Phase transition of $BaTiO_3$ by study of dielectric constant as a function of frequency and temperature

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In electromagnetism, a dielectric (or dielectric medium) is an electrical insulator that can be polarised by an applied electric field. Dielectric Constant (or Relative Permittivity) is the measure of the polarization ability of the dielectric medium in an electric field. In this experiment, we study the dielectric constant of various given materials like $BaTiO_3$, multilayer ceramic capacitors, and disc ceramic capacitors. Then, we study the dependence of the dielectric constant of $BaTiO_3$ with frequency and temperature. We considered $BaTiO_3$ in our experiment because of its special behavior with temperature discussed later. We also study the phase transition of $BaTiO_3$(by the temperature dependence of dielectric constant), which includes the discussion on the Curie temperature.

I. OBJECTIVES

- Study the frequency and temperature dependence of dielectric constant of $BaTiO_3$.

- Study the dissipation factor with frequencies.

- Study the diffusion parameter for different frequencies.

II. THEORY

A. Dielectric constant

Dielectric constant or Relative permittivity(ϵ) is a measure of the electric polarizability and ability to store the electrical energy in a material when an electric field is applied to it. In general, permittivity is a complex quantity. The real part of permittivity signifies the energy stored in a material and the imaginary part is related to energy lost by the material in the presence of an electric field. Permittivity is also dependent on the frequency of the applied electric field. The real part of permittivity is dependent on the polarizability of a material.

B. Polarization types

Polarizability is usually divided into the following four parts:

1. Electronic Polarization:

It generally occurs in neutral atoms due to the displacement of the nucleus w.r.t. the electrons surrounding it. The displacement of the nucleus results in induced charges on the atom thus developing a dipole moment. This mechanism is the fastest of all and remains active
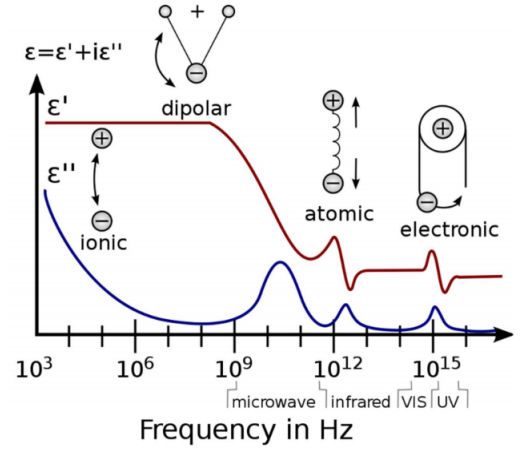

FIG. 1. Different mechanisms of polarization and their dependence with frequency

up to the optical frequencies. Induced moments are dependent on the polarizability of atoms or molecules.

2. Ionic Polarization:

It generally occurs in solids with ionic bonding. They have dipoles that get canceled due to the symmetry of the crystals. When an external field is applied, it causes a small displacement of ions from their equilibrium positions and hence inducing a net dipole moment. This is a relatively slower mechanism and persists till 109 - 1013 Hz.

3. Dipolar Polarization:

It generally occurs in molecules having a permanent dipole moment. The molecular dipoles are randomly distributed in the absence of an electric field due to thermal

randomization. These dipoles align in the direction of the applied electric field and contribute to the total polarization of the molecule. This mechanism is slower than ionic polarization and is active below 10^9 Hz.

4. Space Charge Polarization:

This mechanism is prevalent in composite materials which are made up of more than one material. It is produced by the separation of mobile charge carriers under an electric field, which forms positive and negative space charges in the bulk of the material or at the interfaces between different materials. This mechanism is effective in the range of audio frequencies.

Each polarization mechanism has a characteristic relaxation frequency. As we increase the frequency of the electric field, slower mechanisms of polarization cannot respond to the changing frequency of the electric field and drop off. This results in a decrease in the polarization of the material as lesser mechanisms are contributing to the total polarization, thus we see a decrease in dielectric constant/capacitance.

C. Significance of dielectric constant

The real part of the dielectric constant (ϵ') represents the polarizability of a material by an external electric field thus its ability to store energy. On the other hand, the imaginary part represents the dielectric loss factor (ϵ'') represents the ability of the material to dissipate the absorbed electromagnetic energy, converting it into heat. The ratio $\frac{\epsilon''}{\epsilon'}$ suggests the capability of the material to convert electromagnetic energy into heat at specific temperatures and frequencies. Thus we define the dissipation factor as:

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

D. Barium Titanate ($BaTiO_3$) And Its Properties

Barium Titanate is a perovskite material and has a very large room-temperature dielectric constant. Perovskite is a name of a class of compounds which have the same type of crystal structure as $CaTiO_3$ having a structure of the type ABO_3. The structure of the perovskite is shown in Fig.(2) and (3). Barium Titanate ($BaTiO_3$) has a ferroelectric tetragonal phase below its Curie point of about $120°C$ and a paraelectric cubic phase above the Curie point. The temperature of the Curie point of a particular sample depends on the impurities present in the sample and the synthesis process.

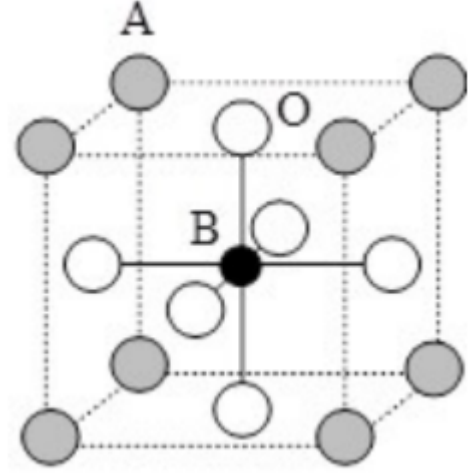In the paraelectric cubic phase, the center of positive

FIG. 2. Perovskite structure of type ABO_3.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.
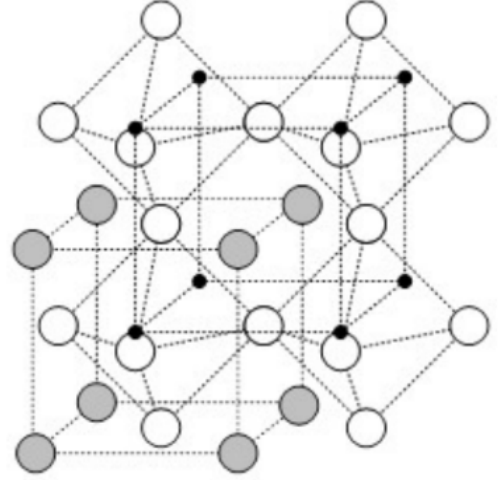

FIG. 3. Perovskite structure of $BaTiO_3$, where Ba occupies grey dots, Ti occupies black dots and O occupies white dots

charges (Ba^{2+}, Ti^{4+}) coincides with the center of negative charges (O^{-2} ion) and on cooling below T_C, we observe a tetragonal phase where the center of Ba^{2+} and Ti^{4+} ions are displaced relative to the O^{-2} ion, forming electric dipoles.

Due to the above properties the dielectric constant of $BaTiO_3$ increases till T_C and becomes the highest at T $=T_C$ due to divergence of susceptibility at that point. After crossing this temperature the dielectric constant starts decreasing due to the formation of a cubic phase.

E. Diffuseness Parameter

The diffuseness parameter,δ, is defined as the slope of the $ln(\frac{1}{\epsilon} - \frac{1}{\epsilon_{max}})$Vs ln(T - T_C) plot. Here, ϵ is the dielectric constant at a temperature T greater than T_C, and ϵ_{max} is the maximum value of the dielectric constant at the Curie temperature T_C.
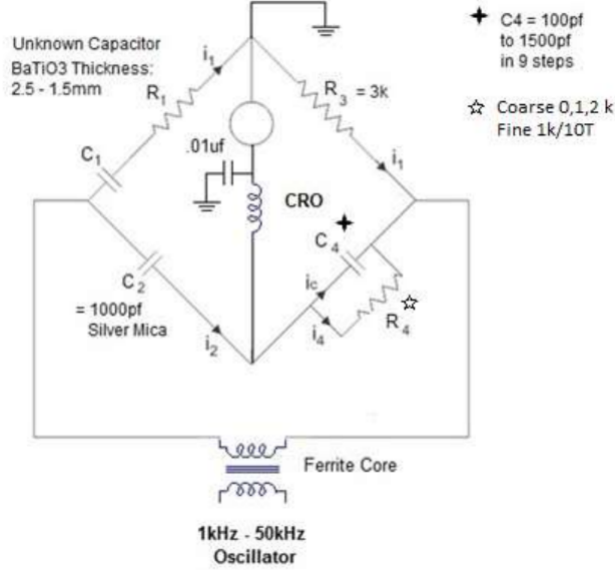
F. Schering Bridge

FIG. 4. Schering bridge for capacitance measurement

The Schering bridge is an AC analogue of the Wheatstone bridge. It is used for measuring the capacitance and dissipation factor of a capacitor. The Schering bridge works on the principle of balancing the load on its arm. Applying the bridge balance condition, we get:

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

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

Here, C_1 is the unknown capacitor, and R_1 is the equivalent series resistance reflecting losses. The dissipation factor is given by:

$$tan\delta = \omega C_1 R_1 = \omega C_4 R_4 = 2\pi fCR \qquad (2)$$

III. EXPERIMENTAL SETUP

A. Apparatus required

The apparatus required for the experiment is as follows:

- Probe arrangement: to hold the material and complete the circuit through it.
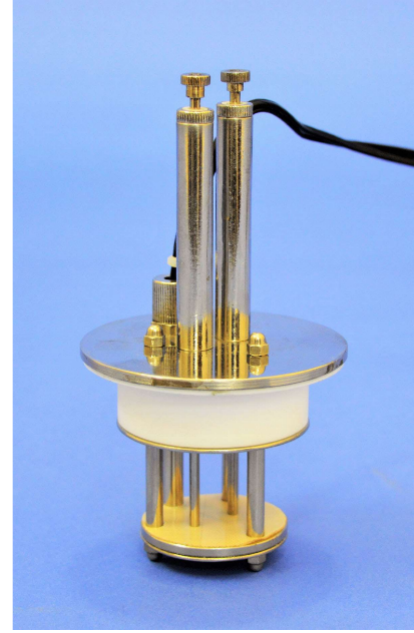

FIG. 5. Probe arrangement

- Samples: Barium Titanate ($BaTiO_3$), Multilayer ceramic capacitor, disc ceramic capacitor.

- Main unit comprising the Schering bridge.

- PID controlled oven: to control the temperature.

IV. OBSERVATIONS AND DATA

The observed data for the frequency and the temperature dependence of the dielectric constant are shown in Fig. (6) and (7) respectively.
The required plots are attached further.
In fig. (8a), we can see that the dielectric constant is decreasing exponentially when we increase the frequency, as it is supposed to be.

Barium titatnate						
Frequency(kHz)	C4(pF)	R4(kohm)	C1(Pf)	R1(kohm)	Dielectric constant	Diss. Factor
1	1150	0.872	290.6667	3.45	839.4652835	0.006297584
3	1150	0.84	280	3.45	808.6592181	0.01819944
5	1150	0.832	277.3333	3.45	800.9577017	0.03004352
7	1150	0.828	276	3.45	797.1069435	0.041858712
10	850	0.824	274.6667	2.55	793.2561853	0.04398512
15	600	0.82	273.3333	1.8	789.4054272	0.0463464
20	500	0.816	272	1.5	785.554669	0.0512448
25	400	0.814	271.3333	1.2	783.6292899	0.0511192
30	400	0.812	270.6667	1.2	781.7039108	0.06119232
35	350	0.812	270.6667	1.05	781.7039108	0.06246716
40	350	0.81	270	1.05	779.7785317	0.0712152
50	300	0.812	270.6667	0.9	781.7039108	0.0764904

t=2.28 mm
d=10.66 mm

Multilayer ceramic capacitor				
Frequency(kHz)	C4(pF)	R4(kohm)	C1(Pf)	R1(kohm)
1	1150	1.83	610	3.45
3	800	1.812	604	2.4
5	500	1.81	603.3333	1.5
7	400	1.808	602.6667	1.2
10	300	1.802	600.6667	0.9
15	250	1.798	599.3333	0.75
20	200	1.79	596.6667	0.6
25	200	1.79	596.6667	0.6
30	200	1.794	598	0.6
35	150	1.776	592	0.45
40	150	1.772	590.6667	0.45
50	150	1.768	589.3333	0.45

Disc ceramic capacitor				
Frequency(kHz)	C4(pF)	R4(kohm)	C1(Pf)	R1(kohm)
1	1150	1.68	560	3.45
3	800	1.66	553.3333	2.4
5	450	1.658	552.6667	1.35
7	400	1.652	550.6667	1.2
10	300	1.648	549.3333	0.9
15	250	1.646	548.6667	0.75
20	200	1.642	547.3333	0.6
25	200	1.638	546	0.6
30	200	1.636	545.3333	0.6
35	200	1.632	544	0.6
40	200	1.632	544	0.6
50	150	1.626	542	0.45

FIG. 6. Signed data for the frequency dependence of the dielectric constant for $BaTiO_3$, Multilayer ceramic capacitor, and disc ceramic capacitor.

In fig. (8b), we can see that the dissipation factors we got for different frequencies are randomly arranged in the plots but there is a gradual increase in those with increasing frequency, maybe due to more energy loss at higher frequencies.

In fig. (8c) and (8d), we can see that the capacitance for both multilayer ceramic capacitor and disc ceramic capacitor decreases with an increase in frequency which is supposed to be as C is inversely proportional to ω.

Frequency=5kHz			
Temperature(C)	R4(kohm)	C1(Pf)	Dielectric constant
60	0.81	270	779.7785317
70	0.816	272	785.554669
80	0.824	274.6667	793.2561853
90	0.838	279.3333	806.733839
100	0.862	287.3333	829.8383881
110	0.892	297.3333	858.7190744
120	0.93	310	895.3012771
130	0.998	332.6667	960.7641662
140	1.032	344	993.4956108
150	0.988	329.3333	951.1372708
160	0.914	304.6667	879.8982444
170	0.854	284.6667	822.1368717
180	0.814	271.3333	783.6292899

Frequency=15kHz			
Temperature(C)	R4(kohm)	C1(Pf)	Dielectric constant
60	0.802	267.3333	772.0770153
70	0.808	269.3333	777.8531526
80	0.818	272.6667	787.4800481
90	0.826	275.3333	795.1815644
100	0.844	281.3333	812.5099762
110	0.87	290	837.5399044
120	0.92	306.6667	885.6743817
130	0.984	328	947.2865126
140	1.022	340.6667	983.8687153
150	0.976	325.3333	939.5849962
160	0.912	304	877.9728653
170	0.85	283.3333	818.2861135
180	0.808	269.3333	777.8531526

Frequency=25kHz			
Temperature(C)	R4(kohm)	C1(Pf)	Dielectric constant
60	0.802	267.3333	772.0770153
70	0.808	269.3333	777.8531526
80	0.816	272	785.554669
90	0.826	275.3333	795.1815644
100	0.842	280.6667	810.5845972
110	0.868	289.3333	835.6145253
120	0.912	304	877.9728653
130	0.98	326.6667	943.4357544
140	1.018	339.3333	980.0179571
150	0.974	324.6667	937.6596171
160	0.908	302.6667	874.1221071
170	0.844	281.3333	812.5099762
180	0.806	268.6667	775.9277735

Frequency=35kHz			
Temperature(C)	R4(kohm)	C1(Pf)	Dielectric constant
60	0.8	266.6667	770.1516362
70	0.806	268.6667	775.9277735
80	0.814	271.3333	783.6292899
90	0.824	274.6667	793.2561853
100	0.84	280	808.6592181
110	0.866	288.6667	833.6891462
120	0.91	303.3333	876.0474862
130	0.978	326	941.5103753
140	1.016	338.6667	978.092578
150	0.972	324	935.734238
160	0.906	302	872.1967281
170	0.844	281.3333	812.5099762
180	0.806	268.6667	775.9277735

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FIG. 7. Signed data for the temperature dependence of the dielectric constant for $BaTiO_3$

In Fig.(9), we can see that the dielectric constant increases up to a particular temperature and then reduce with an increase in temperature. This particular temperature is called Curie temperature. In our data, we found it out to be $T_C = 140°C$.

From Fig.(10), we found the Diffusion parameters from the slope for different frequencies.

- For f=5kHz, diffusion parameter= 1.3126 ± 0.0997

- For f=15kHz, diffusion parameter= 1.263 ± 0.055

- For f=25kHz, diffusion parameter= 1.295 ± 0.0757

- For f=35kHz, diffusion parameter= 1.285 ± 0.076

V. RESULTS

- The Curie temperature for $BaTiO_3$ is found out to be $T_C = 140°C$ which is 16.66 % deviated from the theoretical value of $T_C = 140°C$.
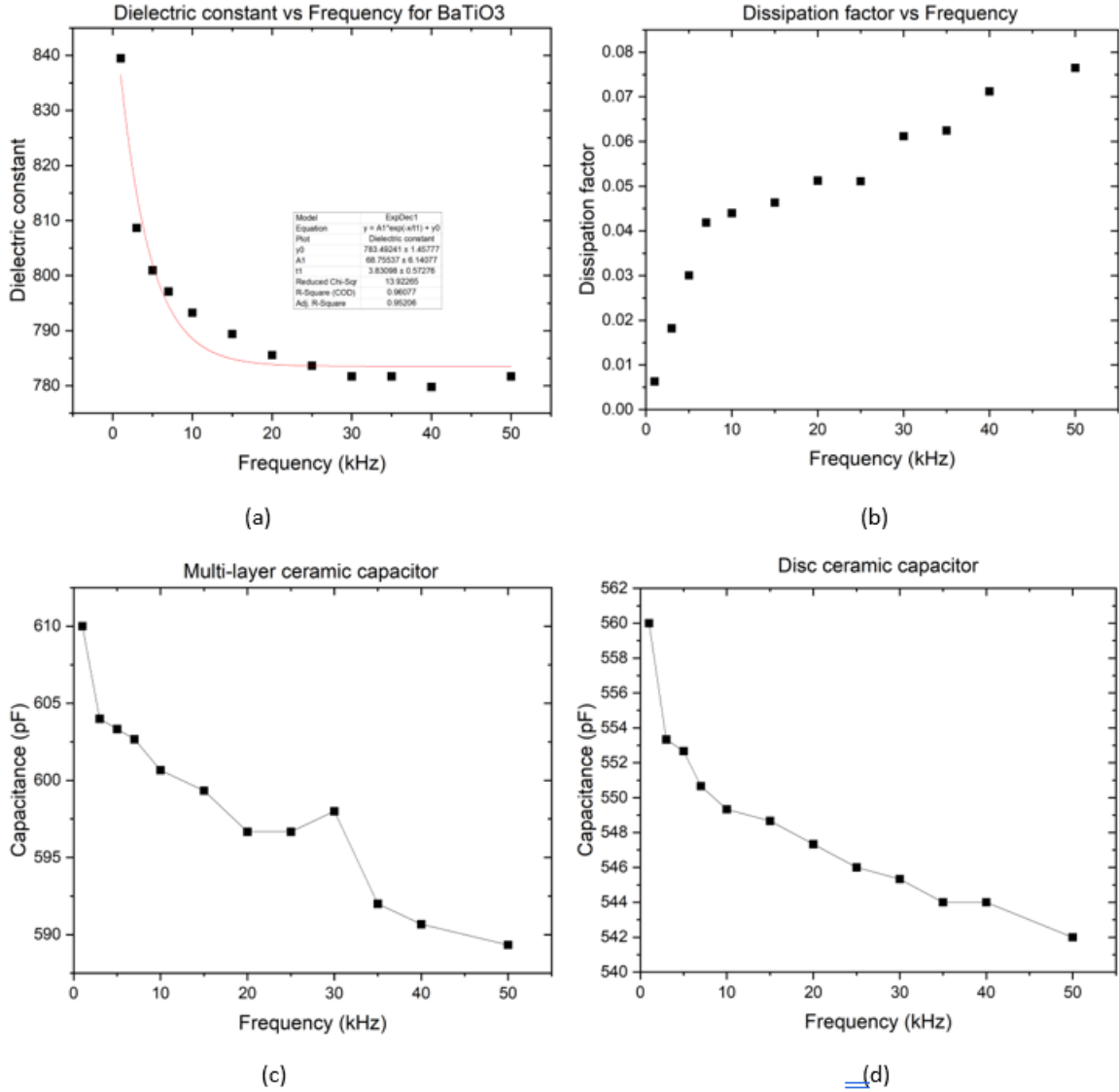
FIG. 8. (a) Plot of dielectric constant vs frequency for $BaTiO_3$
(b) Plot of dissipation factor vs frequency for $BaTiO_3$
(c) Plot of capacitance vs frequency for multilayer ceramic capacitor
(d) Plot of capacitance vs frequency for disc ceramic capacitor

VI. CONCLUSIONS AND DISCUSSIONS

- The plots of dielectric constant or capacitance for $BaTiO_3$, Multi-Layer Ceramic capacitor, and disc ceramic capacitor showed that the dielectric constant or capacitance decreases with an increase in frequency. This can be due to the slower alignment of polarization vectors in the direction of the electric field as compared to the frequency of the electric field and thus many polarisation mechanisms are rendered ineffective at higher frequencies decreasing the total polarization.

- The dielectric constant of Barium Titanate ($BaTiO_3$) increases up to the Curie temperature and then decreases after it. This also verifies the theoretical behavior. This indicates that Barium Titanate ($BaTiO_3$) behaves as a ferroelectric material (existing in the tetragonal phase with a net dipole moment) till the Curie temperature and as a paraelectric (existing in cubic phase without a net dipole moment) after T_C.

- The dissipation factor for different frequencies are found to be random but it is increasing with frequency in our case, which might indicate more energy loss at higher frequencies.
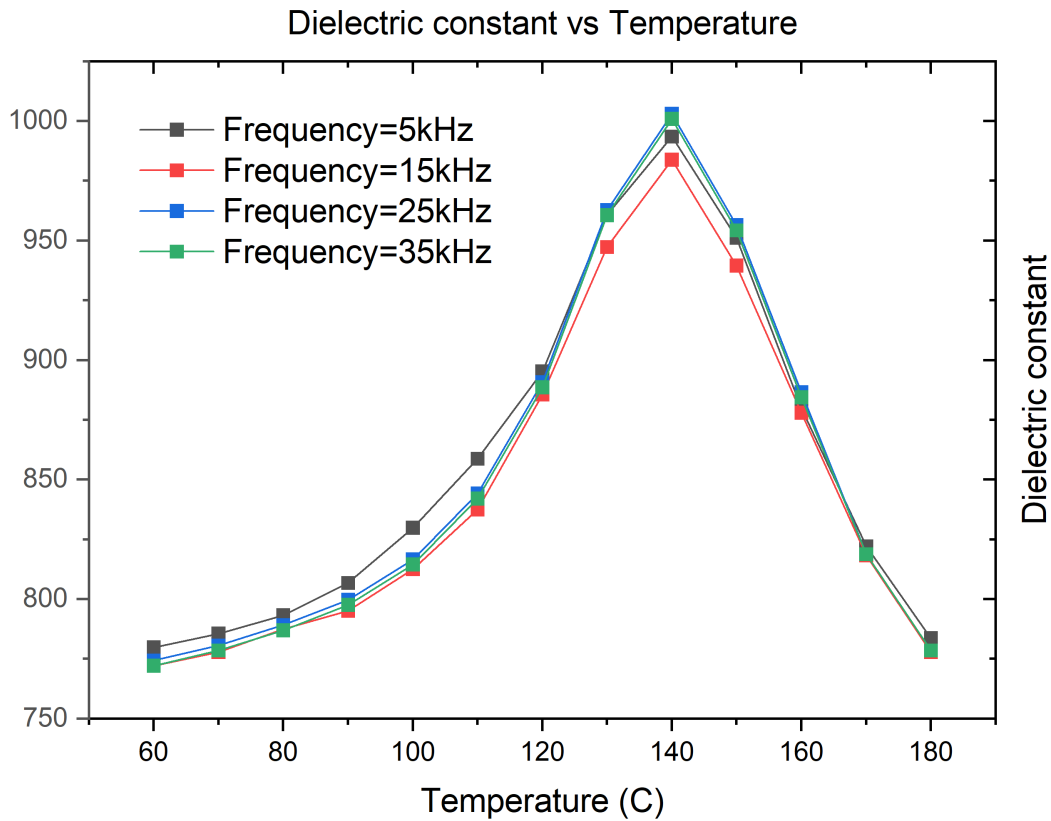
FIG. 9. Plot for dielectric constant vs Temperature for $BaTiO_3$

- By observing the temperature dependence of the dielectric constant of Barium Titanate($BaTiO_3$) at different frequencies we can conclude that the Curie temperature is independent of the frequency of the applied electric field.

- The plots for diffusion parameter fit well with the linear fit as expected in the theory with accuracy described in the sections before.

VII. SOURCES OF ERRORS

- Improper contact of the given sample with the probes. The probes should connect approximately at the center of the sample.

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

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

- Improper balance in Schering bridge at low frequencies, because at low frequencies, changing capacitance was not affecting the required minimum ouput voltage value much.
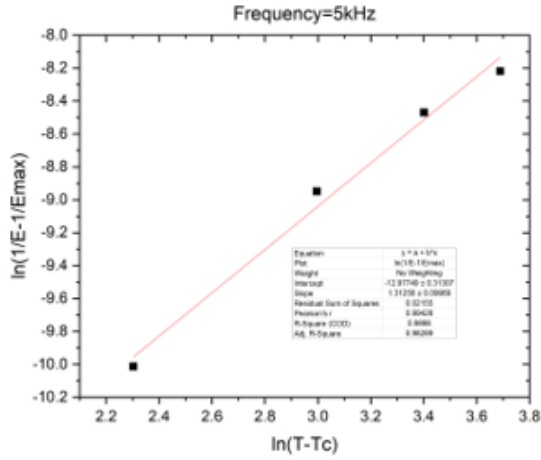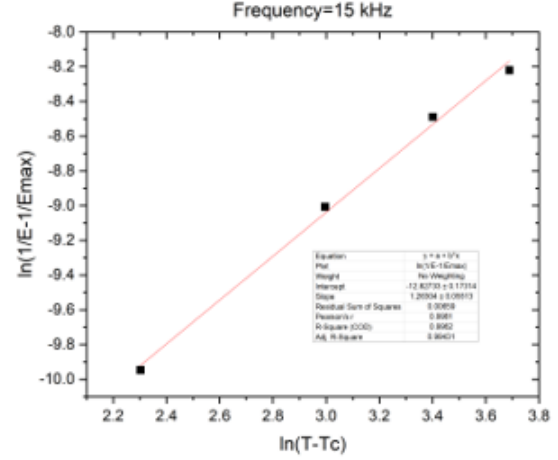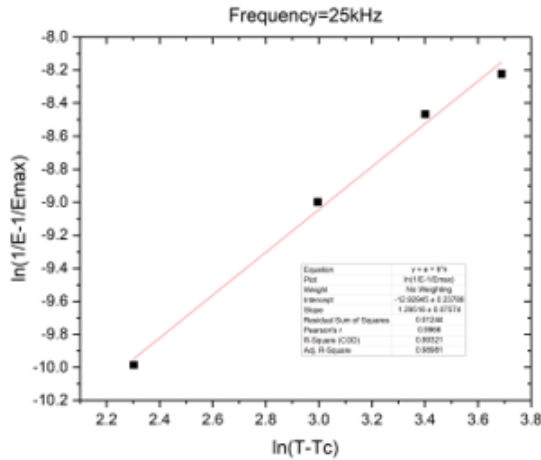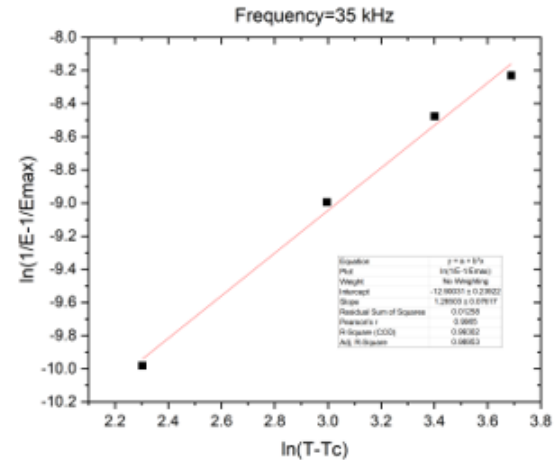
FIG. 10. Plots to determine diffusion parameter at different frequencies

VIII. REFERENCES

- NISER Lab Manual

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  articlehtml/2018/ra/c8ra00794b#:~:
  text=The%20dielectric%20constant%20(%CE%
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