspace{1cm} (1.8)

\[ S = s^E T + dE \] \hspace{1cm} (1.9)
The first equation describes the direct and second, the converse piezoelectric effect. It is a characteristic consequence of the piezoelectric effect that the elastic and dielectric constants are affected by electric and elastic boundary conditions respectively.

There are the five permittivity’s sometimes indicated by the superscript T. Similarly the elastic compliances $S_{11}$ denote the interaction of a strain and a stress with the condition of constant field. They are the short circuit compliances denoted sometimes by superscript E field. Each elastic compliance relates to application of single stress component while the others are kept fixed. Within the limitations, stress and strain are interchangeable: $s_{31} = s_{13}$.

1.4 Electromechanical Properties

When a piezoelectric ceramic is excited at resonant frequency $f_r$, it will resonate freely with a greater amplitude than at other frequencies. Following this resonant frequency is an anti-resonant frequency $f_a$, where the impedance of the ceramic is at a maximum and the oscillation amplitude is at minimum. Different modes of vibration of the ceramic, such as thickness give insight to the different constants associated with that mode [Jordan et al., (2001)]. A typical resonance plot of Impedance Vs frequency for a piezoelectric ceramic is shown in figure 1.3. Here $f_r$ is the resonant frequency at the point of minimum impedance and $f_a$ is the anti-resonant frequency at the point of maximum impedance.

Figure 1.3 Impedance Vs frequency of a poled piezoelectric ceramic
The values of the piezoelectric properties of a material can be derived from the resonance behavior of suitably shaped specimens subjected to a sinusoidal varying electric field. The behavior of the piezoelectric specimen close to its fundamental resonance can be represented by an equivalent circuit as shown in the figure 1.4 this circuit is recommended by the IEEE standard on piezoelectricity [IEEE standard 176 – 1987]. Below \( f_r \) and above \( f_a \) the ceramic behaves capacitively. However between these two frequencies the sample behaves inductively. This model is only valid near the resonance.

An important parameter of a piezoelectric specimen is the effective electromechanical coupling coefficient \( k_{\text{eff}} \), which is defined as follows:

\[
\begin{align*}
   k_{\text{eff}}^2 &= \frac{\text{Mechanical energy converted to electrical energy}}{\text{Input mechanical Energy}} \quad \text{(1.11)} \\
   \text{or} \quad k_{\text{eff}}^2 &= \frac{\text{Electrical energy converted to Mechanical energy}}{\text{Input electrical Energy}} \quad \text{(1.12)}
\end{align*}
\]
Since the conversion of mechanical to electrical energy is always incomplete, always \( k_{	ext{eff}}^2 < 1 \), hence \( k_{	ext{eff}} < 1 \). Typical values of \( k_{	ext{eff}} \) are 0.4 for BaTiO\(_3\) ceramic and 0.10 for quartz [Jaffe et al., (1971)].

The coupling factors can be calculated for each individual vibration mode by using \( f_r \) and \( f_a \) from Capacitance Vs frequency plot and the applicable formula for ceramic disc are shown below:

\[
\frac{k_{	ext{eff}}^2}{f_r} = \frac{f_a^2 - f_r^2}{f_a^2} = (2.51) \frac{f_a - f_r}{f_r}
\]

Coupling Coefficient:

\[
k_t^2 = \frac{k_{33}^2}{1 - k_{33}^2} = \left( \frac{\pi}{2} \right) \frac{f_a}{f_r} \cot \left( \frac{f_a - f_r}{f_r} \right)
\]

Elastic compliance:

\[
S_{11}^E = \frac{1}{\rho(2l_x f_r)^2} ; \quad S_{33}^D = \frac{1}{\rho(2l_x f_a)^2} ; \quad S_{33}^E = \frac{S_{33}^D}{1 - k_{33}^2}
\]

Where \( l_x, \rho, k_{	ext{eff}}, k_p \) and \( k_{31} \) are length of the crystal rod, density, effective electromechanical coupling coefficient, planar mode coupling coefficient and coupling coefficient length wise vibration respectively. [Geng et al., (1998)].

1.5 A brief review of previous work on related systems

An introduction to Bismuth layer – structured ferroelectrics (abbreviated to BLSF’s) has already been given in an earlier section. They are group of important and potential ferroelectric oxide materials useful for dielectric, piezoelectric and pyroelectric applications. They are characterized by (1) low dielectric constants, (2) low loss tangents, \( \tan \delta \), (3) high Curie temperature \( (T_c) \) and (4) large anisotropy in their electromechanical coupling coefficient \( (k_{33}, k_{31}) \) as compared to those of conventional pyroelectric ceramics such as BaTiO\(_3\) and PZT (Subba Rao, 1962;
Ikegami and Ueda, 1974; Takenaka et al., 1984). Hence, the BLSF ceramics are considered to be superior candidates for piezoelectric applications requiring high $T_c$'s and anisotropy characteristics (Takenaka et al. 1985; Takenaka and Sakata, 1986). Therefore the utility of these compounds is based on their piezoelectric properties which make it possible to use them at high temperatures and high frequencies, or as pyroelectric materials with large figures of merit. Thus, there is an ever growing interest in the family of BLSF’s (Subba Rao, 1962; Newnham et al., 1971; Ikegami and Ueda 1974).

Hiroshi et al. (2001) investigated the dielectric and ferroelectric properties of SrBi$_4$Ti$_4$O$_{15}$ single crystal. The dielectric permittivity at 1MHz is 1900 along the axis. The saturated remanent polarization and coercive field are 29 $\mu$C/cm$^2$ and 26kV/cm respectively.

Ng et al. (2002) have investigated high temperature piezoelectric strontium Bismuth titanate [SBT] from mechanical activation of mixed oxides. The mechanical activation derived SBT can be sintered to a relative density of 98% theoretical at 1175 $^\circ$C which exhibits a maximum dielectric constant of 2770 at the Curie temperature 539 $^\circ$C when measured at 100 kHz. A piezoelectric coefficient of 24 pC N$^{-1}$ is measured at room temperature.

Ferrer et al. (2003) studied mechanical activation assisted synthesis of bismuth layered perovskites SrBi$_4$Ti$_4$O$_{15}$. The mechanical treatment was carried by two different methods vibrating and planetary mill. In some samples a new transitory fluorite–type phase appears, depending on the milling time and the kind of mill used. The synthesis of SBT from activated precursors is obtained at a temperature about 450$^\circ$C lower than it would have been required by a conventional solid state reaction.
Zhao et al. (2003) studied the dielectric and pyroelectric properties of SrBi$_4$Ti$_4$O$_{15}$ based ceramics for high temperature applications. Sr (Sr, Ca, Ba)$_{0.1}$Bi$_{3.9}$Ti$_{3.9}$(Ta, Nb)$_{0.1}$O$_{15}$ ceramics were prepared by conventional sintering technique. Among these materials Sr$_{1.1}$Bi$_{3.9}$Ti$_{3.9}$Ta$_{0.1}$O$_{15}$ was found to have the highest Curie temperature, large piezoelectric constant $d_{33}$ and pyroelectric coefficient.

Xie et al. (2003) studied the mechanism of hydrolysis and polymetric reaction of precursor solution and the influence of annealing condition on crystal structure and microstructure of Sr$_{1-x}$Ba$_x$Bi$_4$Ti$_4$O$_{15}$ (SBBT) $[x =0,0.2,0.5,0.8,1]$ ferroelectric materials are studied by Infrared Spectroscopy. The sintering temperature of SBBT powder is about 700°C and the particle size is about 100 nm.

Chang et al. (2003) compared Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ (BLT) ferroelectric thin films by the sol gel method annealed at 650 and 700°C for 30 min. the BLT film showed better crystallization, electrical properties and also denser microstructure with a granular grain shape.

Macedo et al. (2004) studied the electrical and dielectric properties using the impedance spectroscopy of Bi$_4$Ti$_3$O$_{12}$ ferroelectric ceramics synthesized by self – propagating high- temperature synthesis technique. On comparison with reference sample produced by solid state reaction, at high temperatures a notable difference in the electrical conductivity and relative permittivity is found. This is attributed to the differences in the grain size and defect concentration.

Li et al. (2004) investigated the internal friction and young’s modulus of Bi$_{3.5}$Nd$_{0.85}$Ti$_3$O$_{12}$ ceramics is determined using the reed vibration method. The concentration of oxygen vacancies among the unequal oxygen positions in the lattice and also interaction between oxygen vacancies and 90° domain walls can be easily determined using the above method.
Tellier et al. (2004) had done a comparative study on the ferroelectric CaBi$_4$Ti$_4$O$_{15}$ (CBT) and BaBi$_4$Ti$_4$O$_{15}$ (BBT) by means of single crystal X-ray diffraction. Due to the difference in the ionic radii of the Ca$^{2+}$ and Ba$^{2+}$ both these samples have different cation environments. CBT showed a significant deformation of the perovskites blocks where as BBT showed only a weak variation.

Sim et al. (2004) investigated layer structured calcium bismuth titanate (CBT) by mechanical activation for 30 hrs in a nitrogen atmosphere at room temperature. The particle size obtained was about 50nm in size. Sintered CBT exhibited a maximum dielectric constant of 1049 at the Curie temperature 774$^\circ$C, when measured at 1MHz.

Hou et al. (2004) studied the composition SrBi$_{4-x}$La$_x$Ti$_4$O$_{15}$, ($0 < x < 1.9$) and investigated the dielectric properties. The Curie temperature shifts to lower temperature with increasing x. The dielectric constant anomaly is concealed with the substitution. No dielectric relaxation mechanism is observed.

Ogawa (2004) studied the ferroelectric domain structure in SrBi$_4$Ti$_4$O$_{15}$ (SBT) ceramics. The effect of domain clamping on electromechanical coupling factor and dielectric constant at the coercive field was confirmed in BLSF ceramics. The minimum frequency constant due to domain rotation was also observed in BLSF ceramics.

Hou et al. (2005) synthesized and studied the dielectric properties of layer-structure compounds A$_{n-3}$Bi$_4$Ti$_n$O$_{3n+3}$ (A = Ba, Sr, Ca) with $n > 4$. The average radius of A-site cations was found to be closely related to the lattice parameters in the a-b plane and also to the stability of the structure.

Jun et al. (2005) have studied the properties of Vanadium doped SrBi$_4$Ti$_4$O$_{15}$ ferroelectric ceramics by standard solid state reaction method. Several vanadium
doped ferroelectric ceramics of type $\text{SrBi}_{4-x/3}\text{Ti}_{4-x} \text{V}_x\text{O}_{15}$ (SBTV-x) were synthesized. The $2P_r$ of (SBTV – 0.03) reaches a very large value, above $50 \mu\text{C/cm}^2$ and is twice greater than at zero doping. The curie temperature of V- doped samples decreased slightly when compared to SBT ceramics.

Srinivas et al. (2005) prepared a new set of Aurivillius based BLSF materials synthesized by replacing up to 50% of the Bi ions by Sm ions in the conventional $\text{SrBi}_2\text{Nb}_2\text{O}_9$ compound with increase in Sm content showed increase in the ferroelectric polarization and magnetization.

Moure et al. (2005) investigated crystalline structure, dielectric and piezoelectric properties of bismuth-layer $\text{Ca}_x\text{Bi}_4\text{Ti}_{3+x}\text{O}_{12+3x}$ ($x = 1, 2$) compounds. High density was obtained at relatively low temperature. Incorporation of $\text{CaTiO}_3$ led to a slight increase of the orthorhombicity. Compounds with $\text{CaTiO}_3$ showed high resistivity values and could be polarized under very high electric fields.

Raghavender et al. (2006) studied the electrical properties of La-modified strontium bismuth titanate (SBT). They synthesized $\text{SrBi}_{4-x}\text{La}_x\text{Ti}_4\text{O}_{15}$ with $x = 0.25, 0.50$ and 0.75. The powders were prepared using chemical route. The dielectric properties showed interesting changes in the transition temperature. The lattice distortion is calculated using lattice parameters.

Stojanovic et al. (2006) studied mechanically activated formation of layered structured bismuth titanate $\text{Bi}_4\text{Ti}_4\text{O}_{12}$ (BIT). The nucleation and phase formation of BIT, crystal structure, microstructure and powder particle size were followed by XRD, Rietveld refinement analysis, thermal analysis and SEM. The BIT prepared with excess of $\text{Bi}_2\text{O}_3$ shows the orthorhombic crystalline structure. The powder particle size was around 30nm. It is shown that bismuth oxide has the leading role in the formation of bismuth titanate phase during mechanical activation of starting oxides.
Fan et al. (2007) studied the effects of excess bismuth (0 – 15%) on structure and properties of SrBi$_4$Ti$_4$O$_{15}$ (SBT) ceramics. The SBT ceramics with 10% excess Bi showed a pure layered perovskites structure with enhanced dielectric properties. However father addition of Bi led to form of pyrochlore phase and Bi$_2$O$_3$ the ceramic with 10% of excess Bi content had the highest volume fraction of a-axis oriented grains.

Anand et al. (2007) studied Synthesis and characterization of Strontium Bismuth Titanate (SBT) ceramics via high energy mechanical milling. A significant reduction in processing temperature and time was able to achieve. An enhancement was found in dielectric constant and lowering of dielectric loss in comparison to the previous work. Mechano-chemical activation is seen to improve the synthesis, characteristics and dielectric properties of the SrBi$_4$Ti$_4$O$_{15}$.

Rout et al., (2009(a)) studied impedance spectroscopy and morphology of SrBi$_4$Ti$_4$O$_{15}$ (SBT) ceramics prepared by soft chemical route. The presences of peak in the dielectric loss indicate that the hoping of charge carriers is responsible for the relaxation. Impedance studies revealed a non – Debye type relaxation and relaxation frequency shift to higher value with increase in temperature. The Nyquist plot shows overlapping semicircles for grain and grain boundary of SBT ceramics.

Rout et al., (2009(b)) studied a series of compounds, CaBi$_4$Ti$_4$O$_{15}$ (CBT), SrBi$_4$Ti$_4$O$_{15}$ (SBT), BaBi$_4$Ti$_4$O$_{15}$ (BBT) prepared by a modified chemical route. Considering the tolerance factor, a significant deformation of the perovskite block is observed and that increases with decrease in ionic radius of A site atom. The BBT ceramic showed a relaxor behavior near phase transition.

Rout et al., (2010) studied impedance and modules spectroscopy characterization of CaBi$_4$Ti$_4$O$_{15}$ (CBT) ceramic prepared by soft chemical route. Single phase
orthorhombic formation was confirmed by XRD. Simultaneous analysis of the complex impedance and electric modulus spectroscopy was done in the temperature range 100 – 850°C. The plot shows the negative temperature coefficient of resistance.

Anand et al. (2010) studied the processing conditions, microstructure and dielectric properties of strontium bismuth titanate (SBT) were studied by means of Ca substitution in the strontium site referred to hereinafter as SCBT. The electric properties of SBT are notably improved by Ca substitution. The $T_C$ of SBT shows a slight shift to higher temperature upon Ca substitution. Ca substitution also results in a significant enhancement of $P_t$ of SCBT. It is believed that SCBT is potentially an attractive candidate for piezoelectric sensor applications.

Bismuth titanate (BIT) is the prototype for bismuth oxide layer structures and is probably the most widely studied among BLSF compounds. It is a ferroelectric and has high Curie temperatures of 675 °C and also high breakdown strength. It has a monoclinic distortion (which is very nearly orthorhombic) and is one of the most well known and important materials of the Aurivillius family of compounds. It is regarded as the ‘second cousin of Barium Titanate’. It is a polar crystal with useful electro-optic and related properties. It is composed of three perovskite layers between $\text{Bi}_2\text{O}_2$ layers per unit cell. Armstrong and Newnham (1972) examined the solubility limits of various cations in the A and B sites of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and concluded that the bismuth atoms in the perovskite like layer can be replaced by dia and trivalent ions with ionic radii ranging from 1Å to 1.3Å, where as ions with radii ranging from $0.58\text{Å}$ to $0.65\text{Å}$ would substitute for $\text{Ti}^{4+}$ in the octahedral site. Thus, a large number of compounds can be synthesized based on Bismuth Titanate.

1.6 Stimuli for the present work
In the foregoing sections, a brief outline of some salient features of ferroelectrics in general, Bismuth layer structured ferroelectrics in particular have been given. Specific emphasis has been laid upon BLSF’s and an attempt to correlate their structures and properties has been made. Some features of systems related to the present compounds undertaken in this study were outlined. The present work forms a part of a general programme of ongoing activity in our laboratory on the synthesis, characterization and structure property correlations in BLSF’s having their origin in the aurivillius phases. As we are very well aware that PZT/PLZT materials show excellent properties for Sensor applications but due to their low transition temperature (approx 200 °C), its operating range is limited. Whereas for aerospace engines, high temperature applications these materials are not suitable on the other hand BLSF materials show high transition temperature. So here our profound interest is to fabricate lead free-based BLSF ceramics, which offer high transition temperature and good integrated properties for high temperature sensor applications and can be used as a substitute for PZT/PLZT materials. As reviewed in section 1.5, detailed and systematic work in the compounds Sr$_{1-x}$Ca$_x$Bi$_4$Ti$_4$O$_{15}$ (where $x = 0, 0.1, 0.2, 0.4, 0.6$ and $0.8$) for their electrical, dielectric and impedance spectroscopy are not available in literature. Hence the author had undertaken the present work with the following aims:

1. To synthesize SrBi$_4$Ti$_4$O$_{15}$ in the single phase form and dope it with different compositions of Ca.

2. To employ different synthesis techniques i.e. mechanical milling and solid state method.

3. To characterize them by XRD and SEM for phase analysis and observe their microstructures respectively.
4. To study in detail the impedance response of the materials in question and from the extensive impedance and modulus spectroscopic data so acquired, study their electrical properties as a function of both temperature and frequency.

5. To examine the (A.C and D.C) conductivity behavior of these materials and propose a possible mechanism for observed conductivity of these materials on the basis of defects created due to incorporation of Ca.

6. To study their dielectric properties to understand the nature of ferroelectricity in the materials on the basis of defects present in them.

7. To evaluate Electromechanical coupling coefficients

8. To correlate the structure of these compounds with physical properties and also to compare them with other analogous four layered compounds.

9. Ultimately to check the suitability of the materials for high temperature sensor applications as a replacement for PZT materials.