

INTRODUCTION AND LITERATURE REVIEW

1.1 Ferroelectrics: An important class of electronic materials

Ferroelectrics are materials that possess spontaneous electric polarization which can be reoriented in at least two directions with the help of an externally applied electric field. These have wide variety of technological applications such as PTC thermistors, miniature high value capacitors, IR sensors, varistors, memory devices, piezoelectric actuators, gas lighters, tuneable and miniaturized microwave devices etc. [Moulson et al. (2003); Lines et al. (1977); Jaffe et al. (1971); Popovici et al. (2011); Whatmore (2017); Keyrouz et al. (2017); Sebastian (2008, 2017); Gevorgian (2009); Ahmad et al. (2015)]. The applications are based on their linear and non linear properties, viz. dielectric behaviour and hysteresis, that depend upon local structure and microstructure which in turn are controlled by composition and processing variables such as route of synthesis, sintering temperature, time and atmosphere.

All crystalline material may be divided into 32 crystal classes or point groups in which 11 are centro-symmetric and 21 lack centre of symmetry. Out of these, 20 can show piezoelectricity i.e. electric polarization is developed when stress is applied (phenomenon called direct piezoelectric effect) or strain is created when electric field is applied (called converse piezoelectric effect). The cubic class 432, although lacking a center of symmetry, does not permit piezoelectricity. Among these, there are 10 crystal classes which contain unique polar axis (an electric dipole moment) in the unstrained condition. When uniformly heated, such crystals can develop an electric charge owing to change in magnitude of the dipole moment with temperature. This effect is called

pyroelectricity. The pyroelectrics are spontaneously polarized. However, the polarization is masked by the surface charges accumulating from the atmosphere. When the temperature is altered the polarization changes and this change can be observed. A material can be non polar but piezoelectric such as quartz. In some of pyroelectric materials, the direction of the electric polarization can be altered by an externally applied mechanical stress or electric field. Where the change is primarily due to a stress, the material is said to be ferroelastic and when it is due to an external electric field, the material is said to be ferroelectric. [Jaffe et al. (1971); Jona et al. (1962); Lines et al. (1977); Moulson et al. (2003)]. These details are schematically shown in Figure 1.1.

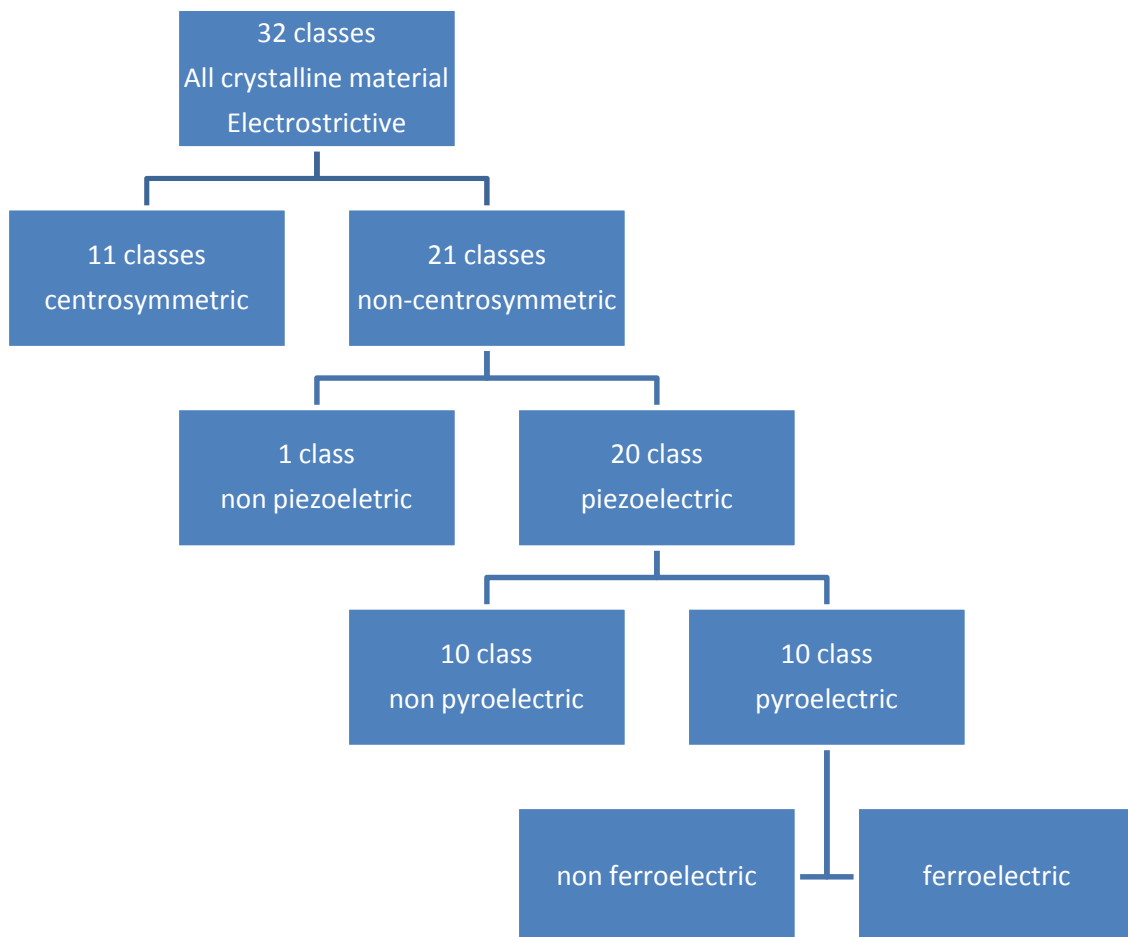


Figure 1.1: Schematic representation of general ferroelectric materials landscape.

The two ferroelectric states are separated by small energy hump so that when temperature is raised, relative stabilities change and the material transforms to a nonpolar state (called the paraelectric state) at certain temperature, T_c , called the Curie point. From above the Curie point, the approaching transition is manifested as diverging dielectric permittivity ϵ' which, close to T_c , varies with temperature in Curie-Weiss manner

$$1/\epsilon' = C/(T - T_0) \quad \dots (1.1)$$

Here T_0 is the Curie-Weiss temperature which is equal to the Curie temperature only for the case of a continuous transition. C is a constant called the Curie constant and is usually of the order of 10^3 - 10^5 degrees. The Curie -Weiss temperature T_0 is a formula constant obtained by extrapolation of the experimental data, while the Curie point is the actual temperature of inversion of the structure. They generally do not coincide. In the case of first order transitions (in which lattice constants, dielectric constant, polarization etc., change discontinuously), the Curie - Weiss temperature can be more than 10 degrees lower than the Curie point. In a ferroelectric undergoing a second order phase transition (i.e. where properties such as lattice constants, dielectric constant, polarization, etc., change continuously with temperature, but generally with a discontinuity of slope) the two temperatures may be essentially identical [Jaffe et al. (1971); Jona et al.(1962); Lines et al. (1977); Moulson et al. (2003)].

There are cases where the dielectric constant vs temperature curve does not show a sharp peak, but, due to inhomogeneities, has a smeared broad peak. Such transitions are popularly known as diffuse phase transitions (DPT) and materials having such a behaviour over larger temperature range are very useful for certain applications.

In these cases, Curie-Weiss law is not obeyed. Rather, modified Curie-Weiss law, expressed as

$$1/\epsilon' - 1/\epsilon'_m = (T-T_m)^\gamma/C \quad \dots (1.2)$$

is followed where ϵ'_m is the maximum permittivity, T_m is the corresponding temperature and γ is diffusivity parameter. Here $\gamma = 1$ corresponds to normal ferroelectric phase transition, $\gamma = 2$ to the so called complete relaxor while $1 < \gamma < 2$ indicates diffuse phase transition [Uchino et al. (1982)]. If the peak in the ϵ' vs. T curve shifts towards higher temperatures as the frequency of dielectric measurement is raised, the ferroelectric is said to be of relaxor type. At temperatures above the transition temperature, the ferroelectric is said to be in paraelectric state. The value of permittivity is still high. Therefore, ferroelectrics whose transition temperature is below room temperature, such as Sr doped BaTiO₃, are highly useful for applications.

If the overall electric polarization arises due to ordering of group of ions, the ferroelectric is called an order-disorder ferroelectric, such as NaNO₂. The NO₂ groups have a flipping motion approximately about the O-O axis and the difference between the number of NO₂ groups along and in opposite direction at any moment defines the effective value of electric polarization. If the polarization arises due to displacements of ions that exist in a structure at a temperature so that the centre of all the positive charges does not coincide with the centre of the negative charges giving rise to a dipole moment, the ferroelectric is said to be a displacive ferroelectric such as perovskite BaTiO₃ [Kittel (2005); Dekker (1958)].

In general, the direction of the spontaneous polarization is not the same throughout a macroscopic crystal. Rather the crystal contains the so called domains that are regions of uniform polarization. Within each domain, polarization has a specific

direction and the direction of polarizations varies from one domain to another. The overall polarization (P) has a nonlinear dependence on the applied electric field (E) and shows a P-E hysteresis. When a ferroelectric is stressed, strain is created and the positions of ions change resulting in change in polarization. Conversely, when electric field is applied, positions of ions change i.e. strain appears. Therefore, a ferroelectric would behave as a piezoelectric as well. The device applications of ferroelectrics have been derived based on the characteristic features [Moulson et al. (2003)] are given in Table 1.1 and also summarized below:

(i) P-E hysteresis showing two reorientational polarization states which can be switched to one another by external electric field which makes the basis of binary states 0 and 1 in memory devices). The non-linear dependence of P on E is useful in second harmonic generation etc.

(ii) Possibility of altering the usable value of dielectric constant by applying external field (exploited to achieve tuneability in microwave devices).

(iii) General high value of dielectric constant (so much desired for fabrication of miniaturized high value capacitors and microwave circuit components).

(iv) Appearance of peak in dielectric constant vs. temperature curve (to be exploited in dc voltage sources etc.).

(v) Piezoelectric behaviour (highly used in microphone pick- ups, ultra sound systems etc.).

Table 1.1: Properties and some applications of ferroelectric materials

Properties	Applications
High permittivity	DRAM storage ,capacitors ,frequency and phase agile microwave circuit
Piezoelectricity	Actuators and Sensors
Polarizability	Non-Volatile ferro-electric memory
Pyroelectricity	Infrared Sensors
Electro-Optical properties	Thermal infrared switch

For various device applications intrinsic nature including the origin of the polarization, effect of additives and processing variables etc has to be understood and this has been the driving force towards various type of continued studies in ferroelectrics. Ferroelectric materials have further gained much more importance in recent years due to possibility of inducing magnetism by incorporating magnetic ions in the matrix with a view to control the dielectric and magnetic behaviour by application of magnetic or electric field . This has given rise to the so called ferroic and magneto-dielectric materials which are supposed to simultaneously exhibit at least two of the ferroelectric, ferromagnetic and ferroelastic properties, generally the former two. Such materials are being seen as the future technological materials which will tremendously widen the range of applications in various areas such as microwave phase shifters and other miniaturized devices, delay lines, magnetic recording read heads, multiferroic random access memories and multi-state memories, photovoltaic solar cells etc [Mosallaei et al.(2004); Vopson (2014); Fiebig et al.(2016); Fiebig (2005); Zhang et al. (2015); Rocha et al. (2008); Su et al. (2014); Min et al. (2006)]. With a view to

develop a theoretical understanding of this and synthesize such materials, intense research activities are being carried out.

Ferroelectrics can be of single crystal or of polycrystalline ceramic form. Ceramics are inorganic non-metallic solids that have been processed and shaped by heating at high temperatures. Due to ease in preparation, processing, casting in desired shapes and sizes, possible enhancement in certain properties by controlling the interplay between grain and grain boundary behaviour, materials in ceramic form are preferred for applications. The polarization based responses of a ferroelectric ceramic can be enhanced by subjecting the sample to the so called poling process which involves heating the system and then cooling it in presence of high electric field [Moulson et al. (2003)].

1.2 Electric Polarization Behavior

Overall polarization behaviour of a system is manifested through the response of various polarizations present in the system to the external electrical stimulus. The electric dipole moment \mathbf{p} , of charges $+q$ and $-q$ separated by a distance \mathbf{r} is defined as

$$\mathbf{p} = q \mathbf{r} \quad \dots (1.3)$$

The polarization of a region is defined as the total dipole moment ($\sum \mathbf{p}$) per unit volume (V)

$$\mathbf{P} = \frac{\sum \mathbf{p}}{V} \quad \dots (1.4)$$

When an electric field (E) is applied to a material, electric charges are displaced in it, and a dipole moment is induced which is proportional to the applied field for a paraelectric material

$$\mathbf{P} = \alpha \mathbf{E} \quad \dots (1.5)$$

where α is the polarizability. For a ferroelectric, a P-E hysteresis is observed. A typical P-E hysteresis curve of a ferroelectric sample is shown in Figure 1.2.

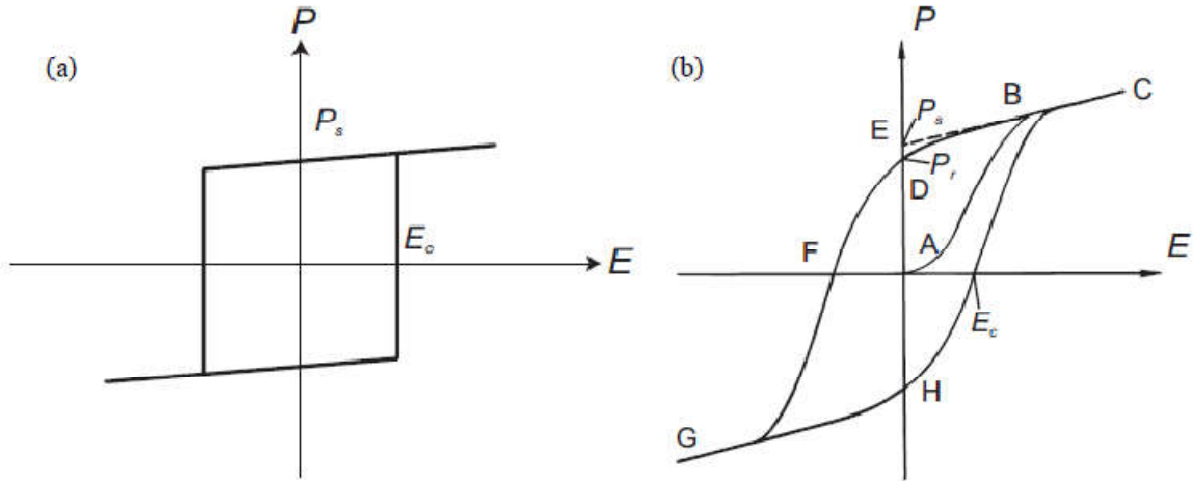


Figure 1.2: Schematic diagram of a ferroelectric hysteresis loop for (a) Single domain
(b) Poly-domain sample. [Jona et al. (1962)]

Starting at the virgin state (the polarization is pointing, in an equal portion of volume, to the positive and negative direction), a part of the negatively oriented domains in a poly domain sample will be switched over the positive direction by increasing the electric field (path AB), and the polarization increases strongly until the saturation state is reached (path BC). Here, the complete volume is aligned in the positive direction and the crystal consists now of one single domain. Decreasing the field does not bring the net polarization back to zero but rather follows the path CD , which means that some of the domains will stay positively oriented without applied field and the crystal exhibits a remanent polarization P_r . Extrapolating the saturation path BC back to the polarization axis, the intercept represents the spontaneous polarization P_s . To decrease the polarization then further to zero, it is necessary to apply a negative electric field (portion DF). The electric field corresponding to this zero polarization state is called the *coercive field* E_c . Additional decrease of the field will cause all dipoles to align in the negative orientation (portion FG), after which the cycle can be completed by reversing the field once again (portion GHC). One then finds a hysteresis loop ($CDFGHC$) as the relation between P and E , which is the most important electrical characteristic of a ferroelectric crystal.

Actually, the y-axis in Figure 1.2 should be denoted as the dielectric displacement

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad \dots (1.6)$$

where in general $\epsilon_0 E$ denotes the vacuum contribution to the displacement D caused by an externally applied field E , and P represents the electrical polarization of the material, independent of its cause. Since in ferroelectric materials the polarization is by many

orders of magnitude larger than the vacuum term, the approximation $\mathbf{D} \approx \mathbf{P}$ is justified. Additional to the ferroelectric contributions, the polarization consists of dielectric contributions from the susceptibility of the material (ionic and electronic polarization) [Dragan et al. (2005)].

According to an electrostatic approach, the real permittivity or dielectric constant ϵ' is defined as the derivative of the dielectric displacement D with respect to the field E . The dielectric susceptibility χ_e is analogously defined as the derivative of the polarization P with respect to the field E , divided by the vacuum permittivity ϵ_0 . Applying this derivation on and dividing by ϵ_0 , the dielectric constant* (or real permittivity) can be expressed as [Von Hippol (1954)]

$$\epsilon' = 1 + \chi_e \quad \dots (1.7)$$

This definition is valid only for normal *linear* dielectrics, in which the relationship between D and E is linear up to high values of E . In ferroelectric crystals however, the definition of ϵ' becomes more complicated due to the *non-linear* relationship between D and E . Here, the dielectric constant ϵ' is defined as the slope of the D - E curve at the origin:

$$\epsilon' = \frac{1}{\epsilon_0} \frac{\partial D}{\partial E} \Big|_{E=0} \quad \dots (1.8)$$

In the case of materials in their paraelectric phase, the spontaneous polarization disappeared and the polarization is simply related to the electric field by

$$\mathbf{P} = \epsilon_0 \chi_e \mathbf{E} \quad \dots (1.9)$$

Combining together, this leads to

$$\mathbf{D} = \epsilon_0 (1 + \chi_e) \mathbf{E} = \epsilon_0 \epsilon' \mathbf{E} \quad \dots (1.10)$$

giving the linear relation between electric displacement and electric field. It has to be mentioned that the dielectric permittivity does not have to be constant and in certain circumstances also depends on the applied field [Jona et al. (1962), Von Hippol (1954)].

* For brevity we have used the terms permittivity for real permittivity or dielectric constant and loss for $\tan\delta$.

Another description of the dielectric response of ferroelectrics is given by the conventional Landau theory and is based upon an expansion of the Helmholtz free energy F with respect to the vector macroscopic polarization \mathbf{P} . For the situation where the polarization is collinear with the macroscopic electric field \mathbf{E} in the material, the first two terms of this expansion read

$$F = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 \quad (1.11)$$

The equation of state $\partial F/\partial P = E$ then leads to a relation between the polarization and electric field

$$E = \alpha P + \beta P^3 \quad \dots (1.12)$$

Equation (1.10) enables us to present the relative dielectric permittivity of the material in the form

$$\varepsilon' = \frac{1}{\varepsilon_0} \frac{\partial P}{\partial E} = \frac{1}{\varepsilon_0} \frac{1}{\alpha + 3\beta P^2} \quad \dots (1.13)$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m. This expression describes the dielectric permittivity both in the absence of a bias field and under it. In the first case, one sets $P = 0$ in Eq. (1.11) to obtain:

$$\varepsilon' = \varepsilon'(0) = \frac{1}{\varepsilon_0 \alpha} \quad \dots (1.14)$$

whereas, for the situation under the bias, one sets $P = P_{dc}$ in Eq. (1.2.11) (P_{dc} is the polarization induced by the bias field) [Tagantsev et al. (2003)].

Various types of polarization can be induced in dielectrics which are schematically shown in Figure 1.3. They are as follows:

- (i) **Electronic Polarization:** It is due to the displacement of electrons with respect to the positive nuclei within the atom under the effect of an external electric field.
- (ii) **Ionic Polarization:** It is due to the displacement of ions with respect to each other in ionic crystals, such as rock salt under the effect of an external electric field.

- (iii) **Dipole Polarization:** It is due to the re-orientation of molecules having permanent dipole moment under the action of an applied field.
- (iv) **Interfacial Polarization:** It is caused by the accumulation of charges at the interfaces of materials having different conductivities.

1.3 Dielectric Constant and Dielectric Loss

The relative dielectric constant ϵ_r is equal to the ratio between the charge stored on an electroded slab of material brought to a given voltage and the charge stored on a set of identical electrodes separated by vacuum. It is often simply denoted as *the dielectric constant* and is the dimensionless multiplier of the vacuum permittivity ϵ_0 ($8.8542 \cdot 10^{-12}$ As/Vm). For general materials, the value of ϵ_r is low, under 5 for organic materials and under 20 for most of the inorganic solids. Ferroelectrics, however, may possess a much higher dielectric constant, with values typically about several hundreds or even several thousands. When an alternating voltage is applied, the charging current in a dielectric slab has both real (in phase) as well as imaginary (out of phase) components, which may be due to resistive leakage or dielectric absorption. The loss is then expressed by the ratio of the out-of-phase component to the in-phase component, which is usually called the loss tangent or $\tan\delta$. This fact is expressed by making the permittivity a complex quantity, $\epsilon^* = \epsilon' - j \epsilon''$, where ϵ' and ϵ'' are real and imaginary components of the complex permittivity and $j = \sqrt{-1}$. The loss tangent can be calculated by

$$\tan\delta = \epsilon''/\epsilon' \quad \dots (1.15)$$

Usually, ϵ' is designated as ϵ_r .

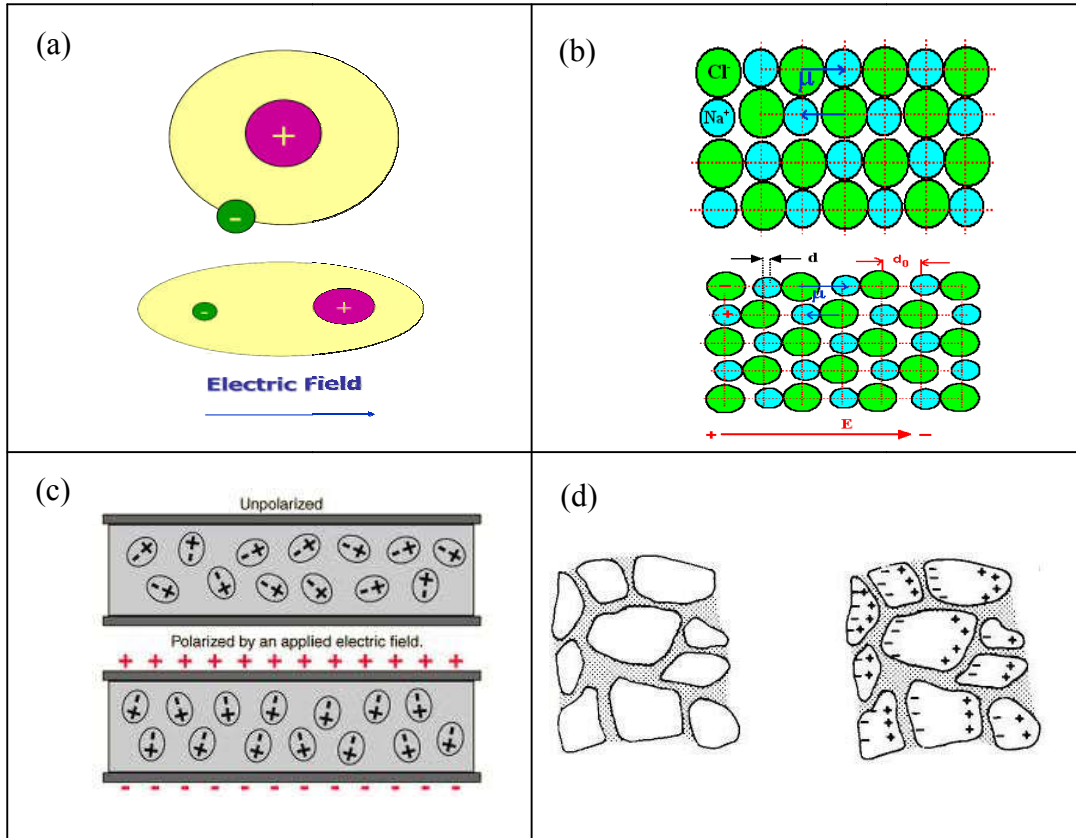


Figure 1.3: Types of Polarizations (a) electronic, (b) ionic, (c) dipole (d) interfacial [Dielectric Terminology Glossary (2016)]

Materials in polycrystalline ceramic form are widely used in commercial applications due to ease of processing and casting in desired sizes and shapes. A polycrystalline ceramic comprises a large number of small crystallites called grains joined in random crystallographic orientations. The inter-grain region, called the grain boundary has, because of their mismatch, strained bonds. Therefore, the properties of inter-grain regions are different from those of the bulk i.e. grains. This fact gives rise to some very interesting and useful properties which are exploited in commercial devices [Moulson (2003)]. Usually, it is the interplay of ‘grain’ and ‘grain boundary’ behavior that bestows ceramics with several technologically useful properties. The understanding and controlling of this interplay with the help of

processing variables, additives, ingredients or reduction in grain size dwelling in nanometers range is the subject of intensive research activities at present.

A ceramic material prepared in powder form or as a glass – ceramic is processed and fabricated in some shape to which usually suitable electrodes are connected for device applications. Thus the overall property of a ceramic sample would get contributions from grains, grain boundaries and electrode interfaces and an electronic ceramic component may be treated as a grain – grain boundary – electrode system. In order to get a reproducible behavior and to develop materials having desired properties, these contributions must be separated out. For this purpose, the method of Impedance Spectroscopy or Complex Impedance Analysis has emerged as a very powerful tool in recent years. Basics of impedance spectroscopy and its applications to various type of materials are discussed in detail by Macdonald (1987) and Jonscher (1983). By using this technique, PTCR behaviour of ferroelectric BaTiO₃ has been studied and electrodes yielding largest PTCR were developed [Maiti et al. (1986)]. West and his co-workers have used impedance spectroscopy for study of PTCR in BaTiO₃, La doped BaTiO₃, characterization and modelling of electroceramics etc. [Sinclair et al. (1989); West et al. (1997); Irvine et al. (1990); Morrison et al. (2001a, 2001b); Abram et al. (2003)].

The impedance spectroscopic analysis proceeds by representing the system by suitable equivalent circuit models which are chosen by looking at the experimental behaviour and the charge transfer processes thought to be possibly present in the system. A parallel RC circuit (a resistor R connected in parallel to capacitor C) has one time constant, giving maximum response at frequency $1/(RC)$ and can be conveniently used to represent one charge transfer process. A general practice is to connect more RC's in series if there are more processes. Thus, a ceramic sample (which can be

considered as a grain – grain boundary – electrode system) can be represented by an equivalent circuit model comprising series combination of three parallel RC's viz. R_1C_1 , R_2C_2 and R_3C_3 where these correspond respectively to grain, grain boundary and electrode behaviour. When these time constants are widely separated, three distinct semicircular arcs appear in complex plane impedance plots [Moulson et al. (2003)]. Choice of a model is a difficult process becoming much more so as same impedance behaviour can be obtained from different models. However, for easy interpretations, simple models are considered to begin with. The choice is greatly facilitated by comparing the experimental plots with those simulated for different possible models. Number of equivalent circuit models and their simulated impedance patterns have been reported [Macdonald (1987); Macdonald (2005); Pandey et al. (1995)].

The situations where possibility of distribution in time constants exists (manifested as depressed arcs in complex plane impedance experimental plots) are analysed by including constant phase angle element (CPE) in the model [Macdonald (1987); Kanoun (2011); Orazem et al. (2013); Boukamp et al. (2004); Garcia et al. (2006); Abram et al. (2003)]. A CPE is a mathematical realization of a system in which the phase angle between applied ac voltage and resulting current remains independent of frequency. If experimental data fit well to a model involving CPE, then presence of distribution in certain properties of the system is inferred. However, a clear method about how a CPE is to be incorporated in the model circuit is not available. Therefore, simulation of impedance behaviour of some models involving CPE was carried out in the present work so that development of equivalent circuit be facilitated by comparing the experimental plots with the simulated ones. This is described in greater details in Chapter 3. Development of equivalent circuit models not only facilitates separating the

contributions from grain, grain boundary and electrodes but also may be useful in simulation work related to optimum intersegment power transfer in a device.

1.4 Ferroelectric Materials: Perovskite BaTiO₃

Ferroelectric materials include oxides, triglycine sulphate (TGS) family and polymeric ferroelectrics (such as polyvinylidene fluoride, PVDF). Among these, ferroelectric oxides, specially perovskites, are by far the most technologically important class of ferroelectric materials [Whatmore (2017); Moulson et al. (2003)]. Perovskites have the general formula ABO₃ where A are divalent and B are tetravalent ions. The perovskite structure may be visualised as a cube with A atoms occupying the corners, B the body centre and Oxygen (O²⁻) ions occupying the face centers. The oxygen atoms form an octahedral cage inside which the Ti atom resides. Variety of isovalent or heterovalent substitutions are possible on A and B sites which alter the properties. Number of research publications are available on studies of dielectric properties on valence compensated perovskites such as those by Upadhyay et al. (1996, 2001), Parkash et al. (1990, 2007) etc. Ever since its discovery in 1941, BaTiO₃ has been found to be the most versatile ferroelectric material for taking up basic studies as well as for developing applications using ferroelectrics [Randall et al. (2009)]. BaTiO₃ is a fascinating perovskite which has various polymorphs existing at different temperatures: rhombohedral (T < -90⁰C), orthorhombic (-90⁰C < T < 5⁰C), tetragonal (5⁰C < T < 120⁰C), cubic (130⁰C < T < 1460⁰C) and hexagonal (T > 1460⁰C) [Dang et al. (2015)]. The Ba atoms (Ba²⁺ ions) occupy the corners, Ti (Ti⁴⁺ ions) the body centre and Oxygen (O²⁻) ions occupying the face centers. The Ti atom resides at the centre of the oxygen octahedron. In the ferroelectric phase the O²⁻ ions are little displaced in one direction as compared to the Ti⁴⁺ ion which is displaced in opposite direction with

respect to the body centre giving rise to a dipole. The BaTiO_3 perovskite structure is schematically shown in Figure 1.4.

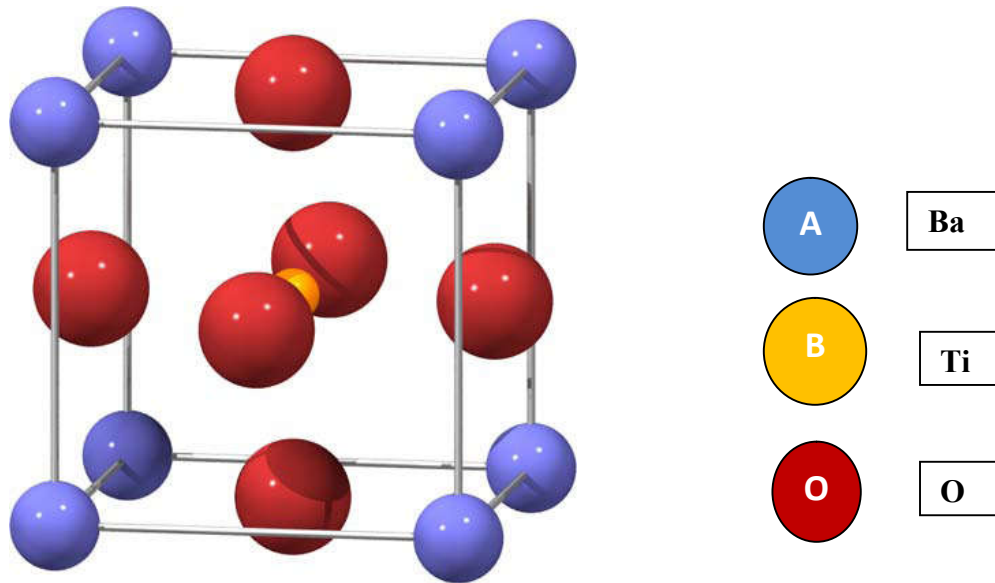


Figure 1.4: Schematic diagram of BaTiO_3 perovskite structure [Popovici et al. (2011)]

Its properties can be modified due to flexibility of substitution of various ions at Ba and/or Ti sites. Thus, based on BaTiO_3 , materials suitable for large variety of technological applications such as PTCR thermistors, DRAMs, piezoelectric devices etc have been developed [Moulson et al. (2003); Lines et al. (1977); Jaffe et al. (1971); Popovici et al. (2011); Acosta et al. (2017)]. As the dielectric constant values are high, these are also suitable for applications in miniaturized capacitors, resonators etc. Enormous amount of literature exists with ever increasing trend where various possibilities of development of technologically useful systems have been explored by using suitable substitutions/dopants at the Ba and Ti sites, different preparation methods and processing procedures such as sintering temperature and time giving a control over microstructure [Lines et al. (1977); Popovici et al. (2011)]. Possibilities of developing ferroic/magneto-dielectric systems are being currently explored by using doped BaTiO_3 as a prototype [Apostova et al. (2013); Lin et al. (2008a, 2008b); Xu et

al. (2009); Qiu et al. (2010); Wei et al. (2011); Mishra et al. (2012); Venkataraman et al. (2013); Valant et al. (2013); Mikulska (2014); Samuel et al. (2015); Deka et al. (2014)]. It has resulted in intensive research activities and a continuous succession of new BaTiO₃ based materials and technology developments that have led to a significant number of industrial applications. Renewed interest has emerged in BaTiO₃ based materials due to search for lead free non-toxic compounds for applications [Whatmore (2017); Juarez et al. (2011)].

As mentioned earlier, BaTiO₃ (general formula ABO₃) is a fascinating perovskite which has various polymorphs existing at different temperatures [Dang et al. (2015)]. The technological applications are based on BaTiO₃ in tetragonal phase as the material remains ferroelectric near room temperature. Interesting ceramic systems are obtained by using substitutions at Ba and/or Ti sites in thin film forms as well as bulk. For several applications, such as microwaves dielectric resonators, cooling systems based on electrocaloric properties etc., knowledge of dielectric behaviour in bulk form is essential. Looking at large number of applications, BaTiO₃ ceramics with isovalent substitutions of Sr at A site, Sn at B site and heterovalent substitution by Fe at B site were explored. These solid solutions have the formulae Ba_{1-x}Sr_xTiO₃, BaFe_xTi_{1-x}O₃ and BaTi_{1-x}Sn_xO₃. Vast literature is available on these materials. In what follows a literature survey on these systems is presented keeping in view compositions studied, polarization and dielectric behaviour, impedance spectroscopy and dielectric measurements at microwave frequencies. One of the promising applications is in the field of microwave communication. The frequencies being presently used in mobile communication are around 2 GHz. In order to provide larger bandwidths, present fast advancing microwaves based communication technology is tending towards higher

frequency bands of microwaves [Keyrouz et al. (2017)]. Therefore, attention was paid to dielectric measurements in the X-band of microwaves (8-12 GHz).

1.4.1 Ba_{1-x}Sr_xTiO₃ ceramic system

Ba_{1-x}Sr_xTiO₃ (henceforth designated as BST) is a solid solution of perovskites BaTiO₃ and SrTiO₃ covering the whole range of x (0 to 1) with Sr occupying the Ba sites. Ba_{1-x}Sr_xTiO₃ has been extensively studied due to its wide variety of potential applications in energy storage devices, capacitors, microwave dielectric resonators, filters, varactors, lens antennas for electromagnetic beam steering, etc. [Ahmad et al. (2015); Popovici et al. (2011); Tagantsev et al. (2003); Gevorgian (2009)]. Its popularity and technological usefulness stems from the fact that the ferroelectric to paraelectric transition temperature T_c of pure BaTiO₃ which is about 395 K decreases almost linearly by increasing the Sr content in the matrix [Moulson et al. (2003); Jaffe et al. (1971); Ahmad et al. (2015); Hilton et al. (1996); Jackson et al. (1945); Tiwari et al. (1995); Ioachim et al. (2006); Bunting et al (1947)]. Strontium titanate has maximum permittivity at about 20 K. Therefore by suitably choosing the value of x, it is possible that the maximum permittivity for the system Ba_{1-x}Sr_xTiO₃ occurs at any desired temperature in the range 20 – 395 K [Hilton et al. (1996)]. In addition, the value of dielectric constant is more than that of BaTiO₃ and the sharpness of ε' vs. temperature curve of BaTiO₃ becomes diffused by addition of Sr. Huge amount of literature is available regarding work devoted to develop an understanding of the mechanism of this diffusiveness [Hilton et al. (1996); Jackson et al. (1945); Tiwari et al. (1995); Ioachim et al. (2006); Bunting et al. (1947); Menoret et al. (2002); Dulian et al. (2014); Liou et al. (2008); Kim et al. (2013); Bengugui et al. (1978); Rushman et al. (1946); Popovici et al. (2011); Tagantsev et al. (2003); Gevorgian et al. (2009); Wang

et al. (2001)]. The smearing out of the dielectric constant vs. temperature peak, popularly known as diffuse phase transition (DPT), has been attributed to inhomogeneities [Sanvordenker (1967); Tikhomirov et al. (2000)] or relaxational freezing of cluster of dipoles [Tiwari et al. (1995); Menoret et al. (2002)]. A value of T_c below room temperature so that no peaks appears as the device gets heated during its operation and a smeared out ϵ vs. temperature curve so that its capacitance does not change much as temperature rises make this material highly promising for technological applications.

Polycrystalline BST is commonly manufactured by solid state reaction method. It can also be prepared by sol-gel, hydrothermal and high energy ball milling processes [Dulian et al. (2014); Liou et al. (2008); Kim et al. (2013)]. Barb et al. (1982) have observed coexistence of tetragonal and cubic phases for $x = 0.24$ with structure becoming almost entirely cubic at $x = 0.285$. McQuarrie et al. (1955) and Durst et al. (1950) found cubic phase for $x \geq 0.30$. Tiwari et al. (1995) have reported that the structure becomes cubic at some composition in the range $0.25 \leq x \leq 0.30$. Rushman et al. (1946), on the other hand, have found that structure remains tetragonal up to $x = 0.35$ at room temperature. Elbasset et al. (2013) observed presence of tetragonality even at $x = 0.40$. The findings of these authors are based on only XRD studies. It is observed that, there is no clear consensus about the composition (x) up to which the room temperature structure remains tetragonal (i.e. the samples show ferroelectricity).

Ioachim et al. (2005, 2006, 2007) have reported dielectric measurement on Sr doped BaTiO_3 with $x = 0.25, 0.50, 0.75$ and 0.90 near 1 GHz. Teranishi et al. (2009a, 2009b) have carried out dielectric studies at frequencies up to a few GHz. Wee et al. (2011) have measured dielectric permittivity upto 3 GHz for $x = 0.50$.

Singh et al. (1996) have carried out P-E loop measurements on this system with $x = 0.12$. Curechriu et al. (2009) have reported P-E loops for $x = 0.20$ and 0.30 for confirmation of ferroelectricity. Kim et al. (2013) have reported decrease in the saturation polarization with increasing x , keeping x below 0.30 .

Surprisingly, to the best of our knowledge, no results for equivalent circuit models for $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ are available. Part of the work presented here involves preparation of this system with $x = 0.15, 0.20, 0.25, 0.30$ and 0.35 and characterization using XRD, P-E loop, dielectric measurements in rf and GHz range, impedance spectroscopy and equivalent circuit modelling.

1.4.2 $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ceramic system

It is known that addition of iron promotes formation of hexagonal BaTiO_3 (h- BaTiO_3) at relatively lower temperatures [Jaffe et al. (1971)]. Therefore Fe doped BaTiO_3 usually possesses both tetragonal as well as hexagonal phases whose ratio depends upon the amount of Fe doping [Qiu et al. (2010); Deka et al. (2014); Dang et al. (2015); Kolodiazhnyi et al. (2008)]. Substituting more than 10% Fe at Ti site leads to fully hexagonal BaTiO_3 . Qui et al. (2010) have studied the phase evolution in BaTiO_3 with doping levels of 1 to 10%. They found that at 1% of Fe doping hexagonal phase was not formed whereas for higher doping levels hexagonal phase was present. Also it was observed by them that higher sintering temperatures (1400°C) and higher sintering times (20 h) would be necessary for synthesising Fe doped BaTiO_3 with hexagonal structure. Room temperature ferromagnetism was observed in samples with doping levels of 2% and above. But magnetization M did not reach saturation indicating presence of some paramagnetic and /or antiferromagnetic components within the ceramic samples. The possible technological applications of this system would thus

depend upon the overall properties resulting from different phases and their interactions.

Formation of pure hexagonal phase was reported by Lin et al. (2008a). Combination of two phases (tetragonal and cubic) was observed by Rajan et al. (2016). Xu et al. (2009) and Khirade et al. (2016) found the formation of pure tetragonal phase. Qiu et al. (2010), Deka et al. (2014), Rani et al. (2016) and Dang et al. (2015) have reported formation of mixture of hexagonal and tetragonal phases. It has been reported by Dang et al. (2015), Nguyen et al. (2011) and Xue et al. (2012) that 6H-BaTiO₃ polymorph is thermodynamically stable above 1460 °C.

Keith et al. (2004) has reported room temperature stabilization of hexagonal phase for $0.10 \leq x \leq 0.50$. It is generally accepted that hexagonal phase is formed for x above 0.10. However, there is no clear consensus about the phases being formed when Fe doping level is changed keeping $x \leq 0.10$ and further investigations may be desirable.

It has been reported by Mishra et al. (2012), Dutta et al. (2016), Maso et al. (2006) and Rajan et al. (2016) that the peak in ϵ' vs. temperature curve gets broadened when BaTiO₃ is doped with Fe. The diffusiveness of this broadening (Diffuse Phase Transition, DPT) varies with level of doping. Maso et al. (2006) has applied impedance spectroscopy to study tetragonal-cubic solid solution in Fe doped BaTiO₃. Using this technique Sitko et al. (2015) have studied grain-grain boundary behaviour in single phase and Xue et al. (2012) studied single phase hexagonal BaTiO₃. No work is available in the literature about impedance spectroscopic studies in Fe doped BaTiO₃ possessing coexisting tetragonal and hexagonal phases. Also, no work has been found on dielectric measurements at microwave frequencies in the X-band (8-12 GHz). As it

is known that the system becomes entirely hexagonal for $x > 0.10$, it was considered worthwhile to prepare and characterize these materials with $x \leq 0.10$.

1.4.3 BaTi_{1-x}Sn_xO₃ ceramic system

BaTi_{1-x}Sn_xO₃ (BTS) is a solid solution of ferroelectric barium titanate and non ferroelectric barium stannate. BaTi_{1-x}Sn_xO₃ has promising properties that can be used for various applications such as sensors, piezoelectric actuators or high permittivity dielectric devices, multilayer capacitors, photoluminescence, non-volatile memories and pyroelectric detectors, tuneable microwave devices etc. This material has attracted considerable interest recently due to its promising electrocaloric properties that can be used for development of eco-friendly room-temperature refrigeration systems and cooling devices. Strong electrocaloric effect was observed by Luo et al. (2014) near the composition $x = 0.105$ (called x_c) which corresponds to the quasi-quadruple critical point of the cubic-tetragonal-orthorhombic-rhobohedral phase transition sequence in the phase diagram. At this composition they have observed greatly enhanced electrocaloric effect near room temperature (~ 28 °C) which is very promising for developing cooling devices. However there are varying reports about the composition where permittivity is maximum.

BTS has stable ferroelectric properties in the vicinity of Curie point and the behaviour becomes more relaxor like as Sn content increases. Zhang et al. (2015) have studied this material for $0.1 < x < 0.18$ ($x = 0.1, 0.12, 0.15, 0.18$) and reported DPT behaviour. They observed fairly wide electrocaloric operating temperature range near room temperature for $x = 0.18$. Markovic et al. (2010) have prepared samples using $x = 0.025, 0.05, 0.07, 0.10$ and 0.15 and found that structure remains tetragonal upto $x = 0.10$ and becomes cubic for $x = 0.15$. In yet another report they had observed phase becoming cubic at

becoming cubic at $x=0.12$ [Markovic et al. (2007)]. Study of dielectric behaviour has been carried out by Shvartsman et al. (2006) using samples with $x= 0.10, 0.15$ and 0.20 . They find that the system remains ferroelectric with $x \leq 0.15$ and dielectric permittivity attains maximum value when $x = 0.15$ and relaxor behaviour is observed for $x=0.20$. Lei et al. (2007) studied temperature dependence of permittivity for $x = 0.06, 0.12, 0.18, 0.20, 0.30$ and found that relaxor behaviour appears for $x > 0.19$. Zhang et al. (2015) studied samples with $x = 0.01, 0.03, 0.05$ and found that permittivity was maximum for $x =0.03$. Mueller et al. (2004) observed deviation from Curie-Weiss law (that is specific for relaxor ferroelectrics) in a narrow temperature region above Curie point even when BaSnO_3 content (x) is between 0.10 and 0.20 . It has been reported that dielectric constant attains a maximum value for $x = 0.15$ [Shvartsman et al.(2006)].

Upadhyay et al.(2014) reported P-E measurements for $x= 0.02, 0.05$ and 0.10 and found high electrocaloric effect at low field for $x = 0.05$. $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ ceramic has shown high value of tuneability and has been projected as material having a potential to replace the so popular $(\text{Ba,Sr})\text{TiO}_3$ in microwave applications [Lu et al.(2004)]. They studied the system for $x = 0.1, 0.2, 0.3, 0.4$ and observed that 54% tuneability can be achieved which decreases as x is increased.

Dielectric measurements upto 67 GHz were reported for $x= 0.02$ thin film samples and it was found that the structure remains tetragonal for $0.05 < x < 0.10$ around room temperature and becomes cubic for $x > 0.10$ [Waldhoff (2014)]. However, dielectric measurements in bulk systems in the microwave X –band are not available. Similarly impedance spectroscopy and equivalent circuit models for representing the dielectric behaviour in RF range are not available except that by Markovic et al. (2010) where they used impedance spectroscopy to study the influence of varying x on grain and grain boundary behaviour in functionally graded samples. As the useful properties

of this system has been attributed to arise for compositions close to the four-phase quadruple point x_c (~ 0.11), it was considered worthwhile to prepare this material with values $x = 0.05$ ($ie < x_c$), $x = 0.10$ ($ie \sim x_c$) and $x=0.15$ ($ie > x_c$) and characterize by XRD , impedance spectroscopy etc.

1.5 A Possible Application: Design of Rectangular Dielectric Resonator Antenna (RDRA)

As a possible application of the materials studied in the present work, effort was made to develop a design of rectangular dielectric resonator antenna (RDRA) operating in X-band of microwaves (8-12 GHz) based on dielectric constant values found for these materials. The X band is used for radar, satellite communication and terrestrial broadband. In modern radars, the shorter wavelengths of the X band allow for higher resolution imagery from high-resolution imaging radars for target identification and discrimination. In general, higher bands offer larger bandwidth capabilities in communication. Dielectric resonator antennas (DRA) have attracted much attentions recently due to their low cost, absence of losses at high frequencies that arise because of presence of metallic parts in usual antennas and flexibility in design [Huitema et al. (2012); Keyrouz et al. (2016); Yaduvanshi et al. (2016)]. RDRA's have recently been used in medical diagnostics with magnetic resonance imaging as well [O'Reilly et al. (2018)]. A DRA consists of a small puck of a dielectric material of certain shape and size and suitably excited to resonate with some desired modes [Keyrouz et al. (2016); Sebastian (2008); Yaduvanshi et al. (2016)]. The size varies as $(\epsilon)^{-1/2}$ so that desired miniaturization is possible by using suitable high permittivity dielectrics. The design essentially involves solving Maxwell electromagnetic equations for given boundary conditions of antenna shape and size. These can be analytically solved for certain regular shapes such as cylindrical or

rectangular etc. For general shapes, numerical methods have to be adopted. With the availability of software packages, such as Ansys High Frequency Simulation Software (HFSS), design and simulation of any shape has become possible. HFSS applies Finite Element Method with element auto-sizing capabilities that gives fast convergence. Vast literature has appeared in very recent years on search of materials as well as novel designs aimed at achieving high gain and large bandwidths [Keyrouz et al. (2016); Tripathi et al. (2015)].

