Study of phase transition in $BaTiO_3$

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For $BaTiO_3$, we investigated the phase transition from the ferroelectric to the paraelectric state and the frequency and temperature dependence of the dielectric constant in the aforementioned experiment. We also noticed the frequency dependence of capacitance for multilayer and disc ceramic capacitors operating at room temperature. We determine the balancing capacitance to arrive at the balancing resistance of the sample at various temperature settings using the Schering bridge, and we plot the result to confirm with the theoretical overview. We discover that the $BaTiO_3$ sample's curie temperature is $140°C$, which is higher than the value predicted by theory and indicating the presence of impurities in the sample. Additionally, the computed diffuseness parameter ranges from 1 to 2 for all frequencies.

I. THEORY

The dielectric constant, also known as permittivity, is a complicated number whose real portion, (ϵ'), represents energy stored and whose imaginary part, (ϵ''), represents energy lost. It may alternatively be described as the difference between the capacitance of a capacitor that contains a dielectric and a capacitor that is similar but empty. The material's capacity to release the absorbed electromagnetic energy is represented by the dielectric loss factor, (ϵ''). EM waves tend to penetrate samples less deeply the greater their dissipation capacity.

The real part of permittivity depends on the polarizability of the material. The total polarizability can be separated into four parts:

1. **Electronic Polarization:** because of the nucleus's displacement with respect to the electron cloud that surrounds it. The displacement induces charges on the atom, leading to the development of a dipole moment. The mechanism operates quickly and continues to function up to optical frequencies (1013-1015 Hz). takes place in neutral atoms.

2. **Ionic Polarization:** It happens in solids with ionic bonding when the net dipole is zero because of the crystal symmetry. Ions are moved out of their equilibrium position by an external field, which induces a dipole moment. This mechanism operates at low frequencies and is comparatively sluggish. Only losses are introduced into a system through ionic conduction.

3. **Dipolar/Orientation Polarization:** It happens in molecules with an ongoing dipole moment. When an external electric field is introduced, randomly distributed dipoles align, increasing the overall polarization. This process operates below 109 Hz and is slower than ionic polarization.

4. **Space Charge Polarization:** This process happens when translating charge carriers become caught at the interfaces of these heterogeneous systems, such as in composite materials or when segregation happens in a material with incompatible chemical sequences. Positive and negative space charges arise in the bulk of the material or at the interfaces between various materials as a result of the separation of mobile charge carriers under an electric field. This method works well in the audio frequency spectrum.
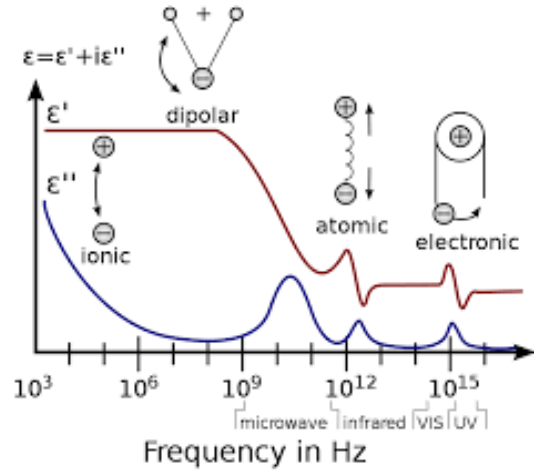

FIG. 1: Real and Imaginary part of permittivity (dielectric constant) as a function of frequency

A. Variation of the dielectric constant in alternating fields

We are aware that an electric field causes a dielectric to become polarised. In a field that changes direction, the polarisation will likewise change direction to match the new field. The transfer of charges or the rotation of dipoles requires time, therefore this cannot happen instantly.

The average dipole orientation adjusts over a particular period of time known as the relaxation time when the field is altered. 10 to 11 seconds are typical relaxing times. As a result, if the electric field alternates directions at a frequency greater than 1011 Hz, the polarization mechanism no longer contributes to the polarisation of the dielectric because the dipole orientation is unable to "keep up" with the alternating field and cannot maintain its alignment with it. The polarization process stops helping to polarise the dielectric at higher frequencies because the flow of charge cannot keep up with the alternating field. As frequency rises, the material's net polarisation decreases because it no longer contributes to the overall polarisation, and as a result, its dielectric constant decreases.

B. Variation of the dielectric constant in Temperature

The electrostatic forces generated by the field cause the molecules to rotate and align with it. However, due to the thermal motion the molecules are experiencing, not all of them are perfectly aligned with the field.

Because the molecules have more thermal energy as the temperature rises, the amplitude of random thermal motion also increases. As a result, the molecules are less tightly aligned with one another, which results in less orientation polarisation of the material and a lower dielectric constant. This indicates that the range of departure from a perfect alignment with the external electric field is higher.

As the temperature is reduced, the dielectric constant does not, however, rise continuously. At phase boundaries, the dielectric constant will abruptly alter. This is because during a phase transition, the structure alters, and as we've shown above, the structure has a significant impact on the dielectric constant.

C. $BaTiO^3$ Properties

Perovskite substance barium titanate has a relatively high dielectric constant at ambient temperature. the name of a group of substances that have the perovskite crystal structure, which is the same as that of calcium titanium oxide ($CaTiO_3$). Perovskite has the following structure. While B-site cations sit in the centre of the body, A-site cations take up the corners of a cube. On the faces are three oxygen atoms per cell.
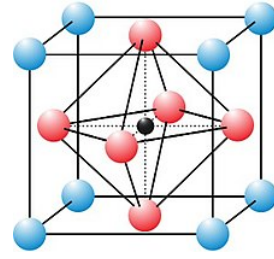

FIG. 2: Perovskite Structure

Below and beyond its $120°C$ Curie point, barium titanate exhibits a paraelectric cubic phase and a ferroelectric tetragonal phase. The contaminants in a sample and the synthesis method have an impact on the Curie point temperature of that sample. In the paraelectric cubic phase, the centres of positive charges (Ba^{2+}, Ti^{4+}) coincide with the centres of negative charges ($O^{-2}ion$). However, when the temperature is cooled below Tc, we observe a tetragonal phase in which the centres of the Ba^{2+} and Ti^{4+} ions are dislocated in relation to the $O^{-2}ion$, resulting in the formation of electric dipoles. As a result, the of BaTiO3 rises until T_c and reaches its maximum value at $T = T_c$ due to the divergence of susceptibility at that point. After crossing this temperature it starts decreasing due to the formation of the cubic phase.

D. Study of diffuseness parameter

The diffuseness parameter δ is defined as the slope of the $\log(\frac{1}{\epsilon} - \frac{1}{\epsilon_c})$ vs $\log(\frac{1}{T} - \frac{1}{T_c})$ plot where ϵ is the dielectric constant at a temperature T ¿ T_c, ϵ_c is the maximum value of the dielectric constant at the Curie temperature T_c. δ is expected to lie between 1 and 2.
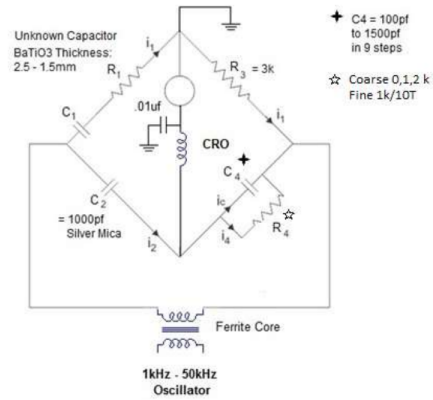
II. EXPERIMENTAL SETUP

FIG. 3: Schering Bridge

A frequency dependence of dielectric constant. The main unit is used in the setup to measure capacitance at frequencies between 1kHz and 50kHz. A built-in oscillator and a Schering Bridge Figure 3 are used to accomplish this. Here, the value of the unknown capacitance ($BaTiO_3$) C1 is to be ascertained by using R1 as a series electrical resistance. C2 is a typical 1000 pf silver mica capacitor. C4 is a variable capacitor with Coarse and Fine values. The metal film resistance, R3, is 3.0 k. R4 is a variable resistance with "Coarse" and "Fine" 1k/10T potentiometers in series and parallel to C4, respectively. From the bridge balance condition we get:

$$R_1 = \frac{R_3 C_4}{C_2}$$

and,

$$C_1 = \frac{R_4 C_2}{R_3}$$

Here C1 is the unknown capacitor and R1 is the equivalent series resistance reflecting losses. The loss factor (dissipation factor) can be defined as:

$$\tan \delta = \frac{\epsilon'}{\epsilon''}$$

from setup it can be calculated as:

$$\tan \delta = \omega C_1 r_1 = 2\pi f C_1 R_1$$

III. OBSERVATIONS AND CALCULATIONS

A. Frequency dependence of Dielectric Constant/Capacitance

1. $BaTiO_3$

- Permittivity of Space $(\epsilon_0) = 8.85 \times 10^{-3} pF mm^{-1}$

- Thickness $(t) = 1.45 mm$

- Diameter $= 10 mm$

- Area $(A) = 78.53 mm^2$

- $R_3 = 3k\Omega$

- $C_2 = 1000 pF$

- $C = \frac{\epsilon A}{t}$

frequency	c4	r4	c1	r1	ϵ	dissipation
kHz	pF	kΩ	pF	KΩ		factor
1	1150	1.10	366.67	3.45	737.76	0.0079
3	1050	1.00	333.33	3.15	670.69	0.0197
5	1000	0.98	326.67	3.00	657.28	0.0307
10	900	0.98	326.67	2.70	657.28	0.0553
15	800	0.96	320.00	2.40	643.86	0.0723
20	500	0.96	320.00	1.50	643.86	0.0602
25	300	0.94	313.33	0.90	630.45	0.0442
30	200	0.94	313.33	0.60	630.45	0.0354
35	150	0.92	306.67	0.45	617.03	0.0303
40	100	0.90	300.00	0.30	603.62	0.0226
50	100	0.90	300.00	0.30	603.62	0.0282

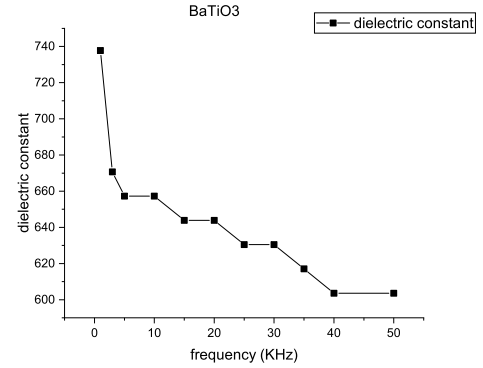TABLE I: observed capacitance value for $BaTiO_3$ at different frequency

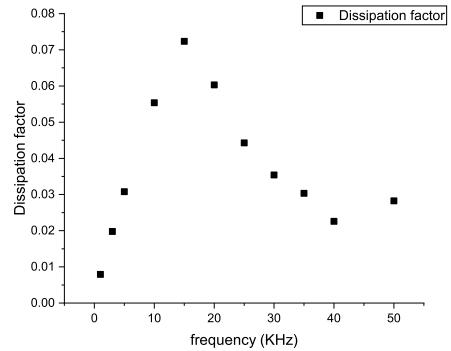FIG. 4: Dielectric constant vs frequency graph for $BaTiO_3$

FIG. 5: Dissipation factor vs frequency graph for $BaTiO_3$

2. Multi-layer Ceramic Capacitor (MLCC)

frequency	c4	r4	c1
kHz	pF	kΩ	pF
1	1150	1.938	646.00
3	900	1.936	645.33
5	600	1.934	644.67
10	200	1.932	644.00
15	150	1.930	643.33
20	100	1.928	642.67
25	100	1.926	642.00
30	100	1.922	640.67
35	100	1.918	639.33
40	100	1.906	635.33
50	50	1.902	634.00

TABLE II: observed capacitance value for MLCC at different frequency

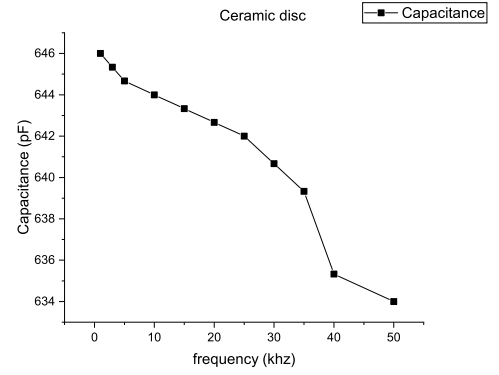FIG. 7: capacitance vs frequency graph for DCC

FIG. 6: capacitance vs frequency graph for MLCC

B. Study of the temperature dependence of dielectric constant at different frequencies using Barium Titanate Sample

3. Disc Ceramic Capacitor (DCC)

frequency	c4	r4	c1
kHz	pF	kΩ	pF
1	1150	0.648	216.00
3	1100	0.588	196.00
5	1050	0.568	189.33
10	600	0.568	189.33
15	400	0.564	188.00
20	100	0.560	186.67
25	50	0.558	186.00
30	50	0.554	184.67
35	50	0.552	184.00
40	50	0.552	184.00
50	50	0.550	183.33

TABLE III: observed capacitance value for DCC at different frequency

Temperature	R	c(pF)	C1	ϵ
°C	KΩ	pF	pF	
50	1.111	1150	370.33	745.14
60	1.118	750	372.67	749.83
70	1.146	700	382.00	768.61
80	1.16	750	386.67	778.00
90	1.182	750	394.00	792.76
100	1.22	750	406.67	818.24
110	1.25	750	416.67	838.36
120	1.3	750	433.33	871.90
130	1.384	800	461.33	928.24
140	1.47	800	490.00	985.92
150	1.38	800	460.00	925.55
160	1.26	800	420.00	845.07
170	1.2	800	400.00	804.83
180	1.12	650	373.33	751.17

TABLE IV: observed capacitance value for $BaTiO_3$ at different temperature at 5kHz

Temperature	R	c(pF)	C1	ϵ
°C	KΩ	pF	pF	
50	1.09	200	363.33	731.05
60	1.14	200	380.00	764.59
70	1.13	200	376.67	757.88
80	1.152	200	384.00	772.64
90	1.182	200	394.00	792.76
100	1.198	200	399.33	803.49
110	1.232	200	410.67	826.29
120	1.28	200	426.67	858.48
130	1.36	200	453.33	912.14
140	1.466	200	488.67	983.23
150	1.4	200	466.67	938.97
160	1.32	150	440.00	885.31
170	1.26	150	420.00	845.07
180	1.2	150	400.00	804.83

TABLE V: observed capacitance value for $BaTiO_3$ at different temperature at 15kHz

Temperature	R	c(pF)	C1	ϵ
°C	KΩ	pF	pF	
50	1.08	100	360.00	724.35
60	1.14	100	380.00	764.59
70	1.18	100	393.33	791.42
80	1.142	100	380.67	765.93
90	1.172	100	390.67	786.05
100	1.186	100	395.33	795.44
110	1.224	100	408.00	820.93
120	1.266	100	422.00	849.09
130	1.342	100	447.33	900.07
140	1.39	100	463.33	932.26
150	1.36	100	453.33	912.14
160	1.28	50	426.67	858.48
170	1.2	50	400.00	804.83
180	1.14	50	380.00	764.59

TABLE VI: observed capacitance value for $BaTiO_3$ at different temperature at 25kHz

Temperature	R	c(pF)	C1	ϵ
°C	KΩ	pF	pF	
50	1.07	50	356.67	717.63
60	1.08	50	360.00	724.34
70	1.09	50	363.33	731.05
80	1.13	50	376.67	757.88
90	1.16	50	386.67	778.00
100	1.18	50	392.00	788.73
110	1.21	50	403.33	811.53
120	1.25	50	418.00	841.04
130	1.32	50	439.33	883.97
140	1.36	50	453.33	912.13
150	1.32	50	440.00	885.31
160	1.20	50	400.00	804.82
170	1.18	50	393.33	791.41
180	1.14	50	380.00	764.58

TABLE VII: observed capacitance value for $BaTiO_3$ at different temperature at 35kHz

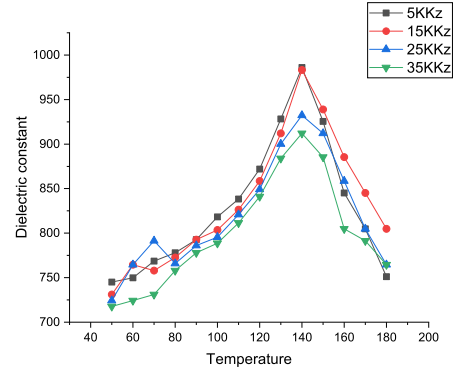

FIG. 8: Dielectric constant vs Temperature T($°C$)

1. *Study of diffuseness parameter at a single frequency*

$\log(\frac{1}{T} - \frac{1}{T_c})$	$\log(\frac{1}{\epsilon} - \frac{1}{\epsilon_c})$			
1.00	-4.19	-4.32	-4.63	-4.48
1.30	-3.77	-3.95	-4.04	-3.84
1.48	-3.64	-3.78	-3.77	-3.78
1.60	-3.50	-3.65	-3.63	-3.67

TABLE VIII: Diffuseness parameter for $BaTiO_3$ at different temperature and frequency
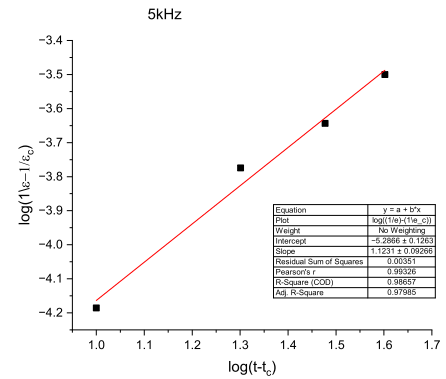

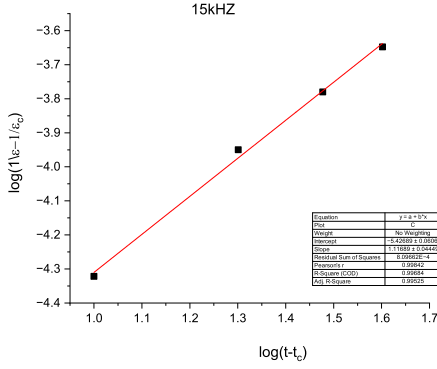FIG. 9: $\log(\frac{1}{\epsilon} - \frac{1}{\epsilon_c})$ vs $\log(\frac{1}{T} - \frac{1}{T_c})$ at 5KHz

FIG. 10: $\log(\frac{1}{\epsilon} - \frac{1}{\epsilon_c})$ vs $\log(\frac{1}{T} - \frac{1}{T_c})$ at 15KHz
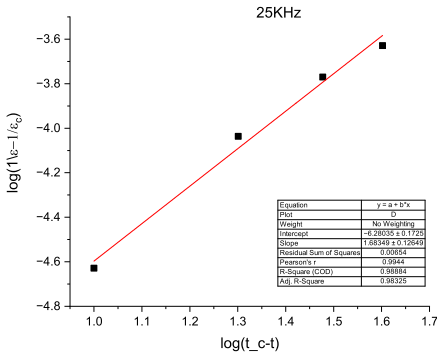

FIG. 11: $\log(\frac{1}{\epsilon} - \frac{1}{\epsilon_c})$ vs $\log(\frac{1}{T} - \frac{1}{T_c})$ at 25KHz
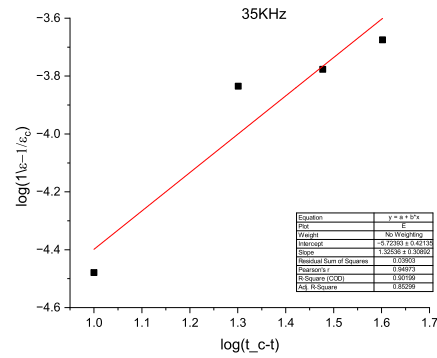

FIG. 12: $\log(\frac{1}{\epsilon} - \frac{1}{\epsilon_c})$ vs $\log(\frac{1}{T} - \frac{1}{T_c})$ at 35KHz

IV. ERROR ANALYSIS

Error in Curie temperature:

$$\delta T_c = \quad \mathrm{mod} \; \frac{T_c(theoretical) - T_c(observed)}{T_c(theoretical)}$$

$$\delta T_c\% = 16.6\%$$

Error in diffuseness parameter δ = error in slope.

- For frequency = 5 kHz: error in slope dδ = 0.092

- For frequency = 15 kHz: error in slope dδ = 0.044

- For frequency = 25 kHz: error in slope dδ = 0.1264

- For frequency = 35 kHz: error in slope dδ = 0.306

V. RESULTS AND DISCUSSION

- Curie temperature $T_c = 140°C$ From the graphs show the diffuseness parameter (δ) for each frequency and the corresponding error.

- For frequency = 5 kHz: slope of the line (δ) = 1.1231

- For frequency = 15 kHz: slope of the line (δ) = 1.1689

- For frequency = 25 kHz: slope of the line (δ) = 1.68349

- For frequency = 35 kHz: slope of the line (δ) = 1.32536

- The plots of dielectric constant or capacitance for $BaTiO_3$, MLCC and DCC matched reasonably with the theoretical expectations and we can observe that the capacitance/dielectric constant decreases with an increase in the frequency of the external field.

- For the temperature dependence plot, we find that is plot is similar to the expected plot however, curie temperature is shifted, and The decrease occurs after $140°C$. Temperature. This significant difference in curie temperature can be due to a broken and thick sample of $BaTio_3$ and impurities. Also, as the oven temperature was increasing rapidly, the temperature at the reading time might not be accurate.

- The plots for the diffuseness parameters show minimum deviation from the linear curve. The observed value is more than 1, where the theoretically expected is between 1 and 2; thus, the observation is correct.

- Error in curie temperature is large and can be minimized by controlling the temperature properly and optimum size of $BaTiO_3$.

A. Scope of Error:

- Impurities in the sample which increase the curie temperature.

- Improper contact of the sample with the probes.

- Loose connections of the cables with the oscilloscope and Schering bridge apparatus.

- Taking a sample with high sample resistance can cause the variable resistor to saturate before Curie temperature, resulting in a different plot shape than the expected one.

- Taking readings above the minimum possible voltage amplitude can give error in variable resistance.

VI. CONCLUSION

In this experiment, we studied the frequency and temperature variation of dielectric constant and capacitance of $BaTiO_3$, MLCC and DCC, which decreases with an increase in frequency. The dielectric constant decreases as the relaxation time of different polarization mechanics cause the slower alignment of polarisation vectors in the direction of the electric field as compared to the frequency of the electric field, thus decreasing the total polarisation.

We also study the phase transition of $BaTiO_3$. We observe that the dielectric constant of ($BaTiO_3$) increases up to the Curie temperature then decreases after it validates our theoretical prediction. This indicates that Barium Titanate behaves as a ferroelectric material(existing in a tetragonal phase with a net dipole moment) below the Curie temperature and as a paraelectric (existing in a cubic phase without a net dipole moment) above Tc. Since the Curie temperature is the same for each frequency curve, we can conclude that the Curie temperature is independent of the frequency of the applied electric field.

As the observed curie temperature is different from the theoretical value, we can say that sample contains impurities leading to this increase.

We noted that the variable resistance didn't change much with frequency Changing the capacitance of the variable capacitor only affected the amplitude of the signal on the oscilloscope. However, since the resistance of the the sample is not required, we can conclude that the balancing resistance is more or less independent of C.