

Study of Frequency and Temperature Dependence of Dielectric Constant and Ferroelectric to Paraelectric Phase Transition of BaTiO₃

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We also noticed the frequency dependence of capacitance for BaTiO₃ and multilayer and disc ceramic capacitors operating at room temperature. We determine the balancing capacitance to arrive at the balancing resistance of the sample at increasing temperatures using a Schering bridge setup to find out the Curie temperature of the sample, which came out to be around 135°. Additionally, we also computed the diffuseness parameter for the samples which ranges from 1 to 2 for all frequencies.

I. THEORY

The dielectric constant of a material, also known as its permittivity (ϵ), 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 ($10^{13} - 10^{15}$ 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 10^9 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 seg-

regation 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, because charge carriers require time to build up at interfaces.

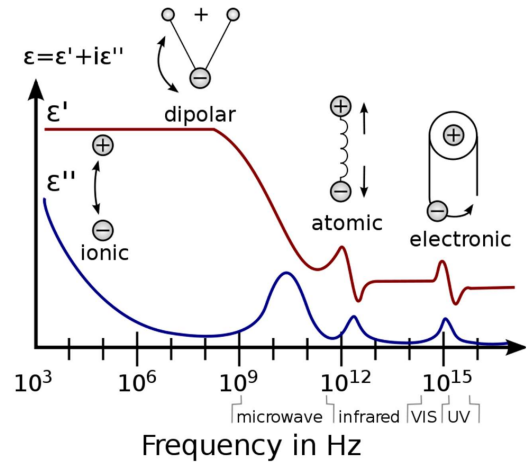


FIG. 1: Real and Imaginary part of permittivity (dielectric constant) as a function of frequency

Variation of the dielectric constant with 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. Around 10^{-11} s is the typical relaxation time. As a result, if the electric field alternates directions at a frequency greater than 10^{11} 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.

Only the fastest mechanism (electronic polarization) contributes, as the slower mechanisms (ionic, orientational, and space charge) cannot follow rapid field changes. 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.

The ratio ϵ''/ϵ' (loss tangent or $\tan \delta$) is a crucial parameter in microwave heating, as it quantifies the efficiency of converting microwave energy into heat. A higher ϵ''/ϵ' means more effective heating.

Variation of the dielectric constant with 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.

A. The Dissipation factor

To quantify the broadening of the phase transition, the diffuseness parameter, δ can be written as the slope of the $\log\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_C}\right)$ vs. $\log\left(\frac{1}{T} - \frac{1}{T_C}\right)$ plot,

$$\log\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_C}\right) = \delta \cdot \log\left(\frac{1}{T} - \frac{1}{T_C}\right) \quad (1)$$

where ϵ is the dielectric constant at a temperatures $T > T_C$, ϵ_C is the maximum value of the dielectric constant at the Curie temperature T_C .

B. Properties of BaTiO₃

Perovskite substances like Barium Titanate or CaTiO₃ have a relatively high dielectric constant at ambient temperature. In the perovskites crystal 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.

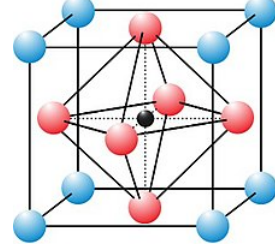


FIG. 2: Perovskite Structure

The lattice constant of perovskites is typically around 4 Å due to the rigid oxygen octahedral network and the oxygen ionic radius of 1.35 Å. A key advantage of the perovskite structure is the ability to substitute various cations on the A and B sites without significantly altering the structure. This allows for the formation of complete solid solutions, enabling the manipulation of material properties like Curie Temperature and dielectric constant through small cation substitutions.

Below and beyond its 120°C Curie point, barium titanate exhibits a paraelectric cubic phase and a ferroelectric tetragonal phase respectively. 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 T_C , 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. The spontaneous polarization vanishes as the centers of positive and negative charges coincide. After crossing this temperature it starts decreasing due to the formation of the cubic phase.

II. EXPERIMENTAL SETUP

Apparatus

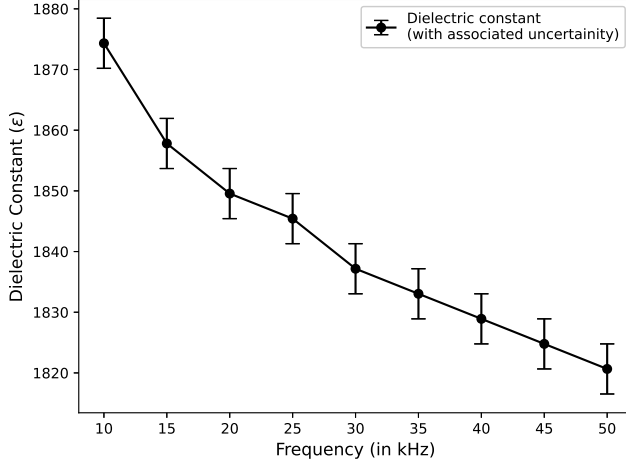
1. BaTiO₃ capacitor sample
2. Standard Multilayer Ceramic Capacitor
3. Disc Ceramic Capacitor
4. Aluminium plate
5. Oscilloscope

Similarly the error in δ can be calculated from Eq. 6 as

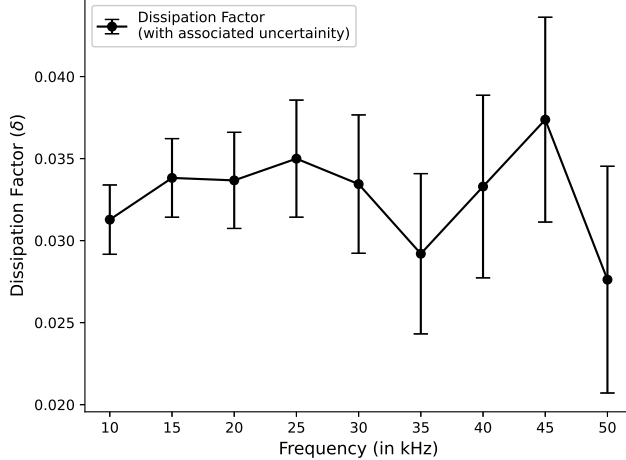
$$\frac{\Delta\delta}{\delta} = \sqrt{\left(\frac{\Delta C_1}{C_1}\right)^2 + \left(\frac{\Delta R_1}{R_1}\right)^2 + \left(\frac{\Delta f}{f}\right)^2} \quad (8)$$

$$= \sqrt{\left(\frac{\Delta R_4}{R_4}\right)^2 + \left(\frac{\Delta C_4}{C_4}\right)^2 + \left(\frac{\Delta f}{f}\right)^2} \quad (9)$$

where $\Delta C_4 = 50$ pF and $\Delta f = 1$ kHz.



(a) Dielectric constant vs frequency



(b) Dissipation factor vs frequency

FIG. 4: Frequency dependent plots for BaTiO₃

These observations show a noticeable decline in the dielectric constant as the frequency increases. This behavior is expected, as at higher frequencies, the polarization response of BaTiO₃ becomes insufficient to keep up with the swiftly varying electric field, resulting in a reduced effective dielectric constant.

The curve for dissipation/loss factor however demonstrates a non-monotonic trend. This could be due to the

multiple energy dissipation mechanisms, such dipolar relaxation and domain wall dynamics, contributing differently across the frequency spectrum. It is also to be noted that due to the low precision in the variation of C_4 , the error bars associated with the dissipation factor are too large to make any proper remarks.

2. Multi-layer Ceramic Capacitor (MLCC)

Similarly, we now study the variation of dielectric constant with frequency for a standard MLCC. Here, the DC capacitance of the capacitor was measured to be, $C_0 = 473.1$ pF.

f (kHz)	C_4 (pF)	R_4 (k Ω)	C_1 (pF)	R_1 (Ω)	ϵ	δ
10	600	0.590	590	600	1.247	0.0222
15	450	0.589	589	450	1.245	0.0249
20	350	0.587	587	350	1.241	0.0257
25	250	0.587	587	250	1.241	0.0230
30	250	0.586	586	250	1.239	0.0275
35	200	0.586	586	200	1.239	0.0257
40	200	0.586	586	200	1.239	0.0294
45	150	0.584	584	150	1.234	0.0247
50	150	0.584	584	150	1.234	0.0274

TABLE II: Measured values of ϵ for a standard MLCC

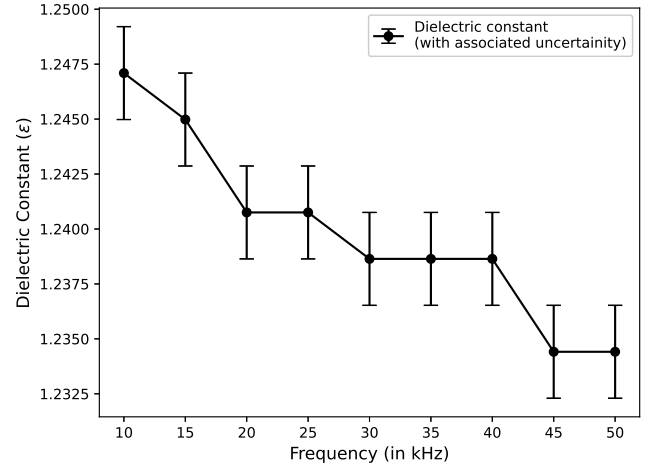


FIG. 5: Dielectric constant (ϵ) vs frequency graph for MLCC

The above plot shows the general trend in the variation of ϵ with frequency, which is decreasing as expected. The plateaus might indicate a shift in the dominant polarization mechanism, leading to a brief period of capacitance stability before it begins to decline further.

We have not plotted the variation in the dissipation factor as the values obtained showed no general trend along with the associated error bars being of the order of the variations (see Fig. 4b).

3. Disc Ceramic Capacitor (DCC)

We now study the variation of dielectric constant with frequency for a standard DCC. Here, the standard capacitance of the capacitor was measured to be, $C_0 = 423.3$ pF.

f (kHz)	C_4 (pF)	R_4 (k Ω)	C_1 (pF)	R_1 (Ω)	ϵ	δ
10	550	0.526	526	550	1.243	0.0181
15	400	0.524	524	400	1.238	0.0197
20	300	0.524	524	300	1.238	0.0197
25	250	0.523	523	250	1.236	0.0205
30	200	0.522	522	200	1.233	0.0196
35	200	0.522	522	200	1.233	0.0229
40	150	0.522	522	150	1.233	0.0196
45	150	0.521	521	150	1.231	0.0220
50	150	0.520	520	150	1.228	0.0244

TABLE III: Measured values of ϵ for a standard DCC

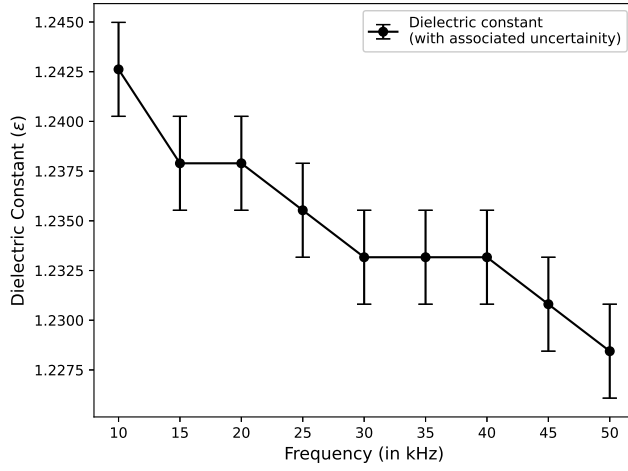


FIG. 6: Dielectric constant (ϵ) vs frequency graph for DCC

As expected, the above plot shows the general decreasing trend in the variation of ϵ with frequency, as explained in the previous part for MLCC.

Again, we have not plotted the variation in the dissipation factor as the values obtained showed no general trend along with the associated error bars being of the order of the variations (see Fig. 4b).

B. Temperature dependence of dielectric constant at different frequencies using BaTiO₃

In the second part of the experiment, we obtained data to study the variation of dielectric constant of BaTiO₃ with temperature for various frequencies.

For this setup, the probe arrangement is mounted in suitable stand as before, which also hold the sample plate

and RTD (Resistance Temperature Detector) 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.

After setting the temperature in the oven, we wait around 10 minutes for the temperature to stabilise before taking any readings.

T (°C)	C_4 (pF)	R_4 (k Ω)	C_1 (pF)	R_1 (Ω)	ϵ
50	550	931	931	550	1921.80
60	600	946	946	600	1952.77
70	550	982	982	550	2027.08
80	700	1020	1020	700	2105.52
90	750	1084	1084	750	2237.63
100	900	1156	1156	900	2386.26
110	850	1282	1282	850	2646.35
120	900	1505	1505	900	3106.67
125	950	1658	1658	950	3422.50
130	800	1804	1804	800	3723.88
135	850	1922	1922	850	3967.46
140	700	1867	1867	700	3853.93
145	650	1742	1742	650	3595.90
150	550	1600	1600	550	3302.78
160	600	1369	1369	600	2825.94
170	700	1216	1216	700	2510.11

TABLE IV: Dielectric constant as a function of temperature for the frequency 10 kHz

T (°C)	C_4 (pF)	R_4 (k Ω)	C_1 (pF)	R_1 (Ω)	ϵ
50	250	914	914	250	1886.711
60	250	932	932	250	1923.867
70	250	963	963	250	1987.858
80	350	1002	1002	350	2068.363
90	350	1059	1059	350	2186.025
100	300	1130	1130	300	2332.585
110	400	1246	1246	400	2572.036
120	450	1450	1450	450	2993.14
125	400	1574	1574	400	3249.105
130	400	1706	1706	400	3521.584
135	400	1816	1816	400	3748.65
140	350	1764	1764	350	3641.31
145	400	1656	1656	400	3418.373
150	350	1548	1548	350	3195.435
160	350	1366	1340	350	2766.075
170	350	1190	1190	350	2456.439

TABLE V: Dielectric constant as a function of temperature for the frequency 25 kHz

T (°C)	C ₄ (pF)	R ₄ (kΩ)	C ₁ (pF)	R ₁ (Ω)	ε
50	200	908	908	200	1874.325
60	200	928	928	200	1915.61
70	200	954	954	200	1969.28
80	200	998	998	200	2060.106
90	300	1048	1048	300	2163.318
100	300	1120	1120	300	2311.943
110	300	1234	1234	300	2547.266
120	300	1431	1431	300	2953.92
125	300	1548	1548	300	3195.435
130	300	1673	1673	300	3453.465
135	300	1768	1768	300	3649.567
140	300	1738	1738	300	3587.64
145	250	1620	1620	250	3344.06
150	300	1521	1521	300	3139.701
160	300	1296	1296	300	2675.248
170	300	1178	1178	300	2431.669

TABLE VI: Dielectric constant as a function of temperature for the frequency 35 kHz

T (°C)	C ₄ (pF)	R ₄ (kΩ)	C ₁ (pF)	R ₁ (Ω)	ε
50	150	902	902	150	1861.94
60	150	922	922	150	1903.224
70	150	946	946	150	1952.766
80	150	990	990	150	2043.592
90	250	1036	1036	250	2138.547
100	250	1116	1116	250	2303.686
110	300	1216	1216	300	2510.109
120	250	1406	1406	250	2902.314
125	300	1528	1528	300	3154.151
130	200	1632	1632	200	3368.831
135	200	1744	1744	200	3600.025
140	200	1706	1706	200	3521.584
145	200	1589	1589	200	3280.069
150	250	1500	1500	250	3096.352
160	200	1280	1280	200	2642.22
170	250	1160	1160	250	2394.512

TABLE VII: Dielectric constant as a function of temperature for the frequency 50 kHz

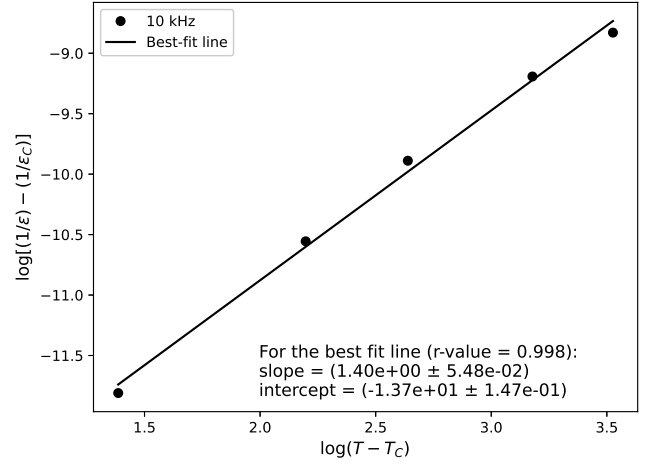
Fig. 7 shows the variation in the dielectric constant with temperature, at four different frequencies. The curves are nearly symmetrical, and the dielectric constant peaks at a specific temperature (the Curie temperature). While the magnitude of the dielectric constant increases as the frequency decreases (as explained in the previous sections), the difference is not quite noticeable at this scale.

The Curie temperature is found to be around 135 °C from the graph. Since we took measurements only at every °C, the standard deviation associated with the readings must be 5°C.

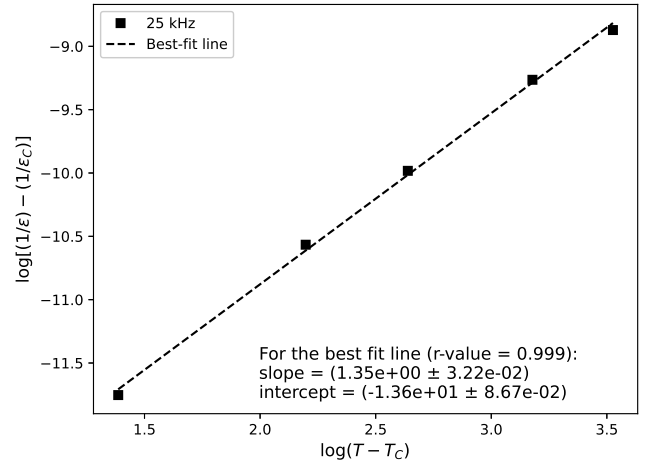
Study of diffuseness parameter at a single frequency

Diffuseness parameter can be calculated as the slope of $\log\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_c}\right)$ and $\log(T - T_C)$, for all values above the

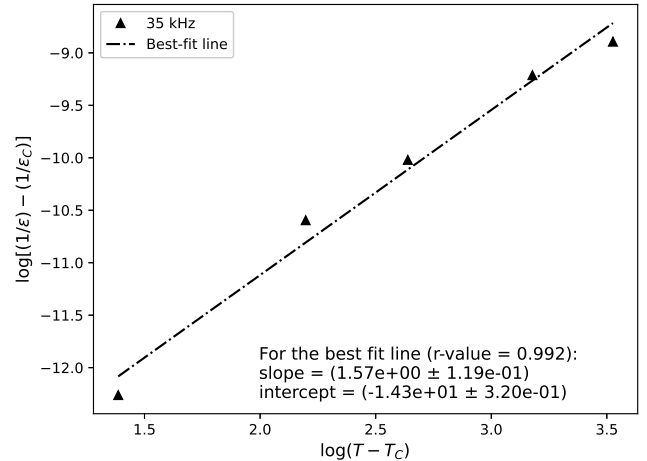
Curie Temperature. ϵ_c is the maximum dielectric constant, which is obtained at the Curie temperature. We have plotted the required quantities for all four values of frequencies below.



(a) 10 kHz



(b) 25 kHz



(c) 35 kHz

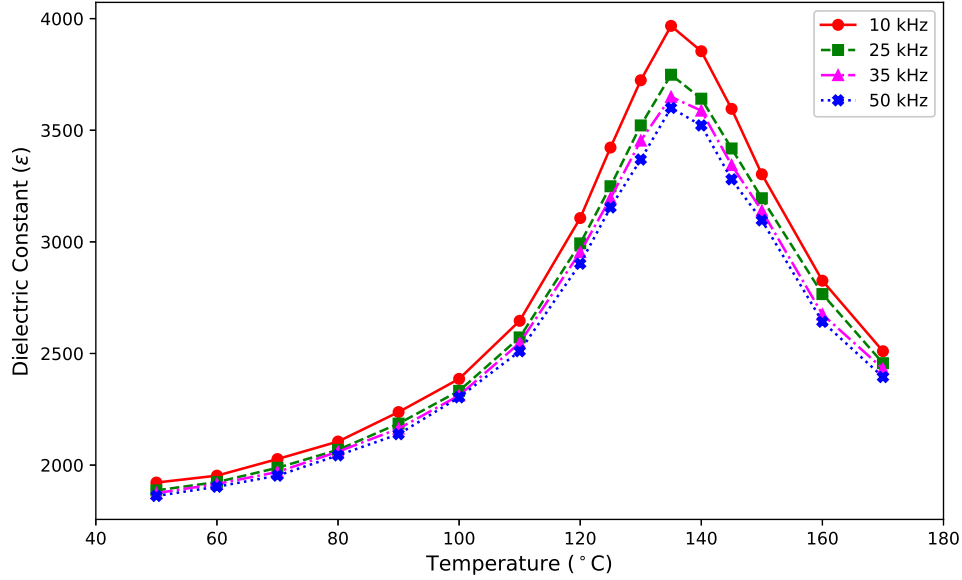
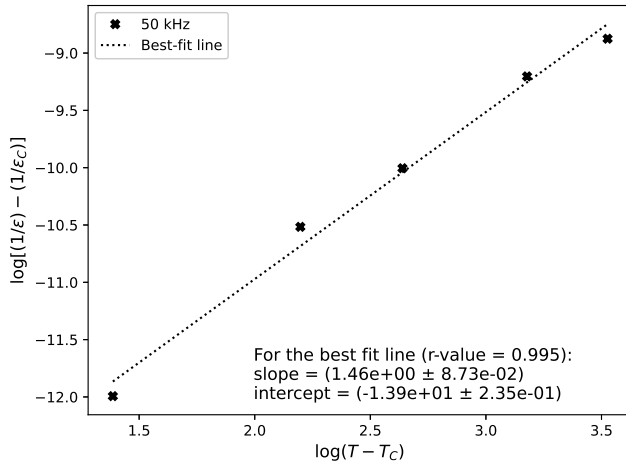


FIG. 7: Variation of Dielectric constant with Temperature T ($^{\circ}\text{C}$) for four different frequencies



(d) 50 kHz

FIG. 8: $\log\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_C}\right)$ vs. $\log(T - T_C)$ at different frequencies

From the above plots, the average value of δ can be taken as the slops obtained using linear regression.

IV. DISCUSSION & CONCLUSION

In this experiment, we looked at how the dielectric constant and the capacitance of BaTiO_3 , vary with frequency. We saw that the dielectric constant lowers as the total polarisation decreases and the relaxation times of various polarisation mechanics result in slower alignment of polarisation vectors in the direction of the electric field

as compared to the frequency of the electric field. We also compared it to the variation in standard MLCC and DCC to observe a general trend.

We also investigated BaTiO_3 's phase transition. The dielectric constant of BaTiO_3 is seen to increase up to the Curie temperature and then decrease symmetrically after. From this we have obtained the value of Curie temperature as

$$T_C = (135 \pm 5) ^{\circ}\text{C}$$

This shows that barium titanate exhibits ferroelectric behaviour below the Curie temperature (where it exists in a tetragonal phase with a net dipole moment) and paraelectric behaviour above T_C (where it exists in a cubic phase without a net dipole moment). We may infer that the Curie temperature is unaffected by the frequency of the applied electric field because it is the same for each frequency curve.

We can probably attribute the slight deviation in T_C to the impurities in the sample since the measured curie temperature deviates from the predicted value of around $120 ^{\circ}\text{C}$.

We found that frequency had little effect on the variable resistance. Only the amplitude of the signal on the oscilloscope was impacted by adjusting the variable capacitor's capacitance. But since the sample's resistance is not necessary, we may infer that the balancing resistance is essentially independent of C .

By plotting $\log\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_C}\right)$ vs. $\log(T - T_C)$, we calculated the diffuseness parameter of the sample at different frequencies,

- at 10 kHz: (1.40 ± 0.05)
- at 25 kHz: (1.35 ± 0.03)

- at 35 kHz: (1.57 ± 0.12)
- at 50 kHz: (1.46 ± 0.09)

Here we observed no general trend and all the values of diffuseness parameter lie in the theoretically expected range between 1 – 2.

V. PRECAUTIONS AND SOURCES OF ERROR

1. The sample not being properly in touch with the probes. and loose connections in any place of the circuit. improperly connected wires can increase the capacitance in the circuit.
2. The variable resistor may saturate before the Curie temperature if a sample is taken with a high sample resistance, which will alter the predicted plot form.
3. Readings beyond the lowest allowable voltage amplitude may result in variable resistance inaccuracy.
4. Sample impurities that raise the curie temperature.
5. The spring-loaded probes may introduce additional contact resistance, leading to an inaccurate measurement of capacitance. This occurs due to improper probe placement or oxidation of the sample's conductive surfaces
6. The accuracy of the capacitance measurement depends on precise balancing of the Schering Bridge. Small misalignments in tuning the variable capacitors and resistors can introduce systematic errors
7. Slight variations in the thickness of the BaTiO_3 sample can introduce errors in the dielectric constant calculation. Since permittivity depends on the capacitance-to-thickness ratio, any deviation in thickness directly affects the computed values.

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- [1] SPS, *Study of Frequency Dependence of Dielectric Constant and Ferroelectric to Paraelectric Phase Transition of BaTiO_3 by Study of Dielectric Constant as a Function of Temperature and Frequency*, NISER (2023).
- [2] C. Kittel, *Introduction to Solid State Physics* (Wiley, 2004).