Chapter 1

INTRODUCTION

1.1 Introduction

Ferroelectric ceramics were born in the early 1940’s with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramics. Since that time, they have been the heart and soul of several multi-billion-dollar industries, ranging from high dielectric constant capacitors to later developments of piezoelectric transducers, PTC devices and electro-optic light valves. The era of ferroelectricity began in early 1940’s under a cloud of secrecy, because World War 2 was under way. Materials based on two compositional systems, barium titanate and lead zirconate titanate, have dominated the field throughout their history. The more recent developments in the field of ferroelectric ceramics, such as medical ultrasonic composites, high-displacement piezoelectric actuators (Moonies, RAINBOWS), photostrictors, and thin and thick films for piezoelectric and integrated-circuit applications have served to keep the industry young amidst its growing maturity.

The tungsten bronze type ferroelectric crystals have a structure similar to tetragonal tungsten bronze KxWO3 (x<1). Lead niobate (PbNb2O6) was one of the first crystals of the tungsten bronze type structure to show useful ferroelectric properties. The site occupancy formula for this type of structure is given by (A1)2(A2)4(C)4(B1)2(B2)8O30. Figure 14 shows the schematic of the projection of the tungsten bronze type structure on the (001) plane. For lead niobate the B1 and B2 sites are occupied by Nb5+ ions. The open nature of the structure as compared to the perovskite allows a wide range of cation and anion substitutions without loss of ferroelectricity. At present, tungsten bronze family of oxide ferroelectrics, numbers more than 85.The ferroelectric crystals grown from solid solutions of alkali and alkaline earth niobates have shown great potential for being used as a material for laser modulation, pyroelectric detectors, hydrophones, and ultrasonic applications. The high Curie point (T_c = 560 ^oC for lead niobate) of their compounds makes them suitable for high temperature applications.

1.2 Applications of ferroelectric materials

Ferroelectrics are excellent candidates for the applications in data storage in digital memory systems, in addition to many other important applications such as piezoelectrics, pyroelectrics, and electro-optics in sensors, actuators, and microelectromechanical systems (MEMS).1–5 Random-access memories (RAMs) based on semiconductor integrated technology have been a great success; however, these semiconductor RAMs can retain information only when power is on. A serious drawback is that when power is interrupted, all information is lost (volatile memory). Furthermore, these RAMs are very sensitive to radiation and this is detrimental for military and space applications.

Among ferroelectric materials, Pb(Zr,Ti)O3 (PZT) is one of the most popular materials attracting many investigators for many years. PZT has an isotropic perovskite crystal structure with a high remanent polarization (30–50 mC/cm2).6–8 Unfortunately, PZT films tend to degrade most of the initial amount of switching charge (so-called “fatigue”) after 106–108 cycles of full polarization switching.9 To be competitive with electrically erasable read-only memories (EEPROM), ferroelectric memories (FeRAMs), which are also called nonvolatile random-access memories (NvRAMs), must be improved to withstand at least 1012 erase/rewrite operations or they must have qualitatively different nondestructive read operations.

- **Capacitors**

The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. This fact makes ferroelectric capacitors smaller compared to dielectric (non-tunable) capacitors of similar capacitance.

- **Non-volatile memory**

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function. Indeed, ferroelectric capacitors are used to make ferroelectric RAM for computers and RFID cards. These applications are usually thin films of ferroelectric materials as this allows the high coercive field required to switch the polarization to be achieved with a moderate voltage, though a side effect of this is that a great deal of attention needs to be paid to the interfaces, electrodes and sample quality for devices to work reliably.

- **Piezoelectrics for ultrasound imaging and actuators**

All ferroelectrics are required by symmetry considerations to be also piezoelectric and pyroelectric. The combined properties of memory, piezoelectricity, and pyroelectricity make ferroelectric capacitors very useful, e.g., for sensor applications. Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body).

- **Electro-optic materials for data storage applications**

High quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. Also, the electro-optic modulators that form the backbone of the Internet are made with ferroelectric materials.

- **Ferroelectric tunnel junctions**

One new idea of recent interest is the *ferroelectric tunnel junction* (*FTJ*) in which a contact made up by nanometer-thick ferroelectric film placed between metal electrodes. The thickness of the ferroelectric layer is thin enough to allow tunneling of electrons. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electroresistance (GER) switching effect.

- **Multiferroics**

Another hot topic is multiferroics, where researchers are looking for ways to couple magnetic and ferroelectric ordering within a material or heterostructure; there are several recent reviews on this topic.

- **Thermistors**
- **Switches known as transchargers or transpolarizers**
- **Oscillators and filters**
- **Light deflectors, modulators and displays**.

SPECIAL ROLE OF SBN IN INDUSTRIAL APPLICATION:

Recently, bismuth oxide layered perovskite materials, such as SrBi2Nb2O9 (SBN), SrBi2Ta2O9 (SBT), and SrBi2(Nb,Ta)2O9 (SBTN), for FeRAM applications have attracted an increasing attention in the research community, because they are fatigue-free and lead-free and possess ferroelectric properties independent of film thickness.10,11 Layered perovskite ferroelectrics, however, suffer from two drawbacks: a relatively low remanent polarization and a high processing temperature. Recently, efforts have been made to enhance the properties of layered perovskite ferroelectrics by theaddition or substitution of alternative cations.

For example,partial substitution of Sr2+ by Bi3+ has resulted in the most noticeable improvement of ferroelectric properties. Both the Curie point and the peak dielectric constant increased significantly with an increased Bi3+ substitution. The enhancement of ferroelectric properties was reported to be accompanied with a linear decrease in lattice parameters due to the substitution of relatively larger cations (Sr2+: 143 pm) at A sites by relatively smaller cations (Bi3+: ~130 pm).

However, the substitution of bivalent Sr2+ cations by trivalent Bi3+ required introduction of cation vacancies to maintain electroneutrality. Although the influences of such cation vacancies on the ferroelectric properties have not been studied, cation vacancies may result in a structural distortion of oxygen octahedron and, thus, degrade the polarizability. The incorporation of barium ions into strontium positions was also reported to exhibit higher remanent polarization than the intrinsic SrBi2Ta2O9 thin films.

1.2 Classes of ferroelectric materials

Dielectrics are electrically non-conducting materials such as glass, porcelain etc, which exhibit remarkable behavior because of the ability of the electric field to polarize the material creating electric dipoles.

Ferroelectricity: Some dielectric materials spontaneously acquire an electric dipole moment below a certain temperature. This is referred to as spontaneous polarization. Analogy with magnetic material results in a type of dielectric materials called ferroelectric materials. Similar to Ferromagnetic materials Ferroelectric materials also exhibit ferroelectric hysteresis. It is a plot of polarization (P) versus Electric field strength (E). Ferroelectric hysteresis is the lagging of the polarization with respect to applied electric field Strength during the positive polarization and negative polarization of the specimen.The static dielectric constant of a ferroelectric material changes with temperature which is given by i*r* Where C is a constant, T is the temperature and q is a temperature very close to a temperature called Curie temperature (Tc). Ferroelectric materials exhibit Piezoelectricity and Pyro-electricity. Quartz, Lithium Niobate and Barium Titanate are the few examples of ferroelectric materials. Ferroelectric materials are used in pressure transducers, Ultrasonic transducers, microphones, Infrared detectors and capacitors.

Piezoelectric Materials:

Certain dielectric materials are electrically polarized when their surfaces are stressed. This phenomenon is called piezoelectric effect and the materials are called piezoelectric materials. The charges produced on the surface due to stressing are proportional to the applied force which is utilized in the conversion of mechanical energy into electrical energy. When crystals like Tourmaline, Rochelle salt and Quartz are sliced in a particular fashion they exhibit piezoelectric effect. In the crystal the distribution of the ionic charges about their lattice sites is symmetrical. Thus the net internal field is zero. But when the crystal is stressed the symmetry is altered due to the displacement of charges which results in non zero internal field. Piezoelectric strains are very small. Hence the corresponding electric fields are very high. For quartz for a strain of the order 10-7 the corresponding electric field is 1000v/cm. The inverse of Piezoelectricity is called electrostriction. Electrostriction is a phenomenon of straining a crystal by applying an electric field. Hence the piezoelectric materials are also called electro-strictive materials. The piezoelectric crystals are used in electro-mechanical transducers, as Oscillators to generate highly stable frequency and measurement of velocity of ultrasonics in solids and liquids.

The types of ferroelectric materials discussed in this chapter have been grouped according to their structure. The four main types of structures discussed include the corner sharing oxygen octahedra, compounds containing hydrogen bonded radicals, organic polymers and ceramic polymer composites.

1.2.1 Corner Sharing Octahedra

A large class of ferroelectric crystals is made up of mixed oxides containing corner sharing octahedra of O^{2-} ions schematically shown in Fig. 4. Inside each octahedron is a cation B^{b+} where 'b' varies from 3 to 6. The spaces between the octahedra are occupied by A^{a+} ions where 'a' varies from 1 to 3. In prototypic forms, the geometric centers of the A^{a+}, B^{b+} and O^{2-} ions coincide, giving rise to a non-polar lattice. When polarized, the A and B ions are displaced from their geometric centers with respect to the O^{2-} ions, to give a net polarity to the lattice. These displacements occur due to the changes in the lattice structure when phase transitions take place as the temperature is changed. The formation of dipoles by the displacement of ions will not lead to spontaneous polarization if a compensation pattern of dipoles are formed which give zero net dipole moment. The corner sharing oxygen octahedra discussed in this chapter includes the perovskite type compounds, tungsten bronze type compounds, bismuth oxide layer structured compounds, and lithium niobate and tantalate.

1) Perovskites

Perovskite is a family name of a group of materials and the mineral name of calcium titanate ($CaTiO_3$) having a structure of the type ABO_3. Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate ($KNbO_3$), Potassium Sodium Niobate ($K_xNa_{1-x}NbO_3$), and Potassium Tantalate Niobate ($K(Ta_xNb_{1-x})O_3$) have a perovskite type structure. Most of the above are discussed in detail below.

(a) Barium Titanate ($BaTiO_3$, BT)

Barium titanate ($BaTiO_3$) has a paraelectric cubic phase above its Curie point of about 130^o C. In the temperature range of 130^o C to 0^o C the ferroelectric tetragonal phase with a c/a ratio of ~ 1.01 is stable. The spontaneous polarization is along one of the [001] directions in the original cubic structure. Between 0^o C and -90^o C, the ferroelectric orthorhombic phase is stable with the polarization along one of the [110] directions in the original cubic structure. On decreasing the temperature below -90^o C the phase transition from the orthorhombic to ferroelectric rhombohedral phase leads to polarization along one of the [111] cubic directions.

The spontaneous polarization on cooling $BaTiO_3$ below the Curie point T_c is due to changes in the crystal structure. As shown in Fig. 2 the paraelectric cubic phase is stable above 130^o C with the center of positive charges (Ba^{2+} and Ti^{4+} ions) coinciding with the center of

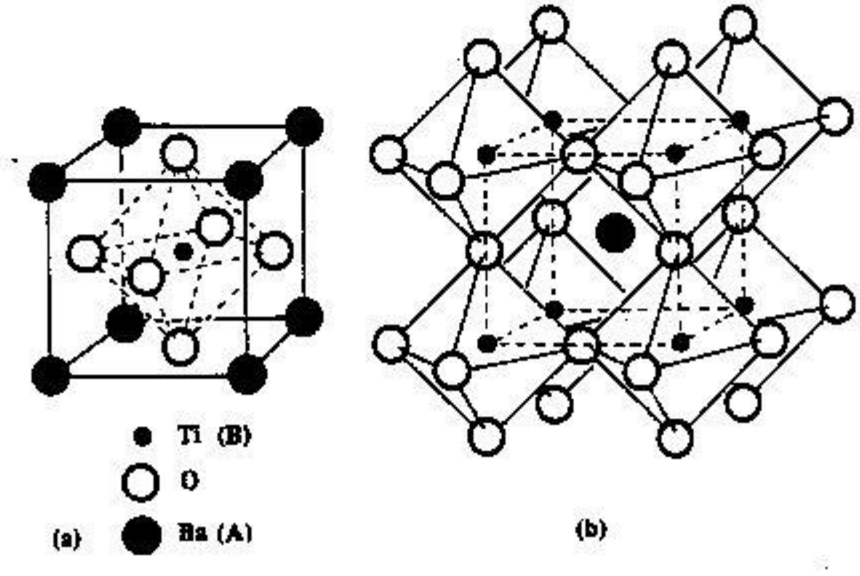


Fig. 1 (a) A cubic ABO_3 ($BaTiO_3$) perovskite-type unit cell and (b) three dimensional network of corner sharing octahedra of O^{2-} ions.

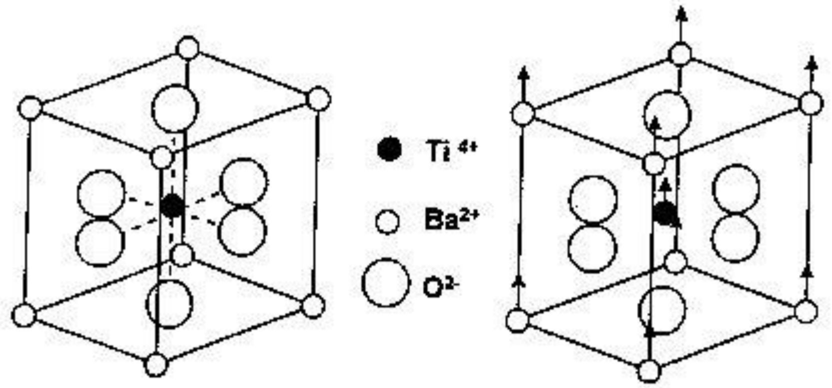


Fig. 2 The crystal structure of $BaTiO_3$ (a) above the Curie point the cell is cubic; (b) below the Curie point the structure is tetragonal with Ba^{2+} and Ti^{4+} ions displaced relative to O^{2-} ions.

negative charge (O^{2-}). On cooling below the Curie point T_c, a tetragonal structure develops where the center of Ba^{2+} and Ti^{4+} ions are displaced relative to the O^{2-} ions, leading to the formation of electric dipoles. Spontaneous polarization developed is the net dipole moment produced per unit volume for the dipoles pointing in a given direction.

Various A and B site substitutions in different concentrations have been tried to see their effect on the dielectric and ferroelectric properties of $BaTiO_3$. Sr^{2+} substitutions to the A site have been found to reduce the Curie point linearly towards room temperature. The substitution of Pb^{2+} for Ba^{2+} raises the Curie point. The simultaneous substitution into both A and B sites with different ions can be used to tailor the properties of $BaTiO_3$. The effect of various isovalent substitutions on the transition temperatures of $BaTiO_3$ ceramic are shown in Fig. 6

(b) Lead Titanate ($PbTiO_3$, PT)

Lead titanate is a ferroelectric material having a structure similar to $BaTiO_3$ with a high Curie point (490^oC). On decreasing the temperature through the Curie point a phase transition from the paraelectric cubic phase to the ferroelectric tetragonal phase takes place.

Lead titanate ceramics are difficult to fabricate in the bulk form as they undergo a large volume change on cooling below the Curie point. It is the result of a cubic (c/a = 1.00) to tetragonal (c/a = 1.064) phase transformation leading to a strain of > 6%. Hence, pure $PbTiO_3$ ceramics crack and fracture during fabrication. The spontaneous strain developed during cooling can be reduced by modifying the lead titanate with various dopants such as Ca, Sr, Ba, Sn, and W to obtain a crack free ceramic. One representative modified lead titanate composition that has been extensively investigated recently is $(Pb_{0.76}\ Ca_{0.24})\ ((Co_{0.50}\ W_{0.50})_{0.04}\ Ti_{0.96})O_3$ with 2 mol. % MnO added to it. This composition has a decreased c/a ratio and Curie point of 255 ^oC).

(c) Lead Zirconate Titanate [$Pb(Zr_xTi_{1-x})O_3$, PZT]

Lead Zirconate Titanate (PZT) is a binary solid solution of $PbZrO_3$ an antiferroelectric (orthorhombic structure) and $PbTiO_3$ a ferroelectric (tetragonal perovskite structure). PZT has a perovskite type structure with the Ti^{4+} and Zr^{4+} ions occupying the B site at random. The PZT phase diagram is shown in Fig. 8. At high temperatures PZT has the cubic perovskite structure which is paraelectric. On cooling below the Curie point line, the structure undergoes a phase transition to form a ferroelectric tetragonal or rhombohedral phase. In the tetragonal phase, the spontaneous polarization is along the <100> set of directions while in the rhombohedral phase the polarization is along the <111> set of directions. As shown in Fig. 9 most physical properties such as dielectric and piezoelectric constants show an anomalous behavior at the morphotropic phase boundary (MPB). The MPB separating the two ferroelectric tetragonal and orthorhombic phases has a room temperature composition with a Zr/Ti ratio of □ 52/48. PZT ceramics with the MPB composition show excellent piezoelectric properties. The poling of the PZT ceramic (see Section 4) is also easy at this composition because the spontaneous polarization within each grain can be switched to one of the 14 possible orientations (eight [111] directions for the rhombohedral phase and six [100] directions for the tetragonal phase). Below the Zr/Ti ratio of 95/5 the solid solution is antiferroelectric with an orthorhombic phase. On the application of an electric field to this composition a double hysteresis loop is obtained. This is because of the strong influence of the antiferroelectric $PbZrO_3$ phase.

(d) Lead Lanthanum Zirconate Titanate ($(Pb_{1-x}La_x)\ (Zr_{1-y}Ti_y)_{1-x/4}\ O_3\ V^B_{0.25x}\ O_3$, PLZT)

PLZT is a transparent ferroelectric ceramic formed by doping La^{3+} ions on the A sites of lead zirconate titanate (PZT). The PLZT ceramics have the same perovskite structure as $BaTiO_3$ and PZT. The transparent nature of PLZT has led to its use in electro-optic applications. Before the development of PLZT, the electro-optic effect was seen only for single crystals. The two factors that are responsible for getting a transparent PLZT ceramic include the reduction in the anisotropy of the PZT crystal structure by the substitution of La^{3+} and the ability to get a pore free ceramic by either hot pressing or liquid phase sintering.

The general formula for PLZT is given by $(Pb_{1-x}La_x)\ (Zr_{1-y}Ti_y)_{1-x/4}O_3V^B_{0.25x}O_3$ and $(Pb_{1-x}La_x)_{1-0.5x}(Zr_{1-y}Ti_y)V^A_{0.5x}O_3$. The first formula assumes that La^{3+} ions go to the A site and vacancies (V^B) are created on the B site to maintain charge balance. The second formula assumes that vacancies are created on the A site. The actual structure may be due to the combination of A and B site vacancies.

The room temperature phase diagram of PLZT system is shown in Fig. 10. The different phases in the diagram are a tetragonal ferroelectric phase (F_T), a rhombohedral ferroelectric phase (F_R), a cubic relaxor ferroelectric phase (F_C), an orthorhombic antiferroelectric phase (A_0) and a cubic paraelectric phase (P_C).

The electro-optic applications of PLZT ceramics depends on the composition. Figure 11 shows the hysteresis loops for various PLZT compositions from the phase diagram. PLZT ceramic compositions in the tetragonal ferroelectric (F_T) region show hysteresis loops with a very high coercive field (E_C). Materials with this composition exhibit linear electro-optic behavior for $E < E_C$. PLZT ceramic compositions in the rhombohedral ferroelectric (F_R) region of the PLZT phase diagram have loops with a low coercive field. These PLZT ceramics are useful for optical memory applications.

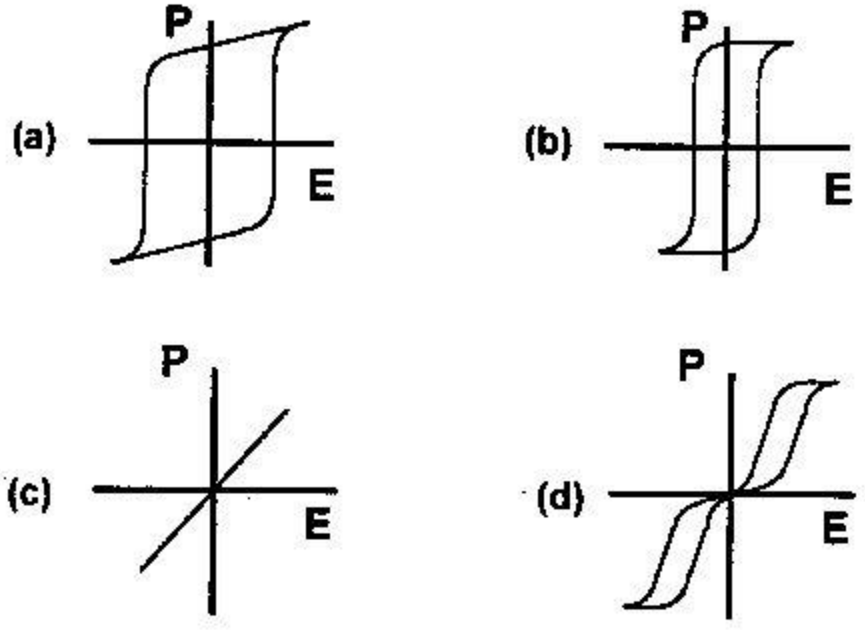


Fig. 3 Representative hysteresis loops obtained for different ferroelectric compositions (a) F_T (b) F_R (c) F_C and (d) A_O regions of the PLZT phase diagram. PLZT ceramic compositions with the relaxor ferroelectric behavior are characterized by a slim hysteresis loop. They show large quadratic electro-optic effects which are used for making flash protection goggles to shield them from intense radiation. This is one of the biggest applications of the electro-optic effect shown by transparent PLZT ceramics. The PLZT ceramics in the antiferroelectric region show a hysteresis loop expected from an antiferroelectric material. These components are used for memory applications.

(e) Lead Magnesium Niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$, PMN)

Relaxor ferroelectrics are a class of lead based perovskite type compounds with the general formula $Pb(B_1,B_2)O_3$ where B_1 is a lower valency cation (like Mg^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}) and B_2 is a higher valency cation (like Nb^{5+}, Ta^{5+}, W^{5+}). Pure lead magnesium niobate (PMN or Pb

$(Mg_{1/3}Nb_{2/3})O_3$) is a representative of this class of materials with a Curie point at -10° C. The main differences between relaxor and normal ferroelectrics are shown in Table 2.

Relaxor ferroelectrics like PMN can be distinguished from normal ferroelectrics such as $BaTiO_3$ and PZT, by the presence of a broad diffused and dispersive phase transition on cooling below the Curie point. Figure 12 shows the variation in the dielectric properties with temperature for PMN ceramic. It shows a very high room temperature dielectric constant and a low temperature dependence of dielectric constant. The diffused phase transitions in relaxor ferroelectrics are due to the compositional heterogeneity seen on a microscopic scale. For example, there is disorder in the B site for Pb $(Mg_{1/3}Nb_{2/3})O_3$. The composition of Mg and Nb is not stoichiometric in the micro regions, leading to different ferroelectric transition temperatures which broaden the dielectric peak.

The relaxors also show a very strong frequency dependence of the dielectric constant. The Curie point shifts to higher temperatures with increasing frequency. The dielectric losses are highest just below the Curie point T_c. For relaxors which have a second order phase transition, the remnant polarization, P_r, is not lost at the Curie point but gradually decreases to zero on increasing the temperature beyond T_c.

The most widely studied relaxor material is the PMN-PT solid solution system. The phase diagram of PMN-PT is shown in Fig. 13. The addition of PT, which has a Curie point of 490°C, shifts the T_c of the composition towards higher temperatures. The morphotropic phase boundary composition (0.65 PMN and 0.35 PT) is piezoelectric in nature. Ceramics with this composition are excellent candidates for piezoelectric transducers. Compositions with a Curie point near room temperature (like 0.95 PMN and 0.10 PT) have very large dielectric constants ($\varepsilon_r > 20{,}000$) which make them very attractive for multilayer capacitor and strain actuator applications.

2) Tungsten Bronze type Compounds

The tungsten bronze type ferroelectric crystals have a structure similar to tetragonal tungsten bronze K_xWO_3 ($x<1$). Lead niobate ($PbNb_2O_6$) was one of the first crystals of the tungsten bronze type structure to show useful ferroelectric properties. The site occupancy formula for this type of structure is given by $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. Figure 14 shows the schematic of the projection of the tungsten bronze type structure on the (001) plane. For lead niobate the B_1 and B_2 sites are occupied by Nb^{5+} ions. The open nature of the structure as compared to the perovskite allows a wide range of cation and anion substitutions without loss of ferroelectricity. At present, tungsten bronze family of oxide ferroelectrics, numbers more than 85.

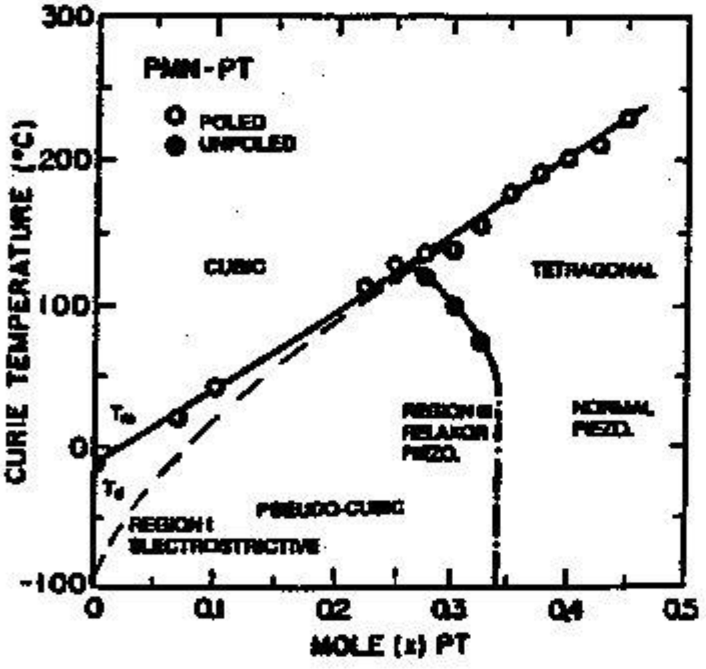


Fig 4 Phase diagram for PMN-PT solid solution.

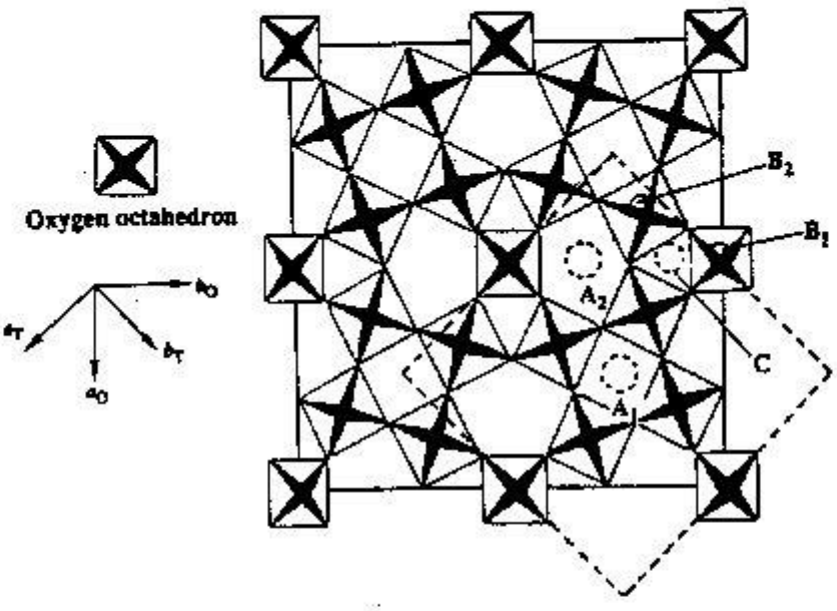


Fig. 5 Schematic diagram showing a projection of the tungsten-bronze structure on the (001) plane. The orthorhombic and tetragonal cells are shown by solid and dotted lines respectively.

The ferroelectric crystals grown from solid solutions of alkali and alkaline earth niobates have shown great potential for being used as a material for laser modulation, pyroelectric detectors, hydrophones, and ultrasonic applications. The high Curie point (T_c = 560 ^{o}C for lead niobate) of their compounds makes them suitable for high temperature applications.

It is difficult to fabricate piezoelectric $PbNb_2O_6$ ceramics because of the formation of a stable non-ferroelectric rhombohedral phase on cooling to room temperature. Rapid cooling from the sintering temperature is used to prevent the formation of the rhombohedral phase. Another problem associated with this type of materials is the large volume change due to phase transformation on cooling below the Curie point, leading to cracking of the ceramic.

2) Bismuth Oxide Layer Structured Ferroelectrics

The two most important piezoelectric materials with the $(Bi_2O_2)^{2+}$ layer structure are bismuth titanate ($Bi_4Ti_3O_{12}$) and lead bismuth niobate ($PbBi_2Nb_2O_9$). As shown in Fig. 15, the structure of $PbBi_2Nb_4O_9$ consists of corner linked perovskite-like sheets, separated by $(Bi_2O_2)^{2+}$ layers.

The plate like crystal structure of these compounds leads to highly anisotropic ferroelectric properties. The ceramics fabricated from the $(Bi_2O_2)^{2+}$ layer compounds do not have very good piezoelectric properties because of a very low poling efficiency. The piezoelectric properties have been shown to be improved by grain orientation during the processing step. One fabrication method involves the tape casting of plate like $Bi_4Ti_3O_{12}$ and $PbBi_2Nb_4O_9$ powders. The powders get aligned during the formation of the green tape. The orientation is further enhanced on sintering. In the other method, the ceramic is hot forged leading to the orientation of the grains along the forged direction.

The bismuth oxide layer structured ferroelectrics may become important piezoelectric ceramics because of their higher stability, higher operating temperature (T_c = 550-650^{o}C), and higher operating frequency. These ceramics are mainly useful for piezoelectric resonators which need to exhibit a very stable resonant frequency.

4) Lithium Niobate and Tantalate

Lithium niobate ($LiNbO_3$) and lithium tantalate ($LiTaO_3$) have similar structures. As shown in Fig. 16 the $LiNbO_3$ structure is actually a variant of the perovskite structure with a much more restrictive arrangement. The ferroelectric behavior of $LiNbO_3$ and $LiTaO_3$ was first discovered in 1949. Their crystals are very stable with very high Curie points of 1210^o C and 620^o C for $LiNbO_3$ and $LiTaO_3$ respectively. These compounds are mainly used in the single crystal form and have found applications in piezoelectric, pyroelectric and electro-optic devices.

1.2.2 Compounds Containing Hydrogen Bonded Radicals

Several water soluble ferroelectrics usually made in the single crystal form have hydrogen bonded radicals in them.

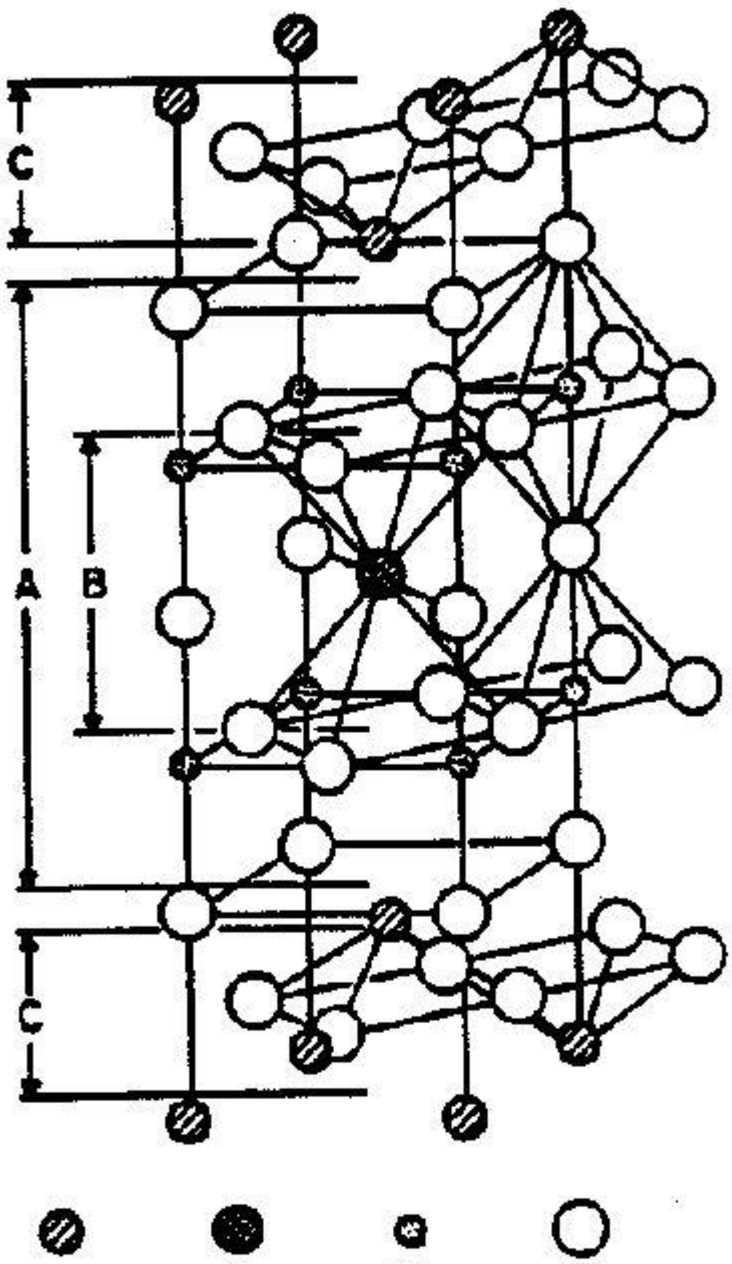


Fig. 6 One half of the tetragonal (4/mmm) unit cell of $PbBi_2Nb_2O_9$. A denotes the perovskite double layer $(PbNb_2O_7)^{2-}$; B is a hypothetical $PbNbO_3$ and C denotes the $(Bi_2O_2)^{2+}$ layers.

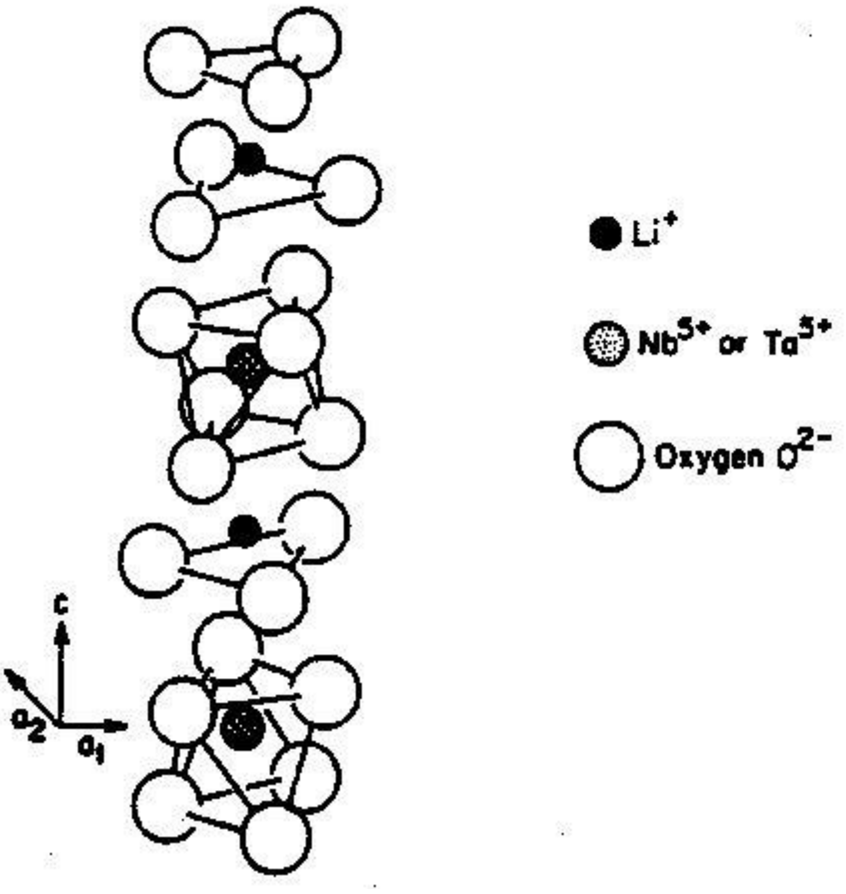


Fig. 7 Structure of Ferroelectric $LiNbO_3$ and $LiTaO_3$

Potassium dihydrogen phosphate (KH_2PO_4, KDP) has a tetragonal point group 42m. Hence this crystal shows only piezoelectricity and no ferroelectric behavior at room temperature. On decreasing the temperature below the Curie point (T_c = -150° C) it transforms into a ferroelectric orthorhombic phase. KDP single crystals exhibit very good electro-optical and non-linear optical properties. Triglycine sulfate ($(NH_2CH_2COOH)_3H_2SO_4$, TGS) has a ferroelectric monoclinic point group 2 at room temperature. On heating the crystal above the Curie point (T_c = 49.7° C) the crystal structure changes from the ferroelectric monoclinic point group to a centrosymmetric monoclinic point group 2/m. The TGS crystals show good pyroelectric properties. Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$, sodium potassium tantalate tetrahydrate) was the first ferroelectric material to be discovered. Between the two Curie points of -18° C and +24° C, Rochelle salt is ferroelectric with a monoclinic point group 2. In the non-ferroelectric region, Rochelle salt has an orthorhombic point group 222 and hence it shows piezoelectric effect. Single crystals of Rochelle salt are widely used for piezoelectric transducers. These water soluble crystals are still used due to their superiority over other crystals in some properties. Yet these crystals have many deficiencies such as weak ferroelectricity, low Curie point, poor mechanical properties, and deliquescence. For these reasons, KDP, TGS and Rochelle salt single crystals are being gradually replaced by piezoelectric ceramics.

1.2.3 Organic Polymers

Polyvinylidene fluoride (PVDF, $(CH_2\text{-}CF_2)_n$) and copolymers of PVDF with trifluoroethylene {P(VDF-TrFE)} have found applications as piezoelectric and pyroelectric materials. The piezoelectric and pyroelectric properties of these polymers are due to the remnant polarization obtained by orienting the crystalline phase of the polymer in a strong poling field. Hence the piezoelectric and pyroelectric properties depend on the degree of crystallinity of the polymer and the ferroelectric polarization of the crystalline phase.

The piezo-polymers have some properties which make them better suited for use in medical imaging applications. The density of these polymers is very close to that of water and the human body tissues, hence there is no acoustic impedance mismatch with the body. The piezo-polymers are also flexible and conformable to any shape. However, there are also some problems associated with the piezoelectric polymers including the very low dielectric constant (K = 5-10) which could lead to electrical impedance matching problems with the electronics. The dielectric losses at high frequencies are very large for these piezopolymers. The polymers also have a low Curie point and the degradation of the polymer starts occurring at low temperatures ($70\text{-}100^{o}$ C). The poling efficiency is very low for polymer specimens with large thickness (>1mm).

1.2.4 Ceramic Polymer Composites

The drive for piezoelectric composites stems from the fact that desirable properties could not be obtained from single phase materials such as piezoceramics or piezopolymers. For example, in an electromechanical transducer, the desire is to maximize the piezoelectric sensitivity, minimize the density to obtain good acoustic matching with water, and make the transducer mechanically flexible to conform to a curved surface. Neither a ceramic nor a polymer satisfies these requirements. The requirement can be optimized by combining the most useful properties of the two phases which do not ordinarily appear together. Piezoelectric composites are made up of an active ceramic phase embedded in a passive polymer. The properties of the composite depend on the connectivity of the phases, volume percent of ceramic, and the spatial distribution of the active phase in the composite. The concept of connectivity developed by Newnham et al. [65] describes the arrangement of the component phases within a composite. It is critical in determining the electromechanical properties of the composite. Figure 17 shows the 10 different types of connectivity possible in a diphase composite. It is shown in the form A-B where 'A' refers to the number of directions in which the active phase is self connected or continuous. 'B' shows the continuity directions of the passive phase. The density, acoustic impedance, dielectric constant and the piezoelectric properties like the electromechanical coupling coefficient k_t change with the volume fraction of the ceramic. Optimum material and piezoelectric parameters for medical ultrasound applications are obtained for ~ 20-25 vol. % PZT ceramic in the composite.

1.3 Sample and its structure

Introduction

There are 32 symmetry point groups/ crystal classes out of which 11 classes are centrosymmetric and 21 are non-centrosymmetric. Out of 21, 20 crystal classes show piezoelectric behavoiur i.e get polarized under stress. 10 crystal classes among them are pyroelectric. Pyroelectric crystals possess the unusual characteristic of being permanently polarized within a given temperature range. Unlike the more general piezoelectrics that produce a polarization under stress, the pyroelectrics develop this polarization spontaneously and form permanent dipoles in the structure. This polarization also changes with temperature, hence, the term pyroelectricity.

A subgroup of the spontaneously polarized pyroelectrics is a very special category of materials known as ferroelectrics. Similar to pyroelectrics, materials in this group possess spontaneous dipoles; however, unlike pyroelectrics, these dipoles are reversible by an electric field of suitable magnitude less than the dielectric breakdown electric field of the material. Thus, the two conditions necessary in a material to classify it as a ferroelectric are:-

(i) the existence of spontaneous polarization and
(ii) the ability to reverse the direction of polarization.

Ferroelectricity was discovered in single-crystal materials (i.e. in Rochelle Salt $NaC_4H_4O_6.4H_2O$) in 1921 and then in polycrystalline ceramics (i.e. in Barium Titanate $BaTiO_3$) during the early to mid-1940s. Thereafter, large number of new materials have been discovered which show ferroelectricity that leads to significant number of industrial and commercial applications.

These materials have a large number of properties which make them very useful in a variety of applications. These properties are:-

- high dielectric constant
- high piezoelectric constants
- relatively low dielectric loss
- high electrical resistivity
- high electromechanical coupling
- medium hardness
- fairly high pyroelectric coefficients

These materials are characterized by a temperature called Curie temperature (T_c). When heated beyond T_c the material goes to paraelectric phase where there is no spontaneous polarization . When the temperature is reduced below the transition temperature T_c, spontaneous polarization occurs and the crystal becomes slightly elongated , i.e. tetragonal. Ferroelectric materials, especially polycrystalline ceramics, are very promising for a variety of applications such as high permittivity capacitors, ferroelectric memories, pyroelectric sensors, piezoelectric transducers, electro-optic devices and PTC thermistors. For these reasons the materials are often classified as **very smart materials.**

In this general group of ferroelectric materials, based on the basic structure, the following four types of ferroelectric materials are known:-

1) Bismuth Layer-Structured group
2) Perovskites group
3) Pyrochlore group
4) Tungsten-Bronze group.

Of these, the Bismuth Layer-Structured ferroelectrics are a large class of technically important materials. These materials belong to an important family of dielectric materials, which display interesting ferroelectric, pyroelectric, piezoelectric, and excellent fatigue resistance up to -10^{12} switching cycles for applications in various electronic devices, such as transducers, actuators, capacitors and ferroelectric random access memory [1-4].

Bismuth Layer Structured Ferroelectric Ceramics

The crystal structure and chemical composition of these materials was first studied by Aurivillius [5].

The general formula of this group is $[Bi_2O_2]^{2+}$ $[A_{n-1}B_nO3_{n+1}]^{2-}$, consisting of perovskite $[A_{n-1}B_nO3_{n+1}]^{2-}$ layers sandwiched between $[Bi_2O_2]^{2+}$ layers. Here, A can be Ba^{2+}, Sr^{2+}, Pb^{2+} , etc. and B can be W^{6+}, Ta^{5+}, etc [6]. These ceramics are very sensitive to the compositional variations. Changing the stoichiometry or doping with various elements remarkably influences the crystal structure and ferroelectric properties [7-9].

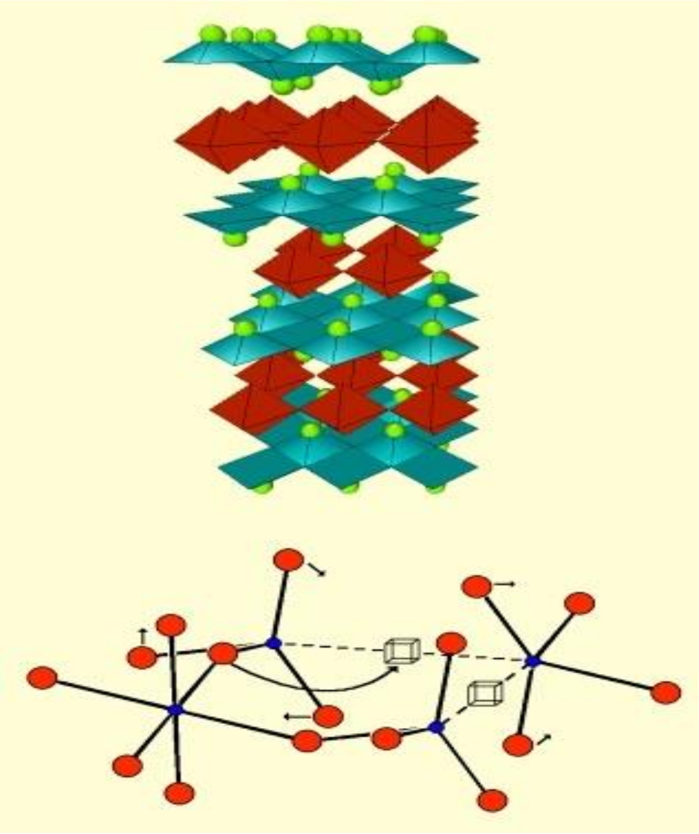
SAMPLE

Strontium Bismuth Niobate (SBN) have been extensively investigated by researchers as the most suitable material for high density ferroelectric random access memory applications because of large remnant polarization, large ferroelectric spontaneous polarization, high dielectric constant and low dielectric loss [10 -12].

AIM OF THE PROJECT:

The aim of my project work is to carry out electrical characterization of a tungsten bronze ferroelectric ceramic. **$SrBi_2Nb_2O_9$ (SBN)** is chosen for this purpose because previous studies suggest that its electrical characteristics vary with temperature and frequency. My aim is to take this work further by characterizing it with respect to different bias voltages along with temperature and frequency. Its dimensions are as follows-

- Sample composition – $SrBi_2Nb_2O_9$ (SBN)
- Thickness – 0.83 mm
- Diameter – 1.32 cm



CHAPTER 2

ELECTRICAL CHARACTERIZATION

2.1 Sample preparation

The sample chosen for the project is a ceramic in form of a pallete formed by sintering the well ground ceramic at high temperature. It has the composition **$SrBi_2Nb_2O_9$ (SBN)**. Its dimensions are as follows-

- Sample composition – **$SrBi_2Nb_2O_9$**
- Thickness – 0.83 mm
- Diameter – 1.32 cm

Silver deposition on sample pallete

To characterize the sample first it has to be made a Metal-Insulator-Metal (MIM) structure. i.e. electrodes must be deposited on both sides of the ceramic sample. Silver is deposited by Vacuum Deposition technique. First silver is deposited on one side of pallete with following conditions-

Pressure – 10^{-5} mBar

VARIAC Voltage – 120 V

Thickness of silver deposited is found out to be 1765 A^0.

Then silver is deposited on the back face with conditions-

Pressure – 9×10^{-6} mBar

VARIAC Voltage – 120 V

Thickness of silver deposition came out to be 1774 A.

Sample was kept insulated from humidity so that oxide is not formed as it can hinder the required characterization.

2.2 Dielectric characterization

The dielectric properties of the various materials used in semiconductor fabrication and packaging play an important role in achieving the desired performance of integrated circuits. A basic understanding of dielectric properties is therefore needed by most engineers working in the semiconductor industry.

Dielectric permittivity

One important property of a dielectric material is its permittivity. Permittivity (ε) is a measure of the ability of a material to be polarized by an electric field.

It is, however, easier to grasp the concept of permittivity by first discussing a closely related property, capacitance (C). Capacitance is a measure of the ability of a material to hold charge if a voltage is applied across it, and is best modeled by a dielectric layer that's sandwiched between two parallel conductive plates.

If a voltage V is applied across a capacitor of capacitance C, then the charge Q that it can hold is directly proportional to the applied voltage V, with the capacitance C as the proportionality constant. Thus, $Q = CV$, or $C = Q/V$. The unit of measurement for capacitance is the farad (coulomb per volt).

The capacitance of a capacitor depends on the permittivity ε of the dielectric layer, as well as the area A of the capacitor and the separation distance d between the two conductive plates. Permittivity and capacitance are mathematically related as follows: $C = \varepsilon (A/d)$.

When the dielectric used is vacuum, then the capacitance $C_o = \varepsilon_o (A/d)$, where ε_o is the permittivity of vacuum (8.85×10^{-12} F/m).

Dielectric constant

The dielectric constant (k) of a material is the ratio of its permittivity ε to the permittivity of vacuum ε_o, so $k = \varepsilon/\varepsilon_o$. The dielectric constant is therefore also known as the relative permittivity of the material. Since the dielectric constant is just a ratio of two similar quantities, it is dimensionless.

Given its definition, the dielectric constant of vacuum is 1. Any material is able to polarize more than vacuum, so the k of a material is always > 1. Note that the dielectric constant is also a function of frequency in some materials, e.g., polymers, primarily because polarization is affected by frequency.

The dielectric constant in polycrystalline ferroelectric materials is due to four types of polarizations; i) Electronic Pe , ii) Ionic Pi, iii) Orientational Po and Space charge Ps represented as :

$$P = Pe + Pi + Po + Ps$$

At lower frequencies, all polarizations are known to contribute to the dielectric constant but with increase in frequency, these are damped out corresponding to respective relaxation/resonance absorption phenomenon. Electronic and ionic polarization modes being less dependent on temperature and frequency normally damp out at high frequencies of the order of 10^{16} Hz and 10^{10-13} Hz respectively. The orientational and space charge polarization modes are strongly temperature and field dependent and are observed to damp out near 10^{3-5} Hz and 10^{8-9} Hz respectively. In polar dielectrics, orientational and space charge polarizations are the major contributors to the total dielectric constant value.

Complex permittivity

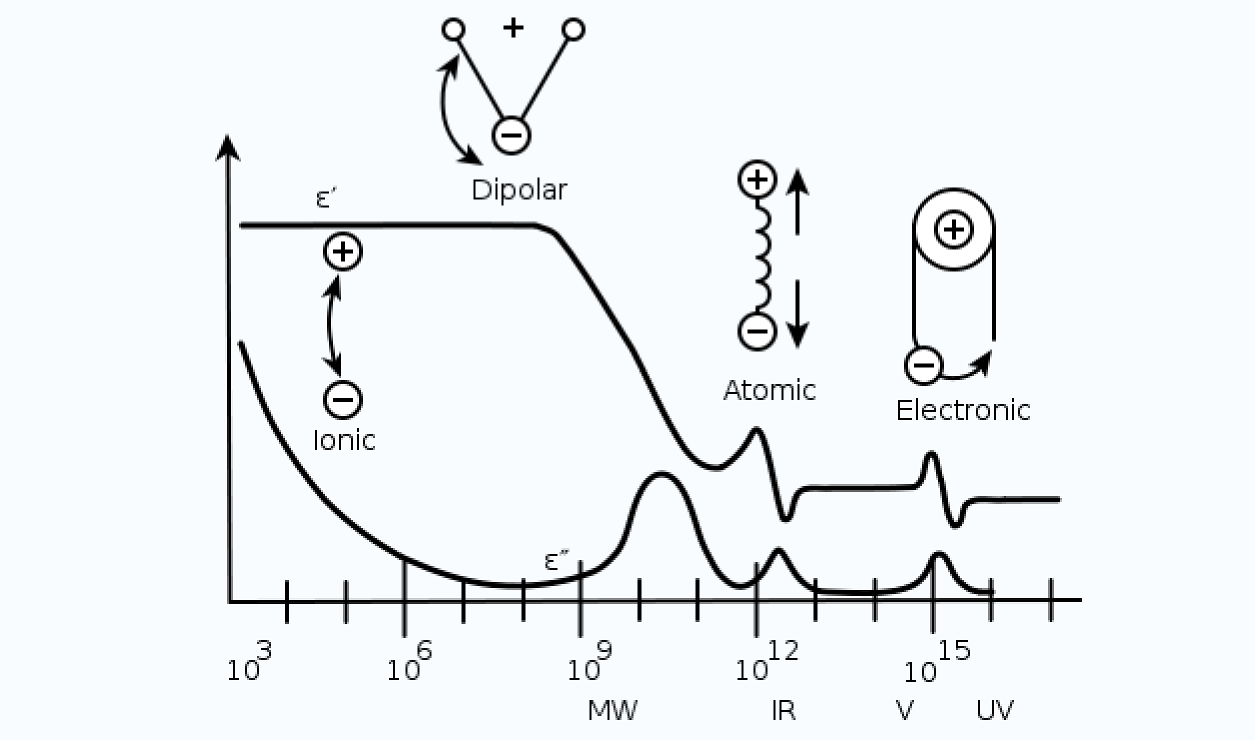


Fig. 9 variation of relative permittivity with frequency.

Dielectric constant as a function of frequency and temperature was measured using the expression

$$C_O = \in_O A/D$$

Where$\in \varepsilon \varepsilon_o = 8.854 \times 10^{-12}$ is the free space permittivity or dielectric constant.

Dielectric loss

The amount of power losses in a dielectric under the action of applied voltage id commonly known as dielectric losses. This is general term determining the in a dielectric when either a dielectric or an alternating voltage is applied. Dielectric loss tangent (tan δ) values were directly measured using the impedence analyzer for frequency as well as temperature variations. Dielectric losses, when a direct voltage is applied, can easily be found out from the equation;

$$P = V^2 / R$$

Where V is the voltage applied and R is the resistance of the insulation. However, the losses under an alternating voltage are determined by regularities that are more intricate. For the case of applied voltage being sinusoidal, charge stored in the dielectric can be expressed as:

$$Q = C\, V_o\, e^{i\omega t}$$

Therefore,

$$I = dQ/dt = i\omega CV = i\varepsilon_r\omega C_oV$$

Where, I represent the current flow on discharge of the dielectric cell in time t. However, for a real dielectric the current I have vector components I_C and I_R, where I_C is the capacitive current proportional to the charge stored in the capacitor. The current I_C is frequency dependent and leads the voltage by 90^0 and the current I_R, is ac conduction current in phase with the voltage V, which represent the energy loss or power dissipated in the dielectric. This condition can be expressed clearly by choosing complex form of dielectric constant ε.

$$I = i\omega\, (\varepsilon' - i\varepsilon'')\, \varepsilon_o C_o V,$$

Where ε is the real part of dielectric constant and ε'' is the imaginary part, ε_o is the absolute permittivity of the air/ free space = 8.854×10^{-12} F/m, ω is the angular frequency of the applied field.

$$I = i\omega\varepsilon'\varepsilon_o C_o V + \omega\, \varepsilon''\varepsilon_o C_o V$$

$$I = I_C + I_R$$

The dissipation factor is defined by the ratio of energy dissipated per cycle to the energy stored per cycle as,

$$\tan\delta = |\, I_R / I_C \,| = \varepsilon''/\, \varepsilon'$$

$$\tan\delta = 1 / \omega\, \varepsilon'\, \varepsilon_o\rho,$$

where ρ is the resistivity of the dielectric material.

Experimental

To characterize the dielectric properties the sample in the form of a capacitor is studied by giving it a bias voltage and a range of frequency over a temperature ranging from room temperature to 580°C. This was done at different bias voltages (such as 0V, 5V, 10V, 20V) and results were compared.

A)<u>VARIATION WITH TEMPRATURE</u>

<u>0Volts</u>

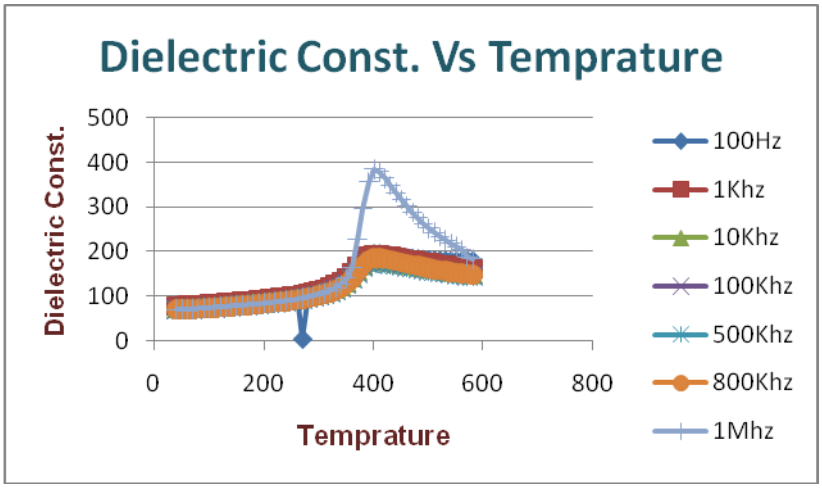


Fig.1.11

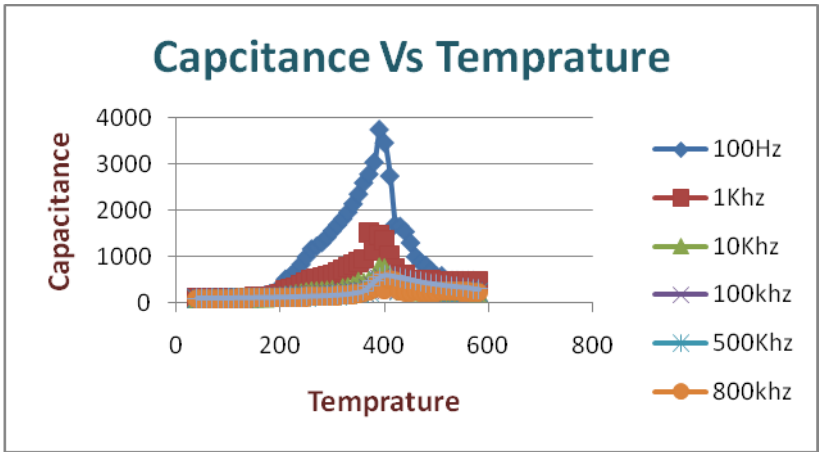


Fig. 1.12

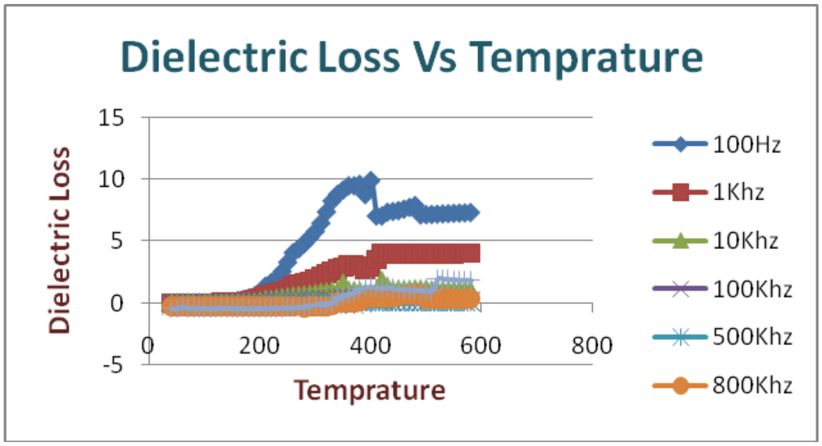


Fig. 1.13

Observation

The variation of dielectric constant or relative permittivity with temperature is shown. The observations were recorded at 0V bias voltage and over a range of frequencies. Frequencies ranged from 100Hz to 800 KHz. Single phase transition from ferroelectric to paraelectric phase is observed at 410^{o}C identified as Curie temperature. The value of dielectric constant is maximum at Curie temperature. The value of dielectric constant increases with temperature till it reaches Curie temperature. Beyond Curie temperature it starts decreasing. The value of dielectric constant at a particular temperature is observed to decrease with increasing frequency.

Inference and explanation

Ferroelectricity depends on temperature. Above θc ferroelectric behavior is lost and the material becomes paraelectric. The change from the ferroelectric to the nonferroelectric state is accompanied either by a change in crystal symmetry (e.g., as in BaTiO3).

The relative permittivity shows a characteristic peak at *T*cw (curie – Weiss temperature) and falls off at higher temperatures following the Curie–Weiss law:

$$\varepsilon_r - 1 = \chi = C / (T - T_{CW}).$$

Observations

The variation of dielectric loss Vs temperature is shown. Dielectric loss remains invariable for some range and then increases with temperature.

Inference and explanation

It is due to increased thermal motion which raises randomness. This increased randomness accounts for the difficulty that dipoles have to overcome in order to get polarized. They have to face increased internal friction and energy dissipates in form of heat. Dissipation of energy in form of heat is called dielectric loss and hence it increases with temperature.

5V

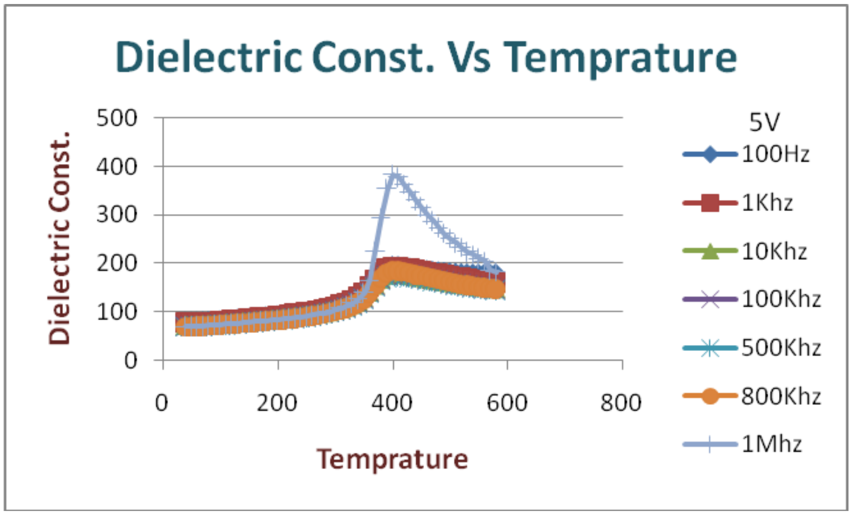


Fig 2.11

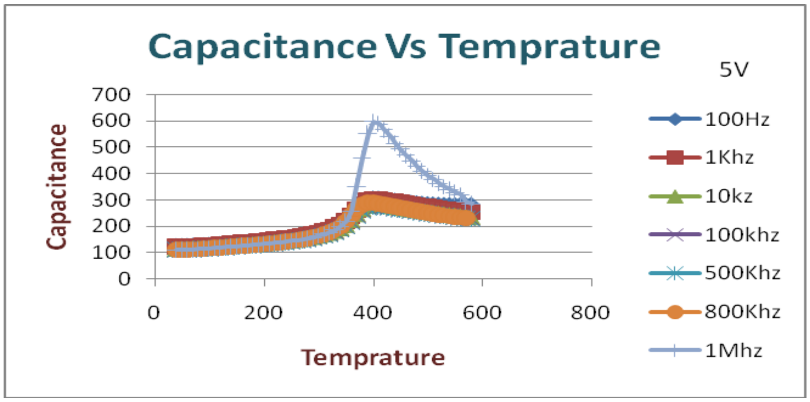


Fig. 2.12

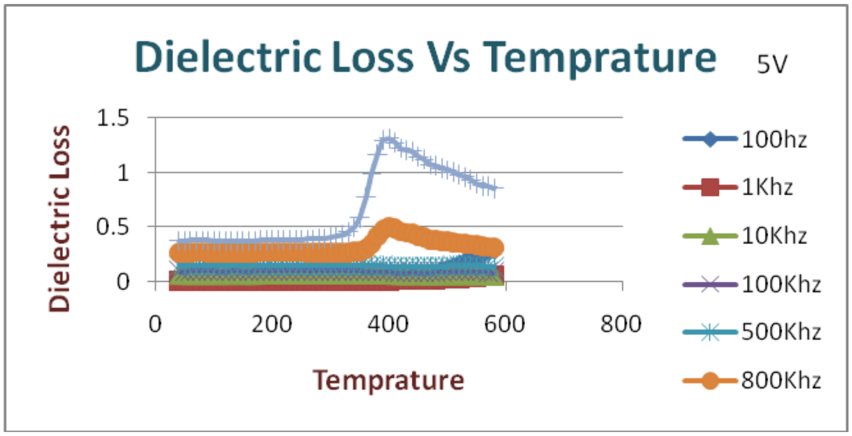


Fig. 2.13

Observations-

For dielectric constant

The variation of dielectric constant or relative permittivity with temperature is shown in fig. 2. The observations were recorded at 5 V bias voltage and over a range of frequencies. Frequencies ranged from 100Hz to 800 KHz. Single phase transition from ferroelectric to paraelectric phase is observed at 410°C identified as Curie temperature at which the value of dielectric constant is (at 100 KHz) maximum. The value of dielectric constant increases with temperature till it reaches Curie temperature. Beyond Curie temperature it starts decreasing with increasing temperature. The value of dielectric constant at a particular temperature is observed to decrease with increasing frequency

Inference and explanation

Ferroelectricity depends on temperature. Above θc ferroelectric behavior is lost and the material becomes paraelectric. The change from the ferroelectric to the nonferroelectric state is accompanied either by a change in crystal symmetry (e.g., as in $BaTiO3$).

The relative permittivity shows a characteristic peak at Tcw (Curie- Weiss temperature) and falls off at higher temperatures following the Curie–Weiss law:

$$\varepsilon_r - 1 = \chi = C / (T - T_{CW}).$$

For dielectric loss-

The dielectric loss remains invariable up to a small temperature rang. Beyond this temperature range, it increases sharply with temperature.

Inference and explanation

It is due to increased thermal motion which raises randomness. This increased randomness accounts for the difficulty that dipoles have to overcome in order to get polarized. They have to face increased internal friction and energy dissipates in form of heat. Dissipation of energy in form of heat is called dielectric loss and hence it increases with temperature.

10V

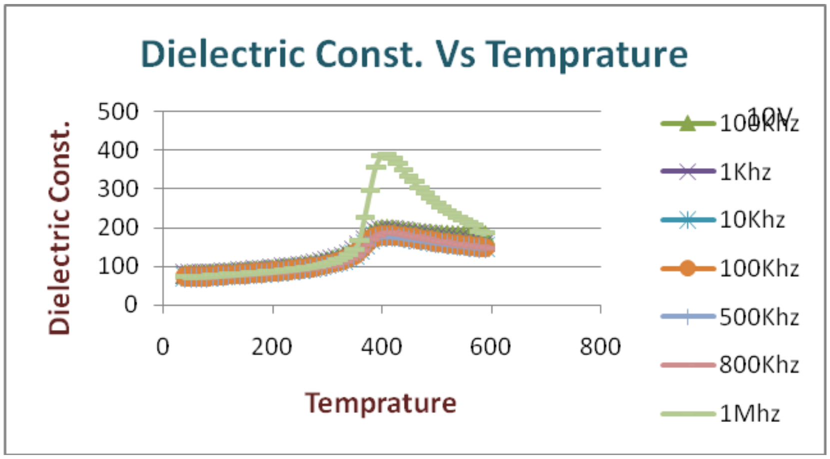


Fig. 3.1

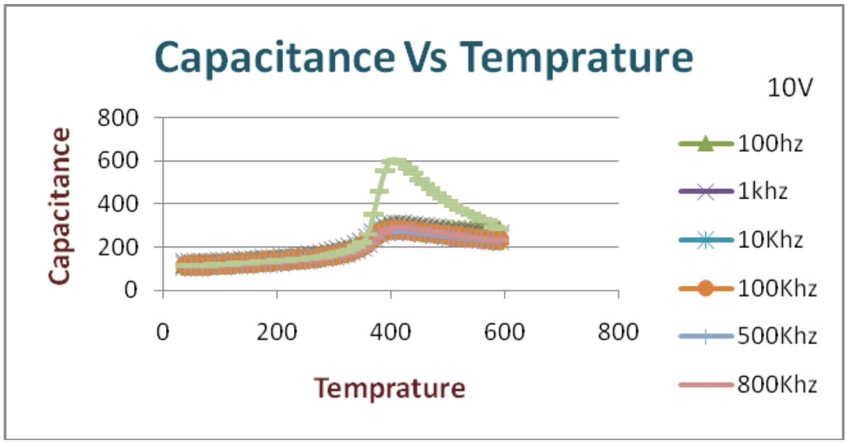


Fig. 3.2

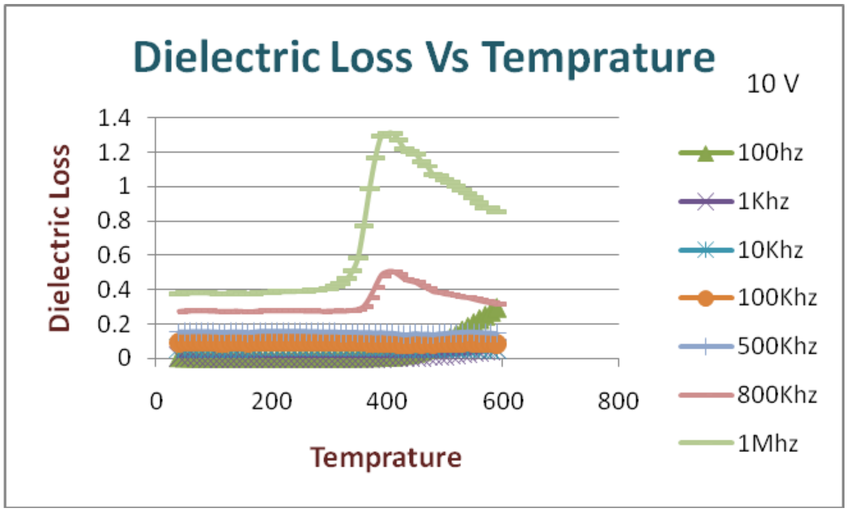


Fig. 3.3

Observations

The variation of dielectric constant or relative permittivity with temperature is shown in Fig. 3. The observations were recorded at 10 V bias voltage and over a range of frequencies. Frequencies ranged from 1 KHz to 800 KHz. Single phase transition from ferroelectric to paraelectric phase is observed at 410^{o}C identified as Curie temperature at which the value of dielectric constant is (at 100 KHz) maximum. The value of dielectric constant increases with temperature till it reaches Curie temperature. Beyond Curie temperature it starts decreasing with increasing temperature. The value of dielectric constant at a particular temperature is observed to decrease with increasing frequency

Inference and explanation

Ferroelectricity depends on temperature. Above θc ferroelectric behavior is lost and the material becomes paraelectric. The change from the ferroelectric to the nonferroelectric state is accompanied either by a change in crystal symmetry (e.g., as in BaTiO3).
The relative permittivity shows a characteristic peak at *T*cw (Curie- Weiss temperature) and falls off at higher temperatures following the Curie–Weiss law:

$$\varepsilon_r - 1 = \chi = C / (T - T_{CW}).$$

For dielectric loss-

The dielectric loss remains invariable up to Curie temperature. Beyond this temperature it increases with temperature.

Inference and explanation

It is due to increased thermal motion which raises randomness. This increased randomness accounts for the difficulty that dipoles have to overcome in order to get polarized. They have to face increased internal friction and energy dissipates in form of heat. Dissipation of energy in form of heat is called dielectric loss and hence it increases with temperature.

20V

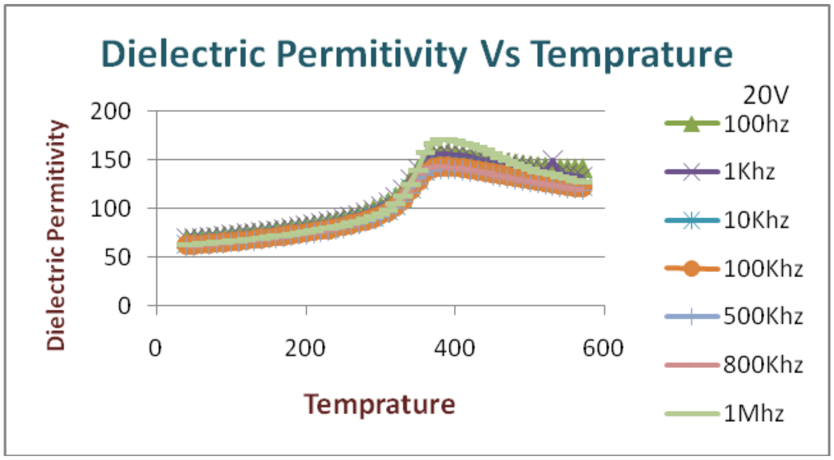


Fig 4.1

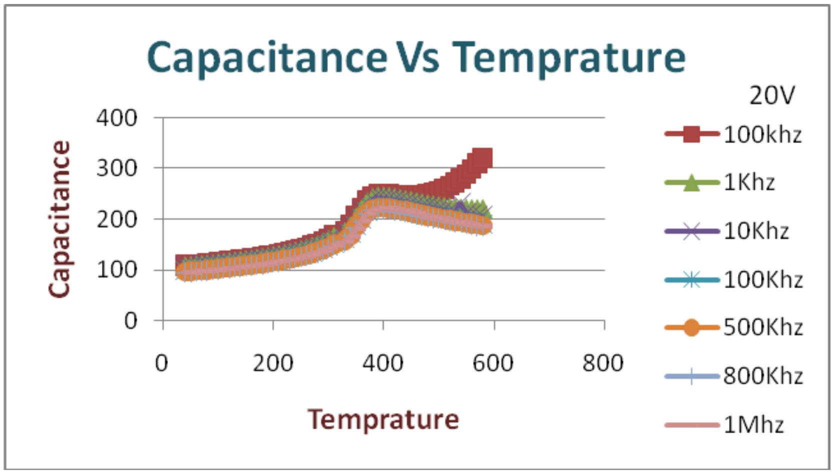


Fig. 4.2

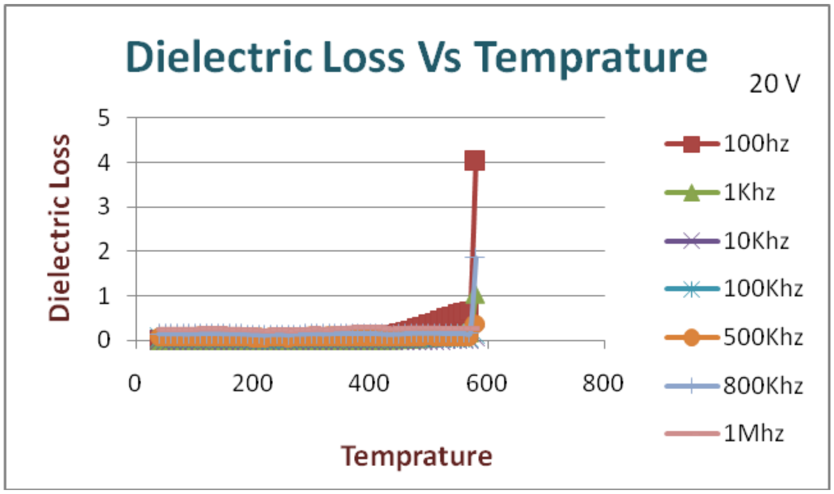


Fig. 4.3

Observations

The variation of dielectric constant or relative permittivity with temperature is shown in fig. 4. The observations were recorded at 20 V bias voltage and over a range of frequencies. Frequencies ranged from 1 KHz to 800 KHz. Single phase transition from ferroelectric to paraelectric phase is observed at 410^{o}C identified as Curie temperature at which the value of dielectric constant is (at 100 KHz) maximum. The value of dielectric constant increases with temperature till it reaches Curie temperature. Beyond Curie temperature it starts decreasing with increasing temperature. The value of dielectric constant at a particular temperature is observed to decrease with increasing frequency.

Inference and explanation

Ferroelectricity depends on temperature. Above θc ferroelectric behavior is lost and the material becomes paraelectric. The change from the ferroelectric to the nonferroelectric state is accompanied either by a change in crystal symmetry (e.g., as in BaTiO3).

The relative permittivity shows a characteristic peak at *T*cw (Curie- Weiss temperature) and falls off at higher temperatures following the Curie–Weiss law:

$$\varepsilon_r - 1 = \chi = C / (T - T_{CW}).$$

For dielectric loss-

The dielectric loss remains invariable up to Curie temperature. Beyond this temperature it increases with temperature.

Inference and explanation

It is due to increased thermal motion which raises randomness. This increased randomness accounts for the difficulty that dipoles have to overcome in order to get polarized. They have to face increased internal friction and energy dissipates in form of heat. Dissipation of energy in form of heat is called dielectric loss and hence it increases with temperature.

B.) VARIATION WITH FREQUENCY

B1.)VARIATION OF DIELECTRIC PERMITIVITY Vs. FREQUENCY

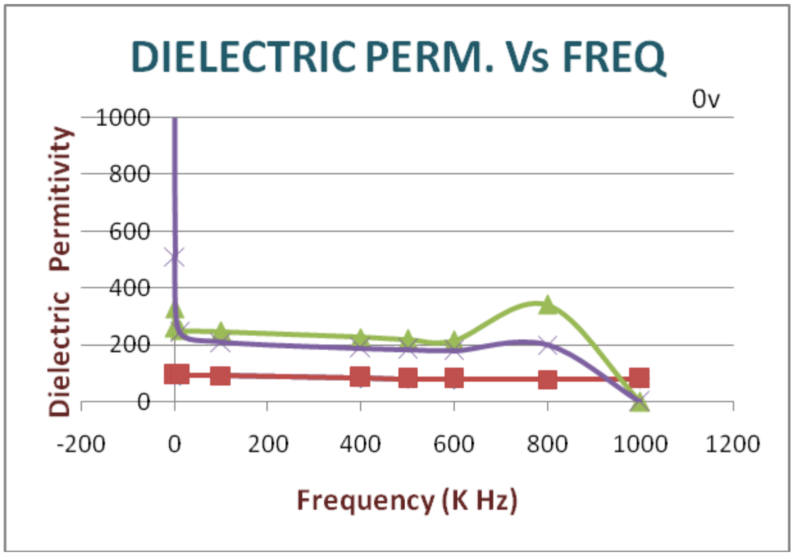


Fig. 5.1

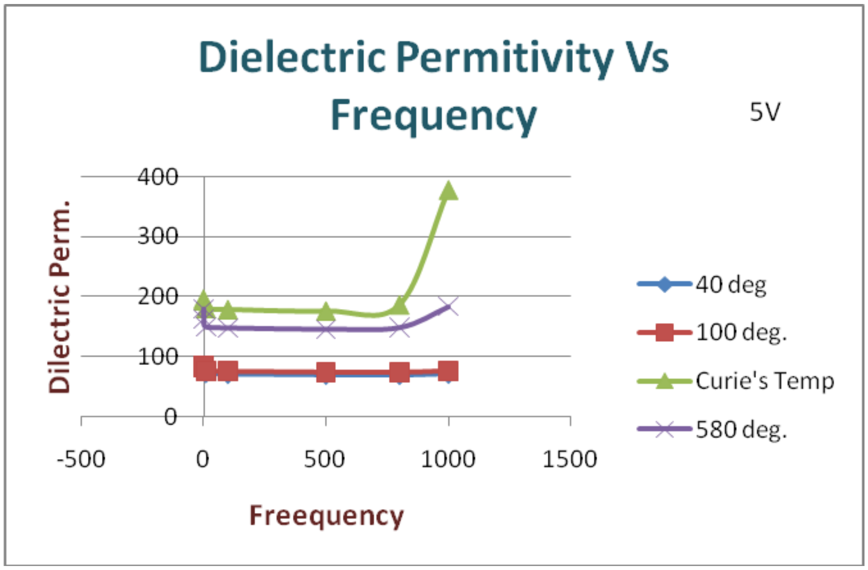


Fig. 5.2

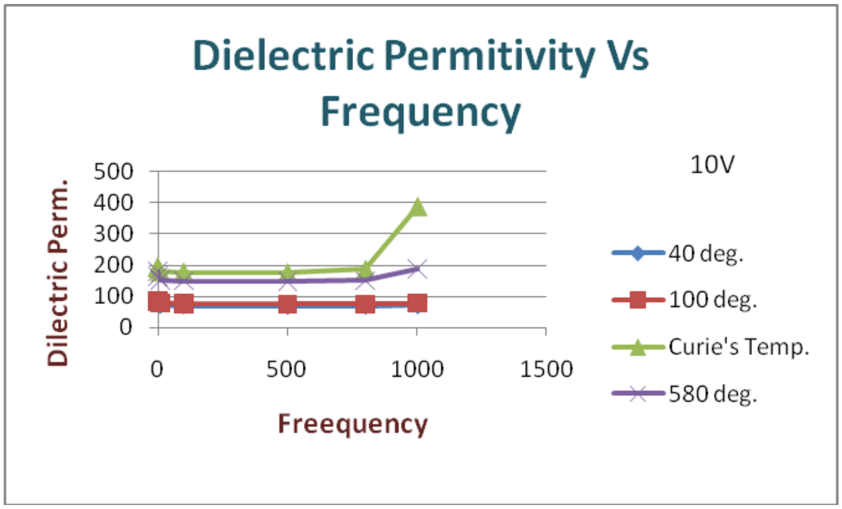


Fig 5.3

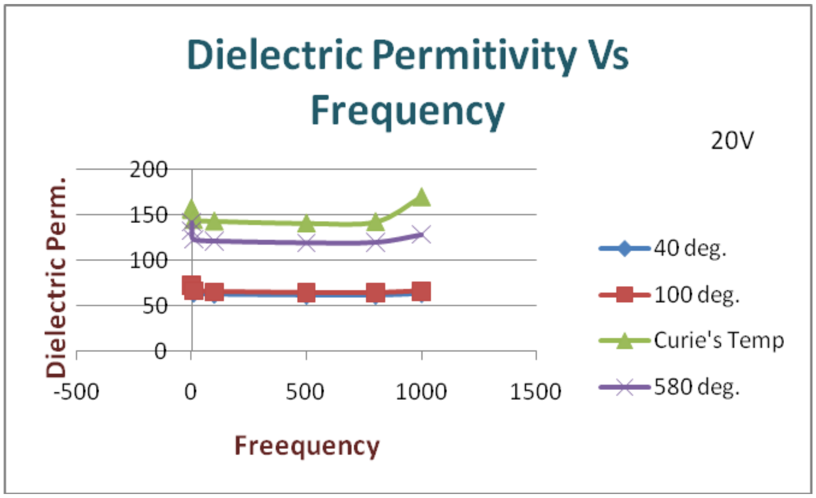


Fig. 5.4

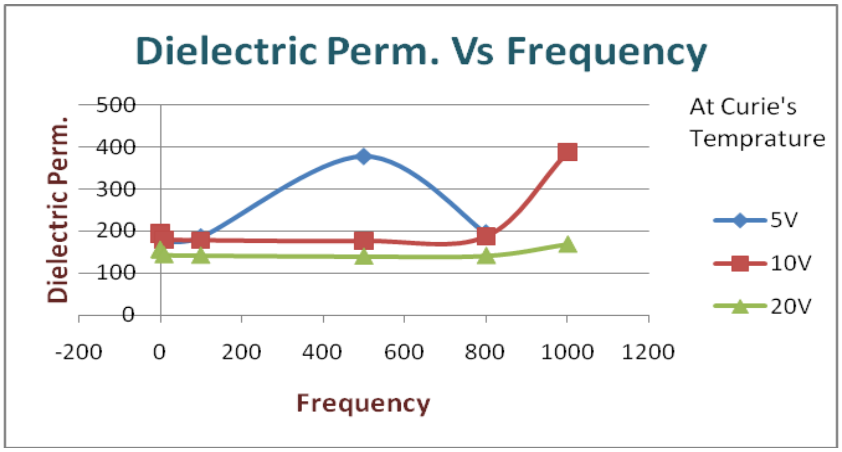


Fig 5.5

Observations

It is observed that dielectric permittivity remains constant for initial frequency range and then shows a small resonance peak. After this point it decreases sharply.

Inference and explanation

We know that a dielectric becomes polarized in an electric field. Now imagine switching the direction of the field. The direction of the polarization will also switch in order to align with the new field. This cannot occur instantaneously: some time is needed for the movement of charges or rotation of dipoles. If the field is switched, there is a characteristic time that the orientational polarization (or average dipole orientation) takes to adjust, called the relaxation time. Typical relaxation times are ~10^{11}s. Therefore, if the electric field switches direction at a frequency higher than ~10^{11} Hz, the dipole orientation cannot 'keep up' with the alternating field, the polarization direction is unable to remain aligned with the field, and this polarization mechanism ceases to contribute to the polarization of the dielectric.

In an alternating electric field both the ionic and the electronic polarization mechanisms can be thought of as driven damped harmonic oscillators (like a mass on a spring), and the frequency dependence is governed by resonance phenomena. This leads to peaks in a plot of dielectric constant versus frequency, at the resonance frequencies of the ionic and electronic polarisation modes. A dip appears at frequencies just above each resonance peak, which is a general phenomenon of all damped resonance responses, corresponding to the response of the system being out of phase with the driving force (we shall not go into the mathematical proof of this here). In this case, in the areas of the dips, the polarisation lags behind the field. At higher frequencies the movement of charge cannot keep up with the alternating field, and the polarisation mechanism ceases to contribute to the polarisation of the dielectric.

As frequency increases, the material's net polarisation drops as each polarisation mechanism ceases to contribute, and hence its dielectric constant drops. The animation below illustrates these effects. At sufficiently high frequencies (above ~10^{15} Hz), none of the polarisation mechanisms are able to switch rapidly enough to remain in step with the field. The material no longer possesses the ability to polarize, and the dielectric constant drops to 1 – the same as that of a vacuum.

Dielectric constant decreases with increasing frequency which suggests that interfaces and dipoles play an important role at low frequency.

B.2. VARIATION OF LOSS Vs. FREQUENCY

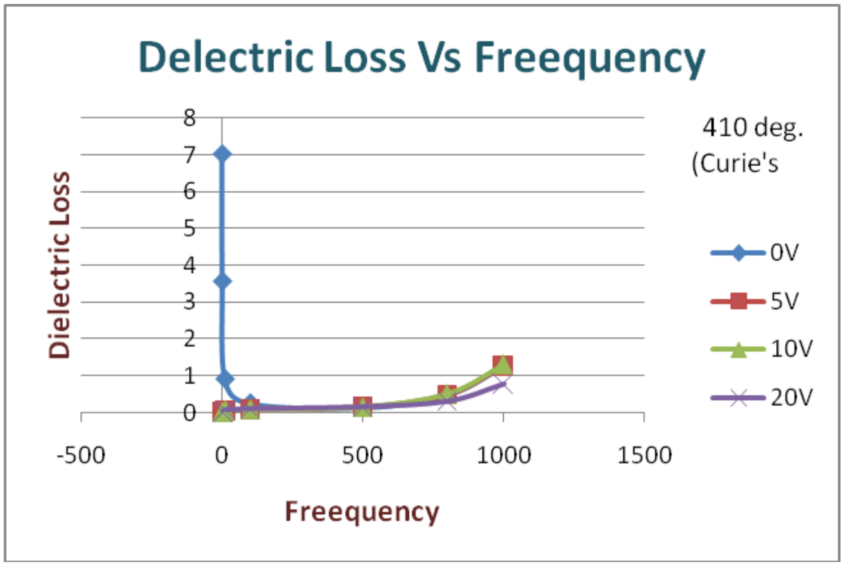


Fig 6.1

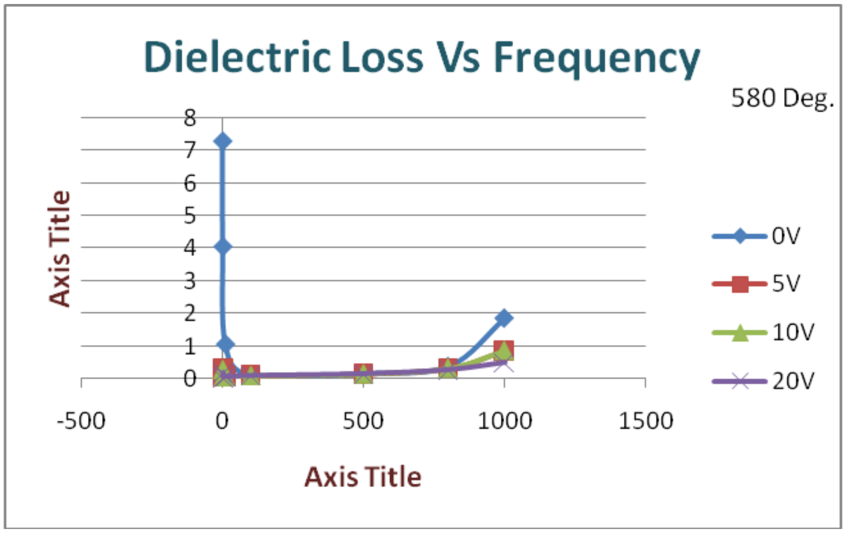


Fig 6.2

Observations

Dielectric loss remains almost constant upto 500 KHz and then rises sharply with increasing frequency. Slope of dielectric loss is maximum at 0V bias voltge and decreases for higher bias potentials - 10 V and 20 V.

Inference and explanation

The dielectric loss increases with increasing frequencies for SBN because in the alternating field conditions during the rotation of dipoles they have to overcome some sort of internal friction, which is dissipated as heat by the material. This is called as dielectric loss. As the frequency increases dipoles moves in opposite directions very rapidly. Therefore internal friction countered is more and more and hence dielectric loss increases with increase in frequency.

Chapter 3

INFERENCES

1.1 Variation of dielectric constant and loss with temperature

a) The dielectric constant increases with temperature till it reaches Curie temperature. After this point dielectric constant decreases with increasing temperature.

b) The dielectric loss increase with temperature after 125^{o}C – 130^{o}c. The increase is more evident for limiting frequencies i.e. 100Hz, 1 KHz, 800 Hz and 1MHz. for intermediate frequencies increase in dielectric loss does not appreciably increase.

Value of dielectric loss at Curie temperature is 0.00855 for 1 V, 0.007107 for 10 V and 0.004534 for 20 V bias voltage (at 100 KHz).

1.2 Variation of dielectric constant and loss with frequency

a) The dielectric permittivity remains constant for initial frequency range and then shows a small resonance peak. After this point it decreases sharply. . Orientational and space charge polarizations damp out as we reach the 1 MHz frequency mark.

b) dilectric loss remains almost constant upto 500 KHz and then rises sharply with increasing frequency. Slope of dielectric loss is maximum at 1V bias voltge and decreases for higher bias potentials - 10 V and 20 V.

3.3 Variation of dielectric constant and loss with bias voltage

a) When relative permittivity is plotted against temperature for different bias votages, it is observed that as thevoltage increases the value of dielectric constant decreases at a particular temperature. At lower frequencies like 100 Hz and 1 KHz the phase transition from ferroelectric to paraelectric phase is not evident. Howeverpattern of dielectric constant for different bis voltage is same as mentioned above. Phase transition appears for 10 Hz and onward frequencies.

b) At lower frequencies dielectric loss remains constant till Curie temperature and increases sharply afterwards. But for higher frequencies say 800 KHz and 1 MHz it starts increasing well before the curie temperature. However at Curie point the phase transition occurs and dielectric loss starts decreasing with increasing temperature.

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