This thesis is devoted to the study of electrical conduction in ferroelectrics. The literature on electrical conduction as a transport property in ferroelectrics has not yet been studied extensively. The conduction in ferroelectrics is associated with the structure details and para- to ferroelectric phase transition in these crystals. The conduction process is measured in terms of an important parameter called the electrical conductivity. Dielectric constant, dielectric loss and ac conductivity of a ferroelectric are very intimately related to its electrical conductivity. Dielectric measurement though studied extensively on single crystal ferroelectric materials but again in their film form the data are scarce. Today when ferroelectric films are being introduced as film detectors and in microelectronics as well we present here in this thesis measurements on dielectric constant, dielectric loss and ac conductivity in addition to dc conductivity as functions of temperature in case of the following ferroelectric material films:

1. Triglycine sulphate (TGS),
2. Triglycine selenate (TGS€),
3. L-alanine doped triglycine sulphate (LATGS),
4. Triglycine sulphate-selenate solid solution (TGS/Se),
5. Polyvinylidene fluoride (PVF₂),
6. Triglycine sulphate-polyvinylidene fluoride multilayer film (TGS-PVF₂),
7. Sodium nitrite (NaNO₂),
8. Potassium nitrite (KNO₂),
9. Sodium nitrite-potassium nitrite solid solution (NaNO₂-KNO₂),
10. Potassium nitrate (KNO₃) and
11. Potassium nitrate-potassium iodate solid solution (KNO₃-KIO₃).

The above ferroelectrics and their solid solutions show anomalous dielectric behaviour around their respective Curie temperatures. To exploit this anomalous behaviour in thermodielectric energy conversion we have selected these materials in the form of parallel plate capacitors in the present study. To enhance the efficiency of the thermodielectric energy converters, all the above materials were investigated in their film forms because they can be conveniently operated with low voltages usually available in the laboratories. Thin film study has been mostly reported on hard ferroelectrics and literature on thin soft ferroelectrics is scarce. This thesis will, therefore, also provide at the same time a few more data on thin soft ferroelectrics for their potential device applications.

All the films have been prepared by the author of this thesis in the department with the equipments designed and fabricated in USIC either by spinning disc
technique or melt-casting technique as per the details given in the relevant chapters. Thin films of soft ferroelectrics, namely TGS, TGSe, LATGS, TGS/TGSe, TGS-PVF$_2$ (multi-layers), PVF$_2$, NaN$_2$O$_2$, KNO$_2$, NaN$_2$O$_2$-KNO$_2$ (solid solution) and KNO$_3$ have been prepared on nearly optically flat glass slides from their respective aqueous or dimethylformamide (for Kynar PVF$_2$ powder) solutions at slightly elevated temperatures by spinning disc technique. The films of KNO$_3$ and KNO$_3$-KIO$_3$ solid solution have been prepared on transparent glass plate by melt-casting technique. The thesis has been divided into seven chapters.

The first chapter introduces the basic concepts and terms used in the study of electrical conduction in ferroelectrics. The electrical conductivity of a ferroelectric is mainly ionic and differs from electronic conduction by the transport of matter. The nature of electrical conduction in typical ferroelectrics has been reviewed. The influence of electrical conductivity of the ferroelectrics on their other properties has been briefly discussed. Since ferroelectrics are essentially a sub-class of dielectrics, the electrical conduction mechanism in dielectrics in general and in ferroelectrics in particular has been briefly presented in this chapter as regards their properties in single crystal and film forms.
A brief review of up-to-date work related to the present study on soft ferroelectrics including solid solutions in their bulk and thin film forms with respect to dielectric constant, loss, ac and dc conductivities has been incorporated in this chapter. The unique properties of thin films and their device applications have also been mentioned in short. In the end, the objectives of the present study have been elaborated.

The second chapter deals with the various experimental techniques adapted for the preparation and measurement of aluminium thin film electrodes, transparent conducting electrodes and ferroelectric thin films. The working principles of important instruments like the vacuum coating unit, the Wayne Kerr Autobalance bridge 942, the Megohmmeter Model 160/3 and Keithley Digital Multimeter Model 160 which were employed in the present study, have been briefly presented. Simple spinning disc used for preparation of soft ferroelectric thin films has been fabricated in the USIC department during the course of present study. Procedures for observing the polycrystalline structure of the ferroelectric films and their birefringence, for estimating the lamellar crystallite size and physical faults through the crossed polarizing microscope are also mentioned. Measurements of the film thickness and their temperature have been also discussed. The usual methods adapted for poling, measurements of electrical parameters such as
dielectric constant, dielectric loss, ac and dc electrical conductivities have been briefly discussed.

The third chapter presents the detailed account of author's investigation on electrical and dielectric properties of thin films of TGS, LATGS and TGSe. For characterization and comparison, single crystals of TGS and TGSe have also been studied. The dielectric constant of a TGS film, of thickness about 10 \( \mu \text{m} \) and lamellar crystallite size \( \sim 1000 \mu \text{m} \) diameter, increases gradually with rise in temperature and a broad peak anomaly occurs at \( 46^\circ \text{C} \) with \( \varepsilon_{\text{max}} \sim 850 \). The dielectric constant then decreases in paraelectric phase and obeys the Curie-Weiss law. The occurrence of dielectric anomaly in the film shows the existence of ferroelectricity in it. The broad peak anomaly with substantial high value of dielectric constant indicates that the crystallites in the film are randomly oriented and the ferroelectric \( \delta \)-axis is favourably oriented perpendicular to the surface of the film for majority of them. The dielectric constant does not fall sharply below and above the transition temperature. This may be attributed to the polarization instability due to presence of strong depolarization fields in the film.

Annealing and poling the film upto 8 kV/cm do not enhance the dielectric anomaly but the decrease in dielectric maximum and slight increase in transition
temperature are observed. It seems that these poling fields, being many orders of magnitude less than the internal bias/depolarization fields could only sweep out the trapped charges at the defect sites and consequently the reduction in dielectric constant is observed.

Slight increase in the transition temperature is due to reduction in domain mobility in polycrystalline samples caused by poling.

Another TGS film of thickness 22.5 µm with lamellar crystallite size of about 50 µm shows very feeble dielectric anomaly with $E_{\text{max}} \sim 8.5$ at 51°C. Thus, the comparison of the dielectric behaviours of the above two films of TGS indicates that the dielectric constant of the film with larger crystallite size is higher by about 100 times than that of the film with smaller crystallite size, irrespective of their thickness. The dielectric loss of the films is comparable to that of the single crystals. The loss of 10 µm thick TGS film is $\sim 1.96 \times 10^{-2}$ (peak value) at 49°C. Poling and annealing reduce the loss slightly. The reduction in loss is due to reduction in the trapped charge carriers caused by poling fields.

L-alanine doping introduces additional internal bias in the matrix of TGS and consequently reduces dielectric maximum, broadens dielectric peak and increases transition temperature with increasing l-alanine content. Addition of asymmetric l-alanine in small quantity (<1%
reduces the conductivity of the film but excess > 1\% of alanine increases conductivity because in excess addition the alanine molecules occupy interstitial positions. Also in addition to substituting the glycine molecules. It is to be emphasised here that it is the first report on successful preparation and investigations on the films of LATGS and TCSe.

Temperature dependence of dielectric constant of TCSe film of thickness 12 \( \mu \)m and lamellar crystallite size of about 1000 \( \mu \)m shows broad dielectric peak (\( \sim 330 \)) at 23.5\(^\circ\)C and its behaviour is very similar to that of the TGS film.

The dc electrical conductivities of films of TGS and TCSe are in the range of 10\(^{-13}\) to 10\(^{-11}\) ohm\(^{-1}\)cm\(^{-1}\) from room temperature to 80\(^\circ\)C. Jumpwise transitions in \( \log \sigma \) vs 1000/T graphs are not seen due to increased conductivity of the films by the large number of defects. Activation energies in films are slightly higher for films being polycrystalline and more defects account for higher conductivity in the films.

The ac conductivities of these films are about 2-3 orders of magnitude higher than the corresponding dc conductivities.

In fourth chapter, the dielectric and electrical properties of thin films of TGS/Se solid solution and TGS-PVF\(_2\) multilayer films have been investigated as
functions of temperature with a view to employ them in thermoelectric energy conversion. Again this is a first report on films prepared and studied on these materials. Dielectric constant variation with temperature of thin film of TGS$_{0.4}$TGB$_{0.6}$ solid solution (thickness~5.5 μm) shows anomalous broad peak ($\varepsilon_{\text{max}} \sim 500$) at 30°C and seems suitable for solar energy conversion (Chapter VII). Its dielectric and electrical behaviours are very similar to that of TGS films. The dc conductivity is of the order of $10^{-12}$ to $10^{-11}$ ohm$^{-1}$cm$^{-1}$ and the dielectric loss having values $2-8 \times 10^{-2}$ between room temperature and 80°C.

The dielectric constant of a PVF$_2$ film (1 μm thick) has values of 3.3 at 30°C, 13 ($\varepsilon_{\text{max}}$) at 109°C and 9.5 at 153°C. The loss values are $4.3 \times 10^{-3}$ at 30°C, $18.3 \times 10^{-2}$ at 77°C, $5.6 \times 10^{-2}$ at 121°C and $60 \times 10^{-2}$ at 153°C. Temperature between 70 - 90°C is region of molecular motion or $\varepsilon$-relaxation of the film. DC conductivity varies between $1.04 \times 10^{-14}$ and $1.45 \times 10^{-11}$ ohm$^{-1}$cm$^{-1}$ from 30 to 155°C.

Technologically important ferroelectric TGS crystals are relatively fragile, have a fairly low thermal conductivity to withstand high incidental power density and are water soluble. Hence they need some protecting housing and optical window to use them to their maximum capacity. With this intention a PVF$_2$ film is prepared on a TGS film and the resulting multilayer film is studied as regards its dielectric constant, loss, ac and dc conductivities as a combined system.
TG$_2$-PV$_2$ multilayer film has intermediate properties of films of TG$_2$ and PV$_2$ with regards to dielectric and electric properties but its transition temperature occurs at 52$^\circ$C. The maximum dielectric constant is 64. The dc conductivity is of the order of $10^{-13}$ to $10^{-11}$ ohm$^{-1}$cm$^{-1}$ and ac conductivity of the order of $10^{-9}$ to $10^{-8}$ ohm$^{-1}$cm$^{-1}$.

The fifth chapter deals with the dielectric and electrical properties of thin films of NaN$_2$, KN$_2$ and NaN$_2$-KN$_2$ solid solution being the first report on thin film preparation. The dielectric constant of NaN$_2$ film ($t\sim1$ μm and crystallite size$\sim50$ μm) increases slowly with temperature upto 90$^\circ$C. Thereafter it rises rapidly and broad anomalous peak ($\varepsilon_{\text{max}}\sim580$) occurs at 148$^\circ$C. It starts decreasing above 148$^\circ$C upto 157$^\circ$C and then increases steeply in paraelectric phase unlike its bulk behaviour. The mechanism of steep rise in dielectric constant in paraelectric phase is related to lattice distortion. Sizeable decrease of about 15$^\circ$C in transition temperature is explained in terms of high internal bias fields. The temperature variation of dielectric loss has two peak values, (i) 0.96 at 123$^\circ$C and (ii) 1.1 at 160$^\circ$C; and one dip value of 0.76 at 147$^\circ$C. Peak value at 123$^\circ$C shows maximum domain mobility within polycrystal at this temperature. Due to steep rise in the dielectric constant in paraelectric phase, the loss in this
phase decreases steeply. Thin films of solid solution of NaN$_2$O and KNO$_2$ show high values ($\sim 10^3$) of dielectric constant and steep rise after about 70°C. Broad anomalous peak is observed in NaN$_2$O-KNO$_2$ (40/60) film at 190°C. No anomalous peak is observed in NaN$_2$O-KNO$_2$ (20/80) film up to 185°C. The thin film of KNO$_2$ (1 µm thick and crystalite size $\sim 50$ µm) shows small dielectric anomalies at 35°C and 60°C. The high values of dielectric constant of the films of these materials in comparison to their bulk values are explained on the basis of space-charge polarization near the electrodes.

dc conductivities of these films are in the range of $10^{-9} - 10^{-7}$ ohm$^{-1}$cm$^{-1}$ and the dc conductivities in the range of $10^{-13} - 10^{-10}$ ohm$^{-1}$cm$^{-1}$ from RT to 220°C. The KNO$_2$ film has dc conductivity of the order of $10^{-7}$ ohm$^{-1}$cm$^{-1}$ and this high value is comparable to bulk values. The high field applied during dc conductivity measurement annuls the effect of space-charge. The losses of these films at high temperatures are high due to increased conductivities and have values in the range 0.01 to 0.76 from room temperature to 220°C.

In the sixth chapter, the results of investigation of the electrical conductivity and dielectric properties as functions of temperature of films of KNO$_3$ (solution grown and melt-casted) and of KNO$_3$-KI$_2$O$_3$ solid solutions (melt-casted) are presented. KI$_2$O$_3$ hitherto a difficult material to melt or dissolve for its film
preparation has been overcome by dissolving it in KNO₃ melt. Hence this bears as the first report on films of the KNO₃-KIO₃ system. Formation of solid solution of KNO₃-KIO₃ has been characterised by IR spectrum. The dielectric constant of solution grown virgin thin film of KNO₃ (about 2 μm thick) increases slowly upto 115°C and suddenly rises to a peak value of about 280 at 117°C showing the phase II → I transition. In paraelectric phase the dielectric constant of this film is found to increase steeply with temperature. Upon cooling the film from 130°C ferroelectric phase III appears at 102°C with Eₘₐₓ ~ 260 and does not disappear till room temperature and the phase II is not observed on cooling. Subsequent repetition of the dielectric measurement hindered the appearance of phase III on cooling while phase II → I transition took place as usual on heating cycle and the dielectric constant is now found increased. The disappearance of ferroelectric phase III on subsequent repetition of the experiment on the same film is attributed to developments of micro-cracks in the film during reconstruction transformation from phase III to phase II. The increase in dielectric constant of the film is attributed to the space-charge polarisation effect. The dielectric loss of the film reduces on repeating the experiment, confirming the existence of space charge polarisation. In paraelectric phase loss increases with temperature. Dielectric measurements on melt-casted films of KNO₃ and KNO₃-KIO₃ solid
solution show second order phase transition around 115°C on heating. The dielectric constant of mixed system is slightly higher at low temperatures but lower at higher temperatures. Phase transitions at 58°C and around 197°C are not pronounced in the mixed system. Thus the behaviour of film of KNO$_3$-KI0$_3$ is intermediate to the behaviours of KNO$_3$ and KI0$_3$.

The loss of mixed system at low temperature is about one order of magnitude higher than that of the KNO$_3$ film. This shows that IO$_3$ ions are more free than NO$_3$ ions to contribute towards electrical conduction.

Conductivity measurements do not show the appearance of phase III explicitly on cooling in solution grown film. However, phase II → I occurs between 113 and 120°C in log $\sigma$ vs 1/T graphs and between 112 and 118°C in log $\sigma$ vs 1/T graphs. The ac conductivities are about 3-4 orders of magnitude higher than the dc values. The dc conductivity of the films of KNO$_3$-KI0$_3$ is found intermediate to those of KNO$_3$ and KI0$_3$ crystals. The activation energy of the film of mixed system is 0.68 eV at low temperatures and 0.51 eV at high temperatures and are less than those of solution grown KNO$_3$ films.

The ac conductivities of these films are between $10^{-10}$ to $10^{-7}$ ohm$^{-1}$ cm$^{-1}$ and the dc conductivities between $10^{-14}$ to $10^{-9}$ ohm$^{-1}$ cm$^{-1}$ from room temperature to 220°C.
Compared to the single crystal study, some of the salient features of thin film study contained in Chapters I.I to VI are summarised as follows:

1. The polar ferroelectric axes are advantageously oriented perpendicular to the plane of the films and such films of ferroelectrics can partially retain ferroelectric behaviour.

2. Anomalous dielectric peaks are not sharp but broadened in the thin films.

3. L-alanine doping reduces dielectric anomaly, increases Curie-temperature and provides a nearly reproducible results. However, it does not yield the desirable result of single crystals doped by l-alanine.

4. Dielectric constants of thin films of inorganic ferroelectrics like NaNO$_2$ and KNO$_3$ are found enhanced in the paraelectric phase.

5. The transition temperatures of the films of the ferroelectrics undergoing second order phase transition increase slightly but those of undergoing first order phase transition decrease significantly.

6. Electrical conductivities of the films are higher by a few orders of magnitude than those of respective single crystals.
7. Jumpwise transitions in \( \log \sigma \) vs \( 1/T \) graphs of the films are not observed in films but anomalous change is obvious.

8. The activation energies in thin films are somewhat higher than the respective single crystal values.

Chapter VII characterises the thin films studied in the present work for thermoelectric energy conversion. The energy ratios for films of respective materials are calculated and they seem to hold promise as energy conversion materials. Earlier work on the investigation of ferroelectric materials as thermoelectric energy conversion has been reviewed. To extend the work further the scope of the dielectric anomalous peak at the transition temperature in the background information on their pyroelectric*, electrical conduction*, thermal expansion*, coercive field, specific heat and density (where some of the data are from the experimental results of our research group starred) were theoretically evaluated in terms of the energy ratio i.e. the electrical energy derivable from the thermal energy input to the materials. In our evaluation mainly the TiS, TGS - \( \beta \mathrm{WO}_2 \), \( \beta \mathrm{WO}_2 \) and \( \mathrm{NaNO}_2 \) films having evaluated value \( \gamma \) between 0.45 and 0.87 show good promise for thermoelectric energy conversion.

Ferroelectrics in thin forms are more suitable materials for such purposes as they enable high field
application to store electrical energy with high dielectric constant (peak value) at the transition temperature. Admixtures of ferroelectrics (e.g. TGS) with the ferroelectric polymers (e.g. PVF₂) are materials for prototype thermal to electrical energy conversion experiments since not only that their energy ratios evaluated by us are comparatively large (e.g. 0.87) but also that mechanical strength, manufacturing and mass production have already a background of thoroughly worked out technology where the success in energy conversion is assured.

For the conversion of solar energy to electrical energy the ferroelectric materials are cycled between the transition temperature (which should be above the ambient temperature and achievable with solar radiation) and room temperature. Shifting to Tc or different ratio of solid solution seems it feasible with TGS-TGSe system to get the desirable Tc ferroelectric solid solution for such purposes.