CHAPTER II

EXPERIMENTAL TECHNIQUES

During our course of investigations, carried out for the study of the mechanism of ferroelectricity in organic materials, the following measurements were made. The main features of the various techniques and the actual procedure of measurements followed have been described below:

1. Ferroelectric coefficient measurements above room temperature by dynamic current method using electrometer amplifier (EA 814).

2. Dielectric constant and dielectric loss measurements using Wayne Kerr Autobalance Universal Bridge (II 642) in the AF range.


4. Sample preparation and other techniques used.

a. Electrode and sample film prepared

   i) Vacuum evaporated metallic thin film electrodes using vacuum coating unit.

   ii) Transparent conducting film electrodes (SnO) by chemical vaporisation and oxidation method.
b. Temperature variation study and measurement cell.

c. Poling and its effect on foregoing measurements.

2.1 Pyroelectric measurements:

Recently a lot of experimental interest has been shown in the measurement of pyroelectric coefficient in materials with high figure of merit, which may be employed as infrared detectors, while the study itself further elucidates the understanding of spontaneous polarization and the ferroelectric mechanism in ferroelectric and related materials.

A variety of techniques have been described in the literature for the measurement of the pyroelectric coefficient by measuring either voltage, charge or current developed during the temperature change of the crystals. The temperature variation leads to a slowly varying interference voltage whose magnitude is practically linearly related to the temperature of the pyroelectric material.

Measurement techniques:

Three types of techniques are usually available for the measurement of pyroelectric coefficient of the pyroelectric materials. They are static, dynamic and indirect methods.
2.1.1 Static Method:

Early measurements in high resistivity pyroelectrics were made by this method (1) by Ackermann.

In this technique the charge developed on the pyroelectric crystal, due to slight raising of the temperature of the sample above that of various constant temperature baths, is compensated by a static charge induced on a capacitor to which the crystal is connected.

Two varieties of the static compensation method are used most frequently:

1) The quasistatic method (2) with a linear variation of the temperature of the sample and
2) the static method or in which the temperature of the sample is varied in steps (3).

Both methods require the use of fairly complex devices for stabilizing and varying the temperature. Moreover, these methods require large time. The accuracy in the determination of the absolute value of pyroelectric coefficient can be increased by the automatic compensation of the pyroelectric charge and by regulating the temperature (4,5). Pyroelectric coefficient can be calculated from the compensating voltage Vc parameters.

\[ p = \frac{V_c}{C_c} \frac{\Delta \theta}{A_{el}} \]

Coupling capacitor \( C_c \) must have minimal leakage resistance and minimal polarization current. \( A_{el} \) is the electrode area, \( \Delta \theta \) is the temperature change.
2.1.2 Dynamic Methods:

The methods used to study the pyroelectric effect by dynamic method can be classified in three ways.

1) Dynamic techniques involving small transient temperature changes around some pre-selected temperature which is usually accomplished by the pulses of radiation (Chynoweth et al. 7).

2) Collection and measurement of the charge released by the sample as a function of temperature (class, 3).

3) Measurement of the current as a function of temperature for a constant heating rate (Chynoweth 9).

Of these, the second method gives the polarization versus temperature curve and the other two yield the slope of the polarization-temperature characteristics of the pyroelectric materials.

In dynamic method the temperature of the crystal is changed continuously by various techniques which are summarized in Table 2.1.

2.1.3 Indirect Method:

(a) Ferroelectric hysteresis loop Method:

For the ferroelectric materials the measurement of the pyroelectric coefficient can be determined easily from the spontaneous polarization/electric field hysteresis loop. This method gives essentially the saturation value of spontaneous polarization and, unless special precautions
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Technique</th>
<th>Principle</th>
<th>Formula used</th>
<th>Accuracy</th>
<th>Applicant</th>
<th>Temperature resolution</th>
<th>Adv./Disadvantages</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Static Compensation Method</td>
<td>Static charge induced on a capacitor is measured</td>
<td>$p = \frac{C \Delta V}{\Delta \theta}$</td>
<td>1. Depends on frequency $1_{X1}$ and $\Delta V_{AC}$</td>
<td>1. Poor</td>
<td>2. Error not exceeding 2.5%</td>
<td>(A) Direct method (1-6)</td>
<td>(1)</td>
</tr>
<tr>
<td></td>
<td>a) Quasi-static method</td>
<td></td>
<td></td>
<td>2. $V_{AC}$</td>
<td>2. Error not exceeding 2.5%</td>
<td>(F) Use of complex devices for stabilizing and varying the temp.</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>b) Static method (Ackermann)</td>
<td></td>
<td></td>
<td>3. $V_{AC}$</td>
<td>2. Error not exceeding 2.5%</td>
<td>(D) Measurements could only be time with unipolar crystals.</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1915)</td>
<td></td>
<td></td>
<td>4. $V_{AC}$</td>
<td>2. Error not exceeding 2.5%</td>
<td>The $C_{T}$ must have maximal leakage and minimal polarization current</td>
<td>(4)</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Pyroelectric Current Method</td>
<td>Pyrocurrent is measured with electro meter</td>
<td>$P = 1/\sqrt{1 + \frac{\Delta V}{\Delta \theta}}$</td>
<td>1. Measured current accuracy is within 1%</td>
<td>(D) is to be held constant.</td>
<td>(A) Straightforward direct method (5)</td>
<td>(D)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2. Dependent on response time detector</td>
<td></td>
<td>(D) Mean temp must be changed steadily throughout</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Shunt Resistor Method</td>
<td>Additional shunt resistance is used for capacitive charging</td>
<td>$P_A(\Delta \theta) = C_p(\Delta V)^{1/2} - kT \Delta \theta$</td>
<td>1. Depends on frequency $1_{X1}$ and $\Delta V_{AC}$</td>
<td>1. Poor</td>
<td>2. $(dV/dt)$ is not measured directly.</td>
<td>(D) Indirect method.</td>
<td>(5)</td>
</tr>
<tr>
<td></td>
<td>(S.B. Lang, 1965)</td>
<td></td>
<td></td>
<td>2. $(dV/dt)$ is not measured directly.</td>
<td></td>
<td>(D) Indirect method.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>and F. Steckel</td>
<td></td>
<td></td>
<td>3. $(dV/dt)$ is not measured directly.</td>
<td></td>
<td>(D) Indirect method.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Radiant Heating Method</td>
<td>Modulated light beam is used to excite pyrocurrent</td>
<td>$P = A (\Delta V)(d\theta/dt)$</td>
<td>1. Depends on frequency $1_{X1}$ and $\Delta V_{AC}$</td>
<td>1. Poor</td>
<td>2. $(dV/dt)$ is not measured directly.</td>
<td>(A) Neither heat flux measurement nor the strain of isothermal conditions required</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2. $(dV/dt)$ is not measured directly.</td>
<td></td>
<td>(D) Indirect method.</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3. $(dV/dt)$ is not measured directly.</td>
<td></td>
<td>(D) Indirect method.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Charge Integration Method</td>
<td>Integrating 1.$V_{AC}$ $\Delta \theta$</td>
<td>$P = \frac{1}{A E_{C}} \int dE$</td>
<td>1. Depends on frequency $1_{X1}$ and $\Delta V_{AC}$</td>
<td>1. Poor</td>
<td>2. $(dV/dt)$ is not measured directly.</td>
<td>(A) Direct method (7-11)</td>
<td>(7)</td>
</tr>
<tr>
<td></td>
<td>1. by capacitor</td>
<td>Amplifier or capacitor is used to collect the pyroelectric charge</td>
<td></td>
<td>2. $(dV/dt)$ is not measured directly.</td>
<td></td>
<td>(D) Indirect method.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. by Amplifier</td>
<td>(A.M. Glass, 1969)</td>
<td></td>
<td>3. $(dV/dt)$ is not measured directly.</td>
<td></td>
<td>(D) Indirect method.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
<td>VI</td>
<td>VII</td>
<td>VIII</td>
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</tr>
</tbody>
</table>
| 6 | Sinusoidal heating method, Hartley, Squire and Putney (1972) | Low freq. sinusoidal variation of θ using thermoelectric module | \( V = P A \times \frac{3h}{2} \times \left( \frac{h+2}{h+1} \right) \), depends frequently on \( V_0 \), \( \Delta \theta \) and \( R \) | 1. Good \((-0.1 \%)
by thermoelectric module
by thermoelectric module (12)
by thermoelectric module
by thermoelectric module |
|  | | | 2. Absolute measurement of \( P \) is within 2% without knowledge of sample resistance and capacitance | |
|  | | | \( 2 \left( \frac{d\theta}{dt} \right) \) is directly measured. | |
| 7 | Step radiation signal method, Sinhony and Shaulov (1972) | Pyroelectric | \( C \left( \frac{dT}{dt} \right) = V \) - \( \frac{E}{R} \) | depends on initial slope rise time, and fall time of the response. | fairly | \( \Delta \theta \) is assumed to be uniform (13) |
| | | | | | | Heat capacity of the sample and intensity of source must be known |
| | | | | | | (D) Indirect method |
| 8 | Ferroelectric Method | Pyro coefficient is estimated from hysteresis loop \( (P_s E) \) | \( P = \left( \frac{dP_o}{dE} \right) \left( \frac{3P}{2} \right) T \) \( T_s \) \( E \) | depends Rarely fairly | \( P_s \) measured through hysteresis loop are not accurate |
| | | | | | | (D) Indirect method |
| 9 | Electromagnetic Method | Based on the electromagnetic effect (converse of pyroelectric effect) | \( q = - \frac{d\phi(x)}{C} \) \( \phi(x) \) \( \theta \) | \( \phi(x) \) \( \theta \) rarely poor | \( \Delta T \) requires large electric field |
| | | | | | | (D) Precise temp. measurement |
are taken, yield approximate value. The pyro-coefficient is obtained as a temperature differential of the spontaneous polarization, viz.

\[ \nu = \left( \frac{d^2 \theta}{d \varphi^2} \right)_T, \]

at constant stress and electric field.

(b) Electrocaloric method:

The electrocaloric effect is the converse of the pyroelectric effect. It is the change in temperature \(d\theta\) of a thermally insulated crystal caused by a change in the electric field \(d\varepsilon\). The pyroelectric coefficient, \(p\), can be calculated from the electrocaloric coefficient \(q\) and the specific heat, \(c\), using the relation:

\[ q = \left( \frac{d\varepsilon}{d\theta} \right)_c, \]

at constant stress and entropy

\[ q = - \frac{\partial P}{\partial T}, \]

cut due to certain experimental limitations this method is rarely used.

2.1.4 Choice of the technique:

In the samples for pyroelectric measurement the two major experimental problems are faced viz (a) the change of temperature in the entire sample is not uniform and (b) there always remains a possibility of electrical leakage through the sample due to conduction loss. The non-uniformly heated samples are more susceptible to
tertiary pyroelectric effect which generally introduces error in dynamic measurements where the temperature is continuously changing. Static methods are supposed to avoid this type of error since the charge or voltage measurement should be made at thermal equilibrium. Since pyroelectricity can be better observed in the absence of conduction, precautions must be taken to avoid conduction or suitable corrections must be made for the same, taking also into the account the input impedance of the measuring instruments. The in effect electrets and solid state electrolytic phenomena, if remotely possible in the samples, are to be dealt with more carefully.

Generally the dynamic technique is more appropriate for the study of small crystals with weak pyroelectric effects. This is also helpful in getting rid of the undesirable conduction in the sample since the temperature modulation of the conduction current is kept out of phase with the pyroelectric current and can be separated.

In case of polarization reversal studies again the dynamic technique is preferred with the condition that the change of polarization is slow compared with the modulation frequency. With the dynamic technique both clamped and unclamped pyroelectric coefficients may be measured. A necessary precaution in low frequency measurement is to ensure that the tertiary pyroelectric effect due to non-uniform heating of the crystal is not significant. Non-uniform heating through piezoelectric effect
currents additional contributions to the pyroelectric effect. However piezoelectric terms are negligibly small compared with the primary and secondary effects. Tertiary effects are relevant to \( \Theta_t \) only for time shorter than the thermal diffusion time across the crystal, while primary and secondary effects persist up to the thermal relaxation time of the crystal with its surroundings.

The major effect of the dynamic technique is the considerable temperature inhomogeneity in the crystal which may produce an additional piezoelectric charge (the so-called tertiary pyroeffect). This can add to the source of error in dynamic measurements. In the static method the temperature of the crystal is changed in only one direction (heating or cooling). Since the charge is measured after final setting of the new crystal temperature the foresaid errors are avoided to a large extent, if the heating or (cooling) at the moment of measurement is reasonably slow to ensure only a small temperature gradient in the crystal.

Static method yields accurate coefficient at discrete temperature values but it is time consuming and rather difficult at very low or very high temperatures. Thus the dynamic technique is generally used for the study of the temperature or time variation of spontaneous polarization for the pyroelectric measurements.
Our method of measurement of pyroelectric coefficient:

Of the various techniques mentioned above for pyroelectric measurements, our choice was the dynamic pyroelectric current measurement method. The purpose of this selection is because of its simplicity and sensitivity. It gives a direct plot of pyroelectric coefficient \( \alpha \) by the measurement of current over that temperature range when the rate of heating or cooling is held constant. During each run the pyroelectric current was measured by vibrating condenser electrometer amplifier. The known values of pyroelectric current

\[ I = \frac{dQ}{dt} \]

and rate of cooling \( \frac{d\theta}{dt} \), permit the calculation of pyroelectric coefficient as follows:

\[ \alpha = \frac{dQ}{I dt} \frac{d\theta}{dt} \quad \text{coul} \text{cm}^{-2} \text{C}^{-1} \]

where \( A \) is the area of the specimen in cm\(^2\) and \( I \) is in amperes.

Our above method was standardized using a well known pyroelectric material such as triglycine sulphate TGS and is, doped with \( \alpha \)-alumina single crystal plates. Another ferroelectric liquid crystal DOBAMBC (p-decylxy benzylidene-p'-amin-3-cyano-4-cinnamate) film is used to observe pyroelectricity in its chiral smectic \( C^* \) phase, to standardize our above technique.
The accuracy of the method, as it can be seen from the above pyroelectric coefficient relation, depends on the temperature resolution that is how the rate of heating/cooling \((-\frac{d\Phi}{dt})\) is held constant. Mean temperature must be changed steadily throughout. For \((-\frac{d\Phi}{dt})\) to be nearly constant, its value is obtained by plotting temperature versus time. The accuracy of the pyrocurent \((-\frac{d\Phi}{dt})\) depends on the accuracy of the amplifier used which is 3 - 5%. Another parameter that counts less in the surface area. The overall accuracy is 5% and in the region of transition around 10°C.

2.1.6 Electrometer amplifier:

The CAL vibrating condenser electrometer (EA 315) which has been used for our measurement is a high-performance electrometer amplifier specially designed to measure very small direct current and low potential from high impedance source and is also used to measure small charges and high resistances.

The electrometer amplifier consists mainly of an operational amplifier \(A\), input resistance \(R_i\) and a meter to read in volts or millivolts.

Pyrocurent of the order of \(10^{-3}\) to \(10^{-15}\) can be measured by measuring the potential across the test sample without any standard voltage source and is given by:

\[
I = \frac{\text{measured potential}}{\text{input resistance}} \quad \text{(in amperes)}
\]
**FIG. 2-1. MEASURING PRINCIPLE OF ELECTROMETER AMPLEIFIER**

\[ V_s = \text{Constant voltage source} \]
\[ R_i = \text{Input resistance} \]
\[ R_x = \text{Resistance of the sample} \]
\[ F = \text{Function switch} \]
The accuracy of current measurement by the electrometer amplifier is $3 \times 10^{-5}$. Fig. 2.1 represents the arrangement for pyrocurrent measurement with standard voltage source $V_s$ removed and the pyroelectric sample itself acting as the source of current when connected to the electrometer amplifier.

2.2 Measurement of dielectric constant ($\varepsilon$):

The dielectric constant ($\varepsilon$) is usually measured by the ratio of the capacity $C$ of a capacitor filled with the substance and the capacity $C_a$ of the corresponding air capacitor, i.e.

$$\varepsilon = \frac{C}{C_a}$$

The air capacity $C_a$ for an area $A$ ($cm^2$) and thickness $t$ ($cm$) is given by

$$C_a = \frac{2.0054}{t} \; \; \; \text{PF}$$

The measurement of $C$ containing the substance has been done as a function of temperature through the transition range using the Wayne Kerr Auto Balance Universal bridge 1542.

2.2.1 Wayne Kerr Auto Balance Universal Bridge 1542 (AF):

It is an autobalance transformer ratio arm bridge for the measurement of capacitance at audio frequencies generally to an accuracy of $0.1\%$. To simplify the derivation of certain values, which are frequency dependent, the measurements are done at a frequency of $15 \times 1.5 \times 10^4$ (at which $\omega = 10^4$).
The arrangement of Wayne Kerr Bridge in principle is similar to that of a sensing bridge with a holder introducing additional load in one of its arms. The basic circuit arrangement is shown in Fig. 2.2. The standard capacitor \( C_2 \) is usually a high quality mica capacitor or an air capacitor.

In balanced condition

\[ Z_n = i_3 \cdot v_1 \]

or

\[ u_3 \cdot \frac{-1}{C_3} = \mu_2 \cdot \left( \frac{-1}{C_1} \right) \cdot \left( \frac{1}{R_1} + j \cdot C_1 \right) \]

equating real and imaginary parts,

\[ \frac{1}{C_3} = \frac{1}{C_1} \cdot \frac{1}{R_1} \]

As can be seen from the circuit diagram, the two variables chosen for the balance adjustment are capacitor \( C_1 \) and resistor \( \mu_2 \).

Because the standards of the 9642 Bridge are in parallel components of in-phase and quadrature terms, the capacitance \( C \) and conductance \( G \) are displayed simultaneously after null balance when the test component is connected.

Eight decades—four for \( C \) and four for \( G \)—are operated in succession; each decade is provided with a numbered readout. Decimal points are indicated by small signal lamps mounted between the decade control knobs, the correct lamp being selected automatically by operation of the range switch.
FIG. 2. SCHERING BRIDGE FOR THE MEASUREMENT OF CAPACITANCE.
Loss tangent:

The loss term, given by 3 display, is the parallel conductance of the component.

The dissipation factor ($\tan \delta$) can then be calculated by the expression

$$\tan \delta = \frac{3}{\omega}$$

where $\delta$ is in ohms and $\omega$ in radians. It can be found very easily by this bridge at an internal frequency 157.5 Hz, (at which $\omega = 10^4$) by taking the direct ratio of $C$ and $G$ readings. Thus

$$\tan \delta = \frac{G \text{ reading}}{C \text{ reading}}$$

The $C$ and $G$ readings referred to are the numerical settings of the decade controls ignoring the decimal points and the unit of measurements. The numbers must be written as if the last fourth decade is in units, the second decade in tenths and so on.

2.3 Measurement of dielectric constant at radio frequency:

During the course of dielectric relaxation studies, the simultaneous plot of real and imaginary parts of complex permittivity $\varepsilon^*$ given by

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

is carried out at different frequencies. The quantity $\varepsilon''$ is known as the dielectric loss coefficient, which gives
the magnitude of the product of \( \varepsilon' = f(t) \) and \( \tan \delta = f(t) \), defined as

\[ \varepsilon'' = \varepsilon' \tan \delta \]

where the \( \tan \delta \) known as the Debye loss is given by the expression\(^{(16)}\)

\[ \tan \delta = \frac{1}{2} \left( \varepsilon_0 - \varepsilon_\infty \right) (\varepsilon_0 \varepsilon_\infty)^{\frac{3}{2}} \]

The Cole Cole diagram\(^{(17)}\) relates the quantities \( \varepsilon'' \) and \( \varepsilon' \). The plot on rectangular co-ordinates of \( \varepsilon'' \) against \( \varepsilon' \), where the values are taken at the individual frequencies measured, will provide a series of points on a semicircle of radius \( \left( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \right) \) meeting the \( \varepsilon' \) axes at \( \varepsilon_0 \) and \( \varepsilon_\infty \). If on the semicircle an experimental point \( P \) at angular frequency \( \omega \) rad \( s^{-1} \) is at distance \( u \) from \( \varepsilon_\infty \) and \( v \) from \( \varepsilon_0 \) then \( C \) can be found from

\[ CE = \frac{v}{u} \]

where \( T \) is relaxation time. The foregoing \( T \) parameters have been measured using the Wayne Kerr Universal Bridge using the accessory Wayne Kerr Source and detector.

2.3.1 Wayne Kerr Universal M.F. Bridge (1962):

The Universal M.F. Bridge (1962) uses self-balancing Transformer Ratio-Amp Bridge principle\(^{(19)}\). It is an M.F. Bridge for the measurement of capacitance, conductance, resistance and inductance with an accuracy of 1% at frequencies between 50.0 kHz and 5 kHz or with
reduced accuracy up to 10 MHz. Being a passive instrument, the B602 requires an external source and detector. Therefore, B602 is used in conjunction with the Wayne Kerr RF source and detector as 266L.

The arrangement of the bridge is such that on the five upper ranges the unknown is measured in terms of its parallel components, while on the lower three ranges the measurement is in terms of the series components. The push-button switch block on the front panel facilitates the selection of sign and multiplier for L/Σ and G/R functions. Selection of the capacitance (C) or inductance (L) standard is made by operation of the central pair of buttons. The appropriate ground and neutral connections must be made according to the type of measurement required.

Since the bridge operates at r.f., all the three of each voltage and current transformers, are miniature components wound on ferrite cores which serve to match the bridge input impedance to the external source output. The full circuit diagram of the B602 is given in Fig. 2.3.

Feed back amplifier is employed to provide a self balancing system for the measurements of impedance Z and admittance Y. Ratio transformers are used to give a very wide range of measurement and the system combines the advantage of a three terminal bridge with the facility of the self-balancing feature. To understand its principle consider the arrangement of Fig. 2.3.
FIG. 2.3. THE PRINCIPLE OF SELF-BALANCING TRANSFORMER RATIO ARM BRIDGE.
(a) The admittance standard 10 \( Y_a \) is fed from \( \alpha \) turns of the voltage transformer.

(b) The admittance standard \( Y_a \) is fed from \( \beta \) turns of the voltage transformer.

The voltage transformer has \( \epsilon \) volts per turn and the voltmeter reading; the output voltage is designed to have a full scale deflection \( \delta \) volts. Equating the fluxes in the current transformers gives

\[
\phi_0 \cdot E_a \cdot Y_u \cdot \alpha \cdot \beta \cdot R = 10 \times Y_a \cdot \epsilon + \beta \cdot Y_a \cdot \epsilon + \delta \cdot n \quad (1)
\]

\[
Y_u = \frac{Y_a}{\epsilon P_1 (1 + \alpha \cdot \beta)} \quad (2)
\]

where \( \alpha \) and \( \beta \) are integers from 0 to 10 and \( S \) is a number lying between 0 and 1. \( E_a \) is the voltage ratio \( \frac{E_0}{E_a} \) and \( P_1 \) is the current transformer ratio \( \frac{N_1}{N_2} \).

Therefore, unknown admittance may be considered to be made up of three parts. The switch positions \( \alpha \) and \( \beta \) are notrical quantities, give the first two significant figures of the unknown. The proportion, \( S \), of full scale indication of the indicator gives the subsequent significant figures with an accuracy dependent upon the voltmeter accuracy and amplifier gain \( u_a \). The self balancing part of the bridge is only conscious of the unknown admittance \( \frac{Y_a}{\phi_0} \) fed from a source voltage of \( V_0 \) volts.

The value of \( Y_a / P_1 \) must be taken as the full scale value of \( Y_u \).
The above arrangement for the measurement of admittance, in general, is also suitable for the measurement of conductance and capacitance. The decade standards to $Y_a$ and $Y_b$ are each duplicated by one capacitance and one conductance standard. Each standard having an individual switch to select the appropriate voltage and the feedback element is conveniently a conductance standard. The accuracy of measurement of capacitance is not dependent on the accuracy of the measurement of frequency.

2.3.2 Wayne Kerr RF source and detector (BR 263L):

The BR 263L is a general purpose bridge source and null detector covering the frequency range 46.5 kHz to 465 kHz, and is used in conjunction with RF bridge (BR02). The frequency range is covered in nine bands and the source and detector tuned circuits are gauged for simple and fast operation. Such button attenuators are provided to control the source output level and detector input sensitivity. A meter facilitates accurate visual detection of the null point.

BR 263L comprises of an RF oscillator, a tuned resonance frequency receiver and a power supply unit, all of which are mounted on a common chassis assembly. The frequency range of both oscillator and detector is covered in nine bands by means of four sets of transformers, each set being carried in its own turret drum. In block diagram Fig. 2.4 shows the progress of the signal from the
FIG. 24. BLOCK DIAGRAM FOR WAYNE KERR RF SOURCE AND DETECTOR.
oscillator to the bridge and from the bridge to the detector and meter.

2.4 Electrode preparation:

For the thin electrode film preparation, the following two techniques were used -

(i) Vacuum evaporation technique for metallic film
(ii) Vaporisation method for transparent conducting SnO₂ films.

2.4.1 Vacuum evaporation technique:

For the metallic thin films, the vacuum evaporation is so far the best technique. The vacuum coating unit (VC-62) (Vacuum Instruments Company) has been used ([15,25]). The electrode films of aluminium or silver (1000 Å thickness) were evaporated on the glass slides/fused silica optically flat plates in the vacuum of the order of 10⁻³ torr. For the deposition of metal films, the source material was taken in the form of thin foils. Tungsten helix was used for the deposition of Al and molybdenum boat was used for evaporation of Ag films. The evaporation temperatures of Al and Ag for vapour pressure 10⁻² torr are 1105°C and 1280°C respectively. After the substrates were transferred to the vacuum chamber prior to vacuum deposition of the electrode films, they were heated for degassing and then final degassing was done by U.V. Ionic bombardment.
FIG. 25. LAYOUT OF VACUUM COATING UNIT.
2.4.2 Preparation of conducting transparent electrodes by vaporisation method:

The conducting glass plates, used in the present study, were prepared in the laboratory following the method suggested by Donor. Vapours of stannous chloride were sprayed on a heated glass plate at a temperature of about 500°C. The experimental arrangement is shown in Fig. 2.6. A few crystals of SnCl₂ · 2H₂O were put in a 10 ml conical flask and heated up to sublimation temperature. Air was then blown in by a rubber blower. In this air the stannous chloride vapours pass over the heated glass plate where it gets decomposed and deposited as stannous oxide film. By this method conducting transparent electrodes on glass plates having resistances of the order of 100 to 200 ohms/cm² were deposited.

2.4.3 Fabrication of sandwich sample cells:

For the various measurements the specimen film under examination is sandwiched between two metallic or transparent electrode films of desired area on the substrates of glass slides (blue star super delux). Before the deposition of the lower metallic electrode film the substrates were thoroughly cleaned with slightly warm chromic acid and then properly rinsed with distilled water after washing them with soap solution. It was dried with air blower. The lower metallic films of aluminium (100 Å thickness) were vacuum deposited on the substrate with the help of
FIG. 26. EXPERIMENTAL ARRANGEMENT FOR PREPARING TRANSPARENT ELECTRODES.
suitable mask for desired area. Transparent conducting electrodes were deposited by stannous chloride vaporisation methods, in lower electrode plate adequate amount of desired liquid crystal powder is sprinkled and melted on a hot plate. Then keeping mica spacers of known thickness over the corners leaving free the two electrode areas, is suitably placed and stuck to give a sandwiched cell of the specimen. Fig. 3.7, before making any measurements the sandwich cells were thoroughly examined by microscope to confirm that the film used for the measurement is free from any physical defects such as presence of pin holes and film discontinuity. Shorting, if any, was checked by ohmmeter.

2.4.4 Measurement of the thickness of the sample film:

Thickness of the film plays an important role in dielectric properties though not in the pyroelectric study. Thickness of the sample film used in the thickness of the mica spacer sandwiched between the two transparent conducting electrodes film on the substrate of glass slides. Thickness of the mica spacer is measured by a thin film mass gauge with a least count of 10 micron (model no. 7001 Japan).

2.4.5 Sample holder and the measuring cell:

For studying the pyroelectric properties of the liquid crystals by dynamic method, a special cell was fabricated, keeping in mind the necessity of the careful
FIG. 27 Sandwiched liquid crystal cell

FIG. 28 Temperature chamber and sample holder for pyroelectric measurements for liquid crystals.
control of the homogeneity of crystal heating or cooling rate in the measurement.

The sample holder consists of screw adjustable upper support holder vertically fitted on iron stand, on a wooden block. This block is mounted inside the centre of the measuring cell (Fig. 2.8). This assembly is centrally fitted within a massive thick walled cylinder of copper with insulated heater windings and it was further shielded with an aluminium sheet to avoid spurious effects due to surrounding charged bodies. This system ensured fairly good thermal insulation and electrical shielding for the specimen. Temperature of the chamber was controlled by Leeds temperature controller and indicator unit, so as to keep crystal heating or cooling rate uniform. Our main criterion was to make measurements under dynamic conditions such that the temperature of the sample was more or less uniform, which was further checked. For avoiding fluctuations in the supply voltage, a clock voltage stabilizer was used.

2.4.6 Temperature Measurement:

Almost all measurements were carried out above room temperature (20°C to 200°C). The temperature was measured using a chromel-alumel thermocouple which had been earlier calibrated in our laboratory. A vernier potentiometer was used to measure thermoelect, having a sensitivity of the order of 10⁻⁵ volts; an external reflex galvanometer was used to balance the potentiometer null point.
2.4.7 Poling

Poling of ferroelectric film materials is essentially done to orient the ferroelectric domains along the sample thickness. This is particularly necessary in poly-crystalline samples. This is all the more essential to study poled and unpoled ferroelectric liquid crystal films. On the other hand, accumulation of surface and volume charges as well as orientation of dipoles in molecules bring about the formation of electric dipoles. Usual method of poling is to heat an electroded film to a poling temperature, apply an electric field for a time, and finally cool the film rapidly to room temperature with the poling field still applied. The film is then short circuited for several hours. The degree of polarization induced depends on the field, temperature and duration of polarizing process. Cooling the film in the presence of strong dc field can orient domains along the direction of the measurement. In case of films, a negligible ripple free dc power supply is sufficient to provide a poling field of several kilo volt/cm; for this purpose twin transistor power supply (641/0) (sytronics) and TEC stabilized power supply were used.
REFERENCES