CHAPTER 1

ELECTRICAL CONDUCTIVITY OF FERROELECTRIC AND
RELAXED CRYSTALS: (1-3)

1.1 INTRODUCTION:

Ferroelectrics form a class of materials which exhibit reversible spontaneous polarisation $P_s$ along polar direction. The spontaneous polarisation can be reversed by applying a suitable electric field. The process involved is associated with dielectric hysteresis. Besides reversible polarisation, other typical characteristics of ferroelectrics are their anomalous behaviour around ferroelectric transition temperature and their nonlinearities. A large number of ferroelectrics cease to exhibit ferroelectricity above a transition temperature $T_c$ known as the Curie point. This anomaly near $T_c$ is of great significance but is not a decisive factor for a ferroelectric.

The various investigations carried out in ferroelectrics have been of utmost importance in view of their very wide and varied applications in technology like memory and logic circuits, optoelectronics, radiation detectors etc. The bulk properties of single crystals and ceramic ferroelectrics have been investigated for their applications in high dielectrics, electromechanical, electrooptic and memory devices (4,5).
With the recent progress in integrated circuitry, ferroelectric thin films have found distinctly a unique place in various device applications on account of their high dielectric constant and hysteresis characteristics which can be incorporated with great deal of superiority in integrated circuits, semiconductor and memory devices. However below a critical thickness with the decreasing thickness of films, spontaneous polarization reduces and coercive field increases. This adversely affects their ferroelectric property from application point of view (6-10).

The important applications of ferroelectrics have been made possible on account of their high dielectric constant especially in the fabrication of thin film capacitors (11), the ferroelectric hysteresis behaviour for memory storage devices, and electrooptic switching characteristic in optical memories and displays (12, 13). They have been further useful as highly sensitive pyroelectric detectors, piezoelectric transducers, thermal imaging devices etc.

Ferroelectrics are generally classified into two groups: the I group comprises of the oxygen-octahedral compounds and others close to them in structure and has the ferroelectric active ion within the octahedra, the II group consists of compounds with octahedral or identical structures which give rise to ferroelectric behaviour as a result of
the displacement of proton in the hydrogen bond, on account of the rotation of groups or other such mechanisms.

The so-called breakdown in solid dielectrics may be either thermal or electrical, the former being caused by the superheating of the dielectric or by very high built up conductivity, whereas the latter occurs due to the application of an electric field. In all ferroelectrics belonging to either the I group or the II group, the dielectric breakdown is electrical. The thermal breakdown can occur in ferroelectrics if their conductivities are very much enhanced as a result of doping or other such process. Intensive 'aging' of the conductivity also, at times, leads to thermal breakdown.

In order to find its application as a detector or a thermistor, the electrical conductivity of a ferroelectric is an important investigation. The loss, being a conduction process in a ferroelectric, affects the squareness of the hysteresis loop and its switching property. However, for pyroelectric applications, materials with low conductivity are chosen. It has been shown that high temperature coefficient of resistance exhibited by BaTiO₃ at Curie point can be attributed to the formation of a thin high resistivity electron-exhaustion layer (14). It has also been postulated that the conductivity anomaly is sensitively dependent on the polarisation conditions of the layer.
The electrical conductivity has to be given due consideration and allowed for in all theoretical calculations on ferroelectrics. Thus, as far example, when energy of the domain wall is calculated, it is found as 0.12 erg/cm$^2$ if no allowance is given for the electrical conductivity and as 0.8 erg/cm$^2$ if it is duly taken into consideration (15).

The electrical conductivity must also be taken into account while measuring the dielectric constant (16, 17), elastic (18), nuclear magnetic (19) and other properties of ferroelectrics.

It may be pointed out that 'aging' of conductivity shown by a small time-dependent increase on applying a constant voltage to a ferroelectric results in deviations from Ohm's law in case of ferroelectrics of group I. However, in a ferroelectric which has been aged previously, Ohm's law remains valid up to the voltage to which the specimen was initially aged. It is, therefore, essential that the ferroelectrics of group I must be 'aged' if they do age so that true electrical conductivity is determined on the basis of the validity of Ohm's law.

The experimental determination of Curie point of known ferroelectrics by the measurement of dielectric constants and the exhibition of ferroelectric or antiferroelectric properties of compounds in which such properties are suspected are hindered on account of an increase in electrical
conductivity for various reasons. It has been pointed out that there is an apparent similarity between high conductivity dielectrics and ferroelectrics. Thus, for example, hysteresis loops are observed even in heated glasses with high electrical conductivity. Due to very strong increase in electrical conductivity with rise in temperature, it is not possible to polarise ferroelectric ceramics near the Curie point limiting thereby their application potentials. To solve this problem, the conductivity is appreciably decreased by addition of special additives.

A fairly substantial amount of information has now accumulated on the properties of ferroelectric and antiferroelectric substances which include over 290 crystalline compounds and more than 1500 materials which are either solid-solutions or contain various additives. Not much work has been reported on the electrical conductivities of these materials particularly in soft ferroelectrics and their related compounds. Nevertheless, conductivity data is of immense importance in a number of applications of ferroelectrics. Such data can also lead to the determination of the crystal structure along with an estimation of the lattice energy. It can also help in getting information regarding defects and impurities in crystals as the individual properties of crystals depend on their respective structures. The main features of electrical conduction can be summarised here for the sake of comparing them with those of ferroelectrics.
1.2 CONDUCTION IN DIELECTRICS (3)

Electrical conduction in materials, in general, can be classified as ionic or electronic. In the former process, transport of matter accompanies the process of conduction. If small amounts of monovalent ions be added to a crystal, its electrical conductivity increases. Various electrical investigations in materials may also reveal information as regards the nature of the charge carriers responsible for electrical conduction in them. In some crystals, when temperature is varied, the carriers of one sign associated with the conduction process may also be joined by carriers of opposite nature to account for overall conduction, e.g. above 600°C, chlorine ions join sodium ions in charge transport in NaCl crystal to some extent.

Certain crystals like α-Ag2S which exhibit predominantly electronic conduction also show mixed electronic-ionic type of conduction. Such crystals include Ag2S, Ag2Se, etc. which exhibit mixed conduction, although they are basically semiconductors and mechanism of conduction in them is predominantly electronic.

Sufficiently large applied electric fields in various crystalline dielectrics give rise to electronic conduction superimposing the ionic process, e.g. in mica, at low temperatures and in strong fields, the conduction
process is predominantly electronic but, at high temperatures and in weak fields, the process of conduction is mainly ionic.

1.3 MECHANISM OF IONIC CONDUCTION:

Irrespective of the exact nature of the process of electrical conduction, it can be shown that electrical conductivity \( \sigma \) can be represented by

\[
\sigma = n e \mu
\]

where \( n \) = no. of charge carriers, \( e \) = electronic charge and \( \mu \) = mobility of carriers.

In ionic crystals, the motion of ions of the host crystal lattice may result in electrical conduction. This is called intrinsic conductivity which has a substantial role at high temperatures. Electrical conduction may also be caused by the movement of the weakly bound ions including impurity ions or ions situated at defect sites in crystal lattice. Such conductivity occurs generally at lower temperatures and is termed extrinsic or impurity conductivity of a crystal. It may be pointed out that both intrinsic as well as extrinsic conductivities may be exhibited by certain crystals. It may further be emphasized that, in spite of the association of the lattice defects with the process of ionic conduction, all ions present in the crystal do not take part in the conduction mechanism.
The movement of ions within a crystal can take place either between the lattice sites or can jump to unoccupied or vacant sites called vacancies or holes. Qualitatively, let \( U_1 \) be the energy of an ion in its bound state at a lattice site, \( U_2 \) the energy at an interstice (metastable) and \( U_0 \) the energy corresponding to the height of the potential barrier between the two metastable states. Then, if the energy of formation of a vacancy in a crystal \( E_2 \) happens to be higher than the energy required for the transfer of an ion to a metastable state, \( E_1 = U_2 - U_1 \), then in a loosely packed lattice, the probability of formation of an interstitial ion will be higher. Consequently, the current in the crystal will be on account of the motion of ions from one metastable position to another overcoming the barrier energy \( U_0 \) during the course of its motion. The true value of interstitial conductivity and its temperature-dependence depend primarily on the number of available ions and the number of sites at which ions are bound. This aspect should, therefore, be taken into consideration as per the following two cases:

(i) when the concentration of free interstices and vacancies in the lattice are sufficiently large with respect to the total number of ions available.

(ii) when the total number of available ions equals the number of sites. This is the case of Frenkel defects in crystals.
In either case, the electrical conductivity can be represented by the general relation,

\[ \sigma = \sum \kappa_1 e^{-\beta_1/T} \]  

(1.2)

where \( \kappa_1 \) and \( \beta_1 \) are the characteristics of each mobile ion.

Presence of impurities in a crystal also affects the low temperature interstitial and vacancy conduction processes. Thus, if conduction mechanism in a crystal happens to be due to the motion of ions along interstices, addition of impurities must result in a tremendous enhancement in conductivity as such ions will go to occupy the interstices in view of the very little availability of vacant sites. This results in an increase in the number of charge carriers only with the distortion of the lattice. This is the second case of interstitial conduction. In case of vacancy conduction, however, addition of some impurity ions should not give rise to any such high increase in conductivity as impurities are free to occupy already existing vacancies. They will, therefore, not produce any distortion of the lattice and the number of vacancies may even cause reduction in conductivity. Further, impurities can also go into the defective regions of the crystal as per provisions in the first case of interstitial conduction process. Thus, in general, the role of impurity ions in the mechanism of electrical conduction is not so simple. It can, however, be said with certainty
that, in general, the electrical conductivity of a crystal is finally governed by the factors like concentration of defects, the mobility of vacancies, the concentration of ions at the interstices and the concentration of impurity ions.

It is also worth mentioning that the nature of intrinsic conduction may also be affected by variation in temperature. In case of alkali halides, for example, variation in electrical conductivity with temperature is governed by the fact that, at low temperatures, conduction mechanism is solely due to alkali ions but at high temperatures, conduction is associated with halide ions also. Some workers have the point of view that in pure ionic crystals like NaCl, high temperature conductivity is controlled solely by the number of interstitial ions (Frenkel defects) and the low temperature conductivity by the number of vacancies (Schottky defects). An associated change in the slope of the straight line log $\sigma$ Vs $\frac{1}{T}$ observed at times may be due to phase transition in crystals. This is, in particular, the characteristic of electrical conduction in ferroelectric crystals.

1.4 Electrical Conductivity in Strong Fields:

It has been found that, for pure single crystals, Ohm's law holds up to values of the fields as high as $\sim 10^4$ volt/cm when polarization emf is also duly considered.
It is known already that the electrical conductivity of natural crystals depends strongly on the impurities present. The electrical conduction process may also be, at times, accompanied by electrolytic purification, thereby changing the value of the electrical conductivity. In some cases, however, the true conductivity of a crystal is not found to depend on the field strength even up to high fields after simple heating is done.

Taking into consideration the presence of defects in ionic crystals, it may be assumed that they should obey Ohm's law up to fields as high as 50-100 KV/cm. Such field strengths are quite close to the breakdown fields in case of real crystals with defects. In 1921, Poole investigated that solid dielectrics exhibited departure from Ohm's law. He gave an empirical relation between electrical conductivity from residual current $\sigma_{\text{res}}$ and the field intensity $E$ as:

$$\sigma_{\text{res}} = ae^{bE} \quad (1.3)$$

where $a$ and $b$ are constants.

1.5 ELECTRICAL CONDUCTIVITY OF FERROELECTRICS:

The true electrical conductivity of a ferroelectric represents the characteristic bulk properties of the material which is unaffected by other intermediate processes. The total current which flows in such a dielectric material consists of the following parts:
(i) the current produced as a result of charging of the geometrical capacitance C of the specimen having a resistance R, the time of decrease of current being $T = RC$

(ii) the current produced as a result of charging of the geometrical capacitance C of a polarization, the current decreasing as per the expression $i = a e^{-t}$

(iii) the current caused by the built up conductance, decreasing with time

and (iv) the current caused by the built up conductance which is independent of time.

The relaxation time of the current caused by the charging of the geometrical capacitance of the specimen can be reduced to zero by possibly designing the system. The relaxation time of all types of polarizations is $\sim 10^{-2}$ secs.

Hence it is rather impossible to observe the built-up conductance current when much stronger current due to dielectric polarization is present, till the dielectric polarization is complete. The value of conductivity determined immediately after the polarization is complete is called the initial electrical conductivity $\sigma_i$. The current slowly reduced to attain a constant value giving rise to the conductivity value called the remanent conductivity $\sigma_0$. 
In the absence of the slow decreasing current, the initial conductivity coincides with remanent conductivity and is termed the true conductivity $\sigma_t$.

A slowly decreasing current can be observed in nearly all ferroelectric materials. However, there are some points of difference in the slow decreasing current obtained in ferroelectrics and in linear dielectrics. It is observed in the ferroelectric region in all ferroelectrics, whereas it is directed along the ferroelectric axis in case of single-axial ferroelectrics. The distribution of potential also remains linear in ferroelectrics unlike the distribution in linear dielectrics. Thus no accumulation of bulk charge takes place in ferroelectrics. It may be noted that the slowly decreasing current in ferroelectrics is not the conductivity current but a ferroelectric polarisation current (20) unlike linear dielectrics in which it constitutes the conductivity current.

The electrical conductivity in ferroelectrics affects their domain configuration. Kanzig (21) postulates the possibility of free charge carriers shielding the interactions which give rise to ferroelectric properties in crystals. He further attributes the difference in numerical values of the Curie constant $C$, investigated by various authors, to different electrical conductivities of the crystal or, in other words, to different concentrations of free charge carriers.
The width of the domain structure is expressed as

$$D = \frac{K_d \varepsilon_l}{(P_0 - P_1)^2} \quad (1.4)$$

where \( \varepsilon_l = \text{e.s. energy of the crystal} \)

\( P_0 = \text{spontaneous polarisation} \)

and \( P_1 = \text{polarisation induced by surface charges} \)

Thus, with increase in the concentration of free charge carriers, \( \varepsilon_l \) and \( P_1 \) are reduced on account of surface charge compensation. Hence the width of the domain also reduces. The domain width \( D \) is also related to the crystal size \( t \) and the energy of domain wall as

$$D \sim t^{\frac{1}{2}} \quad (1.5)$$

Thus as free charge carrier concentration increases, \( \varepsilon_l \) decreases resulting in a decrease in the domain width.

1.6 CONDUCTIVITY ANOMALY AT FERROELECTRIC TRANSITION:

Various studies on electrical conductivity of ferroelectric single crystals of group I reveal a jump in electrical conductivity at phase transition point while passing from ferroelectric to paraelectric phase. The activation energy of the carriers also increases during the change. At times, a temperature hysteresis may also be exhibited for conductivity.
Gurevich (1) thinks of electronic impurity character of group I ferroelectrics as an explanation for the observed conductivity anomaly. The jumpwise decrease in conductivity during transition from ferroelectric to paraelectric region is associated with a jumpwise change in the activation energy of the carriers, agreeing fairly well from qualitative point of view. The anomaly character in ceramics during phase transition has been explained on the basis of the coexistence of both paraelectric and ferroelectric phases over a temperature region above Curie point. Such a transition region instead of a transition point was confirmed by X-ray structure studies for polycrystalline SrTiO₃ (22).

It has been further pointed out that, in case of intrinsic conductivity \( \sigma_i (T) \) temperature dependence determined by the energy gap \( E_g \), it is expected that anomalies on account of the thermal expansion behaviour during phase transition of type first will be exhibited. A jump in the volume \( dV \) affects a change \( dV/dT \), leading to a jump \( dE_g \) of \( \sim 10^{-2} \) ev and a corresponding change \( dE_g/dT \) of \( \sim 10^{-5} \) ev/degree. In case of transitions of type II, there is a change in \( dV/dT \) only. This gives rise to a change \( dE_g/dT \). For \( E_g \sim 1 \) ev, an anomaly in \( \sigma_i (T) \) is exhibited by available methods only below the sensitivity threshold.
It may be assumed, on the basis of experimental data available, that in individual compounds and in solid-solutions internal stress may be one of the causes for phase transitions. The maximum and minimum values of such internal stress have been estimated as +300 to -2500 Kg/cm² from available experimental data and from the shift in the transition temperature under homogeneous stress (23,24). Such internal stresses for ceramics are not homogeneous.

One of the characteristic features of a ferroelectric phase transition is a slowly decreasing current (dependent on the field strength) observed at temperatures below the conductivity-anomaly temperature and no such decrease is observable above the anomaly temperature.

1.7 ELECTRICAL CONDUCTIVITY INVESTIGATIONS IN FERROELECTRIC AND RELATED CRYSTALS:

1.7.1 ELECTRICAL CONDUCTIVITY STUDIES IN HARD FERROELECTRICS:

Gurevich has compiled various electrical conductivity data on ferroelectrics from papers published up to 1965 and from his own work. A brief review of such work along with available data thereafter is being given below for ready reference and utilisation for interpretations as and when required:

\[ \text{BaTiO}_3 \text{ single crystals obey Ohm's law over a wide range of field strengths. Crystals grown by Kembka method} \]
show no 'aging' effect. Exposure to light produces appreciable increase in electrical conductivity (25). Ridpath and Wright (26) have shown the change in electrical conductivity during hydrogen reduction of the crystal. Zabara et al. (27) studied the positive temperature-dependent coefficient of resistance in single crystals and offered an explanation on the basis of a model of the surface layer. Porsien and Starov (28) determined an increase in conductivity to

\[ 0.01 = 1 \ \Omega^{-1} \text{cm}^{-1} \]

under a strong chemical reduction of \( \text{SrTiO}_3 \) single crystals in hydrogen. Zabara and Kudzin (29) detected the existence of an isotropic electrical conductivity in crystals grown in (001) direction from molten \( \text{Sr} \) and found that the conduction at the centre of the crystal is up to 40 times that at the surface. Various additives like Cu\(^{++}\) ions (30), 0.1 mole % of \( \text{Fe} \) (31) 99.99% of \( \text{Co} \) in 0.3 mole %, 0.3 mole % of 99.99% of vanadium (32) etc., when added to crystals, increase its conductivity to an appreciable or marked extent. When additives like \( \text{Fe} \) are added, the conductivity is reduced.

\( \text{SrTiO}_3 \) with additives like lanthanum 1 mole % (33) and 0.05 wt% of niobium has its resistivity reduced, \( \text{CeTiO}_3 \) has the activation energy as 1.8 eV. The conductivity of ceramics containing lanthanum fused in \( \text{H}_2 \)-\( \text{H}_2 \) atmosphere increases tremenously. \( \text{SrTiO}_3 \) has its conductivity increased and zirconium causes a reduction in it. Electron bombardment also increases conductivity producing secondary emission of
electrons. Tokopalo (34) studied the electrical conductivity of lead titanate ceramics and influence of doping. He has given data on the changes in the value and the type of conductivity with reduction. Explanations on the basis of the role of oxygen vacancies have been given.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic has a much lower electrical conductivity and its Seebeck coefficient of differential thermal emf at 973°C is positive (1). Addition of Li in $\text{NaNb}_2\text{O}_6$ shows an increase in conductivity, whereas fixing in oxygen and addition of lanthanum decreases conductivity associated with losses. Electrical conductivity of $\text{BaNb}_2\text{O}_6$ has also been measured but no such data is available for $\text{NaNbO}_3$ which has been shown to have an electric strength as 70 KV/cm (35) and an electric break-down melts the crystals. Thus the effect of dopants like Ti, V, Cr, Mn, etc. in $\text{LiNbO}_3$ crystals as regards electrical conductivity has also been studied along with the mechanism of dopant introduction and nature of electric conductivity at different temperatures. Sarkar et al. (36) have studied conductivity of Fe-doped $\text{LiNbO}_3$ crystals which have a writing sensitivity 500 times higher than that of undoped ones and have sharp changes in conductivity and activation energy. The authors could increase the conductivity by more than eight orders with considerable reduction in the activation energy. Deshmukh and Ingle (37), while measuring $\sigma$ and $\sigma$ of $\text{K}\text{NbO}_3$ single crystals, observed
a sharp rise in electrical conductivity and at the transition temperature viz. 225°C. They interpreted results in terms of anisotropy of conductivity along a- and c-directions in the tetragonal phase of a perovskite type ferroelectric crystal and dielectric approach to impurity conduction.

Fujino et al. (33), while studying the ferroelectric properties of LiTaO₃ single crystals, report that the Curie temperature depends on the composition, but the dependence is not linear. Further, specific resistivity increases as the Li concentration in the melt increases. Agrawal and Rao (39) report the conductivity study of single crystals of pure KTaO₃ and KTaO₃-NaTaO₃ mixed crystals in the temperature range 30-360°C and show that the intrinsic conductivity region is not reached even at 350°C. Deputy and Vest (40) undertook the electrical conductivity measurement for polycrystals and single crystals of KTaO₃ conducted as a function of frequency over the oxygen partial pressure range of the phase field as a function of temperatures up to 1350°C. The conductivity of KTaO₃ at 293°C is reported as 10⁻¹¹ to 10⁻¹² Ωm⁻¹m⁻¹.

The conductivity variation of Mg₃B₇O₁₂Cl with temperature has also been studied (1).

The KIII crystal is a good photo-conductor and has maximum photocconductivity at a wavelength of 6500 Å.
It was found that dark conductivity and photoconductivity depend largely on the electric field strength. Artobolevskya et al. (41) conclude that holes carry the current in semiconductor SbSI. SbSI crystal is also a photoconductor like SbSI. The conductivity variations have been given by Gurevich.

In TiO₂ crystals, the anisotropy is worth-noting. The conductivity increases to a marked extent if O₂ is not present in stoichiometric proportion. MnO₂ shows a phase transition at 413 K along with an anomaly in this region in the electrical conductivity. The conductivity of the non-conducting crystals of SnO₂ has also been reported.

The Hall electron mobility in WO₃ single crystals is reported as 36 Ohm²/V-sec (42). Hanafi and Khilla (43) find that ς is independent of temperature up to 0°C due to the frozen-in impurities. Maximum value of ς is recorded at 18°C due to the triclinic/monoclinic phase transformation. An intrinsic behaviour in the range 140°C to 300°C is followed by an exhaustion range where all impurity atoms are ionised. A decrease in ς is observed between 390°C to 480°C due to the transformation into the orthorhombic modification.

1.7.2 ELECTRICAL CONDUCTIVITY STUDIES IN SOFT FORMOLECTRICS:

Electrical conductivity studies on NaK₄H₄O₆·4H₂O (Rochelle salt) have been carried out by various workers.
Pepinsky et al. (44) have also reported the results. Discrepancies in various results might be due to superconductivity or partial dehydration of the salt. Ohm's law has been found valid up to $E = 60$ to $100$ $kV/cm$. On irradiating the crystals with $x$-rays, the conductivity increases.

Conductivity data on $(\text{CH}_2\text{NH}_2\text{COOH})_3\text{H}_2\text{PO}_4$ (TSP) and $(\text{CH}_2\text{NH}_2\text{COOH})_3\cdot\text{H}_2\text{O}$ (TSG) and $(\text{CH}_2\text{NH}_2\text{COOH})_3\cdot\text{H}_2\text{SeF}_4$ (TSP) have also been provided (1).

Helouet et al. (45) have revealed electrical conductivity inhomogeneities across (001) planes in $\text{KH}_2\text{PO}_4$ and $\text{KD}_2\text{PO}_4$ (KDP) crystals. A correlation is established between the location of inhomogeneities and the position of the crystal defects. Another important correlation is shown between the conductivity and the elastic strains. Sabharwal and Ghosh (46) have very recently presented that the electrical conductivity of KDP increases on gamma irradiation while that of KDPO$_4$ remains unaffected. Results show a single activation energy for conduction in KDP before and after irradiation in the temperature range $30^\circ\text{C}-125^\circ\text{C}$. However, unirradiated KDP shows two activation energies below and after $80^\circ\text{C}$.
The protonic electrical conductivity at 1592 Hz has been measured by Bradley et al. (47) for KIP2, K2H2PO4 and K2NO3 at pressures up to 60 kbar and temperatures up to 350°C, 280°C, and 220°C. It appears that the protonic conductors are differentiated from ionic conductors by the effect of pressure.

Results of electrical conductivity measurements of KHSO4 and K2SO4 from room temperature to the temperature of ferroelectric transition have been communicated by Fairall et al. (48) without observing any anomaly in conductivity.

The conductivities of HSO4-doped (NH2)2SO4 (**) and NH4H2PO4 (KDP) crystals have been investigated in the range 25-180°C by Hairetdinov et al. (49). The results are in good agreement with the known proton dynamic data in KDP type ferroelectric crystals. For (NH4)2SO4, the graph between log $\sigma$ and $10^3/T$ extends beyond the transition region through Curie point.

The electrical conductivity of KLi$_{0.5}$ has been shown as its variation with temperature by Gurevich in a-cut specimens. The phase transition is reported as 726°C.

The conductivities of NaN02 and KNO$_3$ have been measured in single crystals by Isao et al. (50) covering the transition ranges. The electrical resistivity shows a steep
jump at the transition point of about 2-6 times in NaNO₂ and one hundred times in KNO₃. The dc conductivity for KNO₂ and KNO₃ samples have been measured by Bansingh and Smith (51) over a wide range of temperatures. The dc conductivities show anomalies at -13°C and 130°C respectively. Molta et al. (52) have investigated the ac conductivity of films of KNO₃ as a function of temperature and found them to be comparable to that of single crystals. Sioffi (53) has shown experimentally the two transport regions in KNO₃. Selhotra et al. (54) have studied electrical conductivity of RbNO₃ from room temperature to 130°C covering all the phases. Results have been interpreted in terms of the structure of RbNO₃. Electrical conductivities of CsNO₃, KIO₃, H₂O(ice), C₆H₅OH₄ - 6H₂O(gas), LiH₃(SeO₃)₂ have also been reported.

The activation energy Δu for KNO₂₂ crystals along (010) direction has been obtained as 0.40 eV at 40°C by Gesi (55). Slight temperature dependence of Δu is attributed to thermal expansion. Qualitative data on electrical conductivity are also available in case of the materials NH₄H₂PO₄ (56), Li(N₂H₆)₃H₄ (LH₅) (57,58) and(NH₂CH₂COOH)₂ ÷NH₂Cl₂·2H₂O (DGMC) (59). NH₄H₂PO₄ crystals grown from a solution of ammonium sulphate in sulphuric acid and LH₅ crystals grown from lithium and hydrazine sulphate have very high conductivity due to impurities. They may even hinder the dielectric measurements. L/H indicates a sharp increase in conductivity.
above 413°C. In case of CeF₂, the conductivity increases above 328°C and the change is irreversible due to loss of water molecules.

Conductivity measurements in K₂SO₄ and (NH₄)₂SO₄ (60) show only the extrinsic unassociated region while in cobalt-doped crystals extrinsic as well as associated regions are observed. Three distinct regions with slopes 0.86, 1.2 and 0.5 eV are observed in cobalt-doped K₂SO₄. Electrical conductivity studies in CaF₂ by Hens and Egan (61) have concluded that steady state values of current at various applied voltages yield the electronic conductivity as a function of calcium activity. Simze and Patterson (62) during ac conductivity measurements report that ionic transference number for CaF₂ is essentially unity and hence CaF₂ may be employed as a solid electrolyte therein.

\[ \log \sigma = \frac{10^3}{T} \] curve in case of \( \text{K}_4\text{Fe(III)}_6\cdot3\text{H}_2\text{O} \), reveals two segments (63). The activation energies were found as 0.53 and 0.30 eV for ferroelectric and paraelectric phases respectively. In case of semiconducting \( \text{NH}_4\text{SCS} \) (thiourea), it has been concluded by Yogamarasimhan and Good (64) that it is a \( p \)-type semiconductor and the mobility of charge carriers appears somewhat low. Tearing of majority carriers has been suggested as responsible for observed abnormalities. Wurti and Frasch (65) report that excess electrical conductivity is induced by plastic deformation.
in NH₄Cl crystal. Study of the isothermal annealing of the excess conductivity at different temperatures in the range 80-150°C gives an activation energy as 0.08 eV for the carrier responsible for electric conduction which is suggested to be proton.

Gubanov and Chur (66) have shown theoretically that, if charge carriers are polaron, the electric conductivity of a semiconducting ferroelectric may increase strongly just above the Curie point. This may happen as the activation energy of polarons should vanish at the Curie point. Gorbalov and Reinig (67) report the influence of localised electron states on the static electrical conductivity of a ferroelectric semiconductor. The existence of such states leads to changes in the resistivity and the activation energy of carriers on transition from a single domain to a polydomain configuration— the domain wall having been regarded as a surface of discontinuity of the lattice periodicity.

1.7.3 ELECTRICAL CONDUCTIVITY STUDIES ON FERROELECTRIC SOLID-SOLUTION/CERAMICS

The study of electrical conductivity in the ferroelectric solid-solutions/ceramics has been undertaken in a large number of systems. This was also essential in view of tailoring requisite electrical properties for device applications, illustrating a drastic effect of additives in changing the electrical conduction behaviour of these materials.
Reports on the electrical conductivities of solid-solutions and ceramics namely (Ba,Sr)TiO₃ with no specially introduced additives (68), (Ba,Sr)TiO₃ with Ba additives (69,70)
Ba(Ti,Sn)O₃, BaTiO₃-Sr₂(SnO₃)₃, BaTiO₃-CaZrO₃, Ba(Ti,Zr)O₃,
BaTiO₃-(K₀.5Ba₀.5)TiO₃, Ba(Ti,Sn)O₃, (Ba,Ca)TiO₃, Ba(Ti,Hf)O₃,
BaTiO₃-MnO₃, BaTiO₃-Co₃O₄, system BaTiO₃-resite
(beckelite C), system (BaTiO₃)-glass 25-4, (Ba,Ca,Cr)TiO₃
with ceramic additives (Ba,Sr)(Ti,Sn)O₃, (Ba,Sr,Mn)(Ti,Sn)O₃,
(BaTiO₃)₀.₇₅-(BaSnO₃)₀.₂₅-x(BaZrO₃)ₓ (Ba₁-x₀.₈₆Sn₀.₈₆)_x TiO₃,
(Ba,Sr)TiO₃-Cd(Pb,Sn)O₃, Ba(Ti,Sn,Zr)O₃, BaTiO₃-
Cu(Ti,Sn)O₃, (Ba,TiO₃)₁₋ₓ₋₁₋ₓ (SrSnO₃)ₓ₋₁₋₁ (CuZrO₃)ₓ, (Ba,pb)TiO₃,
BaTiO₃-(V₁₀Ta₂O₆, CoTa₂O₆), "Ni₂Ta₂O₇", "CoTa₂O₇", "MnTa₂O₇", 
"CaTa₂O₇", "CaNb₂O₆", "Nb₂O₆", "Ti₂Ta₂O₇", "Ca₂Ta₂O₇",
"Mn₂Ta₂O₇", (Pb, Sr)TiO₃, (Pb,Er)TiO₃, Sr(Ti,Fe)O₃,
PbTiO₃-BaRO₃, PbTiO₃-SrRO₃, PbTiO₃-MnRO₃, PbTiO₃-SrSnO₃,
PbTiO₃-Be₂O₃, PbTiO₃-Fe₂O₃, (PbTiO₃)-25-4 glass,
Pb(Ti,Fe)O₃ (Pb,Ra)Fe₂O₆ (31), (Pb,Sr)Nb₂O₆, (Pb,Er,Sn)
Nb₂O₆, (Pb,Ra,Sr)Nb₂O₆, 25(Nb,Ta)₂O₇, (Pb,Sr)ZrO₃,
Pb₂CO₃-CdMnO₃, (Sr,La)Fe₂O₅, Li(Te,Nb)O₃, (TiO₂,TiSe) are
also available and have been studied mainly by Gurevich.

Recently, Trobel et al. (72), Dudek et al. (73)
and Uzma et al. (74) have also reported results of the
electrical conductivity measurements on Pb(xTi₁₋ₓ)O₃
solid-solutions and lead zirconate monocryystals.
In case of ferroelectrics of group I, various titanates and their ceramics, niobates, tantalates, sulfido-
dides, nitrites, \(\text{SnO}_2\), \(\text{SnO}_2\) and \(\text{WO}_3\)(42,75), Faraday law has been duly verified for most of the materials. The ionic conductivity is conclusively absent and conductivity is electronic in character. In case of \(\text{PbTa}_2\text{O}_6\), \(\text{PbHfO}_3\), \(\text{PbZrO}_3\), \(\text{BiFeO}_3\), however, impurity character of conductivity prevails. In all ferroelectrics of group II, verification of Faraday's law is rather not possible on account of their low conductivity which is ionic, in particular anionic (76). The conductivity has an impurity character.

1.8 IMPORTANT FEATURES OF ELECTRICAL CONDUCTIVITY IN FERROELECTRICS:

(1) In perovskite-structured ferroelectrics, the carrier-release mechanism is the decisive factor in the variation of electrical conductivity (77). The conductivity in \(\text{BaTiO}_3\) and other perovskite-type structure oxides is taken as electronic mainly (1). It is, however, not ruled out that ionic processes also play an important role in electrical conduction (78). It appears that the movement of oxygen vacancies is likely to play an effective role. The vacancies are created as Schottky defects. The perovskite-structure type oxides, when heated, pass from impurity to inherent conduction. In \(\text{BaTiO}_3\), the transition temperature is given as 100-270\(^0\)C (79) or even much higher.
The conductivity in Ba, Sr and Ca-titanates (1,2) is of p-type. Doping may substantially increase $\sigma$ for barium titanate or reduce it to some extent, and it can be assumed that elements with high valency cause some increase in $\sigma$ (34,30). Electrical 'aging' observed in Ba-, Sr-, Ca- and Tb-titanates is attributed to redistribution of oxygen vacancies. On doping $\alpha$TiO$_3$ ceramics to the semiconductor state, the positive temperature coefficient of resistance results, being the characteristic of this particular ceramic.

(i) Ferroelectrics with order-disple structure elements show ionic conduction which may be intrinsic or due to impurities or defects. Thus in case of TGS grown from solution having an excess of $\text{H}_2\text{SO}_4$, the electrical conductivity increases appreciably with the increase in excess $\text{SO}_4$ ions. This is further verified by the fact that electrical conductivity of recrystallised compounds is found to be much lower than the conductivity of freshly grown crystals due to the reduction in concentration of the impurities in the former.

(iii) Oxygen-octahedral ferroelectrics, with usual oxygen deficiency, exhibit electron or hole conduction. In such ferroelectrics, $\beta$TiO$_3$ for example, the activation energy is smaller than the width of the forbidden gap. This is generally due to the presence of impurities and an oxygen-
deficiency. An excess of oxygen may also create impurity levels in such ferroelectrics.

(iv) On account of 'aging' effects, the electrical conductivity of ferroelectrics may increase tremendously when electric field and temperature are increased. However, in low fields and at low temperatures, aging effect is unmeasurably small. Above a certain high temperature, no aging effect is observed whatever the value of the applied field. As aged ferroelectrics exhibit identical properties as an oxygen-deficient ferroelectric, the aging process can be linked with the deficiency of oxygen. Thus 'aging' can be suppressed in ferroelectric materials during their preparation by adding impurities to compensate for the oxygen deficiency or by other such process.

(v) Impurities like Ca, Ni, Co, Ga, Mn, Fe, Nb, Ta, \(\text{Yn, Ce, Cr, V}\) and niobium, when added in small percentage, increase the conductivity. However, rare-earth impurities cause a large increase in conductivity. The energy gap of the donor levels due to these impurities is \(\sim 2.5\) eV which is the same as the energy levels due to oxygen deficiency.

(vi) As most of the crystals possessing orderable structure elements are organic compounds, impurities are likely to give rise to Frenkel defects in them. These impurities are situated at the interstices of the host lattice. However, in some of the organic ferroelectric
compounds possessing hydrogen bonds, the possibility of intrinsic conduction must be taken into due consideration. In these crystals, the conduction mechanism is on account of the protons of the hydrogen bonds leading to vacancy conduction. As a typical example, the pyroelectric lithium sulphate with hydrogen bonds shows intrinsic conduction. Intrinsic conduction in Na2O2 and KIO3 might possibly be due to alkali ions.

(vii) \( \log \sigma \) vs \( 1/T \) graph usually exhibits a bend corresponding to a ferroelectric phase transition which is associated with changes in the spontaneous polarization and structure leading to a change in the activation energy of the carriers. Some of the ferroelectrics exhibit a discontinuity in conductivity at the phase transition point. As a typical example, in TiO2, the activation energies of the carriers are 0.4 eV and 0.6 eV in the ferroelectric and paraelectric regions respectively, the conduction mechanism having been assumed as ionic.

(viii) Slowly decreasing current in some of the ferroelectric crystals is on account of the slow process of reorientation of domains.

(ix) The activation energy at low and high temperatures is dependent on the lattice energy of the crystal, increasing with increase in the lattice constant for a specific series of compounds.
1.9 THERMAL EXPANSION AND ELECTRICAL CONDUCTIVITY:

It is now understood that defects, Schottky or Frankel type, to play an important role in electrical conduction in the extrinsic or lower temperature region, in general. Such defects may also probably affect intrinsic conduction. It has also been shown that defects also affect thermal expansion of materials. As a typical example, in the thermal expansion study of TCO, the x-ray irradiated samples (which may introduce radiation damage/defects) lead to the inference that thermal expansion is a tool which can be adopted for investigations of radiation damage and hence defects caused by radiation (31).

Also, the electrical conductivity of group I compounds namely (CT, LT) has also been shown to be significantly affected by defects. It will, therefore, be interesting to find out some correlation between these two important properties of a material, be it a ferroelectric or otherwise, as both are seen to be distinctly affected by defect density. Not much work has been reported in this direction but for some scanty remarks by Rama Sastry and coworkers (32) and others.

Bradley et al. (51) have pointed out that protonic conduction has analogies to both ionic as well as electronic conduction. Accepting the former analogy applicable to the range of temperatures used and without going into the nature
of the specific defects, for electrical conduction involving a Frenkel type disorder, it is expected that electrical conductivity $\sigma$ should be dependent on the lattice spacing $c$ and the characteristic lattice frequency $\omega$, being proportional to the square of the former and proportional directly to the latter (33).

Pressure dependent electrical conductivity investigations by Shiba et al. (34) lead to the conclusion that in compounds with an open structure such as $\text{Ag}_2\text{Hgl}_4$ and $\text{Cu}_2\text{Hgl}_4$, the electrical conductivity is closely related to the sign and magnitude of $\gamma$, the Seebeck constant, as well as the thermal expansion coefficient $\alpha$ when ionic conduction is dominant. With these references in hand it was tempting to explore the two properties i.e. thermal expansion and electrical conductivity of a material together.

1.10 **PYROELECTRIC CONTRIBUTION TO ELECTRICAL CONDUCTIVITY:**

While measurements of electrical conductivity are carried out with variation in temperature, it may give rise to pyroelectric current, especially in case of materials with high pyroelectric coefficients. This is bound to affect conductivity measurements unless special care is taken to either minimise them or due consideration is given to it while calculating the value of electrical conductivity. It may be noted that pyrocurrent has different signs during
heating and cooling cycles whereas conduction current has the same sign throughout. Study of electrical conductivity in the light of pyroelectricity may be quite useful. However, in materials studied during the present study, the pyrocurrents have been exclusively many orders in magnitude lower than the conduction currents.

1.11 AIM OF THE PRESENT STUDY:

The main intention in taking up the present study is firstly to make available the dc electrical conductivity data in case of certain ferroelectric and related crystals for which such data are not available in literature. It is through these conductivity data that the potentiality of a ferroelectric as a pyroelectric detector or a thermistor is decided. Secondly, so far a correlation of the electrical conductivity of a material and its linear thermal expansion has not been established, although both of them have been shown to be affected by defect density and both, to an extent, can be helpful in the study of the structure of the material. An effort has, therefore, been made to try to explore any correlation that might exist between these two properties of a crystal. Thirdly, conductivity ellipsoids have been drawn superposed over the crystal structure in different planes in order to get the value of electrical conductivity in any desired direction in addition to having a clear idea about its anisotropic behaviour in different directions. Thermal
expansion ellipsoids have also been drawn on the same crystal structure for a comparative study. Fourthly, pyroelectricity has been investigated in a couple of these crystals which were in the doubtful list and further to explore whether pyroelectric current can substantially alter electrical conductivity in ferroelectrics. In the present available literature on electrical conductivity in ferroelectrics this angle of approach has been scarce and hence it was thought worthwhile to undertake this study.

Lastly, a simple dilatometer, cheap and fairly precise and sensitive, has also been jointly devised and presented to determine the linear thermal expansion coefficients of crystals available in needle shapes or are capable of being given such shape. The stress has been laid to undertake both the investigations, namely electrical conductivity and thermal expansion, on materials under study and to search if any correlation exists between these two properties in view of the structure of the material.
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