USER'S MANUAL

Study of Dielectric Constant and Determination of Curie Temperature of Ferroelectric Ceramics

A Product of:

RAMAN SCIENCTIFIC INSTRUMETNS
516, RAM NAGAR, ROORKEE – 247667
Ph. No. +91 1332 270002, FAX No. +91 1332 274950
visit us at www.rsiindia.com, email: rsi_india@yahoo.com

DIELECTRIC AND CURIE TEMPERATURE MEASUREMENT OF FERROELECTRIC CERAMICS

INTRODUCTION:

Ferroelectric ceramics were born in the early 1940s with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramic barium titanate capacitors. Since that time, they have been the heart and soul of several multibillion dollar industries, ranging from high-dielectric-constant capacitors to later developments in piezoelectric transducers, positive temperature coefficient devices, and electro optic light valves. Materials based on two compositional systems, barium titanate and lead zirconate titanate, have dominated the field throughout their history. The more recent developments in the field of ferroelectric ceramics, such as medical ultrasonic composites, high-displacement piezoelectric actuators (Moonies, RAINBOWS), photostrictors, and thin and thick films for piezoelectric and integrated-circuit applications have served to keep the industry young amidst its growing maturity. Various ceramic formulations, their form (bulk, films), fabrication, function (properties), and future are described in relation to their ferroelectric nature and specific areas of application.

A huge leap in the research on ferroelectric materials came in the 1950's, leading to the widespread use of barium titanate ($BaTiO_3$) based ceramics in capacitor applications and piezoelectric transducer devices. Further research in the area of Ferroelectrics is driven by the market potential of next generation memories and transducers. Thin films of ferroelectrics and dielectrics are rapidly emerging in the field of MEMS applications. Ultrasonic micro-motors utilizing PZT thin films and pyroelectric sensors using micro-machined structures have been fabricated. MEMS are finding growing application in accelerometers for air bag deployment in cars, micro-motors and pumps, micro heart valves, which have reached the commercial level of exploitation in compact medical, automotive, and space applications. Extremely sensitive sensors and actuators based on thin film and bulk will revolutionize every walk of our life with Hi-tech gadgets based on ferroelectrics. Wide spread use of such sensors and actuators have made Hubble telescope a great success story. New bulk ferroelectric and their composites are the key components for the defense of our air space, the long coastline and deep oceans.

The quest of human beings for developing better and more efficient materials is never ending. Material Science has played a vital role in the development of society. Characterization is an important step in the development of different types of new materials. This experiment is aimed to expose the young students of Dielectric and Curie Temperature Measurement technique for Ferroelectric Ceramics.

Dielectric or electrical insulating materials are understood as the materials in which electrostatic fields can persist for a long time. These materials offer a very high resistance to the passage of electric current under the action of the applied direct-current voltage and therefore sharply differ in their basic electrical properties from conductive materials. Layers of such substances are commonly inserted into capacitors to improve their performance, and the term dielectric refers specifically to this application.

The use of a dielectric in a capacitor presents several advantages. The simplest of these is that the conducting plates can be placed very close to one another without risk of contact. Also, if subjected to a very high electric field, any substance will ionize and become a conductor.

⊕ ⊖

Dielectrics are more resistant to ionization than air, so a capacitor containing a dielectric can be subjected to a higher voltage. Also, dielectric increases the capacitance of the capacitor. An electric field polarizes the molecules of the dielectric, producing concentrations of charge on its surfaces that create an electric field opposed (antiparallel) to that of the capacitor. Thus, a given amount of charge produces a weaker field between the plates than it would without the dielectric, which reduces the electric potential. Considered in reverse, this argument means that, with a dielectric, a given electric potential causes the capacitor to accumulate a large charge.

The electrons in the molecules shift toward the positively charged left plate. The molecules then create a leftward electric field that partially annuals the field created by the plates. (the air gap is shown for clarity; in a real capacitor, the dielectric is in direct contact with the plates.)

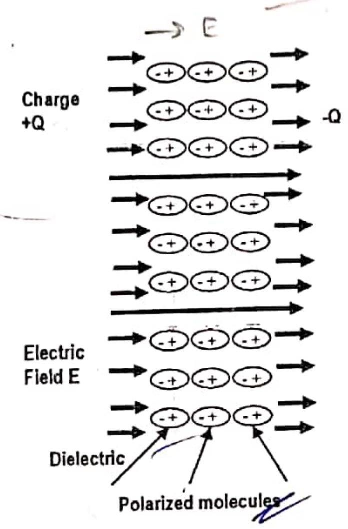


Fig. 1

PEROVSKITE STRUCTURE:

Perovskite is a family name of a group of materials and the mineral name of calcium titanate ($CaTiO_3$) having a structure of the type ABO_3. Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate ($BaTiO_3$), Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate ($KNbO_3$), Potassium Sodium Niobate ($KxNa1\text{-}xNbO_3$), and Potassium Tantalate Niobate ($K(TaxNb1\text{-}x)O_3$) have a perovskite type structure (in the para-electric state) with chemical formula ABO_3 as shown in fig 2 (a) and 2(b).

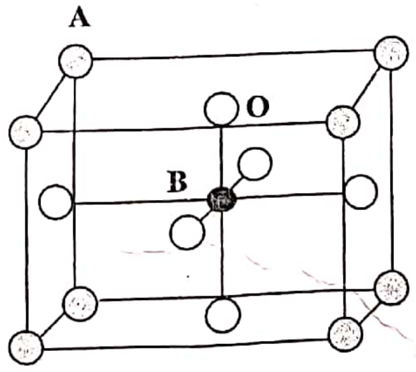


Fig 2(a) Perovskite B3 structure with the A and B cations on the corner and body center positions, respectively. Three oxygen anions per unit cell occupy the faces and form octahedral surrounding the B-site

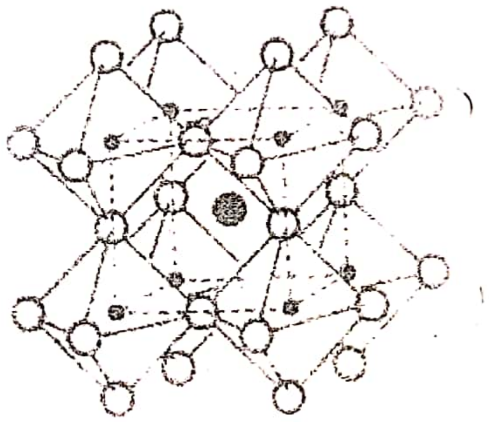


Fig 2(b) Perovskite structure Ba: Grey, Ti: Black. O: White.

As conventionally drawn, A-site cations occupy the corners of a cube, while B-site cations sit at the body center. Three oxygen atoms per unit cell rest on the faces. The lattice constant of the se perovskite is always close to the 4 A due to rigidity of the oxygen octahedral network and the well-defined of oxygen ionic radius of 1.35 A.

$R = R_0 (A)^{1/3}$ constant

A practical advantage of the perovskite structure is that many different cations can be substituted on both the A and B sites without drastically changing the overall structure. Complete solid solutions are easily formed between many cations, often across the entire range of composition. Even though two cations are compatible in solution, their behavior can be radically different when apart from each other. Thus, it is possible to manipulate a material's properties such as Curie Temperature or dielectric constant with only a small substitution of a given cations.

All ferroelectric material has a transition temperature called the Curie point (T_c). AT a temperature $T > T_c$ the crystal does not exhibit ferroelectricity, while for $T < T_c$ it is ferroelectric. On decreasing the temperature through the Curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric (Para electric) phase to a ferroelectric phase.

BARIUM TITANATE ($BaTiO_3$, BT)

$BaTiO_3$ is the chemical formula for Barium Titanates. In powder form it is white to grey in color and has a perovskite structure. It is soluble in many acids including sulfuric, hydrochloric and hydrofluoric acids. It is insoluble in alkalis and water. In the pure form it is an electrical insulator. However, when doped with small amounts of metals, most notably scandium, yttrium, neodymium, samarium etc it becomes semi conducting.

As a semiconductor it exhibits positive temperature of co-efficient of resistivity (PTCR) properties in the polycrystalline form. This means at a certain temperature, called the Curie temperature, the material will exhibit an increase in resistivity, the increase typically being several orders of magnitude. The Curie temperature can to some extent be controlled by the dopant. At the Curie temperature, barium titanate undergoes a phase change from tetrahedral to cubic. It has also been reported that single crystals of barium titanate exhibit negative temperature co-efficient of resistivity (NTCR) properties.

Barium titanate also exhibits ferroelectric properties and is an excellent photorefractive material. Due to its PTCR properties, barium titanate is most often found used as a thermistor e.g. in thermal switches.

Barium Titanate ($BaTiO_3$) has a ferroelectric tetragonal phase Fig 3 (a) below its curie point of about 130°C and Para electric cubic phase Fig, 3 (b) above Curie point. The temperature of the curie point appreciably depends on the impurities present in the sample and the synthesis processes.

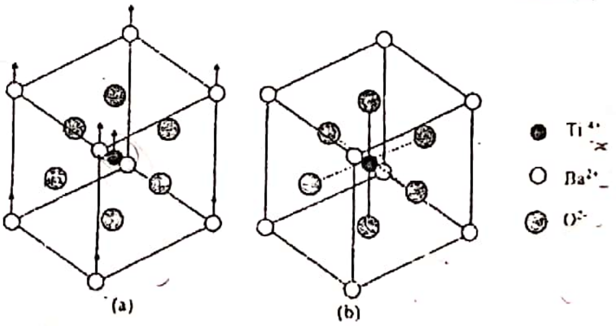


Fig. 3 The crystal structure of $BaTiO_3$ (a) above the curie point (b) below the curie point.

1300

In the Para electric cubic phase the center of positive charges (Ba^{2+}, Ti^{4+}) coincid with the center of negative charges (O^{-2}ion) and on cooling below T_o, a tetragonal phase develops where the center of Ba^{2+} and Ti^{4+} ions are displaced relative to the O^{2-}ions, leading to the formation of electric dipoles.

As the BT ceramics have a very large room temperature dielectric constant, they are mainly used in multilayer capacitor applications. The grain size control is very important for these applications.

DIELECTRIC CONSTANT:

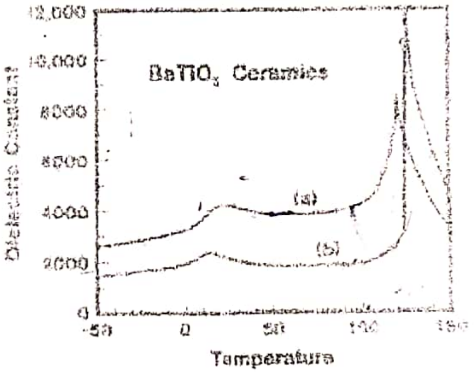


Fig. 4 The variation of relative permittivity (ε_r) with temperature for $BaTiO_3$ Ceramics For grain Size (a) 1 µm (b) for 50 µm

The dielectric properties of $BaTiO_3$ are found to be dependent on the grain size Fig. 4 shows the variation of dielectric constant with temperature for $BaTiO_3$ ceramics with a fine (~1 m m) and coarse (~ 50 m m) grain size. Large grained $BaTiO_3$ (1mm) shows an extremely high dielectric constant at the Curie point. This is because of the formation of multiple domains in a single grain, the motion of whose walls increases the dielectric constant at the Curie point. For a $BaTiO_3$ ceramic with fine grains (~1 mm), a single domain forms inside each grain. The movement of domain walls are restricted by the grain boundaries, thus leading to a low dielectric constant at the Curie point as compared to coarse grained $BaTiO_3$. The room temperature dielectric constant (er) of coarse grained (10 mm) BT ceramics is found to be in the range of 1500-2000. On the other hand, fine grained (~1m m) BT ceramics exhibit a room temperature dielectric constant between 3500-6000.

The dielectric constant of a dielectric material can be defined as the ratio of the capacitance using that material as the dielectric in a capacitor to the capacitance using a vacuum as the dielectric. Typical values of (ε) for dielectrics are:

Material	Dielectric Constant (ε)
Vacuum	1.000
Dry air	1.0059
Barium Titanate	100-1250
Glass	3.8-14.5
Quartz	5
Mica	4-9
Water distilled	34-78
Soil dry	2.4-2.9
Titanium dioxide	100

0.1 = 10

13
23

Pbs

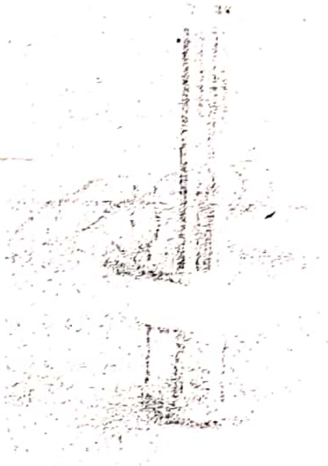
Dielectric Constant (ε) is given by

$$\varepsilon = \frac{C}{C_0}, \quad C_0 = \frac{\varepsilon_0 A}{t}$$

Where

C = capacitance using the material as the dielectric in the capacitor
C_0 = capacitance using vacuum as the dielectric
ε_0 = Permittivity of free space) 8.85×10^{-12} F/M)
A = Area of the plate/sample cross section area
t = Thickness of the sample.

Brief Description of the Apparatus



1. **Probe Arrangement:** It has two spring loaded probes. These probe move in pipes and are insulated by Teflon bush, which ensure a good electrical insulation. The probe arrangement is mounted in suitable stand, which also hold the sample plate and RTD sensor. The RTD is mounted in the sample plates such that it is just below the sample, separated by a very thin sheet of mica. This ensures the correct measurement of sample temperature. This stand also serves as a lid of the oven. The leads are provided for the connection to RTD and capacitance meter.

2. **Sample:** Barium Titanate ($BaTiO_3$) crystal in the form of plate with top and bottom conducting surface.

3. **Oven:** This is a high quality temperature controlled oven. The oven has been designed for fast heating and cooling rates, which enhance the effectiveness of the controller.

4. **Dielectric Constant Set-up** (Main Units): The Set-up consists of two units housed in the same cabinet.

5. **Oven Controller:** Platinum RTD (A class) has been used for sensing the temperature. A Wheatstone bridge and an instrumentation amplifier are used for signal conditioning. Feedback circuit ensures offset and linearity trimming and a fast accurate control of the oven temperature.

Specification of the Oven	
Temperature Range	: Ambient to 200°C.
Resolution	: 0.1°C
Stability	: ± 1°C
Measurement Accuracy	: ± 0.5°C
Oven	: Specially designed for Dielectric measurement
Sensor	: RTD (A class)
Display	: 3 ½ digit, 7 segment LED with autopolarity & decimal indication
Power	: 150W

Platinum RTD Sensor — Platinum ~~Reg~~ Resistance and Temperature Deviation Sensor

(ii) **Digital Capacitance Meter**

This is a compact direct reading instrument for the measurement of capacitance of the sample.

Specification of the Oven	
Range	: 50 to 6000 pf
Resolution	: 1pf
Display	: 3 ½ digit, 7 segment LED

Procedure

1. Put a small piece of aluminum foil on the base plate. Pull the spring loaded probes upward, insert the aluminum foil and let them rest on it. Put the sample ($BaTiO_3$) on the foil. Again pull the top of one of the probe and insert the sample below it and let it rest on it gently. Now one of the probes would be in contact with the upper surface of the sample, while the other would be in contact with the lower surface through aluminum foil.
2. Connect the probe leads to the capacitance meter and oven to the main unit keeping the oven in OFF position.
3. Switch on the main unit and note the value of capacitance. It should be a stable reading and is obtained directly in pf.
4. (i) Switch ON the temperature Controller and approx adjust the set-temperature. The green Yellow LED would light up indicating the oven is ON and temperature would start rising. The temperature of the oven in ^{0}C would be indicated by the DPM.

   (ii) The controller of the oven would switch ON/OFF power corresponding to set-temperature. In case it is less then the desired, the set-temperature may be increased or vice versa.

   (iii) Because of thermal inertia of oven, there would be some oven shoot and under shoot before a steady set-temperature is attained and may take 10 minutes for each reading.

NOTE:-

(a) To save time, it is recommended to under adjust the temperature. eg., it is desired to set at 50 °C, adjust the temperature set knob so that LED is OFF at 45 °C. The temperature would continue to rise. When it reaches 50 °C adjust the temperature set knob so that oven is just ON/OFF. It may go up 1 & 2 °C, but would settle down to 50 °C.

(b) Since the change in temperature at this stage is very slow and response of RTD and sample it fast, the reading can also be taken corresponding to any temperature without waiting for a steady state.

(DPM – Digital Panel Metre)

OBSERVATIONS AND CALCULATIONS

Note:
For Broken sample (29/01/2019)
A = 27 mm²

Sample : Barium Titanate ($BaTiO_3$)
Diameter: 8.56 mm; Area (A): 57.52 mm²
Thickness (t): 1.62 mm
Permittivity of Space (ε_0) : 8.85×10^{-12} F/m or 8.85×10^{-3} pf/mm

$$\varepsilon = \frac{C}{C_0};\ where,\ C_0 = \frac{\varepsilon_0 A}{t} \Rightarrow \frac{8.85\times10^{-3}\times57.52}{1.62} \Rightarrow 314.23\times10^{-3}\ pf$$

S. No.	Temperature (°C)	Capacitance, C (pf)	Dielectric Constant, (ε)
1.	31.5	650	2069
2.	40	648	2062
3.	50	605	1925
4.	60	582	1852
5.	70	572	1820
6.	80	573	1824
7.	90	584	1850
8.	100	596	1897
9.	110	622	1979
10.	120	683	2174
11.	125	728	2317
12.	130	806	2565
13.	133	958	3049
14.	135	1320	4201
15.	137	1460	4646
16.	139	1469	4675
17.	141	1461	4650
18.	143	1413	4497
19.	145	1358	4322
20.	150	1216	3870
21.	155	1121	3568
22.	160	1026	3265
23.	165	945	3007
24.	170	898	2858
25.	175	836	2661

1358
650
705

Typical Results

From the graph, the Curie Temperature (T_c) obtained experimentally is 139 °C.

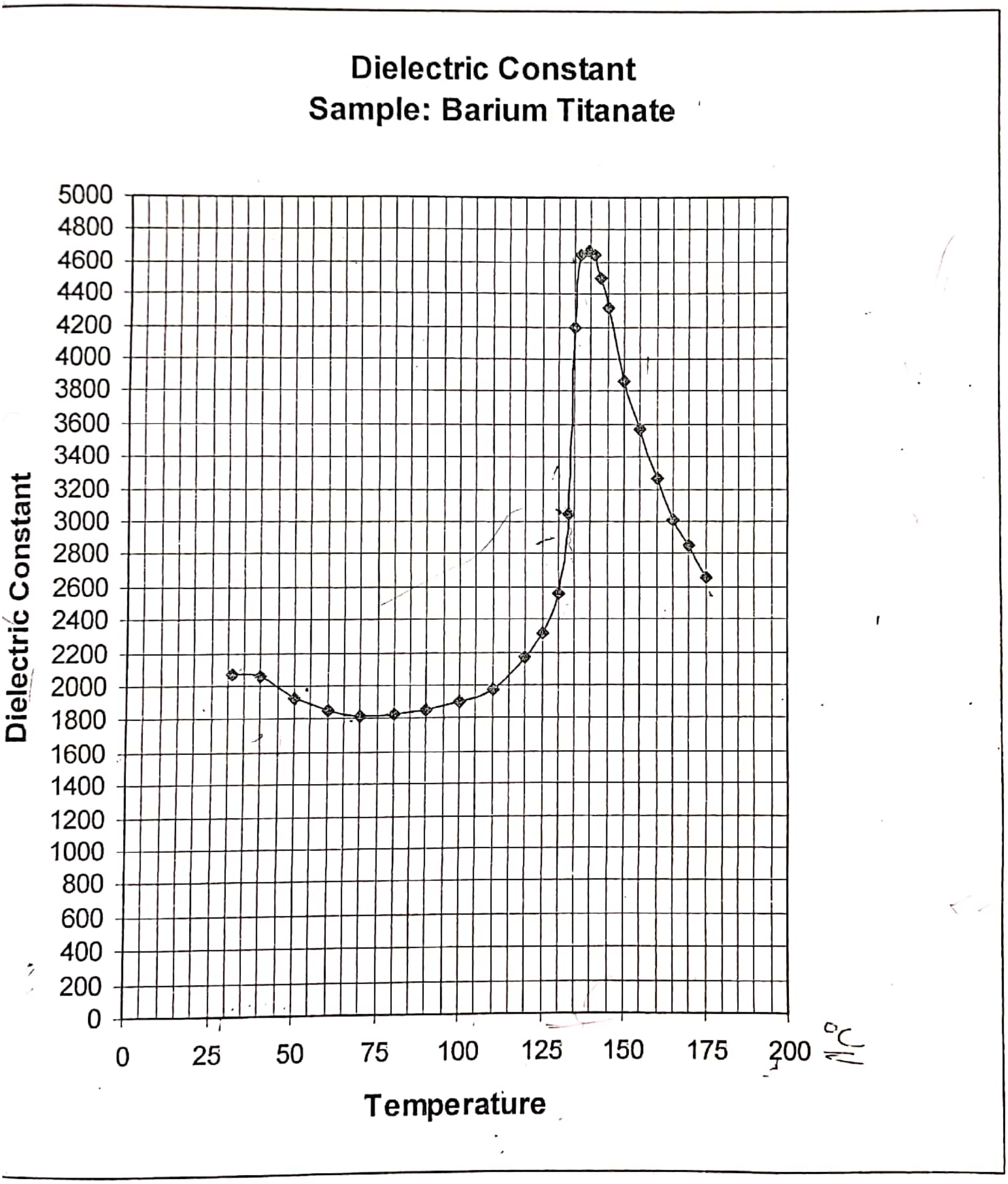
Precautions

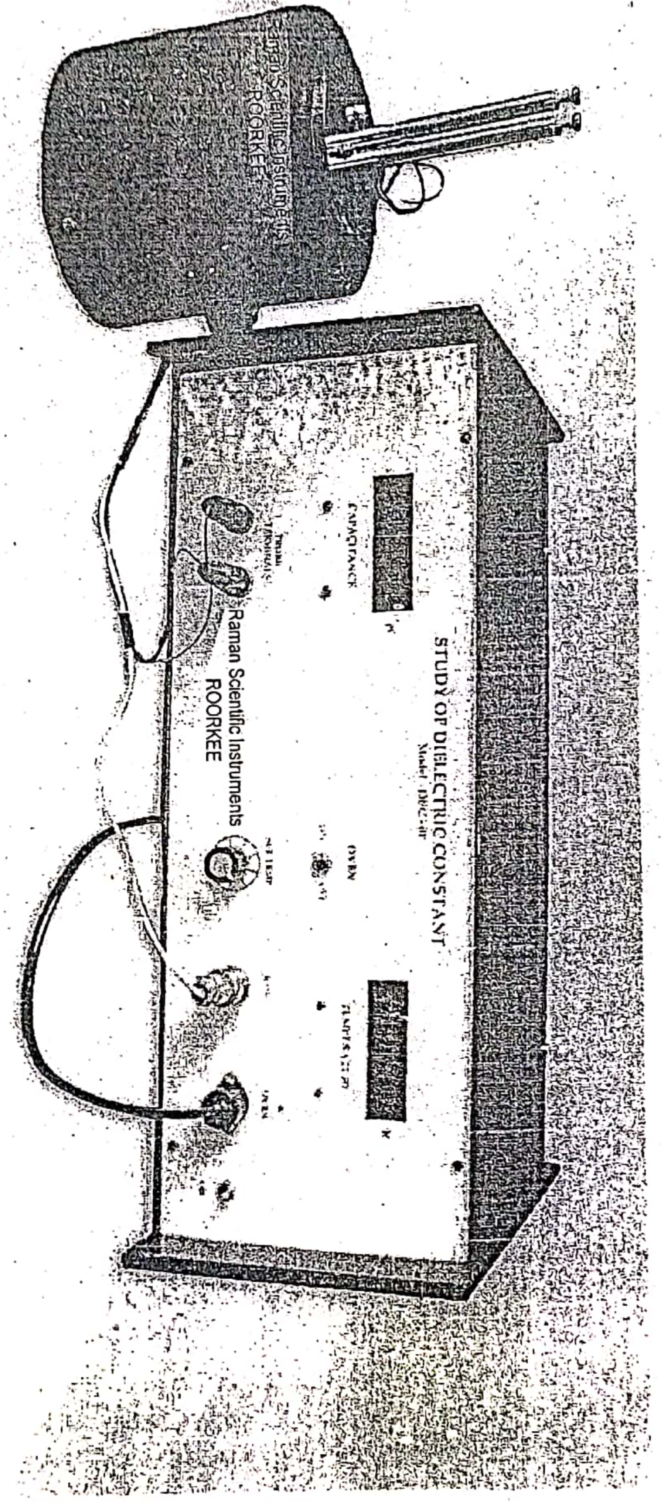
1. The spring loaded probe should be allowed to rest on the sample very gently, other wise it may damage the conducting surface of the sample or even beak the sample.
2. The reading of capacitance meter should be taken when the oven is OFF. This would be indicated by the green LED. In ON position there may be some pick ups.
3. The reading near the Curie Temperature should be taken at close intervals, say 1 °C to 2 °C.

Reference

(1). Introduction to Solid State Physics- C.Kittel, Wiley Eastern Limited (5th Edition).

GRAPH : DIELECTRIC CONSTANT VS TEMPERATURE

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