Chapter 1

Introduction

1.1 Ceramic Research and Development a Global Perspective

The use of ceramics in electronic components is growing rapidly as a result of their superior physical properties and latest developments in device technology. The use of ceramics as insulators, substrates, packages, capacitors, resistors, semiconductors, piezoelectric devices, and superconductors have shown an outstanding growth during the last two decades \cite{1}. Electronic ceramics is a high technology industry driven by rapid innovation and considerable changes. Working with a wide variety of functionally different materials, the electronic ceramic industry is still in the process of strong expansion and redirection. It interfaces smoothly with the electronic industry due to the widespread use of ceramic components as parts of electronic devices and packages. Several of the electronic ceramic market segments have matured, yet some are still growing at a steady pace.

Electronic ceramics (Electroceramics) can be also used as active components, such as semiconductors to control voltage and electrical currents, and in passive components, such as capacitors and resistors to control electrical currents or voltages, or in electromechanical applications, such as ferrite magnets or piezoelectric devices. The significance of electroceramic materials can be gauged with respect to the present demand of the same in the global market and projected demand\cite{2} in the future.
One can easily observe from available data, that, there is an upward trend in global investments in advanced ceramics (functional ceramics developed after World War II). Although research and development in advanced ceramics and related components has been going on for more than three decades in India, its requirements towards competitive commercial needs have neither been systematically studied nor understood. With the onset of globalisation and liberalisation, great emphasis has been imposed on indigenous research and development which therefore has to gear up to the stringent global standards. Global standards on the other hand are ever increasing, therefore to keep up breast with the demands we need considerable inputs in the form of substantial increase in technical manpower as well as cutting edge infrastructure. One needs to maintain a day to day updated database on the consumption and market demands of the ceramics in question. The commercial interest generated for a particular type of advanced ceramic has to be gauged from time to time and the research, development as well as manufacturing schedule has to be planned accordingly.

It can be seen that advanced ceramics can be broadly classified into two areas viz. electronic and structural. Electronic ceramics had generated a lot of commercial interest globally as compared to structural ceramics. This trend will remain so, for more than a decade from now. At present India enjoys just 1% of the global market share. While a smaller country like South Korea holds 7% of the global market share. China which started off much later than India, has now become a prominent player much ahead of India, in the run towards advanced ceramic development and marketing. The reason may be due to less funds available from the Government and industry towards electronic ceramics research or may be apathy on the part of R&D personals, who changed tracks and got involved in alternate and more lucrative fields (Computers for example.). Now
that a lot many developed as well as some developing countries had already invested heavily in the advancement of the industry; India has to bring out a well thought out plan and highly focused R & D to reap some economic benefits from this research. Also some indigenous market has to be developed so as to ensure that economic benefits reach down to the grass roots. Analogous to the world trend, the Indian market’s trend for advanced ceramics is largely dominated by electronic ceramics and therefore R&D efforts and investments were also more in this area. R&D efforts towards product development in this area started at they National Physical Laboratory, (NPL) New Delhi way back in the the year 1960. NPL developed the technology for ceramic ferrites and capacitor grade materials. The products were patented; the technology was transferred to Central Electronics Limited (CEL), Ghaziabad and Bharat Electronics Limited (BEL), Bangalore, both being public sector companies. BEL closed down their capacitor manufacturing units due to problems related to commercial viability, and went in for imported technology. Some of the deficiencies, on analyses, were found to be poor skills in mechanisation, volume production, poor design for quality and robustness into the products, failure in tailoring the product to customer requirements and lack of follow up research

1.2 Ceramic Materials

Ceramic materials are inorganic, non-metallic solids, which consists of an aggregate of randomly oriented crystallites bonded together by ionic bonds and have covalent character \(^3\). In contrast, the Anglo-Saxon term "ceramics" also often includes glass, enamel, glass-ceramic, and inorganic cementitious materials (cement, plaster and lime). Hence ceramics materials can be defined as
polycrystalline materials that acquire their mechanical strength through a sintering processes. Ceramics are good thermal and electric insulators, very much stable, possess high melting point and high chemical resistance and have high compressive strength. Ceramics materials find application in daily life e.g. electronic components, environment sensors, gas igniters, ultrasonic cleaner and intrusion alarm etc. Ceramics are categorized according to its properties like, High performance ceramics, Structural ceramics, Construction ceramics, Industrial ceramics, Engineering ceramics, Functional ceramics, Electrical ceramics, Cutting ceramics and Medical ceramics.

Advanced ceramic materials constitute a mature technology with a very broad base of current and potential applications and a growing list of material compositions. Advanced ceramics are inorganic, nonmetallic materials with combinations of fine-scale microstructures, purity, complex compositions and crystal structures, and accurately controlled additives. Such materials require a level, of processing science and engineering, far beyond that which are used in making conventional ceramics. Collectively, they represent an enabling technology whose continued development is critical to advances in a host of new high-technology applications, ranging from modern microelectronics to superconductors and nanotechnology. The outstanding properties possessed by advanced ceramics are achieved through special compositions and microstructures that require very careful control throughout the successive stages of ceramic processing. Table 1.1 below shows the categorisation of ceramics according to properties and applications.
Table 1.1. Categories of ceramics

<table>
<thead>
<tr>
<th>Materials Group</th>
<th>Property</th>
<th>Application</th>
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<tbody>
<tr>
<td>Traditional Ceramics</td>
<td>Compressive Strength</td>
<td>Bricks</td>
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<tr>
<td></td>
<td>Density + Strength</td>
<td>Ceramic Hollow Ware</td>
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<tr>
<td></td>
<td>Density + Wear Resistance</td>
<td>Structural Clay Products</td>
</tr>
<tr>
<td></td>
<td>Heat and Corrosion Resistance</td>
<td>Refractories</td>
</tr>
<tr>
<td>Structural Ceramics</td>
<td>Hardness</td>
<td>Grinding Grits and Disks</td>
</tr>
<tr>
<td></td>
<td>Strength + Toughness</td>
<td>Engineering Ceramics</td>
</tr>
<tr>
<td></td>
<td>Biocompatibility, Bioactivity</td>
<td>Biocermics</td>
</tr>
<tr>
<td></td>
<td>Nuclear Properties</td>
<td>Nuclear Ceramics</td>
</tr>
<tr>
<td></td>
<td>Corrosion Resistance, Catalytic Properties</td>
<td>Chemocermics</td>
</tr>
<tr>
<td>Functional Ceramics</td>
<td>Electric Resistivity, Dielectric Properties</td>
<td>Electroceramics</td>
</tr>
<tr>
<td></td>
<td>Magnetic Susceptibility</td>
<td>Magnetocermics</td>
</tr>
<tr>
<td></td>
<td>Anisotropic Optical properties</td>
<td>Optocermics</td>
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</tbody>
</table>

Ceramics have traditionally been admired for their mechanical and thermal stability, their unique electrical, optical and magnetic properties and have become increasingly important in many key technologies including communications, energy conversion and storage, electronics and automation. Such materials are now classified under Electroceramics \[^4\], and distinguished from other functional ceramics such as advanced structural ceramics. The term electro ceramic is used to describe ceramic materials that have been specially formulated for specific electrical, magnetic, or optical properties. Their properties can be tailored to
operation as insulators, ferroelectric materials, highly conductive ceramics, electrodes as well as sensors and actuators. The performance of electro-ceramic materials and devices depends on the complex interplay between processing, chemistry, structure at many levels and device physics and so requires a truly interdisciplinary effort by individuals from many fields. Articles in the professional literature tend to deal with the processing, characterization, structure, properties, modeling and performance of electroceramics.

1.3 Ferroelectric ceramics

Ferroelectricity, which at the time was called Seignette-electricity, was reported for the first time by Joseph Valasek[5], who worked at the university of Minnesota in Minneapolis, in his work “Piezoelectricity and Allied Phenomena in Rochelle Salt” at the meeting of the American Physical Society in Washington, in 1920. Since the discovery of ferroelectricity in single-crystal materials (Rochelle salt) in 1921 and its subsequent extension into the realm of polycrystalline ceramics (barium titanate[6], BaTiO₃) during the early to mid-1940s, there has been a continuous succession of new materials and technology developments that have lead to a significant number of industrial and commercial applications that can be directly credited to this most unusual phenomenon. Among these 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 igniters, positive temperature coefficient (PTC) sensors and switches, ultrasonic motors, electro-optic light valves, thin-film capacitors, and ferroelectric thin film memories.
The materials which possess the spontaneous polarization even in the absence of an electric field and the direction of spontaneous polarization can be changed by an applied electric field are called ferroelectric materials and the phenomena is called ferroelectricity\(^\text{[7]}\). The birth of ferroelectric ceramics as a useful class of materials came about as a result of three fundamental steps critical to an understanding of both ferroelectricity and piezoelectricity in ceramics.

1. Discovery of unusually high dielectric constant in barium titanate.

2. Discovery that the origin of this high dielectric constant was due to a permanent internal dipole moment (ferroelectricity). This allowed the development of ABO\(_3\) structure ferroelectrics

3. Discovery of electrical poling process within the ceramics, giving rise to single crystal like properties.

There are several types of ferroelectric materials that are grouped together according to their structure. The four main types of structures include:

1. The corner sharing oxygen octahedral.

2. Compounds containing hydrogen bonded radicals.


1.4. Ceramic polymer composites.
The corner sharing oxygen octahedra include the perovskite type compounds
(ABO$_3$ type structure, for example PCT, PZT, PT, PMN, K$_x$Na$_{1-x}$NbO$_3$, BT etc.),
the tungsten bronze type ferroelectric crystals; have a structure similar to tetragonal
tungsten bronze K$_x$WO$_3$ (x < 1), for example PbNb$_2$O$_6$ etc., bismuth oxide layer
structured ferroelectrics (eg. Bi$_4$Ti$_3$O$_{12}$, PbBi$_2$Nb$_2$O$_9$ etc.) Ferroelectric Curie point
and Phase Transitions Ferroelectric Curie point ($T_c$) is an important characteristic
of ferroelectrics. When the temperature decreases through the Curie point, a
ferroelectric crystal undergoes a structural phase transition from a paraelectric
phase to a ferroelectric phase. When the temperature is above $T_c$, the crystal does
not exhibit ferroelectricity; on the other hand, when the temperature is below $T_c$,
the crystal exhibits ferroelectricity. When the temperature is in the vicinity of the
Curie point, thermodynamic properties (such as dielectric, elastic, optical, and
thermal properties) of a ferroelectric crystal show anomalies and the structure of
the crystal changes. For example, dielectric constant in most ferroelectric crystals
has a very high value near their Curie point. This phenomenon is usually called the
‘dielectric anomaly’. In most ferroelectrics, the temperature dependence of the
dielectric constant above the Curie point (in the paraelectric region) can be
described fairly accurately by a simple law called Curie-Weiss law:

$$\varepsilon = A/(T-T_0)$$

Where, $\varepsilon$ is the dielectric constant, $A$ is the Curie constant and $T_0$ is the Curie Weiss
temperature, which defines the paraelectric phase. In the case of a first order phase
transition, $T_0 < T_c$, while for the second-order phase transition, $T_0 = T_c$. This
anomaly exhibited in the dielectric behaviour of a material with variation in
temperature is a characteristic feature of ferroelectric material. It is graphically, represented, in Figure 1.1 below.

![Figure 1.1](image)

**Figure 1.1** \(\varepsilon^{-1}\) (Inverse of dielectric constant) verses temperature

In fact, both the dielectric anomaly and Curie-Weiss law are predicted in the thermodynamic theory of phase transition. The dielectric anomaly is not a definite proof of ferroelectricity, which is normally confirmed by hysteresis loop. Ferroelectric domains are the regions of uniformly oriented spontaneous polarization within the material. Onset of the spontaneous polarization at \(T_c\), leads to the formation of a surface charge. These surface charges produce an electric field, called depolarizing field, \(E_d\). The depolarizing field may be very strong of the order of several kV/cm, rendering the single–domain state of the ferroelectric energetically unfavourable. The electrostatic energy associated with the depolarizing field may be minimized if

(i) The ferroelectric splits into domains (see Fig. 1.2) with oppositely oriented polarization.
(ii) The depolarizing charge is compensated for by electrical conduction through the material or by charges from the material surrounding.

Splitting of a ferroelectric crystal into domains may also occur due to the influence of mechanical stresses.

Figure 1.2 Representation of domain splitting into $180^\circ$ and $90^\circ$ boundaries

Hysteresis loop is the most important property of ferroelectric materials and measured by the behaviour of polarization reversal or switching by an applied external electric field in the material. The domain-wall switching in a ferroelectric material, results in a ferroelectric hysteresis loop (refer fig.1.3 below).

The value of polarization at zero fields is called the remnant polarization, $P_r$ and the field necessary to bring polarization to zero is called the coercive field, $E_c$. The spontaneous polarization, $P_s$, is usually taken as the intercept of the polarization axis, tangent to the saturated polarization. In polycrystalline materials
(ceramics), true spontaneous polarization equal to that of a single crystal can never be reached and here it is more correct to speak of saturated rather than of spontaneous polarization. Generally, an ideal hysteresis loop is symmetrical. In some materials the coercive field, spontaneous and remnant polarizations and the shape of the loop may be affected by a number of factors including the thickness, the presence of charged defects, mechanical stresses, preparation conditions and pinning centres. Polarization-electric field (P-E) hysteresis loop is also a function of temperature and usually the area of the loop shrinks with the increase in temperature until a phase transition takes place. At this point no P-E loop is observed and this temperature is called Curie temperature T_c.

Figure 1.3. The hysteresis loop.

Poling, which is a process during which a high electric field is applied on the ferroelectric ceramic samples to force the domains to reorient in the direction of
the applied electric field is an important processing condition to bring about macroscopic polarisation in the ceramic sample. This is akin to magnetising a ferromagnetic material by applying a strong external magnetic field. Or alternatively one may say that poling is the electrical analogue of magnetising. Poling is possible only in ferroelectric materials and various poling steps are as follow: graphically represented in Fig.1.4 below.

1. Heating to higher temperature (lower than $T_c$)
2. Application of field in one direction.
4. Switch off the electric field. (at room temperature)

![Figure 1.4 Concept of poling](image)
Before poling, the ferroelectric ceramic does not possess any piezoelectric and pyroelectric properties owing to the random orientation of the ferroelectric domains in the ceramics. For domain reorientation, a poling field must be applied on the sample and maintained for a certain length of time. For a given field and poling time, better domain rearrangement results at higher temperature, but lower than $T_c$. $T_c$ is called the transition temperature where the material phase change occurs from ferroelectric to paraelectric. This happens because with the increase in poling temperature, crystalline anisotropy and coercive field, $E_c$, of the ferroelectric materials decreases.

Also, with increasing temperature, space charges, which act against domain motion, decreases in ceramic materials. However, when the poling temperature is too high, problems arise as the electrical conductivity increases and the consequent increase in leakage current would result in sample breakdown during the period of poling. Sample is allowed to cool to room temperature with the field applied and filed is removed at room temperature. After poling, a remnant polarization and remnant strain are maintained within the material, and it starts exhibiting piezoelectric and pyroelectric effects. A set up of a corona poling unit is as shown in the Figure 1.5 \[8\]
1.4  Piezoelectric Ceramics.

Piezoelectricity stems from the Greek word piezo, which means pressure. It follows that a piezoelectric material develops a potential across its boundaries when subjected to a mechanical stress (or pressure), called direct piezoelectric effect\[^9\]. This property is exploited to make sensors. Conversely, when an electric field is applied to the material, a mechanical deformation ensues, called converse piezoelectric effect and the material can be used to make actuator. Thus the piezoelectric material can be used as sensor and actuator both and hence often called as smart material. These materials are being used extensively in smart systems, which consist of a sensor, actuator and control system. Ferroelectricity is a subgroup of piezoelectricity. It is a linear effect that is related to the microscopic structure of the solid. The microscopic origin of the piezoelectric effect is the displacement of ionic charges within a crystal structure. In the absence of the external stress, the charge distribution within the crystal is symmetric and the net electric dipole moment is zero. However, when an external stress is applied, the charges are displaced and the charge distribution is no longer symmetric. A net polarization develops and results in an internal electric field. A material can only be piezoelectric if the unit cell has no center of inversion. The first practical application for piezoelectric devices was sonar, first developed during World War I. In France in 1917 Paul Langevin\[^{10}\] (whose development now bears his name) and his coworkers developed an ultrasonic submarine detector. The detector consisted of a transducer, made of thin quartz crystals carefully glued between two steel plates, and a hydrophone to detect the returned echo. These materials generally are physically strong and chemically inert, and they are relatively inexpensive to manufacture. The composition, shape, and dimensions of a piezoelectric ceramic element can be tailored to meet the requirements of a specific
purpose. Ceramics manufactured from formulations of lead zirconate / lead titanate exhibit greater sensitivity and higher operating temperatures, relative to ceramics of other compositions, and "PZT" materials currently are the most widely used piezoelectrics\textsuperscript{[11]}. However, high doping levels compromise the chemical and crystalline stability of PZT. These concerns naturally lead to the introduction of compensated doping (i.e. simultaneous acceptor and donor doping) that is equivalent to the dissolution of relaxors in lead zirconate titanate. Thus, a flourishing variety of relaxor-ferroelectric-based compositions exhibiting very high properties appeared in the mid 1960’s. With Curie temperatures close to room temperature, they exhibited properties alike the donor-doped materials with even higher dielectric permittivities and piezoelectric modulus. The next significant improvement was obtained in single crystals of such compositions poled in special directions and hence possessing a particular domain structure. They were shown to exhibit extremely high piezoelectric properties\textsuperscript{[12]}, more than 10 times higher than those of lead zirconate titanate. The increase in properties obtained for piezoelectric materials during the last 50 years is impressive. However, it has been mostly reached by empirical methods as the mechanisms leading to such improvements in soft ferroelectrics are today still under discussion. Moreover, such high properties are often accompanied by strong nonlinearities originating from microscopic mechanisms that are not yet understood. For 40 years, the highest piezoelectric properties were obtained with materials containing lead. Even though lead zirconate titanate, Pb(Zr,Ti)O\textsubscript{3} (PZT), solid solutions were first reported in 1952\textsuperscript{[13,14]}, real interest in PZT was drawn by the discovery of a peak in the dielectric and piezoelectric properties for compositions close to 52 mol\% of PbZrO\textsubscript{3} (PZ) by Jaffe, Roth and Marzullo\textsuperscript{[15]}, as illustrated for the piezoelectric coefficients in Figure 1.6.
Figure 1.6: Piezoelectric properties as a function of composition for lead zirconate titanate

The properties of the undoped 52 mol% PZ composition are compared to those of barium titanate in Table 1.1. Besides the much higher piezoelectric properties of PZT, it also exhibits a higher Curie temperature which is advantageous in applications. Note that the reported properties were obtained for undoped materials. Doping with a few mol% of Nb increases significantly the permittivity and the piezoelectric properties of PZT \cite{16}.

Table 1.1: Comparison of the dielectric and piezoelectric properties of undoped PZT and barium titanate \cite{16}

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon$</th>
<th>$T_C$ [$^\circ$C]</th>
<th>$d_{33}$ [pC/N]</th>
<th>$k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(Zr$<em>{0.52}$, Ti$</em>{0.48}$)O$_3$</td>
<td>1180</td>
<td>386</td>
<td>223</td>
<td>53 %</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>1620</td>
<td>120</td>
<td>191</td>
<td>35 %</td>
</tr>
</tbody>
</table>
The chemically localized increase of properties in PZT was immediately related to the structural change from a rhombohedral to a tetragonal symmetry occurring in this compositional region upon increase of the PbTiO$_3$ (PT) concentration. Such a phase transition was designated as “morphotropic” following the nomenclature introduced by Goldschmidt $^{[17]}$ for structural transformations occurring upon a chemical concentration change. Indeed, the PZT phase diagram (see Figure 1.7) presents an almost vertical morphotropic phase boundary (MPB) separating the tetragonal and rhombohedral ferroelectric phases.

![Figure 1.7: Phase diagram for lead zirconate titanate$^{[16]}$ exhibiting the cubic (paraelectric), antiferroelectric (AF), tetragonal and rhombohedral high/low temperature states.](image)
Figure 1.8: Lattice cells associated with the paraelectric to ferroelectric transition in lead zirconate titanate $^{[18]}$. Top is cubic, left is rhombohedral HT (with the distortion angle, $\alpha$) and right is tetragonal (with lattice parameters, $a$ and $c$)

The phase diagram presents 3 main regions: the cubic paraelectric state, the antiferroelectric (AF) state around pure PZ and the ferroelectric state consisting in two types of rhombohedral phases (R3m at high temperature, and R3c at low temperature) and one tetragonal (P4mm). These ferroelectric phases are obtained by slight deformations of the prototype perovskite cubic cell, ABO$_3$ leading to the
rhombohedral and the tetragonal symmetries, as represented in Figure 1.8. In such phases, the spontaneous polarization partially arises from the off-center position of the B-site atom (Ti or Zr). Its displacement follows the polarization vector ([111] in R3m and [001] in P4mm). Moreover, there are good indications (see e.g. Ref. [19]) that a lead shift also contributes to the total polarization. The transition between the two rhombohedral phases (HT and LT) is related to a tilt in the oxygen octahedra [20,21]. As the spontaneous polarization can take 8 different orientations in the rhombohedral state and 6 in the tetragonal one, ferroelectric domains generally form in PZT ceramics cooled below their Curie temperature. In such symmetries, the permissible domain walls can be separated in two groups: pure ferro-electric and ferro-elasto-electric walls. The former is constituted by 180° domain walls (DW) which separate two oppositely polarized domains. The latter implies a change of both direction of polarization and associated strain across the wall. They are hence confined to mechanical twinning planes. In the tetragonal structure, 90° domain walls (i.e. separating two perpendicular polarization domains) are the only ones of this kind and sit on (110) planes. In the rhombohedral structure, there are two types of such walls, the 109° DW and the 71° DW located on (110) and (100) planes respectively. Note that 109° DW seem to be more frequent as their surface energy is significantly lower than 71° DW [22]. In general, those ferro-elasto-electric domain walls are often referred to as non-180° domain walls. The high properties in PZT being related to the presence of a morphotropic phase boundary, it was natural to look for other perovskite compounds exhibiting a similar feature. For instance, solid solutions of lead hafnate titanate were tested and indeed exhibited a MPB with enhanced properties [23] but not sufficiently elevated to compete with PZT. A significant increase in properties came from the mixing of relaxor ferroelectrics (such as Pb(Mg_{1/3}Nb_{2/3})O_3 (PMN) or Pb(Ni_{1/3}Nb_{2/3})O_3 (PNN)) with normal ferroelectrics such as PT or PZT.
From the analysis of symmetry elements, it is found that symmetry operations can be combined in 32 different ways, resulting 32 crystal classes. Out of these 32, only eleven crystal classes have a center of symmetry and 21 are non-centro symmetric. Out of the remaining 21 non centro-symmetric classes, 20 show the phenomenon of piezoelectricity. The remaining one non-centro symmetric class left does not show any piezoelectric effect because of the combined effect of symmetry elements. Piezoelectric effect is the phenomenon of creation of electric polarization on the application of external stress and vice-versa. Some piezoelectric crystals (10 out of 20) posses spontaneous polarization and are called polar crystals. A summary is represented as a flow diagram below (Figure 1.9[24].)

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Figure 1.9. Summary of symmetry elements and piezo crystals
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In a piezoelectric crystal, the positive and negative electrical charges are separated, but symmetrically distributed, so that the crystal overall is electrically neutral. When a stress is applied, this symmetry is disturbed, and the charge asymmetry generates a voltage. A 1 cm cube of quartz with 500 lbf (2 kN) of
correctly applied force upon it, can produce 12,500 V of electricity. Converse piezoelectricity is revealed by ferroelectrics where application of an electrical field creates mechanical stress (distortion) in the crystal. Because the charges inside the crystal are separated, the applied voltage affects different points within the crystal differently, resulting in the distortion. Materials Exhibit Piezoelectric Effect. Many materials exhibit Piezoelectric effect, including quartz analogue crystals like berlinite (AlPO₄) and gallium orthophosphate (GaPO₄), ceramics with perovskite or tungsten-bronze structures (BaTiO₃, PbTiO₃, CaTiO₃, KNbO₃, LiNbO₃, LiTaO₃, BiFeO₃, NaₓWO₃, Ba₂NaNb₅O₁₅, Pb₂KNb₅O₁₅ etc.) Polymer materials like rubber, wool, hair, wood fiber, and silk exhibit piezoelectricity to some extent. The polymer polyvinylidene fluoride, (-CH₂-CF₂-)_ₙ, exhibits piezoelectricity several times larger than quartz. Bone exhibits some piezoelectric properties (bone remodeling).

The piezoelectric parameters that are of interest when considering the electromechanical effects in piezoelectric materials are the piezoelectric charge coefficients (d₃₁, d₃₃), the piezoelectric voltage coefficients (g₃₁, g₃₃) and the piezoelectric / electro mechanical coupling factors (k₃₁, k₃₃, kₚ and kᵣ). Piezoelectric ceramic is anisotropic, physical constants relate to both the direction of the applied mechanical or electric force and the directions perpendicular to the applied force. Consequently, each constant generally has two subscripts that indicate the directions of the two related quantities, such as stress (force on the ceramic element / surface area of the element) and strain (change in length of element / original length of element) for elasticity. The direction of positive polarization usually is made to coincide with the Z axis of a rectangular system of X, Y, and Z axes. Direction X, Y, or Z is represented by the subscript 1, 2, or 3, respectively,
and shear about one of these axes is represented by the subscript 4, 5, or 6, respectively.

Definitions of the most frequently used constants and equations for determining and interrelating these constants, are summarized here. The piezoelectric charge constant, d, the piezoelectric voltage constant, g, and the permittivity, \( \varepsilon \), are temperature dependent factors.

**Figure 1.10** Direction of forces affecting piezoelectric forces Piezoelectric Charge Coefficient (d)

When a piezoelectric material is subjected to stress, electric charge is generated on the surfaces. The charge generated per unit force is called piezoelectric charge coefficient and is denoted by ‘d’ which is measured in pC/N. Piezoelectric charge\(^{[26]}\) coefficient is a directional property and is usually specified with subscripts to identify the conditions under which it is determined e.g., \( d_{33} \) and \( d_{31} \).
In these piezoelectric charge coefficients, first subscript corresponds to the direction of the applied stress and second corresponds to the direction of the faces of the ceramic on which charges are developed. See fig.1.10 and fig.1.11 for the conventions used in the literature.

Hydrostatic Charge Coefficient \((d_h)\) corresponds to the effect of development of charge when a pressure is applied on the material. Hydrostatic charge coefficient \((d_h)\) is related to \(d_{33}\) and \(d_{31}\) piezoelectric charge constants by the relation:
\[ d_h = d_{33} + 2d_{31} \] [Measured in Coulomb/Newton (C/N) units] …….(1.2)

In a similar manner Piezoelectric Voltage Constant (g) gives the field produced by a stress in a piezoelectric material. Its usual units are meter volts / Newton and ‘g’ constant is related to the ‘d’ constant by the permittivity

\[ g = d / (\varepsilon' \varepsilon_o) \] ........................(1.3)

where g is called the piezoelectric voltage coefficient, \( \varepsilon' \) and \( \varepsilon_o \) are the dielectric constant of the material and permittivity of the free space, respectively.

Corresponding to \( d_{33} \) and \( d_{31} \) piezoelectric constants, there exist \( g_{33} \) and \( g_{31} \) piezoelectric voltage coefficients. High ‘g’ constant is desirable in materials intended to generate voltages in response to a mechanical stress, as in a phonograph pickup.

The Hydrostatic Voltage Coefficient (\( g_h \)) gives the field produced by a pressure. It is related to the \( g_{33} \) and \( g_{31} \) piezoelectric charge coefficients by the relation

\[ g_h = g_{33} + 2g_{31} \] (units are meter volts/Newton.)  .................(1.4)

The Electromechanical Coupling Factor (k) is one of the most crucial measurements related to the strength of the piezoelectric effect, which reflects the efficiency of a piezoelectric material. It gives us the measure of the part of the applied electrical energy converted into mechanical energy or vice-versa and measured by resonance method.
Mechanical energy converted into electrical energy

\[ k_{\text{eff}} = \frac{\text{Mechanical energy}}{\text{Input Mechanical energy}} \quad \ldots \ldots (1.5) \]

Or

Electrical energy converted into mechanical energy

\[ k_{\text{eff}} = \frac{\text{Electrical energy}}{\text{Input electrical energy}} \quad \ldots \ldots (1.6) \]

Depending on the mode of energy conversion, there exist various electromechanical coupling factors, for example \( k_p \), \( k_t \) and \( k_{33} \). Here, \( k_p \) is planar coupling coefficient, related to the energy conversion, when the applied electric field is perpendicular to the generated mechanical vibrations, which are along the plane. \( k_t \) is thickness coupling factor related to the energy conversion, when the applied electric field is in the direction of generated mechanical vibrations and which are along the thickness in the material large \( k_t \) and small \( k_p \) in a piezoelectric material exhibits huge anisotropy behaviour. Due to large anisotropy, transverse modes get suppressed resulting in the prevention of pickups due to transverse mode.

1.5 Ceramics as Capacitors (Dielectric Properties).

Ferroelectrics materials are very often good dielectrics\textsuperscript{[27]}. For most applications of ferroelectric materials, the dielectric constant (\( \varepsilon' \)) and dielectric loss (\( \tan \delta \)) are important practical parameters, studies of the dielectric properties
provide a great deal of information about the suitability of the material for various applications.

For a given substance, the ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric is called dielectric constant of the substance. It is a measure, therefore, of the amount of electrical charge a given substance can withstand at a given electric field strength. The capacitance, C for a parallel plate capacitor is given by

\[ C = \varepsilon_0 \frac{A}{t} \]  

............... (1.7)

Where \( \varepsilon_0 \) is the permittivity of free space and is equal to \( 8.854 \times 10^{-12} \) F/m, A is the area of electrode and t is the separation between two electrodes. When a dielectric (electrical insulator) fills the space between the plates, the capacitance of the capacitor is increased by a factor \( \varepsilon' \), which is called the dielectric constant of the dielectric material. Therefore, for a parallel plate capacitor with a dielectric between the capacitor plates, the capacitance, C is given by

\[ C = \varepsilon'\varepsilon_0 \frac{A}{t} \]  

............... (1.8)

Thus the energy stored in a capacitor of a given volume at a given voltage is increased by the factor of the dielectric constant when the dielectric material is present. For an alternating electric field, the dielectric constant can be written as

\[ \varepsilon_r = \varepsilon' - i\varepsilon'' \]  

............... (1.9)

where \( \varepsilon' \) is the real component of the dielectric constant, in phase with the applied field \( \varepsilon'' \) is the imaginary component, \( 90^\circ \) out of phase with the applied field, caused by either resistive leakage or dielectric absorption. For normal substances, the
value of $\varepsilon_r$ is low, usually under 5 for organic materials and under 20 for most inorganic materials. Generally, ferroelectric ceramics have much higher $\varepsilon_r$, typically several hundreds to several thousands.

The dielectric dissipation factor (dielectric loss factor), $\tan\delta$, for a ceramic material is the tangent of the dielectric loss angle. $\tan\delta$ is determined by the ratio of effective conductance to effective susceptance in a parallel circuit, measured by using an impedance bridge. Values for $\tan\delta$ typically are determined at 1 kHz. Dielectric loss is related to non-instantaneous polarisation due to the inertia of charges and absorption of electrical energy by the dielectric. Polarisation is time-dependant as a new charge distribution will take time to establish. The final static charge distribution forms after the instantaneous atomic and ionic polarizations.

High dielectric ceramics used in industrial applications are Barium Titanate, PZT, PMN, etc. Most of them are relaxor ferroelectrics and are either perovskites or those with tungsten bronze structure.

1.6 Structure of the Ceramics under investigation.

Perovskite-type ferroelectrics (of general formula $ABO_3$) that followed the discovery of barium titanate, Shirane, Hoshino and Suzuki studied lead titanate ($PbTiO_3$) ceramic and reported its ferroelectricity on the basis of the structural analogy between both compositions\cite{28}. Lead titanate is a ferroelectric material with a high Curie temperature ($490^\circ$C) at which the phase transition from the cubic paraelectric phase (above Curie temperature) to the tetragonal ferroelectric phase (below Curie temperature) occurs.
Lead titanate is having perovskite-type structure. This oxide ceramic has the general chemical formula $\text{ABO}_3$, where O is oxygen, A represents a cation with a larger ionic radius and B a cation with a smaller ionic radius. Fig. 1.12 shows a cubic $\text{ABO}_3$ (e.g., A is Pb and B is Ti in $\text{PbTiO}_3$) perovskite-type unit cell.

The packing situation of this structure may be characterized by a tolerance factor, $t$, which is defined by the following equations:

$$R_A + R_O = t \sqrt{2} (R_B + R_O) \quad \cdots \cdots \ (1.10)$$

Where, $R_A$, $R_B$ and $R_O$, are the ionic radii of A, B and O ions respectively. When $t$ is equal to 1, the packing is said to be ideal \[^{30}\]. When $t$ is larger than 1, there is too large a space available for B ion, and therefore this ion can move inside its octahedron. In general, to form a stable perovskite structure, one requires that $0.9 < t < 1.1$. 

**Figure 1.12.** Perovskite Structure\[^{29}\]
1.7 Lanthanum Modified PZT (PLZT) Ceramics.

The doping of La to the basic PZT system results in many effects such as enhanced dielectric and piezoelectric properties, increased squareness of the $P–E$ hysteresis loops, decreased coercive field ($Ec$) and transparency $^{[31]}$. The advantages of this material include not only the optical transparency, but also a fast response, multicolour capability and electrooptic properties. Solid-state nature of the material is based on the simple PbZrO$_3$–PbTiO$_3$ (PZT) solid solution system, the function of the La concentration as well as the Zr/Ti ratio, i.e., the $x$/65/35 composition yields the most transparent ceramics for La concentrations in the range of 8–16 mole per cent $^{[32]}$. Nanocrystalline PLZT materials obtained from the sol-gel derived powders exhibit some features substantially increasing possibilities of their application in electronic and opto-electronic devices such as: segment displays, light shutters, coherent modulators, colour filters, linear gate arrays and image storages. As a result, they have been widely investigated $^{[33]}$. The goal of this study is (i) to utilise sol-gel method for obtaining amorphous PLZT nano powders with the chemical composition corresponding to the $x$/52/48 ratio, where $x = 0$ to 20 mole per cent of La, and (ii) to study their structure and basic dielectric properties. The ferroelectric ceramics have a number of properties, which make them very useful in a variety of applications. As an example of such materials the lanthanum – doped PZT systems, represented also as PLZT. Solid-state nature of PLZT material is based on: the simple PbZrO$_3$-PbTiO$_3$ solid solution system, the function of the lanthanum concentration as well as the Zr/Ti ratio. Donor dopants of higher charge, like a La$^{3+}$ ions, enhance domain wall mobility and result in improved remnant polarization, coupling factors, dielectric constants, dielectric loss tangent and increased optical transparency of electrically “soft” PZT material $^{[32,34]}$. The result of such doping is also attributed to the
creation of vacancies \((V)\) in the A site of perovskite crystal structure, thus the chemical composition of PLZT is given by the formula \([35]\):

\[
Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}V_{0.25x}O_3,
\]

Creations of such vacancies ensure electric neutrality of the lead lanthanum zirconate titanate system. The composition of PLZT is routinely represented by the notation \(x/(1-y)/y\), which denotes the amount of La/Zr/Ti, given in mole fractions or mole per cent. The goal of this study is to obtain PLZT materials, from sol-gel derived powders by the sintering method, subject all samples to polarization by the low temperature method, and to study the influence of \(La^{3+}\) dopant on their basic dielectric and piezoelectric properties.

Application of proper technological methods to the fabrication of ceramic powders are one of the factors improving the control of the stoichiometry of materials, influencing the properties of ferroelectric ceramic materials. The sol-gel method is a low temperature process, which utilizes chemical precursors and makes it possible to obtain fine powders that exhibit high chemical reactivity, as well as better purity, homogeneity and physical properties than those fabricated by conventional high-temperature processes. The lead–lanthanum zirconate–titanate (PLZT) ceramics is one of the ferroelectric materials, which can be successfully obtained by the sol-gel method. The chemical composition namely

\[
Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}V_{0.25x}O_3,
\]

takes into account the charge compensation, assuming that the electrical neutrality is maintained by the creation of \((Zr, Ti)\) vacancies \((V)\). The concentration of La, \(x = \text{La}/(\text{La} + \text{Pb})\), may vary from 0. to 0.2. The ratio \(y\) of \(Zr/(Zr + Ti)\) may take any value 0.52. The composition of PLZT is usually represented by the notation \(x/(1 - y)/y\), which denotes the amounts of
La/Zr/Ti, given in mole fractions or mole per cent (i.e. mole fraction multiplied by 100). For instance, the notation 8/65/35 represents PLZT with the chemical composition \((\text{Pb}0.92\text{La}0.08)(\text{Zr}0.65\text{Ti}0.35)0.98\text{O}_3\) \cite{32}. Lanthanum-doped lead zirconate–titanate ceramics, with variable dopant concentration and the ratio of Zr/Ti exhibit a variety of phases such as ferroelectric (FE), antiferroelectric (AFE), paraelectric (PE) and mixed (MPh) phases, shown in the room temperature phase diagram in Fig. 1.13 \cite{35,36}.

![Phase diagram of the PLZT system at room temperature](image)

*Fig. 1.13. Phase diagram of the PLZT system at room temperature* \cite{35}
References:


