During the course of investigations carried out to measure the properties of ferroelectric and related crystals, the following measurements were made:

1. DC electrical conductivity by using BPL Megohmmeter Model RM 160/3 and ECIL Electrometer Amplifier Model EA 815.


3. Thermal expansion measurements using newly devised Dilatometer Technique.

4. Temperature measurements using chromel-alumel thermocouple.

In addition, the crystal holder and the cell for dc electrical conductivity measurements and the crystal holder and cell for pyroelectric current measurements were also designed and fabricated in the department. The main features and principles of the physical properties of the materials involved, the measuring technique and the actual procedure of measurement followed have been described below.
2.1. **D.C. ELECTRICAL CONDUCTIVITY MEASUREMENTS** (1,2):

2.1.1. **INTRODUCTION**:

In dc electrical conductivity measurements, especially in case of ferroelectrics, a number of factors have to be considered otherwise several difficulties may arise. If pyroelectric effects are also present, an emf develops on the faces of the polarised specimen and, with variation of temperature, the pyroelectric current can contribute to the conduction current. However, this difficulty can be easily eliminated if the emf of the specimen can be compensated by means of the measuring device. It was believed till a few years ago that if the electric field applied is less than the coercive, it will not change the polarisation of the ferroelectric. But later experiments (3-9) showed that the constant electric field which leads to polarisation changes in the ferroelectric has no lower limit. If the applied field is reduced to 0.005 of the coercive field for ferroelectrics or to 0.8 of the critical field for the antiferroelectrics, the ferroelectric polarisation current is less than the conductivity current which can be recorded almost immediately after the field is applied provided the measuring instruments are sensitive enough. If the applied field \( \sigma > 0.005 \varepsilon_c \), the ferroelectric polarisation changes and true conductivity can be measured only after the ferroelectric polarisation is complete. It is, therefore, convenient to first polarise
the ferroelectric by a field higher than the coercive
provided the ferroelectric was not in such state before
measurement. This procedure should prevent the appearance
of a ferroelectric polarisation current in single crystals
with a stable single-domain configuration.

It has been observed further that 'aging' of the
conductivity indicated by the small time-dependent increase
when a constant voltage is applied to a ferroelectric,
leads to deviations from Ohm's law in ferroelectrics of
group I. On the other hand, if a ferroelectric is
previously aged, Ohm's law holds up to a voltage at which
the material was preliminarily aged. Since the principle
involved in the measurement of measuring the true conductivity
is the validity of Ohm's law, the ferroelectrics of group I
must be aged if they do 'age'; this will polarise the
ferroelectric also.

Another principle involved is that the electrodes
used must have an ohmic nature. This can be checked by
extrapolating the volt-ammere characteristic of the specimen
with the applied electrodes to the origin of the coordinate
system. A linear characteristic signifies that Ohm's law
is satisfied in the applied voltage range.

As in course of time the ferroelectric gets polarised
not only underneath the electrodes by the field effect (10,11)
the entire surface of the specimen must be covered by the electrodes if an electrode system without a guard ring is used otherwise the current produced by the slow polarisation might unduly complicate measurements.

The possibility of photoconductivity in ferroelectrics may lead to photocurrent measurements also under certain illuminated conditions. The electrical conductivity measurements are, therefore, likely to be affected due to this contribution. Fridkin (12) therefore suggests that, in all electrical conduction, particularly in semiconductor ferroelectrics, it is advisable to do the measurements in dark.

2.1.2. **METHODS OF MEASURING DC ELECTRICAL CONDUCTIVITY:**

Various methods are available for the measurement of the electrical conductivity of materials, in general, and of ferroelectrics, in particular. They are briefly discussed as follows:

(i) **Voltmeter-ammeter method:** In this method, as shown in fig. (2.1), the current flowing through the specimen $R_x$ is measured by a galvanometer joined in series. The method has, however, low sensitivity and accuracy of measurement. The use of the mirror zero galvanometer $G$ for null deflection is not quite convenient in view of unstandardised accuracy. A photo-compensation galvanometer with 3.5% accuracy can be conveniently used.
FIG. 2·1 VOLTMETER AMMETER CIRCUIT FOR MEASURING ELECTRICAL CONDUCTIVITY.

FIG. 2·2 DIRECT DEFLECTION METHOD.

FIG. 2·3 CIRCUIT WITH STANDARD CURRENT OSCILLATOR.

FIG. 2·4 TWO PROBE CIRCUIT.

**SYMBOLS.**

- **U** = APPLIED VOLTAGE.
- **V** = VOLTMETER.
- **G** = GALVANOMETER.
- **E** = ELECTROMETER.
- **A** = MILLI AMPERETTER.
- **Rsh** = SHIELDING RESISTANCE.
- **B** = TUMBLER SWITCH.
- **Ro** = STANDARD RESISTANCE.
- **C0** = STANDARD CAPACITOR.
- **R** = STANDARD ELECTRIC SPECIMEN.
- **Rx** = STANDARD WITH THREE ELECTRODE SYSTEM.
- **G** = SAW TOOTH VOLTAGE OSCILLATOR.
- **P** = LOW RESISTANCE POTENTIOMETER OF HIGH PRECISION.
(ii) **Direct-deflection method**: As shown in the fig. (2.2), the current through the specimen $R_x$ is determined by the voltage drop across a standard resistor $R_0$ joined in series. The method is suitable for high temperature range and also over a narrow range below 0°C.

(iii) **Method of charging standard capacitor**: A standard capacitor is joined in series with the specimen $R_x$ and the charge on the capacitor is either measured directly with a ballistic galvanometer or by calculating the voltage acquired by the capacitor as shown in fig. (2.3) in which $I_0$ is a standard current oscillator. Even with a variation in voltage on the ferroelectric from $10^{-2}$ to 1 V, the conductivity can be measured. The lower temperature limit depends upon the sensitivity of the circuit and $R_z < 0.01$ of the input resistance of the electrometer.

(iv) **Two probe method**: This method can be conveniently used to measure the conductivity at high temperatures when the ferroelectric-electrode interaction is large. Such methods are more suitable at elevated temperatures in the para- and ferroelectric regions since the resistance between the probes must be at least two orders of magnitude less than the input resistance of the electrometer amplifier ($\sim 10^{11}$ to $10^{13}$ ohms) (fig. 2.4).
(v) **The Megohmmeter method:** The methods described so far apply only within the limits of their sensitivity in the ferroelectric region and then in the para-electric region above the Curie point. Bridge methods are not suitable for measurements in the ferroelectric region for practical difficulties.

The method used during the present measurements of dc electrical conductivity allows for ferroelectric absorption and uses direct deflection technique (13). The set up consists of a Megohmmeter, NEL Model M-160/3, the details of which are described separately.

(vi) Henderek (14) suggests a method of determining electrical conductivity from thermoelectric current, particularly in case of ferroelectric materials with a high Curie temperature. Such materials, in general, exhibit high conductivity which changes quite rapidly with temperature. High voltage generally applied in various existing methods of measuring \( \sigma \) may cause changes in the ferroelectric polarization state and hence the conductivity itself. Also, a high conductivity current may produce additional heating of the sample producing a temperature gradient, resulting on account ofeltier effect. The suggested method is based on the measurements of the various quantities in the following relation:

\[
\sigma = \frac{d}{S} \left( \frac{J}{\phi} - 1 \right)
\]
where \( A \) is the surface area of electrodes, \( J \) the density of thermoelectric current measured at resistance \( R \), \( J_0 \) is the maximum value of current at \( R \to 0 \) and \( d \) is the volume of the sample.

(vii) Høen et al. (15) have proposed another method for measuring the temperature dependence of electrical conductivity of ferroelectrics which allow measurement of conduction current of samples in the low temperature range and near phase transition where pyrocurrents considerably exceed the conduction currents.

The sample is mounted in vacuum and can be cooled by liquid nitrogen. The current through the sample is measured by an electrometer and recorded by an automatic recording potentiometer. The temperature of the sample is measured by a thermocouple. A potentiometric compensator is connected in the thermocouple circuit, the difference emf is applied to the microvoltmeter and then to automatic recording potentiometer.

Liquid nitrogen reduces the temperature of the sample slowly. At a certain temperature the heaters of the oven are turned on so that the temperature of the sample begins to increase at nearly the same rate. Under these conditions, an external point appears on the curve. The oven is then switched off; the temperature begins to drop again. Thus a maximum develops on the dependence \( T(t) \), where \( t \) is time.
Slow fluctuations develop against the background of a continuous upward temperature drift. At the extremum points $I_n = 0$. Actually, $I_n = \frac{d\phi}{dt}$ where $\phi$ is spontaneous polarisation.

Taking $T = T(t)$ we get the relation,

$$I_p = \frac{d\phi}{dt} \cdot \frac{dT}{dt}$$

At the extremum points $\frac{dT}{dt} = 0$ and hence $I_p = 0$. During the process of variation of $\phi$, the current through the sample is continuously recorded by an electrometer and the potentiometer.

2.1.3. **The Megohmmeter**

The main feature of the Megohmmeter is the fully automatic delay circuit which computes the charging time delay time required for the test sample. It is only after the elapse of the computed delay time that the test sample is presented to the measuring circuit. The instrument has also been rendered drift free by the incorporation of a 'chooper' amplifier which dispenses with the conventional inherently unstable dc amplifier.

The very high upper limit of the resistance measurement viz. 400 million megohms along with negligible drift has been achieved in this instrument by the novel use of a synchronous converter working in conjunction with a condenser.
The basic input circuit of the megohmmeter is shown in fig. (2.5). Under stable condition, a continuous chain of pulses is developed across $R_g$, whose amplitude is inversely proportional to $R_x$, the resistance of the sample under test.

The resistance in megohms of the test sample is given by the expression,

$$R_x = \text{meter reading in megohms} \times \text{multiplier} \times \text{test voltage} \times \frac{1}{500}$$

with an accuracy of 5 to 6%.

The indicating meter together with the sensitive measuring circuitry has complete overload protection preventing damage that could be caused by breakdown of the test sample or by the selection of incorrect range. A signal lamp indicates when the overload protection is in operation. In the interest of safety, the course resistance has been kept high to minimise the risk of serious shock to the operator. The instrument is thus safe and simple to use and is suitable for electrical conduction measurement in ferroelectrics.

Continuously variable test voltage from 5 to 1000 V in four ranges is available. Of these, the first three ranges are suitable for testing the insulation resistance of capacitors as well as for pure resistance measurement. The 500 to 1000 V range is meant for pure resistance
FIG. 25 BASIC INPUT CIRCUIT OF MEGOHMMETER
measurement only. Seven ranges covering 9 megohms to 400 million megohms can be used to measure resistance of the test sample.

A selector switch works in three different positions. In the 'test voltage' position, the meter is automatically arranged to measure the test voltage applied to the test sample. In the 'normal' position the test sample is partially short circuited by a 10,000 ohms resistance, while in the 'measure R x' position, the test sample is presented to the measuring circuit after charging delay time has elapsed.

An indicator lamp automatically flashes for periods of approximately one second if any parallel capacitance component present in the test sample is not approximately fully charged. When the capacitance is charged, the test sample is presented to the measuring circuit and indicator lamp will remain off. Since the delay calculator initiates an overload protection, the lamp will also flash if the test sample should break down during test, or if the range selected is too sensitive.

Provision is also there of a balance control, the purpose of which is to cancel any spurious potentials that may occur in the synchronous converter or circuits prior to the converter itself. These can take the form of thermal emfs, contact potentials, noise or potentials resulting
from moisture paths. Whilst these are random in nature they are obviously a function of ambient temperature and relative humidity. The magnitude of these spurious potentials only reach detectable proportions on the highest sensitivity range. Thus the balance control provides ready means for adjustment of both the phase and amplitude of the injected cancelling voltage.

2.1.4. THE SAMPLE HOLDER FOR DC ELECTRICAL CONDUCTIVITY MEASUREMENTS:

The sample holder used for electrical conductivity measurements of different materials was designed and fabricated in the department. It is shown in fig. (2.6) and has the following parts:

- $R$ is an iron rod fixed at its upper end to the centre of a thick circular mica sheet $m_1$ by screws on either side of the sheet. This mica sheet has three holes near its periphery equidistant from each other. Three iron rods $R_1, R_2, R_{1r_2}$ and $R_{1r_2}$ fixed to this mica sheet project upwards supporting two other mica sheets $m_2$ and $m_3$ such that all the three mica sheets are parallel to each other. These two mica sheets can be kept in their respective positions by screws fixed to the iron rods. The second circular mica sheet $m_2$ carries through a central hole in it a silver electrode $S_2$ which rests in a groove of iron with a spring in between. This serves as the lower
FIG. 2-6 THE SAMPLE HOLDER FOR ELECTRICAL CONDUCTIVITY MEASUREMENTS.
electrode to which one junction of a thermocouple Th can be inserted through a groove in it for recording the temperature of the specimen. Electrical connection can also be made to this electrode to be finally connected to one of the input terminals of the megohmmeter. The upper surface of this electrode is plane and circular in shape so that the test specimen may rest on it with the entire lower surface of the latter in contact with the electrode. A screw head $H$, also made of iron, passes through a central hole in the micro sheet $m_2$ has its lower end connected to another silver electrode $E_1$ which forms the upper electrode moveable in such a way that it can be brought in contact with the upper surface of the specimen. A connecting wire joined to this electrode leads to the megohmmeter as the second input terminal. The entire set up is surrounded by an electric oven $F$ which can be raised to a desired high temperature using a Variac in series for manual control.

2.1.5. MEASUREMENT OF DC ELECTRICAL CONDUCTIVITY:

Electrical resistances of various specimens were measured using the megohmmeter Model RM 160/3, E.L. India and electrometer amplifier Model $E_A$ 316 the principles of which have already been referred to above. The crystals were suitably cut and grounded in plate forms with the cross section kept rectangular in order to measure the cross-sectional area accurately. Silver electrodes were
used to avoid rectifying contacts, the crystals having been coated with conducting silver paint. The experimental set up is shown in fig. (2.6).

D and E are the upper and lower electrodes between which the crystal rests in such a way that the pressure of the upper electrode on the crystal is constant and small at all temperatures. Use of a small spring below the lower electrode helps in achieving this requirement. The chromel-alumel thermocouple, previously calibrated, measures the temperature of the crystal with an accuracy of about $\frac{1}{4}^\circ C$. The two electrodes are connected to the megohmmeter which measures directly the resistance of the specimen. The entire set up viz. the electrodes and crystal is kept inside an electric furnace FF run by ac mains with a variac in series to control the rate of heating manually. The rate of heating was generally kept as $\frac{1}{2}^\circ C$ or $1^\circ C$ per minute.

The crystal was heated steadily and electrical resistance measured at different increasing temperatures after ensuring that the crystal had attained the temperature of the surroundings. Electrical conductivities at various temperatures were then calculated with the help of the formula already given. $\log \sigma$ vs $\frac{10^3}{T}$ graphs were plotted for three axial directions and polar diagrams in conductivity drawn superposed over the crystal structure for proper and valid interpretations.
Various macroscopic properties of a crystal can be explained in terms of tensors. One such property is the electrical conductivity. In case of an isotropic crystal, the electrical conductivity is fully represented by a vector. For anisotropic crystals, however, the electrical conductivity varies with the direction along which measurement is done. It is regarded as a tensor of rank two. The components of current are then related to the electric field components as

\[ J_i = - \sigma_{ik} \cdot \frac{\partial \phi}{\partial x_k} = \sigma_{ik} \cdot \varepsilon_k \quad (2.1) \]

where \( J_i \) is the current density, \( \sigma_{ik} \) the electrical conductivity tensor, \( \phi \) the potential and \( \varepsilon_k \) the electric field intensity. This expression is based on the generalised form of Ohm's law.

Isotropic crystals obey Ohm's law. Hence

\[ J = - \sigma \text{ grad } \phi \quad (2.2) \]

where \( \sigma \) is a positive coefficient, the electrical conductivity. In suffix notation, therefore,

\[ J_i = - \sigma \cdot \frac{\partial \phi}{\partial x_i} \quad (2.3) \]

In a crystal, in general, \( J \) is not parallel to grad \( \phi \) and equation (2.3) can be written as \( J_1 = - \sigma_{1k} \frac{\partial \phi}{\partial x_k} \), the same as equation (2.1).
As the crystal is anisotropic, each component of $j$ must depend on all the three components of potential gradient. Since the coefficients $\sigma_{ik}$ correlate two vectors, they form the second rank tensor, the electrical conductivity tensor.

It can be shown that $\sigma_{ik} = \sigma_{ki}$

Thus $[\sigma_{ijk}]$ is a symmetrical tensor represented as

$$
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{bmatrix}
$$

(2.4)

when referred to the principal axes of the crystal, it can be written as

$$
\begin{bmatrix}
\sigma_1 & 0 & 0 \\
0 & \sigma_2 & 0 \\
0 & 0 & \sigma_3
\end{bmatrix}
$$

(2.5)

Referred to the principal axes, equation (2.1) becomes

$$
\begin{align*}
J_1 &= -\sigma_1 \frac{\partial \phi}{\partial x_1}; \\
J_2 &= -\sigma_2 \frac{\partial \phi}{\partial x_2}; \\
J_3 &= -\sigma_3 \frac{\partial \phi}{\partial x_3}
\end{align*}
$$

(2.6)

The representation quadrif for electrical conductivity is

$$
\sigma_{ij} \cdot x_i \cdot x_j = 1 \text{ or referred to the principal axes,}
$$

$$
\sigma_1 \cdot x_1^2 + \sigma_2 \cdot x_2^2 + \sigma_3 \cdot x_3^2 = 1
$$

(2.7)
Experimentally, \( \sigma_1, \sigma_2, \sigma_3 \) are always found to be positive and so equation (2.7) is always an ellipsoid, termed the electrical conductivity ellipsoid. Its shape and orientation must be in conformity with the symmetry of the crystal.

Thus in order to determine the conductivity ellipsoid, what is required is the measurement of electrical conductivities of the single crystal along the three axial directions using the megohmmeter method already described. The values of electrical conductivities of the crystal in a particular plane along different directions are then estimated using the relation

\[
\sigma = \sigma_1 \cos^2 \theta + \sigma_2 \sin^2 \theta
\]  

(2.8)

where \( \sigma \) is the electrical conductivity of the crystal along a direction making an angle \( \theta \) with axis-1 in the plane \((1-2)\), \( \sigma_1 \) and \( \sigma_2 \) are the values of electrical conductivities along axes 1 and 2 respectively. The values of conductivities so calculated are then plotted on a polar graph paper to get the required conductivity ellipsoid in a given plane. The structure of the crystal projected on this plane is then suitably superposed to get an idea as to how conductivity variation occurs in the specific crystal plane with respect to the crystal structure.
In order to describe completely the electrical conductivity behaviour of a crystal, the values of principal electrical conductivities have to be specified, in general, along with the principal axes of the ellipsoid along with the orientation of these axes with respect to the crystallographic axes. The symmetry of the crystal, however, reduces the number of parameters. As shown in Table (2.1), only one value of conductivity is sufficient for a cubic system, whereas two values of conductivity are required in case of the tetragonal, hexagonal and trigonal systems to describe completely the conductivity behaviour of the crystal. In case of crystals with lower symmetry, the number of parameters is increased from three for orthorhombic and four for monoclinic systems to six for the least symmetric triclinic system. These numbers, therefore, represent the minimum number of measurements required for a crystal system to study its anisotropic electrical conductivity.

2.2. PYROELECTRIC CURRENT MEASUREMENTS

2.2.1. PYROELECTRICITY: (15)

Hdan et al. (15) have pointed out that, in high resistance ferroelectrics, investigations on the temperature dependence of electrical conductivity are usually not quite easy, particularly at low temperatures. The difficulty is enhanced when measurements are carried out
<table>
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<tr>
<th>Crystal system</th>
<th>Axial relations</th>
<th>Characteristic symmetry</th>
<th>Electrical conductivity tensor components</th>
<th>Representation quadric</th>
<th>No. of independent values required</th>
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in the ferroelectric phase and near the phase transition point due to the presence of pyrocurrents which result on account of insufficiently high stability of temperature. As an example, in LiO, which is a typical ferroelectric semiconductor, pyrocurrents \( I_p \approx 10^{-10} \) A flow in the specimen when \( T < T_f \), corresponding to a variation rate \( \approx 0.1^\circ K/sec \). When \( T = T_f \), the pyrocurrents increase attaining a maximum value at \( T_f \). The conduction current \( I_0 \) in an electric field \( \approx 50 \) V/cm comes to \( 10^{-11} \) to \( 10^{-13} \) A at these temperatures. It is, therefore, concluded that \( I \) should remain independent of \( T \) at low temperatures.

Pyroelectricity is produced on account of the temperature dependence of spontaneous polarisation \( P_s \) of a group of solids in single crystal or polycrystalline forms. If a piece of such material be held at a fixed temperature for some time, it attains electrical neutrality by acquiring free electric charges from the surrounding media through its surface and due to internal conduction of free charges. If the temperature of the specimen be raised a bit, its electrical polarisation changes whereby a voltage is developed between the faces of the crystal. Conversely, if the temperature of the specimen be lowered an equal amount, the same magnitudes of polarisation and voltage would be developed. Their signs would, however, be opposite.
A simple model of a pyroelectric crystal based on its structure has been suggested thus: For a substance to behave as pyroelectric, each unit cell in the structure must have a dipole which is produced as a result of the non-coincidence of the centres of positive and negative charges. If the alignment of dipoles within the specimen is such that they do not cancel each other, the substance will show a resultant electrical polarisation termed as spontaneous polarisation which must be clearly distinguished from what is called induced polarisation occurring in dielectrics kept in an electric field. If the temperature of the pyroelectric specimen be maintained constant for a sufficiently long time, surface charges get accumulated on the sample, which will mask the internal spontaneous polarisation. A change in temperature will change the strength of the dipoles by shifting the positions of the atom or by modifying the interatomic bonding. The surface charges will then undergo a redistribution to compensate for the new internal spontaneous polarisation. This redistribution will then be observed in an ammeter connected between the conducting electrodes in contact with the surfaces of the material under investigation. The flow of electric charge so observed now is due to pyroelectricity.

Analytically, spontaneous polarisation can be expressed as dipole moment per unit volume $\mu$ considered over the entire volume of the specimen.
\[ \mathbf{s} = \frac{1}{V} \iiint \mathbf{\mu} \, dv \] (2.9)

Both \( s \) and \( \mu \) are polar vectors. In order that \( \mathbf{s} \) may have a nonzero value, it is essential that firstly, \( \mu \) be different from zero at least some part within the material. Secondly, the integration should not cancel out all the terms. The above equation allows for the consideration of the pyroelectric behaviour of polycrystals as well as single crystals. The temperature derivative of spontaneous polarization \( \mathbf{s} \) under a fixed stress and electric field is termed the pyroelectric coefficient given by

\[ s^T = \left[ \frac{\partial s^T}{\partial T} \right]_{s, \mathbf{E}} \] (2.10)

Thus pyroelectricity may be represented by a polar vector. For it to be invariant, the only symmetry considerations are rotation through an angle about the vector and reflection in a plane passing through the vector. Pyroelectric effect can, therefore, be exhibited by those crystals only for which there is at least one direction which remains invariant under all symmetry operations. This condition can be fulfilled by crystals under the following symmetry requirements:

(i) Pyroelectric crystals cannot have a centre of symmetry and

(ii) Pyroelectric crystals have either no axis of rotational symmetry or have a single axis of rotational
symmetry which is not included in the inversion axis.

It is evident from the first symmetry requirement given above that all pyroelectrics may also be piezoelectrics. However, the converse of this is not true.

2.2.2. Types of Pyroelectric Effects:

Any change in the temperature of a crystal can give rise to a number of electrical effects classified under 'pyroelectricity'. The origin of such effects is due to the thermal, mechanical and electrical constraints on the crystal. If, during measurement of pyroelectric coefficient, a crystal be kept free to expand or contract thermally, then in the first stage no change in its dimensions is possible i.e. the crystal is held under a constant strain. Any change in temperature affected will give rise to a change in electric displacement. In the second stage, the crystal is free to deform. Thermal expansion produces a strain which then causes a change in electric displacement through piezoelectric process. Combining the two stages, the total pyroelectric effect can be shown to yield,

\[ \tilde{d}_i = d_i + \tilde{d}_{ijk} \cdot \tilde{C}_{jklm} \cdot \kappa_{lm} \quad (2.11) \]

where \( d_i \) represents the primary pyroelectric effect (at constant stress) and \( \tilde{d}_{ijk} \cdot \tilde{C}_{jklm} \cdot \kappa_{lm} \) the secondary pyroelectric effect (the piezoelectric-thermal strain).
The symmetry role in respect of secondary pyroelectricity is important. It is known that pyroelectricity as well as piezoelectricity can exist only in crystals which belong to certain specific classes. The symmetry of only 20 of the point groups permits piezoelectricity, whereas only ten of them exhibit pyroelectricity. The nonoccurrence of secondary pyroelectricity, caused by the actions of thermal expansion and piezoelectricity in a nonpyroelectric crystal, can be explained from the symmetry point of view. Secondary pyroelectricity cannot exist as the product of piezoelectric coefficient, the elastic stiffness and thermal expansion coefficient happens to be a vector. Vector properties are allowed only in ten polar point groups. Thus, as an example, piezoelectric but at the same time non-pyroelectric crystal is α-quartz.

Various other processes can produce surface charges resembling pyroelectricity. Non-uniform change of temperature in a piezoelectric crystal can cause creation of electric charges giving rise to what is termed as tertiary pyroelectric effect. The process is quite clear. Non-uniform heating can create different thermal strains along the three two-fold axes. The resulting piezoelectric charge then remain uncompensated producing tertiary pyroelectric effect. As an alternative, it can also be
argued that non-uniform strain arising from non-uniform heating may reduce the crystal symmetry from that of a piezoelectric but non-pyroelectric point group to that of a pyroelectric one. However, it may be noted that non-uniform heating may at times lead to incorrect results about the pyroelectric nature of a substance.

2.2.3. PIEZOELECTRICITY AND PYROELECTRICITY:

A polar material whose electric dipoles can be reversed in direction by an electric field is termed a ferroelectric. Ferroelectrics form a subgroup of pyroelectrics. Jaffe et al. (19) have very clearly drawn a distinction between the relationship of ferroelectricity to pyroelectricity and that of pyroelectricity to piezoelectricity. Although all pyroelectrics have a dipole, it is not always possible to reverse it on applying an electric field. Thus, for example, a field greater than the electrical breakdown field of a substance might be necessary or the dipole might be due to an asymmetric and non-reversible arrangement of atoms as in tourmaline and hexagonal CdCit. Thus ferroelectricity is an empirical distinction between one type of pyroelectric crystal and another on the basis of experimental observation. Even though all pyroelectrics are necessarily piezoelectrics, pyroelectricity is basically distinct from piezoelectricity as the two depend on different symmetry considerations.
Ferroelectrics usually, but not always, exist in a non-polar (paraelectric) phase above the Curie point, although a few ferroelectric crystals like Rochelle salt also exhibit a lower Curie point below which they exist in paraelectric phase. Thus, as such, all ferroelectric phenomena should be included in the study of pyroelectrics.

2.2.4. **PYROELECTRIC MEASUREMENT TECHNIQUES**

Three techniques are usually available for the measurement of pyroelectric coefficient directed mainly towards the elucidation of ferroelectric phenomena and a search for promising materials for application: static, dynamic and indirect methods.

(1) **Static methods**: In this technique the sample is heated slightly in order to raise its temperature above that of various constant temperature baths. The charge thus developed on the pyroelectric crystal is compensated by a static charge induced on a capacitor to which the crystal is connected. Pyroelectric coefficient can be calculated using the relation

\[ dD = d\theta \]

The set up can be made sensitive by using electrometer circuit for charge compensation and null detection. Static methods yield accurate coefficients at discrete
temperature values. However, measurements are time-consuming, and, at very high or very low temperatures, often difficult.

(ii) Dynamic method: In the dynamic method actually followed for investigations on pyroelectric effect, the sample is heated and cooled at a uniform rate. The sample is mounted in a cell with least possible contact pressure between the electrodes. The cell is heated through an a.c heater coil, a temperature controller and a variac. The current is measured by an electrometer amplifier model 5A/515.

The test sample was heated to a constant high temperature at a uniform rate and kept constant at that temperature for a reasonably good time. It was then cooled at a uniform rate. The change in sign of the pyrocurrent during cooling cycle establishes the primary pyro-effect. The measurement of pyro-electric coefficient was done during cooling cycle in order to avoid any contribution from thermocurrent (depolarisation current). The time and temperature records are carefully and regularly maintained throughout the measurement of pyrocurrent. The pyro-electric coefficient $p$ is calculated as follows:

$$ p = \frac{1}{k} \left( \frac{1}{\alpha^2} \right) \text{Coul./cm}^2/\text{C} $$ (2.13)
where \( A \) is the area of the sample in \( \text{cm}^2 \)

\[ I \] is the pyroelectric current in amperes

and \( \frac{d\theta}{dt} \) is the rate of heating/cooling

Dynamic methods are most useful in measuring data over broad temperature ranges, but most of them require careful determination of the rate of temperature change. Errors due to tertiary pyroelectricity (non-uniform heating) may also be significant.

(iii) **Indirect methods:** The spontaneous polarisation of a ferroelectric material can be determined from hysteresis loop measurements using the method of Sawyer and Tower. Differentiation of the spontaneous polarisation with respect to temperature yields the pyroelectric coefficient. The method requires extremely accurate measurements of the spontaneous polarisation and is, thus, rarely used.

The pyroelectric coefficient can also be calculated from the electrocaloric coefficient and the specific heat using the equation \( q_i = -\frac{\partial T}{\partial T'} \). As the method requires the use of large electric fields and precise temperature measurement, it is not frequently used.

Among the most serious errors encountered in quantitative measurements on pyroelectrics are those due to non-uniform temperature change and to electrical leakage. Any electrical measurement made during the time when the crystal
temperature is changing may be erroneous because of a
tertiary pyroelectric effect resulting from non-uniformity
in temperature. Static methods are not subject to this type
of error if the charge or voltage measurements are made at
thermal equilibrium states. Because pyroelectricity can only
be observed in insulators, precautions must be taken or
corrections made for the electrical conductivity of the
crystals, the finite input impedance of the electrical
measuring instruments and the imperfect insulating
materials in the instrument. Special care should be taken
for the possibility of errors due to electret-type charges
and solid state electrolytic phenomena. If possible,
pyroelectric measurements should be made while cooling the
material as well as during heating.

2.2.5. **THE ELECTROMETER AMPLIFIER:**

The E&IL Vibrating Condenser Electrometer type
E& 815 is a high performance electrometer amplifier specially
designed to measure very small direct current, low dc
potential from high impedance source, small charges and high
resistances. The extremely rapid response combined with its
good stability and low drift characteristics makes it a very
useful instrument in various measurements.

The E& 815 consists of two units, a measuring head
and the indicator unit. The measuring head is a rugged
moisture proof assembly and can be located at the site of
measurement and remotely monitored by the indicator unit from
a safer distance. Shielded high impedance antineedlemic tone
cable is provided to couple the two units.

Voltage ranges of 10 mV, 30 mV, 100 mV, 300 mV, 1 V,
3 V and 10 V and current ranges of 10^{-9} to 10^{-14} of both
calorities are provided, whereas the input resistance of
10^9 to 10^{12} ohms selectable ranges are provided by a front
panel selector on the measuring head. The input sensitivities
are 10^{-16} per division for current measurements and 0.1 mV
per division for voltage measurements. The accuracy of
measurement is 3\% in 10^{6} and 10^{10} ohms ranges and 5\% in
10^{11} and 10^{12} ohms ranges. The accuracy of voltage measure-
ments on all ranges is 1\% \pm 0.1 mV.

Conservative circuit design and careful lay out have
mainly rendered artificial cooling unnecessary even when the
Electrometer Amplifier is used continuously over long periods.

The Electrometer Amplifier consists mainly of an
operational amplifier A, input resistance R_i and a meter to
read in volts or millivolts as shown in fig. (2.7). In
order to measure resistance, the given sample is connected
to a standard voltage source V_s and current through it is
measured. The reading in the meter is recorded in volts and
resistance R_x of the test sample calculated as follows:
FIG. 27. MEASURING PRINCIPLE OF ELECTROMETER AMPLIFIER

Vs = Constant voltage source
Rx = Resistance of the sample
Ri = Input resistance
F = Function switch
\[ I = \frac{V_s}{R_{\text{in}}}, \text{ where } I \text{ is the current flowing through the sample} \]

or

\[ I = \frac{V_s \times \text{input resistance}}{\text{measured potential}} \text{ in ohms} \quad (2.14) \]

Pyrocurrencts of the order of \(10^{-15}\) to \(10^{-16}\) can be measured by measuring the potential across the test sample without any standard voltage source and is given by

\[ I = \frac{\text{measured potential}}{\text{input resistance}} \text{ in amperes.} \]

Fig. (2.7) represents the arrangement for pyrocurrent measurement with standard voltage source \(V_s\) removed and the sample itself acting as the source of current when connected to the electrometer amplifier.

2.2.6. The Sample Holder for Pyrocurrent Experiments

The crystal specimen \(\sigma\) is held by relay strip contacts \(R_1\) and \(R_2\) at the centre of a furnace \(F\) enabling the measurements to be done under dynamic conditions such that the temperature of the specimen is maintained more or less uniform. The sample holder is mounted inside a massive thick walled cylinder \(S_1S_2\) of copper with insulated heater windings \((W_1, W_2)\). Further, it is shielded with an aluminium shield. This system ensures fairly good thermal insulation and electric shielding for the specimen as shown in fig. (2.8).
FIG. 2-8 THE SAMPLE HOLDER FOR PYROCURRENT MEASUREMENTS.
The temperature of the specimen is measured using a chromel-alumel thermocouple Th passing through a central hole in the massive copper lid L to which terminals T₁ and T₂, with due insulation from the lid, are provided. These terminals are joined to the relay strips R₁R₂ at their lower ends, whereas the upper ends are connected to ECIL electrometer amplifier for pyrocurrent measurements. Inside the hot chamber the heating/cooling rate is maintained uniform by using a Tempo temperature controller and an indicator unit.

2.3. MEASUREMENT OF THERMAL EXPANSION COEFFICIENT:

The linear thermal expansion coefficient at varying temperatures was measured with the help of a newly devised dilatometer technique described in Chapter III. It is essential for this technique that the crystal be in needle-form. Crystals which grow directly in needle shapes can be grown like that and suitable specimens chosen. However, crystals which do not grow in needle shapes can be suitably shaped in the desired form if large crystals of the substance are available.

The crystal of suitable length, depending upon the size of the miniature furnace available, is selected, its ends made plane and then it is inserted in the miniature furnace. Its temperature can be varied at a rate ~ 1°C or 1°C per minute using a variac in series with the heater coil
of the furnace. After usual adjustments of the spectrometer
and that of the crystal assembly, a reflected image of the
slit is seen on the cross-wire of the telescope. As
temperature of the crystal increases, it expands along its
length thereby rotating the optically plane glass cover
slide. By rotating the telescope, the reflected image is
again obtained on the cross-wire. Half this angle of rotation
gives $\Delta \theta$ corresponding to a rise in temperature by $\Delta T$.
The temperatures of the crystal are measured with an accuracy
of $\pm 0.5^\circ C$ using a chromel-alumel thermocouple which was previously
calibrated. The value of coefficient of linear expansion
along the desired direction is calculated using the formula,

$$\Lambda = \frac{0.2}{T} \cdot \frac{\Delta \theta}{\Delta T} \quad (2.15)$$

$\Lambda$ vs $T$ plot is then obtained. It will exhibit the variation
of coefficient of linear thermal expansion with
temperature and can be used to correlate with the crystal
structure or any other microscopic or macroscopic parameter
of the specimen.

2.4 MEASUREMENT OF TEMPERATURE:

Almost all measurements were carried out above room
temperature. The temperatures were measured using a chromel-
alumel thermocouple in conjunction with a portable potentiome-
ter of Toshniwal make. The latter measured the thermo-emfs
in steps of 0.01 mV in the range of 0 to 18 mV. An external
polyflex galvanometer of high sensitivity was used to increase the sensitivity of measurement. Both the potentiometer and the galvanometer were kept on a separate insulated portable table. It was ascertained that there was very good insulation between the heater and thermocouple circuits. For good and sustained stability during measurements, a 6 V storage battery was used in the potentiometer circuit. The following table gives the calibration of the chromel-alumel thermocouple.

Table 2.2

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point/Boiling point $^\circ$C</th>
<th>$E_{\text{std}}$ (mV)</th>
<th>$E_{\text{obs}}$ (mV)</th>
<th>$E_{\text{std}} - E_{\text{obs}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>4.095</td>
<td>4.11</td>
<td>0.015</td>
</tr>
<tr>
<td>Zinc</td>
<td>419.5</td>
<td>17.220</td>
<td>17.23</td>
<td>0.010</td>
</tr>
</tbody>
</table>
REFERENCES:


