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 FRQUENCY

The dielectric constant or permittivity is frequency dependent (Figure 1). 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. The dielectric loss (imaginary part) will correspondingly peak at each critical frequency. 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. Both electronic and atomic polarization create induced moments depending on the polarizability of the atoms or molecules. A permanent dipole moment is caused by unbalanced sharing of electrons by atoms of a molecule. In an absence of an external electric field, these moments are oriented in a random order such that no net polarization is present. Under an external electric field, the dipoles rotate to align with the electric field causing orientation polarization to occur. 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.

Even though permittivity is function of frequency, in engineering terms it is known as dielectric constant. Why it got the name as **dielectric constant**?

Both real and imaginary part are important for applications. For example, in the microwave heating, the dielectric constant (ε') represents a measure of the ability of a material to be polarized by an external electric field (as that of microwaves) 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 microwaves into the same sample. Thus, the ratio $\varepsilon''/\varepsilon'$ suggests the capability of each material to convert electromagnetic energy (microwaves) into heat at specific temperatures and frequencies.

In this experiment, along with real part of permittivity, loss factor (dissipation factor) can be measured, which is defined as $tan\delta = \dfrac{\varepsilon'_r}{\varepsilon''_r}$.
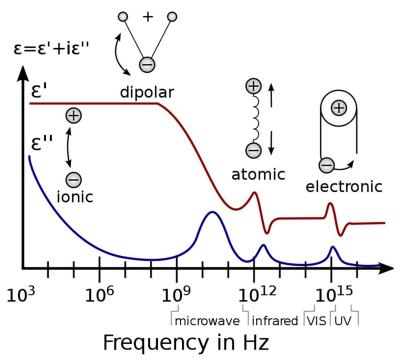
Fig.1 real and imaginary part of permittivity (dielectric constant) as function of frequency (source:https://web.archive.org/web/20010307184808/http://www.psrc.usm.edu/mauritz/dilect.html)

BARIUM TITANATE (BaTiO₃, BT)

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 (Figure 2 a, b).

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

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. Even though two cations are compatible in solution, their behaviour 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 caution.

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.

In the paraelectric cubic phase the centre of positive charges (Ba^{2+}, Ti^{4+}) coincide with the centre of negative charges (0^{-2} ion) and on cooling below T_c, a tetragonal phase develops where

the centre of Ba^{2+} and Ti^{4+} ions are displaced relative to the 0^{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 of these polycrystalline sample used in the experiment is very important for these applications.
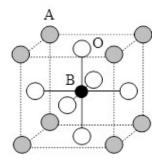

Figure 2 (a).   Perovskite ABO_3 structure with the A and B cations on the corner and body centre positions, respectively. Three oxygen anions per unit cell occupy the faces and form octahedra surrounding the B-site.
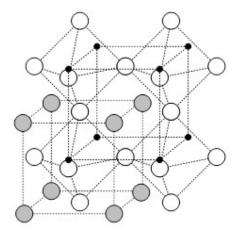

Figure 2 (b)   Perovskite structure (Ba: Grey; Ti: Black; O: White)

Fig. 6: Dielectric Constant Arrangement

DIELECTRIC CONSTANT OF DIFFERENT MATERIALS

Typical values of dielectric constant are:

Material	DIELECTRIC CONSTANT (ε)
Vacuum	1.000
Dry Air	1.0059
Barium Titanate	100-2500
Glass	3.8-14.5
Quartz	5
Mica	4-9
Water distilled	34-78
Soil dry	2.4-2.9
Titanium dioxide	100

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)
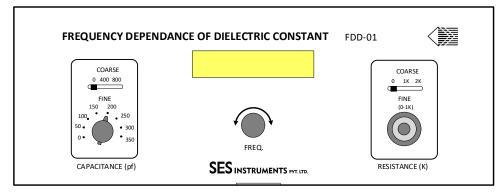A = Area of the plate/ sample cross section area
t = Thickness of the sample

BRIEF DESCRIPTION OF THE APPARATUS

1. **Probe Arrangement**
   As shown in Fig. 6, it has two spring loaded probes. These probes 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. **Samples**
   (a) Barium Titanate ($BaTiO_3$) plate with top and bottom conducting surface.
   (b) Standard Multilayer Ceramic Capacitor.
   (c) Disc Ceramic Capacitor

3. **Setup** The set-up in the present experiment, covers frequencies only up to 50 KHz.

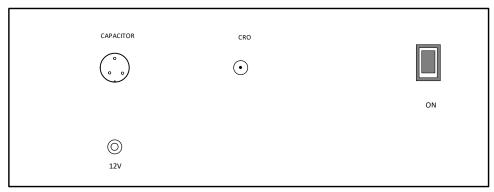4. **Oscilloscope** Required for balancing the bridge.

FREQUENCY DEPENDANCE OF DIELECTRIC CONSTANT FDD-01

COARSE
0 400 800

FINE
150   200
100   250
50   300
0   350

CAPACITANCE (pf)

FREQ.

SES INSTRUMENTS PVT. LTD.

COARSE
0 1K 2K

FINE
(0-1K)

RESISTANCE (K)

Front Panel

CAPACITOR   CRO

ON

12V

Fig.7 Panel Diagram of the Unit

Unknown Capacitor
BaTiO3 Thickness:
2.5 - 1.5mm R_1

C_1

.01uf

$R_3 = 3k$

CRO

C_4

i_c

i_4 R_4

C_2
= 1000pf
Silver Mica

i_2

$C4 = 100pf$
to 1500pf
in 9 steps

☆ Coarse 0,1,2 k
Fine 1k/10T

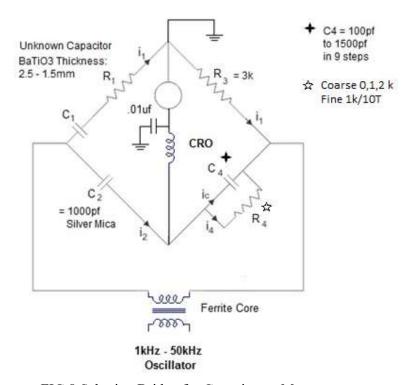Ferrite Core

1kHz - 50kHz
Oscillator

FIG.8 Schering Bridge for Capacitance Measurement

3. Main Unit

The set-up consists of the main unit (Fig. 7) for the measurement of capacitance at different frequencies from 1kHz to 50kHz. This is done with the help of a Schering Bridge and a built-in oscillator. The basic bridge structure is shown in Fig. 8.

Here,

C_1 is the unknown capacitance ($BaTiO_3$) whose value is to be determined with series electrical resistance R_1.

C_2 is a standard silver mica capacitor of 1000 pf

C_4 is a variable capacitor divided in two levels – Coarse and Fine. Coarse variation is divided in 3 steps (0-400-800) and correspondingly Fine variation in further 8 steps [(0-50-100-150-200-250-300-350)/ (400-450-500-550-600-650-700-750)/ (800-850-900-950-1000-1050-1100-1150)].

R_3 is a metal film resistance of 3.0k.

R_4 is a variable resistance, 'Coarse' 0, 1k, 2k, 3k (selectable) in series with 'Fine' 1k/10T potentiometer, connected in parallel with C_4.

From the bridge balance condition,

$$R_1 = \frac{R_3 C_4}{C_2} \quad \text{and} \quad C_1 = \frac{C_2 R_4}{R_3}$$

Here C_1 is the unknown capacitor and R_1 is the equivalent series resistance reflecting losses.

The dissipation factor may be calculated from,

$$\tan\delta \text{ (Dissipation factor)} = \omega C_1 R_1 = \omega C_4 R_4 = 2\pi f (CR)$$

Note: Derivation of the above expressions may be seen in APPENDIX-I

EXPERIMENTAL PROCEDURE

1. Put the small piece of aluminium foil on the base plate. Pull the spring-loaded probes upward, insert the aluminium foil and let them rest on it. Put the sample ($BaTiO_3$) on the foil. Again, pull the top of one of the probes 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 aluminium foil.

2. Connect the probe leads (capacitor terminals) to the main unit at the back as also a Oscilloscope.

3. 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.

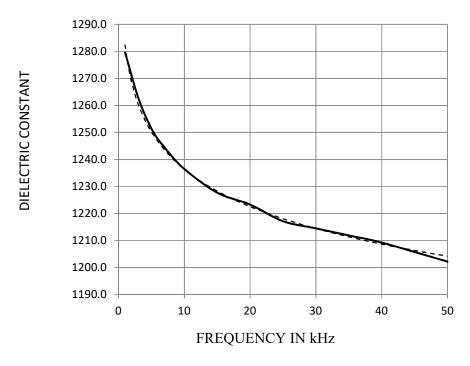4. Complete the calculations and plot a graph as shown in the sample results.

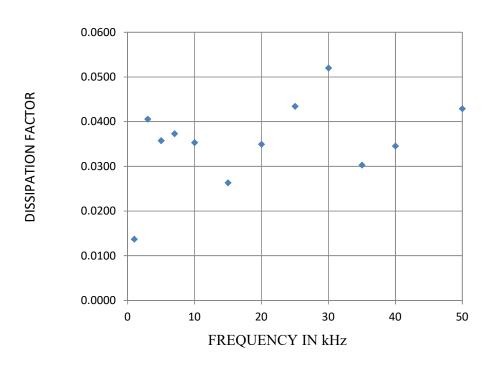Fig. 9 Plot of Dielectric Constant as a function of frequency

Fig. 10 Plot of Dissipation Factor as a function of frequency (BT)

OBSERVATIONS AND CALCULATIONS

FREQUENCY DEPENDENCE OF DIELECTRIC CONSTANT/CAPACITANCE

(a) Barium Titanate (BT)

Sample: Barium Titanate ($BaTiO_3$): Dia = ----

Area (A): ----

Thickness (t): ----

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

$$\varepsilon = \frac{C_1}{C_0}; \quad \text{where,}$$

$$C_0 = \frac{\varepsilon_0 A}{t}$$

R_4 = Dial Reading (divided in Coarse and Fine)

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

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

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

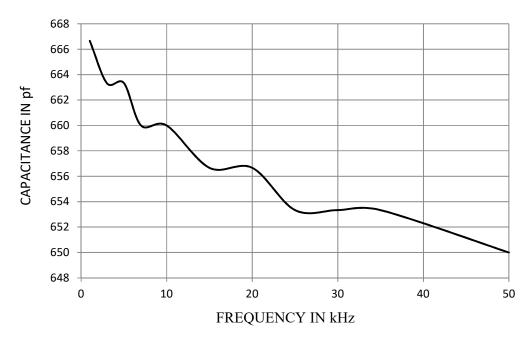| Freq., kHz (f)	C_4, pf	R_4, kohm	C_1, pf	R_1, ohm	Dielectric Constant $\varepsilon = C_1/ C_0$	Diss. Factor $(2\pi f C_1 R_1)$
1						
3						
5						
7						
10						
15						
20						
25						
30						
35						
40						
50						

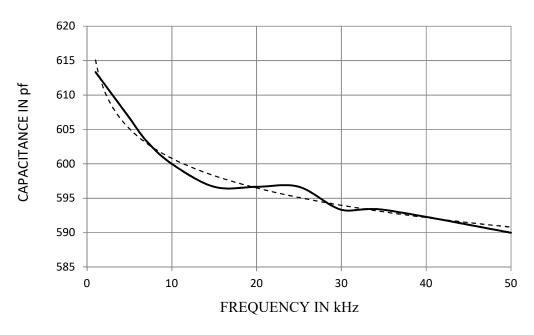Fig. 11 Plot of Capacitance as a function of frequency (MLCC)

Fig. 12 Plot of Capacitance as a function of frequency (Disc)

(b)   Multi-layer Ceramic Capacitor (MLCC)

Variation of Unknown Capacitance as a function of Frequency

(In the absence of dimensional information of commercially available capacitors, the value of C_0 cannot be computed. Hence, we tabulate value of capacitance, which is proportional to the dielectric constant, as a function of frequency.

Freq., kHz	R_4, kohm	C_1, pf
1		
3		
5		
7		
10		
15		
20		
25		
30		
35		
50		

(c)   Disc Ceramic Capacitor

Variation of Unknown Capacitance as a function of Frequency

(In the absence of dimensional information of commercially available capacitors, the value of C_0 cannot be computed. Hence, we tabulate value of capacitance, which is proportional to the dielectric constant, as a function of frequency.

Freq., kHz	R_4, kohm	C_1, pf
1		
3		
5		
7		
10		
15		
20		
25		
30		
35		
50		

TYPICAL RESULTS

Figure 9 shows the variation of dielectric constant of BaTiO$_3$ with frequency over a frequency range 0-50KHz. This follows the same general variation as shown in Fig. 3 over this frequency range. It is contributed by space charge polarization caused by mobile charge carriers whose motion is impeded by interface due to a grain or phase boundary.

Figure 10 shows the variation of the dissipation factor of barium titanate sample with frequency. The increase with frequency reflects the increase in friction between dipoles due to their inability to follow up the first variation of the applied alternating electric field.

The variation obtained in Fig. 11 and 12 for the standard multilayer ceramic capacitor and disc ceramic capacitor show the general trend.

USING BARIUM TITANATE SAMPLE

1. Study of temperature dependence of dielectric constant at different freq.

Step-1 Insert the Dielectric Constant Arrangement Fig.6 in the oven.

Step-2 Set a frequency of 5 kHz on the main unit.

Step-3 Switch the oven unit ON and set a temperature of 50°C.

Step-4 Measure the capacitance by balancing the bridge as in the previous experiment. Note down R_4 and C_4 in the table below.

Step-5 Now repeat Steps 2 to 4 for different frequencies like 15 kHz, 25 kHz, and 35 kHz

Step-6 Increase temperature by steps of 10°C and repeat Step-4 above till 180°C. Take closer readings near the curie temperature of 130°C.
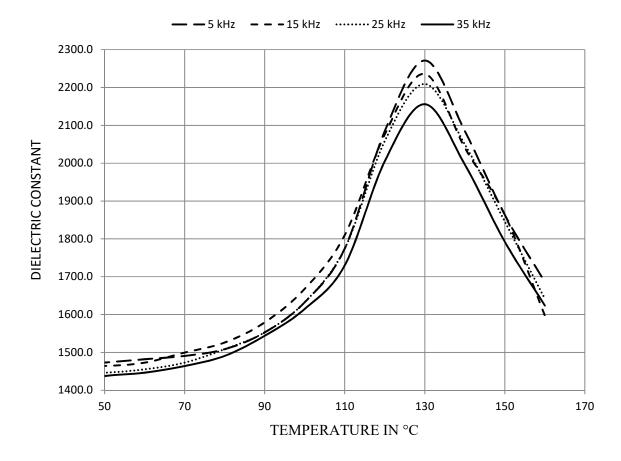
Step-7 Plot a graph as in Fig.13.

Fig 13: Typical plot of Dielectric Constant as a function of Temperature for various Frequencies

OBSERVATIONS AND CALCULATIONS

Temp., C	Operating Frequency – 5kHz			Operating Frequency – 15kHz		
	R_4, kohm	C_1	ε	R_4, kohm	C_1	ε
50						
60						
..						
..						
..						
180						

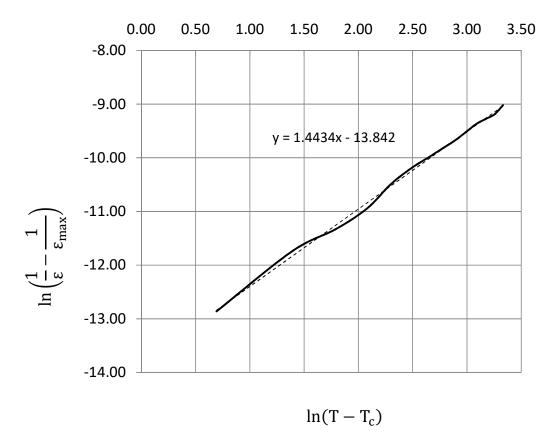| Temp., C	Operating Frequency – 25kHz			Operating Frequency – 35kHz		
	R_4, kohm	C_1	ε	R_4, kohm	C_1	ε
50						
60						
..						
..						
..						
180						

Fig 14: Plot of Diffuseness Parameter

2. Study of diffuseness parameter at a single frequency

The diffuseness parameter, δ, is defined as the slope of the,

$$\ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}}\right) \quad vs \quad \ln(T - T_c) \quad \text{plot, where,}$$

ε is the dielectric constant at a temperature T, ε_{max} is the maximum value of the dielectric constant at the curie temperature, T_c. The above is valid in the paraelectric phase, i.e., beyond the curie temperature.

A plot for a BT sample is shown in Fig.14 along with a linear approximation (shown dotted). The slope of the linear plot is found to be 1.4434 which is the value of the diffuseness parameter, δ, and is expected to lie between 1 and 2. The user can either get the results on an excel sheet as above, or plot the readings on a graph paper and calculate the slope of the linear approximation.
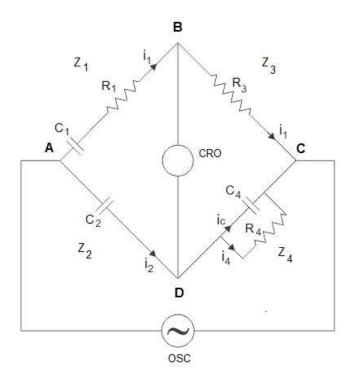
TYPICAL RESULTS

Figure 13 shows the variation of dielectric constant of barium titanate (BT) with temperature over the temperature range 50-160°C at four different frequencies 5, 15, 25 and 35 KHz. The variation follows the same general trend of normal ferroelectrics with the dielectric constant peaking (Curie Temperature) at 130°C in all the four cases. This aspect shows that the Curie temperature of the given sample BT does not change with the frequency. This aspect which is a structural phase change [Tetragonal to Cubic in the case of BT] with temperature therefore does not depend on the frequency. The value of the dielectric constant however decreases as the frequency increases in conformity with the results in Fig. 9.

PRECAUTIONS

(1) The spring loaded probe should be allowed to rest on the sample very gently, otherwise it may damage the conducting surface of the sample or even break the sample.

(2) It would be desirable to take readings at smaller intervals of temperature around the curie point, say from 120°C – 140°C for better results.

REFERENCES

1) Introduction to Solid State Physics – C. Kittel, Wiley Eastern Limited (5th Edition).
2) **https://www.doitpoms.ac.uk/tlplib/dielectrics/printall.php**
3) **https://web.archive.org/web/20010307184808/http://www.psrc.usm.edu/mauritz/dilect.html**
4) https://www.sciencedirect.com/topics/chemical-engineering/microwave-heating

The figure above shows the configuration of the Schering Bridge, where,

C_1 is the unknown capacitance with series electrical resistance R_1,

C_2 is a standard capacitor,

C_4 is a variable capacitor,

R_3 is a pure resistor (i.e. non inductive in nature), and,

R_4 is a variable non inductive resistor connected in parallel with variable capacitor C_4.

Now the supply is given to the bridge between the points A and C, and the detector (Oscilloscope) is connected between B and D. In the balance condition the Oscilloscope shows zero signal, i.e., there is no potential difference between points B and D. This implies the balance equation as,

$$Z_1/Z_3 = Z_2/Z_4, \text{ or } Z_1.Z_4 = Z_2.Z_3$$

Substituting the values of Z_1, Z_2, Z_3 and Z_4 in the above equation, we get

$$\left(R_1 + \frac{1}{j\omega C_1}\right)\left(\frac{R_4}{1 + j\omega C_4 R_4}\right) = \frac{R_3}{j\omega C_2}$$

$$\left(R_1 + \frac{1}{j\omega C_1}\right) R_4 = \frac{R_3}{j\omega C_2}(1 + j\omega C_4 R_4)$$

$$R_1 R_4 - \frac{jR_4}{\omega C_1} = -\frac{jR_3}{\omega C_2} + \frac{R_3 R_4 C_4}{C_2}$$

Equating the real and imaginary parts and the separating we get,

$$R_1 = \frac{R_3 C_4}{C_2} \quad , \quad and, \quad C_1 = \frac{R_4 C_2}{R_3}$$

The unknown capacitor and its equivalent series resistance may therefore be computed from the above equation.

The equivalent series resistance or ESR of a capacitor act like any other resistor giving rise to voltage drops and energy dissipated as heat. Although the ESR figure of a capacitor is mentioned more often, dissipation factor and loss tangent are also widely used and closely associated with the capacitor ESR. When a sinusoidal alternating voltage is applied to an ideal capacitor, the current leads by $\square/2$ in phase. In the case of a practical capacitor, however, advance in phase is ($\square/2$ - $\square$), which is smaller than $\square/2$. "$\square$" is referred to as Loss Angle.

$$I = \frac{V}{Z}$$

$$\tan\delta = \frac{R}{X_C} = \frac{ESR}{X_C} = 2\pi fCR$$

$$= \frac{1}{Q} , \quad (Q: \text{Quality Factor})$$

$$= \text{Dissipation Factor}$$

For Demonstration of Structure: Structure of Barium titatnate in tetragonal and cubic forms with simulated X-ray diffraction patterns: For tetragonal: **https://materialsproject.org/materials/mp-5986/#** For cubic: https://materialsproject.org/materials/mp-2998/

For structural phase transition in $BaTiO_3$: Figure 1 of $BaTiO_3$-based piezoelectrics: Fundamentals, current status, and perspectives Applied Physics Reviews 4, 041305 (2017); https://doi.org/10.1063/1.4990046