A THESIS

On

STUDIES ON STRUCTURAL, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF DOPED PCT CERAMICS

Submitted in the partial fulfillment of requirement for the award of the degree of

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IN

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Submitted by
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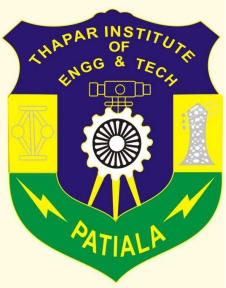

School of Physics and Materials Science

THAPAR INSTITUTE OF ENGINEERING AND TECHNOLOGY

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CERTIFICATE

This is to certify that the thesis entitled **STUDIES ON STRUCTURAL, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF DOPED PCT CERAMICS** submitted by **Mr. Mohit Sharma** in the partial fulfillment of the requirement for the award of the degree of **M. Tech** in **Materials Science and Engineering** from the **School of Physics and Materials Science, Thapar Institute of Engineering and Technology (Deemed University), Patiala,** is a record of candidate's own work carried out by him under my supervision and guidance. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

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Dedicated To My Parents

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ABSTRACT

Ceramics have traditionally admired for their mechanical and thermal stability, their unique electrical, optical and magnetic properties. These features make ceramics important in many key technologies including communication, energy conversion and storage, electronics and automation. Electroceramics are the advance structural ceramics materials used for electronic applications. Developments in these materials are categorized as smart materials, have paralleled the growth of new technologies. Example includes Ferroelectrics – high dielectric constant, non-volatile memories; Ferrites – data and information storage; Solid electrolytes, energy storage and conversion; Piezoelectrics – sensors, actuators, transducers, sonar etc.

Lead titanate (PT) ceramics are very promising piezoelectric materials for high temperature and high frequency applications because of their high curie temperature and low dielectric constant. Pure lead titanate ceramics are difficult to sinter because of their large anisotropy. On cooling through the curie temperature, the large anisotropy cause the ceramics to become fragile. By addition of small amount of suitable additives, cracking can be prevented.

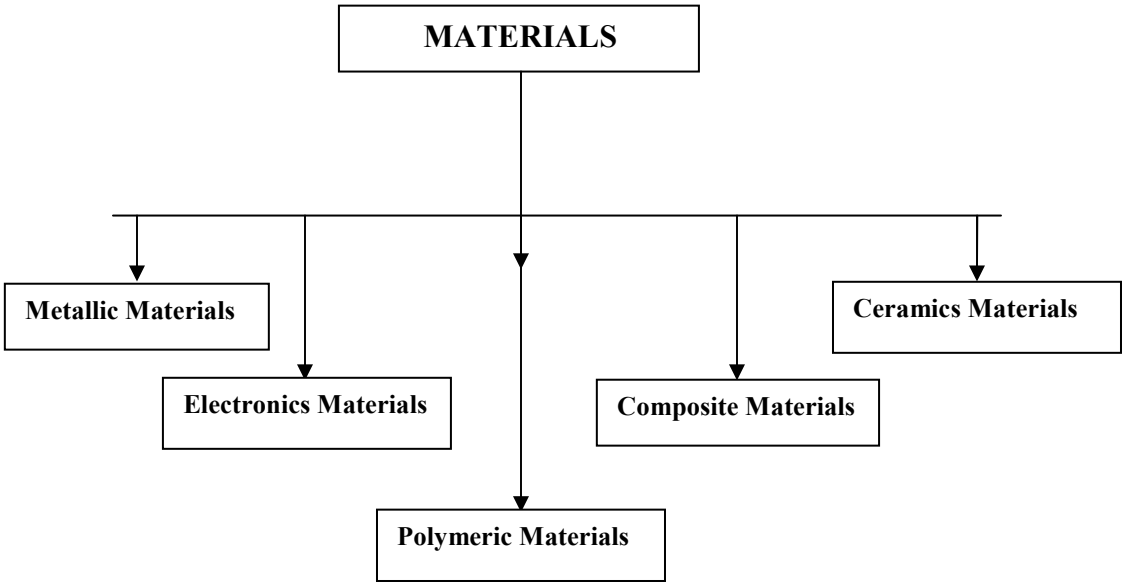
In the present work, the effect of lanthanum substitutions on the structural, dielectric and piezoelectric properties of lead calcium titanate (PCT) ceramics going to be investigate. The sample with composition formula $Pb_{0.76-x/2}La_xCa_{0.24}(Ti_{0.98}Mn_{0.02})_{1-x/2}O_3$ and $Pb_{0\cdot76}Ca_{0.24}Mn_{0.02}Ti_{0.98-5x/4}Ta_xO_3$, with x = 0 - 0.02 prepared by solid state reaction method. Structural and phase analysis carried out by SEM and XRD. Dielectric and piezoelectric parameters study helps to show that La^{3+}, Ta^{5+} substitution improves the electromehanical properties of lead calcium titanate.

1. INTRODUCTION

Materials are broadly a group of substances required for the development of newer products with use in moving the technological engine. There is always a need to synthesize and /or prepare materials with varied functionalities supported by the standard processing methodologies.

Modern materials can be divided into following classes. Each class plays significant role depending up on their range of applications and use in industry.

Flow Chart Classification of materials



1.1 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. 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 are polycrystalline materials that acquire their mechanical

strength through various sintering processes. Ceramics [1] are good thermal and electric insulators, more stable, 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 ignitors, ultrasonic cleaner and intrusion alarm etc. Ceramics are categorized as High performance ceramics, structural ceramics, construction ceramics, industrial ceramics, engineering ceramics, functional ceramics, electrical ceramics, cutting ceramics and medical ceramics.

Table 1. Classes of ceramics materials and their application

Materials Group	**Property**	**Application**
Traditional Ceramics	Compressive Strength	Bricks
	Density + Strength	Ceramic Hollow Ware
	Density + Wear Resistance	Structural Clay Products
	Heat and Corrosion Resistance	Refractories
Structural Ceramics	Hardness	Grinding Grits and Disks
	Strength + Toughness	Engineering Ceramics
	Biocompatibility, Bioactivity	Bioceramics
	Nuclear Properties	Nuclear Ceramics
	Corrosion Resistance, Catalytic Properties	Chemocermics
Functional Ceramics	Electric Resistivity, Dielectric Properties	Electroceramics
	Magnetic Susceptibility	Magnetoceramics
	Anisotropic Optical properties	Optoceramics

1.2 Electroceramics

Electroceramics are the basic science of the origins of a wide range of physical properties including conductive, dielectric, magnetic and piezoelectric and how these properties influence the components such as capacitors, thermistors, microwave [2] device and actuators. Their properties are controlled by composition, processing conditions and complexities of the shape. Various types of electronic ceramics are: insulators, ferrites, capacitors, substrates (PTCS), ferroelectrics, pyroelectrics, piezoelectric and electr-ooptic ceramics. A variety of smart materials used in today's state of art military and other intelligent systems are based on ceramics materials.

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 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 [3] 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.

Ceramics have traditionally been admired for their mechanical and thermal stability, their unique electrical, optical and magnetic properties have become of increasing importance in many key technologies including communications, energy conversion and storage, electronics and automation. Such materials are now classified under *Electroceramics* as 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.

History

Historically, developments in the various subclasses of Electroceramics have paralleled the growth of new technologies. Examples include: Ferroelectrics - high dielectric capacitors, non-volatile memories; Ferrites-data and information storage; Solid Electrolytes-energy storage and conversion; Piezoelectrics-sonar; Semiconducting Oxides environmental monitoring.

The exploitation of piezoelectric property in sonar, and its success created intense development in piezoelectric devices. Over the past few decades, new piezoelectric materials and their applications were explored which led to the development of novel devices like smart systems, actuators, sensors SAW devices, MEMS and multilayer capacitors. Quartz crystals were the first commercially [4] exploited piezoelectric material, but scientists searched for higher-performance materials.

Definition

Ceramics materials which are used for electronic applications are called electroceramics. 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 electro-ceramic. Topical areas cover a wide spectrum with recent active areas including sensors and actuators, [5] electronic packaging, photonics, solid state ionics, defect and grain boundary engineering, magnetic recording, nonvolatile ferroelectric memories, wide band gap semiconductors, high T_c superconductors, integrated dielectrics and nano-technology.

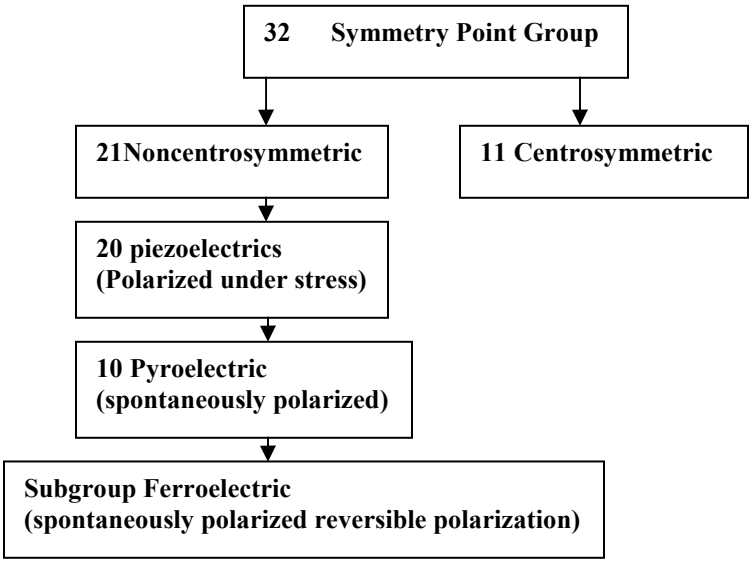
Key Features

The key features that generally describe ceramics, and consequently electroceramics are:

- The presence of ionic-covalent bonding.
- Microstructures comprising inorganic crystal compounds and/or amorphous glass in varying proportions
- Thermal processing conducted at elevated temperatures

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.

Flow Chart Inter-relationship of piezoelectric and subgroups



These polar crystals are also known as pyroelectric crystals and give pyroelectric effect i.e. the appearance of an electric charge at the surface of the polar material with change in temperature i.e. under uniform heating or cooling. Current generated due to these electrical charges is called the pyroelectric current. If the direction of the pyroelectric current (or spontaneous polarization) in pyroelectric crystals can be reversed by the application of high electric field then these materials are [6] known as ferroelectrics. As all pyroelectric materials are polar, and ferroelectrics are a sub-group of these pyroelectric materials; all ferroelectrics are pyroelectrics and piezoelectrics both. These crystals show large dielectric constant and high electro-mechanical coupling factor. Polycrystalline ceramics of these materials also show the ferroelectric effect after poling. Electroceramics includes dielectric ceramics, ferrites, ferromaganates, electrostrictive ceramics and piezoelectric ceramics.

1.3 Ferroelectricity

Ferroelectricity, which at the time was called Seignette-electricity, was reported for the first time by **Joseph Valasek**, who worked at the university of Minnesota in Minneapolis, in his work "Piezoelectricity and Allied Phenomena in Rochelle Salt" at the meeting of the Americal 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, $BaTiO_3$) 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 [7] 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 ignitors, positive temperature coefficient (PTC) sensors and switches, ultrasonic motors, electro-optic light valves, thin-film capacitors, and ferroelectric thin film memories.

General Features of Ferroelectrics

Definition

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.

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.

Types of Ferroelectric Materials

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.
3. Organic polymers.
4. Ceramic polymer composites.

The corner sharing oxygen octahedra include the perovskite type compounds (ABO_3 type structure, for example PCT, PZT, PT, PMN, $K_xNa_{1-x}NbO_3$, BT etc.), the tungsten bronze type ferroelectric crystals; have a structure similar to tetragonal tungsten bronze K_xWO_3 ($x < 1$), for example $PbNb_2O_6$ etc., bismuth oxide layer structured ferroelectrics (eg. $Bi_4Ti_3O_{12}$, $PbBi_2Nb_2O_9$ 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 [4] 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:

$$\varepsilon' = A/(T-T_0) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.1)$$

Where, ε' 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 [7] with variation in temperature is a characteristic feature of ferroelectric material.

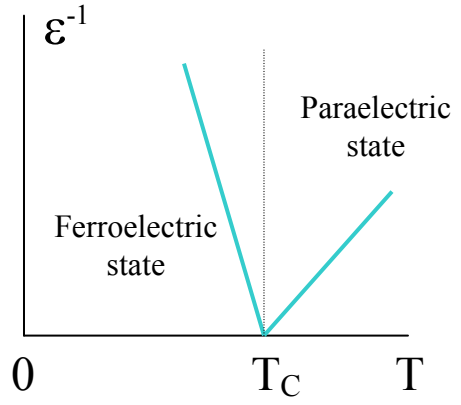


Figure 1.1 ϵ^{-1} (Inverse of dielectric constant) verses temperature

In fact, both the dielectric anomaly and Curie-Weiss law are predicted in the thermodynamic theory of transition. The dielectric anomaly is not a definite proof of ferroelectricity, which is normally confirmed by hysteresis loop.

Ferroelectric Domains

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 unfavorable. The electrostatic energy associated with the depolarizing [8] field may be minimized if

(i) The ferroelectric splits into domains 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.

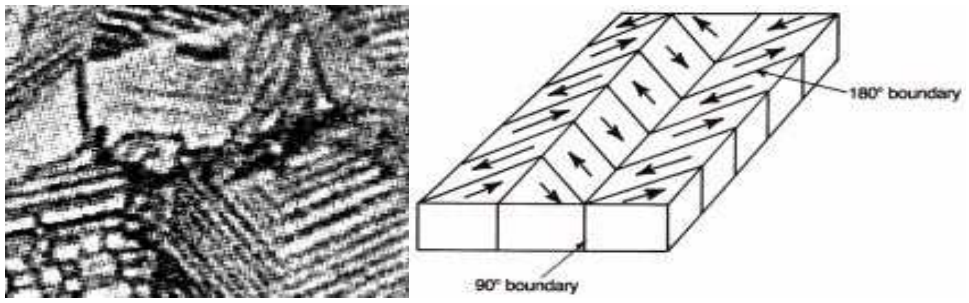


Figure 1.2 Schematic diagram of $90^o$and 180^odomains.

1.4 Hysteresis Loop Behavior

Hysteresis loop is the most important property of ferroelectric materials and measured by the behavior 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.

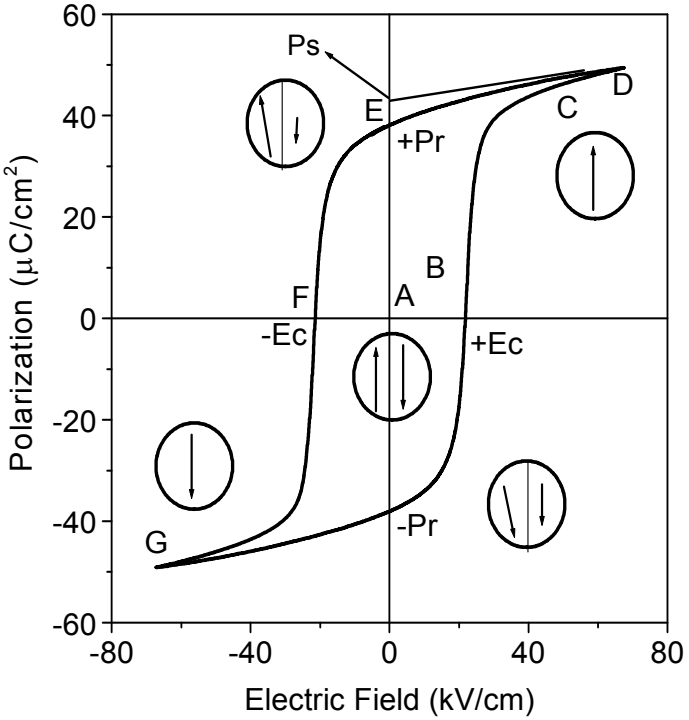


Figure 1.3 Polarization versus electric field loop behaviour.

The value of polarization at zero field 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, 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 centers. 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.

1.5 Poling

Poling 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. The poling is possible only in ferroelectric materials and various poling steps are as follow:

1. Heating to higher temperature (lower than Tc)
2. Application of field in one direction.
3. Removal of temperature.
4. switch off the electric field .(at room temperature)

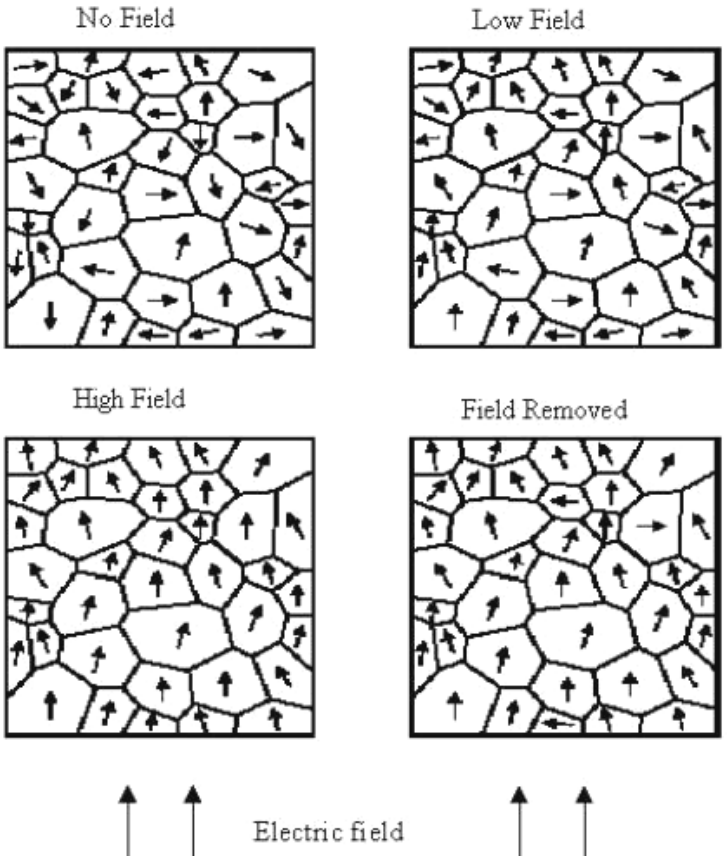


Figure 1.4 Concept of poling

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, [3] better domain rearrangement results at higher temperature, but lower than T_c. This happens because with the increase in poling temperature, crystalline anisotropy and coercive field, E_c, of the ferroelectric materials decreases.

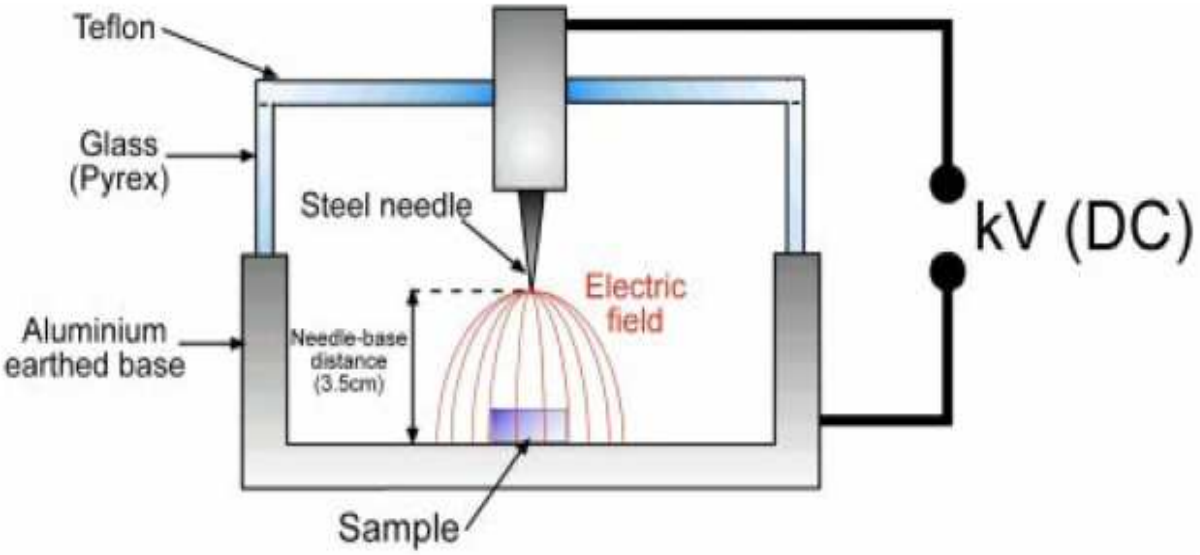


Figure 1.5 Poling set-up

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

1.6 Piezoelectricity

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. 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 [9] 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 (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.

Mechanism

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 reveal 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 [10] the crystal differently, resulting in the distortion.

Materials Exhibit Piezoelectric Effect.

Many materials exhibit Piezoelectric effect, including quartz analogue crystals like berlinite ($AlPO_4$) and gallium orthophosphate ($GaPO_4$), ceramics with perovskite or tungsten-bronze structures ($BaTiO_3$,$PbTiO_3$, $CaTiO_3$, $KNbO_3$, $LiNbO_3$, $LiTaO_3$, $BiFeO_3$, Na_xWO_3, $Ba_2NaNb_5O_5$, $Pb_2KNb_5O_{15}$ etc.) Polymer materials like rubber, wool, hair, wood fiber, and silk exhibit piezoelectricity to some extent. The polymer polyvinylidene fluoride, $(-CH_2-CF_2-)_n$, exhibits piezoelectricity several times larger than quartz. Bone exhibits some piezoelectric properties (bone remodeling).

1.7 Piezoelectric Parameters and Relations.

The piezoelectric parameters that are of interest when considering the electromechanical effects in piezoelectric materials are the piezoelectric charge coefficients (d_{31}, d_{33}), the piezoelectric voltage coefficients (g_{31}, g_{33}) and the piezoelectric/electromechanical coupling factors (k_{31}, k_{33}, k_p and k_t).

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, e, are temperature dependent factors.

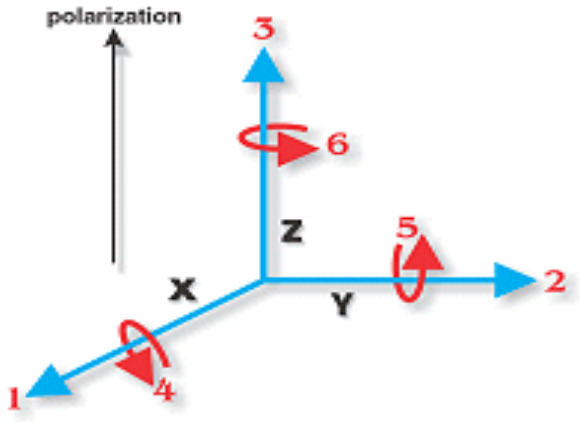


Figure 1.6 Direction of forces affecting piezoelectric forces

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 [7] 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}.

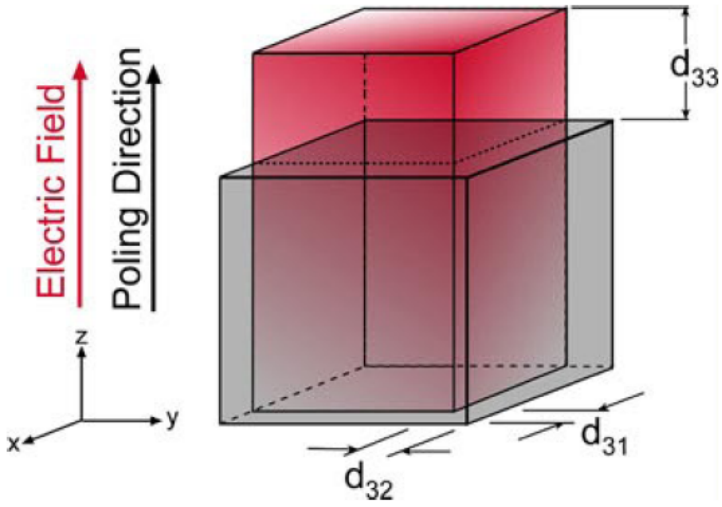


Figure 1.7 Measurement of Piezoelectric Charge Coefficient

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.

Hydrostatic Charge Coefficient (d_h)

It corresponds 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:

$$d_h = d_{33} + 2d_{31} \text{ (Measured in Coulomb/Newton (C/N) units)} \ldots\ldots.(1.2)$$

Piezoelectric Voltage Constant (g)

It 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

$$g = d / (\varepsilon' \varepsilon_o) \ldots\ldots\ldots\ldots\ldots(1.3)$$

where g is called the piezoelectric voltage coefficient, ε' and ε_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.

Hydrostatic Voltage Coefficient (g_h)

It gives the field produced by a pressure. It is related to the g_{33} and g_{31} piezoelectric charge coefficients by the relation

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

Electromechanical Coupling Factor (k)

Most powerful measurement of the strength of the piezoelectric effect is the electromechanical coupling factor k, which reflects the efficiency of a 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 [24].

$$k^2 = \frac{\text{Mechanical energy converted into electrical energy}}{\text{Input Mechanical energy}}$$

or

$$k^2 = \frac{\text{Electrical energy converted into mechanical energy}}{\text{Input electrical energy}}$$

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 behavior. Due to large anisotropy, transverse modes get suppressed resulting in the prevention of pickups due to transverse mode.

1.8 Dielectric Properties

Ferroelectrics materials are very often good dielectrics. For most applications of ferroelectric materials, the dielectric constant (ε') and dielectric loss (tanδ) are important practical parameters, studies of the dielectric properties provide a great deal of information about the suitability of the material for various applications.

Dielectric Constant (ε')

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

$$C = \varepsilon_0 A/t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.5)$$

Where ε_0 is the permittivity of free space and is equal to 8.854×10^{-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 ε', 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

$$C = \varepsilon' \varepsilon_0 A/t \quad \ldots\ldots\ldots\ldots\ldots \quad (1.6)$$

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

$$\varepsilon_r = \varepsilon' - i\varepsilon'' \text{ …….. (1.7)}$$

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

Dielectric Dissipation Factor

The dielectric dissipation factor (dielectric loss factor), tan δ, for a ceramic material is the tangent of the dielectric loss angle. tan δ is determined by the ratio of effective conductance to effective susceptance in a parallel circuit, measured by using an impedance bridge. Values for tan δ typically are determined at 1 kHz.

Dielectric loss is related to non-instantaneous polarisation due to the inertia of charges and absorption of electrical [14] 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.

1.9 Structural Aspects of Lead Titanate [$PbTiO_3$, (PT)] Ceramics

New 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.

Lead titanate is a ferroelectric material with a high Curie temperature (490^oC) at which the phase transition from the cubic paraelectric phase (above Curie temperature) to [9] the tetragonal ferroelectric phase (below Curie temperature) occurs.

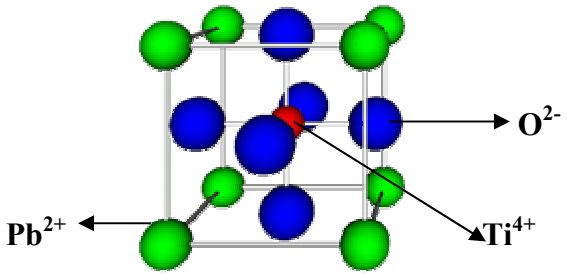


Figure 1.8 Perovskite Structure

Lead titanate is having perovskite-type structure. This oxide ceramic has the general chemical formula 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. 1.4 shows a cubic ABO_3 (e.g., A is Pb and B is Ti in $PbTiO_3$) perovskite-type unit cell.

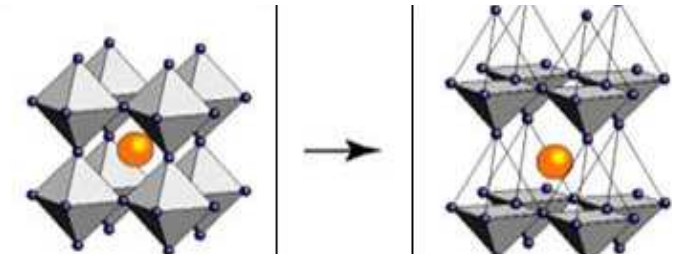


Figure 1.9 Perovskite structure Perovskite with cation displaced from the center

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

$$R_A + R_O = t\sqrt{2}\,(R_B + R_O) \quad \ldots\ldots\ldots\ldots\ldots \quad (1.8)$$

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. [10] 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 $0.9 < t < 1.1$.

1.10 Applications

Lead titanate is a well-known ferroelectric material with high Curie point and low dielectric constant, which make them attractive for high-temperature and high frequency transducer applications. A piezoelectric system can be constructed for virtually any application for which any other type of electromechanical transducer can be used. For any particular application, however, limiting factors include the size, weight, and cost of the system. Piezoceramic devices fit into four general categories: generators, sensors, actuators, and transducers.

- **Sensors**

  A sensor converts a physical parameter, such as acceleration or pressure, into an electrical signal. In some sensors the physical [1] parameter acts directly on the piezoelectric element; in other devices an acoustical signal establishes vibrations in the element and the vibrations are, in turn, converted into an electrical signal. A piezo sensor attached to the body of an instrument is known as a contact microphone.

  Piezoelectric elements are also used in the generation of sonar waves. Piezoelectric microbalances are used as very sensitive chemical and biological sensors.

- **Acoustic wave sensors (SAW)**

  Acoustic wave sensors are extremely versatile devices that are just beginning to realize their commercial potential**.** Acoustic wave sensors are so named because their detection mechanism is a mechanical, or acoustic, wave. As the acoustic wave propagates through or on the surface of the material, any changes to the characteristics of the propagation path affect the velocity and/or amplitude of the wave.

Figure 1.10. Acoustic wave sensors

. Changes in velocity can be monitored by measuring the frequency or phase characteristics of the sensor and can then be correlated to the corresponding physical quantity being measured.

- **Actuators**

  A piezoelectric actuator converts an electrical signal into a precisely controlled physical displacement, to finely adjust precision machining tools, lenses, or mirrors. Piezoelectric actuators also are used to control [7] hydraulic valves, act as small-volume pumps or special-purpose motors, and in other applications. Piezoelectric motors are unaffected by energy efficiency losses that limit the miniaturization of electromagnetic motors, and have been constructed to sizes of less than 1 cm^3. A potentially important additional advantage to piezoelectric motors is the absence of electromagnetic noise.

  Alternatively, if physical displacement is prevented, an actuator will develop a useable force. As very high voltages correspond to only tiny changes in the width of the crystal, this width can be changed with better-than-micrometre precision, making piezo crystals the most important tool for positioning objects with extreme accuracy.

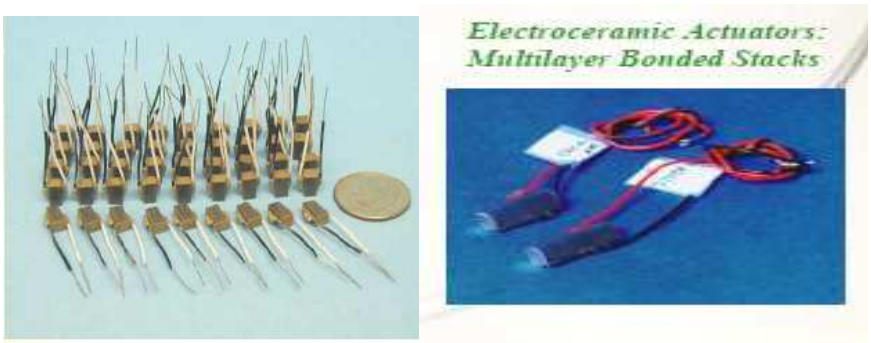


Figure 1.11 Electroceramics Actuators

- Loudspeaker: Voltages are converted to mechanical movement of a piezoelectric polymer film.

- Piezoelectric motor: piezoelectric elements apply a directional force to an axle, causing it to rotate. Due to the extremely small distances involved, the piezo motor is viewed as a high-precision replacement for the stepper motor.

- Piezoelectric elements can be used in laser mirror alignment, where their ability to move a large mass (the mirror mount) over microscopic distances is exploited to electronically align some laser mirrors. By precisely controlling the distance between mirrors, the laser electronics can accurately maintain optical conditions inside the laser cavity to optimize the beam output.

- A related application is the acousto-optic modulator, a device that vibrates a mirror to give the light reflected off it a Doppler shift. This is useful for fine-tuning a laser's frequency.

- Atomic force microscopes and scanning tunneling microscopes employ converse piezoelectricity to keep the sensing needle [9] close to the probe.

- **Transducers**

  Large anisotropy of lead titanate consequently allows transducer designs with simple flat plates of piezoelectric material as opposed to the hollow cylindrical or spherical geometries commonly used with PZT ceramics.

Figure 1.12 High-intensity ultrasonic transducers for cleaning applications

Piezoelectric transducers convert electrical energy into vibrational mechanical energy, often sound or ultrasound which is used to perform a task. Piezoelectric transducers that generate audible sounds afford significant advantages, relative to alternative electromagnetic devices they are compact, simple, and highly reliable, and minimal energy can produce a high level of sound. These characteristics are ideally matched to the needs of battery-powered equipment.

Piezoelectric effect is reversible; a transducer can both generate an ultrasound signal from electrical energy and convert incoming sound into an electrical signal. Some devices designed for measuring distances, flow rates, or fluid levels incorporate a single piezoelectric transducer in the signal sending and receiving roles, other designs incorporate two transducers and separate these roles.

Piezoelectric transducers also are used to generate ultrasonic vibrations for cleaning, atomizing liquids, drilling or milling ceramics or other difficult materials, welding plastics, medical diagnostics etc.

- Hydrophone

  Lead titanate is being used widely in hydrophone applications. A hydrophone is the element of a sonar system used to detect the ultrasound. The sensitivity of a hydrophone is determined by the hydrostatic voltage coefficient, g_h, which relates the voltage appearing across the transducer to the applied pressure. Another useful parameter is the

hydrostatic charge coefficient, d_h, which relates the charge develops to the applies stress. A useful figure of merit for hydrophone piezoceramics is reflected in the product $d_h x g_h$ since the maximum energy obtainable form a material is proportional to this product. For hydrophone applications, it is not sufficient to have a high d_{33} coefficient, and it is because of this that dense lead zirconate titanate (PZT) is far from ideal material for hydrophones. These materials may also have some uses in underwater projectors, but the applications would be much more specialized. In the last decades or so, several manufacturers in U.S. and Japan have developed conventional ceramics with superior sensitivity under quasi-hydrostatic stress.

- **Relaxors**

  In relaxor materials, the transition between piezoelectric behavior and loss of piezoelectric capability does not occur at a specific temperature (Curie point), but instead occurs over a temperature range (Curie range). In addition to relative insensitivity to temperature, single crystals of some relaxor formulations exhibit very high electromechanical coupling factors -- values greater than 0.9, versus values of 0.7-0.8 for conventional, lead-zirconate-titanate ceramics. This combination makes relaxors very attractive materials for actuator, transducer, [6] and other applications. Lead magnesium niobate, lead magnesium niobate / lanthanum formulations, and lead nickel niobate currently are among the most studied relaxor materials.

- **Nonvolatile memory devices**

  Ferroelectric lead titanate thin films, grown directly on a semiconductor such as Si, form a very promising combination for nonvolatile memory [2] devices as well as piezoelectric and pyroelectric sensor applications.

2. LITERATURE REVIEW

- **Quartz:**

  Properties

  1. Great physical and chemical stability
  2. Small coupling coefficient

  Applications:

  Oscillators and resonators

- **Rochelle salt ($NaKC_4H_4O_6*4H_2O$)**

  Properties

  1. Great piezoelectric effect
  2. Water soluble and had poor temperature characteristics

  Applications:

  Various transducers such as a phonograph pickups.

- **Barium Titanate**

  Discovered independently

  1. United States (Waigner and Salomon 1942)
  2. Soviet Union (Wul and Goldman, 1945)
  3. Japan (Miyake and Ueda, 1946).

  Structure

  Perovskite structure: ABO_3

  The absence of center symmetry in crystal structure gives spontaneous polarization.

  1. Cubic above Curie temperature; tetragonal as it cools down.
  2. The first material to be developed as a piezoceramics available in single crystal form.

  Applications:

  Detection of mechanical, actuators, acoustic and ultrasonic vibrations.

- **PZT (Lead titanate)**

  Discovered in 1955:

  1. Takagi, Shirane, Sawagachi, Japan.

  Properties High coupling coefficient, high Curie temperature

Pure $PbTiO_3$ ceramics [8] are generally too fragile and porous to be polarized. Attempts have been made to produce dense $PbTiO_3$ ceramics with good piezoelectric properties by adding additives or forming solid solutions. Improvement in various properties is achieved, by modifying the ceramics to an extent that they become very promising piezoelectric materials for high temperature and high frequency applications because of their high Curie temperature and low dielectric constant. Modified PT ceramics show usually large anisotropy in electromechanical factors and a large anisotropic piezoelectric coupling

Calcium modified PT ceramics (PCT), dielectric [9] and thermal expansion measurements as a function of temperature suggest that the phase transition in these ceramics is of diffusive character and their exist a local polarization which disappear at 460^oC much above the Curie temperature.

Advanced electroceramics have played a [10] critical role in the development of new and modern technologies such as computers, telecommunications and aerospace and they will continue to play the leading role in the technology of the future.

The materials cobalt-mangan oxides used as negative temperature coefficient thermistors, semiconducting doped barium titanate used for positive temperature coefficient thermistors with large applications in thermal protections and piezoelectric electroceramics of PZT type, which find new application as ceramic transducers and sensors in biomedical and aerospace industries or as simply buzzers, filters, igniters, ultrasonic cleaners, towed array sonars, medical imaging system.

Electromechanical [12] and piezoelectric properties of lanthanum modified ceramics prepared by conventional solid state reaction method with lanthanum variation from 2 to 20 mol% are reported. The samples poled in silicone oil at 150^0C under the application of 30 kV cm^{-1} electric field exhibit increase in electromechanical thickness coupling coefficient (k_t) and piezoelectric longitudinal coefficient (d_{33}) with increase in lanthanum

substitution. Decay of piezoelectricity above 15 mol% La^{3+} substitution level could be due to the onset of relaxor like properties at higher La^{3+} concentrations.

Effect of additives on $PbTiO_3$, Tien and Carlson [11] has attempted several additives and dense polycrystalline specimens are achieved. A very high d_{33} value of 130 pC/N has been reported for specimens containing one mole percent CaF_2 which had a dielectric constant of 160 at room temperature.

Yashihiro Matsuo et al. [13] on 0.1 to 2 mol% MnO_2 doped ceramics, the temperature range suitable for sintering is found to become broader with increasing MnO_2. The grain has been reported to increase with increasing sintering temperature. It has also been found that the addition of 2 mol% MnO_2 results in high mechanical strength, high electrical resistivity of the order of 10^{13} ohm-cm, small dielectric constant of 250, dissipation factor of 0.75 and a small planar coupling coefficient of around 4%.

Lanthanum modified ceramics [14] extensive piezoelectric and electromechanical studies provide a k_t value of 0.51 and k_p value of 0.077 indicating a large electromechanical anisotropy in the ceramic system.

Hennings [15] and Rosenstein [16] investigated the range of existence of perovskite phases in the system $PbO\text{-}TiO_2\text{-}La_2O_3$ by means of X-ray diffraction, chemical analysis and microscopic analysis. Depending on the partial pressure, conversion of A-site vacancies into B-site vacancies by taking up PbO from vapour phase has been suggested. Strong evidence in favour of lanthanum incorporation at A-site is reported.

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The ferroelectric properties of lead titanate ceramics modified by (La = Mn) have been investigated by Carl [17] under quasi-static driving fields. Information about the reorientation processes was obtained from lateral switching strain and hysteresis loop measurements with low-frequency fields. It was shown that microcracking is the cause of the degradation effects found in hysteresis loop of PLMT (lead lanthanum manganese titanate) specimens during 10 - 50 Hz excitation.

New piezoelectric ceramics with zero temperature coefficients of surface wave delay time were developed by Ito et al. [18]. These lanthanum, niobium, manganese and indium modified ceramics have a temperature coefficient less than $1x10^{-6}/^{o}C$. The electromechanical coupling factor of 0.1, mechanical quality factor of 1400 and a dielectric constant of 225 was reported [19] have suggested these ceramics to be potential materials for high frequency surface acoustic wave (SAW) devices.

Yamamoto et al. reported the investigated dielectric and electromechanical properties of complete tetragonal range of lanthanum modified PT ceramics [20]. These hot pressed, single dopant ceramics exhibits a decrease in tetragonality, Curie point, remnant polarization and coercive field while the planar and thickness mode electromechanical factors exhibits a maximum of 15 mol% La composition, the reported values being 0.49 and 0.29, respectively.

R. Ticoo explains series of doped lead calcium titanate based ceramic compositions has been synthesized using [21] a conventional attrition milling process. The influence of dopants and the powder processing conditions on the density, microstructure, dielectric and piezoelectric properties. The most favorable piezoelectric properties, having a thickness coupling coefficient of 0.47, a planar coupling coefficient 0.040 and a $d_{33} > 60$. These characteristics make them promising candidates for use as transducer elements for non-destructive testing of materials and similar device applications

Another research group attracted to investigate the calcium modified PT ceramics (PCT) further. In their first work, [22] on PCT ceramics, dielectric and thermal expansion measurements as a function of temperature suggest that the phase transition in these ceramics is of diffusive character and their exist a local polarization which disappear at $460^{o}C$ much above the Curie temperature.

Large electromechanical anisotropy was observed in lead titanate ceramics modified by 24 mol% calcium with cobalt and tungsten and by 8 mol% rare earth elements with

manganese, prepared by Duran et al. [23, 24]. The hydrostatic figure of merit for hydrophone applications was ~ 2200 in case of calcium modified lead titanate.

Disruption of sintered ceramics [25] is strongly influenced by their grain size. For grain size > 10 μm, a complete disruption of the fired compacts has been observed, while with grain size of 3 μm, mechanically string ceramics were obtained. This was attributed to intergranular cracking or grain separation due to grain boundary stresses setup by incompatible expansion of the individual grains owing to different coefficients of thermal expansion in different crystallographic directions..

In a report by King et al. [26], the strain induced ferroelectric domain structure was found to be absent in $(Pb_{1-x}Ca_x)TiO_3$ when $x \geq 0.39$ because the c/a ratio approaches unity. A simple model was presented to predict the conditions under which the ferroelectric strain-induced domain structure is absent.

Piezoelectric and dielectric properties of calcium and samarium modified PT ceramics for hydroacoustic applications were studied by Rittenmyer et al. [27]. The results showed that the piezoelectric sensitivity changes little with the addition of samarium after a certain concentration is reached, whereas the dielectric constant can be substantially varied over the range of substitution that was investigated. In contrast the addition of calcium into lead titanate produces a minimum in the dielectric constant for 15% calcium substitution and causes the voltage sensitivity of the material to reach a maximum for the compositions with about 20% calcium.

Takahashi [28] did an extensive study on the large anisotropy in modified lead titanate ceramics and their applications. A large k_t (0.56) and small k_p (0.4) in calcium modified lead titanate provided a large anisotropy ratio of 12 for this composition. It was suggested that the vanishingly small value of k_p could be achieved if 90^o domain rotation exceeds 20% though it is not always observed and depends on grain size, measuring temperature and a special agreement of 180^o and 90^o domains. Using Ca substituted PT ceramics; an ultrasonic high-resolution NDT array probe for metal flaw detection was designed,

fabricated and analyzed. Further due to high hydrostatic figure of merit of 2067, this material was composed with $PbNb_2O_6$, which was considered to be the best material for hydrophones.

In a report by Frutos and Jimenez [29] on the spatial distribution of polarization in calcium modified lead titanate ceramics, it was confirmed that when crystalline anisotropy increases, the reorientation of 90^o domains predominantly takes place near the surface, d_{33} values arise mainly from 180^o domains polarization, but a contribution due to high internal stresses caused by poling electric fields have to be taken into account.

A method to increase the figure of merit of infrared detectors was proposed for calcium modified lead titanate ceramics with a composition of $Pb_{0.76}Ca_{0.24}[Ti_{0.96}(W_{0.5}Co_{0.5})_{0.04}]O_3$ by Mendiola et al. [31]. In their work, by subjecting the modified PCT ceramics to electric poling reversal upto 10 times, a controlled microcracking state was caused, with a considerable decrease of the dielectric permittivity and a moderate decrease of the pyroelectric coefficient. Therefore, an increase of the voltage response Vrms close to 50% was obtained.

A discussion on the concentration and temperature dependence of the lattice parameters of calcium modified lead titanate ceramics was given by Windsch et al. [32]. They showed that the temperature dependence of the lattice parameters for a sample with 24 mol% Ca reveals a second order transition near to tricritical behaviour. Different models were used to describe the pure ferroelectrics and substantially mixed ferroelectrics.

In their work of Jimenez et al. [33], extrinsic contributions to the low frequency piezoelectric properties of Ca/Sm modified lead titanate ceramics were discussed. They concluded that the behaviour of piezoelectric ceramics, with high piezoelectrical anisotropy and tetragonal distortion at very low frequencies, must be attributed to their microstructural states (grain and microcrack sizes) and to the space charge that comes into play during poling processes.

In a study by Ranjan et al. [34], the superlattice reflections observed for the first time in the room temperature powder neutron diffraction patterns of $(Pb_{0.5}Ca_{0.5})TiO_3$ were shown to arise due to an orthorhombic distortion resulting from tilted TiO_6 octahedra and off-center location of Pb^{2+}/Ca^{2+}.

Materials prepared as thin layers are nowadays of great interest for research laboratories and industries, due to their possible integration in novel multifunctional devices that have prospective use in [35] microelectronic technology. Ferroelectric thin films are of great interest because of their applications as ferroelectric nonvolatile memories and in other integrated technologies. A large number of the work related to ferroelectric thin films is based on modified lead titanate because of the possibility to tailor the material performance for specific applications. Recent developments in micro-mechanical systems have opened new potential applications of ferroelectric thin layers in actuators and infrared sensors [36].

Chu and Chen [37] were studied the effect of calcium on the piezoelectric and dielectric properties of samarium modified lead titanate ceramics by varying the amount of calcium from 11 mol% to 17 mol% in $(Pb_{0.88-x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ system. They observed that the coupling coefficient, k_t was 0.57 as Ca = 13-15 mol%, which can be used for high-temperature and high frequency applications.

Very recently Chen et al. [39] reported the comparison of the piezoelectric properties of microwave sintered PCT ceramics modified by cobalt and tungsten with conventionally sintered.

Doping effects of strontium [40] on the dielectric and piezoelectric properties of calcium additive samarium modified lead titanate ceramics prepared by conventional dry ceramic technique with composition, $(Pb_{0.73-x}Ca_{0.15}Sr_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O_3$; x = 0.05 - 0.1. The maximum value of k_t was observed to be 0.565 with k_p = 0.05 and TCF = 14.5 ppm/^oC for x = 0.06.

The effect of lanthanum substitution on the structural, dielectric and piezoelectric properties of lead calcium titanate (PCT) ceramics is studied by S. Singh et. al. Samples prepared by the conventional dry ceramic technique. [41]Dielectric properties were studied in detail as a function of frequency and temperature. The Curie temperature (TC) and tetragonality (c/a) was found to decrease with increase in lanthanum content. The Curie temperature was also confirmed from the thermal-expansion behaviour of the sintered samples. Piezoelectric coefficients (d_{33}, d_{31}, g_{33}, g_{31}, g_h, d_h, k_t and kp) measured at room temperature. Increase of degree of [44-48] diffusiveness (γ) suggests a microscopic heterogeneity in the samples. The highest value of k_t/kp occurs at La 0.06%, which we believe is the preferred La content ratio, and can be used for high-temperature and high frequency applications.

S. K. Pandey et all explain influence of Lamon piezoelectric properties of PZT sintered at different temperature. Density [42,] measured by Archimedes principle found to be decrease with sintering temperature. Piezoelectric properties (d_{33}) decreases with increasing Ts. Optimum grain size of ~1μm gives better piezoelectric properties.

- **Electroceramics Research in India**

Electroceramics research is driven by the technology development needs and the device applications in the fields of microelectronics, communications, automation, energy conservation, MEMS. Ferroelectric ceramics have been technically exploited because of their unique properties such as high dielectric permittivity, high piezoelectric & electromechanical coupling and discovery of electrical poling process. They show high optical transparency and electro-optic coefficients. High permittivity barium titanate based piezoelectric ceramics and their [43] polymer composites show unusual properties for a wide range of applications in sonars, ultrasonic cleaners, micro-accelerometers, hydrophones, surface acoustic wave filters, delay lines, and microactuators etc. A number of organizations in India viz. academic institutions, research laboratories and industries are involved in the preparation, characterization and device fabrication of the electroceramics materials. In the recent years, there has been considerable interest in combining desirable properties of PZT and different piezoelectric polymers to forms

electro active materials for advance sensors. The materials oriented research is becoming more and more interdisciplinary and nanotechnology methods offer new challenges for materials integration as well as modeling studies. In the future, the field of electroceramics materials will continue to grow and unfold new application domains

3. REVIEW OF MODIFIED LEAD TITANATE CERAMICS

3.1 Aim of the work.

Thesis work entails the following objectives: -

- Subject understanding
- Familiarity with material preparation techniques
- Proficiency in the working of various equipments
- To prepare modified lead calcium titanate ceramics (Bulk form) and to study effect of dopant (La and Ta) on lead calcium titanate ceramics

Study the effect of dopant on A site, La substitution at A site.

- $Pb_{0.76-x/2}La_xCa_{0.24}(Ti_{0.98}Mn_{0.02})_{1-x/2}O_3$, x = 0
- $Pb_{0.76-x/2}La_xCa_{0.24}(Ti_{0.98}Mn_{0.02})_{1-x/2}O_3$, x = 0.02

Study the effect of dopant on B site, Ta substitution at B site.

- $Pb_{0.76}Ca_{0.24}Mn_{0.02}Ti_{0.98-5x/4}Ta_xO_3$, x = 0
- $Pb_{0.76}Ca_{0.24}Mn_{0.02}Ti_{0.98-5x/4}Ta_xO_3$, x = 0.02

- To systematically characterize characterization of these ceramics for various;
  - Structural
  - Electrical
  - Piezoelectric properties.

- To understand the composition-property relationships in the modified lead calcium titanate ceramics.

Lead titanate, (PT) ceramic is a perovskite-type ferroelectric with many attractive properties, such as

1. High Curie temperature, 490^0C (A stable piezoelectric material for high temperature).
2. Large anisotropy in electromechanical coupling factor.

3.2 Problem with $PbTiO_3$ (Need Of Doping)

1. Large lattice anisotropy (c/a = 1.064)

On cooling through Curie temperature, it causes fragileness. **(Difficult to sinter)**

It is very difficult to produce pure and dense lead titanate ceramics because of its too fragile and porous nature due to its high vapour pressure and large tetragonal distortion (lattices anisotropy c/a = 1.064).

2. Low resistivities (107-108 ohm-cm). **(Difficult to pole)**

It is very difficult to pole these ceramics because of the large coercive field. Many attempts have been made to produce dense $PbTiO_3$ ceramics with good piezoelectric properties by adding additives or forming solid solutions.

Substitutions for A-site, lead (Pb^{2+}) that maintains the perovskite crystal structure responsible for strong ferroelectric behaviour:

Iso-valent additives are Ca^{2+}, Ba^{2+}, Cd^{2+}, Sr^{2+} etc.

Off-valent additives are La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Y^{3+} etc.

Substitutions for B-site, titanium (Ti^{4+}) that serves to compensate charge due to A-site substitution :

Ta^{5+}, Mn^{4+}, fe^{3+}, Sb^{5+}, Ni^{2+}, etc.

The effect of substitution is a complex matter but, with caution number of important generalization can be made regarding substitution in perovskite.

3.3 Effect of off-valent substitution.

Donor dopant, those of higher charge than that of the ion they replace, are compensated by cation vacancies. Acceptor dopant, those of lower charge than that of replaced ion ,are compensated by oxygen dopant. Each dopant type tends to suppress the vacancy type that other promotes.

Table 3.1 Common off-valent substituents.

A-site donars	La^{3+},Bi^{3+},Nd^{3+}
B-site donars	Nb^{5+},Ta^{5+}, Sb^{5+}
A-site acceptors	K^{+}, Rb^{+}
B-site acceptors	Co^{3+},Fe^{3+},Sc^{3+},Ga^{3+},Cr^{3+},,Mn^{2+},Mg^{2+},Cu^{2+}

The significant different between oxygen vacancies and cation vacancies in perovskite structure is the highest mobility of the former. Cation and cation vacancies tend to be separate by oxygen ions so that there is a considerable energy barrier to be overcome before the ion and its vacancy can be interchanged. Oxygen ions however form a continuous lattice structure so that oxygen vacancies have oxygen ion neighbors with they can easily exchange.

3.4 Lead Calcium Titanate (Pb, Ca)TiO_3 Materials.

Lead calcium titanate (PCT) materials have recently attracted much attention for their use in various applications based on their special characteristics.

1. Properties that can be modified on substitution ;
2. Large electromechanical anisotropy (k_t/k_p) which makes then attractive for high-frequency transducer (SAW) application and piezoelectric transducer.
3. Lattice anisotropy (c/a) is reduced, hard and dense samples can be obtained.
4. High dielectric constant (Єr).
5. Large remnant polarization (Pr) used for non-volatile ferroelectric random assess memories (NVFRAMs)
6. Lower in value of curie point (Tc)
7. Low power consumptions.

4. EXPERIMENTAL

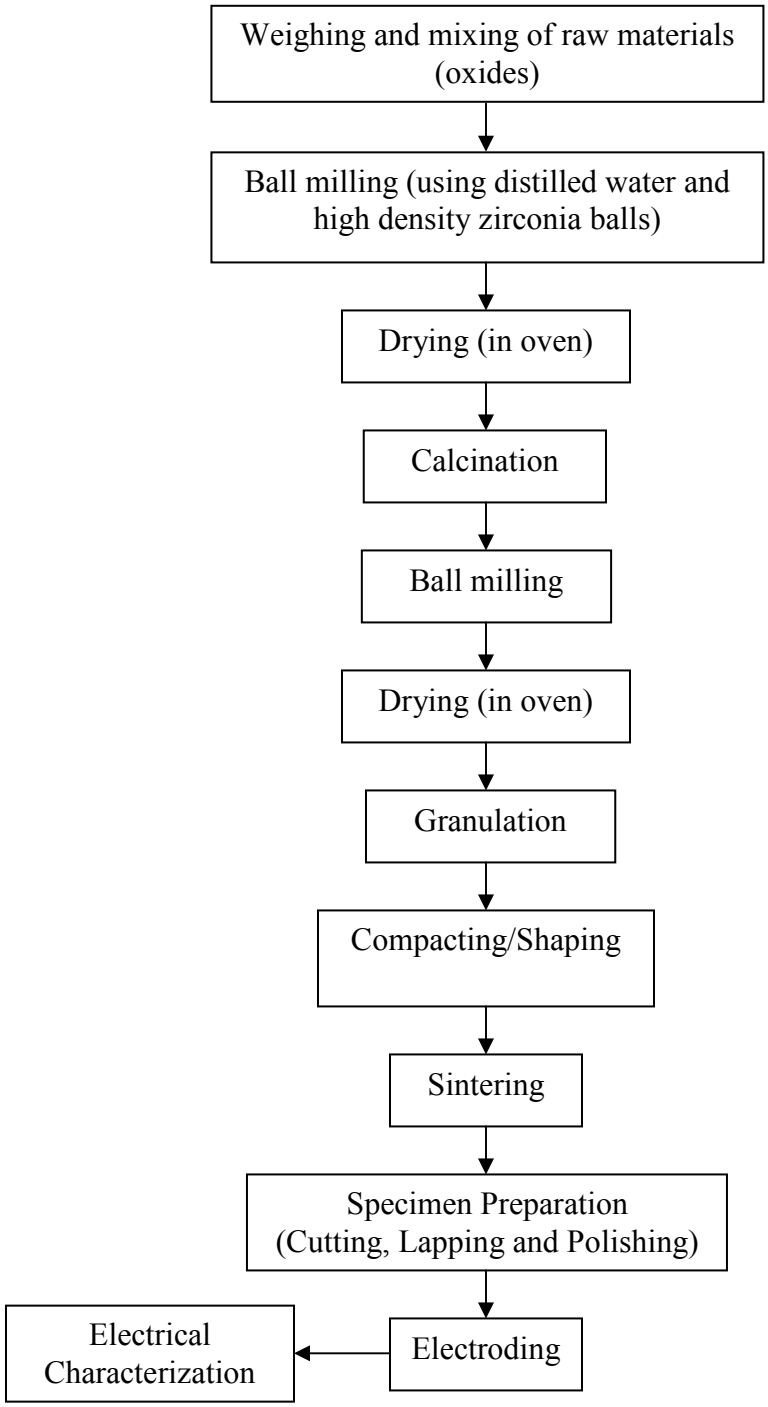
The details of synthesis techniques, various characterization equipments used and inherent parameters are explained here. The ceramic samples were prepared in bulk form via techniques namely conventional dry ceramic method

The properties of ferroelectric materials are strongly influenced by preparation methodology. There may be excellent compositional control of the material with improper processing, but the properties of the resulting ceramics are not necessarily good. Generally, in lead based materials, depending on the processing steps, there can be development of unwanted pyrochlore phase in the material. Therefore, it is important to understand the various process intricacies taking place during material synthesis. A study of calcination and sintering parameters is therefore essential. The properties that characterize a ferroelectric material for various applications include: phase and microstructure, dielectric constant and loss, ferroelectric and piezoelectric. Discussion on each one of the processes and the parameters is presented in following sections. A brief description about the synthesis and characterization parameters adopted for the material synthesis (bulk) and also for the study of various physical properties (structural, dielectric, ferroelectric and piezoelectric) of modified PCT ceramics are given in proceeding sections.

4.1 Conventional Dry Ceramic Method

A solid-state reaction is a direct reaction between starting reagents (usually powders) at high temperature. High temperature provides the necessary energy for the reaction to occur. Solid-state reaction is usually slow because during the reaction, a large amount of bonds break, and the ions migrate through a solid unlike gas phase and solution reactions. The limiting factor in solid state reaction is usually diffusion. So the rate-controlling step in a solid-state reaction is the diffusion of the cations through the product layer. Solid-state reaction occurs much more quickly with increasing temperature and reaction does not normally occur until the reaction-temperature reaches at least $2/3^{rd}$ of the melting point of one of the reactants.

Flow Chart Showing Conventional Dry Ceramic Method



Batch calculation

Batch of raw ceramic materials using powders PbO, $CaCO_3$, MnO_2, TiO_2, La_2O_3, Ta_2O_5 (>99% purity, Aldrich) are made by using batch calculations. These raw materials were weighed according to the given formula. Excess PbO (2 mol%) was taken to counteract the volatisation of lead during sintering.

Batch Description

All Batch 20 gm.

Study the effect of dopant on A site

1. $Pb_{0.76-x/2}La_xCa_{0.24}(Ti_{0.98}Mn_{0.02})_{1-x/2}O_3$, x = 0
2. $Pb_{0.76-x/2}La_xCa_{0.24}(Ti_{0.98}Mn_{0.02})_{1-x/2}O_3$, x = 0.02

Study the effect of dopant on B site

3. $Pb_{0.76}Ca_{0.24}Mn_{0.02}Ti_{0.98-5x/4}Ta_xO_3$, x = 0
4. $Pb_{0.76}Ca_{0.24}Mn_{0.02}Ti_{0.98-5x/4}Ta_xO_3$, x = 0.02

Ball Milling

In solid state reaction method, raw materials are weighed out according to the stoichiometry of the compound with due consideration for impurity and moisture contents. Raw materials are mechanically mixed and then grinding operations are performed to control the particle size and to make mixture homogeneous. For this purpose milling operation is performed which can reduce the particle size to 1-10 μm range. An attempt to reduce the size of the particles further may affect the homogeneity and purity of the material. Distilled water is usually used as wetting medium as it is available with adequate purity at low cost and is non-inflammable.

Experimental Profile:

1^{st} & 2^{nd} ball milling No. of balls 20, milling media water, time 4hrs.

3^{rd} ball milling No. of balls 20, milling media water, time 1hrs

This may be either dry or with a liquid medium. A typical liquid medium is the organic ethanol as it has a faster evaporation rate in comparison to distilled water. However, water may be used in preference as it has less environmental implications. The liquid type will depend on any reactions between water/matrix and how much powder it can disperse.

Calcination

Calcination is a chemical reaction process during which either the partial or complete phase of the compound is formed. It also helps in removing the unwanted gases and products during the decomposition of the constituent compounds. Calcination also helps in homogenizing the materials and reducing the shrinkage during the subsequent sintering process of the finally shaped samples.

Four physical processes are involved in the calcinations of the raw materials:

(i) Linear expansion of the particles ($< 400^0$C)
(ii) Solid phase reaction (400-750^0C)
(iii) Contraction of product (750-850^0C) and
(iv) Grain growth ($> 850^0$C).

Usually, the calcination temperature is chosen high enough to cause reaction, but low enough to facilitate subsequent grinding. In the materials, having volatile constituents, the calcination temperature must be kept low enough to avoid loss of the volatile parts.

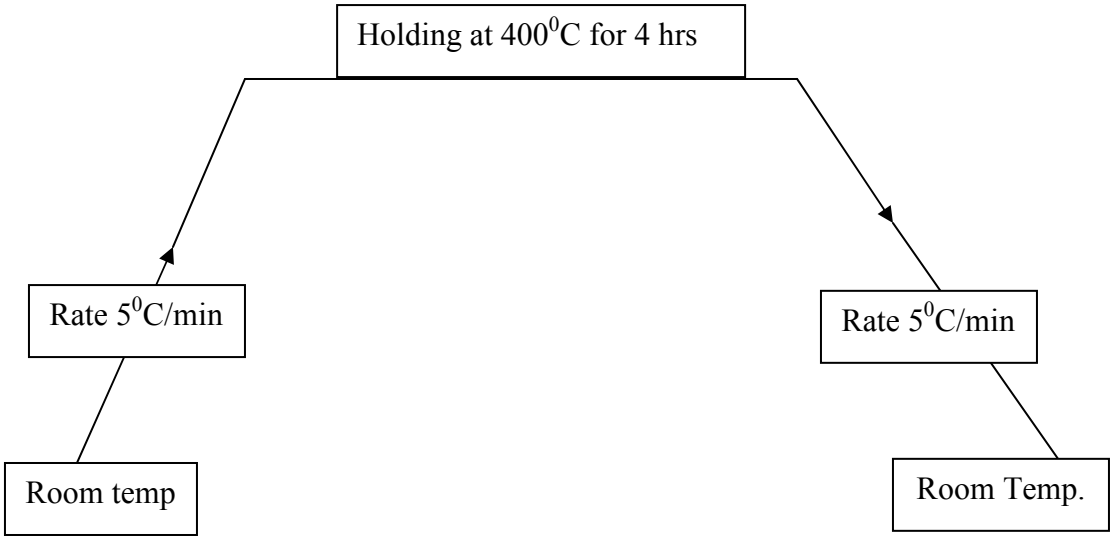


Figure 4.1 Calcination Profile

During calcination, control over stoichiometry is essential, and for it, volatile constituents have to be compensated. Calcination causes the constituents to interact by inter diffusion of their ions and resulting in a homogeneous body. Hence, it is considered that calcination is the part of the mixing process. Calcination also controls the shrinkage during sintering. After calcination powder is compacted to give desired shape, known as green body, and this green body is densified through sintering process. A general discussion on calcination and sintering is given in the coming sections. Also, in lead based ceramics, density of the materials greatly affects the materials properties. Density of the material depends on the technique used for shaping of the material, as some green body formation techniques do not require addition of binder, which is detrimental to the densification of the material. Hence, a general discussion on the shaping of the material is also presented.

Shaping

Calcined powders are ball-milled again to give suitable shaping to the powder. Generally, an organic binder is incorporated into the powder, for giving sufficient strength to green samples, so that handling between shaping and sintering may not be difficult. One of the

most important requirements of the binder is that it should be possible to remove the binder from the pressed shapes without any disruptive effect.

Isostatic Pressing

Isostatic pressing is used to form samples of larger size. Many of the difficulties encountered in dry pressing are overcome by using isostatic pressing. In this technique, the calcined powder is filled in a flexible mould and the mould is immersed in liquid filled in pressure chamber of the press. More and more liquid is pumped to apply pressure. Pressure of the range 200 MPa can be applied using this method. This method is based on the Pascal's Law. Any change in the hydrostatic pressure is distributed uniformly through out the liquid.

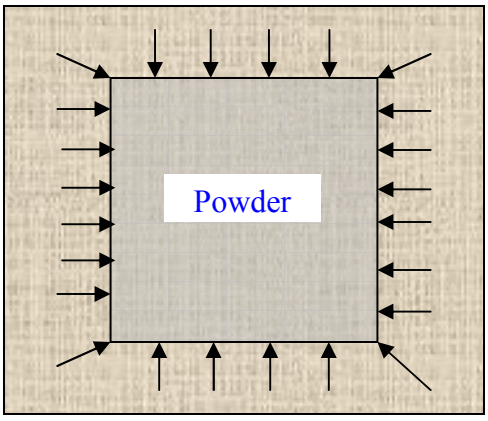


Figure 4.2 Principle of Isostatic Pressing

Therefore, calcined powder in the flexible container receives a uniform pressure from all directions .This results in higher and uniform density of the green body. The advantage of this method is that one can achieve high degree of reproducibility with intricate shapes and sizes, which are otherwise very difficult to obtain.

Sintering

Sintering is the process in which the green compacts are consolidated into strong and dense polycrystalline aggregates. During sintering at an appreciable temperature, the atomic motion is more violent and the area between grains in contact increases due to the thermal expansion of the grains and finally only one interface between two grains remains. This corresponds to a state with much lower surface energy. In this state, the atoms on the grain surfaces are affected by neighboring atoms in all directions, which results in densified ceramic.

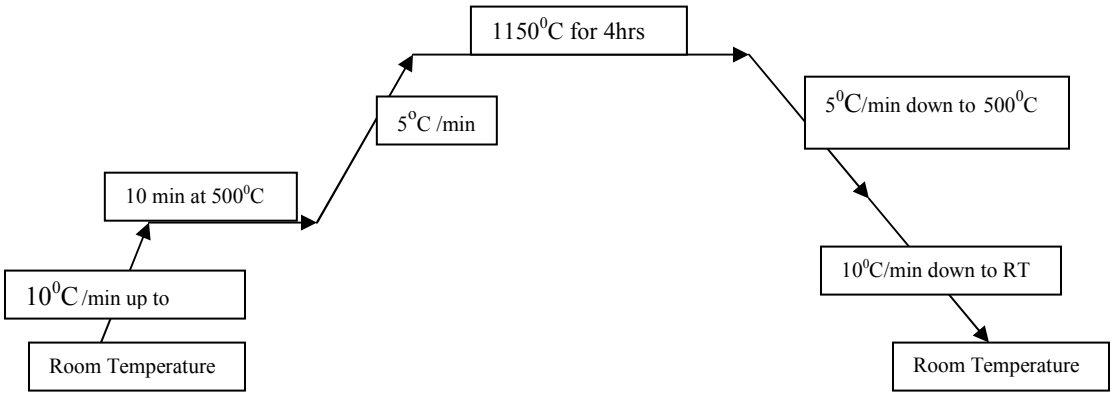


Figure 4.3 Sintering Profile

At the beginning of the sintering process, but rather at high temperature, the lattice distortion and internal strain are reduced by atomic diffusion and this is frequently called as 'the recovery process'. With the further increase in temperature, a recrystallization process takes place through atomic diffusion. During recrystallization, new crystal nuclei form and grow at grain boundaries and in other regions inside the grain with higher free energies. Meanwhile, some grains grow by swallowing up other smaller grains. In the recrystallization stage, grain growth is usually realized through the motion of grain boundaries. In general, higher the sintering temperature, larger the grains would grow, as the grain growth is caused by atomic diffusion, which increases with the increase in

sintering temperature. However, the density of a ceramic is affected by the sintering temperature and time in a more complex fashion. If the sintering temperature is too high or the sintering time is too long, the density of the lead based ceramics will be reduced owing to PbO evaporation at high temperatures. Since, the grain growth is caused by atomic diffusion; it follows that a higher sintering temperature and a larger hold time would result in larger grains.

4.2 Characterization Techniques and Studied Parameters

Structural Characterization

- **Density**

The bulk density (d_{ex}) was measured by the method based on the Archimedes principle and is given by:

$$d_{ex} = (W_a / W_a\text{-}W_w)\ g/cc \quad \ldots\ldots\ldots\ldots (4.1)$$

where d_{ex} is the density of the sample. Here, W_a and W_w are the weights of the material in air and in water, respectively.

Theoretical density (d_{th}) was computed from the lattice parameters using the relation,

$$d_{th} = (Z \cdot M)/(N \cdot V)\ g/cc \quad \ldots\ldots\ldots\ldots (4.2)$$

where Z is the number of molecules in a unit cell and is equal to 1 for the present system, M is the molecular weight, N is the Avogadro's number and V is the unit cell volume.

Relative density (d_{rel}) was computed using the relation,

$$d_{rel} = [(d_{th}\text{-}d_{ex})/d_{th}] \times 100\ (\%) \quad \ldots\ldots\ldots (4.3)$$

- **X-ray Diffraction (XRD)**

The X-ray diffraction technique is used for the structural/phase analysis of the material under investigation. The basic principle is that for a fixed wavelength (λ), the constructive interference occurs for a fixed set of an interplaner spacing (d) and incidence angle (θ). According to Bragg's condition of diffraction:

$$\lambda = 2d \sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

For cubic system, d is given by

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \ldots\ldots\ldots\ldots \quad (4.5)$$

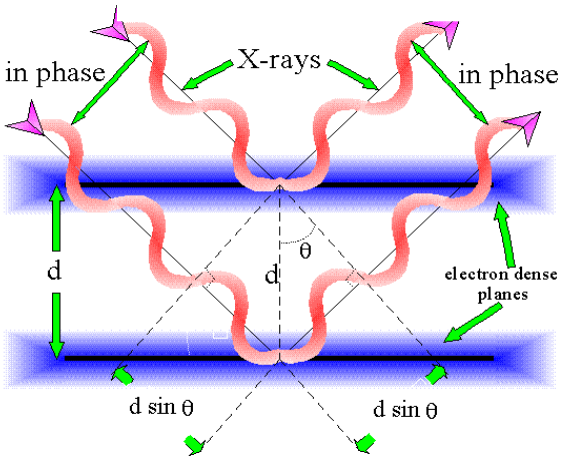


Figure 4.4 Principle X- ray diffraction of beam from assembly of lattice-atoms.

Generally, X-ray diffraction provides information about the:

(a) Long range order structure

(b) Phase composition

(c) Crystallinity, crystal size and shape

(d) Micro-stress and strain

(e) Texture (crystal orientation)

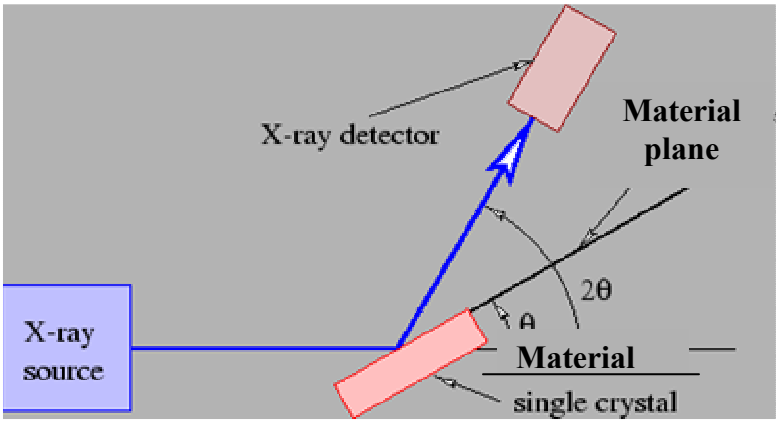


Figure 4.5 Schematic diagram of Bragg's diffraction

- **Scanning Electron Microscope (SEM)**

The scanning electron microscope was used to determine the average crystallite size and the surface morphology. It gives information about the grain evolution and grain size. It also gives the information about the inter-granular and the intra-granular pores and the distribution of grains in the bulk samples. SEM measurements are based on the principle of irradiating the specimen with a finely focused electron beam. The secondary electrons, backscattered electrons, auger electrons, characteristic x-rays and several other radiations are released from the specimen. Generally, the secondary electrons are collected to form the image in the SEM mode.

Electrical Characterization

- **Dielectric Properties**

Dielectric measurements (dielectric constant, loss, curie temperature) carried out using LCR meter model HP 4284A interfaced to a PC via IEEE 488, measurement jig and software. Signal of 1V rms was applied to the sample. Measurements of the samples were done as a function of frequency and temperature. Data were recorded at the interval of two degrees.

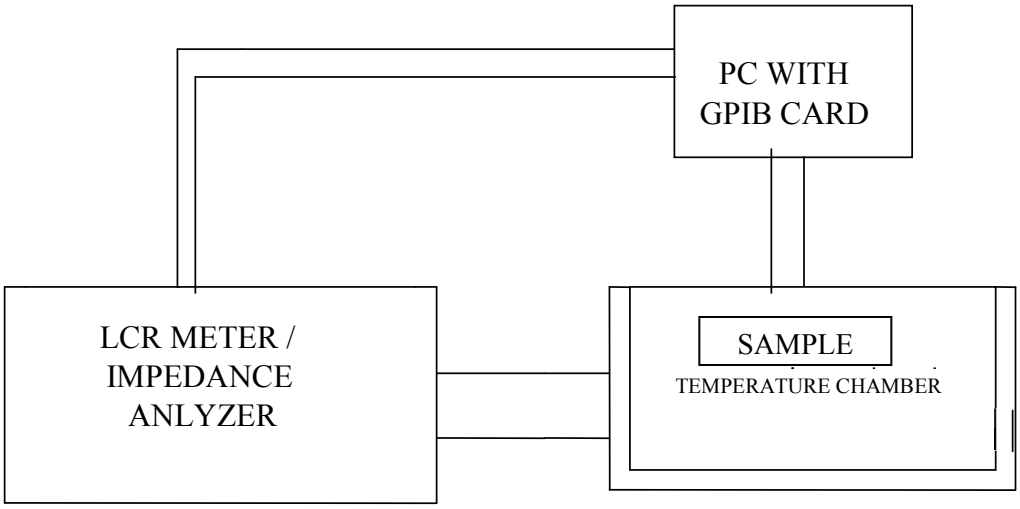


Figure 4.6 Dielectric measurement setup

- **Electrode Deposition**

Study the electrical properties of modified PCT ceramics, the electrical contacts were made by depositing gold electrodes on both bulk and thin films using Desk II TSC Cold Sputter/Etch Unit.

The sintered pellets were polished to a smooth finish and cleaned thoroughly using an ultrasonicator. The flat surfaces of pellets were coated with gold using sputtering, which gives the metal-insulator-metal structure to the pellets which are ready for electrical measurements.

- **Hysteresis Measurements**

Ferroelectric hysteresis (P-E) loops at room temperature recorded using an Automatic PE Loop Tracer of M/S AR Imagetronics. The system consists of a PC, Software, programmable voltage source (up to 5 kV) and Silicon oil bath. The measurement is based on modified Sawyer Tower circuit, operating at 50 Hz.

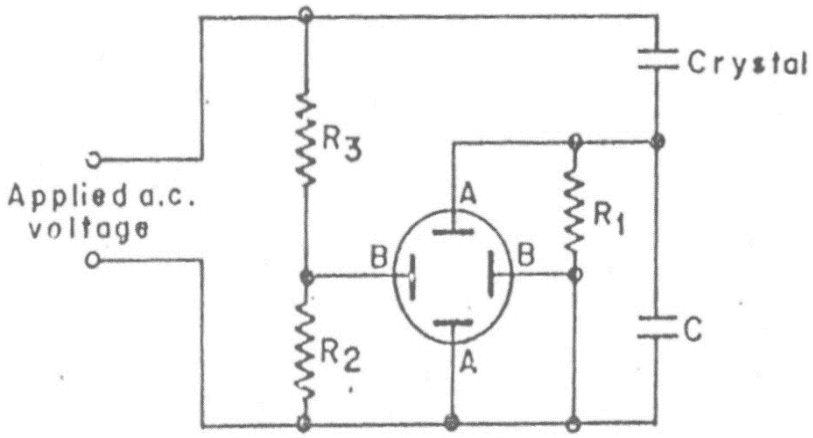


Figure 4.7 Sawyer - Tower circuit for P - E loop measurements of bulk samples

For measurement, specimen was kept in a spring-loaded jig and immersed in silicon oil. The loop is recorded by the system and the software computes all the parameters e.g. P_s, P_r and E_c. Software has the facility of cycling and averaging of the data points.

Piezoelectric Property Measurements.

- **Piezoelectric Constants (d_{33} and d_{31})**

Piezoelectric charge coefficients, d_{33} and d_{31} were been directly measured using a Piezometer System (Model PM 35, Take Control, U.K.)

- **Piezometer System**

The PM35 is a model in a range of instruments from Take control for measuring the properties of piezoelectric materials. By a simple, direct measurement, the PM35 gives an indication of d_{33} coefficient of all type of piezoelectric materials. The PM35 system consists of two units-force head and the PM35 system electronics unit. The later item provides the facility to store measurements. The block diagram shows the principle of operation of piezometer system

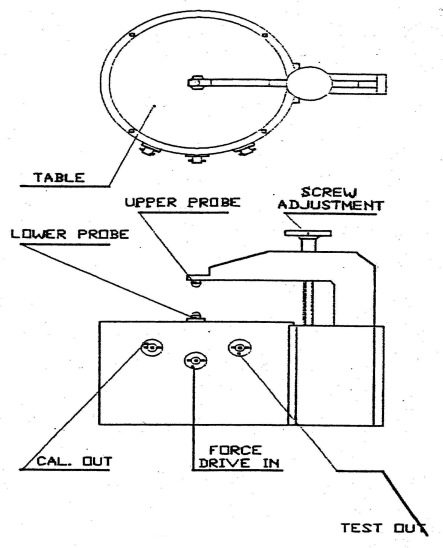


Figure 4.8 Block diagram of P35 Piezometer System

- **Planar (k_p) and Thickness (k_t) Coupling Coefficients**

Electromechanical coupling factors were determined by the resonance–antiresonance method using impedance-frequency data from an impedance analyzer (HP4294A) and piezoelectric resonance analysis program (PRAP) software.

5. RESULTS AND DISCUSSION

The properties of ferroelectric materials are strongly influenced by preparation methodology. There may be excellent compositional control of the material with improper processing, but the properties of the resulting ceramics are not necessarily good. Various methods of sample preparation and characterization techniques used for studying properties (like structural, dielectric, ferroelectric and piezoelectric) of modified PCT ceramics. It is important to understand the various process intricacies taking place during material synthesis. A study of calcinations and sintering parameters is therefore essential. The properties that characterize a ferroelectric material for various applications include: phase and microstructure, dielectric constant and loss, ferroelectric and piezoelectric.

5.1 Characterization Techniques

Various characterization techniques including the details of operating principles and various parameters for studying structural, electrical and piezoelectric properties. Piezo and ferroelectric behaviour of the ceramics is greatly influenced by their density after sintering, so one should first try to get the samples with higher green density so that good amount of percentage relative density achieved after sintering. Also sintering temperature and duration play a very important role in the development of microstructure and densification. Hence all the powders were first isostatically pressed into the rod form and then sintered at 1150^{o}C for 4 hrs to get sufficiently dense samples as at 1150^{o}C, maximum density (6.77 g/cc, ~ 95.1% relative density) of the pure PCT ceramics was achieved. Sintering temperature and duration were optimized after several experiments.

5.1.1 Density

The values of experimental density (measured by Archimedes Principle), theoretical (XRD) density and relative density of isostatically sintered rods are measured with respect to La and Ta addition as dopant. La doping increases the experimental density with the large continuous reduction in the theoretical density.

Table 5.1 Variation of experimental (d_{ex}, g/cc) and theoretical density (d_{th}, g/cc)

	La Doping		Ta Doping		
x	d_{ex}	d_{th}	x	d_{ex}	d_{th}
0	6.77	7.12	0	6.77	7.12
0.02	6.81	7.01	0.02	6.07	7.13

Theoretical density is decreasing with La doping on PCT lattice, this is due to the replacement of Pb with La (A-site substitution) because the atomic weight of lead is more than that of lanthanum so the molecular weight decreases as La is added.

La doping reduced tetragonality of the PCT crystal lattice, which leads to a reduction in internal stresses, thus allowing crystallites in grains to accommodate more closely to form a denser micro-structure.

Ta replaces Ti in the B-site making modified PCT ceramics less dense. Thus it can be concluded that the La doping increase densification of PCT ceramics whereas Ta doping reduces its density. The relative density $d_{rel,\ x=0}$ = 95.09% also computed from equation (4.3) and we noted that $d_{rel\ La}$= 97.15% & $d_{rel\ Ta}$=85.14%

5.1.2 X-ray Diffraction (XRD) Study

Studies study for lanthanum and tantalum substitution was carried out by XRD (Philips, PW3020 Diffractometer, Holland). A single-phase with tetragonal structure has been observed. The phase analysis is carried out by comparing the patterns with standard JCPDS file (6-0452) for $PbTiO_3$. The analysis showed all the samples to be single-phase with tetragonal structure.

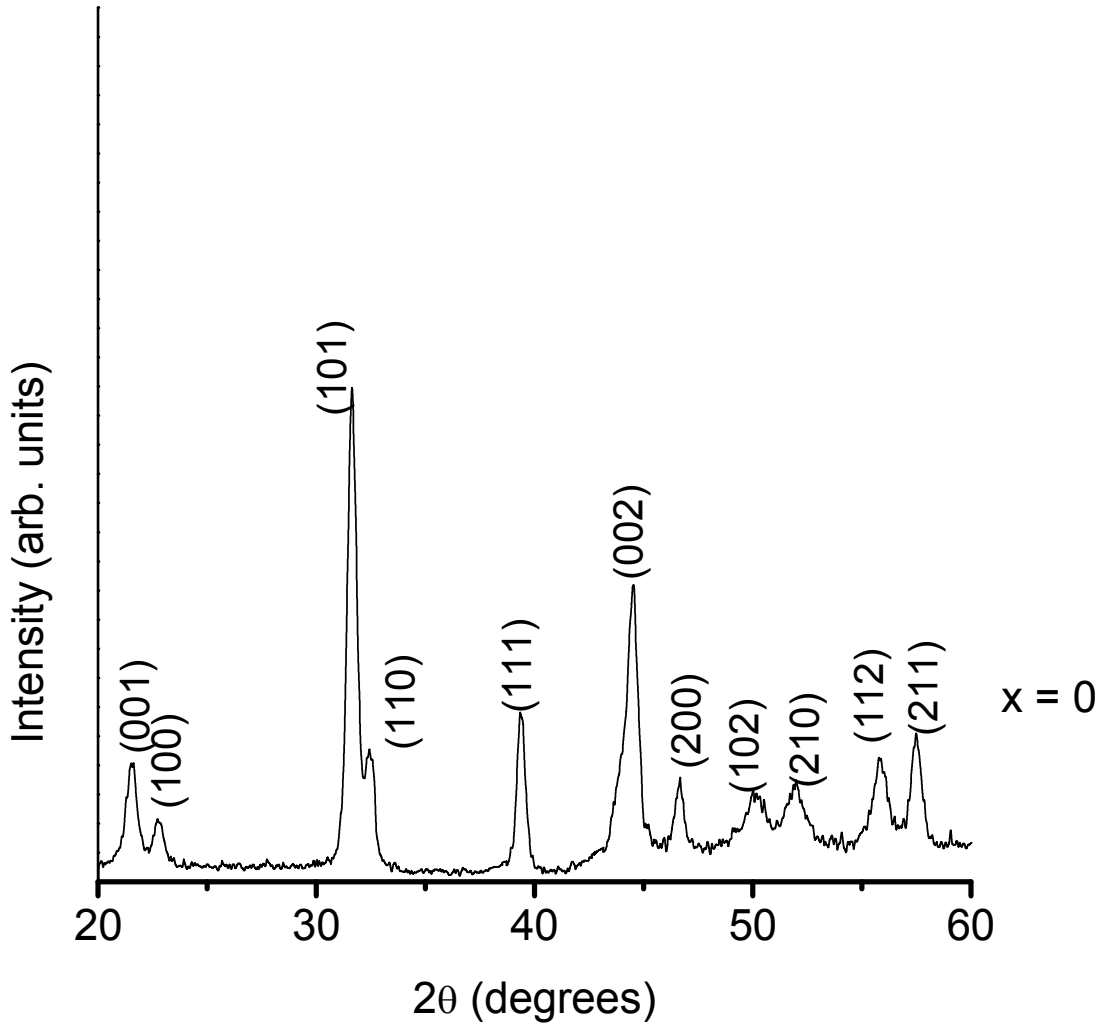


Figure 5.1 XRD Pattern for La doped (X=0) PCT ceramics.

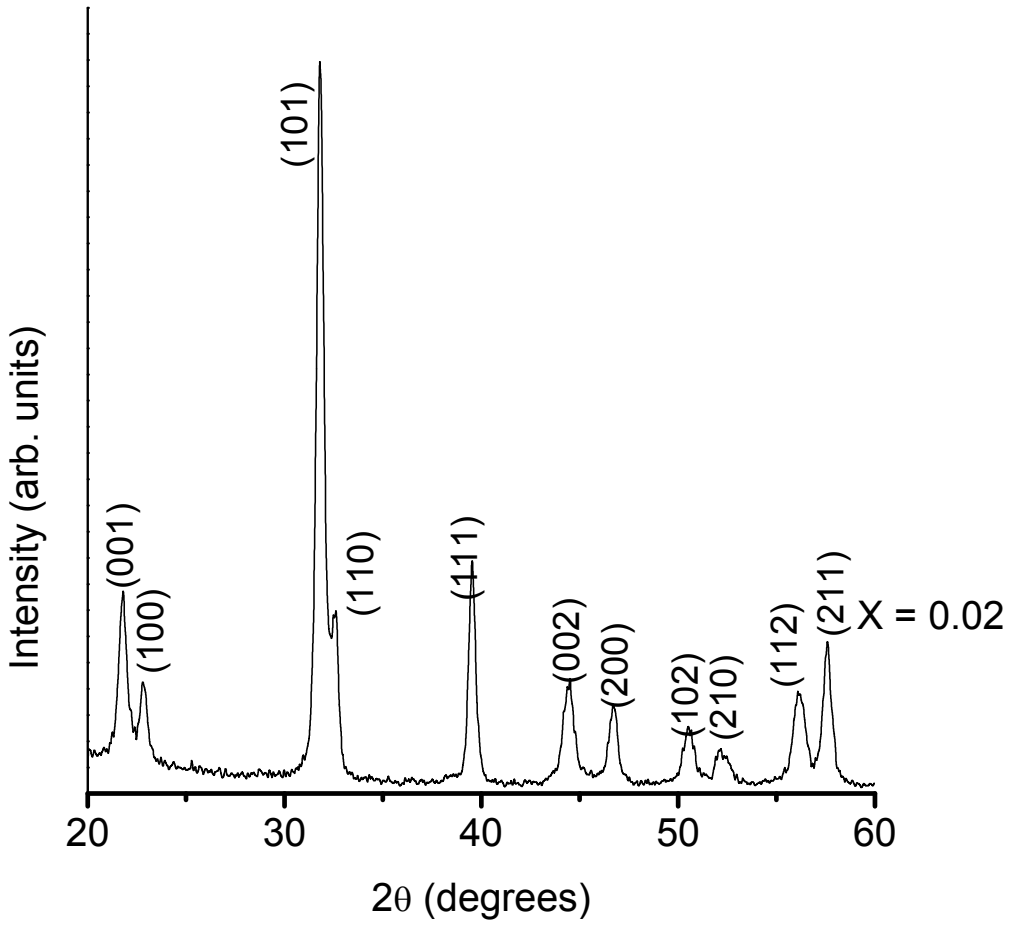


Figure 5.2 XRD pattern La doped (X=0.02) PCT ceramics

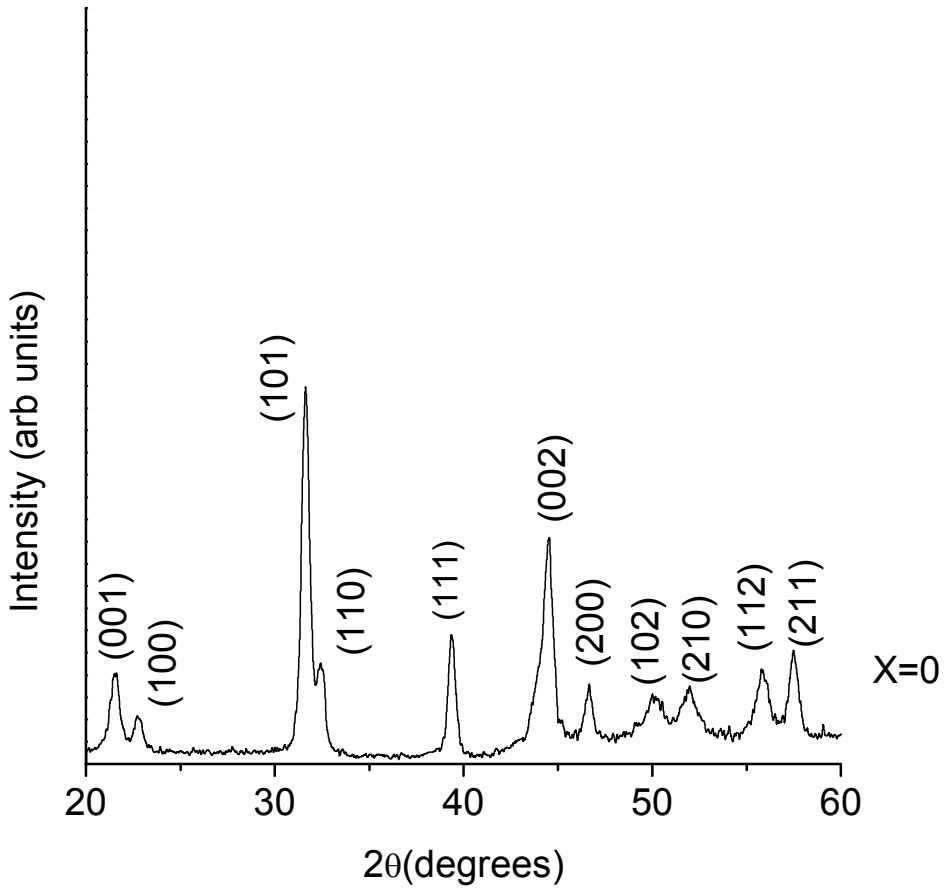


Figure 5.3 XRD pattern Ta doped (X=0) PCT ceramics

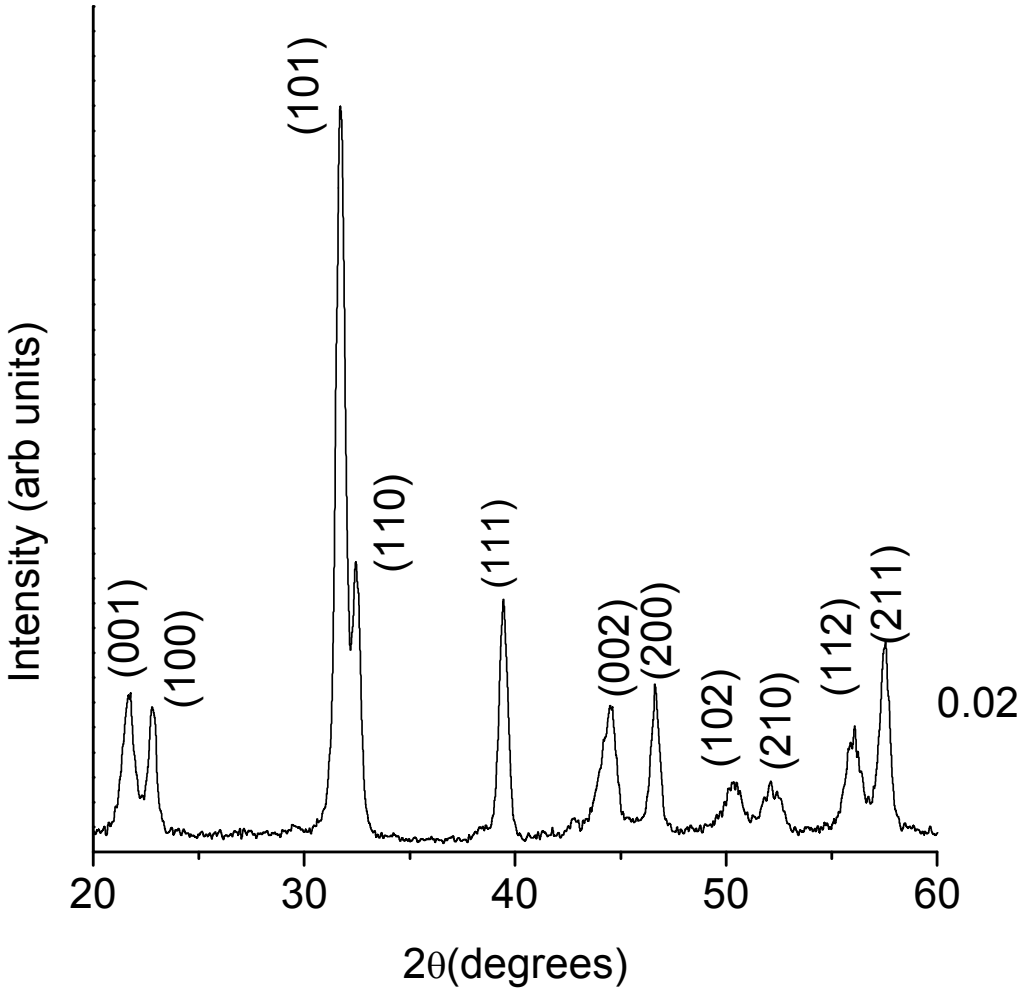


Figure 5.4 XRD pattern Ta doped (X=0.02) PCT ceramics

5.1.3 Microstructural Study

Microstructural parameters i.e. average crystallite size and the surface morphology concluded by scanning electron (SEM JSM840) microscope. Various microstructural aspects grain types, grain size and their distributions. SEM measurements are based on the principle of irradiating the specimen with a finely focused electron beam. The secondary electrons are collected to form the image in the SEM mode.

The microstructures of the freshly fractured sintered samples of all the compositions are shown as follows.

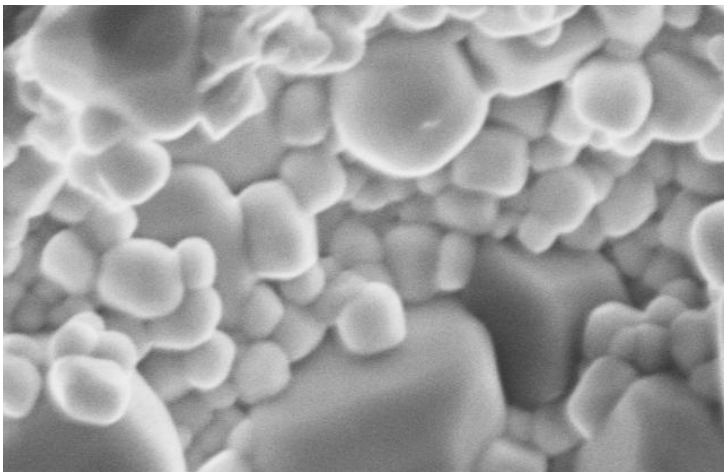


Figure 5.5 SEM micrograph La doped PCT ceramics for X=0 at 8KX.

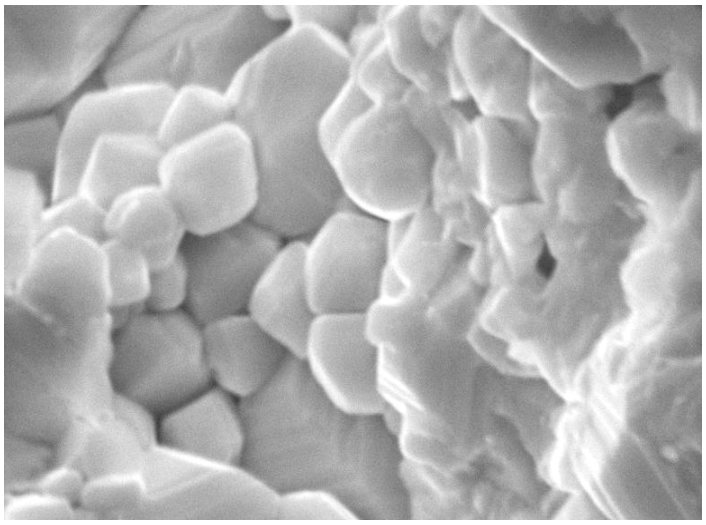


Figure 5.6 SEM micrograph La doped PCT ceramics for X=0.02 at 8KX.

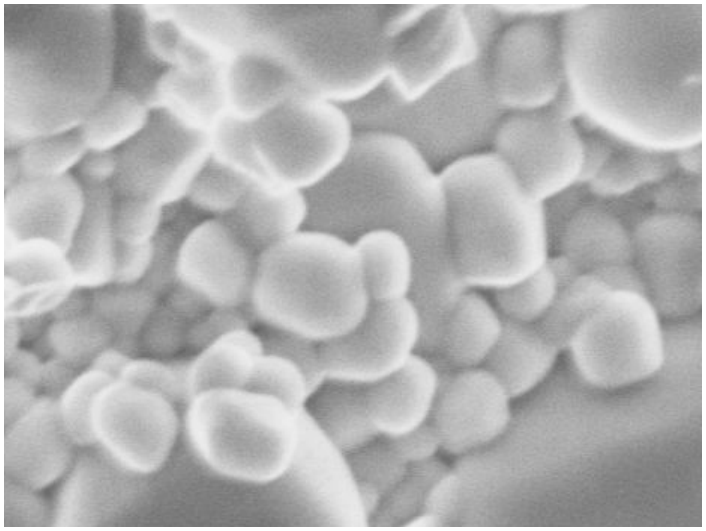


Figure 5.7 SEM micrograph Ta doped PCT ceramics for X=0 at 8KX.

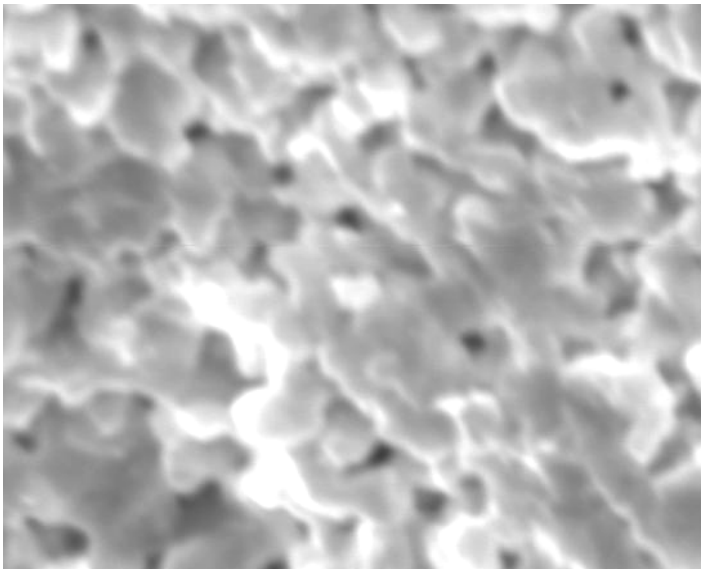


Figure 5.8 SEM micrograph Ta doped PCT ceramics for X=0.02 at 5.7KX.

With La doping increase in grain size arises due to the fact of dissolution of lanthanum in perovskite lattice. Micrographic analysis for Ta doping shows that porosity increase with increase in the amount of tantalum, which is in good agreement with density results where we found a decrease in density with tantalum substitution.

5.1.4 Piezoelectric Properties

Piezoelectric properties, piezoelectric charge coefficients (d_{33}, d_{31}), voltage coefficients (g_{33}, g_{31}), piezoelectric anisotropy (d_{33}/d_{31}, g_{33}/g_{31}), thickness electromechanical coupling coefficient (k_t), planar electromechanical coupling coefficient (k_p) and electromechanical anisotropy (k_t/k_p) tabled for La and Ta dopants. The effect of various substituted elements on the behaviour of these properties is explained.

Both d_{33} and $-d_{31}$ increases with La substitution in modified PCT series whereas decreases for Ta substituted on PCT. The increase in d_{33} value may be due to the reorientation of domains, which is facilitated by decrease in crystal tetragonality. In case of Ta

substitution, the decreasing trend of d_{33} may be due to the dominating effect of relative density of the modified PCT samples on the small decrease in crystal tetragonality.

Voltage Coefficients g_{33} and $-g_{31}$ effectively decreases with the substitution of La and Ta, which may be due to large increase in dielectric constant (relative permittivity) at room temperature. A high value of piezo-figure of merit, $d_h.g_h$ is observed for both the modified PCT samples.

Table 5.2 Piezoelectric coefficients for La doping

X	d_{33} (pC/N)	$-d_{31}$ (pC/N)	$-d_{33}/d_{31}$	g_{33} ($x10^{-3}$ Vm/N)	$-g_{31}$ ($x10^{-3}$ Vm/N)	$-g_{33}/g_{31}$	d_h (pC/N)	g_h ($x10^{-3}$ Vm/N)	FOM= $d_h.g_h$ ($10^{-12}m^2N^{-1}$)
0	43.00	2.00	21.50	35.95	1.67	21.52	39.00	32.64	1272.96
0.02	48.00	2.20	21.81	33.47	1.53	21.87	43.60	30.42	1326.31

Table 5.3 Piezo coefficients for Ta doping

X	d_{33} (pC/N)	$-d_{31}$ (pC/N)	$-d_{33}/d_{31}$	g_{33} ($x10^{-3}$ Vm/N)	$-g_{31}$ ($x10^{-3}$ Vm/N)	$-g_{33}/g_{31}$	d_h (pC/N)	g_h ($x10^{-3}$ Vm/N)	FOM = $d_h.g_h$ ($10^{-12}m^2N^{-1}$)
0	43.00	2.00	21.50	35.95	1.67	21.52	39.00	32.64	1272.96
0.02	33.00	1.10	30.00	29.83	0.99	30.13	30.80	27.84	857.47

The high value of electromechanical anisotropy (k_t/k_p) is observed for various substituted on PCT ceramics, which is desirable for high frequency applications.

Table 5.4 Variation Electromechanical coefficients wit Dopants

	La Doping			Ta doping			
X	k_t	k_p	k_t/k_p	x	k_t	k_p	k_t/k_p
0	27	2.3	11.7	0	27	2.3	11.7
0.02	32	3	10.6	0.01	23	2.6	8.8

5.1.5 Ferroelectric Properties: Hysteresis Study

Hysteresis loop is an important characteristic of ferroelectrics i.e., the polarization, P, as the function of applied electric field, E. It can be observed by means of a Sawyer-Tower circuit. Polarization vs. electric field (P-E) loops was observed for La substitution but not for Ta substitution because of high porosity and low resistivity.

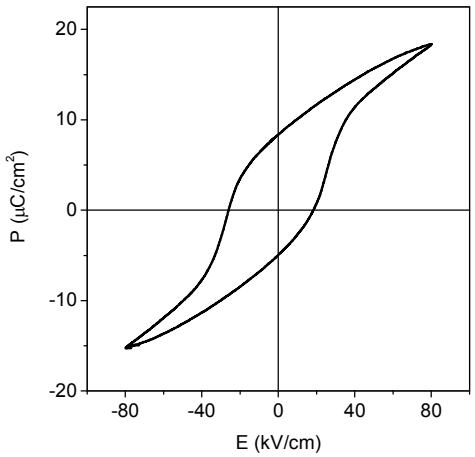


Figure 5.9 Hysteresis loop for lead calcium titanate, X=0

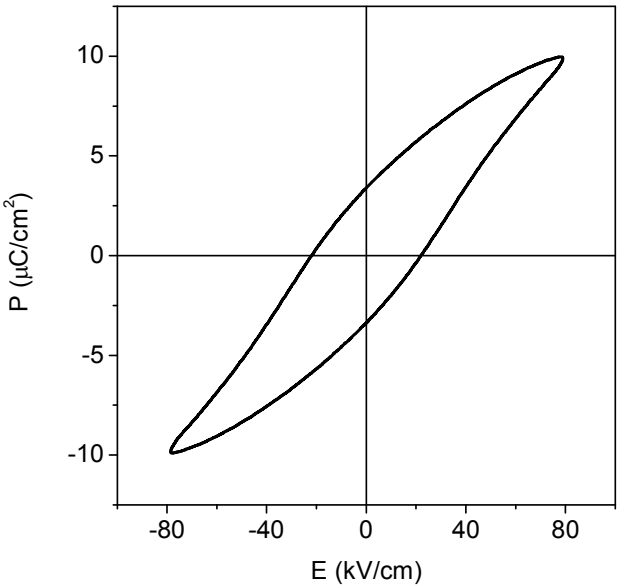


Figure 5.10 Hysteresis loop for La doped lead calcium titanate, X=0.02

5.1.6 Dielectric and Ferroelectric Properties

The dielectric constant (ε') and loss (tanδ), frequency (100 Hz - 1 MHz) is measured. The effect of substituents (La and Ta) on the dielectric behaviour and Curie temperature was studied. Ferroelectric properties include the study of polarization vs. electric field (P-E) hysteresis loops.

Table 5.5 Variation of ε' and tanδ at Frequency (10kHz)

	La Doping		**Ta Doping**	
X	DC (ε')	Loss (tanδ)	DC (ε')	Loss (tanδ)
0.0	135	0.01	135	0.01
0.02	162	0.02	125	0.07

Dielectric constant & loss (ε' and tanδ) shows decreasing trend with increase in frequency. The fall in dielectric constant arises from the fact that polarization does not

occur instantaneously with the application of the electric field because of inertia. The delay in response towards the impressed alternating electric field leads to loss and decline in dielectric constant. At low frequencies, all types of polarization contribute. As frequency is increased, those with large relaxation times cease to respond and hence the decrease in dielectric constant. At lower frequencies, the contribution from the space charge polarization is maximum, which reduces slowly with the increase of frequency. The space charge arises from the charge accumulation at grain boundaries and at the electrode interface, mainly due to vacancies of lead and oxygen. With the increase of frequency, these dipoles due to space charge do not respond at higher frequencies resulting in decrease in the dielectric constant.

In contrast to increase of dielectric constant, the loss factor (tanδ) shows a decreasing trend with La in PCT ceramics, whereas it increases for Ta substitution. This trend of loss may be due to the decrease in porosity with the increase of the La substitution and an opposite trend in case of Ta substitution.

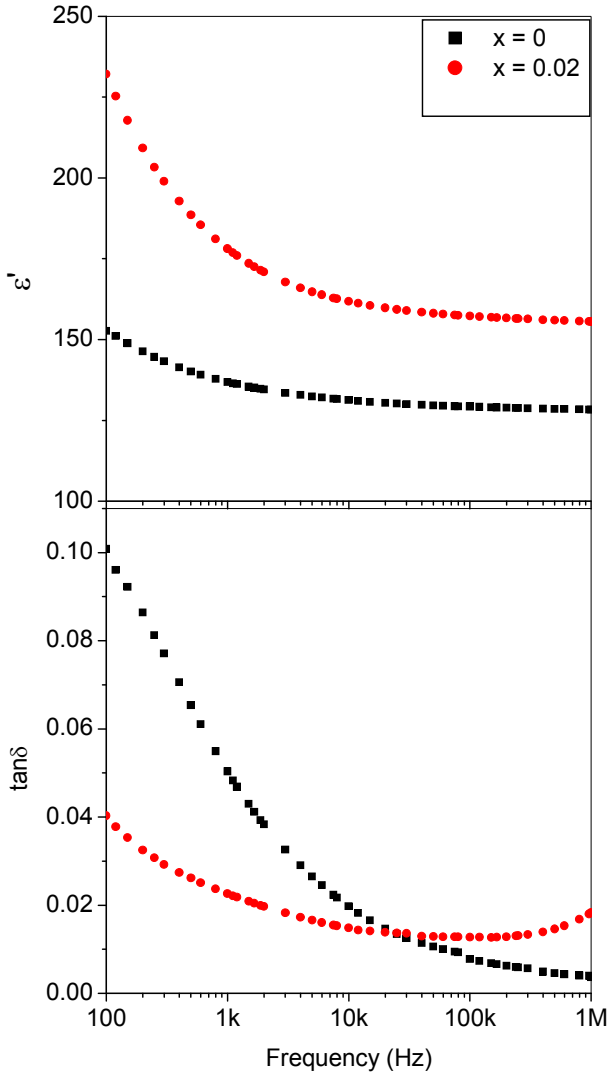


Figure 5.11 Frequency dependence of (ε') dielectric constant & dielectric loss (tanδ) for La X= 0, 0.02

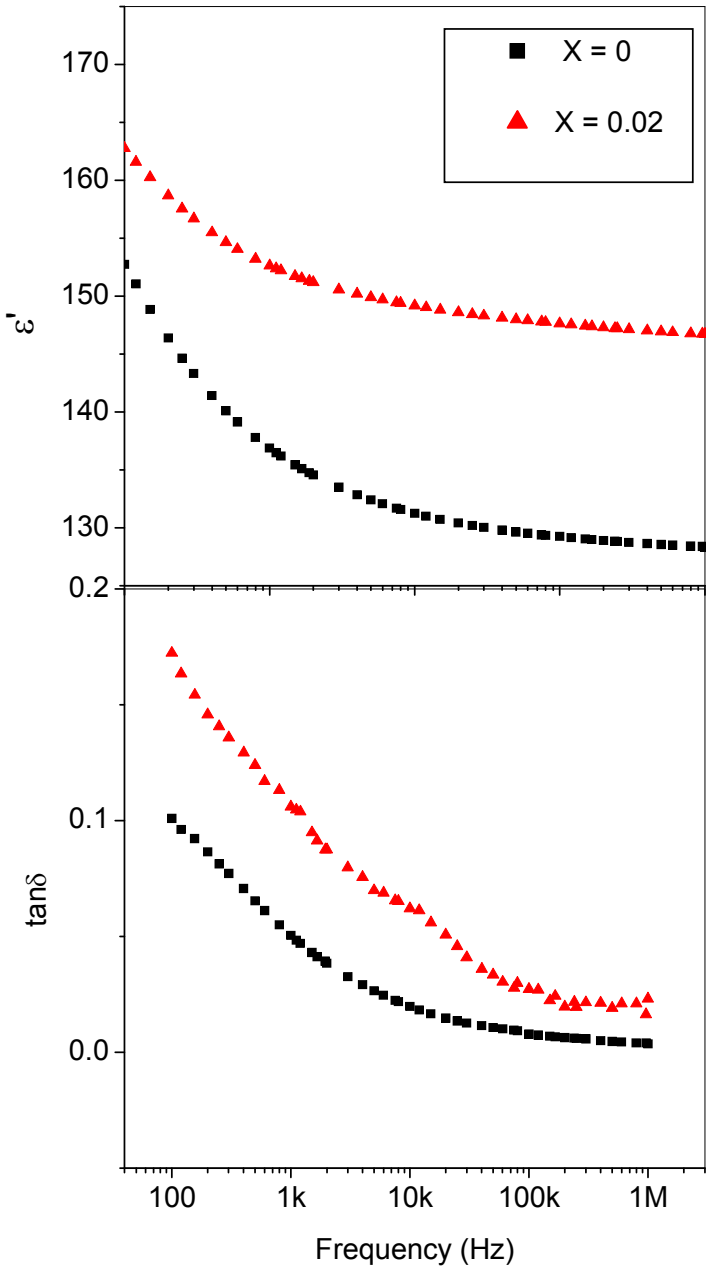


Figure 5.12 Frequency dependence of (ε) dielectric constant & dielectric loss (tanδ) for Ta, X= 0, 0.02

5.1.7 Temperature Variation of dielectric constant (ε') and loss (tanδ)

The temperature variation of dielectric constant and loss studied at 10 KHz. Dielectric constant increases with increment in the temperature due to interfacial polarization becoming more dominant as compared to the dipolar polarization and passes through a maximum (Curie temperature, T_c) and then decreases due to the phase transition from ferroelectric to the paraelectric phase. The decrease of tanδ at the phase transition is due to the reduction in the domain wall contribution to loss. The dispersive loss at high temperature is probably due to the localized ionic mobility. Curie transition temperature is found to decrease with La and Ta in PCT ceramics. This can be attributed to the decrease in crystal tetragonality caused by the La, Ta substitution that reduces internal stress and which in turn transition temperature. For Ta substitution curie temperature decreases.

Table 5.6 Variation of Curie temperature with amount of X

X	La doping (T_c^0C)	Ta doping (T_c^0C)
0.0	353	353
0.02	316	345

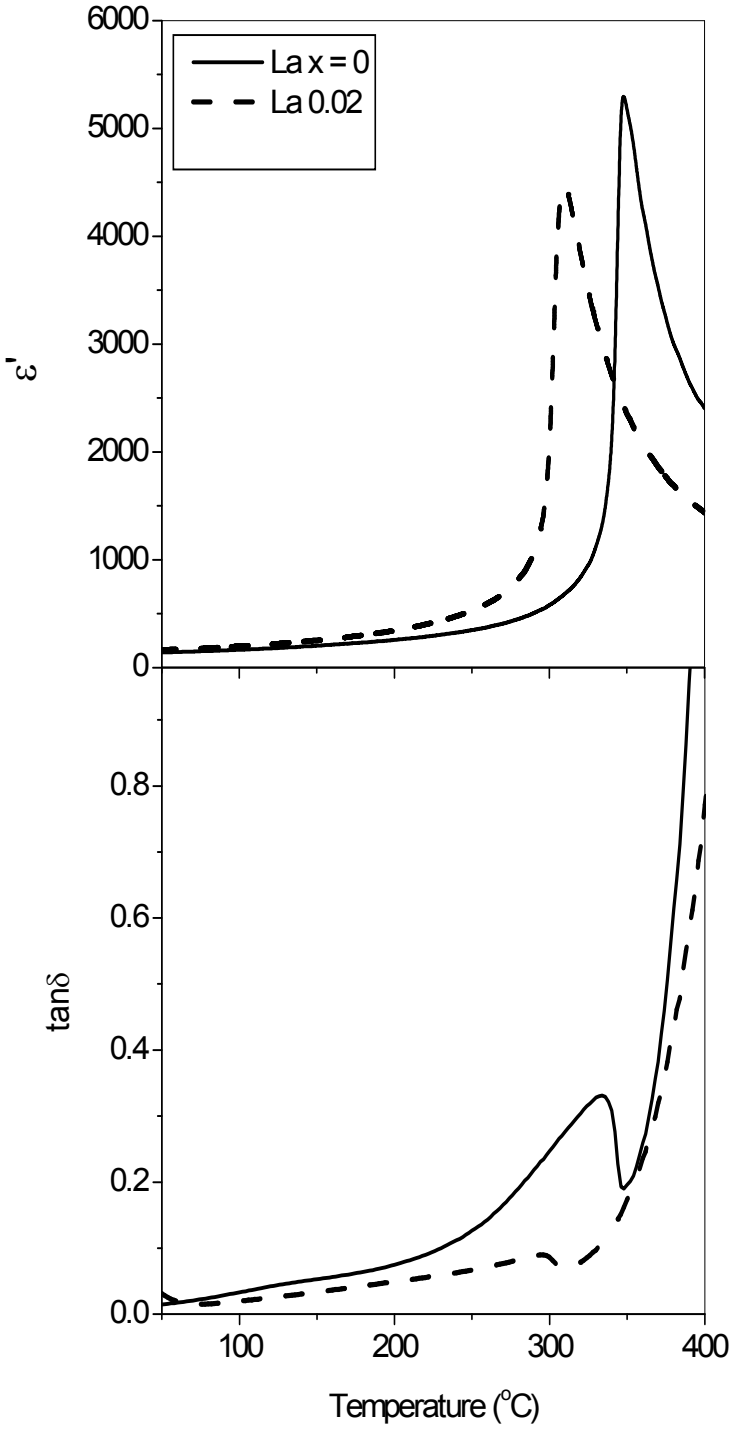


Figure 5.13 Temperature depends of dielectric constant (ε') and dielectric loss (tanδ) for La 0.02, at frequency 10 KHz

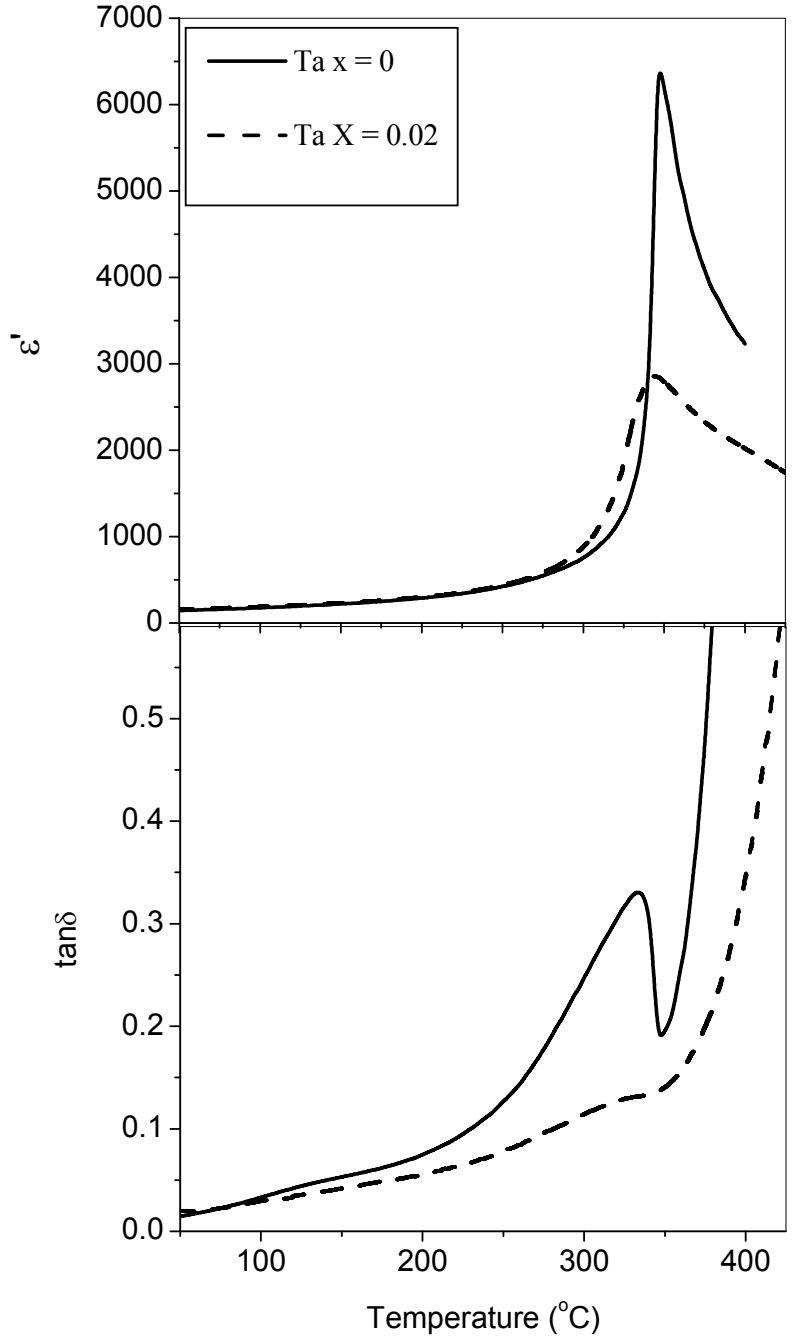


Figure 5.14 Temperature dependence of dielectric constant (ε') and dielectric loss (tanδ) for Ta 0.02 at frequency 10 KHz

6. CONCLUSION AND SCOPE OF FUTURE WORK

The present work was an attempt to understand the synthesis and characterization of PCT ceramics. Dopants on PCT Ceramics were used to enhance and modify its properties. La and Ta were added as dopants, we observed that the dopants do contribute to increase in dielectric properties especially with the La addition.

With the substitution of dopants like La and Ta on lead calcium titanate following structural, physical and electrical parameters obtained that makes them ideal as futuristic materials.

Modification in PCT ceramics via La^{3+} ions in A site and Ta^{5+} ions in B site is done. This substitution was undertaken with a view to know the suitability of the substituting elements for the enhancement of various structural, dielectric, ferroelectric and piezoelectric properties of PCT ceramics.

La doping increases the experimental density with the reduction in tetragonality of the PCT crystal lattice, which leads to the formation of denser micro-structure. Ta replaces Ti in the B-site making modified PCT ceramics less dense and porous. XRD studies confirm the single perovskite phase with tetragonal structure for La and Ta substitution in PCT ceramics.

Microstructural study reveals that almost uniform grain growth and grain compaction with well-defined grain boundaries is observed with the increase in substitution of La in PCT ceramics whereas for Ta substituted PCT series microstructure is indicative of porous material.

Dielectric constant increases gradually with increment in the temperature and passes through a maximum (Curie temperature, T_c) and then decreases due to the phase transition from ferroelectric to the paraelectric phase in La and Ta substituted PCT ceramics.

Polarization vs. electric field (P-E) loops that explains the ferroelectric behavior are obtained for La compositions not for the samples substituted with Ta because of their high porosity and low resistivity. Well-defined ferroelectric behaviour is observed.

The values of piezoelectric charge coefficients (d_{33}, d_{31}), piezoelectric voltage coefficients (g_{33}, g_{31}), hydrostatic coefficients (d_h, g_h), electromechanical coupling coefficients (k_p, k_t) are obtained for all the samples. Both d_{33} and $-d_{31}$ shows an increasing trend with increasing La substitution in modified PCT series whereas they show opposite trend for Ta substituted PCT series.

The work also exposed us to get familiarized with several instruments used in the present study.

Scopes of Future Work

The area of electroceramics has very interesting features with respect to the development and advancement of new materials for various device applications.

Lead titanate ($PbTiO_3$) ceramics exhibit many attractive properties. These attributes make them attractive for devices in many electronic applications in the form of bulk, thin film, composite and single crystal. These applications include surface acoustic wave (SAW) devices, actuators and piezoelectric transducer etc.

Recently much attention paid to use these materials for pyroelectric devices , ferroelectric memories (NVFRAMs), smart materials and pressure sensors and hydrophones due to their inherent properties like high speed, low power consumption, high dielectric constant.

Following steps for further extension of work can be done

- Novel techniques (microwave sintering, mechanochemical alloying) can be adopted for La and Ta modified PCT ceramics.
- For proper domain understanding, TEM study can be done. .
- X-ray diffraction can be studied at different temperatures.
- Dilatometric studies can be studied for analyzing thermal strain generated during heat treatments, thermal expansion, and anisotropies.
- Dependence of grain size and other properties particularly piezoelectric parameters on sintering temperature can be studied.
- Dielectric and piezoelectric characterization of thin films can be made for their integration in memory devices

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