

Ferroelectric phase transition in BaTiO₃ and dielectric constant with frequency, and demonstration of structures of BaTiO₃.

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Abstract:

Barium titanate (BaTiO₃) is a ferroelectric oxide that undergoes a transition from a ferroelectric tetragonal phase to a paraelectric cubic phase after crossing Curie Temperature. Ferroelectricity in tetragonal (BaTiO₃) is due to an average relative displacement along the c-axis of titanium from its centrosymmetric position in the unit cell and consequently the creation of a permanent electric dipole. The dielectric constant varies frequency as well as temperature, but the transition of ferroelectric to paraelectric is only temperature dependant.

Aim

- *To Study the frequency dependence of Dielectric Constant*
- *To Study the Dielectric Constant as a function of Temperature and Frequency and determine the ferroelectric to paraelectric phase transition.*

Apparatus Required

- *Oscilloscope*
- *Samples-Barium Titanate (BaTiO₃), Standard Multilayer Ceramic Capacitor, Disc Ceramic Capacitor*
- *Main Unit*
- *Probe arrangement*

Theory:

The dielectric constant or permittivity is a complex quantity with real part signifying energy stored and imaginary part signifying energy loss. Real part of permittivity depends on the polarizability. The total polarizability may usually be separated into three parts or four parts (when interfaces are involved): electronic, ionic (or atomic), dipolar (or orientation) and space charge. Each dielectric mechanism effect has a

characteristic relaxation frequency. As the frequency becomes larger, the slower mechanisms drop off. This in turn leaves only the faster mechanisms to contribute to the dielectric storage or real part.

Electronic polarization occurs in neutral atoms when an electric field displaces the nucleus with respect to the electrons that surround it. Atomic polarization occurs when neighboring positive and negative ions "stretch" under an applied electric field. In an absence of an external electric field, these moments are oriented in a random order such that no net polarization is present.

The ionic polarization is composed of ionic conductivity and interfacial or space charge polarization. At low frequencies ionic conduction is the most prevalent mechanism. Ionic conduction only introduces losses into a system.

Space charge polarization occurs when more than one material component is present or when segregation occurs in a material containing incompatible chemical sequences and when translating charge carriers become trapped at the interfaces of these heterogeneous systems. The electric field distortion caused by the accumulation of these charges increases the overall capacitance of a material which appears as an increase in real part of dielectric constant. The dielectric permittivity at optical frequencies arises almost entirely from the electronic polarizability.

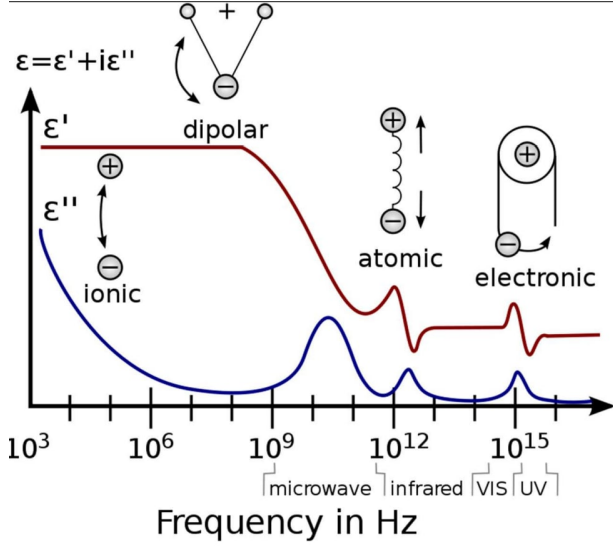


Figure 1: Permittivity Variable with Frequency

Both real and imaginary part are important for applications. The dielectric constant (ϵ') represents a measure of the ability of a material to be polarized by an external electric field storing energy within it. On the other hand, the dielectric loss factor (ϵ'') represents the ability of the material to dissipate the absorbed electromagnetic energy, converting it into heat. The higher the dissipation capacity for a sample the lesser will be the penetration of EM wave into the same sample. Thus, the ratio $\frac{\epsilon''}{\epsilon'}$ suggests the capability of each material to convert electromagnetic energy into heat at specific temperatures and frequencies.

The loss factor (dissipation factor) is defined as:

$$\tan \delta = \frac{\epsilon'_r}{\epsilon''_r} \quad (1)$$

BARIUM TITANATE ($BaTiO_3$)

Barium Titanate has a very large room temperature dielectric constant. It has 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 ($PbTiO_3$), Potassium Niobate ($KNbO_3$) etc. have a cubic perovskite type structure (in the paraelectric state) with chemical formula ABO_3 .

A practical advantage of the perovskites 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. 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 cation.

Barium Titanate ($BaTiO_3$) has a ferroelectric tetragonal phase below its curie point of about 120°C and paraelectric cubic phase above Curie point. The temperature of the curie point appreciably depends on the impurities present in the sample and the synthesis process.

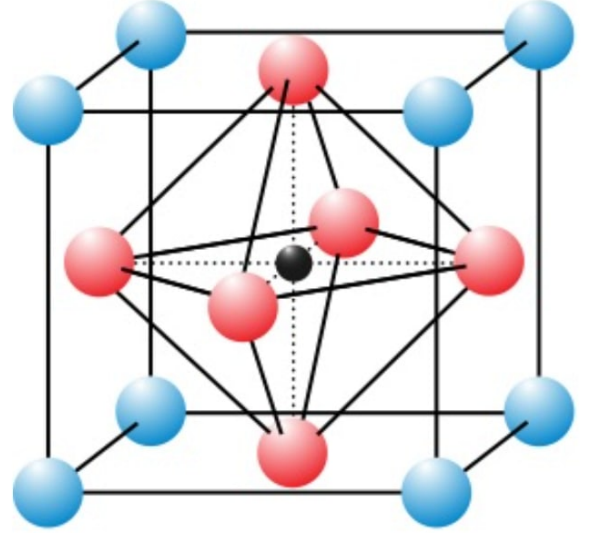


Figure 2: Perovskite ABO_3 structure with the A and B cations on the corner and body centre positions, respectively. Three oxygen anions per unit cell occupy the faces

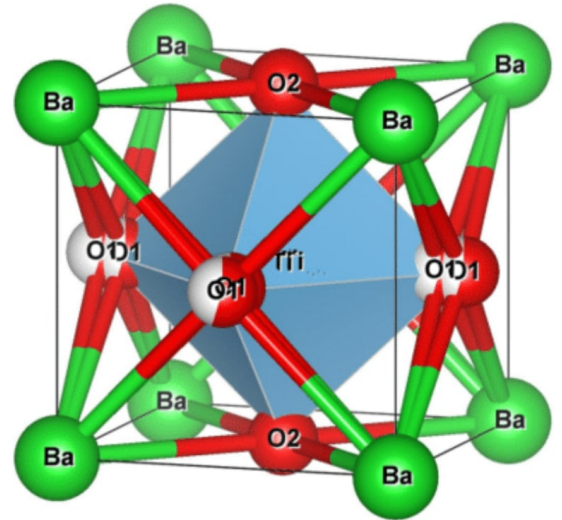


Figure 3: Lattice Structure of $BaTiO_3$

Procedure:

- Pull the spring-loaded probes upward, place the aluminium foil on the base plate and let it rest.
- Put the sample (BaTiO_3) on the foil such that one of the probes is in contact with the upper surface of the sample, while the other would be in contact with the lower surface through aluminium foil.
- Connect the probe leads (capacitor terminals) to the main unit at the back as also

a Oscilloscope.

- Switch on the main unit. Set the frequency to 1 kHz and balance the bridge to see minimum amplitude displayed on the Oscilloscope. It may be necessary to choose a suitable value of C_4 to obtain the lowest amplitude displayed on the oscilloscope. Record the readings as suggested in the table below and continue with different frequencies up to 50 kHz.
- Calculations and plot a graph.

Observations and Calculations:

For BaTiO_3

Diameter (D): 10.65 mm

Area (A): 89.75×10^{-6}

Thickness (t): 2.24 mm

Permittivity of Space (ϵ_0) : 8.85×10^{-12} F/m or 8.85×10^{-3} pf/mm

$\epsilon = \frac{C}{C_0}$;

where,

$$C_0 = \frac{\epsilon_0 A}{t} = \frac{8.85 \times 10^{-12} \times 89.75 \times 10^{-6}}{2.36 \times 10^{-3}}$$

$$C_0 = 336.57 \times 10^{-15}$$

R_4 = Dial Reading

Standard values of C_2 & R_3 used for Schering bridge balancing are as follow:

$$C_1 = C_2 \left(\frac{R_4}{R_3} \right), \quad \text{where } C_2 = 1000 \text{ pf}, \quad R_3 = 3\text{k}$$

Freq. kHz	C_4 (pF)	R_4 (Ω)	C_1 (pF)	R_1 (Ω) -	Dielectric $\epsilon = \frac{C_1}{C_0}$	Dissipation $2\pi f C_1 R_1$
1	1150	1284	428	3450	1278.81	9.2E-03
3	1100	1256	418.67	3300	1250.92	2.61E-02
5	1100	1244	414.67	3150	1238.96	4.1E-02
7	950	1218	406	3000	1213.073	5.35E-02
10	950	1208	402.67	2850	1203.114	7.21E-02
15	500	1200	400	2700	1195.14	10.17E-02
20	500	1192	397.34	2500	1187.178	1.91E-02
25	350	1155	385	2400	1150.32	2.9E-02
30	300	1146	382	2250	1141.37	3.76E-02
35	300	1143	381	2100	1138.37	5.03E-02
40	300	1140	380	2050	1136.45	4.54E-02
45	250	1138	379	1950	1135.39	2.32E-02
50	250	1137	379	1800	1132.41	3.01E-02

Table 1: Variation of Capacitance parameters (C_1 and R_1) and Dielectric Constant as a function of Frequency

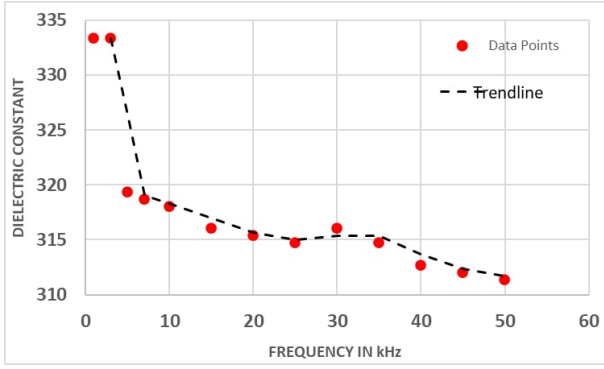


Figure 4: Plot of Dielectric Constant as a function of frequency for $BaTiO_3$

Freq. kHz	R_4 (k Ω)	C_1 (pF)
15	1961	653.6666667
20	1958	652.6666667
25	1956	652
30	1952	650.6666667
35	1948	649.3333333
40	1946	648.6666667
45	1938	646
50	1932	644

Table 3: Variation of Capacitance of Disc Ceramic as a function of Frequency

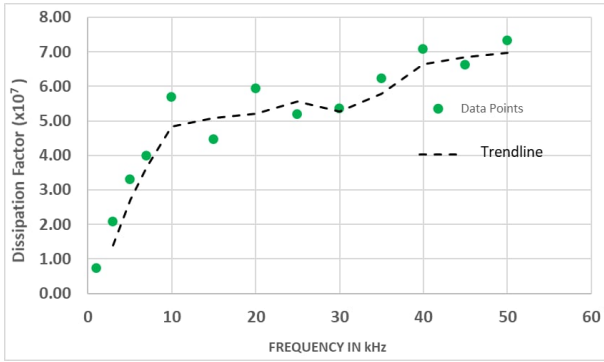


Figure 5: Plot of Dissipation Factor as a function of frequency $BaTiO_3$

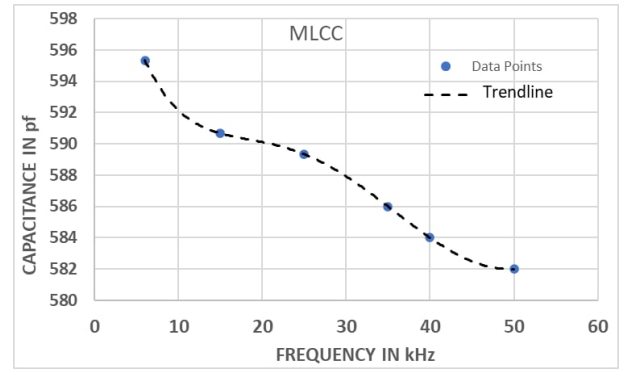


Figure 6: Plot of Capacitance as a function of frequency (MLCC)

Freq(KHz)	R_4	C_1
1	2148	716
3	2110	703.3333333
5	2100	700
7	2071	690.3333333
25	2068	689.3333333
30	2059	686.3333333
35	2055	685
50	2040	680

Table 2: Variation of Capacitance of MLCC as a function of Frequency

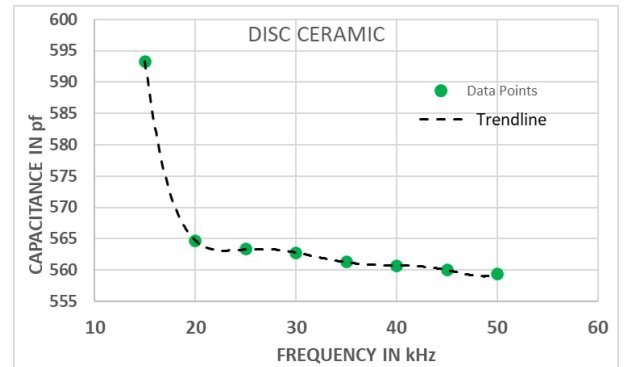


Figure 7: Plot of Capacitance as a function of frequency (Disc)

Temperature dependence of dielectric constant at different frequency

Temperature	Operating Frequency – 5kHz			Operating Frequency – 15kHz		
$^{\circ}C$	R_4 (k Ω)	C_1 (pF)	Dielectric $\epsilon = \frac{C_1}{C_0}$	R_4 (k Ω)	C_1 (pF)	Dielectric $\epsilon = \frac{C_1}{C_0}$
80	1171	390.33	1,166.26	1175	391.67	1,170.25
85	1191	397.00	1,186.18	1189	396.33	1,184.19
90	1210	403.33	1,205.11	1200	400.00	1,195.15
95	1220	406.67	1,215.07	1210	403.33	1,205.11
100	1224	408.00	1,219.05	1214	404.67	1,209.09
105	1226	408.67	1,221.04	1224	408.00	1,219.05
110	1235	411.67	1,230.00	1230	410.00	1,225.03
120	1310	436.67	1,304.70	1280	426.67	1,274.82
130	1376	458.67	1,370.43	1358	452.67	1,352.51
135	1390	463.33	1,384.38	1372	457.33	1,366.45
140	1410	470.00	1,404.30	1400	466.67	1,394.34
145	1370	456.67	1,364.46	1365	455.00	1,359.48
150	1335	445.00	1,329.60	1340	446.67	1,334.58
155	1310	436.67	1,304.70	1316	438.67	1,310.68
160	1275	425.00	1,269.84	1285	428.33	1,279.80
170	1248	416.00	1,242.95	1200	400.00	1,195.15

Table 4: Variation of dielectric with Temperature for 5 & 15 kHz

Temperature	Operating Frequency – 25kHz			Operating Frequency – 35kHz		
$^{\circ}C$	R_4 (k Ω)	C_1 (pF)	Dielectric $\epsilon = \frac{C_1}{C_0}$	R_4 (k Ω)	C_1 (pF)	Dielectric $\epsilon = \frac{C_1}{C_0}$
80	1169	389.67	1,164.27	1166	388.67	1,161.28
85	1180	393.33	1,175.23	1181	393.67	1,176.22
90	1198	399.33	1,193.15	1196	398.67	1,191.16
95	1208	402.67	1,203.11	1206	402.00	1,201.12
100	1220	406.67	1,215.07	1210	403.33	1,205.11
105	1228	409.33	1,223.03	1218	406.00	1,213.07
110	1229	409.67	1,224.03	1224	408.00	1,219.05
120	1272	424.00	1,266.86	1256	418.67	1,250.92
130	1340	446.67	1,334.58	1330	443.33	1,324.62
135	1375	458.33	1,369.44	1365	455.00	1,359.48
140	1390	463.33	1,384.38	1380	460.00	1,374.42
145	1356	452.00	1,350.52	1359	453.00	1,353.50
150	1339	446.33	1,333.58	1341	447.00	1,335.58
155	1318	439.33	1,312.67	1326	442.00	1,320.64
160	1270	423.33	1,264.86	1235	411.67	1,230.00
170	1179	393.00	1,174.23	1160	386.67	1,155.31

Table 5: Variation of dielectric with Temperature for 25 & 35 kHz

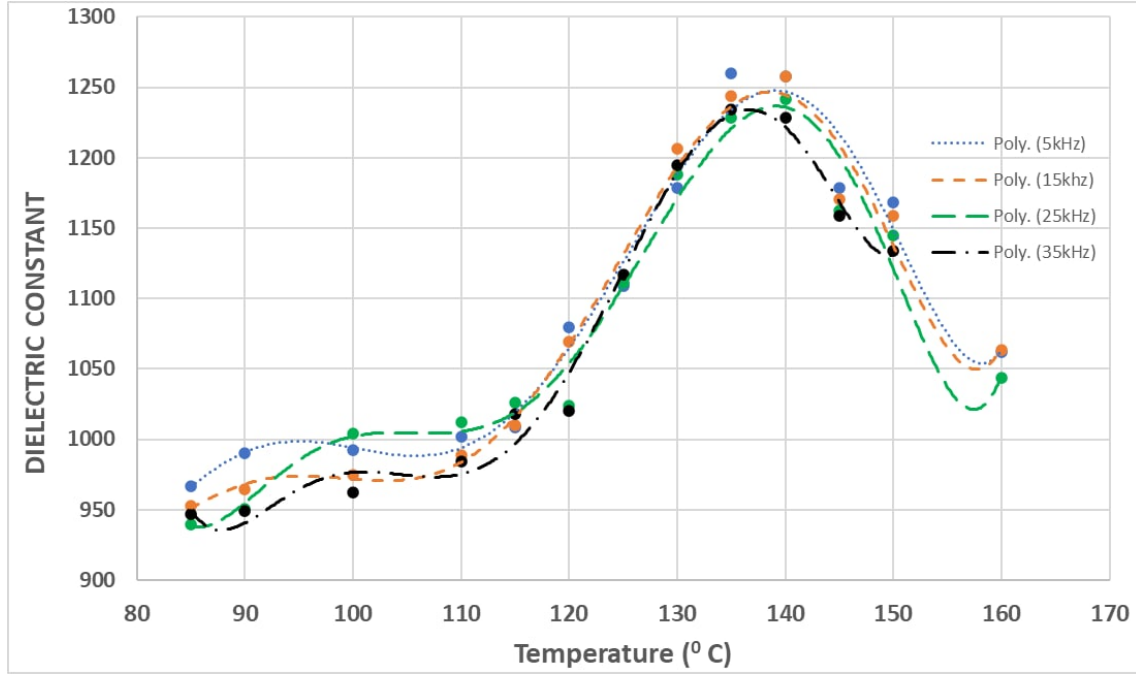


Figure 8: Typical plot of Dielectric Constant as a function of Temperature for various Frequencies

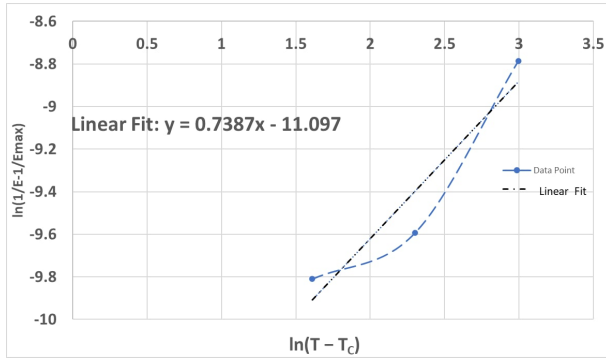


Figure 9: Plot of Diffuseness Parameter

Results

- The dielectric Constant for $BaTiO_3$, MLCC, Disc Ceramic decreased with increasing frequency (i.e. inverse relation) before reaching a plateau, which is the expected behaviour.
- The dielectric Constant for $BaTiO_3$ increases till curie point after which it decreases indicating para electric phase. This behaviour is independent of frequency.
- The curie temperature for 5kHz, 15kHz and 35kHz came out to be: $135^{\circ}C$. While

the curie temperature for 25kHz came out to be: $140^{\circ}C$, this could be due to parallax error in taking the readings.

- The Dielectric Constant for $BaTiO_3$ varies within the range 939-1065
- The best fit line for Diffuseness Parameter of $BaTiO_3$ came out to be:

$$y = 0.7387x - 11.097$$

Source of Error:

- Loose Connections will make bridge balancing very difficult.
- The sample is placed improperly in the PID controlled oven.
- Parallax error while taking the readings.

Acknowledgement

I, along with my experiment partner, Simran, would like to acknowledge the gesture of the other group, Sarthak & Sarbajit, for lending us their setup as our equipment was not properly functioning at the moment.