DEVELOPMENT OF HIGH DIELECTRIC CONSTANT MATERIALS FOR MEMORY APPLICATIONS

A DISSERTATION
Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
SOLID STATE ELECTRONIC MATERIALS

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CERTIFICATE

This is to certify that this work which is being presented by **Abhishek Kumar Singh** for his dissertation entitled **"Development of High Dielectric Constant Materials for Memory Applications"**, in partial fulfillment of the requirements for the award of degree of **Master of Technology** in **"Solid State Electronic Materials"** submitted in the Department of Physics, Indian Institute of Technology Roorkee, is an authentic record of his own work.

Dissertation Guide

Date: June, 2006
Place: IIT Roorkee, INDIA

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CANDIDATE’S DECLARATION

I hereby declare that the work which is being presented in this dissertation entitled, **“Development of High Dielectric Constant Materials for Memory Applications”** submitted towards the partial fulfillment of the requirements for the award of the degree of **Masters of Technology** in **“Solid State Electronic Materials,”** in the Department of Physics, IIT Roorkee, Roorkee is an authentic record of my own work under the supervision of **Dr. K. L. Yadav**, Department of Physics

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Date: 13-06-06

Place: ROORKEE **Abhishek Kumar Singh**

Abstract

Neodymium doped polycrystalline samples of PNdZT, $Pb_{1-3x/2}$ Nd_x $(Zr_{.65}Ti_{.35})$ O_3 wh x=.01,.03,.05,.07,.1 were prepared using conventional solid reaction route technique Studies the Nd^{+3} doped PZT reveal that donor doping at A-site. X-ray diffraction of these compou show that they can be formed in single phase at 1050°C.Pellets prepared from the ab powders were sintered at 1150°C.Detailed studies of the Dielectric constant(K) and loss tang of the compounds at different frequencies at room temperature and temperature(RT to criti temperature 350°C) suggest that the compounds undergo ferroelectric phase transition. T dielectric constant (K) is found to increase initially and then to decrease with increasing concentration.

Motivation

PNdZT with high dielectric constant can be used as a capacitor for high speed devices High materials are required for ULSI circuits, especially for DRAM (dynamic random acc memory).The storage capacitance in a DRAM has to maintain a certain value of capacitance proper operation .For a given capacitance, usually a minimum'd' is required to meet conditions of the maximum allowed leakage current and the minimum required break do voltage. For a planar structure area 'A' is reduced with increasing DRAM density. Therefo the dielectric constant of the material must be increased. Several high K-materials have b prepared, including titanates such as BST (Barium strontium titanate) and PZT (Lead Zirconi Titanate).

In the present work, we have synthesized Nd doped PZT ceramics with a general formula $Pb_{1-3x/2}$ Nd_x $(Zr_{.65}Ti_{.35})$ O_3 (X=.01,.03,.05,.07,.1) using the solid state reaction route .The eff of the Neodymium doping on the structural and electrical properties of the samples have b studied.

Organization of Report

The dissertation report focused on to study the dopant effects on the dielectric behaviour of the PZ

The rest of report is organized as follows

Chapter 1 presents brief description of the ceramics, its properties and different mode of synthesis.

Chapter 2 presents brief description about the dielectric and its existence in the materials.

Chapter 3 presents brief description about the Ferroelectricity , its properties and applications.

Chapter 4 presents brief description about the PZT and dopant effect on it.

Chapter 5 describes the different techniques involved in the process.

Chapter 6 discusses about the effect of the dopant on the PZT on its properties.

Chapter 7 conclusion and future scope of ?

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Chapter 1

Introduction to Ceramics

Ceramics

The word **ceramic** is derived from the Greek word (keramikos, "having to do with pottery"). The term covers inorganic non-metallic materials whose formation is due to the action of heat. Up until the 1950s or so, the most important of these were the traditional clays, made into pottery, bricks, tiles and the like, along with cements and glass. The traditional crafts are described in the article on pottery. A composite material of ceramic and metal is known as cermets.

Historically, ceramic products have been hard, porous and brittle. The study of ceramics consists to a large extent of methods to mitigate these problems, and accentuate the strengths of the materials, as well as to offer up unusual uses for these materials. While 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.

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; Piezoelectric - sonar; Semiconducting Oxides - environmental monitoring. Recent advances in these areas are described in the Journal of Electroceramics.

1.1 Dielectric ceramics

Dielectric materials used for construction of ceramic capacitors include zirconium barium titanate, strontium titanate (ST), calcium titanate (CT), magnesium titanate (MT), calcium magnesium titanate (CMT), zinc titanate (ZT), lanthanum titanate (TLT), and neodymium titanate (TNT), barium zirconate (BZ), calcium zirconate (CZ), lead magnesium niobate (PMN), lead zinc niobate (PZN), lithium niobate (LN), barium stannate (BS), calcium stannate (CS), magnesium aluminium silicate, magnesium silicate, barium tantalate, titanium dioxide, niobium oxide, zirconia, silica, sapphire, beryllium oxide, and zirconium tin titanate

Some piezoelectric materials can be used as well; the EIA Class 2 dielectrics are based on mixtures rich on barium titanate. In turn, EIA Class 1 dielectrics contain little or no barium titanate.

1.2 Piezoelectric ceramics

Commercially used piezoceramic is primarily lead zirconate titanate (PZT). Barium titanate (BT), strontium titanate (ST), quartz, and others are also used. Even non-ceramic materials can be used.polyvinylidene fluoride is a plastic used for its piezoelectric properties

The American Society for Testing and Materials (ASTM) defines a ceramic article as "an article having a glazed or unglazed body of crystalline or partly crystalline structure, or of glass, which body is produced from essentially inorganic, nonmetallic substances and either is formed from a molten mass which solidifies on cooling, or is formed and simultaneously or subsequently matured by the action of the heat."

The word ceramic can be an adjective, and can also be used as a noun to refer to a ceramic material. Ceramics is a singular noun referring to the art of making things out of ceramic materials

Commonwealth English, ceramic can also be used as a singular noun, referring to an object made of ceramic material Classifications of technical ceramics

Technical Ceramics can also be classified into three distinct material categories:

- Oxides: Alumina, zirconia
- Non-oxides: Carbides, borides, nitrides, silicides
- Composites: Particulate reinforced, combinations of oxides and non-oxides.

Each one of these classes can develop unique material properties

Examples of ceramic materials

- Barium titanate (often mixed with strontium titanate) displays ferroelectricity, meaning that its mechanical, electrical, and thermal responses are coupled to one another and also history-dependent. It is widely used in electromechanical transducers, ceramic capacitors, and data storage elements. Grain boundary conditions can create PTC effects in heating elements.
- Bismuth strontium calcium copper oxide, a high-temperature superconductor
- Boron carbide (B_4C), which is used in some helicopter and tank armor.
- Boron nitride is structurally isoelectronic to carbon and takes on similar physical forms: a graphite-like one used as a lubricant, and a diamond-like one used as an abrasive.
- Bricks (mostly aluminium silicates), used for construction.
- Earthenware, which is often made from clay, quartz and feldspar.
- Ferrite (Fe_3O_4), which is ferrimagnetic and is used in the core of electrical transformers and magnetic core memory.
- Lead zirconate titanate is another ferroelectric material.
- Magnesium diboride (MgB_2), which is an unconventional superconductor.
- Porcelain, which usually contains the clay mineral kaolinite.
- Silicon carbide (SiC), which is used as a susceptor in microwave furnaces, a commonly used abrasive, and as a refractory material.
- Silicon nitride (Si_3N_4), which is used as an abrasive powder.
- Steatite is used as an electrical insulator.
- Uranium oxide (UO_2), used as fuel in nuclear reactors.

- Yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$); another high temperature superconductor.
- Zinc oxide (ZnO), which is a semiconductor, and used in the construction of varistors.
- Zirconia, which in pure form undergoes many phase changes between room temperature and practical sintering temperatures, can be chemically "stabilized" in several different forms. Its high oxygen ion conductivity recommends it for use in fuel cells. In another variant, metastable structures can impart transformation toughening for mechanical applications; most ceramic knife blades are made of this material.

1.3 Properties of ceramics

1.3.1 Mechanical properties

Ceramic materials are usually ionic or covalently-bonded materials, and can be crystalline or amorphous. A material held together by either type of bond will tend to fracture before any plastic deformation takes place, which results in poor toughness in these materials. Additionally, because these materials tend to be porous, the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength. These combine to give catastrophic failures, as opposed to the normally much more gentle failure modes of metals.

These materials do show plastic deformation. However, due to the rigid structure of the crystalline materials, there are very few available slip systems for dislocations to move, and so they deform very slowly. With the non-crystalline (glassy) materials, viscous flow is the dominant source of plastic deformation, and is also very slow. It is therefore neglected in many applications of ceramic materials.

1.3.2 Electrical properties

1. Semiconductivity

There are a number of ceramics that are semiconductors. Most of these are transition metal oxides that are II-VI semiconductors, such as zinc oxide.

While there is talk of making blue LEDs from zinc oxide, ceramicists are most interested in the electrical properties that show grain boundary effects.

One of the most widely used of these is the varistor. These are devices that exhibit the unusual property of negative resistance. Once the voltage across the device reaches a certain threshold, there is a breakdown of the electrical structure in the vicinity of the grain boundaries, which results in its electrical resistance dropping from several megaohms down to a few hundred ohms. The major advantage of these is that they can dissipate a lot of energy, and they self reset — after the voltage across the device drops below the threshold, its resistance returns to being high.

This makes them ideal for surge-protection applications. As there is control over the threshold voltage and energy tolerance, they find use in all sorts of applications. The best demonstration of their ability can be found in electrical substations, where they are employed to protect the infrastructure from lightning strikes. They have rapid response, are low maintenance, and do not appreciably degrade from use, making them virtually ideal devices for this application.

Semiconducting ceramics are also employed as gas sensors. When various gases are passed over a polycrystalline ceramic, its electrical resistance changes. With tuning to the possible gas mixtures, very inexpensive devices can be produced.

2 Superconductivity

Under some conditions, such as extremely low temperature, some ceramics exhibit superconductivity. The exact reason for this is not known, but there are two major families of superconducting ceramics.

1.4 Ferroelectricity and subsets

Piezoelectricity, a link between electrical and mechanical response, is exhibited by a large number of ceramic materials, including the quartz resonators used to measure time in watches and other electronics. Such devices use both properties of piezoelectric, using electricity to produce a mechanical motion (powering the device) and then using this mechanical motion to produce electricity (generating a signal). The unit of time measured is the natural interval required for electricity to be converted into mechanical energy and back again.

The piezoelectric effect is generally stronger in materials that also exhibit pyroelectricity, and all pyroelectric materials are also piezoelectric. These materials can be used to interconvert between thermal, mechanical, and/or electrical energy; for instance, after synthesis in a furnace, a pyroelectric crystal allowed to cool under no applied stress generally builds up a static charge of thousands of volts. Such materials are used in motion sensors, where the tiny rise in temperature from a warm body entering the room is enough to produce a measurable voltage in the crystal.

In turn, pyroelectricity is seen most strongly in materials which also display the ferroelectric effect, in which a stable electric dipole can be oriented or reversed by applying an electrostatic field. Pyroelectricity is also a necessary consequence of ferroelectricity. This can be used to store information in ferroelectric capacitors, elements of ferroelectric RAM.

The most common such materials are lead zirconate titanate and barium titanate. Aside from the uses mentioned above, their strong piezoelectric response is exploited in the design of high-frequency loudspeakers, transducers for sonar, and actuators for atomic force and scanning tunneling microscopes.

1.4.1 Positive thermal coefficient

Increases in temperature can cause grain boundaries to suddenly become insulating in some semiconducting ceramic materials, mostly mixtures of heavy metal titanates. The critical transition temperature can be adjusted over a wide range by variations in chemistry. In such materials, current will pass through the material until joule heating brings it to the transition temperature, at which point the circuit will be broken and current flow will cease. Such ceramics are used as self-controlled heating elements in, for example, the rear-window defrosts circuits of most automobiles.

At the transition temperature, the material's dielectric response becomes theoretically infinite. While a lack of temperature control would rule out any practical use of the material near its critical temperature, the dielectric effect remains exceptionally strong even at much higher temperatures. Titanates with critical temperatures far below room temperature have become synonymous with "ceramic" in the context of ceramic capacitors for just this reason.

1.4.2 Processing of ceramic materials

Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten, by casting, or when in a state of toffee-like viscosity, by methods such as blowing to a mould. If later heat-treatments cause this class to become partly crystalline, the resulting material is known as a glass-ceramic.

Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories - either makes the ceramic in the desired shape, by reaction in situ, or by "forming" powders into the desired shape, and then sintering to form a solid body. Ceramic forming techniques include shaping by hand (sometimes including a rotation process called "throwing"), slip casting, tape casting (used for making very thin ceramic capacitors, etc.), injection molding, dry pressing, and other variations. A few methods use a hybrid between the two approaches.

1.5 In situ manufacturing

The most common use of this method is in the production of cement and concrete. Here, the dehydrated powders are mixed with water. This starts hydration reactions, which result in long, interlocking crystals forming around the aggregates. Over time, these result in a solid ceramic.

The biggest problem with this method is that most reactions are so fast that good mixing is not possible, which tends to prevent large-scale construction. However, small-scale systems can be made by deposition techniques, where the various materials are introduced above a substrate, and react and form the ceramic on the substrate. This borrows techniques from the semiconductor industry, such as chemical vapour deposition, and is very useful for coatings. These tend to produce very dense ceramics, but do so slowly.

1.5.1 Sintering-based methods

The principles of sintering-based methods are simple. Once a roughly held together object (called a "green body") is made, it is baked in a kiln, where diffusion processes because the green body to shrink. The pores in the object close up, resulting in a denser, stronger product. The firing is done at a temperature below the melting point of the ceramic. There is virtually always some porosity left, but the real advantage of this method is that the green body can be produced in any way imaginable, and still be sintered. This makes it a very versatile route.

There are thousands of possible refinements of this process. Some of the most common involve pressing the green body to give the densification a head start and reduce the sintering time needed. Sometimes organic binders such as polyvinyl alcohol are added to hold the green body together; these burn out during the firing (at 200-350°C). Sometimes organic lubricants are added during pressing to increase densification. It is not uncommon to combine these, and add binders and lubricants to a powder, then press. (The formulation of these organic chemical additives is an art in itself. This is particularly important in the manufacture of high performance ceramics such as those used by the billions for electronics, in capacitors, inductors, sensors, etc.Slurry can be used in place of a powder, and then cast into a desired shape, dried and then sintered. Indeed, traditional pottery is done with this type of method, using a plastic mixture worked with the hands.

If a mixture of different materials is used together in a ceramic, the sintering temperature is sometimes above the melting point of one minor component - a liquid phase sintering. This result in shorter sintering times compared to solid state sintering.

1.6 Other applications of ceramics

In the early 1980s, Toyota researched production of an adiabatic ceramic engine which can run at a temperature of over 6000 °F (3300 °C). Ceramic engines do not require a cooling system and hence allow a major weight reduction and therefore greater fuel efficiency. Fuel efficiency of the engine is also higher at high temperature. In a conventional metallic engine, much of the energy released from the fuel must be dissipated as waste heat in order to prevent a meltdown of the metallic parts.

Despite all of these desirable properties, such engines are not in production because the manufacturing of ceramic parts in the requisite precision and durability is difficult. Imperfection in the ceramic leads to cracks, which can lead to potentially dangerous equipment failure. Such engines are possible in laboratory settings, but mass-production is infeasible with current technology.

Work is being done in developing ceramic parts for gas turbine engines. Currently, even blades made of advanced metal alloys used in the engines' hot section require cooling and careful limiting of operating temperatures. Turbine engines made with ceramics could operate more efficiently, giving aircraft greater range and payload for a set amount of fuel.

Since the late 1990s highly specialized ceramics, usually based on boron carbide, formed into plates and lined with Spectra, have been used in ballistic armored vests to repel large-caliber rifle fire. Such plates are known commonly as small-arms protective inserts (SAPI). Very similar technology is used for armoring of cockpits of some military airplanes, because of the low weight of the material.

Recently, there have been advances in ceramics which include bio-ceramics, such as dental implants and synthetic bones. Hydroxyapatite, the natural mineral component of bone, has been made synthetically from a number of biological and chemical sources and can be formed into ceramic materials. Orthopedic implants made from these materials bond readily to bone and other tissues in the body without rejection or inflammatory reactions. Because of this, they are of great interest for gene delivery and tissue engineering scaffolds. Most Hydroxyapatite ceramics are very porous and lack mechanical strength and are used to coat metal orthopedic devices to aid in forming a bond to bone or as bone fillers. They are also used as fillers for orthopedic plastic screws to aid in reducing the inflammation and increase absorption of these plastic materials. Work is being done to make strong-fully dense nano crystalline Hydroxapatite ceramic materials for orthopedic weight bearing devices, replacing foreign metal and plastic orthopedic materials with a synthetic natural bone mineral. Ultimately these ceramic materials may be used as bone replacements or with the incorporation of protein collagens, synthetic bones [2].

Dielectric polarization

The source of the dielectric displacement _D is given by the density of free (conducting) charges ρ:

$$divD = \rho \quad (1)$$

The overall charge neutrality of matter in an external field is described by

$$D = \varepsilon_0 E + P \quad (2)$$

The vacuum contribution caused by the externally applied electric field is represented by the term ε_0 E, and the electrical polarization of the matter in the system is described by P. This relation is independent of the nature of the polarization which could be pyroelectric Polarization, by piezoelectric polarization or dielectric polarization (by an external electric field).

For a pure dielectric response of the matter the polarization is proportional to the electric field in a linear approximation by

$$P = \varepsilon_0 \chi E \quad (3) \qquad D = \varepsilon_0 \varepsilon_r P \quad (4)$$

The macroscopic polarization P is the sum of all the individual dipole moments pj of the material with the density Nj

$$p = \sum_j N_j P_j \quad (5)$$

A dipole moment is induced by the electric field at the position of the particle which is called the local electric field E_{loc}

$$P = \alpha E_{loc} \quad (6)$$

where α is the polarizability of an atomic dipole. If there is no interaction between the polarized particles, the local electric field is identical to the externally applied electric field $E_{loc} = E_0$, resulting in a simple relation between the susceptibility and the polarizability

$$\varepsilon_0 \chi = N_j \alpha_j \quad (7)$$

For cubic structures and for induced dipoles (ionic and electronic polarization), the calculation reveals a relation between the atomic polarizability α and the macroscopic permittivity $\varepsilon = \varepsilon_0 \varepsilon_r$ which is referred to the Clausius-Mossotti equation

$$\varepsilon = \frac{\varepsilon_0 + 2N_j\alpha_j}{\varepsilon_0 - N_j\alpha_j} \qquad (8)$$

2.1 Mechanisms of polarization:

- **Electronic polarization** exists in all dielectrics. It is based on the displacement of the negatively charged electron shell against the positively charged core. The electronic polarizability α_{el} is approximately proportional to the volume of the electron shell.

- **Ionic polarization** is observed in ionic crystals and describes the displacement of the positive and negative sub lattices under an applied electric field.

- **Orientation polarization** describes the alignment of permanent dipoles. At ambienttemperatures, usually all dipole moments have statistical distribution of their directions.An electric field generates a preferred direction for the dipoles, while the thermal movement of the atoms perturbs the alignment. The average degree of orientation is given by the Langevin function $<\alpha_{or}>= P^2/3k_BT$ where k_B denotes the Boltzmann constant and T the absolute temperature

- **Space charge polarization** could exist in dielectric materials which show spatial in homogeneities of charge carrier densities. Space charge polarization effects are not only of importance in semiconductor field-effect devices, they also occur in ceramics with electrically conducting grains and insulating grain boundaries (so-called Maxwell-Wagner polarization).

- **Domain wall polarization** plays a decisive role in ferroelectric materials and contributes to the overall dielectric response. The motion of a domain wall that separates regions of different oriented polarization takes place by the fact that favored oriented domains with respect to the applied field tends to grow.

The total polarization of dielectric material results from all the contributions discussed above. The contributions from the lattice are called intrinsic contributions, in contrast to extrinsic contributions

$$\varepsilon = \varepsilon_{elec} + \varepsilon_{ion} + \varepsilon_{or} + \varepsilon_{dw} + \varepsilon_{sc} \qquad (9)$$

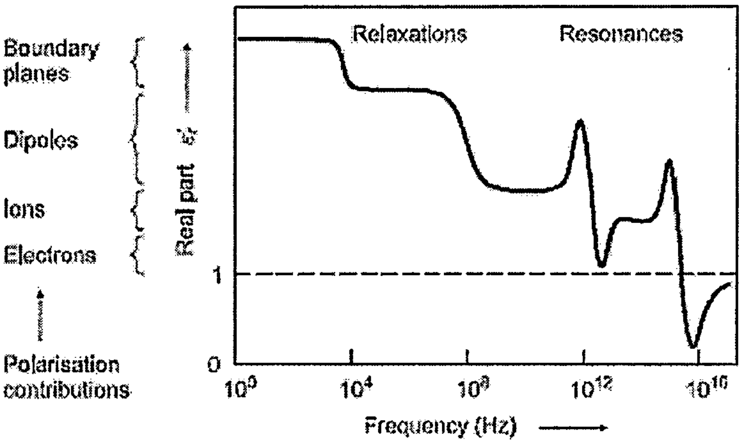


Figure 2.1: Frequency dependence of real part of the dielectric function

The dispersion of the dielectric response of each contribution leads to dielectric losses of the matter which can be mathematically expressed by a complex dielectric permittivity:

$$\varepsilon = \varepsilon' + i\varepsilon'' \qquad (10)$$

Dielectric losses are usually described by the loss tangent:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (11)$$

It should be taken into account that the general definition of the tan δ is related to the ratio of loss energy and reactive energy (per period), i. e. all measurements of the loss tangent also include possible contributions of conductivity of a non-ideal dielectric given by[1].

$$\tan\delta = \frac{\sigma}{\omega\varepsilon'} \qquad (12)$$

Chapter 3

FERROELECTRICITY AND ITS APPLICATIONS

In physics, the **ferroelectric effect** is an electrical phenomenon whereby certain ionic crystals and piezoelectric polymers may exhibit a spontaneous dipole moment, which can be reversed by the application of an electric field. The term ferroelectricity is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment.

There are two main types of ferroelectrics: displacive and order-disorder. The effect in barium titanate, a typical ferroelectric of the displacive type, is due to a polarization catastrophe, in which, if an ion is displaced from equilibrium slightly, the force from the local electric fields due to the ions in the crystal increase faster than the elastic restoring forces. This leads to an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment. In an order-disorder ferroelectric, there is a dipole moment in each unit cell, but at high temperatures they are pointing in random directions. Upon lowering the temperature and going through the phase transition, the dipoles order, all pointing in the same direction within a domain. Another important ferroelectric material is lead zirconate titanate.

Ferroelectric crystals often show several Curie points and domain structure hysteresis, much as do ferromagnetic crystals. By analogy to magnetic core memory, this hysteresis can be used to store information in ferroelectric RAM, which has ferroelectric capacitors as memory cells. The nature of the phase transition in some ferroelectric crystals is still not well understood.

Ferroelectrics often have very large dielectric constants, and thus are often used as the dielectric material in capacitors. They also often have unusually large nonlinear optical.

3.1 Structural Phase Transitions:

It is not common for crystals to transform from one crystal structure to another as the temperature or pressure is varied. The stable structure A at absolute zero generally has the lowest accessible internal energy of all the possible structures. Even this selection of a structure A can be varied with application of pressure, because a low atomic volume will favour closest-packed or even metallic structures.

Some other structure B may have a softer or lower frequency phonon spectrum than A. As the temperature is increased the phonons in B will be more highly excited (higher thermal average occupancies) than the phonons in A.Becauese the entropy of B will become higher than the entropy of A as the temperature is increased.

It is thereby possible for the stable structure to transform from A to B as the temperature is increased. The stable structure at a temperature T is determined by the minimum of the free energy F=U-TS. There will be a transition from A to B if a temperature Tc exists (below the Melting point).

Often several structures have nearly the same internal energy at absolute zero. The phonon dispersion relations for the structure may, however be rather different .The phonon energies are sensitive to the number and arrangement of nearby atoms; these are the quantities that change as the structure is changed.

Some structural phase transitions have only small effects on the macroscopic physical properties of the material [2].

3.2 Ferroelectric polarization

An ideal single crystal shows a P(E) behavior as depicted in Figure 1.6. The non-ferroelectric dielectric ionic and electronic polarization contributions are clearly linear, and are supposed by the spontaneous polarization Ps (dashed curve in Figure 1.6). To reverse the polarization an electrical field with an amplitude > Ec is required. In opposite to single crystals in polydomain ferroelectric ceramics, the remnant polarization Pr is smaller than the spontaneous one Ps due to back switching even for opposite fields as shown in Figure. In that case Ps can be estimated by extrapolation of (non-switching) P-values to E →0 [1].

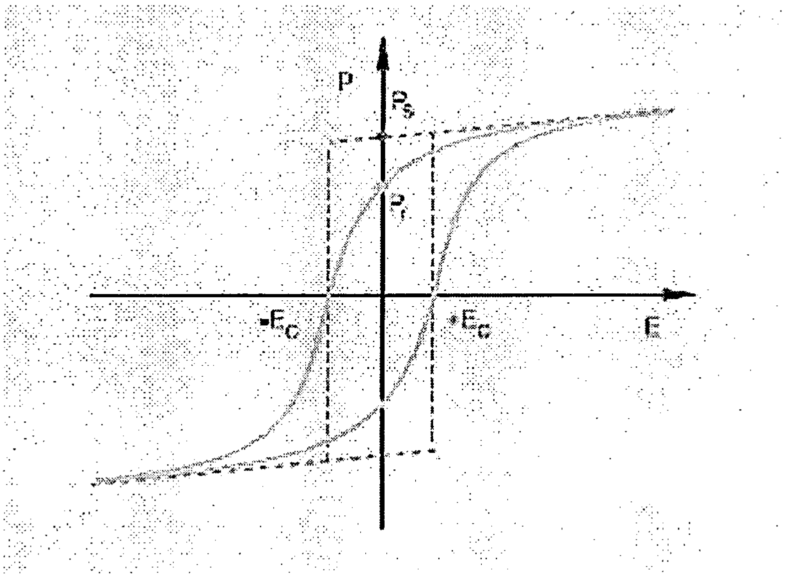


Figure 3.1: Ferroelectric hysteresis of single domain single crystal (dashed line) and polylycrystalline sample (full line)

The inverse susceptibility as well as the dielectric permittivity follows a Curie-Weiss law

$$\chi^{-1} \approx \varepsilon^{-1} \propto (T - \Theta) \qquad (1)$$

3.3 Theory of Ferroelectric Phase Transition

Ginzburg-Landau Theory

The Ginzburg-Landau theory is equivalent to a mean field theory considering the thermodynamic entity of the dipoles in the mean field of all the others. It is reasonable if the particular dipole interacts with many other dipoles. The theory introduces an order parameter P, i.e. the polarization, which for a second order phase transition diminishes continuously to zero at the phase transition temperature Tc [3]. Close to the phase transition, therefore, the free energy may be written as an expansion of powers of the order parameter. All the odd powers of P do not occur because of symmetry reasons

$$F(P,T) = \frac{1}{2} g_2 P^2 + \frac{1}{4} g_4 P^4 + \frac{1}{6} g_6 P6 \qquad (2)$$

The highest expansion coefficient (here g_6) needs to be larger than zero because otherwise the free energy would approach minus infinity for large P.All coefficients depend on the temperature and in particular the coefficient g_2. Expanding g_2 in a series of T around the Curie temperature Θ which is equal to or less than the phase transition temperature Tc, we can approximate:

$$g_2 = \frac{1}{c}(T - \Theta) \qquad (3)$$

Stable states are characterized by minima of the free energy with the necessary and sufficient conditions:

$$\frac{\partial F}{\partial P} = P(g_2 + g_4 P^2 + g_6 P^4) = 0 \qquad (4)$$

and

$$\frac{\partial^2 F}{\partial P^2} = \frac{1}{\chi} = g_2 + 3g_4 P + 5g_6 P^3 > 0 \qquad (5)$$

Two cases are to distinguish: (i) $g_4 > 0 \Rightarrow g6 \approx 0$ which corresponds to a phase transition of second order, and (ii) $g4 < 0 \Rightarrow g6 > 0$ which is related with a phase transition of first order. In both cases, the trivial solution P = 0 exists, representing the paraelectric phase
A comparison of above equation found the curie-wiess law (3),

$$\chi = \frac{C}{(T - \theta)} \qquad (6)$$

3.4 Ferroelectric Random Accessory Memory:

3.4.1 Ferroelectric RAM (FRAM or FeRAM) is a type of non-volatile computer memory that uses a ferroelectric capacitor to store a binary state (0 or 1) as two voltages. It uses one or two transistors to read and write the capacitor similar to EEPROM but based on electric field orientation and with near-unlimited number (exceeding 10^{10} for 5V devices and even more for 3.3V ones) of write-erase cycles. The main vendor of FRAM chips is Ramtron International.

Constructionally, FRAM is an array of ferroelectric capacitors, a DRAM with the dielectric layer in the memory capacitors replaced with a thin ferroelectric film, typically made of Lead Zirconium Titanate (PZT). The resulting cell is electrically similar to the capacitors used in a conventional DRAM cell, but the ferroelectric film will retain a electric field even after the charge in the capacitors (quickly) drains. Depending on the direction of the current flow when the cell is charged, the film will be polarized into one of two directions.

The bit is read by applying an electric field across the capacitor. If the cell is currently in a "1" state the magnetic field will resist the voltage, and will not allow current to flow until it reaches a critical point at a somewhat higher voltage. Measuring this voltage allows the memory device to read the current state of the cell, revealing it to be "1". If the cell had been in the "0" state, the voltage would remain lower, revealing the "0". However reading the cell also flips the polarity of the magnetic field, meaning that all reads must be followed by a write to restore the contents, just as on DRAM.

Generally the operation of FRAM is similar to ferrite core memory, one of the primary forms of computer memory in the 1960s. In comparison, FRAM requires far less power to flip the state of the film's polarity, and does so much faster. The requirement for a write cycle for each read cycle, together with the high but not infinite write cycle limit, poses a potential problem for some special applications.

Physically FRAM is almost identical to current DRAMs, with the additional ferroelectric layer. Since the charge quickly drains from the capacitor, DRAMs must be continually "refreshed" with additional current. Unlike DRAM, the charge stored in the capacitor does not form the memory in FRAM cells. Although the power needed to read or write an FRAM cell is thus slightly higher than in a DRAM, there is no need for power when idle, meaning that overall power use is dramatically reduced. Additionally FRAM will retain its contents with no power at all.

It is possible to make FRAM cells using two additional masking steps during normal semiconductor manufacture, leading to the possibility of full integration of FRAM into microcontrollers and other chips. Flash typically requires nine masks. This makes FRAM particularly attractive as an embedded non-volatile memory on microcontrollers, where the simpler process can reduce costs. However, the materials used to make FRAMs are not commonly used elsewhere in integrated circuit manufacturing. Both the PZT ferroelectric layer and the noble metals used for electrodes raise process compatibility and contamination issues.

FRAM does not yet offer the bit density of DRAM and SRAM, but is non-volatile, is faster than Flash/EEPROM memory (write times under 100 nanoseconds, roughly as fast as reading), and has very low power requirements, as unlike the EEPROMs they do not require a charge pump. It is expected to replace EEPROM chips in applications where very many write cycles are required. The very low current consumption makes them suitable for contact less chip cards.

In theory, however, FRAM can be scaled to much smaller cell sizes than currently being utilized. Bulk ferroelectric materials can be self-organized into small magnetic domains only a few nanometers across, known as quantum dots. If a manufacturing technique evolves that allows circuits to be able to interact with these dots, FRAM will have cell sizes on the order of 5 nm, in comparison with Flash which is currently having real difficulty scaling below 65 nm.

Even without this sort of miniaturization, FRAM uses less components per cell (bit) than Flash. Each Flash cell consists of several transistors and a single high-quality insulator. FRAM is much simpler, consisting of a single transistor and the capacitor/magnet. Using the same production lines as modern DRAM devices, even in its current form FRAM should be much less expensive and higher density than Flash. However, Flash production lines have been scaled up to meet massive demand, while DRAM lines are already at capacity. FRAM may not become common until the market demands higher density than Flash can provide.

Ferroelectric Of or relating to a crystalline dielectric that can be given a permanent electric polarization by application of an electric field.

Refers to a material that functions similarly to a ferromagnetic material in that it can be polarized into two states. Ferroelectric devices generally do not have any "ferrous" (iron) them[1].

3.4.2 Ferroelectric capacitor:

A capacitor made of crystals that can retain a polarized state, making it useful for storing binary data (0 and 1). It differs from a regular capacitor, which will polarize when electricity is applied, but does not retain the state when the voltage is reduced to zero. Ferroelectric capacitor is a capacitor used in digital electronics as a component of Ferroelectric RAM, a type of non-volatile computer memory. In a ferroelectric capacitor, the dielectric layer is replaced with a thin ferroelectric film, typically made of lead zirconate titanate (PZT).

The stored value is read by applying an electric field on the memory capacitor. The amount of charge needed to flip the memory cell to the opposite state is measured and the previous state of the cell is revealed. This means that the read operation destroys the memory cell state, and has to be followed by a corresponding write operation, in order to write the bit back. This makes it similar to the ferrite core memory. The requirement for a write cycle for each read cycle, together with the high but not infinite write cycle limit, poses a potential problem for some special applications.

FeRAM was designed to replace flash memory because it writes faster and uses less power. It can also be more easily integrated with other circuits on a semiconductor chip than flash.

3.4.3 Non-Volatile Random Access Memory:

NVRAM is a type of computer memory chip which does not lose its information when power is turned off. NVRAM is mostly used in computer systems, routers and other electronic devices to store settings which must survive a power cycle (like number of disks and memory configuration). One example is the magnetic core memory that was used in the 1950s and 1960s. Magnetic core memory was invented by Jay Forrester of MIT.

Today, most NVRAM is Flash memory, which is used primarily in cell phones and portable MP3 players. The many types of NVRAM under development are based on various technologies, such as carbonnanotube technology, magnetic RAM (MRAM) based on the magnetic tunnel effect, Ovonic Unified Memory based on phase-change technology, and FeRAM based on the ferroelectric effect.

3.4.4 Random-access memory:

Random-access memory (commonly known by its acronym **RAM**) refers to data storage formats and equipment that allow the stored data to be accessed in any order -- that is, at random, not just in sequence. In contrast, other types of memory devices (such as magnetic tapes, disks, and drums) can access data on the storage medium only in a predetermined order due to constraints in their mechanical design.

Generally, RAM in a computer is considered main memory (or primary storage): the working area used for displaying and manipulating data. This type of RAM is usually in the form of integrated circuits (IC). These are commonly called memory sticks or RAM sticks because they are manufactured as small circuit boards with plastic packaging and are about the size of a few sticks of gum. Most personal computers have slots for adding and replacing memory chips.

RAM is typically erased when a computer is shut down, though some RAM chips maintain data indefinitely without electrical power. Technically, RAM devices are not limited to memory chips and random - access memory as a storage format is not limited to use as working memory. In a broad sense, modern storage devices for long-term or secondary storage, including magnetic media and laser-readable CDs and DVDs, are forms of random-access memory.

Most RAM can be both written to and read from, so "RAM" is often used interchangeably with "read-write memory." In this sense, RAM is the opposite of read-only memory (ROM). Strictly speaking, however, "RAM" and "ROM" are not mutually exclusive designations because "RAM" refers only to the method of accessing stored data, not whether data can be written.

Overview

Computers use RAM to hold the program code and data during computation. A defining characteristic of RAM is that all memory locations can be accessed at almost the same speed. Most other technologies have inherent delays for reading a particular bit or byte.

Early main memory systems built from vacuum tubes behaved much like modern RAM, except the devices failed frequently. Core memory, which used wires attached to small ferrite electromagnetic cores, also had roughly equal access time (the term “core” is still used by some programmers to describe the RAM main memory of a computer). The basic concepts of tube and core memory are used in modern RAM implemented with integrated circuits.

Alternative primary storage mechanisms usually involved a non-uniform delay for memory access. Delay line memory used a sequence of sound wave pulses in mercury-filled tubes to hold a series of bits. Drum memory acted much like the modern hard disk, storing data magnetically in continuous circular bands. (See primary storage for a greater discussion of these alternatives and others.)

Many types of RAM are volatile, which means that unlike some other forms of computer storage such as disk storage and tape storage; they lose all data when the computer is powered down. Modern RAM generally stores a bit of data as either a charge in a capacitor as in "dynamic RAM,", or the state of a flip-flop, as in "static RAM".

Currently, there are several types of non-volatile RAM under development, which will preserve data while powered down. Technologies that are being used include carbon nanotube technology and magnetic tunnel effect.

In the summer of 2003, a 128 KB Magnetic RAM chip was introduced, which was manufactured with 0.18 µm technology. The core technology of MRAM is based on the magnetic tunnel effect. In June of 2004, Infineon Technologies unveiled a 16 MB prototype based on 0.18 µm technology once again.

As for carbon nanotube memory, a high-tech startup Nantero built a functioning prototype 10 GB array in 2004.

Software can "partition" a portion of a computer's RAM, allowing it to act as a much-faster hard drive, which is referred to as a RAM disk. Unless the memory used is non-volatile, a RAM disk does not maintain the stored data if the computer is shut down.

Some types of RAM can detect or correct random unintentional faults known as memory errors in the stored data.

3.4.7 Static RAM

Static Random Access Memory (SRAM) is a type of semiconductor memory. The word "static" indicates that the memory retains its contents as long as power remains applied, unlike dynamic RAM (DRAM) that needs to be periodically refreshed. (Nevertheless, SRAM should not be confused with read-only memory and flash memory, since it is volatile memory and preserves data only while power is continuously applied.) SRAM should not be confused with SDRAM, which stands for synchronous DRAM and is entirely different from SRAM, or with pseudostatic RAM (PSRAM), which is DRAM disguised as SRAM.

A fast memory technology that requires power to hold its content. Static random access memory (SRAM) is used for high-speed registers, caches and relatively small memory banks such as a frame buffer on a display adapter. In contrast, the main memory in a computer is typically dynamic RAM (DRAM, D-RAM). Static RAM chips have access times in the 10 to 30-nanosecond range, while dynamic RAM is usually above 30 ns. Bipolar and ECL memories are under 10 ns.

More Real Estate Static RAM is fast because the six-transistor configuration of its pretzel-like flip-flop circuits keeps current flowing in one direction or the other (0 or 1). The 0 or 1 state can be written and read instantly without waiting for a capacitor to fill up or drain; however, the six transistors take more space than dynamic RAM cells made of one transistor and one capacitor.

Earlier asynchronous static RAM chips performed read and write operations sequentially. Newer synchronous static RAM chips overlap reads and writes. Contrast with dynamic RAM.

When opposite voltage are applied to the column wires, the flip-flop is oriented in one of two wires, the flip-flop is oriented in one direction for a 0 or 1.At that point, the flip-flop becomes a self-perpetuating storage cell as long as a constant voltage is applied.

Design

Random access means that locations in the memory can be written to or read from in any order, regardless of the memory location that was last accessed.

Each bit in an SRAM is stored on four transistors that form two cross-coupled inverters. This storage cell has two stable states which are used to denote **0** and **1**. Two additional access transistors serve to control the access to a storage cell during read and write operations. It thus typically takes six MOSFETs to store one memory bit.

Access to the cell is enabled by the word line (WL in figure) which controls the two access transistors M_5 and M_6 which, in turn, control whether the cell should be connected to be bit lines: BL and BL. They are used to transfer data for both read and write operations. While it's not strictly necessary to have two bit lines both the signal and its inverse are typically provided since it improves noise margins.

The symmetric circuit structure allows the value of a memory location to be read much faster than in a DRAM. Another difference with DRAM that contributes to making SRAM faster is that commercial chips accept all address bits at a time. As opposed to this, commodity DRAMs have the address multiplexed in two halves, i.e. higher bits followed by lower bits, over the same package pins in order to keep their size and cost down.

The size of an SRAM with m address lines and n data lines is 2^m words, or $2^m \times n$ bits.

Types of SRAM

By transistor type

- Bipolar transistor (not much used now: consumes a lot of power but is very fast)
- CMOS (the most common type)

By function

- Asynchronous: Independent of clock frequency, data-in and data out are controlled by address transition
- Synchronous: All timings are initiated by the clock rise/fall time. Address, data-in and other control signals are associated with the clock signals

SRAM operation

To understand the operation of a CMOS SRAM cell, let us try to get some idea of how the cell works during standby, read and write operations.

Standby

If the word line is not asserted, the access transistors M_5 and M_6 disconnect the cell from the bit lines. And the two cross coupled inverters formed by M_1- M_4 will continue to reinforce each other as long as they are disconnected from the outside world.

Reading

Assume that the content of the memory is a **1**, stored at Q. The read cycle is started by precharging both the bit lines to a logical **1**, then asserting the word line WL, enabling both the access transistors. The second step occurs when the values stored in Q and Q are transferred to the bit lines by leaving BL at its precharged value and discharging BL through M_1 and M_5 to a logical **0**. On the BL side, the transistors M_4 and M_6 pull the bit line towards Vdd, a logical 1. If the content of the memory was a **0**, the opposite would happen and BL would be pulled towards **1** and BL towards **0**.

Writing

The start of a write cycle begins by applying the value to be written to the bit lines. If we wish to write a **0**, we would apply a **0** to the bit lines, i.e. setting BL to **1** and BL to **0**. This is similar to applying a reset pulse to a SR-latch, which causes the flip flop to change state. A **1** is written by inverting the values of the bit lines. WL is then asserted and the value that is to be stored is latched in. Note that the reason this works is that the bit line input-drivers are designed to be much stronger than the relatively weak transistors in the cell itself, so that they can easily override the previous state of the cross-coupled inverters. Careful sizing of the transistors in a SRAM cell is needed to ensure proper operation.

Applications

Fast SRAM is faster than DRAM and is used where speed is the most important requirement, as in all the storage inside a CPU (Eg: Pipeline and prefetch buffers, the general register set, the entire Cache, holding registers and much more). Also used for external caches, DRAM burst circuits and in its dual-ported form for digital signal processing circuits. Slow, low-capacity SRAMs are used where low power consumption and low cost are the most important requirements, as in battery-powered backup RAM. SRAM is less dense than DRAM (fewer bits per unit area) and is therefore not suitable for high-capacity, low-cost applications such as PC extended memory.

The power consumption of SRAM varies widely depending on clock speed. Fast SRAM is much more power-hungry than DRAM, and some ICs can consume many watts at full speed. Slow SRAM, such as the battery-powered "CMOS" RAM on PC motherboards, can have very low power consumption, in the region of a microwatt when sitting idle.

Drum memory was an early form of computer memory that was widely used in the 1950s and into the 1960s, invented by G. Taushek in 1932 in Austria. For many machines, a drum formed the main working memory of the machine, with data and programs being loaded on to or off of the drum using media such as paper tape or punch cards. Drums were so common that the machines were often referred to as drum machines. Drums were later replaced by core memory, which was faster and had no moving parts, and which lasted until semiconductor memory entered the scene.

A drum is a large metal cylinder that is coated on the outside surface with a ferromagnetic recording material. It is, simply put, a hard disk platter in the form of a drum rather than a flat disk. A row of read-write heads runs along the long axis of the drum, one for each track.

A key difference between a drum and a disk is that on a drum, the heads do not have to move, or seek, in order to find the track they are looking for. This means that the time to read (or write) any particular piece of data is smaller than it would be on a disk; the controller simply waits for the data to appear under the proper head as the drum turns. The performance of the drum is defined almost entirely by the rotational speed, whereas in a disk, both rotational speed and head movement rates are important.

Performance was still an issue, however, and programmers often took to hand-writing the code onto the drum in a particular fashion in order to reduce the amount of time needed to find the next instruction. They did this by carefully timing how long it would take for a particular instruction to run and the computer to ready itself to read the next instruction, then placing that instruction on the drum so that it was just arriving under the heads at that point in time. This method of timing compensation is called the Skip Factor, and is still used today in modern hard disk controllers

The basic operation of a ferroelectric memory device is then discussed. Following this, the advantage and disadvantage of the most widely investigated Ferroelectric materials are discussed.

3.5 FERROELECTRIC MEMORIES AND ITS BASIC OPERATION

Nonvolatile memory is an essential part of all computer systems. It is especially important for specific use such as military systems where vital information has to be stored in some type of a nonvolatile memory-memory that does not lose information when power is lost in a hostile, environment. Among the available nonvolatile memory technologies, disk memories offer large, capacities, and are widely used in such items as personal computers. However, they are slow, bulky, and susceptible to breakdown because of their mechanical nature. Magnetic core and magnetoinducive plated wire memories are very limited in capacity, are very bulky, have large power requirements and are very expensive. Erasable programmable read-only memories (EPROM) and electrically erasable programmable read-only memory (EEPROM) have slower write speed, are susceptible to radiation damage, and fatigue faster than either core or silicon random access memories. Silicon oxide nitride oxide silicon (SONOS) memory is a type of nonvolatile memory option that is fast to read and can be radiation hard. Unfortunately however, SONOS is yet to be programmed for long retention (over five years) with programmable pulses of 1 μs or shorter. Another memory option currently under development is the magneto resistive random access memory (MRAM), which has the potential to provide high density, radiation hardness, and nondestructive readout (NDRO) operation with unlimited endurance. Major disadvantages of this device are its slower read cycle time and larger cell design. Key characteristics of some of the current and future nonvolatile memory technology are listed in Table 1-1. When one considers all the selection requirements for a nonvolatile memory, namely fast read/write, radiation hardness,

	FLOATIN GATE EEPROM	FLASH EEPROM	SNOS nvSRAM (Shadow)	MNOS EEPROM (SNOS)	SONOS EEPROM	DRO FRAM	NDRO FRAM	MRAM	CORE
SPEED (ACCESS TIME)	150 nsec	120 nsec	35 nsec	150 nsec	150 nsec	100 nsec	200 nsec	Density Dependent 200 ns-2μs	350 nsec
WRITE TIME	10 msec Byte/Page	High	SRAM write 35 nsec; Download 11 msec	10 msec Byte	10 msec Byte	100-200 nsec	100-200 nsec	100-200 nsec	900 nsec
ENDURANCE	10E4-10E5 write cycles	10E4 Write cycles	10E5 Power cycles	10E5 Write cycles	10E6 Write cycles	10E10 Read/Write	10E10 Write cycles	No known Limitations	No Limits
RADIATION HARDNESS	Low-Moderate	Low-Moderate	Moderate	High	High	High	High	High	Moderate-High
LIMITATIONS	Write speed Endurance	Write speed Endurance	Density	Write speed	Write speed	Endurance DRO	None	Read speed, Density	Speed, Density Power
COST	Moderate	Low	Moderate to High	Low	Moderate	Potentially Low	Potentially Low to Moderate	Potentially Moderate	High

Table 3.1: Characteristics of the Nonvolatile Memory

Cost effectiveness and compatibility with currently used integrated circuit (IC) processing technology, high endurance and retention, and nondestructive readout capability, the ferroelectric memory stands out as the logical choice for all applications where submicro-second programming is needed [3].

Ferroelectric materials are characterized by a reversible spontaneous polarization in the absence of an electric field [4-6].

Spontaneous polarization in a ferroelectric arises from a noncentrosymmetric arrangement of ions in its unit cell that produces an electric dipole moment.

Adjacent unit cells tend to polarize in the same direction and form a region called a ferroelectric domain. The most common ferroelectrics have the ABO_3 perovskite structure shown in Fig 1.

Above the Curie temperature, these materials have a Centrosymmetric structure and therefore lose all spontaneous polarization. In this state, the material is termed paraelectric. As the temperature is lowered through the Curie point, a phase transformation takes place from the paraelectric state to the ferroelectric state. The center ion is displaced from its body-centered position and the cubic unit cell deforms to assume one of the noncentrosymmetric structures such as tetragonal, rhombohedral or monoclinic structures.

When an alternating electric field is applied to a ferroelectric, the polarization shows a hysteretic behavior with the applied field (Fig 2). In these initial stages, the ferroelectric domains that are oriented favorably with respect to the applied field direction grow at the expense of other domains. This continues until total domain growth and reorientation have occurred. At this stage, the material has reached its saturation polarization P_{sat}. If the electric field is then removed, some of the domains do not return to their random configurations and orientations. The polarization at this stage is called the remnant polarization, Pr. The strength of the electric field required to return the polarization to zero is the coercive field, Ec.

Although it is possible to utilize these ferroelectric properties for a wide variety of applications. The primary impetus of recent research activity in this field is directed towards the development of nonvolatile random access memories [4]. In principle, the memory application is based on the hysteretic behavior of polarization with electric field as shown in Fig 2. When an external voltage is applied to a ferroelectric capacitor, there is a net ionic displacement in the unit cells of the ferroelectric material. The individual unit cells interact constructively with their neighbors to produce domains within the material. As voltage is

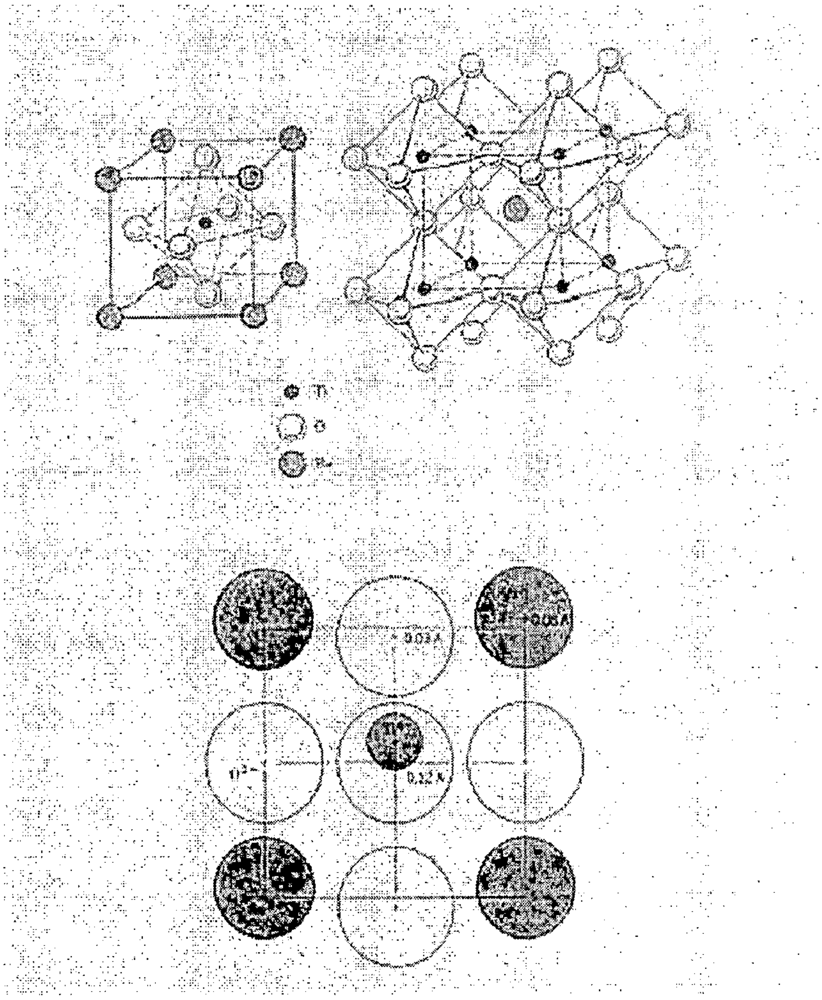


Figure 3. 2: Unit cell of ABO3 type perovskite structured material

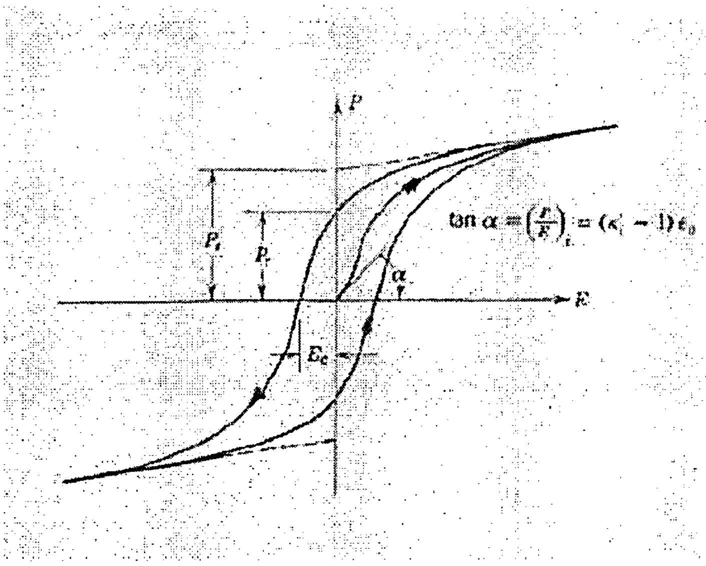


Figure 3. 3: A typical ferroelectric hysterisis loop

removed, the majority of the domains will remain poled in the direction of applied field, requiring compensation charge to remain on the plates of the capacitor. It is this compensation charge that causes the hysterisis in the polarization with applied external voltage [5]. At zero applied fields, there are two states of polarization, ±Pr. Furthermore; these two states of polarization are equally stable. Either of these two states could be encoded as a "1" or a "0" and since no external field is required to maintain these states, the memory device is nonvolatile.

Clearly, to switch the state of the device, a threshold field greater than ±Ec is required. Additionally, in order to reduce the required applied voltage (to within 5 V) for a given Ec, the Ferroelectric materials need to be processed in the form of thin films.

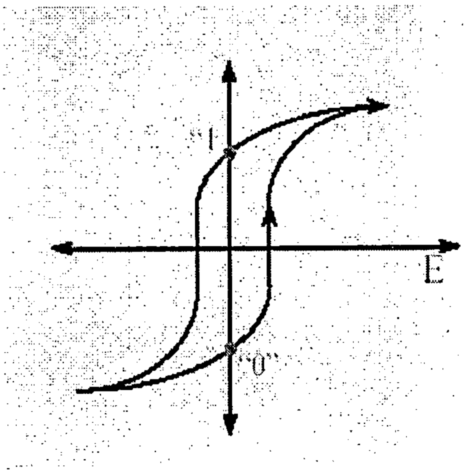
From a digital point of view, if a voltage is applied to a ferroelectric capacitor in a direction opposite of the previous voltage, the remnant domains will switch, requiring compensating charge to flow onto the capacitor plates [7].

If the field is applied in the direction of the previously applied field, no switching takes place, no change occurs in the compensating charge, and a reduced amount of charge flows to the capacitor. This property can be used to read the state or write a desired state into the capacitor. In most ferroelectric memories, the memory cell is read destructively by sensing the current transient that is delivered to a small load resistor when an external voltage is applied to the cell. For example, if a memory cell is in a negative state (-Pr) and a positive switching voltage is applied to it, there will be a switching charge given by [1-2]:

$$Q = A\varepsilon E_a + A\int_0^{\alpha} \frac{dP}{dt}\,dt$$

where A is area of the cell, ε_r is the dielectric constant of the ferroelectric material, Ea is the applied field and P is the polarization of the ferroelectric. Equation 1.1, as depicted in Fig 1-3, indicates that this current transient, known as the "switching current", consists of a linear dielectric response $(A\varepsilon E)$ and a displacement current. A "nonswitching current" transient, for example, is the response of a memory cell in a positive state (+Pr) to a positive applied voltage.

In this case, $Q = A\varepsilon E$ (7)



Reading Pulse

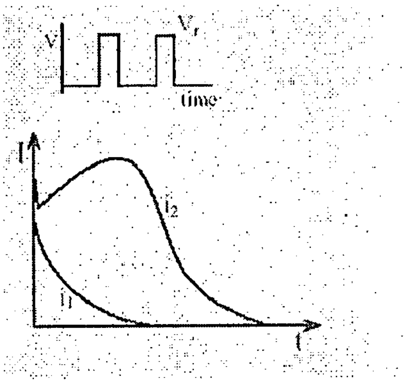


Figure 3. 4-5. Schematic of the read/write operation in a ferroelectric memory cell

A sense amplifier and other associated circuitry is used in a FRAM device to determine these current transients and thereby read the state of the device.

The basic operation discussed so far describes the working of a typical destructive readout (DRO) single transistor-single capacitor ferroelectric. However, there are actually two basic types of integration and operation schemes utilizing the ferroelectric materials:

(1) Destructive readout (DRO) where the information must be rewritten after every read operation; and,

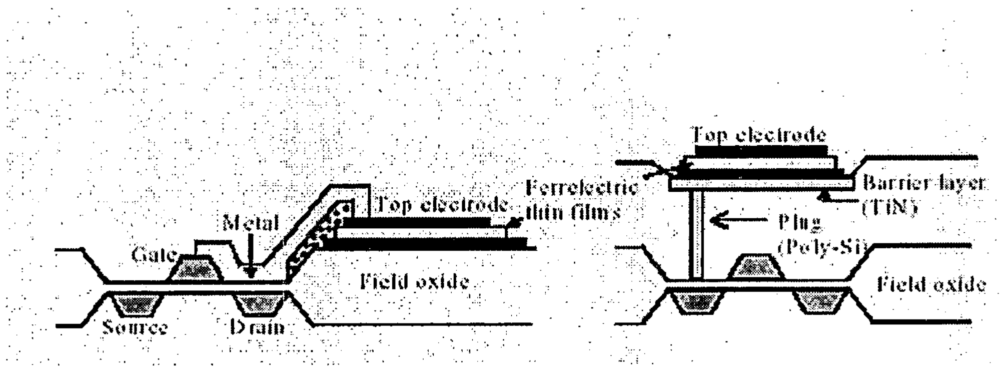
(2) Nondestructive readout (NDRO) where the information can be read over and over again until the next write operation. However, throughout this dissertation, our focus will be on the DRO single transistor-single capacitor ferroelectric memories. Integrated ferroelectric random access memory using the DRO scheme closely resembles dynamic random access memory (DRAM).

A DRO FRAM is close to realization. The basic structure of such memory includes a thin film ferroelectric capacitor sandwiched between two chemically stable metal electrodes, integrated on top of, in case of high density memory, or next to a semiconductor IC fabricated using existing CMOS technology as shown in Fig 1-4. The chip design consists of a matrix array of memory elements and transistors, with each memory element integrated to appropriate transistor circuitry. A typical memory element is also shown in Fig 4. A transistor known as the pass-gate transistor or select transistor is connected between the ferroelectric capacitor (Cf) and a sense capacitor (Cs). The need for this transistor arises from the fact that ferroelectrics do not exhibit well defined coercive fields or switching voltages, thus creating the so called "half-select disturb problem", i.e., the possibility of unintentional switching of cells adjacent to the ones being addressed in a large array of memory elements. The selected transistor provides electrical

isolation to each memory cell, allowing the circuit to select which capacitor is to be switched and creating individually addressable bits. Voltage is applied to the ferroelectric capacitor by the drive line, the select transistor is controlled by the word line, and the cell is sensed via the bit line. The signal is measured by means of a sense amplifier at the end of the bit line which identifies the state of the bit [8].

3.5.1 MATERIALS AND PROBLEM DEFINITION

The current surge in interest in ferroelectric nonvolatile memories can be traced to the development of thin film technologies in the 1970's and 1980's allowing the fabrication of



Low density memory device(64Kbit)   High density memory device(1Mbit)

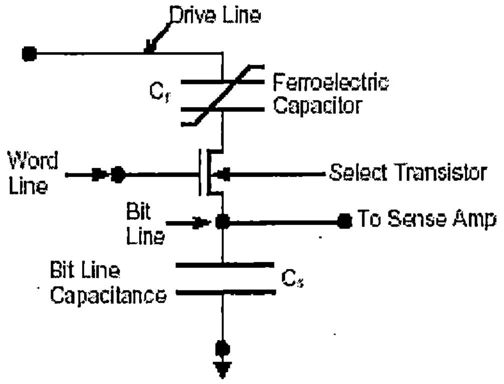


Figure 3.6-9. Proposed ferroelectric memory cell device configuration

film capacitors at temperatures compatible with semiconductor processing. An ideal ferroelectric should have small dielectric constant, reasonable (~ 5 μ C/cm ^{2})

Spontaneous polarization and high Curie temperature (beyond the storage and operating temperature range of the device).

Required low voltage operation (< 5V) necessitates submicron layer thickness with low coercive field and adequate dielectric breakdown. Inherent switching speed should be in the nanosecond range, and the ferroelectric capacitor should have good retention and endurance. Radiation hardness is another desirable property for military applications; and, of course, the material should be chemically stable. Additionally, to be useful, a ferroelectric material in a memory array must have good retention and imprint characteristics. The films must have very uniform composition and thickness over the surface of the integrated circuit

(IC) so that the capacitance associated with each memory cell is the same. Also, the processing required to produce the ferroelectric thin film must not have a detrimental effect on the underlying circuitry.

Many materials show Ferro electricity and two families of materials, perovskite (e.g.$PbZr_{1-x}Ti_xO_3$) and layered perovskite (e.g. $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$), have been widely investigated for memory applications. However, the realization of a commercially viable nonvolatile FRAM technology based on PZT has been hampered by the lack of reliable performance of the PZT ferroelectric capacitor or to problems related to the growth and processing of ferroelectric capacitor layers. The PZT films grown on metal electrode such as Pt show high fatigue, i.e. loss of polarization with switching cycles [4-5]. The polarization fatigue problem can be solved for all practical purposes only by replacing the metallic Pt electrodes with metal-oxide electrodes such as RuO_2, or with any array of the perovskite metal oxides such as $La_{0.5}Sr_{0.5}CoO_9$, or with hybrid metal-oxide electrodes, among others. The lead based ferroelectrics have been extensively studied, but recently issues with fatigue, environmental safety, and health concerns have prompted interest in $SrBi_2Ta_2O_9$ (SBT) which belongs to layered perovskite family. The bulk bismuth layer-type ferroelectric compounds were discovered in 1959 [9-14]. The family of bismuth layered oxides has the formula

$(Bi_2O_2)^{2+}$ $(Me_{m-1}R_mO_{3m+1})^{2-}$

Where Me = mono-, di-, or trivalent

Advantages:

- PZT based capacitors have larger switchable polarization (40–50 μC/cm 2) than the Bismuth layer-type ferroelectric
- PZT layers with a pure perovskite structure and good electrical properties can be generally produces at lower temperatures (600-700 ° C)
- PZT based capacitors require oxide or hybrid-metal-oxide electrodes technology to yield negligible fatigue and imprint, two important electrical properties for FRAMs. TheseElectrodes are more complicated to synthesize than pure metal electrodes such as Pt.

Disadvantages: PZT based capacitors involve Pb, which may present contamination and hazardous problems during fabrication.

4.1 Lead zirconate titanate

Lead zirconate titanate was discovered by Jaffe et al [9] is very important and interesting ferroelectrics because of its high spontaneous polarizations and Curie temperature above room temperature. This complex compound Pb(ZrTi)O_3(generally referred to as PZT),belonging to the ferroelectric family of perovskite structure with a general formula ABO_3,(A=mono or divalent=tri to hexavalent ions) is a solid solution of ferroelectrics $PbTiO_3$(Tc=490^0) and antiferroelectric $PbZrO_3$(Tc=230^0)[10].The complex ceramics are very sensitive to compositional fluctuation.Gerson showed that the electro-mechanical properties of PZT ceramics can be altered by adding small quantity of tri or pentavalent ions(e.g., Lanthamum,Neodymium, Tantalum or niobium)[11].

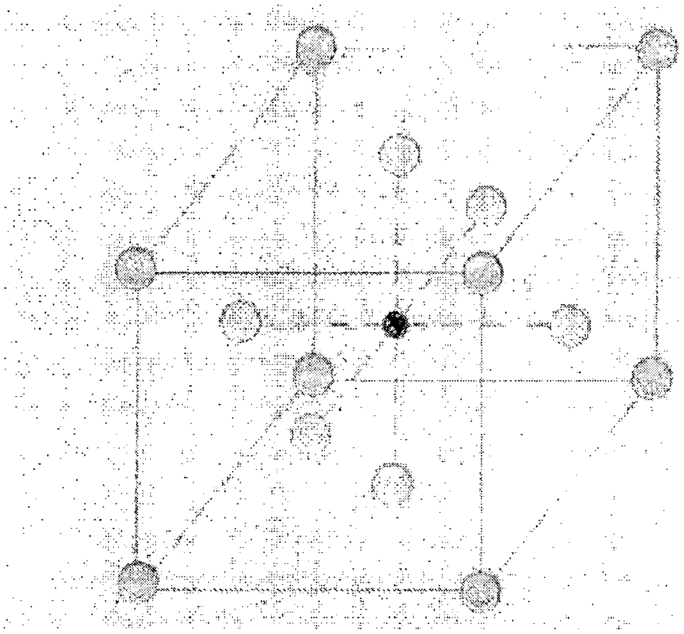


Figure 4.1:shows the perovskite structure of PZT where at the corner Pb2+,O2- at the centre of each face .

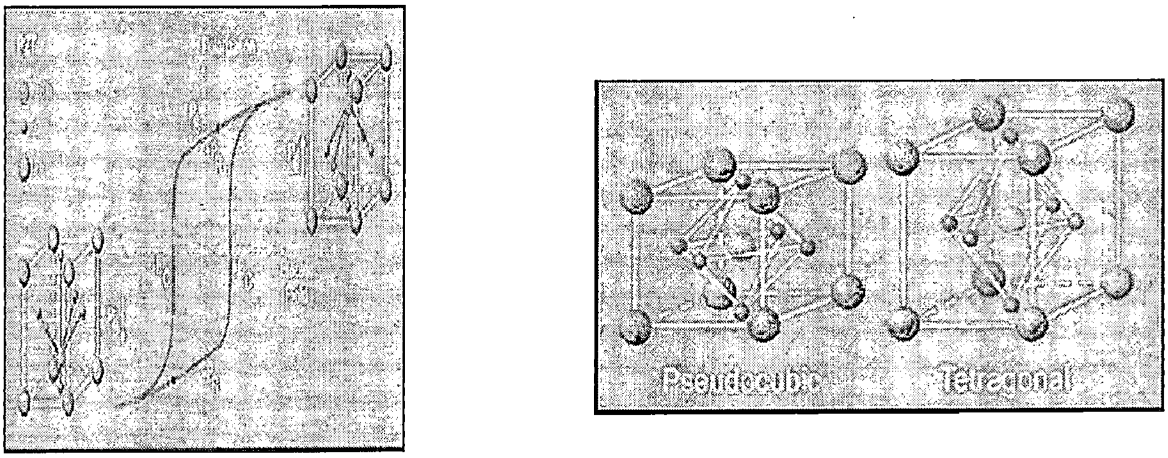


Figure 4.2: shows the structure of PZT before and after phase transition.

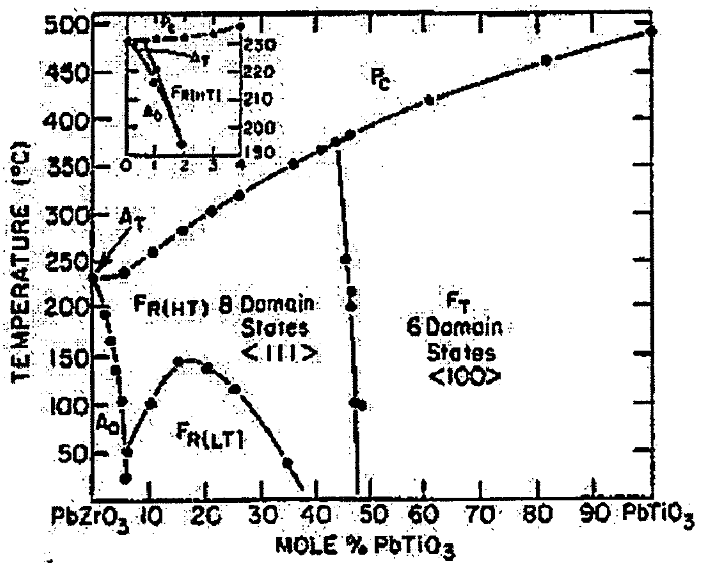


Figure 4.3: shows the phase diagram of PZT.

ceramic perovskite material that shows a marked piezoelectric effect—that is, it develops a voltage difference across two of its faces when compressed. It is also ferroelectric, in other words, it has a spontaneous polarization which can be reversed in the presence of an electric field.

Modifications of the PZT ceramics and the effects of dopant had been researched extensively to improve its piezoelectric properties for various applications in actuators, Piezoelectric resonators, transducers, micropositioners, etc [12-14]

This is long known as doping, depending on the site occupied of a type ABO3 perovskite and has to comply with Goldschmidt or tolerance factor [12].

The material features an extremely large dielectric constant at the morphotropic phase boundary (MPB) near $x = 0.65$. These properties make PZT-based compounds one of the most prominent and useful electro ceramics. Commercially, it is usually not used in its pure form, rather it is doped with either acceptor dopants, which create oxygen (anion) vacancies, or donor dopants, which create metal (cation) vacancies and facilitate domain wall motion in the material. In general, acceptor doping creates *hard* PZT while donor doping create soft PZT. In general, soft PZT has higher piezoelectric constant, but larger losses in the material due to internal friction. In hard PZT, domain wall motion is pinned by the impurities thereby lowering the losses in the material, but at the expense of a reduced piezoelectric constant.

PZT is used to make ultrasound transducers and other sensors and actuators, as well as high-value ceramic capacitors and FRAM chips.

4.2 Dopant Distribution between A and B sites in the PZT Ceramics of Type ABO3

The influence of doping oxides on the $PbZr_{.95}$ $Ti_{.05}$ 0 composition is studied. A theoretical model allows the doping ion distribution between A and B sites to be established from its ionic radius. The tolerance factor t, calculated for each doped composition, has a minimum value when the antiferroelectric (AF) property is at the maximum .The experimental results agree well with theoretical calculations.

It is known that the ferroelectric (F) or antiferroelectric (AF) state of a type ABO_3, perovskite structure is related to its Goldschmidt or tolerance factor t (I):

$$t = \frac{R_A + R_o}{\sqrt{2}(R_A + R_o)} \qquad (1)$$

Where R_A,R_B,Ro indicate the ionic radius of the large cation, the small cation, and the oxygen ion, respectively. Generally, for a Goldschmidt factor above approximately 0.92, the AF property does not appear. More precise results were obtained while studying the doping effect on a given composition near the F-AF transition phase.

A dopant which decreases the tolerance factor produces an extension of the AF phase, that is, a temperature increase of the AF -> F phase transition, the reverse effect is also observed. If the doping ion decreases the average volume of the A or B ions, the unit cell volume is decreased. The reverse effect is also observed. The extension of the AF phase is caused by the

increase of the hydrostatic stress on the B- ion sites. According to the rules of Goldschmidt, site can be determined if the ion and the substituted ion radii do not differ by more than 15% [13]. These rules cannot be applied for a dopant with an ionic radius very different from RA, and RB. We propose to evaluate the distribution of a given dopant between two sites in relation to its ionic radius, taking into account the effect on the AF -> F transition temperature. Most of the dopants used belong to the rare earth for they present two advantages-their homogeneity and a large
range of ionic radii.

Ion	Pb^{2+}	O^{2-}	Ti^{4+}	Zr^{4+}	Sc^{3+}	Yb^{3+}	Ho^{3+}	Bi^{3+}	Tb^{3+}	Gd^{3+}	Eu^{3+}	Sm^{3+}	Nd^{3+}
Ionic radius (Å)	1.32	1.32	0.64	0.87	0.83	0.92	0.95	0.96	0.98	1.00	1.01	1.02	1.06

Table 4.1: The ionic radius of the cations.

It appears that the change of the AF-F phase transition temperature by a doping oxide is directly related to the cation ionic radius of this oxide and the gradual distribution of this cation between the A and B sites. The distribution of an ion on the A and B sites seems to be a regular function of the ionic radius. A large ionic radius favors the A sites.

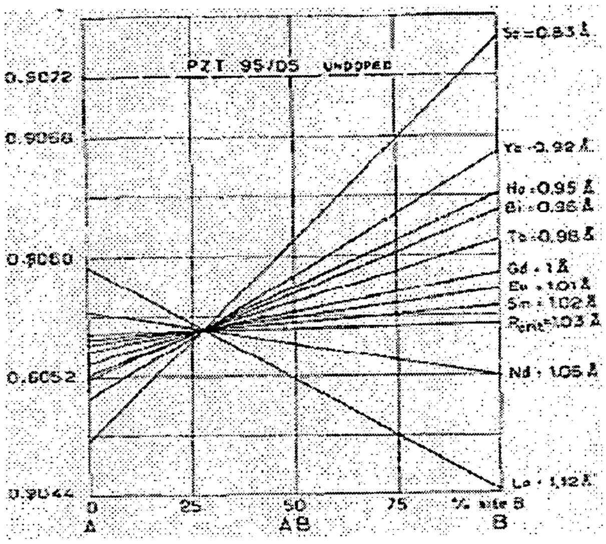


Figure 4.4: Tolerance factor variation related to the Doping ion distribution between the A and B sites PZT 95/05+$10^0/_0$ oxide.

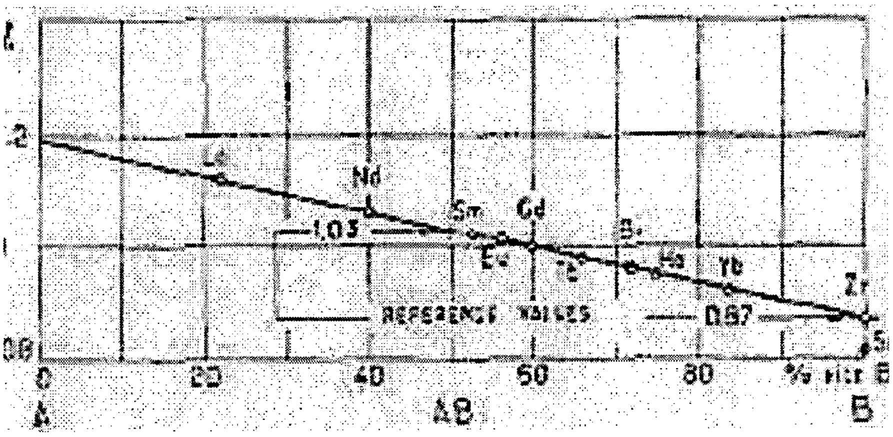


Figure 4.5: Theoretical distribution between the A and B sites: PZT $95/05+10^{0}/_{0}$ oxide.

Chapter 5

EXPERIMENTAL TECHNIQUE

FURNACE

The most essential point in good fireclays, or in the bricks or other objects made from them, is the power of resisting fusion at the highest heat to which they may be exposed. This supposes them to be free from metallic oxides forming easily fusible compounds with silica, such as lime or iron, the presence of the former even in comparatively small proportion being very detrimental. As clays they must be sufficiently plastic to be readily moulded, but at the same time possess sufficient stiffness not to contract too strongly in drying, whereby the objects produced would be liable to be warped or cracked before firing. In most cases, however, the latter tendency is guarded against, in making up the paste for moulding, by adding to the fresh clay a certain proportion of burnt material of the same kind, such as old bricks or potsherds, ground to a coarse powder. Coke dust or graphite is used for the same purpose in crucible making.

Alumina as a refractory material is chiefly used in the form of bauxite, but its applications are somewhat special. It has been found to stand well for the linings of rotatory puddling furnaces, where, under long-continued heating, it changes into a substance as hard and infusible as natural emery.

The electric furnace has led to the discovery of several important materials, which have been employed as furnace linings. They are four sic rod with resistance 10 ohms each and they are connected in series.

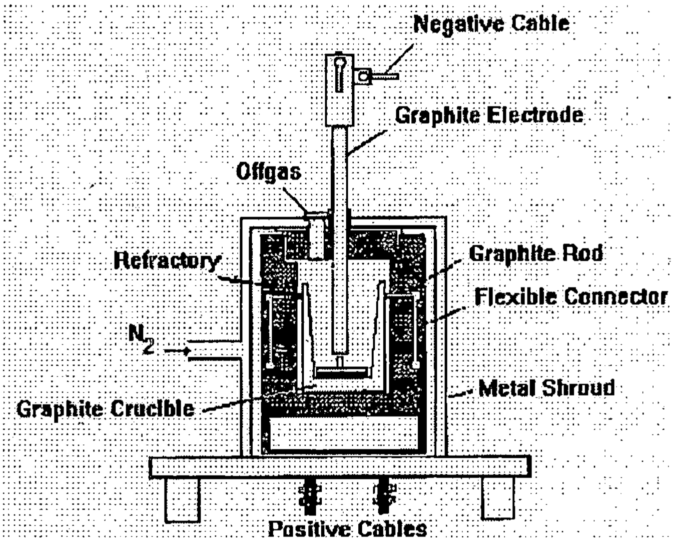


Figure 5.1: furnace

5.1 Thermo-electric sensors:

The most common electrical methods of temperature measurement thermo-electric sensor, also known as the thermocouple (TC).The thermocouple is a temperature transducer that develops an emf which is a function of the temperature between hot junction and cold junction.

Construction:

It consist of two wire of different metals twisted and brazed or wielded together with each wire covered with insulation which may be either :

1. Mineral (magnesium oxide) insulation for normal duty or
2. Ceramic insulation for heavy duty

5.1.1 Basic Principle (discovered by seeback in 1821):

When two conductors o dissimilar metals, are joined together to form a loop (thermocouple) and two unequal temperatures T_1 and T_2 are interposed at two junctions j_1 and j_2, respectively then an infinite resistance voltmeter detects the electromotive force

'E'. Experimentally it was found that the magnitude of E depends upon the materials as well as the temperature T_1 and T_2.

5.1.2Thermocouple materials:

The choice of materials for thermocouples is governed by the following factors;

1. Ability to withstand the temperature at which they are used.
2. immunity from contamination /oxidation ,etc which ensures maintenance of the precise thermocouple properties with continuous use, and
3. linearly characteristics ,

$$E=aT+bT^2$$

relationship between thermo-electric (emf) and difference between hot and cold junction temperatures.

In the laboratory use Platinum- Platinum/$10^0/^0$ Rhodium with appropriate sensitivity in ($\mu v/^0c$) 5-12 having temperature range 0 to 1400^0c + or -0 .$25^0/_0$ accuracy and Platinum-Platinum/$13^0/_0$Rhodium 5-12 ($\mu v/^0c$).

5.2 Pellet Technique:

Simple die and pellet holder which give very satisfactory results, including high energy and yet require only *2* to 10 mg. of sample. The 7cm-diameter pellet is pressed directly into **a** holder designed to fit. A die was constructed which could be used in the unmodified laboratory hydraulic pressure .The die shown in the figure5.2 consists of five parts: base, pellet holder, sleeve, plunger, and spring to ensure vacuum tightness during evacuation previous to pressing, O ring seals are used between the base and pellet holder, the pellet holder and sleeve, and on the shaft of the plunger.

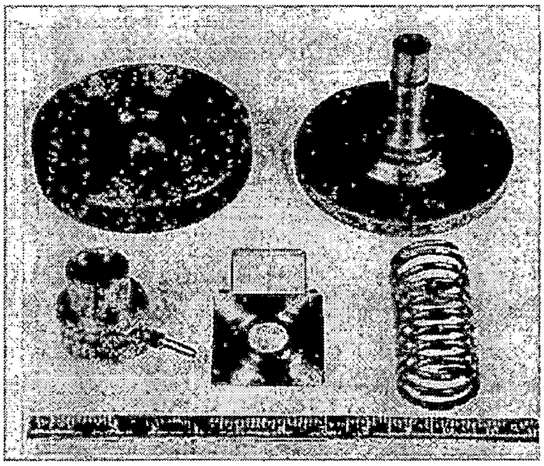


Figure 5.1: shows the Unassembled die

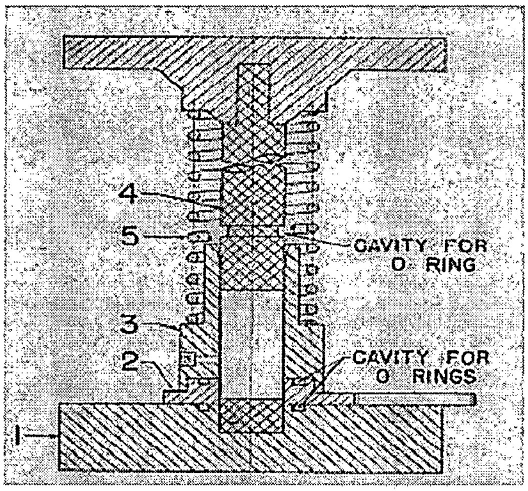


Figure5.2: Die

When the die is compressed slightly, the spring exerts enough pressure to give a good seal. A 1-inch stainless steel rod serves to insert the seal ring into its O-ring groove without damage and to pack initially the powdered Lead Zirconium Titanate (PZT) into the lead ring the filling sleeve provides a means of in traducing the powdered PZT into the die body. A constraining sleeve for the upper plunger makes it possible for the pressing surfaces to compress the powder within the lead ring. O-rings within the die body and on the under side of the top cap provide adequate seals for evacuation. 7/4-inch inside diameter and a length of 1/8-inch can either be machined by use of simple jigs or punched out from a sheet of alloyed lead.

Pressing Operation: The lower plunger, attached to the top of the ram by the retaining ring, and the die are placed at the top of the recess of the briquetting press. The ram and plunger are lowered to the bottom position and the lead ring and filling sleeve are inserted into the bole. The powder charge is introduced and leveled nith a straight edge of a spatula. The plunger-tamper further flattens and compacts the charge within the lead ring. The top plunger with its retainer sleeve is inserted into the die bore; the bridge of the prms is secured in pressing position, and the die cavity is evacuated for *2* minutes. 4 pressure of 80,000 pounds total force or approximately 133,000 p.s.i. is applied for *2* minutes. The pressure is gradually released to zero dial reading and the vacuum line is opened to the atmosphere. The bridge support is swung to the ejection position, holding the die body with one edge of the bridge, while the compressed pellet is ejected by the ram action. If the lead ring adheres to the punch, a simple twist removes ring and pellet.

5.3 X- Ray diffractrometer (XRD)

Siemens D5000 X-Ray Diffractometer

The D5000 measures atomic spacing in crystals using diffraction of approximately monochromatic x-radiation. It can be used to characterize solid samples ranging in size from about 1 millimeter square up to intact four-inch wafers. The radiation used is copper k-alpha with a wavelength of 1.5418 A°. The instrument has two fundamentally different modes of operation.

5.3.1 Definitions & Process Terminology

RUA: Radiation Usage Authorization. A permit issued by the University's radiation safety to let a radiation-producing machine be operated on campus. Both the machine and all operators must be explicitly identified.

Monochrometer: A device which selects x-rays of a specific energy, traveling along a specific axis. Two channel cut germanium crystals are mounted as periscopes in opposition. The radiation diffracts from the first surface to the second, where it diffracts again with direction unchanged but position displaced by the projected width of the channel. The second crystal reverses the displacement, so the beam direction and position are identical to the original beam.

The crystal lattice spacing in the monochrometer is effectively the "metric standard" to which the sample is compared.

Goniometer: The mechanism which supports the sample and detector, allowing precise movement.

Available Processes

Our D5000 offers two fundamentally different modes of operation. High-resolution mode is used to examine well-ordered single crystal films. High throughput mode is used to examine textured polycrystalline films. Non-textured or powdered samples can be examined also.

Diffraction measurements commonly take two forms, a "normal coupled scan" and a "rocking curve". Normal coupled scans provide information about what materials are present and lattice type. Rocking curves allow estimates of crystal quality and in good crystals can also provide quantitative measurements of layer thickness. They can also be helpful in locating a known peak on a sample of uncertain orientation.

Operation

It is quite possible to make a life's work out of doing x-ray diffraction. This guide tries only to give the barest sketch, sufficient to get started.

Preliminary Steps
Mounting the sample in the holder
Loading the mounted sample in the holder
Locating initial diffraction peak
Saving the data
Printing the data
Exporting the data

Working:

DURING recent years x-ray diffraction methods have been have been extensively applied to problems of quantitative analysis Diffraction methods possess the unique advantage of detecting not only the presence of chemical elements but also their state 'If chemical combination. Quantitative measurements of greatly improved quality can now be made with the aid of Geiger counter tubes for receiving the diffracted energy. Finally, particular impetus has been given to the use of quantitative diffraction techniques by the development and widespread commercial distribution of the Norelco Geiger-counter x-ray spectrometer.

In spite of this extensive activity in the field of diffraction analysis, no investigator to date has published a detailed statement of the simple but important mathematical relationships Ehich relate the diffracted intensity to the absorptive properties of the sample and thereby determine the particular procedure that is suitable for the analysis of any given sample. This communication presents these mathematical considerations for the case of diffraction from the surface of a flat powder specimen, the arrangement employed in the Norelco x-ray spectrometer. The measurement of the absolute intensities of x-rays diffracted by the components of a binary powder mixture has been discussed theoretically by Brentano and he has applied the results the measurement of atomic scattering factors. Glocker and Schafer have shown in a similar manner that the fundamental intensity formulas of Laue can be used as a basis for the quantitative diffraction analysis of binary powder mixtures and alloys. However, they did not extend their mathematical treatment to the point of evolving a systematic practical when if analysis.

5.3.1 INTENSITY DIFFRACTED BY ONE COMPONENT OF A POWDER MIXTURE

will be initially assumed that the sample is a uniform mixture of ***1c*** components, that the particle size is very small so that extinction and so-called micro absorption effects are negligible, and that the thickness of the sample is sufficient to give maximum diffracted

intensities. Satisfactory criterion for the latter condition is that $\mu ss \geq 6.4$,*a* being the linear absorption coefficient of the sample and s being the maximum path length traversed by the x-rays through the sample. Applied to the geometrical arrangement of the Geiger-counter x-ray spectrometer, this

$$t \geq \frac{3.2}{\mu} x \frac{\rho}{\rho^{s}} x \sin\theta \qquad (1)$$

Criterion takes the form in which t is the thickness of the powder sample, ρ is the average density of the solid material composing the powder, p' is the density of the powder (including the interstices), θ is the Bragg reflection angle, and ,u is the mean linear absorption coefficient of the solid material composing the powder.

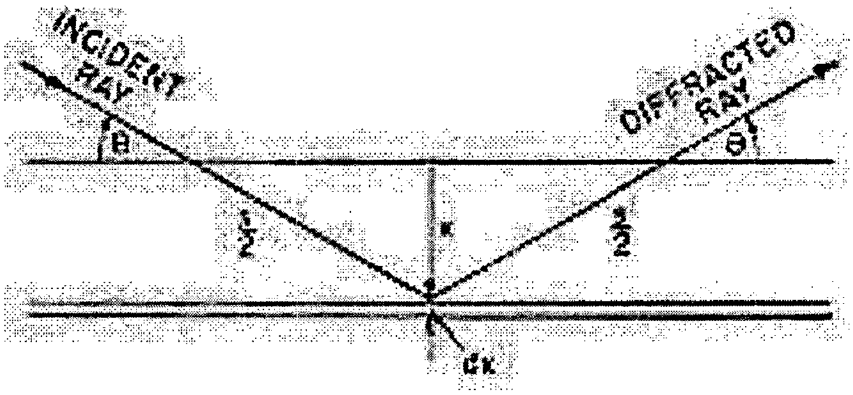


Figure 5.3: Diffraction from a Layer of Powder at Depth x

Consider such a powder sample consisting of ***n*** Components and irradiated by an incident x-ray beam of cross-sectional area ***A*** which impinges upon the sample at angle 0. Under

these conditions the area of sample surface irradiated is A/sin 0. Referring *to* Figure 1, consider the diffraction taking place from a layer ***cd*** thickness ***dx*** at depth ***x***. The volume of this layer is

$$dV = \frac{Adx}{\sin\theta} \tag{2}$$

$$x = \frac{1}{2}s\sin\theta \tag{3}$$

$$dV = \frac{1}{2}Ads \tag{4}$$

Let us now define **$(I_0)_i$** as the intensity diffracted by unit volume of pure ith component at the angle 2θ to the primary beam and under conditions of nonabsorption, and let f_i be the volume fraction occupied by the ith component, neglecting the interstices. The intensity diffracted from element *dV* by component ***i*** of the mixture is then

$$dI_i = \frac{1}{2}(I_0)f_iAe^{-\mu s}ds \tag{5}$$

and, integrating between the limits $\mathbf{s} = 0$ and m, we obtain for that total intensity of the diffracted beam from the ith component.

5.3.2 X-ray Diffractometry (XRD)

X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials this method has been traditionally used for phase identification, quantitative analysis and the determination of structure imperfections. Important advances in structural studies of materials ranging from high temperature superconductors and high pressure research have relied heavily on the powder diffraction technique.

Some solids can be prepared only as micro crystalline powders and hence their structure cannot be determined using single crystal diffraction techniques. Also the structures of some materials which are in the form of hydrocarbons and resins cannot be determined by single crystal diffraction methods. In such cases we can determine the structure of the material using powder diffraction data. The ability to determine crystal structures using powder diffraction promises to open up many avenues in structural sciences. Powder diffractometry projects the three-dimensional lattice into a one-dimensional lattice. We can determine the orientation, unit cell dimensions, stress/strain, crystal structure, etc from the information obtained in the powder diffraction pattern.

5.3.3 Deriving Bragg's Law

Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, □). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda □ is the **wavelength** of the incident X-ray beam (see applet); n is an integer

This observation is an example of X-ray **wave interference** (Roentgenstrahlinterferenzen), commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest

Bragg's Law can easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z (Fig.). The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance AB + BC if the two beams are to continue traveling adjacent and parallel. This extra distance must be an integral (n) multiple of the wavelength (λ) for the phases of the two beams to be the same:

$$n\lambda = AB + BC \qquad (6)$$

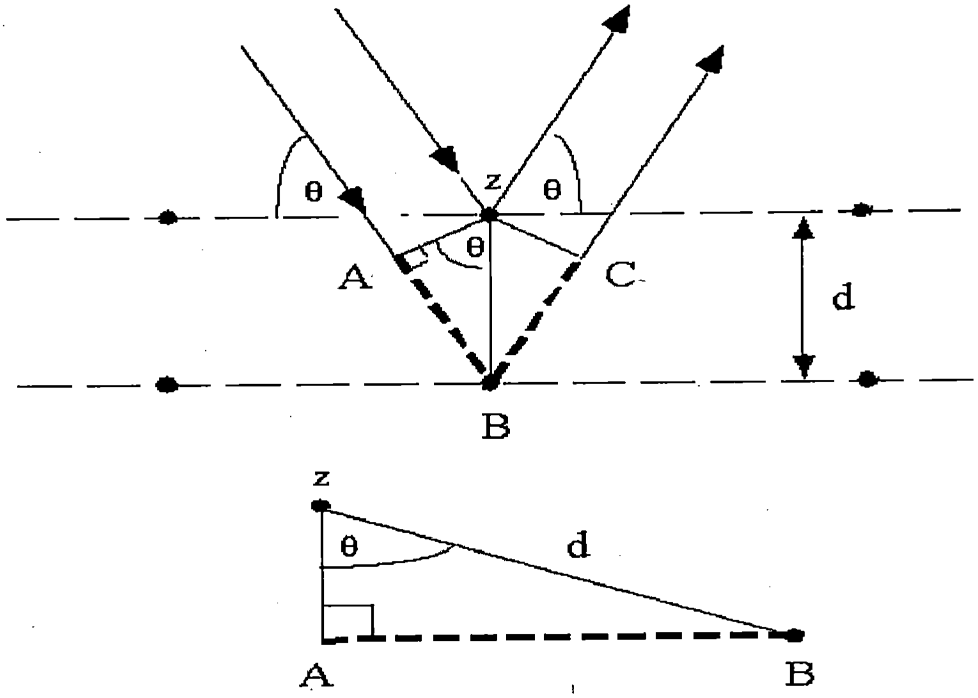


Fig 5.4: Deriving Bragg's Law using the reflection geometry and applying trigonometry.

The lower beam must travel the extra distance (AB + BC) to continue traveling parallel and adjacent to the top beam. Recognizing d as the hypotenuse of the right triangle Abc, we can use trigonometry to relate d and λ to the distance (AB + BC). The distance AB is opposite λ so,

$$AB = d \sin\theta \qquad (7)$$

Because AB = BC above eq. becomes,

$$n\lambda = 2AB \qquad (8)$$

from Substitution we have,

$$n\lambda = 2\, d \sin\theta \qquad (9)$$

and Bragg's Law has been derived. The location of the surface does not change the derivation of Bragg's Law.

BRAGG'S CONDITION:

Consider a beam of wavelength striking a line of atoms spaced at equal distances. The radiated beam that is in the form of spherical wave fronts will be of maximum intensity when the path difference between the incident and the reflected beam is equal to an integer number of wavelengths. Taking a picture where each atom is giving off a spherical wave front, the directions of scattering thus constitute a series of cones. If we take a 2-D net, in which there is another line of atoms independent from the first line of atoms, another series of cones is generated. Thus a 2-D net produces two families of intersecting cones. Thus a constructive interference in seen only in some specific well defined directions in space. Also when the axes of the cones are non-linear, the intersections of the cones give a series of lines.

Extending this idea to three dimensions, strong constructive interference will occur only for some specific conditions of interference and specific directions. But it is difficult to picture this in three dimensions. However Bragg proposed that the condition for constructive interference is equivalent to that of a simple plane, which can be described by the Miller indices. Now the plane is (hkl) and the spacings between the planes are considered but not the spacings between the atoms or lattice points as was considered previously.

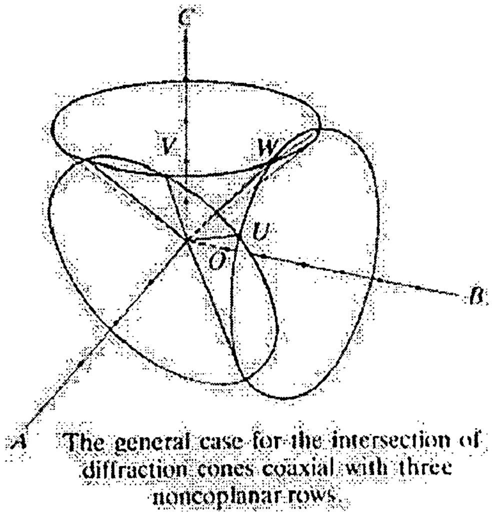


Figure 5.5: A 3-D scattering of x-rays can be seen

Consider a crystal lattice whose interplanar spacing is d. Also the incident radiation strikes the planes (hkl) at an angle θ as shown. The condition for constructive interference is now:

$n\lambda=2d\sin\theta$

where λ = Incident Light wavelength. n=0,12,3......

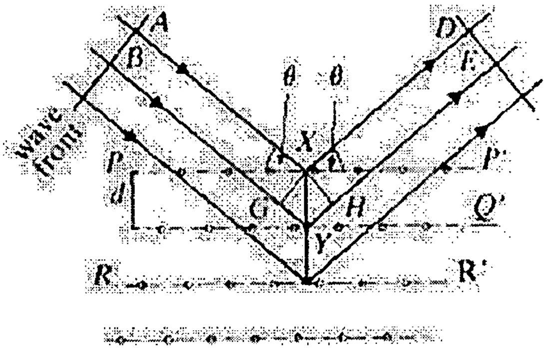


Figure 5.6: Diffraction of the waves from the planes

5.3.4 The Powder Diffractometer :

Modern X-ray techniques give a series of peaks instead of diffraction intensities as in Debye Scherrer method. In this method a detector is used instead of the film. A convergent incident ray is used to give a good peak resolution. The powder is filled in the hole of a sample holder. The set up requires that if reflection is obtained when the beam is incident at an angle θ with the lattice plane, the reflected beam is recorded at an angle of 2θ in what is referred to as θ-2θ scan. This is shown in Fig5. The peak positions and the intensities are readily obtained from the chart. The powder diffractometer uses an x-ray detector like a Proportional or Scintillation Counter to measure the positions of the diffracted beams. Diffractometry is a widely used method because it measures the intensities directly.

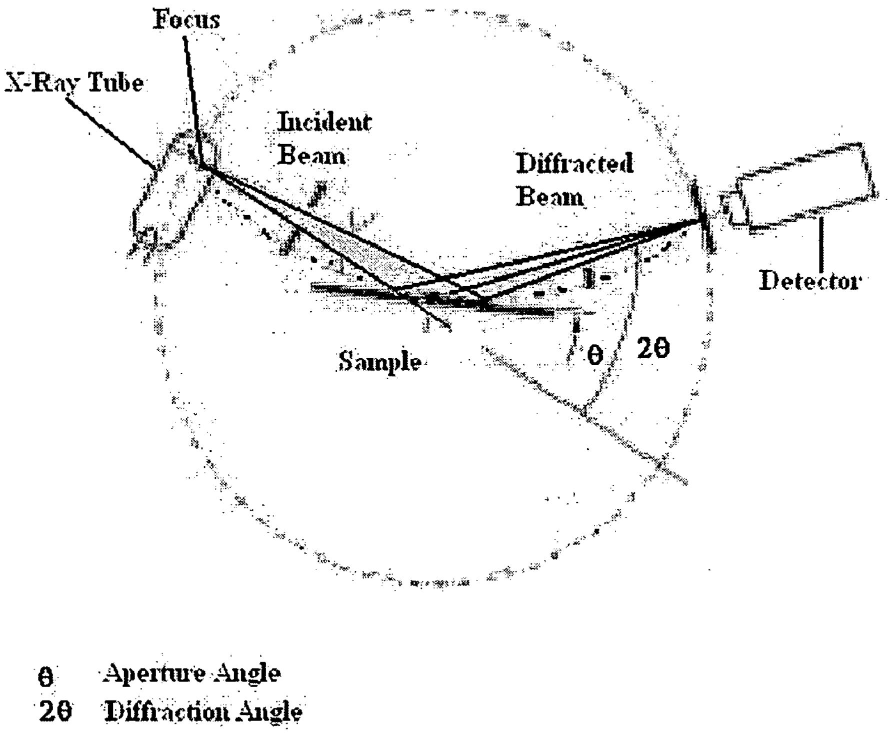


Figure 5.7:X-Ray Diffraction of the samples

5.4 Scanning Electron Microscope (SEM):

The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of a metallic filament. The electron beam follows a vertical path through the column of the microscope. It makes its way through electromagnetic lenses which focus and direct the beam down towards the sample. Once it hits the sample, other electrons (backscattered or secondary) are ejected from the sample. Detectors collect the secondary or backscattered electrons, and convert them to a signal that is sent to a viewing screen similiar to the one in an ordinary television, producing an image.

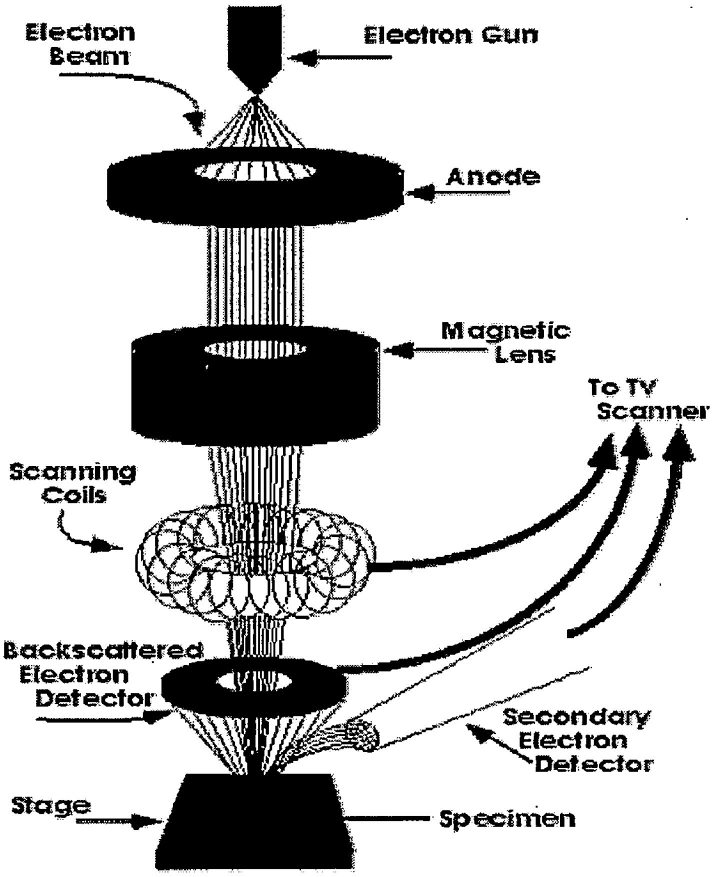


Figure 5.8: Scanning Electron Microscope (SEM)

Specimen Preparation

There are two basic types of SEM's. The regular SEM, which we have in the Iowa State Materials Science Department, requires a conductive sample. An environmental SEM can be used to examine a non-conductive sample without coating it with a conductive material. Three requirements for preparing samples for a regular SEM such as in the Iowa State Materials Science Department are:

1) Remove all water, solvents, or other materials that could vaporize while in the vacuum.
2) It firmly mounts all the samples.
3) Non-metallic samples, such as bugs, plants, fingernails, and ceramics, should be coated so they are electrically conductive. Metallic samples can be placed directly into the SEM. SEMs are patterned after Reflecting Light Microscopes and yield similar information:

Topography

The surface features of an object or "how it looks", its texture; detectable features limited to a few manometers

Morphology

The shape, size and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching; detectable features limited to a few manometers

Composition

The elements and compounds the sample is composed of and their relative ratios, in areas ~ 1 micrometer in diameter

Crystallographic Information

The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles >20 micrometers

A detailed explanation of how a typical SEM functions follows (refer to the diagram):

1. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.
2. The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam
3. The beam is then constricted by the condenser aperture (usually not user selectable), eliminating some high-angle electrons
4. The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob"
5. A user selectable objective aperture further eliminates high-angle electrons from the beam
6. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range)
7. The final lens, the Objective, focuses the scanning beam onto the part of the specimen desired.
8. When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments
9. Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).
10. This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

SPECIFICATIONS :

Operation Mode	Conventional and Variable pressure
Magnification	10x to 300,000x
Resolution	4.0nm (Conventional mode) 6.0nm (VP mode)
ACCELERATION VOLTAGE	30 kV (Continuously variable)
Beam Current	1 mA
STAGE	Eucentric goniometer stage. a.X & Y movement 50mm. b.Tilt -150° to 60°. c.Rotation 360° endless.
DETECTORS	SED & Back Scatter Electron Detector.
Image input/output	a. Recording monitor 7" monochrome. b. 35 mm camera. c. Laser printer (1200 dpi). d. Storage on floppy disk.

5.5 Analysis of Dielectric Material Properties Using LCR Meters

A wide variety of methods exists for the measurement of permittivity; the particular method adopted being determined by the nature of the specimen and the frequency range in which the measurement is made.

Impedance measurements are a basic means of evaluating electronic components and materials. Every material has a unique set of electrical characteristics that are dependent on its dielectric or insulation properties. Accurate measurements of these properties can provide valuable information to ensure an intended application or maintain a proper manufacturing process. And so what are these measurements and how are they made?

5.5.1 Dielectric Constant

The dielectric constant measurement, also known as relative permittivity, is one of the most popular methods of evaluating insulators such as rubber, plastics, and powders. It is used to determine the ability of an insulator to store electrical energy. The complex dielectric constant consists of a real part (k'), which represents the storage capability and an imaginary part (D), which represents the loss.

The dielectric constant is defined as the ratio of the capacitance of the material to the capacitance of air, or $k' = \frac{Cx}{Co}$ where Cx = capacitance with a dielectric material and Co =

capacitance without material, or vacuum. The k' value of dry air is 1.00053, which for most measurement applications is usually close enough to the value of a vacuum, which is 1.0000. Thus if a material is to be used for insulating purposes only, it would be better to have a lower dielectric constant, or as close to air as possible. To the contrary, if a material is to be used in electrical applications for storage of electrical charge, the higher the dielectric constant the better. More charge is stored when a dielectric is present than if no dielectric (air) is present. The dielectric material increases the storage capacity of the plate capacitor; hence the dielectric constant of any solid or liquid would be greater than 1.

5.5.2 Dissipation Factor

Dissipation factor (D) is defined as the ratio of an insulating materials resistance to its capacitive reactance at a specified frequency. It measures the inefficiency or loss of the material, is always greater than 0, but usually much smaller than the dielectric constant. D measurements are an excellent means of quality control which can yield indication of contamination or deterioration. For example, if we wanted to check the purity of epoxy or some raw material for consistency in a production run why not just measure the D. Excessive moisture would increase the dissipation factor value telling us something has changed as compared to previously established values.

The capacitance for a particular dielectric medium can be measured; the dielectric constant of the medium can be determined simply by the equation,

$$\varepsilon_m = C_m / C_o$$

5.5.3 How can these measurements be made?

When making these measurements, connection of the material to the measuring instrument (an LCR Meter) is one of the major challenges faced, special fixtures are generally required depending on the material type. With copier toner, PVC compounds, and other powders the material can be compressed into a test slab or disk at a given thickness so it can be measured in a dielectric cell. In simplest terms a dielectric cell is a nothing more than a test fixture with two adjustable plates into which the sample is installed for evaluation of its electrical properties. The most common piece of test equipment for holding a variety of solid materials is the LD-3, a liquid tight, three terminal connection cells with electrode spacing adjustable by a precision micrometer. When connected to an automatic LCR meter, the capacitance (C) and loss (D) measurements can be readout directly yielding fast, reasonable results.

Working Principle:

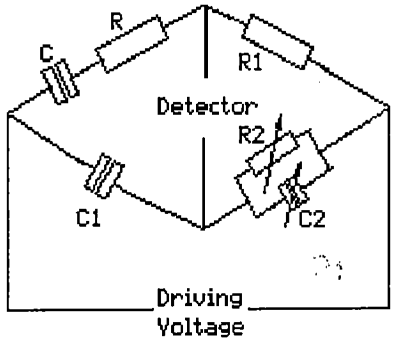


Figure5.9: Schering bridge

For frequencies in the audio to high range (10^2 to 10^7 hz) one of the many a.c. bridges may be used for the measurement of permittivity of these the Schering bridge, shown in above figure is most usually used since it is suitable for higher frequencies and can be calibrated for direct reading of $\tan\delta$.Referring to figure 5.9, 'C' represents the dielectric-filled condenser and R the dielectric loss.C1 and C2 are standard, calibrated condensers and resistors R1 and R2 are usually made equal.

The unknown capacitor (or condenser) is represented by the series grouping of C and R on the same arm of the bridge. C_1 is a good standard condenser, whose magnitude should be of the same order as that of the condenser under test. The balance condition can now be expanded to the following,

$$j\omega c_1\left(R + {}^{1}\!/_{jc\omega}\right) = R_1\left(\left({}^{1}\!/_{R_2}\right)\right) + j\omega \qquad (1)$$

Separating the real and imaginary parts gives both of the balance conditions

$C=C_1(R_2/R_1)$ (2a)

$R=R_1(C_2/C_1)$ (2b)

These conditions fulfill the A.C. bridge prescription, the unknown capacitance is obtained in terms of a standard capacitor and the ratio of two resistances. C_2 is only used in the determination of R, the unknown resistance

$C.R_1=R_2.C_1$ (3a) $R.C1/C_2=R_1$ (3b)

The dielectric constant of the medium can be determined simply by the equation,

$$\varepsilon_m = C_m / C_o \tag{4}$$

5.5.4 Quick, Easy Measurements of Solid Materials

One method that is quick and easy, requires a minimum of calculations, but does sacrifice some accuracy, is the Contacting Electrode Method. The results would generally be within 10% if the sample is reasonably flat, thick and uniform.

Figure 5.10A **Figure 5.10B**

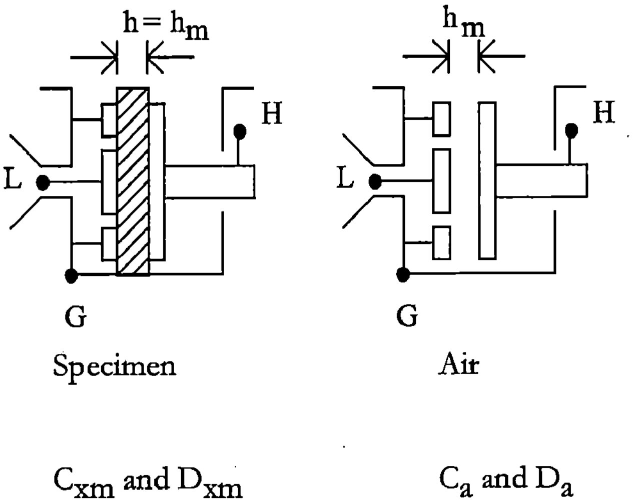


Figure 5.10: Dielectric measurement in air and specimen

This error is smallest for very flat samples, for thicker samples, and for those with low K and D values.

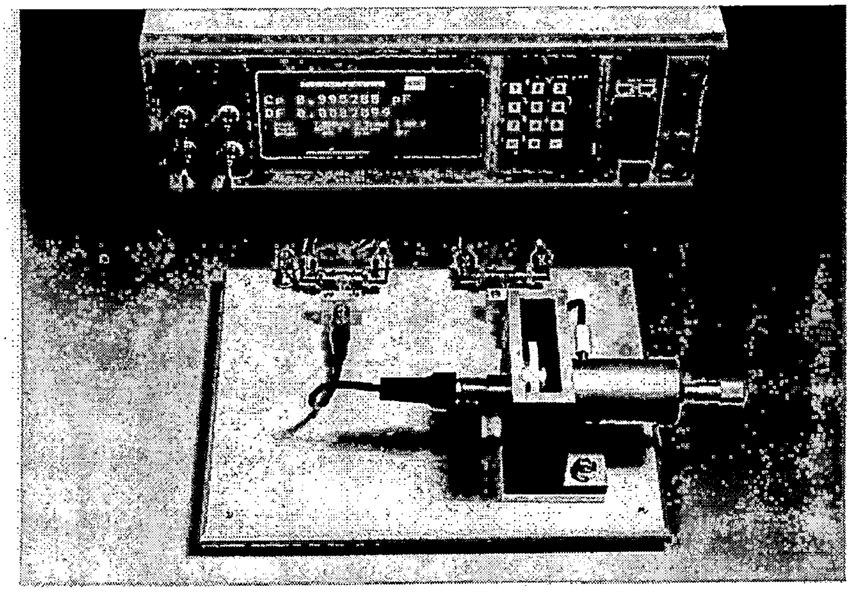


Figure 5.11: QuadTech 7600 Precision LCR Meter shown with Dielectric Products LD-3 Cell

Other Methods for Increased Accuracy

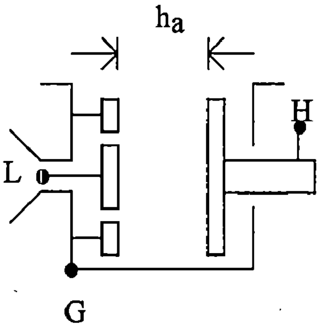
Since a layer of air between specimen and electrodes can't be completely avoided a more accurate result is possible using another calculation and a specimen of known thickness. In this case the thickness of the sample is first measured at several different points and averaged to yield h_m, Figure 5.12. The electrodes of the test cell are opened to 0.01 to 0.02 cm greater than h_m by setting the micrometer to a value of h_a. The capacitance and dissipation factor, C_a and D_a, are measured for h_a, with air as the dielectric. The specimen is then inserted between the electrodes, approximately in the center, and the new values, C_{xa} and D_{xa}, measured. The value for dielectric constant is then calculated from

$$k' = \frac{1}{1 - \frac{\Delta C}{C_{xa}} \frac{h_a}{h_m}}$$

and D calculated from $D = D_{xa} + \left(\frac{h_a}{h_m} - 1 \right) k' (D_{xa} - D_a)$

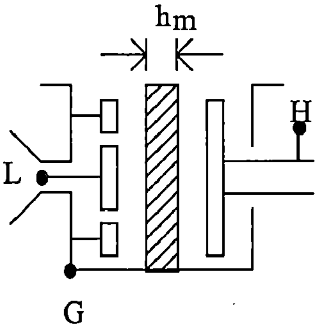
The accuracy of these results depends mainly upon the accuracy with which the two thicknesses (material and cell opening) can be measured. This is called the Air-Gap Method.

Figure 5.12A



C_a and D_a

Figure 5.12B



C_{xa} and D_{xa}

We can even take this one step further. When a specimen whose thickness is difficult to measure, because it is thin or not rigid, it can be measured without regard to its thickness. A measurement is first made with the cell and a fluid, usually air, then the specimen plus air (same as the air-gap method discussed earlier). Two more measurements are then made; the cell with a second fluid, and the specimen with this second fluid. This is called the Two-Fluid Method, which yields accurate results of dielectric constant and loss through a slightly more complex calculation. In this method the choice of fluid must be one that has known and stable dielectric properties, does not react with the test specimen and not too messy to deal with. Usually a silicon fluid base fits this requirement.

LCR Meters and specimen cells are readily available that make it easy to perform impedance measurements on materials. A measuring instrument with a wide programmable frequency range is important since the insulation properties can vary substantially with frequency. Accuracy of results can be enhanced by averaging several measurements and calculating results can be simplified through computer programs, all of which leads to better process control, increased efficiency and superior products. [19-21]

EXPERIMENT

Polycrystalline samples of with $Pb_{1-3x/2}$ Nd_x $(Zr_{.65}Ti_{.35})$ O3 x=1, 3, 5, 7, and10 mole percent were prepared by the conventional solid reaction route method (PNdZT) from the raw materials (commercially available Lead oxide, Neodymium oxide, Zirconium oxide and titanium oxide powders of 99.9% purity) in stochiometric proportions.10% excess Lead oxide was used to compensate for the Lead evaporation during sintering process at the elevated temperature. These raw materials were ball mixed for 2 hrs mixed in the mortar and pestle. More the finer the powder more easily reacts in the calcinations and in less time period is required.

Composition $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$	Weight(gms) X=.01	Weight(gms) X=.03	Weight(gms) X=.05	Weight(gms) X=.07	Weight(gms) X=.1
PbO	19.968	12.997	12.581	12.331	12.008
Nd_2O_3	0.153	0.308	0.513	0.727	1.065
ZrO_2	7.281	4.884	4.883	4.944	5.069
TiO_2	2.542	1.705	1.705	1.726	1.771

Table 6.1: The Stoichiometric weight of the $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$

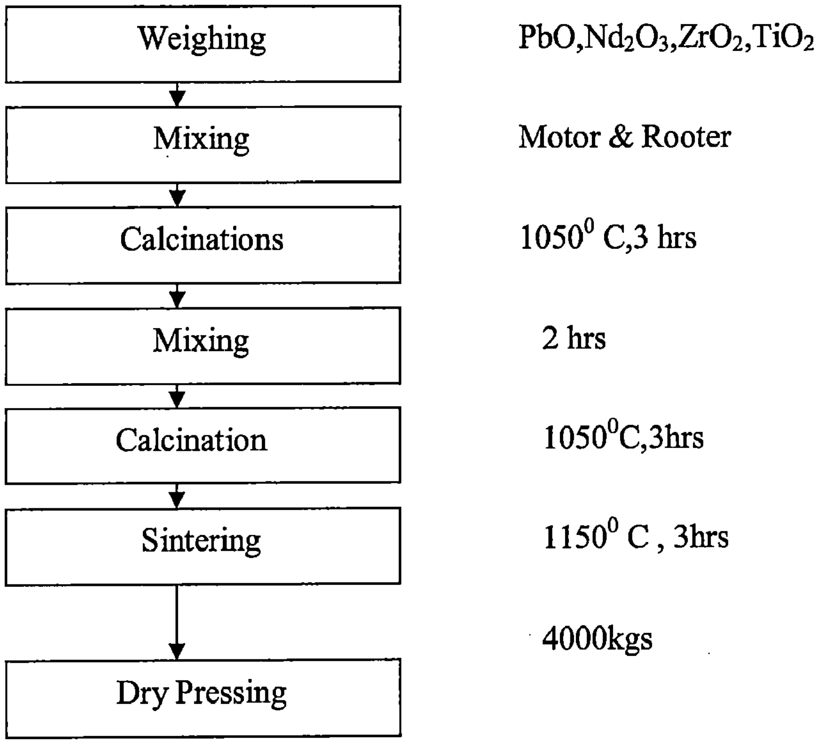


Figure6.1: Flow chart of Experimental Procedure for solid State method

6.1 CALCINATION

The heating of a solid to a high temperature, below its melting point, to yield the degree of sintering and agglomeration of diatomite particles needed to result in particular flow rate permeability. Calcining can be effected over a range of temperatures up to about 1300° C. A powder can immediate be formed into a shape and sintered without prior heat treatment, but usually an intermediate calcinations occur at a lower temperature. Calcinations causes the constituents to interact by inter diffusion of ion and so reduced the extent of the diffusion that must occur during the sintering in order to obtain a homogeneous body. It can therefore be considered to be part of mixing process. The calcinations conditions are important factor controlling shrinkage during the sintering. To minimize the energy of the system, this involves a considerable movement of ions; there inter diffusion to form new phases the minimization of the internal surface area and an increase in grain size.

For the initial heat treatment, the mixture is heated at1050^0 c for 3hrs in the furnace.

SINTERING

Sintering converts a powder into a denser structure of crystalline joined to one another by grain boundaries. Grain boundaries vary in thickness from about 100 pico meter to over 1 micrometer. They may consist of crystalline or vitreous phase or may be simply a disordered form of major phases because of the differing lattice orientation in neighboring grains. They impact strength to the body, typically in the range of 70-350 MPa. Grain boundaries are not generally as dense as the crystals and in the early stages of the sintering at least, allow free diffusion of gas to and from the outside atmosphere. The energetic basis of sintering lies in the boundaries to adjacent pores which are eventually filled. The most mobile available entities are vacant crystal site, which moves from pores into the grain boundaries. Grain boundaries serve as vacancy 'sinks' because of their intrinsic disorder. Grain growth also takes place in parallel with densification and is energetically favored by the reduction in the are of grain boundaries. This is because the crystal lattice has a lower free energy than the defectively grain boundaries region and the ratio of boundaries area to the volume for large grain are smaller than that for small grains. If crystal growth is to rapid, pores may become detached from he grain boundary so that the easy mechanism for their removal is lost, crystal growth should be limited. Grain boundaries can be stabilized to some extend by the presence of finally divided phase that is insoluble in both the main and the inter granular phases.

The heat treatment may be done in a crucible or evaporating dish made of alumina or in a good grade of laboratory porcelain. This forms a basic crystal structure PNdZT. The result of first firing is a porous light yellowish color powder. The coloration should be fairly even. An uneven coloration is an indication that the powders are not as thoroughly mixed as they should have been, and that extra time and care should be taken to ensure thorough grinding and mixing on the subsequent steps. The yellowish powder is ground into a fine powder and placed in the furnace in an alumina dish, at 1050^0c, and for 3hrs for intermediate firing. Intermediate firing ensures the formation of basic structure of the material.

The calcined Powder is mixed with binder and than put into hot air chamber for to remove the moisture in it and again converted into a fine powder. Compressing the powder at 4000 Kgs using a 7mm diameter steel die formed cylindrical pellets using a hydraulic press.Finally,the sintering of the pellets was carried was carried out at 1150^0 for 3hrs with a heating rate of 5.83^0 c/min. It leads to densification of the material and also increases the strength of the material. The maximum sintered temperature is 10% percent above the calcined temperature. All the sintered samples samples were found to be of 95% of the theoretical density. The structural studies of all the samples were performed on PW 3020 Philips X-ray diffractometer using CuKα (k = 1.5405^{0}A) radiation. Scanning electron micrographs were obtained using Cambridge Stereo scan 360 scanning electron for microscope studies. Dielectric constant was measured at different frequencies (1 kHz to 1 MHz) as a function of temperature using computer interfaced 4284A HP LCR meter.

6.2 Results and Discussion

Room temperature XRD patterns of the calcined powders of PNdZT are shown in the figure 6.1. Viz. 1/65/35, 3/65/35, 5/65/35, 7/65/53, 10/65/35.These X-ray diffractograms confirm the formation of single perovskite phase for all the compositions. Sharp peaks indicate the good homogeneity and crystallization of the samples. All the reflection peaks were indexed, and compared with the standard peaks (22).

A good agreement, confirms the formation of PNdZT. However, a weak reflection peak was observed for a 2θ value around 29^0 is due to the presence of pyrochlore in the PNdZT structures (2 percent). Some changes in the intensity of a few reflections have been observed, which may be due to variation of particle size and the presence of Nd^{3+} with different x values.

The average particle size (P) of all the pellet samples was calculated from reflections using Scherrer's equation.

$$P=\frac{k\lambda}{\beta_{1/2}\cos\theta} \quad \text{where k=0.89}$$

$\beta_{1/2}$ =Half-peak width

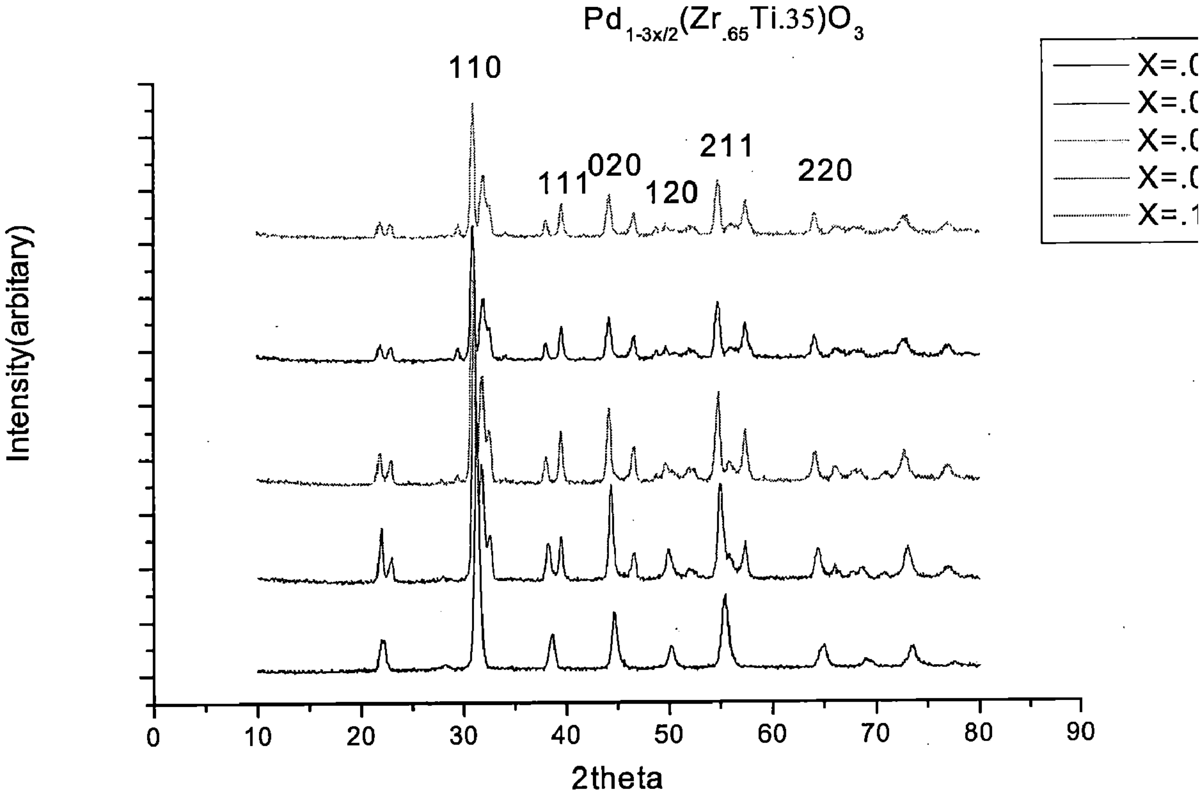
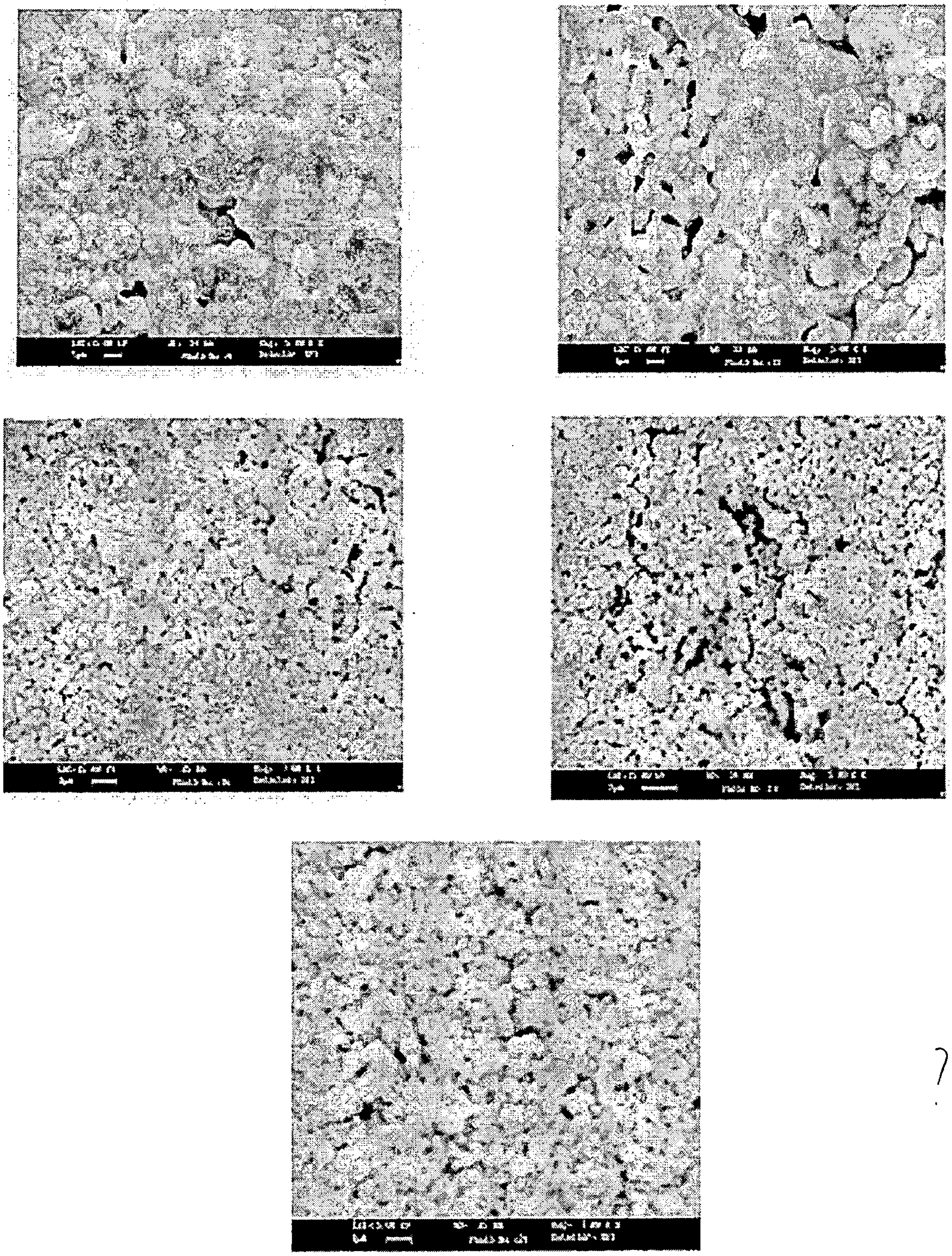


Figure 6.2: The XRD of the PNdZT with x=.01,.03,.05,.07,.1

The morphology studies and grain size measurement of the samples with different x value were obtained using SEM (Scanning electron microscope) are shown in figure 6.2. Some holes and islands can be seen in the figure which suggests that the densities of the compound decreases with increasing dopant concentration small grains are seen in the image. All the compositions show well developed grains. Average size was found to be 1.2958 μm.Another important feature of these micrographs is the fact that, by comparison with the grain size (about 10μm) normally encountered in pure sintered PZT, the addition of Nd^{3+} ion has an inhibiting effect on the grain growth process.

This may be due to the fact that Nd^{3+} ions could be located near the grain boundary, impeding its mobility and enhancement in sintering (23).

Also the micrographs suggest that the sintered pellets were not fully dense.



?

Figure 6.3: SEM of the PNdZT with x=.01, .03, .05, .07, and .1 ?

6.3 Dielectric Measurement:

Dielectric measurements were conducted on an automated system, using HP4192A LCR meter connected with a computer. The dielectric properties of the samples were investigated using an inductance-capacitance-Resistance (LCR) meter in the frequency range 100Hz to 1MHz.

The pellets are polished and coated with silver paint, to form an electrode, for the measurement of dielectric at different frequencies and temperature.

The dielectric constant was measured as a function of temperature for various PNdZT compositions. Plots of dielectric constant measured at different frequencies are shown in the figure 6.4.

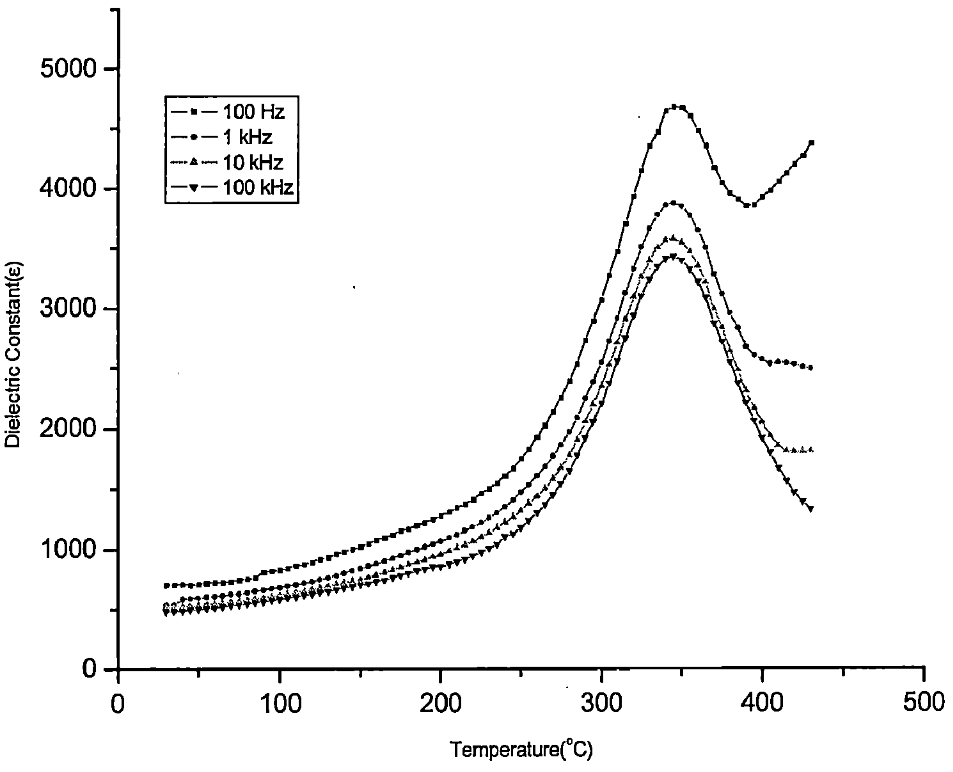


Figure6.4: Dielectric Constant vs Temperature of $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$ with x=.01

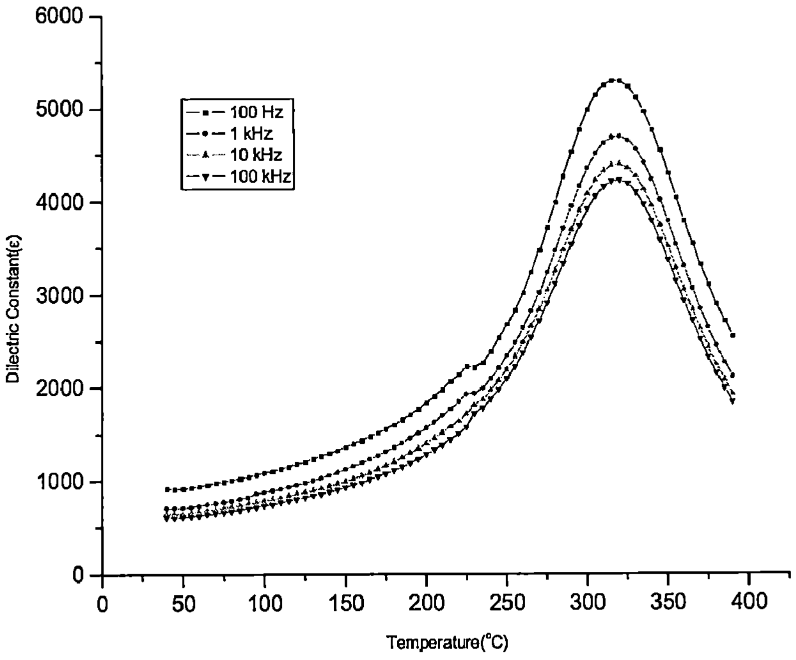


Figure 6.5: Dielectric Constant vs Temperature of $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$ with x=0.03

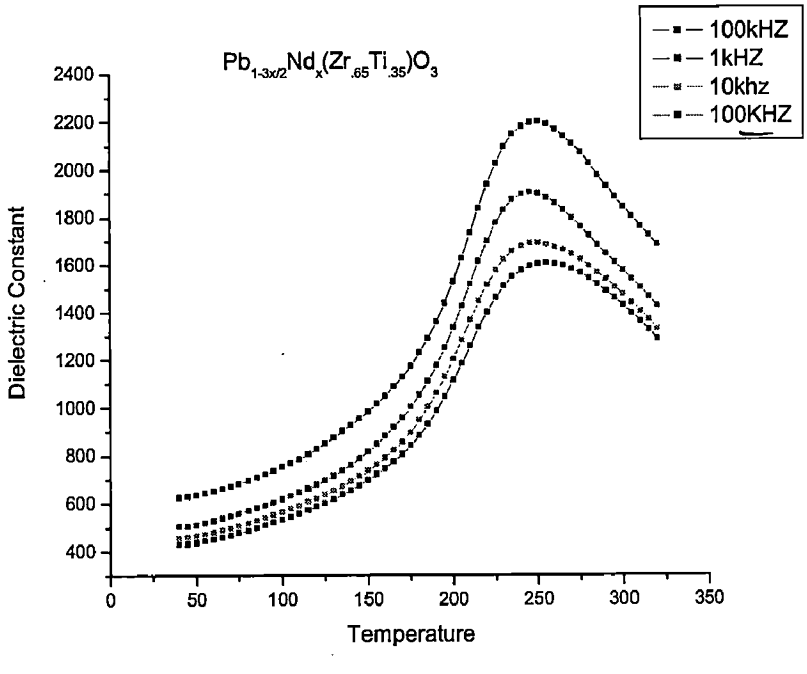


Figure6.6: Dielectric Constant vs Temperature of $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$ with x=.05

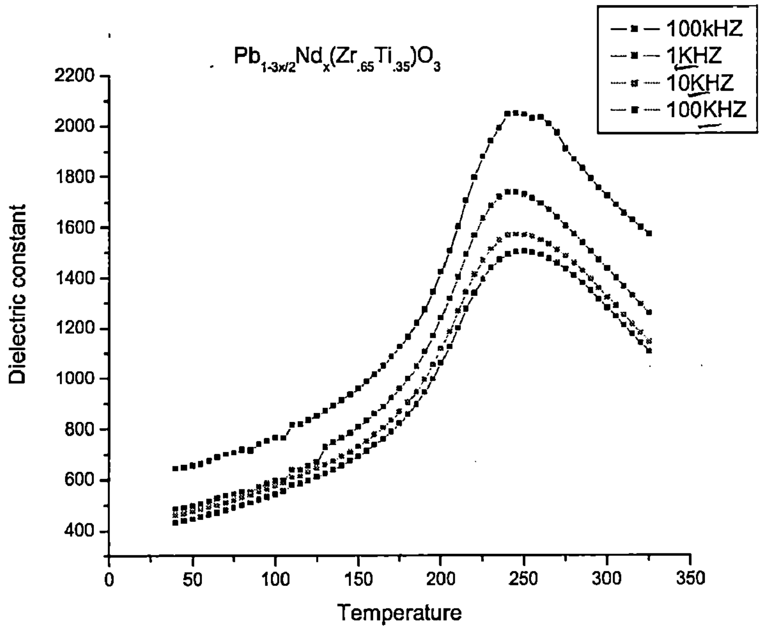


Figure 6.7: Dielectric Constant vs Temperature of $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$ with x=.07

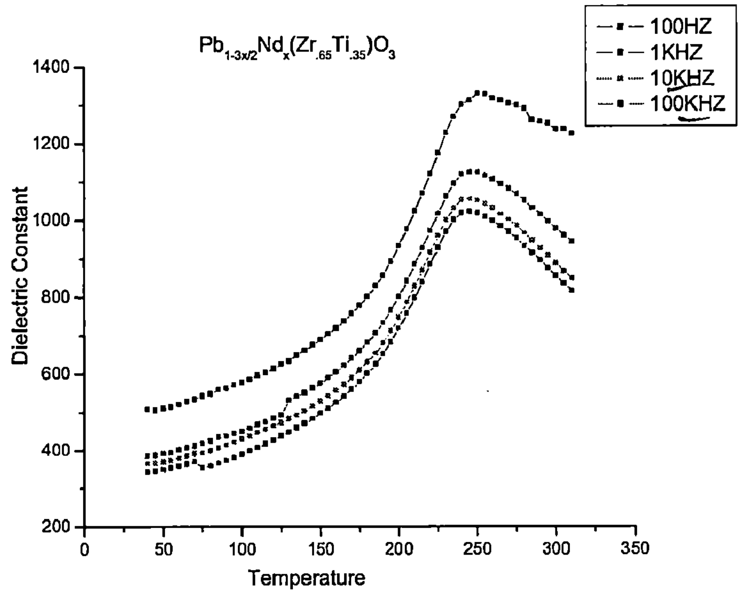


Figure 6.8: Dielectric Constant vs Temperature of $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$ with x=.1

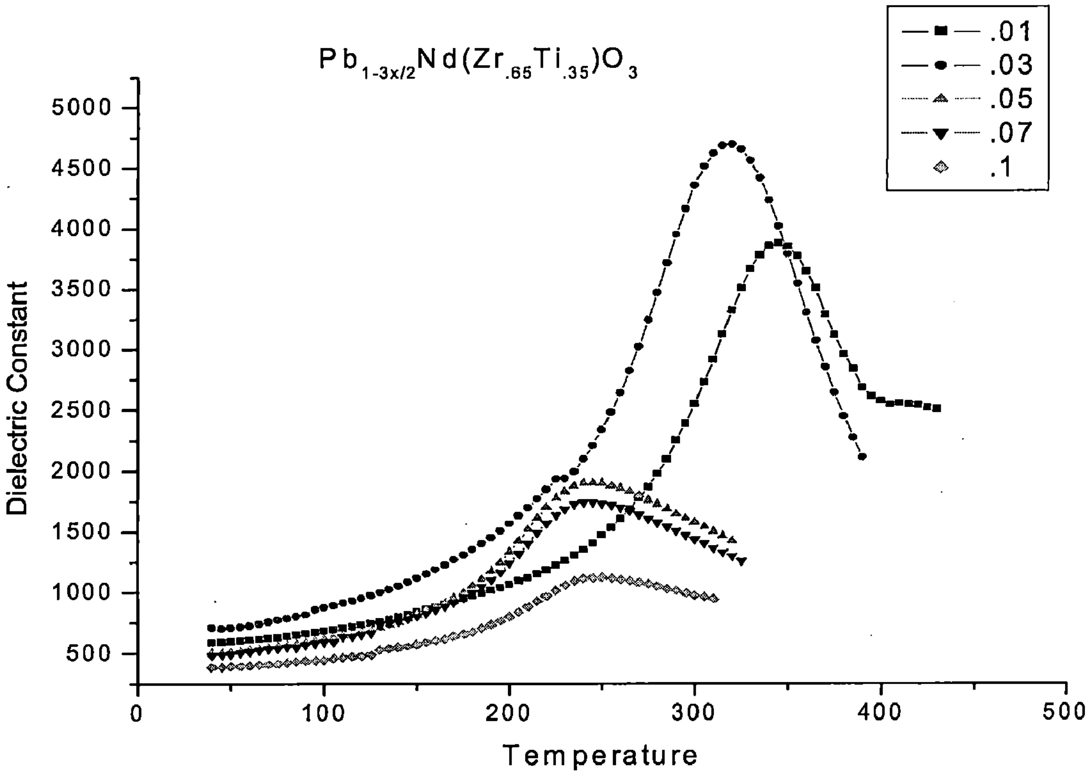


Figure 6.9: Dielectric constant vs Temperature PNdZT with x=.01,.03,.05,.07,.1 at 1khz

With increase in the dopant concentration the Dielectric constant of the compound increases and also the critical temperature (T_c) of the compound. Dielectric permittivity was measured at different frequencies (100 HZ, 1 KHZ, 10KHZ, and 100KHZ).

The difference between the peak dielectric constant and loss is an automatic consequence of the Kramers-Kronig relationships where there is a temperature-dependent relaxation (24).

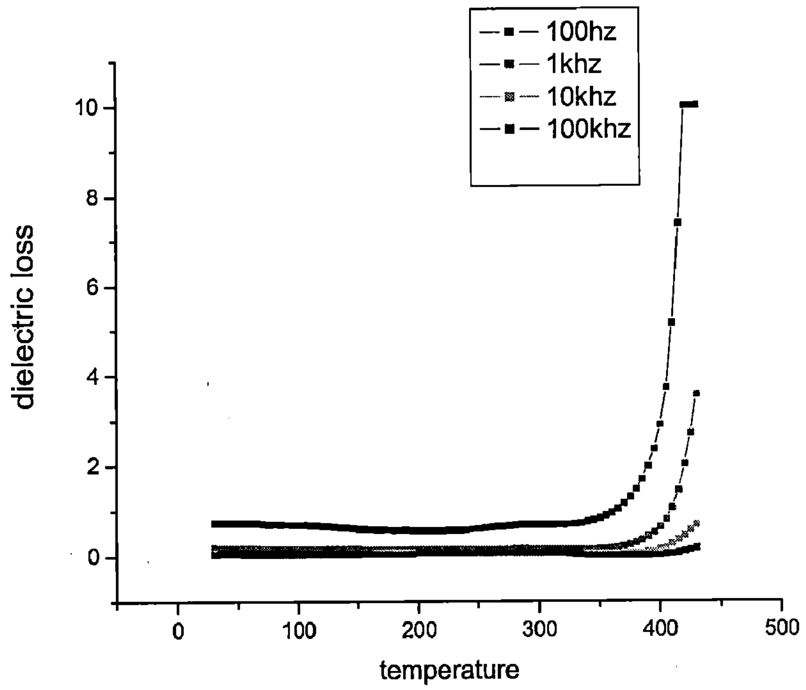


Figure 6.10: Dielectric loss vs Temperature of the $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3x$ with x=0.01

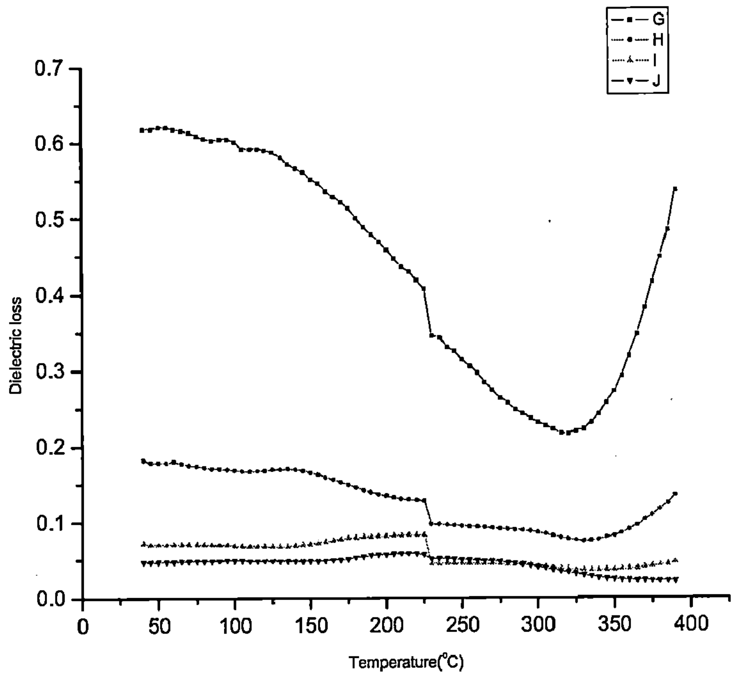


Figure 6.11: Dielectric loss vs Temperature of the $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3x$ with x=0.03

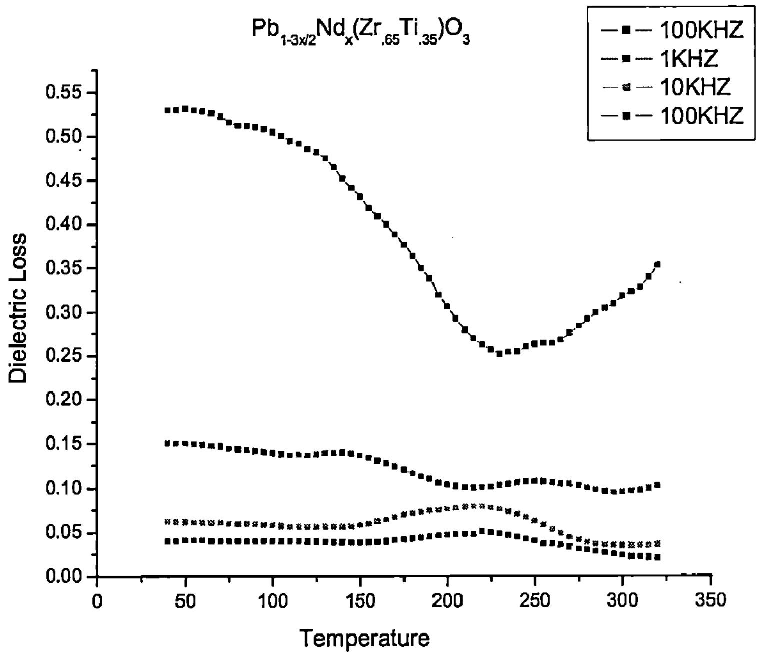


Figure 6.12: Dielectric loss vs Temperature of the $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3x$ with x=0.05

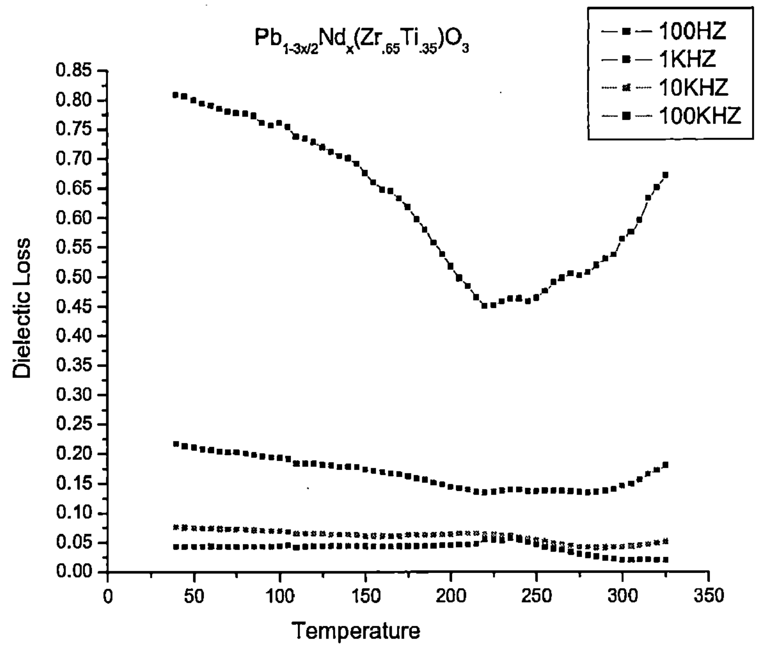


Figure 6.13: Dielectric loss vs Temperature of the $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3x$ with x=0.07

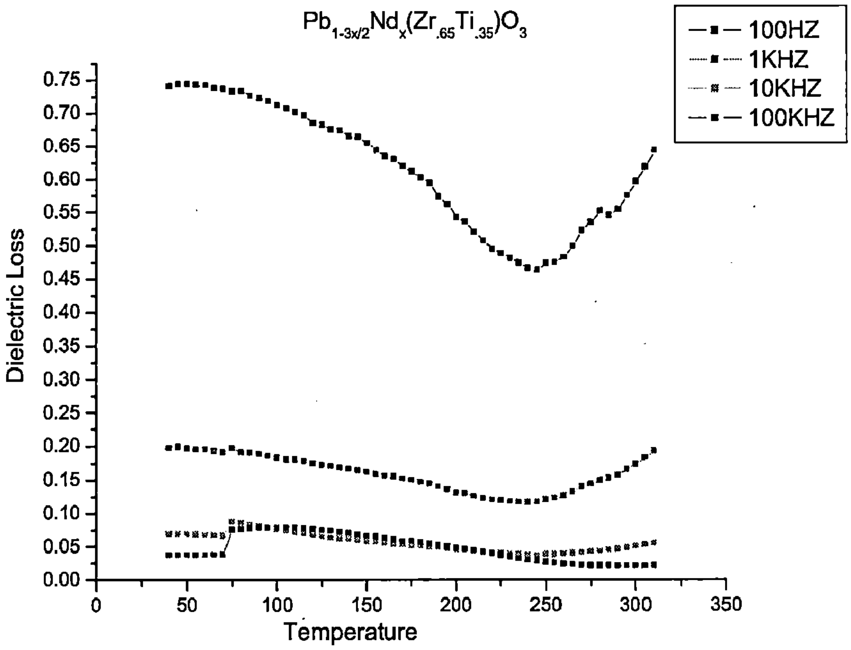


Figure 6.14: Dielectric loss vs Temperature of the $Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3x$ with x=0.1

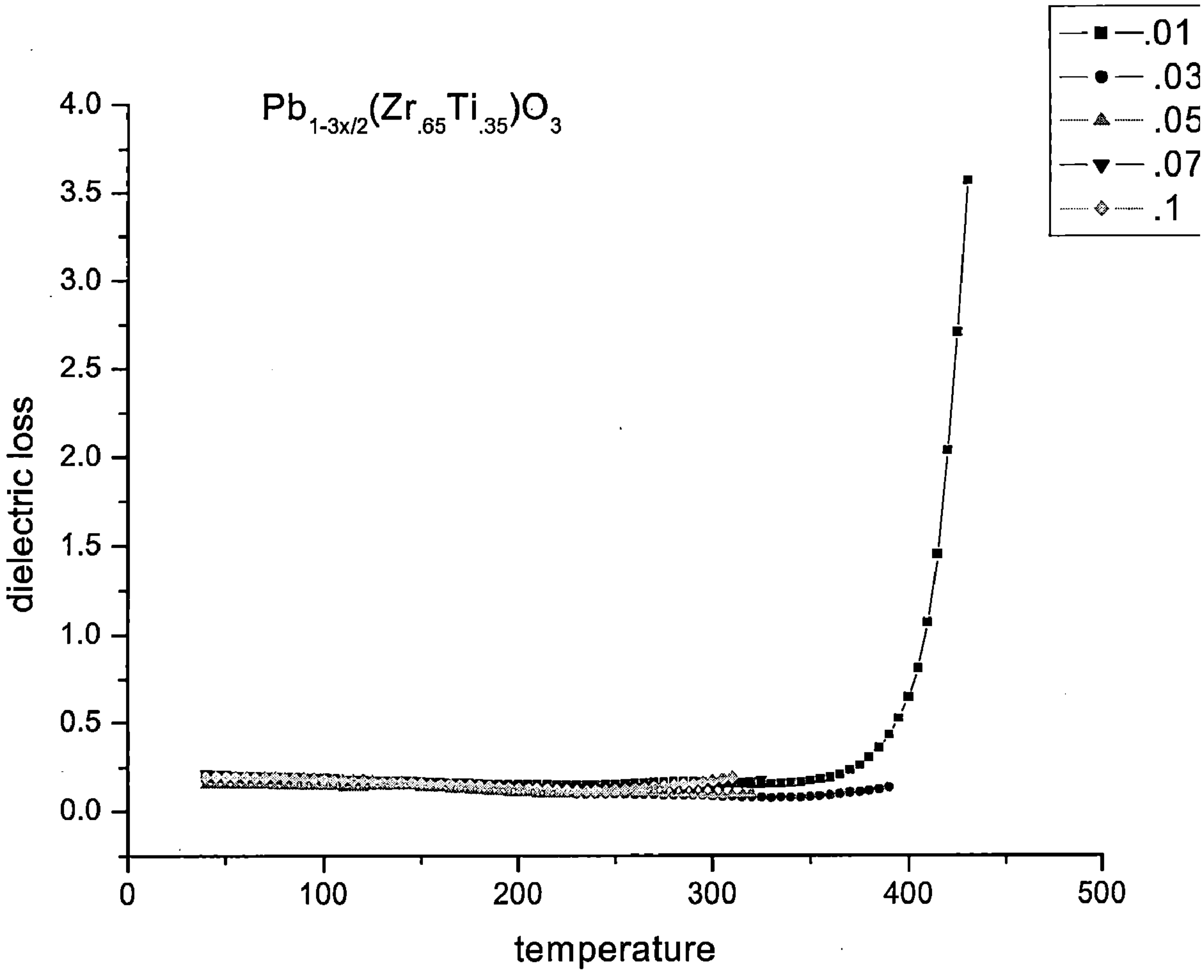


Figure 6.15: Dielectric loss vs Temperature PNdZT with x=.01,.03,.05,.07,.1 at 1khz

$Pb_{1-3x/2}Nd_x(Zr_{.65}Ti_{.35})O_3$	Dielectric constant (K) at 1KHz	T_c	ϱ (gm/cc)	Capacitance (pf)	Particle Size(nm)	Grain size(μm)	Diff ty
X=.01	3864.99	344.74	6.403	0.31121	23.490	1.875	2
X=.03	4682.71	317.17	6.403	0.205	31.519	1.625	1.89
X=.05	1903.39	244.42	6.289	0.3003	33.339	1.3	1.68
X=.07	1738.23	241.47	6.203	0.232	31.764	0.95	1.57
X=.1	1124.74	246.29	6.214	0.316	36.789	0.729	2.01

Table 6.2: Characteristic properties of the PNdZT

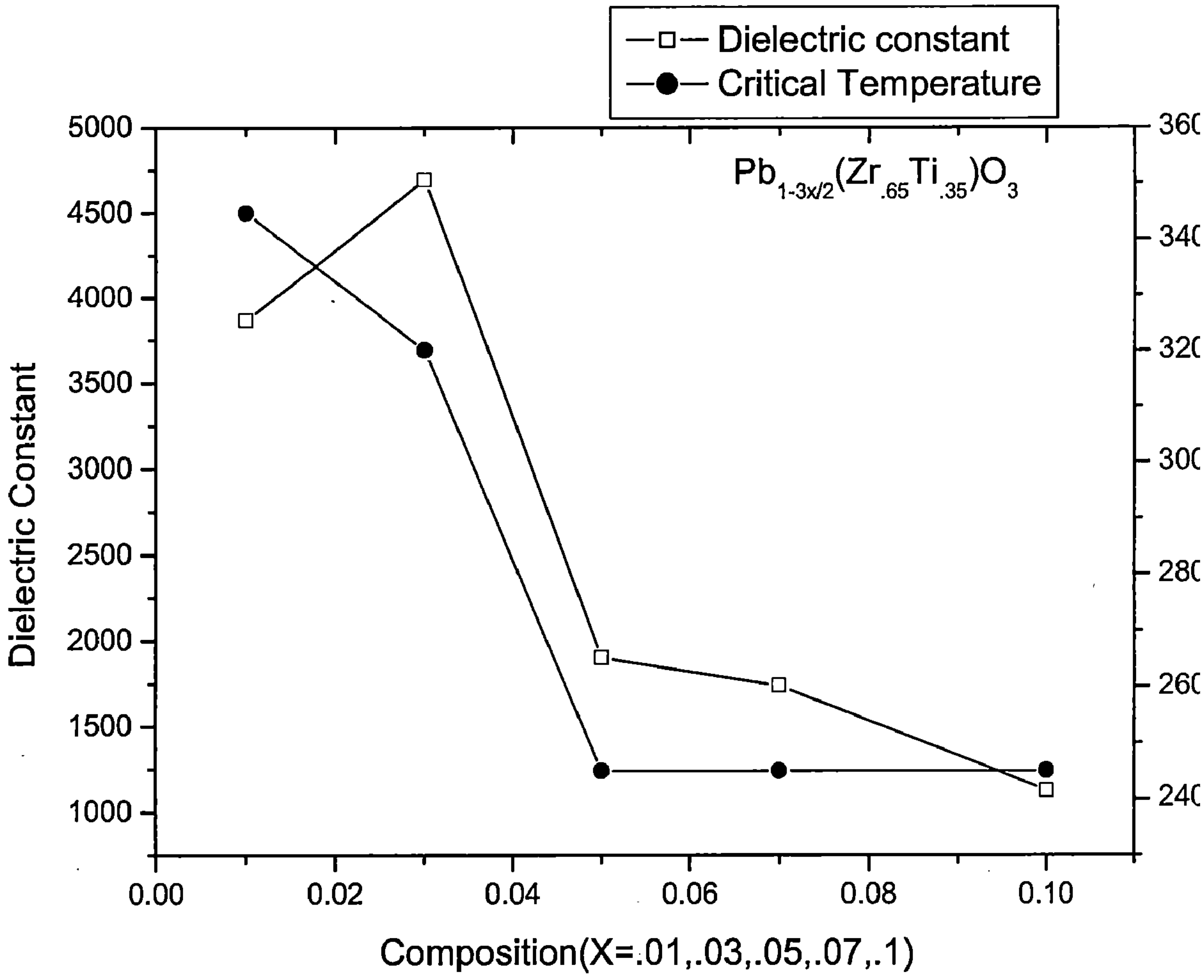


Figure 6.16: Variation of Dielectric constant, Critical Temperature with respect to composition

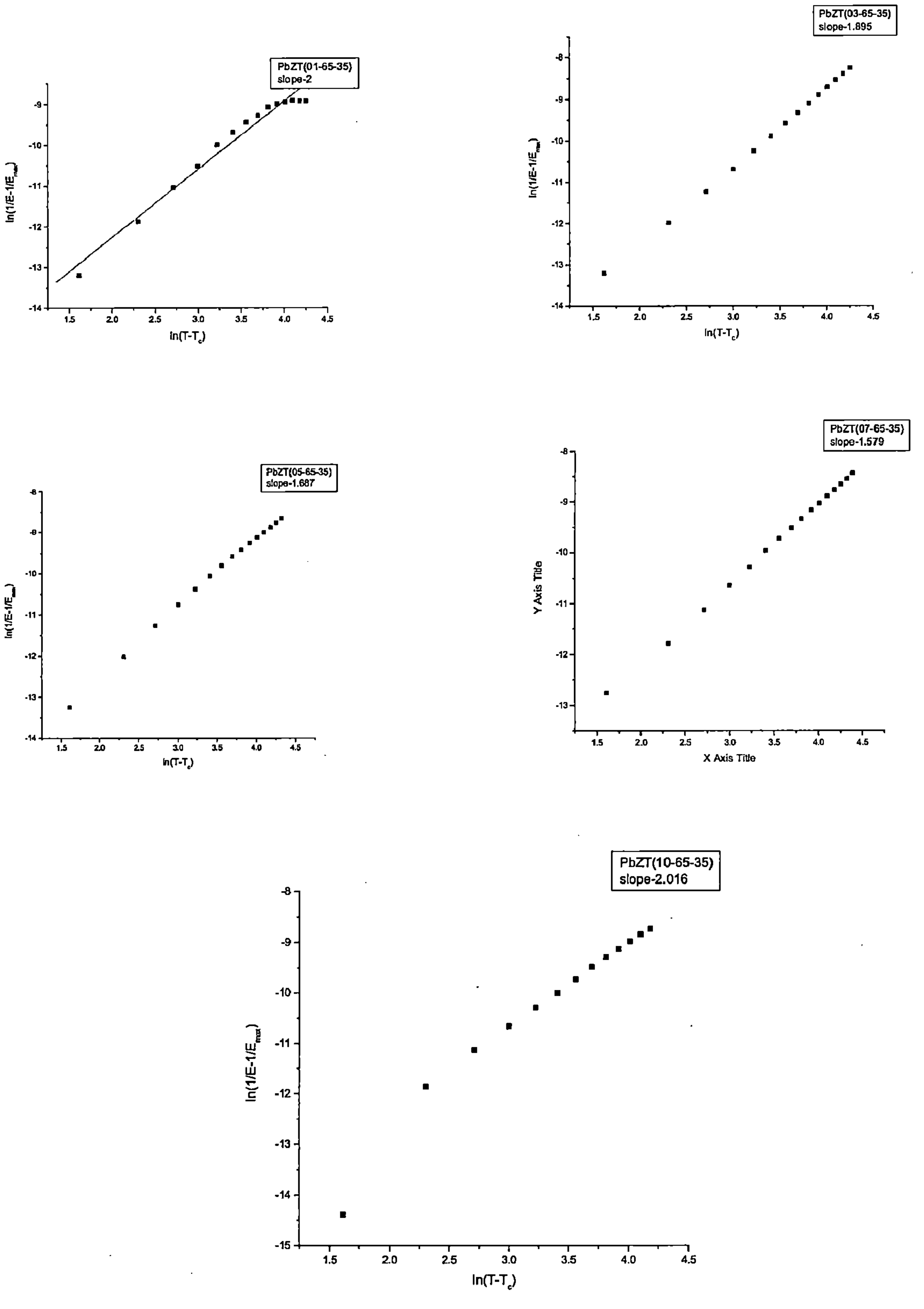


Figure 6.17: shows the diffusivity of $Pb_{1-3x/2}(Zr_{.65}Ti_{.35})O_3$

The region around the dielectric peak is broadened, which is on of the most important characteristics of a disordered perovskite structure with a diffuse phase transition. The broadening is considered to be due to compositional fluctuations. Compositional fluctuations may be developed at the A-site which is occupied by Pb^{+4} or at the site B-site occupied by Zr^{+4} or Ti^{+4} (25, 26). It is also seen that the dielectric peak shifts towards the higher temperature side with increasing frequencies. This dispersion and the shift in Tc of the maximum dielectric permittivity confirm the relaxor behavior of PNdZT ceramics. Further examination of the diffuseness in the materials was carried out by using the following expression $(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_{\max}})\alpha(T-Tc)^{\gamma}$ Where $\varepsilon_{\max}$ is the maximum value of ε at Tc.The value of γ (diffusitivity) was found to be between 1 and 2, which confirms the diffuse phase transition in the material. Ideally sharp phase transition can occur in the thermodynamic limit of infinite systems; phase transitions are rounded and shifted with different characteristic exponents for the first and second order transitions.

When a crystal is cooled from the paraelectric state to the ferroelectric state in the absence of any external field, the uncompensated polarization at the surface acts as the source for an intense depolarization field in insulating systems in order to minimize the energy associated with this field macroscopic systems split into domains of uniform polarization .it is well known that for materials like $BaTio_3$ and PZT , dielectric constant shows a sharp jump at the ferroelectric phase transition temperature characteristic of a first order phase transition.

Conclusion and Future Work

7.1 Conclusion

The PNdZT ceramics prepared by conventional solid reaction route (calcined at 1050°C and sintered at 1150°C) exhibits homogeneity formation of single phase compound and useful dielectric and other electrical properties.

1. The particle sizes calculated on the basis of Scherrer's equation are found to be increasing Nd concentration (except at X=0.07).
2. The dielectric constant and the loss tangent are found to decrease with increasing frequency which is the characteristic property of the ferroelectric materials.
3. The effect of dopant on the property of PZT is studied, it was found that with increasing dopant concentration, initially dielectric constant increases (up to X=0.03) than decreases and also the critical temperature increases due to the addition of Nd^{3+} ions, is lowered.
4. It is found that the dielectric peaks of theses compounds are broad and suggest diffuse (broad) phase transition for the compounds. It can be concluded that there is no change in the basic structure of $Pb_{1-3x/2}(Zr_{.65}Ti_{.35})O_3$ for Nd substitution .

From our dielectric study, we can prescribe the above materials as good dielectric materials due to their high dielectric constant and low dielectric loss which is very much suitable for the Memory applications.

7.2 The future: a vision

We see that in the last ten years significant advances have been made in computing properties and understanding origins of ferroelectric behavior. We now have the ability to predict ferroelectric instabilities, electromechanical coupling, phonon dispersion and optical spectroscopy, elasticity, pressure behavior, order–disorder, and some surface and defect properties of structurally and chemically relatively simple pure compounds. Now the challenge is to address problems in more complex solid solutions, some that are structurally and/or chemically heterogeneous and some with frequency dependent properties.

7.2.1 Relaxor systems

In relaxor systems, the dielectric response has a broad peak as a function of temperature, rather than a sharp peak in a normal ferroelectric, and a frequency dependent response. The origin of this behavior is still controversial, but is most likely due to heterovalent disorder. It will be a challenge to compute this behavior from first-principles(By "first-principles", we mean that experimental data are not used to constrain parameters; rather one starts from the fundamental interactions among electrons and nuclei. Most of the first-principles methods that have been applied to ferroelectrics are based on the density functional theory (DFT) [27] and some are based on Hartree–Focktheory.)

but models can be parameterized using first-principles results, as in the effective Hamiltonian models discussed above, and then molecular dynamics or Monte Carlo simulations could be used to simulate still rather small disordered systems. To simulate much larger, mesoscopic systems, it may be necessary to parameterize models for interactions between nanoregions, leaving the atomic domain all together. But this may be possible using only ab initio results.

7.2.2 Materials by design

The goal of this research program is to lead to the ability to computationally design useful materials. We are clearly on that path, but it will be a few years before one can

Practically hope to routinely design materials by computer. On the other hand, it is also largely a matter of having the right good idea. We understood the role of Pb in the strain of PbTiO3 some years ago, and if we smart enough to think of trying to make "rhombohedral PbTiO3" we might have found this large strain effect before experiments. However, theoretical developments were just a few years behind to realistically do this, because the first-principles computation of piezoelectric constants in pure tetragonal PbTiO3 were only done this last year, and it has not been that long since the Berry's phase approach to computing polarization was discovered. As we make further advances, however, in the next revolution perhaps theory will lead the way rather than follow [28].

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