

Synthesis and Characterizations of Ca, La and Zr Modified PbTiO₃ Ceramics

**A THESIS SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE IN PHYSICS**

by

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CERTIFICATE

This is to certify that the thesis entitled, “Synthesis and Characterizations of Ca, La and Zr Modified PbTiO_3 Ceramics” being submitted by Prativa Adhikari in partial fulfillments for the requirements for the award of Master of Science Degree in Physics Department at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

The work incorporated in this thesis has not been submitted elsewhere earlier, in part or in full, for the award of any other degree of this or any other institution or university.

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Abstract

The compositions of Ca, La and Zr doped PbTiO₃ sample were prepared by sol-gel technique. The phase formation and structural property of all compositions were studied by X-Ray diffraction (XRD) technique.

- The XRD pattern of PCT, PLT & PLZT ceramics indicated the formation of single perovskite phase at 650°C, 650°C & 950°C calcination temperatures, respectively.
- The surface morphology of the sintered pellets were studied by SEM, which showed dense and homogeneous packing of grains with grain size ~0.72 μm, 0.85 μm and ~1.12 μm, respectively for PCT, PLT & PLZT ceramics.
- Temperature and frequency dependence of dielectric behaviors of some of the selected compositions have been studied.
- The formation of saturated PE hysteresis loops in case of La and Zr modified PT ceramics confirmed the ferroelectric nature of these samples.

Chapter 1

INTRODUCTION AND BACKGROUND

1.1 Introduction:

Ferroelectric ceramics were born in the early 1940s with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramic barium titanate capacitors. Since that time, they have been the heart and soul of several multibillion dollar industries, ranging from high-dielectric-constant capacitors to later developments in piezoelectric transducers, positive temperature coefficient (PTC) devices, and electrooptic light valves. Materials based on two compositional systems, barium titanate and lead zirconate titanate, have dominated the field throughout their history. The more recent developments in the field of ferroelectric ceramics, such as medical ultrasonic composites, high-displacement piezoelectric actuators (Moonies, RAINBOWS), photostrictors, and thin and thick films for piezoelectric and integrated-circuit applications have served to keep the industry young amidst its growing maturity. Various ceramic formulations, their form (bulk, films), fabrication, function (properties), and future are described in relation to their ferroelectric nature and specific areas of application.

The discovery of ferroelectricity in lead titanate (PbTiO_3) has given birth to a large number of ABO_3 type materials. Perovskite-type lead titanate (PbTiO_3 , PT), which is a promising ferroelectric ceramics, has a high Curie temperature (T_c)~ 490°C, a large tetragonality ($c/a = 1.06$), a relatively low dielectric constant (ϵ_r), a large pyroelectric coefficient and an easy spontaneous polarization (P_s)[1]. PT ceramics have many important ferroelectric and piezoelectric technological applications in optoelectronics and microelectronics, because of their high T_c , pyroelectric coefficient and P_s . It also shows a high electromechanical coupling coefficient, k_t , a large range of dielectric

constant values and low dielectric and mechanical losses. The major problem associated with PT ceramics is that when it cooled through the Curie temperature, disintegrates due to a large anisotropic thermal expansion (expansion along the tetragonal c axis and contraction along the a axis), due to change in unit cell from cubic to tetragonal, resulting in a tetragonality ratio $c/a = 1.064$. Moreover, these ceramics also have high acoustic impedance and low flexibility [2]. In order to overcome these difficulties, substitution of cations in sites A or B in PT composition has been extensively studied.

There are various synthesis routes reported in the literature by which PT and modified PT ceramics can be synthesized such as solid state reaction route, sol-gel, hydrothermal reactions, co-precipitation, and emulsion techniques. In the present study we have employed the sol-gel method, due to its various advantages, specifically: the reactants are mixed on a molecular level, a better control of stoichiometry, higher purity of raw materials, the easy formation of ultra-fine and crystallized powders [3]. Also, the preparation of the ceramic powders by sol-gel technique allows one to obtain pure ceramic powders with controlled morphology and grain size [4].

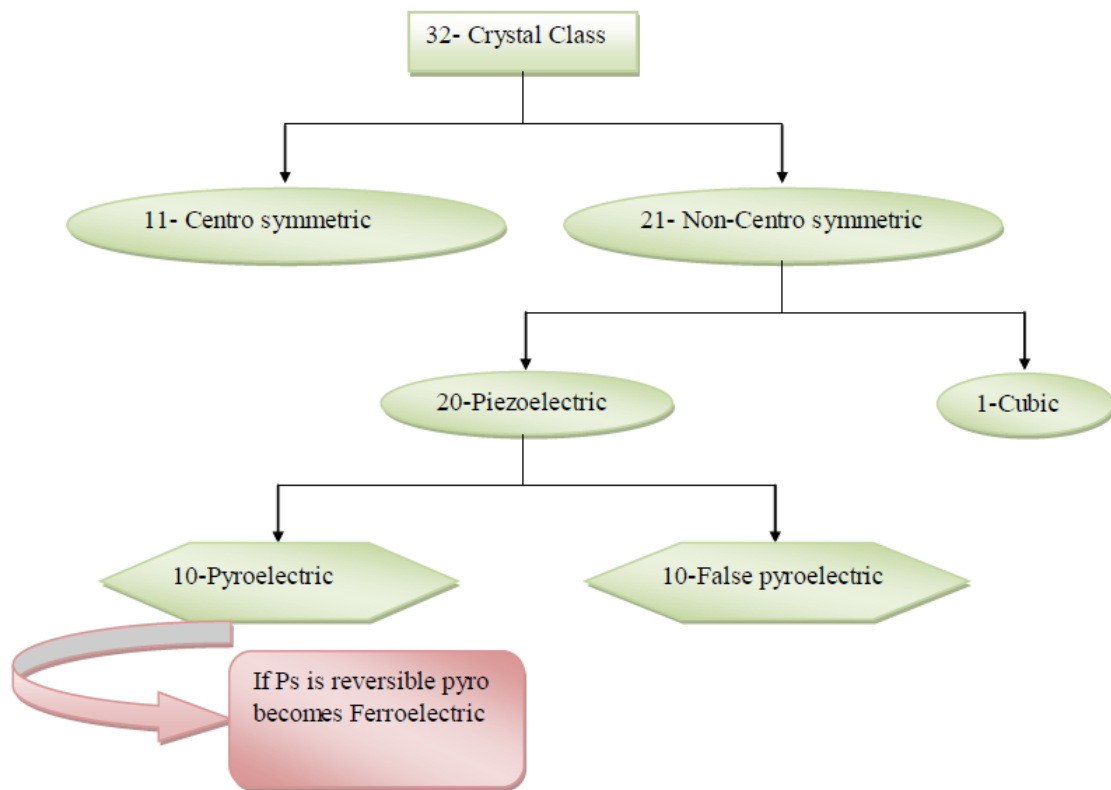
In order to improve the sintering and electrical properties of the pure PT ceramics, Ca and La are substituted in the A-site in place of Pb whereas Zr has been incorporated in B-site in place of Ti ion. The effects of such substitutions on the structural, microstructural and electrical properties are investigated in detail.

1.2Basis of Ferroelectricity in Crystals:

On the basis of the symmetry elements of translational position and orientation, there are 230 space groups. Ignoring translational repetition, these 230 groups break down into 32 classes, known as the 32 point groups. Point groups are based on orientation only. Any point may be defined by coordinates x , y , and z , with respect to the origin of symmetry. A centro symmetric crystal is a crystal in which the movement of each point at x , y , z , to a new point at $-x$, $-y$, $-z$, does not cause a recognizable difference. This implies that centro symmetric crystals are nonpolar and thus do not possess a finite polarization or dipole

moment. Of the 32 classes (or point groups), 11 classes are centrosymmetric and 21 classes are non-centro symmetric, possessing no center of symmetry.

The latter is the necessary requirement for the occurrence of piezoelectricity. However, one of the 21 classes, though classified as the non-centro symmetric class, possesses other combined symmetry elements, thus rendering no piezoelectricity. So, only 20 classes of non-centrosymmetric crystals would exhibit piezoelectric effects. In 10 of these 20 classes, polarization can be induced by a mechanical stress, while the other 10 classes possess spontaneous polarization, so they are permanently polar and thus can have piezoelectric as well as pyroelectric effects. There is a subgroup within these 10 classes that possesses spontaneous polarization and reversible polarization; this subgroup can exhibit all three effects ferroelectric, piezoelectric, and pyroelectric. In fact, the ferroelectric effect is an empirical phenomenon distinct from piezoelectric and pyroelectric effects in that it exists with a reversible polarization. The 32 point groups are subdivisions of seven basic crystal systems, which are based on the degree of symmetry. In the order of ascending symmetry, these seven basic crystal systems are triclinic, monoclinic, orthorhombic, tetragonal, trigonal (rhombohedral), hexagonal, and cubic.



(Fig.1 Crystal point group)

Symmetry

A state in which parts on opposite sides of a plane, line, or point display arrangements that are related to one another via a symmetry operation such as translation, rotation, reflection or inversion.

Application of the symmetry operators leaves the entire crystal unchanged.

Point group symmetry

- Inorganic crystals usually have perfect shape which reflects their internal symmetry
- Point groups are originally used to describe the symmetry of crystal.
- Point group symmetry does not consider translation.
- Included symmetry elements are rotation, mirror plane, center of symmetry, rotary inversion.

Space groups

The combination of all available symmetry operations (32 point groups), together with translation symmetry, within the all available lattices (14 Bravais lattices) lead to 230 Space Groups that describe the only ways in which identical objects can be arranged in an infinite lattice. The International Tables list those by symbol and number, together with symmetry operators, origins, reflection conditions, and space group projection diagrams.

1.3 Ferroelectricity and Polarization

Ferroelectrics have reversible spontaneous polarization. The word spontaneous may mean that the polarization has a nonzero value in the absence of an applied electric field. The word reversible refers to the direction of the spontaneous polarization that can be reversed by an applied field in opposite direction. The spontaneous polarization P_s usually increases rapidly on crossing the transition point and then gradually reaches a saturation value at lower temperatures. The most prominent features of ferroelectric properties are hysteresis and nonlinearity in the relation between the polarization P and the applied electric field F . The simplest method for measuring spontaneous polarization is the Sawyer and Tower method. Ferroelectric materials exhibit ferroelectric properties only at temperatures below T_c because they are polar; at temperatures above it, they are not polar. Obviously, the shape of the hysteresis loop depends on temperature.

Polarizations

Positively charged species in insulators shift towards the negative electrode and negatively charged species align towards the positive electrode; creating dipoles. The dipole moment density is termed the Polarization (P) and has the units of C/m^2 . It is defined as dipole moment per unit volume of a dielectric material.

In a dielectric material, the total polarization has contribution from all the four types of polarization namely electronic, ionic, orientational, and space charge polarization. The total polarization P_T may be written as

$$P_T = P_E + P_I + P_O + P_S$$

Where; P_E is the electronic polarization

P_I is the ionic polarization

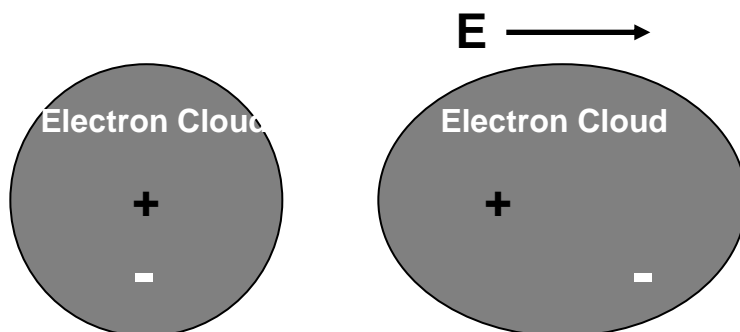
P_O is the orientational polarization

P_S is the space charge polarization

Types of polarization:

Electronic polarization:

It is the displacement of the positively charged nucleus and the electrons of an atom in opposite directions on application of an electric field. The extent of shift is proportional to the field strength. Electronic polarization increases with increase in volume of the atom but independent of temperature. Mono atomic gases exhibit only this kind of polarization.

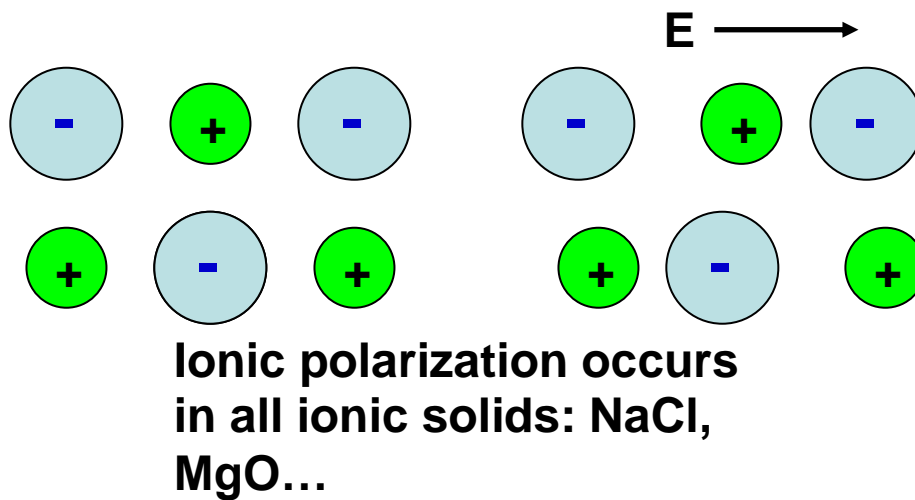


**Electronic polarization, occurs
in all insulators**

(Fig.2)

Ionic polarization:

Ionic polarization is the polarization which is caused by relative displacements between positive and negative ions in ionic crystals. Ionic polarization causes ferroelectric transition as well as dipolar polarization. The transition which is caused by ionic polarizations in crystals is called displacive phase transition. Ionic polarization is also independent of temperature.



(Fig.3)

Orientalional polarization:

This type of polarization only occurs in polar substances. When an electric field is applied on such molecules they tend to align themselves along the applied field. The polarization due to this alignment is called orientational polarization and is dependent on temperature.

Space charge polarization:

It occurs due to accumulation of charges at the electrodes or at the interface in a multiphase material. The ions diffuse over appreciable distance in response to the applied field giving rise to redistribution of charges in the dielectric medium.

1.4 Dielectric:

A dielectric is a non-conducting substance used to describe materials in which all the electrons are tightly bound to the nuclei of the atoms. Here the dielectric polarization is important. It supports charge without conducting it to a significant degree. In principle all insulators are dielectric; the capacity to support charge varies greatly between different insulators.

Dielectric constant:

The dielectric constant is the ratio of the capacitance of a capacitor containing the dielectric to that of an identical but empty capacitor (vacuum). The dielectric constant of a material provides a measure of its effect on a capacitor.

1.5 Piezoelectricity:

Piezoelectric are materials in which electricity can be generated by an applied mechanical stress or a mechanical stress can be reproduced by an applied electric field. This interconvertible behavior was first discovered by Pierre and Jacques Curie in 1880 in certain crystals, such as quartz, zinc blends, tourmaline, and Rochelle salt. The term piezoelectricity has been used by scientists since 1881 to distinguish the piezoelectric phenomena from electrostriction. The piezoelectric phenomena occur in both the ferroelectric and the non-ferroelectric states.

1.6 Pyroelectricity:

(Thermal variation Leads to Charge generation)

Pyroelectric are the bridge between ferroelectric and piezoelectric. They possess a spontaneous polarization which is not necessarily switchable by an electric field. If their polarization is switchable, i.e. they are ferroelectric, then they are mainly used in situations in which ferroelectric properties are required. However, if they are not ferroelectric, then their properties as pyroelectric are more useful. In Pyroelectric, the material has a spontaneous dipole moment, as a result of the ionic positions. This dipole moment induces a polarization. Depending on the formation of the Pyroelectric, the

Pyroelectric may possess a net polarization. This polarization will increase when a stress is applied to the material, as it is piezoelectric. But it will not reverse under the application of an electric field.

Based on the classification of crystals given in Figure the following statements can be made:

- All ferroelectrics possess piezoelectric and pyroelectric effects.
- All pyroelectrics possess piezoelectric effects, but not all are ferroelectric.
- Piezoelectrics may have only piezoelectric effects, both piezoelectric and pyroelectric effects, or all three effects: ferroelectric, piezoelectric, and pyroelectric.

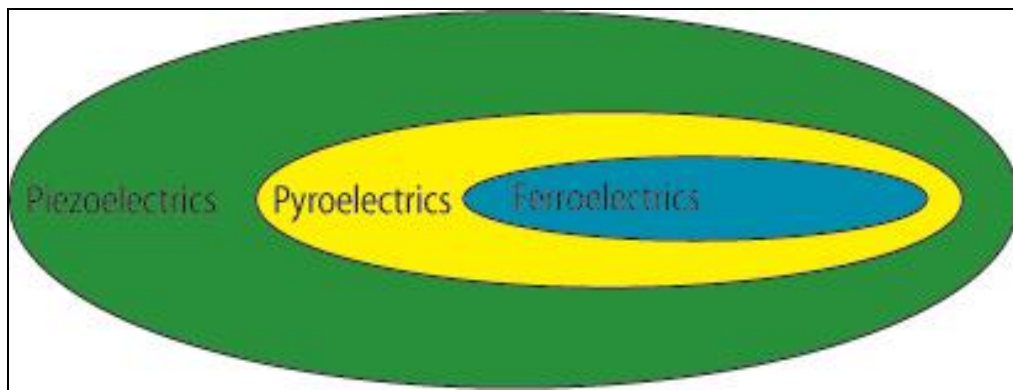


Fig.4 (Venn diagram showing the relationship between ferroelectric, Pyroelectric and piezoelectric)

1.7 Perovskite Crystal Structure

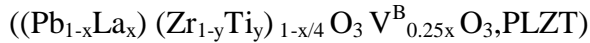
Lead Titanate (PbTiO_3 , PT)

Lead titanate is a ferroelectric material having a structure similar to BaTiO_3 with a high Curie point (490°C). On decreasing the temperature through the Curie point a phase transition from the paraelectric cubic phase to the ferroelectric tetragonal phase takes place. Lead titanate ceramics are difficult to fabricate in the bulk form as they undergo a large volume change on cooling below the Curie point. It is the result of a cubic ($c/a = 1.00$) to tetragonal ($c/a = 1.064$) phase transformation leading to a strain of $> 6\%$.

Hence, pure PbTiO_3 ceramics crack and fracture during fabrication. The spontaneous strain developed during cooling can be reduced by modifying the lead titanate with

various dopants such as Ca, La, Ba, Sn and W to obtain a crack free ceramic. One representative modified lead titanate composition that has been extensively investigated recently is Lead Lanthanum Zirconate Titanate $((\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)_{1-x/4} \text{O}_3 \text{V}^{\text{B}}_{0.25x} \text{O}_3, \text{PLZT})$.

Lead Lanthanum Zirconate Titanate



- PLZT is a transparent ferroelectric ceramic formed by doping La^{3+} ions on the A sites of lead zirconate titanate (PZT).
- The PLZT ceramics have the same perovskite structure as BaTiO_3 and PZT.
- The transparent nature of PLZT has led to its use in electro-optic applications.
- The two factors that are responsible for getting a transparent PLZT ceramic include the reduction in the anisotropy of the PZT crystal structure by the substitution of La^{3+} and the ability to get a pore free ceramic by either hot pressing or liquid phase sintering.
- The general formula for PLZT is given by $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)_{1-x/4} \text{O}_3 \text{V}^{\text{B}}_{0.25x} \text{O}_3$ and $(\text{Pb}_{1-x}\text{La}_x)_{1-0.5x}(\text{Zr}_{1-y}\text{Ti}_y) \text{V}^{\text{A}}_{0.5x} \text{O}_3$.
- The first formula assumes that La^{3+} ions go to the A site and vacancies (V^{B}) are created on the B site to maintain charge balance.
- The second formula assumes that vacancies are created on the A site. The actual structure may be due to the combination of A and B site vacancies.

The room temperature phase diagram of PLZT system is shown in fig. The different phases in the diagram are a tetragonal ferroelectric phase (F_{T}), a rhombohedral ferroelectric phase (F_{R}), a cubic relaxor ferroelectric phase (F_{C}), an orthorhombic antiferroelectric phase (A_0) and a cubic paraelectric phase (P_{C})

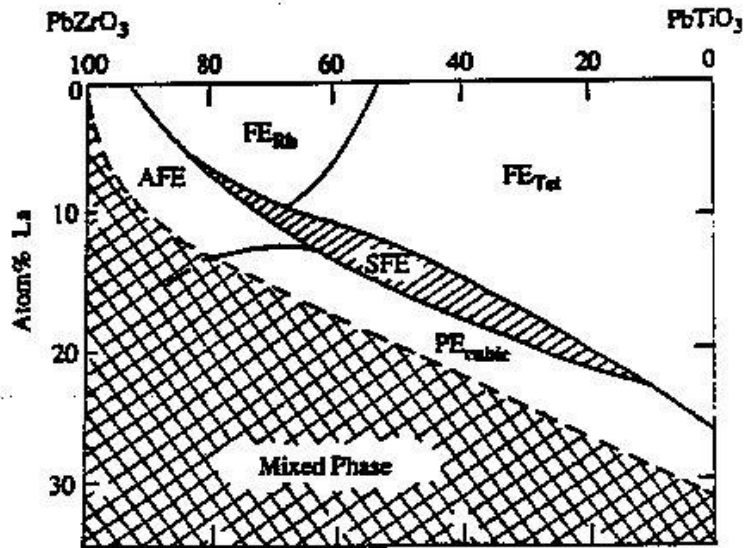


Fig.5 Room temperature phase diagram of the PLZT system. The regions in the diagram are, a tetragonal ferroelectric phase (F_T); a rhombohedral ferroelectric phase (F_R); a cubic relaxor ferroelectric phase (F_C); an orthorhombic antiferroelectric phase (A_O); and a cubic paraelectric phase (P_C).

THESIS OBJECTIVE

- ✓ To synthesize Ca, La and Zr Modified PT Ceramics by sol-gel synthesis route.
- ✓ To optimize the synthesis route.
- ✓ To carry out different characterizations like XRD for phase formation, SEM for surface morphology, Electrical study for dielectric constant and transition temperature and P-E loop measurement to detect the ferroelectric behavior of the ceramics.

Chapter 2

2.1 Sol–Gel Processing

In the sol–gel process, a solution of metal compounds or a suspension of very fine particles in a liquid (referred to as a *sol*) is converted into a highly viscous mass (the *gel*). Starting with a sol, the gelled material consists of identifiable colloidal particles that have been joined together by surface forces to form a network. When a solution is used, typically a solution of metal-organic compounds (such as metal alkoxides), the gelled material in many cases may consist of a network of polymer chains formed by hydrolysis and condensation reactions. As a fabrication route for ceramics, the sol–gel process has a number of advantages. Because of the ease of purification of liquids (as the starting materials for the process), materials with high purity can be produced. Materials with exceptionally good chemical homogeneity, which is very desirable, especially in the case of complex oxides, can also be produced because the mixing of the constituents occurs at a molecular level during the chemical reactions. Another advantage is the lower densification temperature.

However, the disadvantages are also real. The starting materials (e.g., the metal alkoxides) can be fairly expensive. We have already mentioned the difficulties of conventional drying, during which cracking, warping, and considerable shrinkage are common problems. Mainly because of these problems in drying, the sol–gel route has seen little use for the fabrication of monolithic ceramics. Instead it has seen considerable use for the fabrication of small or thin articles, such as films, fibers, and powders, and its use in this area is expected to grow substantially in the future.

The level of mixing in the sol-gel process is in molecular range, which is never possible in solid state mixing. Hence, sol-gel mixing helps to evolve homogenous microstructure, most desirable criteria for compiling a composite. The crystalline temperature of obtained oxide materials is also lower than the conventional approach. Reduction of particle size

of the individual ingredients is obviously at the highest level, which will be helpful in enhancing the sintering process without any additive.

According to Brinker some advantages of the sol-gel method can be summarized as follows;

1. Better homogeneity – from raw materials
2. Lower temperature of preparation
3. Better purity – from raw materials
 - saves energy
 - minimise evaporation losses
 - minimise air pollution
4. New crystalline phases from new non-crystalline solids
5. Better glass products determined by special properties of gel

2.2 SYNTHESIS ROUTE:

2.2.1 Table-1: Steps of synthesis:

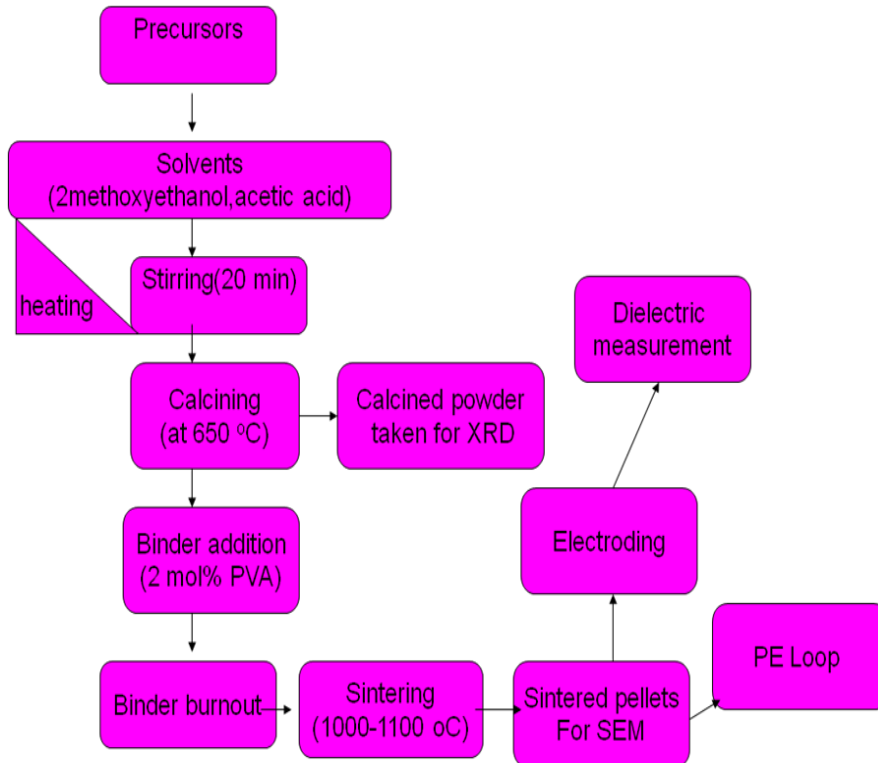
Ferroelectric ceramics can be fabricated by various methods. In the present study modified PT ceramics were prepared by sol-gel synthesis route. The step of synthesis routes are described below:

1.Precursors:	PCT	PLZT	PLT
i. Lead acetate trihydrate($C_4H_6O_4Pb \cdot 3H_2O$) 5%Pb	4.9236gm	5.1946gm	5.1443gm
ii. Calcium acetate hydrate ($C_4H_6CaO_4 \cdot H_2O$)	0.6877gm		
iii. Titanium isopropoxide ($C_{12}H_{28}O_4Ti$)	4.8408 ml	1.3893ml	4.5221ml
iv. Zirconyl nitrate hydrate ($ZrO(NO_3)_2 \cdot H_2O$)		2.7149gm	
v. lanthanum acetate hydrate ($C_6H_9LaO_6(1.5H_2O)$)		0.3251gm	1.5638gm
2.Calcining temperature	650 °C(4hr)	950 °C (4 hr.)	650 °C (4 hr.)
3.Sintering temperature	950-1050°c(4hr)	1050-1100°c(4hr.)	950-1050°c(4hr.)

2.2.2 Optimization of synthesis route:

- The samples are prepared by sol – gel route.
- The solvents chosen for the synthesis is mixture of 2 – methoxy ethanol and acetic acid.
- The starting solutions are prepared by first mixing 5 % extra lead acetate trihydrate and 2-methoxy ethanol. Approximately 40 ml ethanol is used and some extra (10 ml) acetic acid is also mixed with the solution. After this mixing we dissolve lead acetate trihydrate by spinning method for 20 minutes.
- When lead acetate was dissolved completely with the solution 0.6877 gm of calcium acetate is mixed to the solution.
- Now the colour of the solution changes from colourless to milky white. After 1 hour of continuous stirring the solution is heated with stirring at a temperature of 700°C. After 3 hours of heating and stirring the solution became transparent gel.
- Then after few minutes and in some elevated temperature yellow colour precipitation occurred. After some time the powder in the bottom of beaker turned black, gradually the whole powder become blackish.
- The black powder is also found to be hygroscopic. With further heating it is found that the powder burnt with glows, exactly similar to charcoal cavity experiment with evolution of white coloured gases.
- Now the xerogel powder obtained is not hygroscopic.
- The powder collected is then calcined for 4 hours at a temperature of 650⁰C for PCT, PLT and at a temperature 950⁰C for PLZT.
- After cooling, the sample is collected from the furnace and is grinded by agate - mortar.
- The grinded powder is now ready for necessary characterization.
- The sample is then pressed into pellet by dry pressing method and is then sintered at a temperature range from 950 to 1100 ⁰C for electrical characterization.

2.2.3 FLOW CHART:



(Fig.6 Flowchart for the synthesis of Ca, La & Zr modified PbTiO₃ ceramics)

In this thermal process thermal decomposition, phase transition of solid materials takes place. It occurs above transition temperature for phase transition. At transition temperature the standard Gibbs free energy for a particular calcination reaction is equal to zero. The higher the calcining temperature the higher the homogeneity and density of the final ceramic product. Proper calcination at right temperature is necessary to obtain the best electrical and mechanical properties. In calcination process our aim is to remove

water of hydration, CO_2 to form desired solution and as a consequence of reaction to have reduced volume shrinkage in the final firing.

Binder addition:

Binders serve to provide plasticity in the feed material during deformation. The binder must provide the desired chemical properties to the feed materials so that the powder can be consolidated into the desired shape and then must be removed completely from the shaped powder without disrupting the packing of particles in the powder.

Binder burnout:

Binder burnout is a processing step performed before sintering where the green body is heated until the polymer binder is burnt out of the ceramic.

Sintering:

Sintering is the process by which ceramics are densified. Microstructure refers to density, grain shape, grain size and distribution, porosity, pore size and distribution. A full densification of ferroelectric ceramics ensures to achieve the maximized performance. Generally, the densities of ferroelectric ceramics increase with increasing sintering temperature. Sintering aids are required to have relatively low melting points and no reaction with ferroelectric phase during sintering process. Sintering is done because ceramics have high melting temperatures and reactive metals. Sintering temperature is that temperature at which the grains of solid formed from powder start connecting through its boundaries and merge so form a larger grain.

Advantages of sintering:

I. The parts produced have an excellent surface finish, and good dimensional accuracy.

ii. The porosity inherent in sintered components is useful for specialized application such as filters and bearings.

2.3 Characterization Methods:

2.3.1 X-Ray Diffraction:

- In the powder, thousands of grains have random orientations. With random orientations, it is expected that most of the different atomic planes lie parallel to the surface in some of the grains.
- Thus, by scanning through an angle θ of incident X-ray beams from 0 to 90° , diffraction has occurred in a particular angle, and each of these angles would be associated with a different atomic spacing.
- The instrument used to do this is an X-ray powder diffractometer.
- A powdered mineral sample is packed on a sample stage so that it can be irradiated by the X-ray tube. To detect the diffracted X-rays, an electronic detector is placed on the other side of the sample from the X-ray tube, and allowed to rotate the sample to produce angles from 0 to 90° .
- The instrument used to rotate both the X-ray tube and the detector is called a goniometer. The goniometer keeps track of the angle θ , and the detector records the rate of X-rays coming out of the other side of the sample (in units of counts/sec) and sends this information to the computer.
- The identification of different phases is carried out by powder X-ray diffraction study. For the phase analysis of dried gel and calcined powder, X-ray data were collected using a fully automated Philips X-pert system (PHILIPS PW1830) with Cu-K α radiation.
- The voltage and current were set at 35 kV and 30mA respectively with the copper target, with a step size of 0.020 (2θ) and a count time of 1s per step.
- After scan of the sample, the X-ray intensity (counts/sec) was plotted against the angle theta (θ). The angle (2θ) for each diffraction peaks were then converted to d-spacing, using the Bragg equation.
- The crystal structure and associate each of the diffraction peaks with a different atomic plane in terms of the Miller Index for that plane (hkl) was determined through standard APD software.

2.3.2 Scanning Electron Microscope (SEM)

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). SEM is a type of electron microscope that creates various images by focusing a high energy beam of electrons onto the surface of a sample and detecting signals from the interaction of the incident electron with the sample's surface. SEM images have greater depth of field (curved surfaces are resolved properly) yielding a characteristic 3D appearance useful for understanding the surface structure of a sample. Magnification is of order 10,000 X and resolution 10 nm.

Scanning process

A stream of electrons is formed by electron surface and accelerated towards the specimen using positive electric potential. The stream is confined and focused using metal apertures and magnetic lenses into a thin focused monochromatic beam. The beam is focused onto the sample using a magnetic lens. Interactions occur inside the irradiated sample affecting the electron beam.

2.3.3 Dielectric property study:

Ferroelectric ceramics generally have much higher dielectric constants, typically several hundred to several thousand. It is calculated for the pellet from capacitance using the formul:

$$K = C \cdot d / \epsilon_0 A$$

Where C: Capacitance

K: dielectric constant

A: area of the electrode

ϵ_0 : permittivity of the free space

The dielectric constant was measured using HIOKI 3532-50LCR HiTester.

A LCR meter is a device that is used to test the electrical impedance of a piece of equipment. In operation, it is capable of identifying the measurement of an object's resistance to steady electrical current. This is most helpful when dealing with alternating current (AC). It will determine the relative change in magnitude of the repetitive variations of the voltage and current known as amplitudes. Inductance is a change in the flow of current through a circuit and some device such as a resistor prevents that change. This is called electromotive force. Because electrical currents produce magnetic fields that reduce the rate of change in the current, the LCR will measure the ratio of magnetic flux.

2.3.4 P-E hysteresis loop:

The hysteresis loop of the compound was also obtained using our laboratory studied Sower–Tower circuit. The polarization versus electric field (P-E) hysteresis loop is one of the most important electrical characteristics of ferroelectric ceramics. Hysteresis loops can provide a plentiful amount of information for the understanding of ferroelectric materials. The domain concept is well explained by the phenomenon of hysteresis. A high remnant polarization is related to high internal polarizability, strain, electromechanical coupling etc. the coercive field indicates the grain size of a given material. A sudden large change in apparent polarization is usually an indication of incipient dielectric breakdown.

3. Results and Discussions:

3.1 X-Ray Diffraction

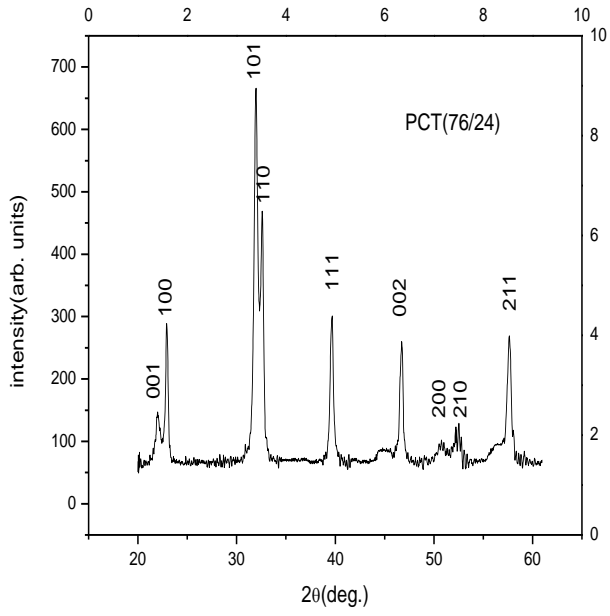


Fig.3. 1(a)

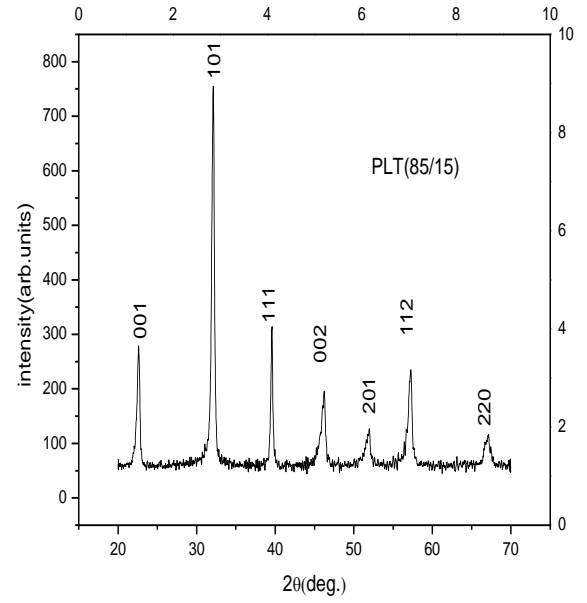


Fig.3.1 (b)

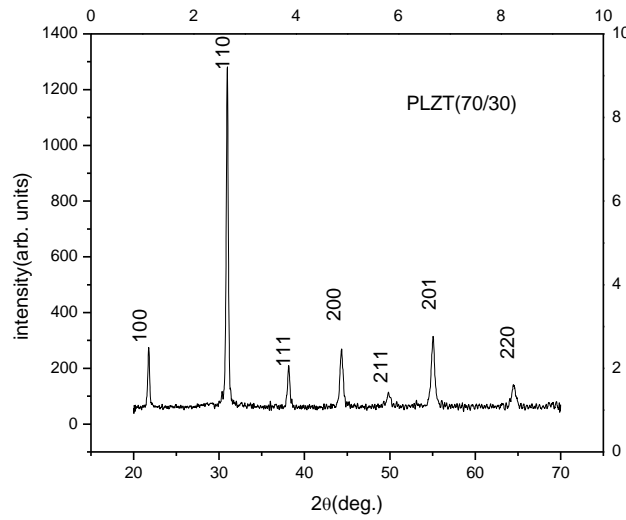


Fig.3. 1(c)

Fig.3. 1(a), (b) & (c) of XRD pattern shows:

- i. The development of single perovskite phase peaks.
- ii. The XRD peaks are found to be sharp, which indicates good homogeneity and crystallization of the ceramic samples.
- iii. There is no unwanted secondary peak in XRD pattern.
- iv. Among PCT, PLT and PLZT, intensity peak of PLZT is sharper than other two ceramics.

The refined lattice parameters so obtained for all compositions are listed in the table below:

Sample name	Lattice parameter	Unit cell Volume (\AA^3)
PCT,	$a = b = 3.89502$ $c = 4.04482$	61.36
PLT	$a = b = 3.69386$ $c = 3.93303$	61.32
PLZT	$a = b = 4.07962$ $c = 4.08217$	67.98

3.2 SEM Analysis:

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). The SEM microstructure of all samples is given in figure below:

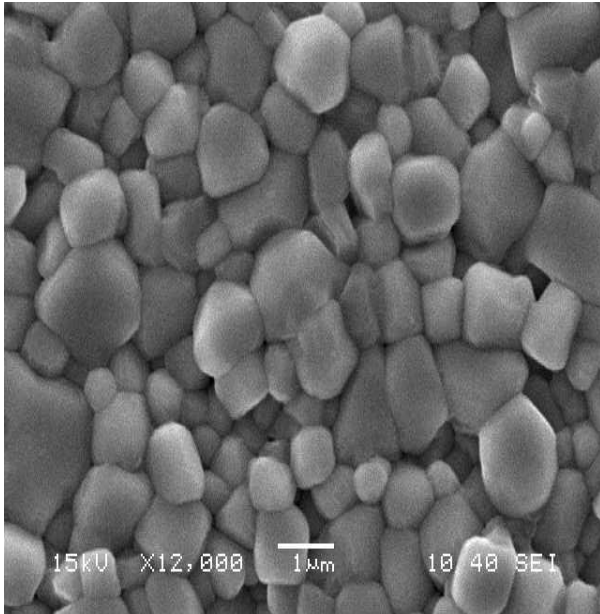


Fig3.2. (a) SEM micrograph of PCT PLT

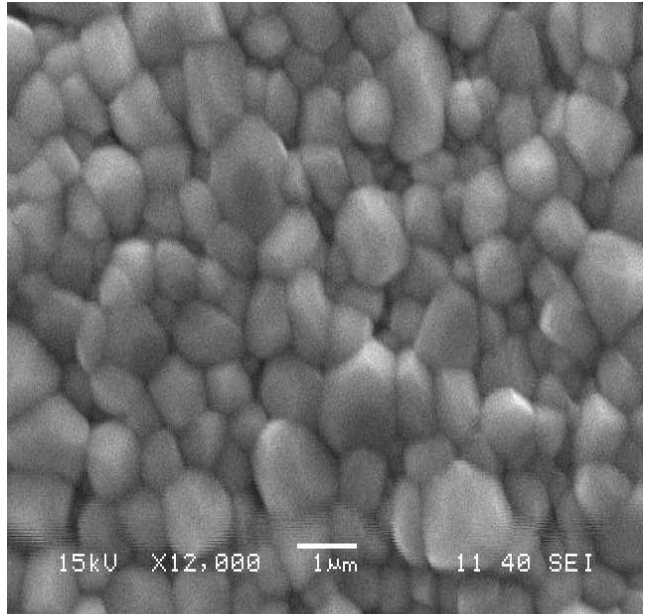


Fig.3.2 (b) SEM micrograph of

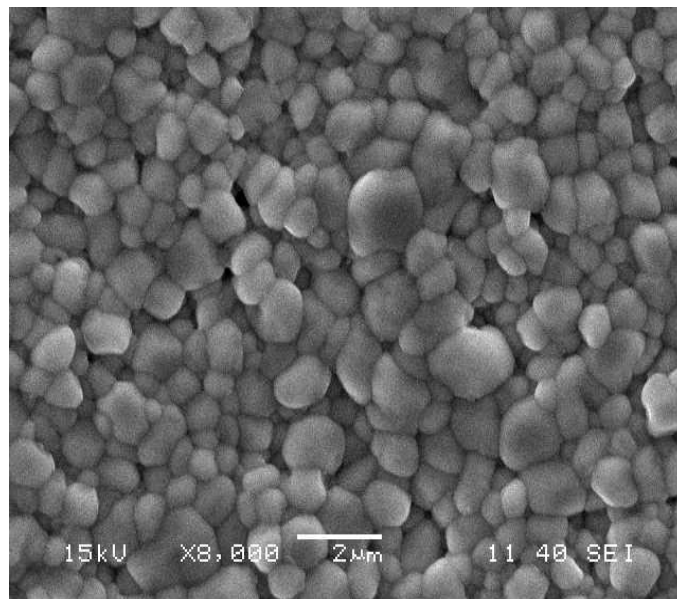


Fig.3.2 (c) SEM micrograph of PLZT ceramic

Fig3. 2. (a), (b) &(c) illustrate the SEM micrographs of PCT, PLT and PLZT ceramic samples respectively. Presence of pore free uniform grains ceramic samples suggests the advantage of using modified chemical route over conventional solid state reaction route. Average grain size, estimated by linear intercept method, was found to be ~ 0.7 , 0.85 & $1.12\mu\text{m}$ in PCT, PLT & PLZT ceramic samples.

3.3 Dielectric Analysis:

i.PCT

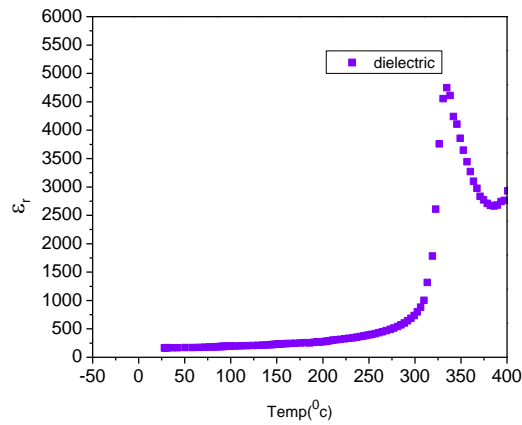


Fig.3.3 (a) Temperature variation of ϵ_r of PCT

ii.PLT

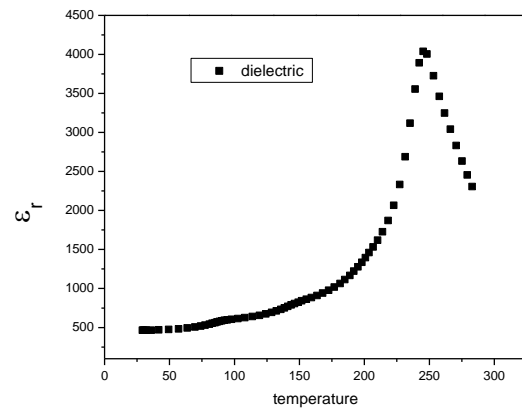


Fig.3.3 (b) Temperature variation of ϵ_r of PLT

iii.PLZT

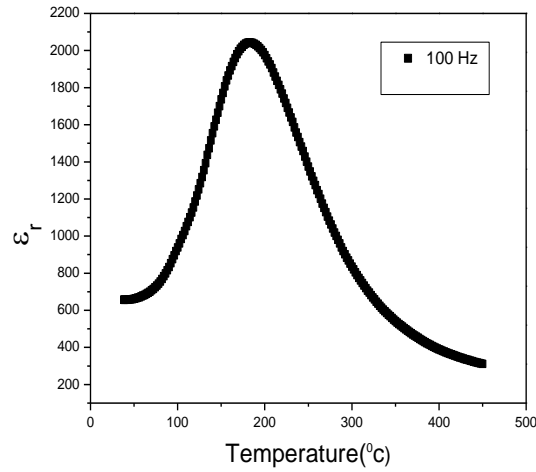


fig3.3(c)

Fig3.3.(a),(b)&(c) shows :Temperature variation of ϵ_r of PCT ,PLT & PLZT ceramics at a frequency of 100 Hz. Values of ϵ_r increases with the increase in temperature and transition temperature (T_c) was found to be 334°C, 245°C & 181°C of PCT,PLT & PLZT samples around ϵ_r 4747 ,4041 ,2058 respectively.

Dielectric constant (ϵ_r) of any material, in general, is influenced by dipolar, electronic, ionic and interfacial polarizations .Interfacial polarization increases due to the creation of crystal defects and dipolar polarization decreases due to the increase in randomness of the dipoles with temperature. However, the temperature effect on ionic and electronic polarizations is very small. The increase in ϵ_r with temperature suggests the increase in interfacial polarization.

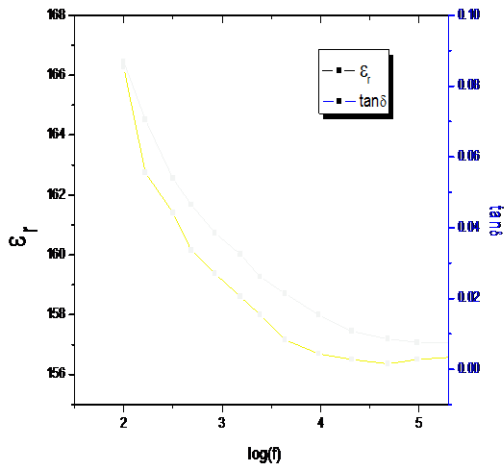


Fig.3.3 (d)

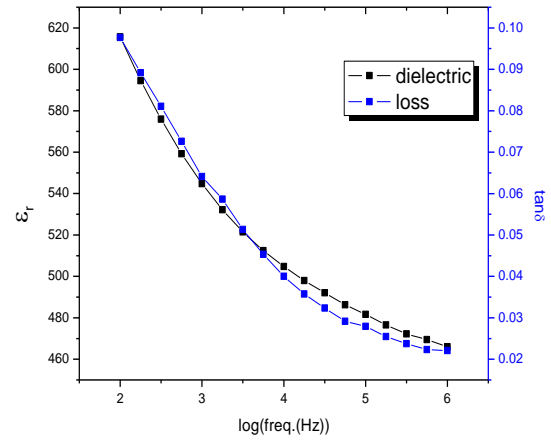


Fig.3.3 (e)

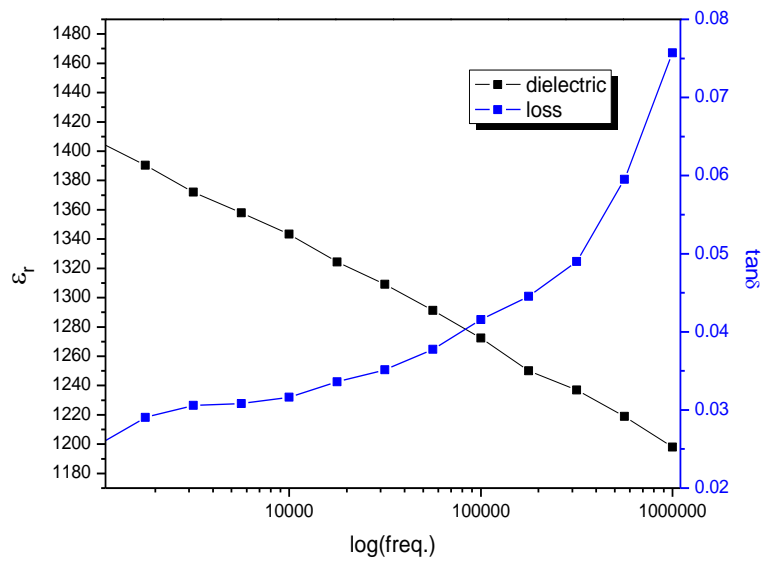


Fig.3.3 (f)

Fig. 3.3(d),(e), (f) shows Variation of ϵ_r and $\tan\delta$ with frequency of PCT, PLT&PLZT ceramic samples respectively sintered at 1050°C, 1050°C & 1100°C.

Initially, both ϵ_r and $\tan\delta$ decreases with the increase in frequency. The fall in arises from the fact that polarization does not occur instantaneously with the application of the electric field, which is further due to the inertia of the dipoles and the delay in response towards the impressed alternating electric field leads to dielectric loss and decline in ϵ_r .

At low frequencies, all types of polarization contribute and as the frequency is increased, polarizations with large relaxation times cease to respond and hence the decrease in ϵ_r . At lower frequencies ϵ_r is maximum because the contributions from the space charge polarization are large. The space charge polarization arises by the accumulation of charges mainly due to vacancies of lead and oxygen at the grain boundaries and at the electrode interface. At higher frequencies, contributions from the polarizations having high relaxation time cease resulting in the decrease in ϵ_r . The same type of frequency-dependent dielectric behaviour is found in many other ferroelectric ceramic systems.

3.4 Ferroelectric polarization versus electric field study:

- The P–E loop for all the compositions are recorded at room temperature and at a frequency of 100 Hz.

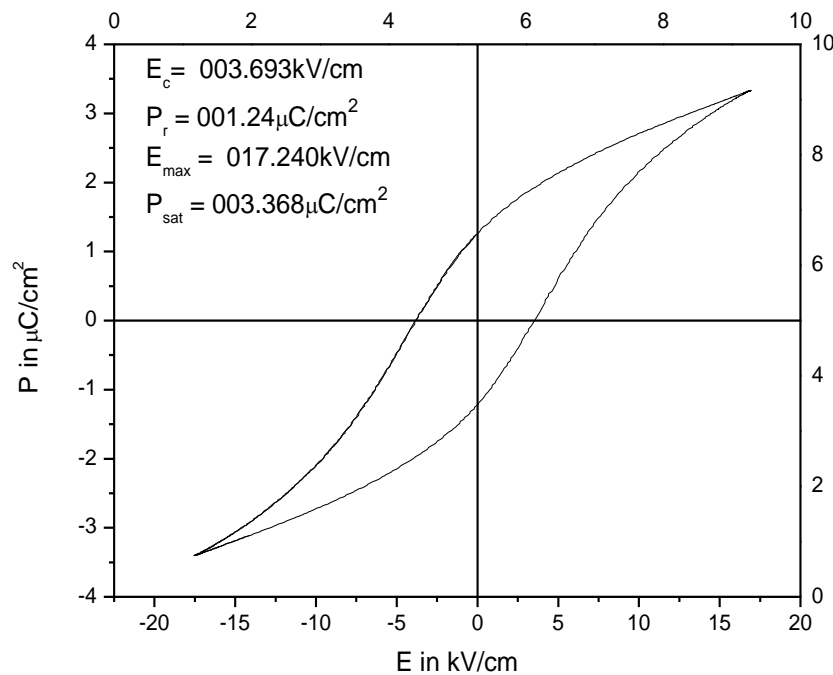


Fig.3.4.1 Shows the ferroelectric hysteresis loop of PLZT with maximum applied electric field of 17.24 kVcm^{-1} . The values of remnant polarization (P_r) and coercive field (E_c) are listed in fig.

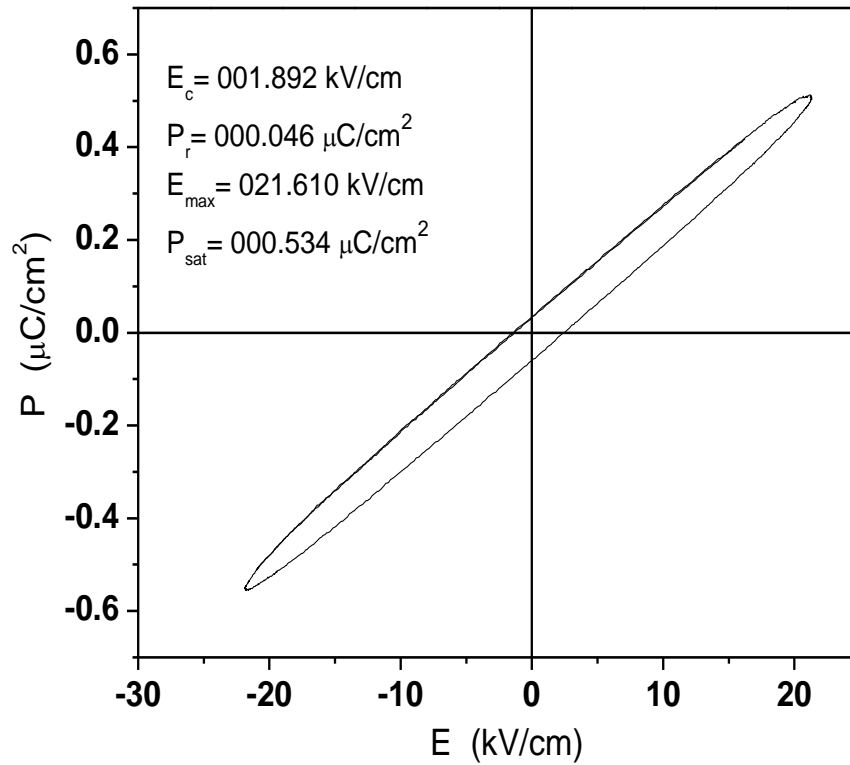


Fig.3.4.2 shows the ferroelectric hysteresis loop of PCT with maximum applied electric field of 21.61 kVcm^{-1} . The values of remnant polarization (P_r) and coercive field (E_c) are $0.534 \text{ } \mu\text{Ccm}^{-2}$ and $0.046 \mu\text{CCm}^{-1}$ respectively.

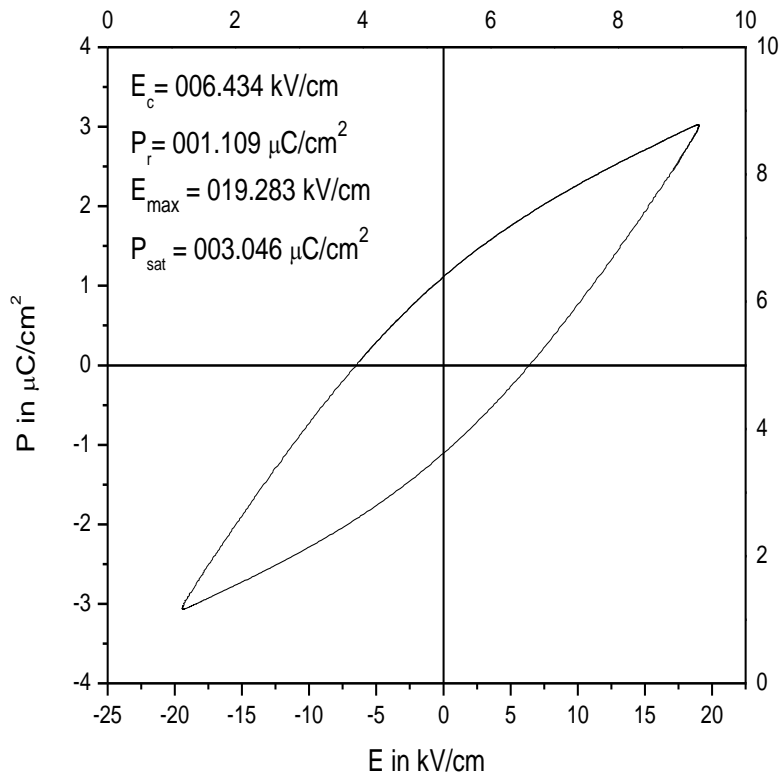


Fig3.4.3: Shows the ferroelectric hysteresis loop of PCT with maximum applied electric field of 21.61 kVcm^{-1} . The values of remnant polarization (P_r) and coercive field (E_c) are $0.534 \text{ } \mu\text{CCm}^{-2}$ and $0.046 \mu\text{CCm}^{-1}$ respectively.

CHAPTER-4

CONCLUSIONS

- XRD peaks revealed the single perovskite phase formation at lower calcination temps. For both PCT and PLT compositions with a tetragonal structure while PLZT showed cubic structure at room temperature.
- SEM micrograph showed homogeneous & dense grain morphology with low porosity in the samples with grain size in the range 0.7-1.12 μ m.
- The temperature dependence dielectric study of PCT, PLT & PLZT composition is studied.
- Near T_c value of ϵ_r at 100 Hz was found to be \sim 4747, 4041, 2058, respectively PCT, PLT & PLZT compositions.
- T_c was found to be \sim 334 $^{\circ}$ C, 245 $^{\circ}$ C, & 181 $^{\circ}$ C for PCT, PLT & PLZT compositions, respectively.
- P-E loop confirmed ferroelectric nature of the PCT, PLT & PLZT ceramics.

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