Synthesis & Characterization of PCT (76/24) Thin Films

A thesis submitted in partial fulfillment of the requirement

For the degree of

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IN

PHYSICS

By

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National Institute of Technology, Rourkela

<u>CERTIFICATE</u>

This is to certify that the thesis entitled "**Synthesis & Characterization of PCT (76/24) Thin Films**" submitted by **Mr. DIPTIRANJAN ROUT** in partial fulfilment for the requirement for the award of degree of Master of Science degree in Physics at National Institute of Technology, Rourkela is an authentic work carried out by his under my supervision and guidance in Electro ceramic Lab of Department of Physics.

       To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or Diploma.

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ACKNOWLEDGEMENTS

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I am also thankful to all the PhD scholars (S.N.Kumar , Sridevi, Subrat, and Punyatoya) in the Electro Ceramic lab for their liberal co-operation with extending their all analytical facilities.

CONTENTS

Abstract:

The thin films of calcium substituted $PbTiO_3$ (76/24)system were prepared by spin coating technique at different temperatures namely at 550^0C, 600^0C and 650^0C, respectively. The phase formation and structural property of all thin films were studied by X-Ray Diffraction (XRD) technique.

- The XRD pattern of PCT thin films indicated the formation of single perovskite phase at 550^0C annealing temperature.
- The surface morphology of the annealed thin films was studied by SEM which showed dense and homogeneous packing of grain with grain size ~1.25µm.
- Temperature and frequency dependence of dielectric behavior of PCT thin films have been studied.
- Thickness of the PCT thin film was measured and found to be ~100nm.

1.1 Introduction

The piezoelectric and pyroelectric materials have unique properties. Due to these unique properties these materials can be used in various applications like developments in integrated circuitry and electro-optic technologies. Over the last few years there has been a rapid increase in research of ferroelectric thin films. Ferroelectric materials have been commercially important to the electronics industry. Best examples include lead zirconium titanate ceramic, the ultrasonic transducer and depth-sounding systems; and modified barium titanate, which is used as ceramic capacitor. There are also other examples ranging from infrared movement detectors to auto focusing cameras. The common and important feature of all ferroelectrics is the presence of a field re-Oriential spontaneous polarization [1].
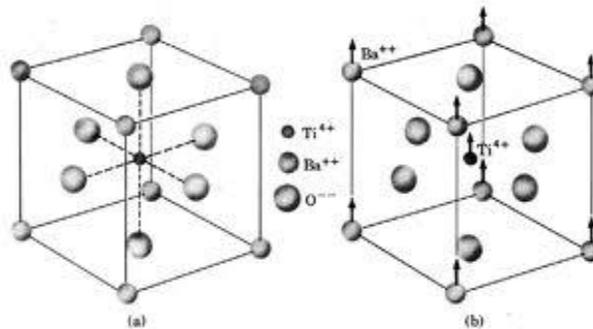
The ABO_3 type materials are known as Perovskite-type materials. Lead titanate PbTiO3 (PT) is a perovskite-type ferroelectric material and it is suitable for pyroelectric infrared detectors because of its relatively large pyroelectric coefficient and spontaneous polarization. It has also a high curie temperature ($T_C = 490^0$ C), a large tetragonality (c/a=1.06) and easy spontaneous polarization (P_s) [2]. $PbTiO_3$ based ceramics are very useful materials for various applications like pyroelectric detectors and ultrasonic transducers. It also shows a high electromechanical coupling coefficient, k_t a large range of dielectric constant values and low dielectric and mechanical losses.

However, one of the biggest problem present in PT systems is the micro-cracking produced in the cubic-tetragonal phase transition when it is cooled and a large anisotropic thermal expansion (expansion along the tetragonal c axis and contraction along the a axis). As a change in unit cell from cubic to tetragonal, resulting in a tetragonality ratio c/a = 1.064. These

ceramics also have high acoustic impedance and low flexibility [3]. Necessary care should be taken for the preparation of such PT based materials. So to avoid these difficulties, substitution of cations in sites A or B in PT composition has been extensively required. Otherwise this will cause the micro or macro cracking in the material. These micro-cracking are considered to be responsible for the decrease in the dielectric and piezoelectric properties of the materials. This material has poor mechanical properties due to its large tetragonal strain. Hence in order to reduce the large tetragonal strain and maintain the high mechanical stability there is need to dope PT systems with proper substituent.

Hence focus should be given on the modification of PT by doping with the purpose of obtaining improved mechanical and electrical properties. The incorporation of off-valent (La^{3+}, $Nd^{3}+$) and isovalent ions (Ca^2+, Ba^2+, Sr^2+) into PT ceramics is reported to enhance the mechanical stability along with good dielectric, piezoelectric, ferroelectric and pyroelectric properties [4]. The substitution of these ions results in the reduction of lattice anisotropy leading to hard and dense ceramics with high mechanical strength [4–16]. Due to thermal responsivity, the pyroelectric detector is better in the form of thin film.

1.2 Preparation of Ferroelectric thin film

Several methods are currently use for making thin films, each of which has its merits and demerit. The methods can be classified into two groups on the basis of deposition:

• Chemical deposition

• Physical deposition

1.2.1 Chemical deposition

In this method a fluid precursor undergoes a chemical change at a solid surface and leaving a solid layer. A normal example is the formation of soot on a cool object when it is placed inside a flame. As the fluid is surrounding the solid object, deposition happens on the surface, in a particular direction; thin film from chemical deposition techniques tends to be conformal, rather than directional.

Chemical deposition is further divided by the phase of the precursor:

1.2.1.1 Electroplating

In electroplating, an ionic metal is required with electrons to form a non-ionic coating on a substrate. A common system consists of a chemical solution with the ionic form of the metal, an anode which may made up of the metal being plated (a soluble anode) or an insoluble anode (usually carbon, platinum, titanium, lead, or steel), and finally, a cathode where electrons are supplied to produce a film of non-ionic metal.

1.2.1.2 Sol-gel

The sol-gel process is a wet-chemical technique and   widely used for the fabrication of both glassy and ceramic materials. Such method is used for the fabrication of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor for an integrated network like structure (or gel) of either discrete particles or network polymers. In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like biphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks.

1.2.1.3 Chemical vapor deposition

Chemical vapor deposition (CVD) is a chemical process used to make high-purity solid materials. The process is basically used in the semiconductor industry to produce semiconductor thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which reacts and decompose on the substrate surface to produce the desired deposit.

Types:

There are several types of CVD process. These processes differ according to their chemical reactions initiated (e.g., activation process) and the processing conditions.

1.2.1.4 Classified by operating pressure:

- *Atmospheric pressure CVD (APCVD)* – CVD processes at atmospheric pressure.
- *Low-pressure CVD (LPCVD)* – CVD processes at sub atmospheric pressure. Reduced pressures tend to decrease unwanted gas-phase reactions and improve film uniformity across the substrate.
- *Ultrahigh vacuum CVD (UHVCVD)* – CVD processes at an ultra high vacuum $(10^{-7} \, Pa)$.

    Most CVD processes are either LPCVD or UHVCVD.

1.2.1.5 Classified by physical characteristics of vapor:

- *Aerosol assisted CVD* (**AACVD**) – A CVD process in which the precursor is transported to the substrate by means of a liquid or gas aerosols, which can be produced ultrasonically. This method is suitable for use with non-volatile precursors.

- *Direct liquid injection CVD* (**DLICVD**) – A CVD process in which the precursor is in liquid form (liquid or solid dissolved in a convenient solvent). Liquid solution is injected in a vaporization chamber towards injectors. Then the precursor vapor is transported to the substrate as in normal CVD process. This method is suitable for use on liquid or solid precursors and high growth rates can be reached using this technique.

1.2.1.6 Plasma methods:

- *Microwave plasma-assisted CVD* (**MPCVD**)
- *Plasma enhanced CVD* (**PECVD**) **–** a CVD process that utilizes plasma to enhance chemical reaction rates of the precursors. PECVD processing allows deposition at lower temperatures, which is often difficult in the manufacture of semiconductor.
- *Remote plasma-enhanced CVD* (**RPECVD**) – PECVD except that the wafer substrate is not directly used in the plasma discharge region. After removing the wafer from the plasma region allows the processing temperature down to room temperature.
- *Atomic layer CVD* (**ALCVD**) – Deposits successive layers of different substances to produce layered crystalline films.

- *Combustion chemical Vapor Deposition* (CCVD)-A Chemical Vapor Deposition process is an open-atmosphere, flame-based technique for depositing high-quality thin films and nanomaterials.
- *Hot wire CVD* (HWCVD) – also known as catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). In this case a hot filament is used to chemically decompose the source gases

Metalorganic chemical vapor deposition (MOCVD) – CVD processes based on Metalorganic chemical vapor deposition precursors.

Rapid thermal CVD (RTCVD) – CVD processes that use heating lamps or other methods to heat the wafer substrate. Heating only the substrate helps reduce unwanted gas phase reactions that can lead to particle formation.

1.2.1.7 Atomic Layer Deposition (ALD)

This method uses gaseous precursor to deposit conformal thin films one layer at a time. The process is divided into two separate reactions, run in sequence and repeated for each layer, in order to confirm total layer saturation before beginning the next layer. Hence one reactant is deposited first and then the second reactant is deposited. In that time a chemical reaction occurs on the substrate, forming the desired composition.

1.2.1.8 Spin coating

This is also known as spin casting, uses a liquid precursor deposited onto a smooth substrate which is subsequently spun at a high velocity to centrifugally spread the solution over the substrate. The velocity at which the solution is spun and the thickness of the deposited film depends upon the viscosity of the solution. Repeated depositions are carried out to increase the thickness of films as desired. Thermal treatment is often carried out in order to crystallize the amorphous spin coated film. Such crystalline films can exhibit certain preferred orientations after crystallization on single crystal substrates.

1.2.2 Physical deposition

In this process mechanical, electromechanical or thermodynamic processes are used to produce a thin film. Commercial physical deposition system tends to require a low-pressure vapor environment to function properly; can be classified as **physical vapor deposition** (PVD).

Examples of physical deposition include:

- **Thermal evaporator:** In this method an electric resistance heater is used to melt the material and raise its vapor pressure to a useful range. This is done in a high vacuum and both to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber and reduce the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapor pressure than the heating element can be deposited without contamination of the film. Molecular beam epitaxy is a sophisticated form of thermal evaporation.

- **Electron beam evaporator:** In this process a high-energy beam is used to (from an electron gun) boil a small spot of material. As the heating is not uniform, lower vapor pressure materials can be deposited. The beam is usually bent through an angle of 270° in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rate for electron beam evaporation range from 1 to 10 nanometers per second.

- **Molecular beam epitaxy** (**MBE**)**:** This is one of the common methods of depositing single crystals. It was invented in the late 1960s at Bell Laboratories by J. R. Arthur and Alfred Y. Cho. This requires high or ultra vacuum. The most important property of MBE is the slow deposition rate (typically less than 1000 nm per hour), which allows the films to grow epitaxially. In this process slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compound like gallium arsenide is usually deposited by repeatedly applying a layer of one element (i.e., gallium), then a layer of the other (i.e., As), so that the process is chemical, as well as physical. The beam of material can be generated by either physical means (that is, by a furnace) or by a chemical reaction (chemical beam epitaxy). During operation, reflection high energy electron diffraction (RHEED) is used for monitoring the growth of the crystal layers.

- **Sputtering**: It requires plasma (usually a noble gas, such as argon) to knock material from a "target" a few atoms at a time. The target has to be kept at a relatively low temperature, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is mostly useful for compounds or mixtures, where different components have different evaporate at rates. Sputtering step coverage is more or less conformal. It is also widely used in the optical media. The manufacturing of CD, DVD, and BD are done with the help of this technique. It is a fast technique and also thickness can be controlled with good accuracy. Presently, nitrogen and oxygen gases can be also used in sputtering.

- **Pulsed laser deposition (PLD):** This is a thin film deposition technique where a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material so that the material can be deposited. This material is vaporized from the target which deposits it as a thin film on a substrate. This process is done in ultra high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films.

- **Cathodic arc deposition (arc-PVD)**: This is a physical vapor deposition technique in which an electric arc is used to vaporize material from a cathode target. The vaporized material then condenses on a substrate and forms a thin film. The technique is being done to deposit metallic, ceramic, and composite films.

- **Electro hydrodynamic deposition (Electro spray deposition):** This is a relatively new process of thin film deposition. The liquid can be deposited either in the form of nano-particle solution or simply a solution and it is fed to a small capillary nozzle (usually metallic) which is connected to a high power source. The substrate on which the film will be deposited is connected to the ground terminal of the power source. Through the influence of electric field the liquid comes out of the nozzle and takes a conical shape (Taylor cone) and at the apex of the cone a thin jet emanates which disintegrates into very fine and small positively charged droplets .The droplets keep getting smaller and smaller and finally get deposited on the substrate as a uniform thin layer.

CHAPTER-2

2.1 Spin Coating Process Theory

Spin coating has been used for several decades for the making of thin films. In this process involves depositing a small puddle of a fluid solution onto the center of a substrate and then spinning the substrate at high speed (typically around3000 rpm).Centripetal acceleration is the cause the solution to spread and the edge of the substrate leaving a thin film of solution on the surface. The film thickness and other properties depend on the nature of the solution (viscosity, drying rate, percent solids, surface tension, etc.) and the parameters taken for the spin process. Factors like rotational speed, acceleration, and fume exhaust contribute to how the properties of coated films are defined.

One of the most important factors in spin coating is repeatability. Any variations in the parameters that define the spin process can result in drastic variations in the coated film.

The followings are an explanation of some of the effects of these variations.

2.1.1 Spin Coating Process Description

A typical spin process consists of a dispense step in which the solution fluid is deposited onto the substrate surface, application of vacuum to hold the substrate tightly, a high speed spin step to thin the fluid, and a drying step to eliminate excess solvents from the film.

There are two common methods of dispense. One is Static dispense and another is Dynamic dispense. Static dispense is simply depositing a small amount of fluid or solution on or near the center of the substrate. It can range from 1 to 10 cc depending on the viscosity of the solution and the size of the substrate. Higher viscosity and or larger substrate typically require a larger puddle to ensure full coverage of the substrate.

Dynamic dispense is the process of dispensing while the substrate is moving at low speed. A speed of about 500 rpm is commonly used during this step of the process. This spreads the fluid over the substrate and results in less waste of solution material since it is usually not necessary to deposit as much to wet the entire surface of the substrate. This is an advantageous

method when the fluid or substrate itself has poor wetting abilities and can eliminate voids that may form.

After the dispense step a sufficient acceleration has to give to the substrate in order to get the desired thickness of the film. Typical spin speeds for this step range from 1500-3000 rpm, again it can be changed depending on the properties of the fluid as well as the substrate. This step takes from 10 seconds to several minutes. The combination of spin speed and time selected for this step generally decides the final film thickness. In general, higher spin speed and longer spin time creates thinner film.

Vacuum Pump

Vacuum is very essential in the process of spin coating. A vacuum pump is required to create vacuum. It holds the substrate tightly so that substrate can't be slipped. In the time of spinning it holds the substrate strongly and hence the sample is unaffected from any kind of breakage.

Spin Speed

Spin speed is one of the most important factors in spin coating. The speed of the substrate (rpm) affects the degree of radial (centrifugal) force applied to the liquid solution and also it's velocity. The high speed spin step generally decides the final film thickness. Relatively minor variations of ±50 rpm at this stage may cause a resulting thickness change of 10%. It can be controlled by the programming.

Acceleration

The acceleration of the substrate towards the final spin speed can also affect the coated film properties. Since the solution begins to dry during the first part of the spin cycle, it is important to accurately control acceleration. Acceleration also plays an important role in the coat properties of patterned substrates. The substrate surface should be smooth so that uniformly coat will occur. While the spin process in general provides a radial (out ward) force to the solution, it is the acceleration that provides a twisting force to the solution. It can be controlled by the programming.

Advantages

- This is a low cost method for preparation of thin film.
- Film uniformity is maintained and thickness can also be controlled.

2.2 Synthesis Route:

The ferroelectric thin film can be prepared in various methods. In the present study modified PT ceramics thin films were prepared by spin coating technique. The steps of synthesis are described below:

2.2.1 Preparation of PCT ($Pb_{0.67}Ca_{0.24}TiO_3$) :

Lead acetate trihydrate ($C_4H_6O_4Pb.3H_2O$) (5% extra Pb) =2.4790gm

Calcium acetate hydrate ($C_4H_6CaO_4.H_2O$) = 0.3109gm

Titanium Isopropoxide ($C_{12}H_{28}O_4Ti$) = 2.4377ml

Annealing Temperature = 600^0C for 20 mins

Annealing Temperature (for 2 hours) =$550^0C,600^0C,650^0C$

2.2.2 Optimization of synthesis route:

- The samples are prepared by spin coating method.
- The solvents chosen for the mixture of synthesis is 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 some extra (10ml) acetic acid is also mixed with the solution. After this mixing we dissolve lead acetate trihydrate by spinning method for 20 mins.
- When lead acetate was dissolved completely with the solution 0.3109gm of Calcium acetate hydrate is mixed with the solution.
- Now the color of the solution becomes milky white. After one hour of continuous stirring the solution is heated with a temperature of 100^0C. Now 3 hours of heating and stirring the solution became transparent.

- Then the Indium Tin Oxide (ITO) coated glasses are taken with proper size.
- This ITO coated glasses are kept on the spin coating machine and proper vacuum was maintained.
- Now the PCT solution is put on the substrate and the spin speed is maintained 2000rpm.
- After every two coatings the film is heated at a temperature 600^0C for 20 mins.
- Similarly we have made three films.
- Finally all the three samples were annealing at 550^0C, 600^0C and 650^0C for 2 hours separately.
- The samples are etched by hydrofluoric acid for the characterizations.
- **FLOW CHART**

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                    │    Precursors    │
                    └──────────────────┘
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         ┌───────────────────────────────────────┐
         │ Solvents (2methoxyethanol, acetic acid)│
         └───────────────────────────────────────┘
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            ┌────────────────────────────────┐
            │ Heating with Stirring (20mins)  │
            └────────────────────────────────┘
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            ┌────────────────────────────────┐
            │  Spin coating on ITO coated glass│
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            │  Annealing (600⁰C) for 20 mins  │
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    │ Annealing (550⁰C, 600⁰C and 650⁰C) for 2hours │
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    │ XRD, SEM, Thickness and Dielectric measurements│
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Precursors

Solvents (2methoxyethanol, acetic acid)

Heating with Stirring (20mins)

Spin coating on ITO coated glass

Annealing (600^0C) for 20 mins

Annealing (550^0C, 600^0C and 650^0C) for 2hours

XRD, SEM, Thickness and Dielectric measurements

2.3 CHARECTRERIZATION METHODS

2.3.1 MEASUREMENT OF THICKNESS OF THE FILM

The MTI-2100 fotonic sensor is a dual – channel fiber optic measurement system that performs noncontact displacement and vibration measurements. By using fiber optic technology, the MTI-2100 imposes no load on measurement target and not affected by magnetic and electrical fields.

The displacement motion ranging from 0.01 micro inch (0.25nm) to 0.2 inch (5.08mm) can be measured at frequencies ranging from DC to over 150 KHz.

PROBE MODULE DESCRIPTIONS:

Standard Probe module

The standard Probe modules and fiber optic probes are designed for making displacement measurements on reflective surfaces. Typically sensitivities of the standard probes range from less than 1 micro inch per volt (µin/mV) (0.025 micron per milivolt) to greater than 40 µin/mV (1 µm/mV). The probe specific sensitivity is labeled on the side of the plug- in module and the fiber optic cable jacket. The frequency responses range is from DC to 190 KHz.

High-resolution Probe module

The high-resolution Probe module and fiber optic probe is designed for making displacement measurements on reflective surfaces. The typical normal gain sensitivity of the high-resolution Probe is on the order of 0.2µin/mV (0.005µm/mV). The probe specific sensitivity is labeled on the side of the plug- in module and the fiber optic cable jacket. Note that two modes are provided. One provides normal range and the second is high sensitivity mode where linear range is usually traded off for higher sensitivity. The gain mode is typically 10 times more sensitivity than normal mode. The maximum liner range in normal gain mode is on the order of 1mil (25µm). The frequency response ranges from DC to 100 KHz.
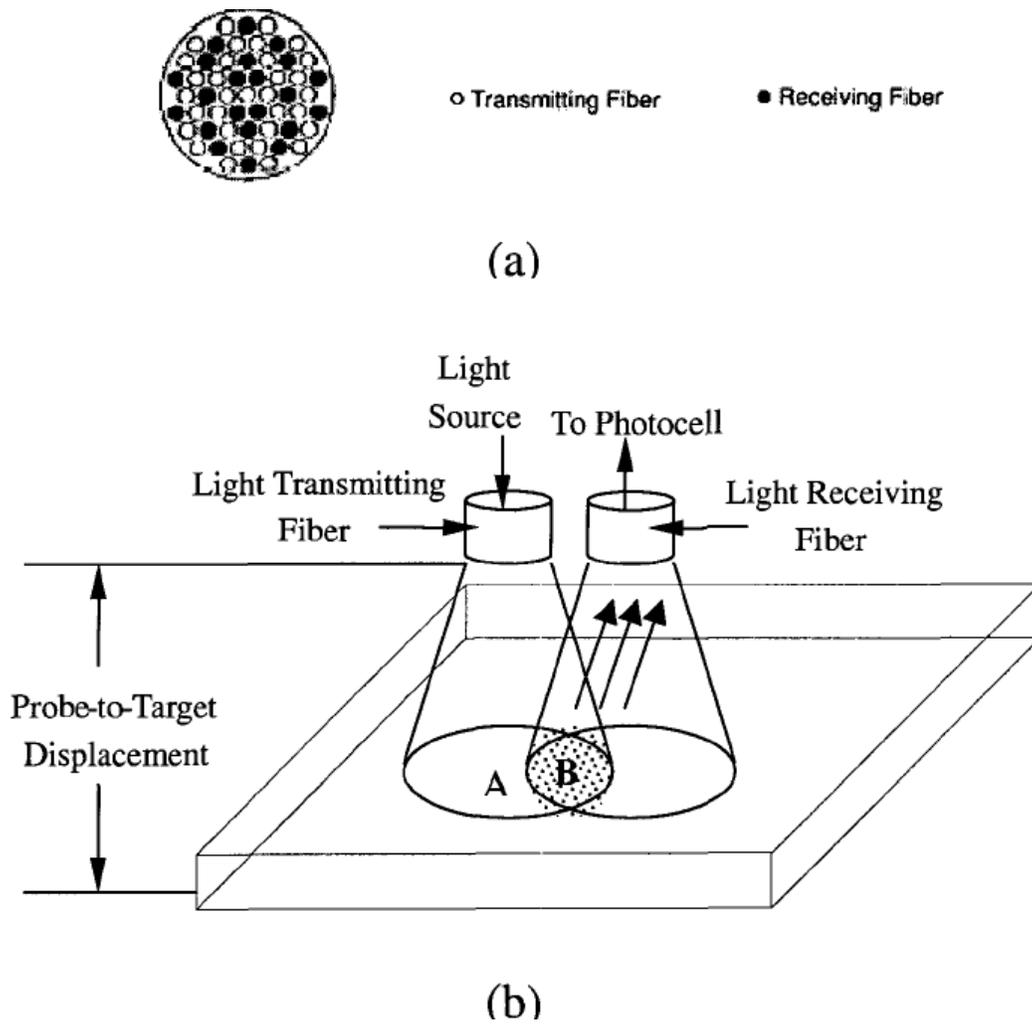
Fig.2.1. A setup for measurements of the strain vs. electric field loop. (a) Fiber – optical probe tip configurations; (b) Displacement sensing mechanism of adjacent fiber-optical elements.

2.3.2 X –RAY DIFFRACTION

- It is a non-destructive analytical technique which gives the information about the crystal structure, chemical composition, and physical properties of materials and thin films. This technique is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy

- The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's law i.e. $n\lambda = 2d\,\sin\theta$. Where n= integer and d= inter planar spacing

- It measures the average spacing between the layers or row of the atoms, find the crystal structure of unknown materials and determine the orientation of single crystal or grain.

- The different phases can be analyzed by the X-ray analysis.

- We can also get all the crystal parameters from the x- ray data by using the software.

Fig.2.2. Illustration of the constructive interference of the X-rays scattered from lattice planes.

2.3.3 SCANING ELECTRON MICROSCOPE (SEM)

- The Scanning Electron Microscope (SEM) is a special type of microscope that uses electrons rather than light to form an image.
- It can produce images of high resolution and with high magnification.
- The sample should be correctly prepared i.e. it should be conductive.
- The SEM can help for direct studying of the surfaces of solid objects
- SEM can allow a greater depth of focus than the optical microscope so for this reason the SEM can produce a better image of the three-dimensional sample.
- In SEM the electron beam moves in a vertical path through the column of the microscope and the beam passes through electromagnetic lenses which focus and direct the beam down towards the sample. When it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors can collect the secondary or backscattered electrons and it converts them to a signal that is sent to a viewing screen similar to the one in a normal television, producing an image.
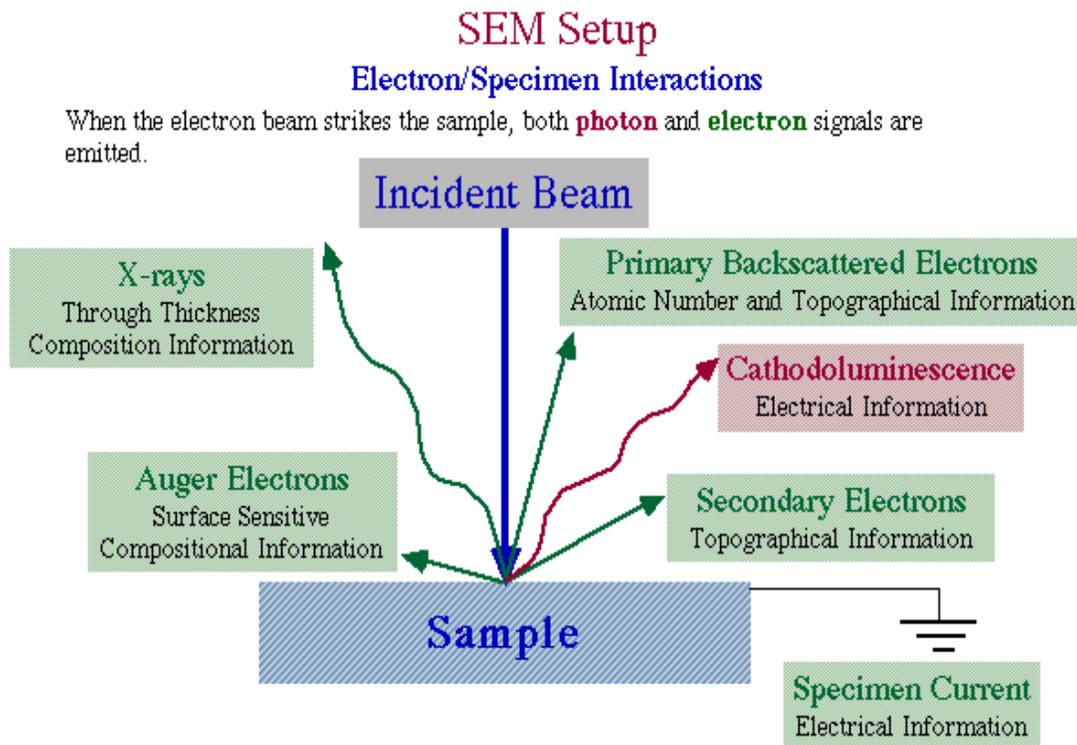
Fig.2.3. Various signals generated when electron beam strikes the sample

2.3.4 Dielectric property study:

Normally ferroelectric materials have high dielectric constant typically several hundred to several thousands. It can be calculated by using the formula

$$\varepsilon_r = (C.t)/\varepsilon_0 A$$

Where ε_r = dielectric constant

C= capacitance value

t= thickness of the film

A= area

ε_0= permittivity of free space

The dielectrics constants were measured by using **HIOKI 3532-50LCR** HIT ester.

The LCR meter is used to measure the electrical impedance. While operating it is capable of indentifying the measurement of steady electrical current. This is mainly helpful when we are dealing with alternative current. It will determine the relative change in the magnitude of the repetitive variation of the voltage and current known as amplitude. Inductance is a change in the flow of current through a circuit and some devices prevents this change, like resistor. This force there by generated is called as electromotive force. Because magnetic fields are produced by electric field which in turn reduces the change in current rate, the LCR will measure the ratio of magnetic flux.

CHAPTER-3

Results and Discussions

3.1 X-ray Diffraction Analysis:
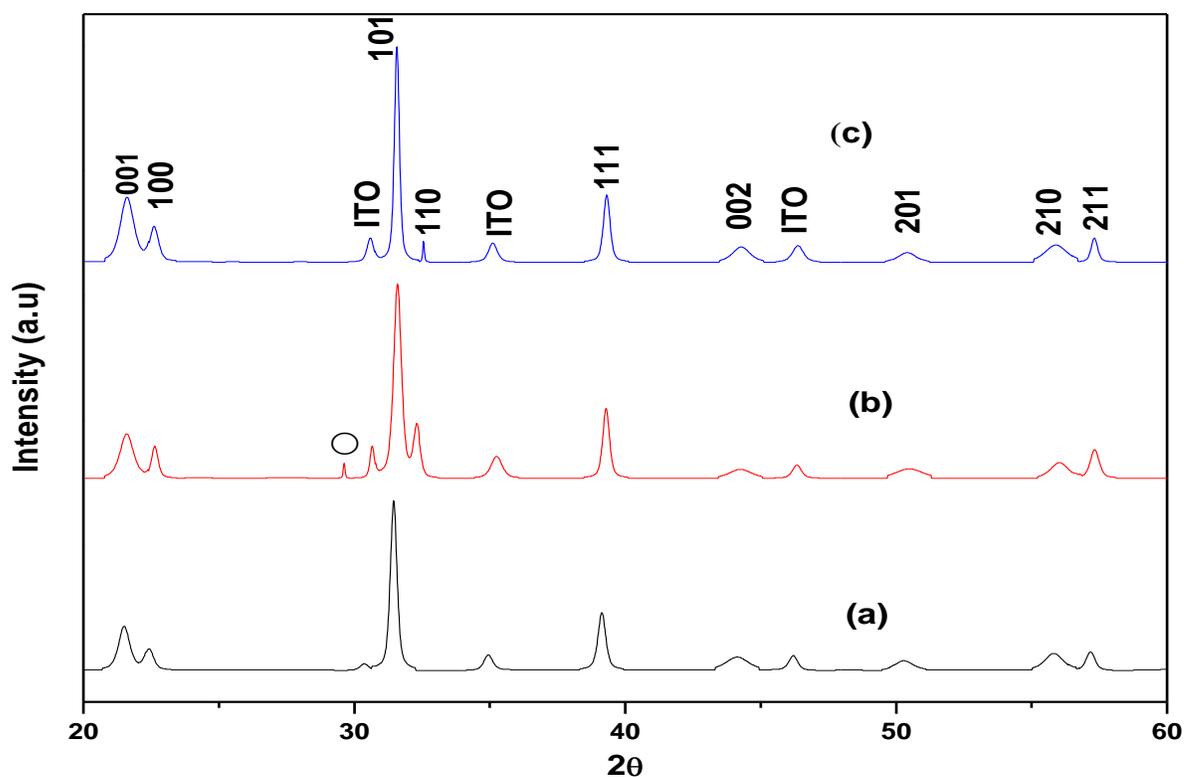
Fig. 3.1. XRD patterns of PCT thin films annealed at (a) 550^0C, (b) 600^0C and (c) 650^0C

The crystallographic structures of the thin films were examined by X-ray diffraction (XRD). These peaks show the film is tetragonal pervoskite structure and the ratio of c/a is nearly equal to 1.021. As we increase the temperature there will be loss of lead so the secondary phase is formed. Just below 30^0C it shows a small peak. This is known as pyrochloro phase [17]. The circle (O) shows the as pyrochloro phase.

3.2 SEM Analysis:

The surface morphology was studied by using the Scanning electron microscope (JSM 6480 LV JEOL,Japan).The SEM microstructure of all the samples are given below:
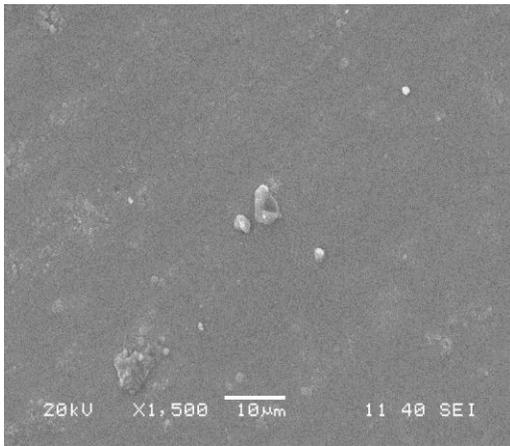
Fig3.2(a) SEM micrograph of PCT-550^{0}C
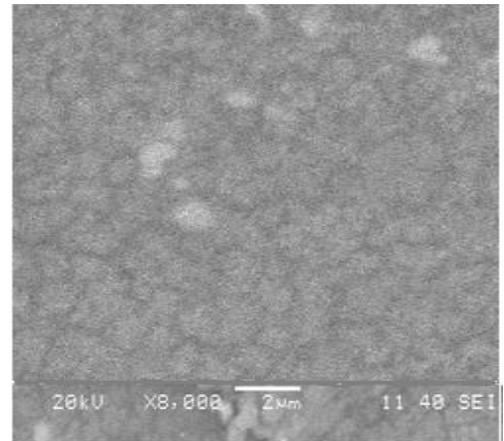
Fig3.2(b) SEM micrograph of PCT600^{0}C
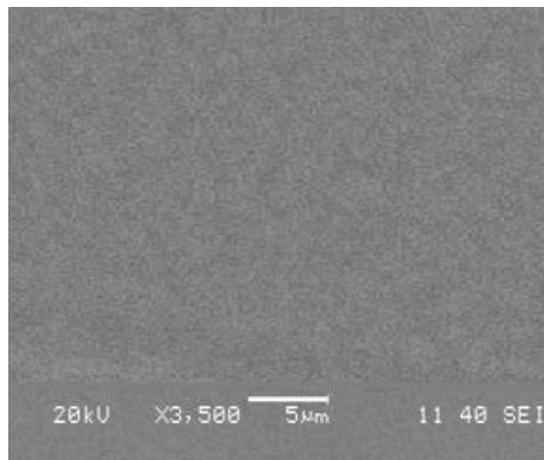
Fig3.2(c) SEM micrograph of PCT-650^{0}C

Fig 3.2. SEM macrographs of PCT thin films annealed at (a) 550^{0}C), (b) 600^{0}C and (c) 650^{0}C. Average grain size was found to be 1.25µm of the PCT thin film.

3.3 Dielectric Analysis:
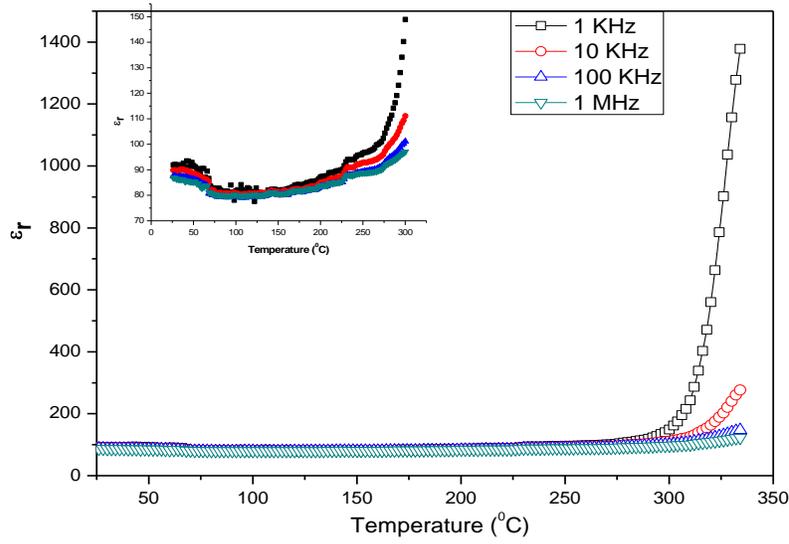
Fig3.3 (a) Temperature variation of ε_r of PCT thin film annealed at 550^0C
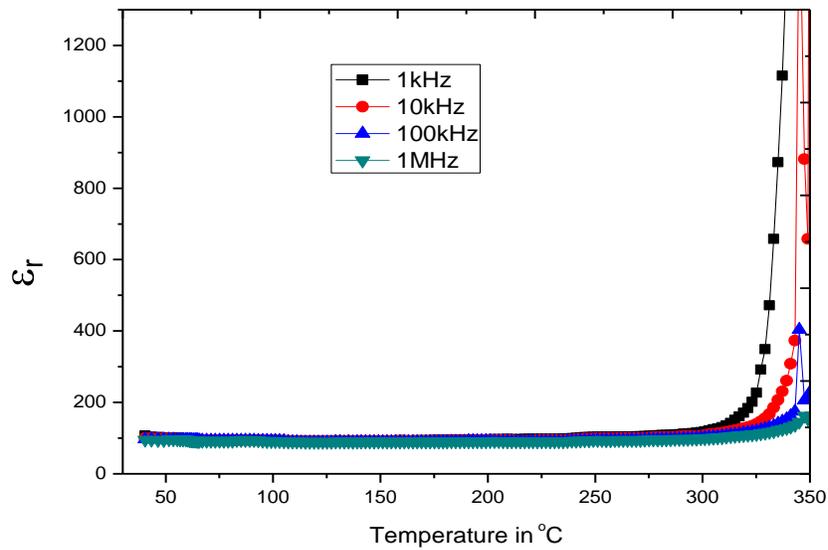
Fig3.3 (a) Temperature variation of ε_r of PCT thin film annealed at 600^0C
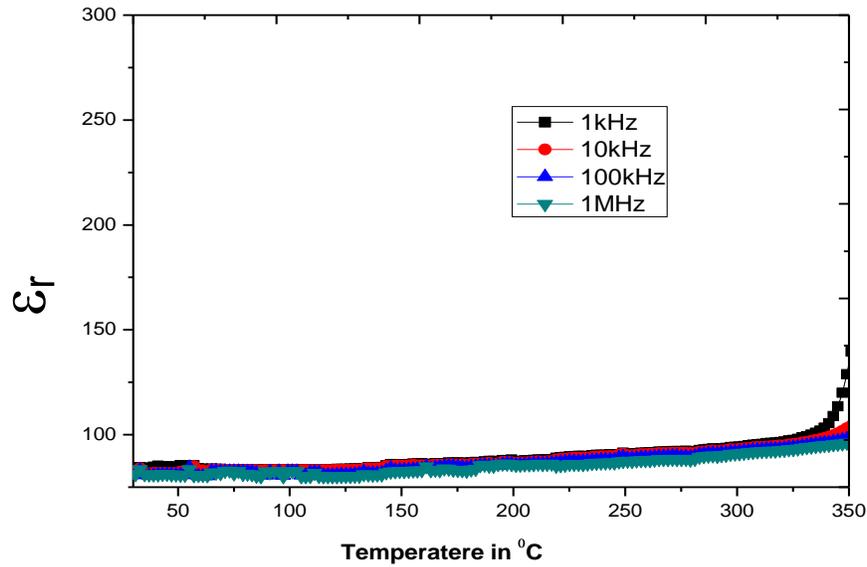
**Fig3.3 (b)** Temperature variation of ε_r of PCT thin film annealed at **650^0C**

Fig 3.3. Shows the temperature variation of dielectric constant of PCT thin films annealed at 550^0C, 600^OC and 650^0C of different frequencies 1 kHz, 10kHz, 100 kHz and 1 MHz, respectively. The value of dielectric constant is increasing with increase in temperature.

The increase in the value of dielectric constant with the increase of temperature is mainly due to large contribution of dipolar and space charge polarization. With the increase of frequency at constant temperature, the dipolar and space charge polarization is not able to cope with the changing field and therefore their contribution reduces. Electronic and ionic polarization is dominated in this range.
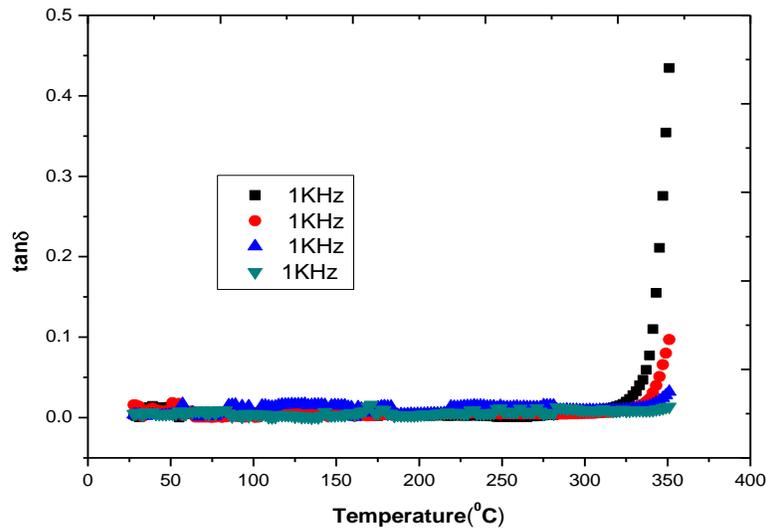
3.4 Dielectric loss:
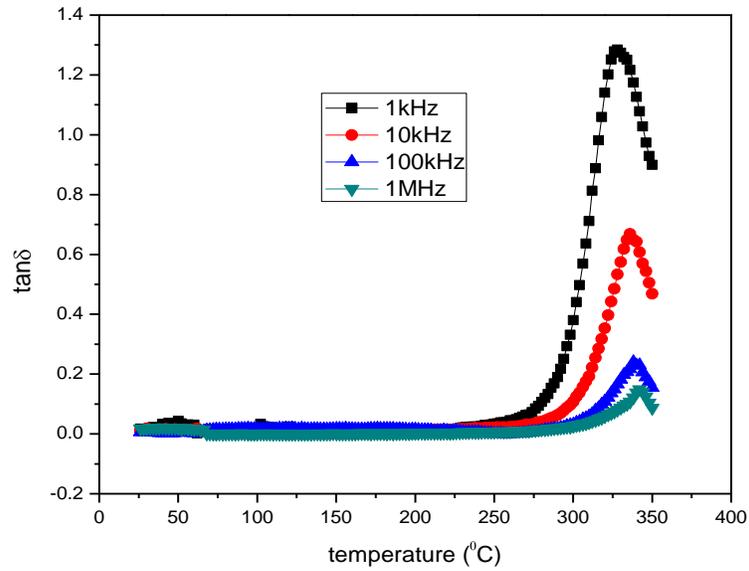
3.4(a) Dielectric loss of PCT thin films annealed at **550^{0}C**
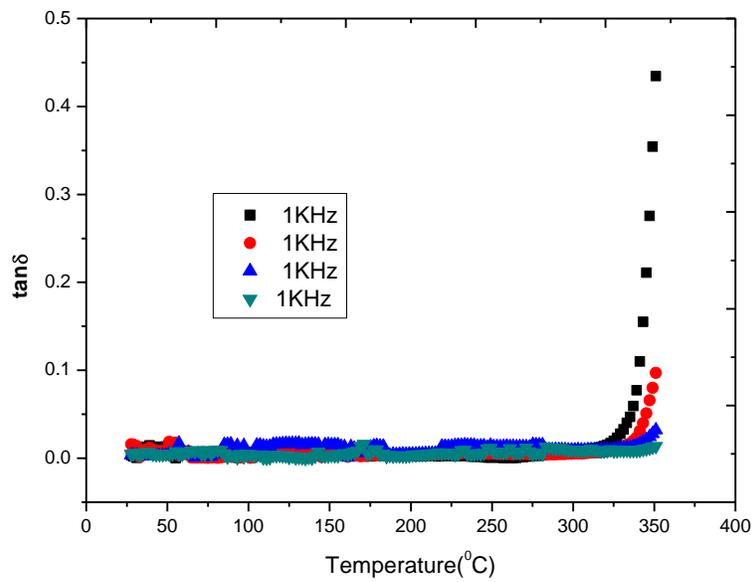
3.4(b) Dielectric loss of PCT thin films annealed at **600^{0}C**

3.4(c) Dielectric loss of PCT thin films annealed at **650⁰C**

Fig3.4 (a),(b)and (c) shows the variation of tanδ with frequency of PCT thin films annealed at 550⁰C, 600⁰C and 650⁰C respectively. Initially both ε_r and tanδ decreases with the increase in frequencies. The fall in arise the fact that polarization does not occur simultaneously with the application of electric field, which further due to the inertia of dipoles and the delay in response towards the impressed alternating electric field to dielectric loss and the decline in ε_r. At low frequencies all types of polarization contribute and as the frequency is increased, the polarization with large relaxation time cease to respond and hence the decrease in ε_r. At lower frequencies ε_r is maximum because the contribution from 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, the contributions from the polarization having high relaxation time cease resulting in the decrease in ε_r. The same type of frequency dependent dielectric behavior is found in many other ferroelectric ceramic systems.

CHAPTER – 4

CONCLUSIONS

- The XRD peaks gave the idea that there is a single pervoskite phase formation at lower annealing temperature (550^oC) and as we increased the annealing temperature, a secondary phase is formed, which is known as pyrochloro phase. The structure of the PCT thin film annealed at 550^oC was found to be tetragonal.

- SEM micrographs showed homogeneous and dense grain morphology of PCT thin films with grain size ~1.25µm.

- The temperature dependence of dielectric of PCT thin films was studied.

- Thickness of the PCT thin film was measured to be ~100nm.

- The dielectric constant of the PCT thin film annealed at 550^oC is ~ 90 and loss 0.01 at room temperature.

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