Ferroelectrics are materials which possess spontaneous electric polarisation, \( P_s \), which can be reoriented by applying a suitable electric field. This process is known as switching, and is accompanied by hysteresis. This reversibility is a consequence of the fact that the polar structure of a ferroelectric is a slightly distorted non-polar structure.

Ferroelectrics find wide scope for applications in high dielectric, electro-optic (1-5), electromechanical and memory devices (6,7). The bulk properties of single crystals and ceramic ferroelectrics were exploited in the past. Recently, with the growth of the integrated circuit technology, the research in ferroelectric thin films has been widely appreciated and efforts were put on their film preparation methods and device applications (6,9). The unique high dielectric constant for high capacitance value capacitors of small volume, square hysteresis properties with low switching voltage and small switching time for memory devices (10,11), low loss, high negative or positive temperature coefficients, large pyroelectric coefficients and low thermal capacity for sensitive
thermal detectors (12-14) and others (15) are of utmost technological importance for optimizing the films.

Ferroelectric materials evaluated for thin film devices have included $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{SrTiO}_3$, doped-$\text{BaTiO}_3$ and ($\text{Ba},\text{Sr})\text{TiO}_3$ for thermistors (16), $\text{LiTaO}_3$ (17), $\text{TGS}$ (18) and $\text{PVF}_2$ (19) for pyroelectric detectors, $\text{LiNbO}_3$ and other niobates for transducers (20-22), $\text{KNO}_3$ and complex pervoskite types solid solution based upon lead-ion niobate zirconate for memory storage, and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (2,23) for optical displays.

However, the field is developing rapidly and the prospect of ferroelectric thin films is clear. Hence, in this research pursuit the ferroelectric samples investigated were mainly in the film form in studies hitherto not reported in the physical properties like electrical conduction and dielectric investigation and to further compare and characterize them with their single crystal properties.

Ferroelectrics in addition to their single crystal studies, have been also investigated in a very large number of their solid solutions in the form of ceramics (24-33), having particularly in mind to obtain ferroelectric materials of desirable characteristics with device potentials. In a solid solution, one group of atoms is substituted for another group in a lattice or made extra group occupy interstitial position in
the crystal lattice without breaking up the crystal lattice structure. Certain dopants have also been tried with an intention to affect the ferroelectric characteristics in a desired way (39-50). Hence it was thought desirable to undertake investigation in thin films of a few useful ferroelectric solid solutions.

The anomalous behaviour of many other transition related physical properties near transition temperature is probably as significant as reversible spontaneous polarization to understand the ferroelectric nature of the given material. One of the vital studies on a ferroelectric to affect its other characteristics is its electrical conduction investigation which this thesis presents in some ferroelectric films. In addition the dielectric loss and the dielectric constant being equally important studies for their potential dielectric application it has been subsequently dealt with as regards to their state of knowledge in ferroelectric films.

The study of electrical conductivity of ferroelectric and related materials enables one to get some information also about their related other properties (51). They can be enumerated as follows:

1. Very strong increase in the electrical conductivity with rise in temperature restricts the polarisation of the ferroelectric ceramic near the Curie point and at the same time to utilize the potentialities of the ceramic.
For example, the lead titanate-zirconate ceramic without any additives, with $T_c = 663^\circ K$, can be polarised at a temperature not above $453^\circ K$. By introducing suitable additives the conductivity can be appreciably decreased, so that it is possible to polarise the ceramic at a temperature as high as $523^\circ K$ (51).

2. An increase in conductivity hinders not only the determination of the Curie point of known ferroelectrics by dielectric measurements (51) but also the revealing of the true ferroelectric (or antiferroelectric) nature of compounds as against the spurious ones (52). There is a superficial similarity between dielectrics with high electrical conductivity and ferroelectrics. For example, hysteresis loops are observed in heated glass with a higher electrical conductivity.

3. Ferroelectric crystals have critical size in the absence of the required amount of free carriers. If the crystal is placed into the conducting medium, which is equivalent to increasing the number of free carriers in the bulk of the crystal, the depolarising field is compensated, the electrostatic energy of the crystal decreases and ferroelectricity can develop in the crystal irrespective of its minimum size (53). This is important for observing ferroelectricity in thin film form.

4. The utilization of several properties of ferroelectrics is significantly influenced by the electrical
conduction in the materials. For example, polarized ferroelectric ceramics should have piezoelectric properties up to the Curie point. Clearly, in the polarized piezoelectric ceramics of barium titanate (Tc = 393°K) the piezoelectric properties are observed up to this temperature. On the other hand, in the polarized piezoelectric ceramic of barium-lead titanate (Tc = 523°K), the piezoelectric effect is observed to a temperature of 473°K only (54) and in the polarized ceramic of lead-metaniobate with an addition of neodymium (Tc = 773°K), the piezoelectric activity was observed up to 593°K, i.e. when the conduction is enhanced the region of piezoelectric effect is accordingly narrowed.

5. The concentration of the free carriers is also responsible for the ability to 'forget' the initial configuration. If the crystal is heated above the Curie point Tc, and the carrier concentration is insufficient to compensate the surface charges in a relatively short time, the initial domain configuration reappears in the crystal when it is cooled to a temperature below Tc (55).

6. A single-domain ferroelectric crystal, which is usually the desirable state, can be formed if the surface charges of the boundary dipoles can be compensated by the free charges in the sample during the onset of the ferroelectric phase through the paraelectric phase (56).
The width of a domain decreases with increase in the concentration of the free charge carriers since these reduce the electrostatic energy of the crystal and the opposite polarization induced by the surface charges by charge compensation (57). The width of the domain also depends on the size of the crystal and energy of the domain wall. The increase in the free carrier concentration leads to a decrease in domain wall energy, and thus to a reduction in the domain width (58).

Correct value of domain wall energy is estimated only after considering the electrical conduction in the material as theoretical calculation of domain wall energy gives a value of 0.12 erg/cm$^2$ if the electrical conductivity of the material is not allowed for, and 0.08 erg/cm$^2$ if it is taken into account (58).

1.1 ELECTRICAL CONDUCTION IN FERROELECTRIC SINGLE CRYSTALS:

The main features of electrical conduction in ferroelectrics are the same as those of conduction in ordinary dielectrics. Ionic conduction in ferroelectrics may be intrinsic or extrinsic (59).

However, electrical conduction in ferroelectrics has also a number of special features, primarily associated with the presence of a domain structure, pyroelectricity and with phase transitions. Moreover, non-stoichiometry, which is practically always observed in oxygen-
octahedral ferroelectrics gives rise to electron or hole conduction. The non-stoichiometry of such crystals is fairly pronounced in the interior and electron or hole conduction in these crystals is stronger than ionic conduction. Thus we can speak of semiconducting properties of oxygen-octahedral ferroelectrics.

Heating in ferroelectrics alters the colour of the sample and reduces the activation energy of electrical conduction.

The most interesting and important is the observation that the dependence \( \log \sigma = f(1/T) \) has a kink which corresponds to a ferroelectric phase transition. This means that a structural change near phase transition and consequently the appearance (or disappearance) of spontaneous polarization are accompanied by a change in the activation energy of the charge carriers. Some ferroelectrics exhibit not only a change in the activation energy but also a conductivity discontinuity in the phase transition region.

In the case of ferroelectrics, slow process of domain polarization (reorientation), which also gives rise to a decay of the current, may be superimposed on the usual polarization and conduction process.

Data on the electrical conductivity of ferroelectrics from research papers published up to 1965 have
been reviewed by Serevich (51). A few more data thereafter are presented here.

Ahdan et al. (60) proposed a method for measuring temperature dependence of electrical conductivity of ferroelectrics, which allows measurement of conduction current of the sample in the range of low temperatures and near the phase transition where the pyrocurrent considerably exceeds the conduction current by adjusting $I_p = 0$. The results of log $\sigma$ vs temperature for SbO single crystal show the conductivity singularities at phase transition temperature. Hence in ferroelectrics the pyroelectric contributions are carefully to be accounted in the conduction current.

Electrical conductivities of $Sb_2S_3$ along three axes a, b and c in the temperature range 100-550°K have been investigated by Roy et al. (51). Electrical conduction below 310°K is extrinsic and between 310-550°K it takes place by jumping of electrons from one antimony site to another.

Mansingh et al. (62) have studied phase transitions in melt pulled and pressed crystalline samples of KNO$_2$ at about -13 and 40°C from dc conductivity measurements. The dielectric anomalies at these temperatures are not sharp showing that room temperature phase of KNO$_2$ is not a ferroelectric. The dc conductivity and activation energies of a melt sample of KNO$_2$ are higher than those of randomly oriented crystal. Dielectric
measurements show phase transitions at 130°C on heating and at 124°C and 108°C on cooling these samples of KNO₃.

Shen et al. (63) have investigated dielectric anomaly at about 65°C in KNO₂ fused sample between two nickel coated copper plates. The dielectric constant after decreasing for a short range of temperature (65-70°C) increases continuously upto 110°C. The dc conductivity measurements on the same sample also show an anomaly at about 65°C. Because no hysteresis loop is observed, the 65°C transition is not a ferroelectric-paraelectric transition but is a transition from a polar phase to non-polar phase.

Nanotaka et al. (54) report that the dc resistivity of U₃ doped PbTiO₃ crystal at room temperature is greater than 10¹⁰ ohm-cm compared with ~10⁶ ohm-cm for undoped PbTiO₃ grown by the same technique. They presume that uranium ions enter the PbTiO₃ lattice substitutionally at the Pb²⁺ ion sites. Below 350°C the conductivity measured at 1 kHz is dominated by dielectric loss, while at higher temperatures dc conductivity is dominant.

Mas看得h et al. (55) have studied the temperature dependence of dc conductivity and thickness dependence of dielectric constant at 1, 10 and 100 kHz of ferroelectric lead germanate (Pb₅Ge₃O₁₁). The activation energies have been found to be 0.91 and 0.52 eV in paraelectric and ferroelectric phases respectively. The dielectric constant decreases with decreasing thickness of the sample at
all frequencies. The results have been explained by assuming surface layer at the metal-insulator junction with a conclusion that electrical conduction at high temperature is mainly electronic.

The same authors (66) have also reported constant and dielectric ac conductivity of ferroelectric lead germanate in frequency range 60 Hz - 100 kHz for particle size 40 to 300 μm. The conductivity decreases with decreasing particle size. These have been explained on the basis of high resistivity surface layer having a lower dielectric constant than that of the bulk.

Lillicrap et al. (67) conclude from the temperature variation of the loss resistivity of doped D(3) TGS samples that it is only reproducible when the rate of change of the sample temperature is not greater than about 0.2°C min⁻¹. Higher rates affect the loss tangent by reducing the loss resistance, and recovery of equilibrium values requires time of the order of an hour.

Mathur et al. (47) reported higher values of electrical conductivity of nitroaniline doped TGS crystals than those of pure crystals. They suggest that nitroaniline molecules enter the TGS lattice interstitially.

The effect of doping (0.1 to 1.5% wt.) in electrical conductivity of PbTiO₃ ceramics has been communicated by Frohkopalo (68).
In high Curie temperature ferroelectrics the dc conductivity is determined by measurement of thermoelectric current (69). Temperature dependencies of dc electrical conductivity obtained by this method for PbTiO$_3$, Pb(Zr$_{0.25}$Ti$_{0.75}$)O$_3$ and Pb(Zr$_{0.40}$Ti$_{0.60}$)O$_3$ agree well with reported values and phase transition anomalies are clearly seen.

Preparation and characterization of a single domain crystal of Ba$_{1-x}$Nd$_x$Ti$_{3}$O$_{11}$ (x = 3x10$^{-3}$ to 3.1x10$^{-2}$) have been investigated by Seltz et al. (70). x = .31 yields Curie temperature of 55$^\circ$C due to distortion of Ti$^{IV}$O$_6$ octahedra by the Nb$^{V}$O$_6$ octahedra. The anisotropy of specific conductivity is about half an order of magnitude at room temperature and decreases at rising temperatures.

1.2 ELECTRICAL CONDUCTION IN DIELECTRIC AND FERROELECTRIC THIN FILMS:

Because of their methods of preparation the thin films of dielectrics are either in uniform deposit of small crystallites or are amorphous. Single crystal films are difficult to prepare and polycrystalline ones are generally much less insulating. Stoichiometric films of compound dielectrics are also difficult to prepare.

Much of the theory outlined for electrical conduction in bulk materials is also applicable to thin films but with a few notable exceptions, namely, the breakdown
process and the high conductivity. Conductivity is generally higher in films due to the presence of 'weak paths' which are a direct result of the method of deposition and resultant stresses.

The thin film dielectrics provide an ideal medium for the study of conduction process at high fields (greater than $10^5$ V/cm) since the voltages necessary to provide such fields are easily attainable in the form of laboratory power-packs.

**DC Conduction Mechanism:**

Most dielectrics conduct ohmically below 0.1 kV cm$^{-1}$ and non-ohmically above 1 MV cm$^{-1}$. Ohmic conduction is always extrinsic near 20°C in practical material, whereas the non-ohmic components may be intrinsic. This is true whether the conduction is ionic or electronic, direct or relaxational.

The high-field conduction in a dielectric can be due to electronic conduction by means of the conduction band of the dielectric. The tunnelling process at high field is also feasible from the metal into the conduction band, between the trapping levels in the dielectric, directly between the trapping levels in the dielectric, directly between the valence band and conduction band and from valence band directly into the metal electrode, or directly between the two metal electrodes. During impurity conduction electrons hop from one trapping
(e.g., impurity) centre to another without going to the conduction band. Space-charge effects may also appear during conduction process where one of the three conduction processes is not the rate-limiting process which acts as impedance and in the limit balance out the applied voltage.

In addition to the processes described above to allow electrons to go through the dielectric, it is also possible for ions, often in the form of impurities or defects, to themselves move through under the influence of an electric field and thus, ionic conduction is said to occur.

Low-field conduction is ascribed with only two processes i.e. impurity conduction and ionic conduction.

TEMPERATURE DEPENDENCE:

It is difficult to generalise the temperature dependence of dc conduction whether it is electronic or ionic since so many processes are possible. However, tunnelling (high-field) conduction usually exhibits a small temperature dependence. Ohmic (low-field) conduction, whether ionic or electronic, gives an exponential temperature dependence given by

\[ \sigma = \sigma_0 \exp \left( -\frac{E_g}{kT} \right) \]

where \( \sigma_0 \) is a constant and \( E_g \) is the activation energy.
Whatever be the ohmic mechanism, a log $\sigma$ vs $1/T$ plot will usually exhibit increasing linear slopes as temperature is raised. At the highest temperatures the intrinsic ionic or electronic conduction may finally appear, although the melting point may hide them.

**AC Conduction and Dielectric Losses**

The ac conduction is generally studied by measuring the dissipation factor or loss tangent ($\tan \delta$) as a function of frequency and temperature. Since we are concerned with electrical insulators (dielectrics), these are best considered in capacitor dielectrics. The capacitance $C$ of a parallel-plate capacitor is given by

$$C = \frac{\varepsilon' \varepsilon_0 A}{d} = \varepsilon' C_0$$

where the symbols have their usual meanings. Insulators always have a finite parallel resistance $R$, and the complex impedance will be given by

$$Z = \frac{1}{j\omega C R}$$

A second method of representing the ac losses is to consider a complex capacitance resulting from a complex permittivity

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

The complex impedance of the capacitor is given by

$$Z = \frac{1}{j\omega C} = \frac{1}{j\omega C_0(\varepsilon' - j\varepsilon'')}$$
Since the above two methods of representation are equivalent, we have

\[ \frac{1}{r} = \omega C \sin \theta \quad \text{and} \quad C = C_0 \epsilon' \]

The energy loss is proportional to \( \cos \theta = \sin \delta = \tan \delta \) (for small values of \( \delta \)),

or

\[ \tan \delta = \frac{1}{\omega C_0 \epsilon'} = \frac{\epsilon''}{\epsilon'} \]

The ac conductance is then given by

\[ \sigma^* = \omega C_0 \epsilon'' \]

1.2.1 Electrical Conduction in Ferroelectric Thin Films:

General concepts of electric conduction on dielectrics are also applicable to ferroelectric film with some special features as outlined here.

Off Ferroelectric Films:

Nolta et al. (22) have studied temperature dependences of dc electrical conductivity of \( \text{KNO}_3 \) in the form of fused layer \((t \sim 100 \mu)\), vacuum evaporated film \((t = 0.75 \mu)\) on stainless steel substrates and \( c \)-cut single crystal \((t \sim 940 \mu)\) from RT to \(260^\circ\) in vacuum.

The conductivity, \( \sigma^* \), vs temperature, \( T \), characteristic of \( \text{KNO}_3 \) did not show any significant difference with thickness or between the three types of specimens.
Phase II $\rightarrow$ Phase I at $\sim120^\circ$C and phase I $\rightarrow$ Phase III transitions at $\sim121^\circ$C were observed but phase III $\rightarrow$ II was not detectable for evaporated film. To shifts towards lower temperature side.

They (71) have also reported ac conductivity vs temperature for the evaporated film of KNO$_3$. It shows the usual single transformation upon heating and also only a single transition on cooling while the ferroelectric transition is suppressed.

Stephen et al. (72) have prepared TGS thin films on microscope cover slides by laser evaporation under high vacuum (0.1 to 50 $\mu$m). The resistivity reported is about $10^{13}$ ohm-cm, very close to the bulk value. The transition temperature was found to be $48^\circ$C.

Yoda et al. (73) have reported the temperature dependence of dc electrical conductivity of 100 $\mu$m thick ferroelectric polymer PVF$_2$ film (40% crystallinity) from crystal melting point ($\sim185^\circ$C) to room temperature.

From 185$^\circ$C down to 150$^\circ$C, conductivity decreases stepwise and ionic conduction is dominant. The conductivity decreases due to capture of carriers on crystal interiors or boundary. From crystallization temperature 150$^\circ$C down to 70$^\circ$C, the decrease in conductivity is reported to be due to capture of carriers at deep energy levels caused by halting of molecular motion in folding portion on crystal boundaries.
The resistivity of unoriented PVF₂ (0.154 to 0.051 cm thick) is \( \sim 2 \times 10^{15} \) ohm-cm which is lower than that of the oriented materials (\( \sim 1-5 \times 10^{16} \) ohm-cm) by at least an order of magnitude as reported by Nur (74). Hence orientation affects electrical properties.

The same author (75) has reported that the resistivity of PVF₂ increases with draw ratio and percentage of total crystallinity which is \( \beta \)-phase. Increase in resistivity is due to the presence of polar crystallites which have an impeding effect on conducting ions because of the large fields at their surfaces.

**Hard Ferroelectric Films:**

Surfoot et al. (75) have reported electrical properties of flash evaporated \( \text{BaTiO}_3 \) thin films (\( t \sim 600 \, \mu \text{m} \)) on cleaved NaF substrates. Thin film structure varied from amorphous to crystalline as substrate temperature was varied from 130 to 540°C. The dielectric constant decreased with decreasing film thickness. The film resistivity is one to two orders higher at low field and it is lossy also.

Spence et al. (77) have prepared \( \text{Pb}_{0.92} \text{Bi}_{0.07} \text{La}_{0.01} (\text{Sr}_{0.405} \text{Nb}_{0.325} \text{Cr}_{0.27})_0 \text{Ba}_3 \) ferroelectric film (\( t \sim 2-10 \, \mu \text{m} \)) at temperature between 100-500°C on gold-coated alumina substrates by r.f. sputtering and reported that the dc resistivity is about \( 10^{14} \) ohm-cm for 4.5 \( \mu \text{m} \) thick sample.
Castellano et al. (78) have studied film resistivity of PZT deposited by focused ion beam sputtering technique in oxygen atmosphere on NiCr-Au film in a Pyrex glass or Invar at 750°C. The resistivity approaches bulk values (10^9 ohm-cm) at 425°C but decreases for films deposited at 450°C.

Temperature variation of electrical conductivity of α-TiO_3 thin film on Pt prepared by r.f. sputtering (t ~ 1-5 μm), by electrophoresis (t ~ 5-65 μm) and by paste burning method the polycrystalline Sr(Ti,Sn)O_3 films (15-100 μm thick) have been investigated by Surowiak (79). The ohmic resistance of a SrTiO_3 film of thickness 5 μm at room temperature was 10^{12} ohm, giving a conductivity value of 3×10^{-11} ohm^{-1} cm^{-1}, comparable to bulk value.

Surowiak et al. (80) have studied semiconducting properties of (α,β)TiO_3 ferroelectric film (t ~ 8-10 μm) obtained by the sintering method. Very slight change in the conductivity as a function of temperature was observed. There is anomaly at a temperature close to the phase transition and a maximum value of conductivity (at room temperature) is of the order of 10^{-4} ohm^{-1} cm^{-1} for a composition with 0.25% Sb_2O_3 admixture, which diminishes as the concentration is increased.
1.3 ANOMALOUS DIELECTRIC BEHAVIOUR OF FERROELECTRICS

IN BULK AND FILM FORM:

The dielectric study investigation on ferroelectric films has been included in this thesis with equal weightage. Though invariably amongst ferroelectrics dielectric study is reported extensively but in their film form still the data is scarce. Ferroelectric films investigated so far for their dielectric investigations are tabulated and summarized in Table 1.1. Since reviewing all dielectric studies in ferroelectrics are too exhaustive. Our main interest in dielectric investigation on ferroelectric films has been with a view to present unreported data in their film form particularly with a view to evaluate their thermodielectric energy conversion efficiency in the last chapter.

The dielectric constant ($\varepsilon$) of a linear dielectric for example, alkali halides, decreases monotonously with decreasing temperature. In contrast to this, the dielectric constant of a ferroelectric in the non-polar paraelectric phase increases with decreasing temperature, passes through a maximum at very high values at the transition temperature and then decreases when the spontaneous polarization begins to rise in ferroelectric phase. This decrease is due to saturation of spontaneous polarization. The very high values of dielectric constant in the neighbourhood of Curie point are referred to as anomalous values.
| No. | Repairative Technique | Ferroelect. Cryst. | Purity & Phase | Transition Temp. (°C) | Dielectric Loss | Dielectric Constant | Composition | Characteristic
|-----|----------------------|-------------------|----------------|----------------------|----------------|-------------------|-------------|-------------------
| (1) | (8)                  | 199                | 1.2            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (2) | (7)                  | 60                 | 1.3            | 90-30                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (3) | (6)                  | 215                | 1.4            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (4) | (3)                  | 225                | 1.5            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (5) | (4)                  | -                  | 1.6            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (6) | (5)                  | -                  | 1.7            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (7) | (6)                  | -                  | 1.8            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |
| (8) | (7)                  | -                  | 1.9            | 95-35                | 10-15         | 0.8               | (Ba0.65Sr)0.37Ti03 | Vap. - PZT    |

Table 1.1 Performance of thin films prepared by different techniques
<table>
<thead>
<tr>
<th>No.</th>
<th>Structure</th>
<th>( \theta ) (°)</th>
<th>Ip (mA)</th>
<th>Intensity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>19</td>
<td>30</td>
<td>0.01</td>
<td>0.17</td>
<td>Spinning drop</td>
</tr>
<tr>
<td>(2)</td>
<td>25</td>
<td>30</td>
<td>0.01</td>
<td>0.17</td>
<td>Spinning drop</td>
</tr>
<tr>
<td>(3)</td>
<td>75</td>
<td>30</td>
<td>0.01</td>
<td>0.17</td>
<td>Spinning drop</td>
</tr>
<tr>
<td>(4)</td>
<td>170-115(111)</td>
<td>30</td>
<td>0.01</td>
<td>0.17</td>
<td>Spinning drop</td>
</tr>
<tr>
<td>(5)</td>
<td>118-229(111)</td>
<td>30</td>
<td>0.01</td>
<td>0.17</td>
<td>Spinning drop</td>
</tr>
</tbody>
</table>

\( \theta \) = 2\theta, \( Ip \) = Ion Beam; \( SC \) = Single Crystal; \( RF \) = Radio Frequency
At low frequencies the piezoelectric deformations can follow the periodic change of the applied ac field and one measures the dielectric constant of the mechanically unconstrained free crystals.

Above the transition temperature in paraelectric phase, the dielectric anomaly appearing as dielectric instability around $T_c$ is frequently of the Curie-Weiss form

$$\varepsilon = \frac{4\pi C}{T - T_0}$$

to a good approximation. $C$ is known as the Curie constant. The value of $T_0$ (Curie temperature) usually coincides with $T_c$ (transition temperature) in materials with first-order transitions. In other materials $T_0$ is a few degree below $T_c$.

The anisotropy of dielectric constant is very pronounced for uniaxial ferroelectrics. The dielectric constant perpendicular to the ferroelectric axis is lower than along the ferroelectric axis and exhibits less or even no anomalous temperature dependence. Poly-axial ferroelectrics that are cubic and dielectrically isotropic in the nonpolar phase become strongly anisotropic in the polar phases.

In linear dielectrics the polarization is strictly proportional to the electric field. Dielectric breakdown occurs before dielectric saturation can be observed. In ferroelectric crystals, however, the dielectric polari-
zation can become so large that non-linear effects become observable. The most drastic manifestation of saturation is the decrease of dielectric constant that occurs together with the spontaneous polarization. Saturation effects are also observable in the paraelectric phase, particularly near the Curie point where the dielectric susceptibility is very high.

For a given ferroelectric material in thin film form its dielectric constant is sensitive to film preparation condition, stoichiometry and crystallinity of the film. Departure from stoichiometry (81) leads to lowering of the dielectric constant e.g. PbTiO₃. Amorphous or microcrystalline nature with appreciable strain and structural disorder amount to considerable reduction in dielectric constant.

Dielectric investigations carried out in the ferroelectric films are summarised with respect to their deposition technique, crystalline form, transition temperature, thickness and dielectric peak value in Table 1.1. It is evident that many of the ferroelectrics have not yet been investigated in their film form hence this work was further included in our investigation. Dielectric loss studies on ferroelectric films are also incorporated in our experimental studies for their relevance with the process of electrical conduction.
1.4 DIELECTRIC LOSSES IN FERROELECTRICS

An alternating current field heats any real dielectrics. That part of the energy of the alternating field which is transformed into heat is known as dielectric losses, corresponding to a constant voltage, and losses due to active component of the displacement current within the material.

Dielectric losses are associated with the process of establishment of polarization. The displacement polarization is established rapidly. Hence the dielectric losses in crystals which exhibit only displacement polarization are very low.

The situation is somewhat more complicated in the case of dielectrics exhibiting relaxational polarization. Numerous dielectrics, exhibiting these types of polarization, have fairly high losses at radio frequencies because of the time required for establishment of polarization is now comparable with the period of an external electric field. There may be losses due to formation of a space-charge.

The conduction current in a dielectric is, in fact, main source of dielectric losses. The conduction current redistributes the field. In such cases, the conduction current not only has an active (ohmic) but also a reactive component.
In weak fields ferroelectrics are polarized similarly to linear dielectrics. Although domain processes do take place, they do not give rise to a hysteretic dependence of the polarization in the weak field. The value of dielectric loss of ferroelectrics increases and passes through a maximum when the temperature approaches the ferroelectric phase transition point.

The losses in ferroelectrics, subjected to strong fields, can be due to various causes but the main losses are due to dielectric hysteresis. The magnitude of these losses is proportional to the area of the hysteresis loop. A ferroelectric with a rectangular hysteresis loop behaves as an ohmic resistance. Hysteresis of real dielectrics (i.e. BaTiO$_3$ and TGS) are nearly rectangular if the losses in them can be minimized. In lossy ferroelectrics the rectangular loops are rounded off. The absolute value of the losses due to dielectric hysteresis can be expressed in terms of the hysteresis loop area. Hence the loss study becomes quite relevant in the characterization of ferroelectric materials and so was a part of our study in the ferroelectric films.

1.5 PURPOSE OF PRESENT STUDY:

The objective of the present study of thin ferroelectric films has been

1) To understand their dielectric behaviour through experimental measurements of the dielectric
constant and loss as a function of temperature to evaluate their ferroelectric nature in film form and persistence of the ferroelectric phase transition in thin films. This has further relevance in characterizing the prepared ferroelectric films by the author and is providing hitherto unreported data on the reported films.

2) To understand the underlying mechanism and provide data on electrical conductivity of a few more soft ferroelectric films as the data available to date on these are not sufficient and the literature on thin films is quite scarce.

3) To prepare through this reported new technique, which is relatively cheap and simple, thin films of more soft ferroelectrics with well crystalline structures which could not yet be prepared by the usual standard techniques.

4) To evaluate these films for thermodielectric energy conversion on the basis of our measured dielectric constant of these films and other supplementary data.
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