Physics 180C, Winter 2020: Dielectric Properties of the Ferroelectric $BaTiO_3$

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Barium Titanate, $BaTiO_3$ is an crystal often used as a dielectric in capacitors since it has a large dielectric constant across a wide range of temperatures. Cooling through 120 °C, $BaTiO_3$ changes from a cubic to a tetragonal crystal structure. Some theoretical understanding of a the transition's effect on the dielectric constant may be gained by studying the theory of second order phase transitions and comparing the transition between paraelectric and ferroelectric, to the transition between paramagnetic and ferromagnetic phases, but the transition observed here is first order. We determined the dielectric constant of a $BaTiO_3$ crystal over 40 °C to 180 °C using the ratio of in-phase and quadrature voltages across the crystal in series with a resistor. We observed a first order phase transition at 119.45 ± 0.55 °C and estimate that if the second order phase transition had not been interrupted it would have occurred at $T_c = 89.96 \pm 0.57$ °C.

INTRODUCTION

Barium Titanate, $BaTiO_3$ is a crystal noted for its high dielectric constant k, which can reach 10^4, where the dielectric constant of a vacuum is $k = 1$. This makes $BaTiO_3$ a useful dielectric material for capacitors. In this lab, we are interested in explaining and understanding the dielectric behavior of $BaTiO_3$ with respect to temperature, and in particular at its transition.

At temperatures above 120 °C at ambient pressures, $BaTiO_3$ exists in a cubic (perovskite) crystal structure. Yet, when cooled below 120 °C, $BaTiO_3$ undergoes a phase transition to tetragonal crystal symmetry. This is significant because in cubic symmetry there is no net electric dipole, while in tetragonal symmetry there is an electric dipole moment. This is the result of broken inversion symmetry in the tetragonal crystal structure.

We can then write the Hamiltonian for this system in the presence of electric field $\boldsymbol{E}$ with polarization $\boldsymbol{P}$:

$$H = H_0(p, q) - \boldsymbol{P} \cdot \boldsymbol{E} \tag{1}$$

The polarization is a first derivative:

$$P = -\left(\frac{\partial H}{\partial E}\right)_T \tag{2}$$

The permittivity is a second derivative:

$$\varepsilon = -\left(\frac{\partial^2 H}{\partial E^2}\right)_T \tag{3}$$

Noting that the formulary is exactly identical to that of the Ising Model transition, with a change of labels, where $H = H_0(p, q) - \boldsymbol{M} \cdot \boldsymbol{B}$, with magnetization $M = -\partial_B H$ and susceptibility $\chi = -\partial_{BB} H$, we may use the results of that model with suitable rebranding to realize some theoretical understanding of the $BaTiO_3$ system.

For a second order phase transition, from the Ising Model, and also the mean field theory of ferromagnets, we expect that for temperatures above the transition temperature, for some constant c:

$$\varepsilon = \frac{c}{T - T_c}$$

This behavior does not happen. The permittivity does not diverge. Rather this second order transition is interrupted by the first-order phase transition corresponding to a discontinuity in the polarization when inversion symmetry is broken. We observed a first order transition at 119.45 ± 0.55 °C and estimate that if the second order phase transition had not been interrupted it would have occurred at $T_c = 89.96 \pm 0.57$ °C with constant $c = 1.0030 \pm 0.0068 \times 10^8$ F K/m.

EXPERIMENTAL METHODS

For this experiment, three circuits are involved in the manipulation and measurement of the crystal sample. Principally, the crystal is connected in series with a resistor, driven by a sinusoidal voltage, with the in-phase and quadrature voltages measured across the capacitor using a lock-in amplifier. Additionally, the sample is heated with a resitive heater coil, and the temperature is measured by the variation in voltage across a platinum resistor at constant current. The sample and platinum resistor were housed in a thermally insulated chamber, surrounded by the heater coil.

Through comparison of the quadrature to the in-phase voltages, with scaling for the resistance and frequency, the capacitance of the sample is determined as a function of temperature.

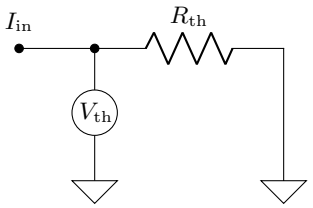

FIG. 1. Thermometer circuit. Current is provided by a constant current power source and resistance variations are determined by measuring the voltage across the resistor and using Ohm's Law, $R(T) = V(T)/I$.

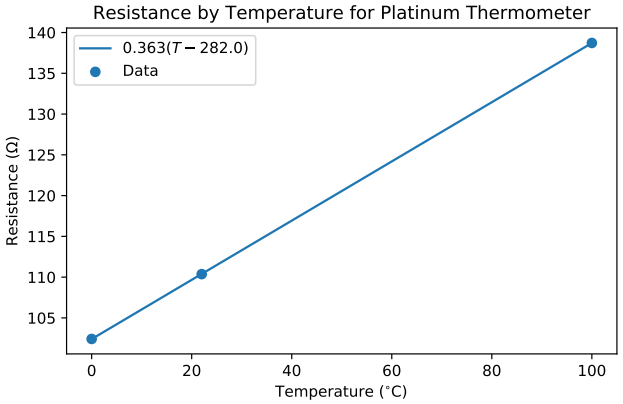

FIG. 2. Resistance as a function of temperature along with a least-squares linear fit. Data from Joshua Buttery and Paul Smigliani: our resistances inexplicably varied on the first day, but obeyed the Buttery-Smigliani relation on the second day. We found that $R(T) = 0.363(T - 282.0)$ for T in Celsius. Note that adding a 1 Ω resistor (such as wires) in series with the platinum resistor insignificantly affects the results and is accounted for by the interpolation. Error bars are smaller than the marker size.

Temperature

For many metals, over a moderate temperature range, their resistance is proportional to the temperature:

$$R_{\text{th}}(T) = r(T - T_0) \tag{4}$$

If a resistive circuit is built with a metal resistor, and a constant current power source, the temperature can be determined by the voltage with Ohm's Law, $R = V/I$:

$$T(V_{\text{th}}) = T_0 + \frac{V_{\text{th}}}{Ir} \tag{5}$$

In particular, we assembled a thermometer circuit with a constant current source of 0.01 A and a platinum resistor, and measured the resistance with a desktop multimeter, as shown in Fig. 1. We determined T_0 and r by measuring the resistance in ice water 0 °C, at room temperature 22 °C, and in boiling water 100 °C, and interpolating a least squares fit, as shown in Fig. 2. We found

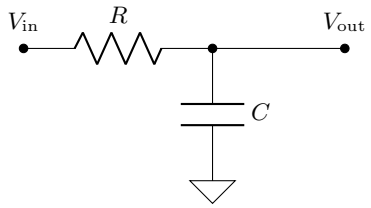

FIG. 3. RC circuit design. V_{in} is a sinusoidal voltage, R is fixed, C is the crystal, and V_{out} connects to a lock-in amplifier.

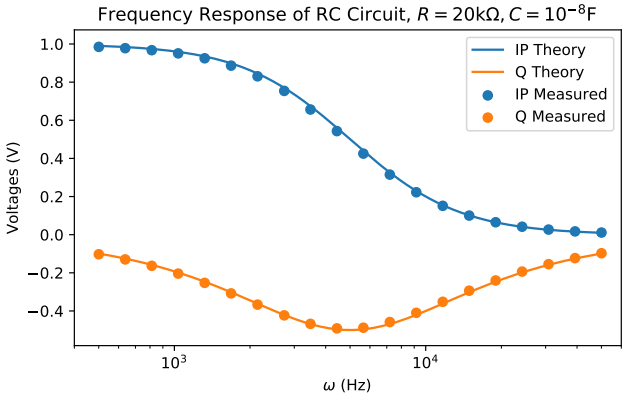

FIG. 4. Frequency response of an RC Circuit to sinusoidal driving. The graph is centered on the 3 dB point, where $|V_{\text{IP}}| = |V_{\text{Q}}|$, of $\omega = 1/\tau = 1/RC$ which is 5 kHz here. We observe good agreement between the theoretical and experimental values. Error bars are roughly the marker size.

$r = 0.36312 \pm 0.00038$ Ω/K and $T_0 = -282.01 \pm 0.34$ °C. At 0.01 A the temperature is found using the expression:

$$T(V_{\text{th}}) = \frac{V_{\text{th}}}{0.0036312} - 282.01 \tag{6}$$

Capacitance

We consider the frequency response of the RC circuit shown in Fig. 3. The impedance of the circuit with nothing attached to the output is:

$$Z = R + \frac{1}{i\omega C} \tag{7}$$

This means that the output voltage is:

$$V_{\text{out}} = \frac{\frac{1}{i\omega C}}{R + \frac{1}{i\omega C}} V_{\text{in}} \tag{8}$$

$$= \frac{1}{1 + iR\omega C} V_{\text{in}} \tag{9}$$

$$= \frac{1}{1 + iR\omega C} \frac{1 - iR\omega C}{1 - iR\omega C} V_{\text{in}} \tag{10}$$

$$= \frac{1 - iR\omega C}{1 + R^2\omega^2 C^2} V_{\text{in}} \tag{11}$$

Thus, the in-phase and quadrature voltages are:

$$V_{IP} = \mathrm{Re}(V_{\mathrm{out}}) = \frac{1}{1+R^2\omega^2C^2}V_{\mathrm{in}} \tag{12}$$

$$V_Q = \mathrm{Im}(V_{\mathrm{out}}) = \frac{-R\omega C}{1+R^2\omega^2C^2}V_{\mathrm{in}} \tag{13}$$

We assembled the circuit shown in Fig. 3 with a 19.98 kΩ resistor and a 0.0100 μF capacitor. We produced a sinusoidal signal with a function generator, and measured the in-phase and quadrature components of V_{out} with a lock-in amplifier. We observed good agreement between the theoretical and experimental values over a range of frequencies as shown in Fig. 4.

Now, we note that by taking the ratio of the quadrature to the in-phase voltage, and dividing by the (known) resistance and angular frequency, we find the total capacitance of the circuit:

$$C(T) = \frac{1}{R\omega}\left|\frac{V_Q(T)}{V_{IP}(T)}\right| \tag{14}$$

Now, the total capacitance is the sum of the capacitance of the sample and the stray capacitance from the wires in the circuit:

$$C(T) = C_{\mathrm{sample}}(T) + C_{\mathrm{stray}} \tag{15}$$

We then assembled the measurement circuit, with $V_{\mathrm{in}} = 1.078$ V and $R = 1.0789$ Ω, but instead of measuring the crystal as the capacitor, we measured a shorting wire. The 3 dB point of this circuit was at $f = 1.4885$ kHz, which corresponds to $C_{\mathrm{stray}} = 1/2\pi Rf = 9.910\times10^{-11}$ F.

We then measured the dimensions and mass of the crystal, shown at left in Fig. 5, and found that it had an area of approximately $A = 1.5$ mm^2 and a mass of 2.3 mg. With a density of 6.02 g/cm^3 this corresponds to a thickness of $d = 2.55\times10^{-4}$ m. For a given dielectric constant k the capacitance is:

$$C(T) = \frac{\epsilon_0 A}{d}k(T) \tag{16}$$

Or, rearranging to find the dielectric constant:

$$k(T) = \frac{d}{\epsilon_0 A}C(T) \tag{17}$$

Measurement

We drove our circuit with a $f = 1488.5$ Hz sine wave of amplitude 1.078 V, used a 1.0789×10^6 Ω resistor and determined that the stray capacitance was 9.910×10^{-11} F. We then measured the quadrature and in-phase voltages across the sample, and the voltage across the platinum resistor, taking one measurement per second using LabView, as we slowly cooled the sample from 180 °C to 40 °C. We then determined the capacitance using:

$$C_{\mathrm{sample}}(T) = \frac{1}{R\omega}\left|\frac{V_Q(T)}{V_{IP}(T)}\right| - C_{\mathrm{stray}}$$

We then determined the dielectric constant using the sample dimensions, as shown in Fig. 6, and the inverse capacitance, as shown in Fig. 7.

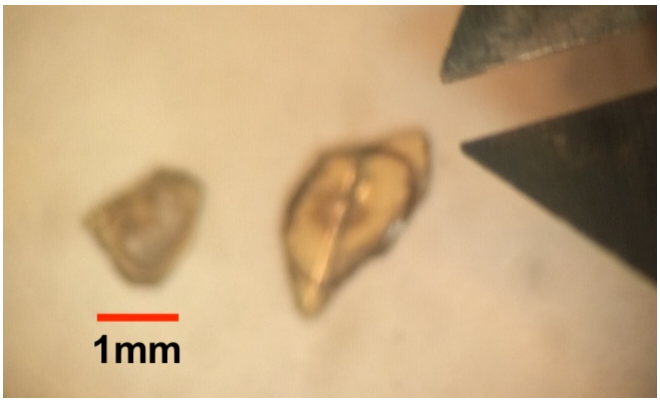

FIG. 5. $BaTiO_3$ samples. The sample we used is at left and has a mass of 2.3 mg and an area of approximately 1.5 mm^2.

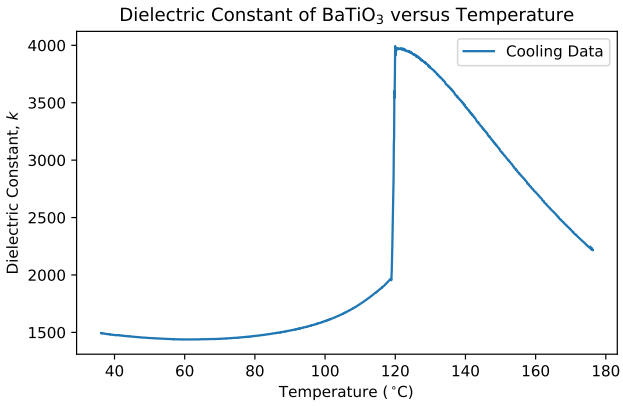

FIG. 6. Temperature dependence of dielectric constant in $BaTiO_3$. Near the critical temperature of 119.4 °C the dielectric constant nearly triples to a measured value of $k = 3994$. Error bars are smaller than the line width.

RESULTS

We observed a first order phase transition in the dielectric constant of $BaTiO_3$ at a temperature of 119.45 ± 0.55 °C. At this point we observed the dielectric constant changed from roughly 1800 to 4000 in a discontinuous transition. This result is in disagreement with mean field theory and the theory of second order phase transitions,

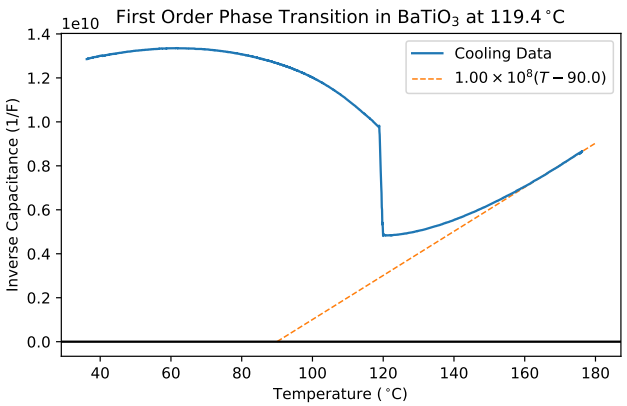

FIG. 7. We observe a first order, discontinuous, phase transition at 119.45 ± 0.55 °C, corresponding to the transition from cubic (paraelectric) to tetragonal (ferroelectric). We estimate that if mean field theory were valid and a second order transition occurred, it would occur at $T_c = 89.96 \pm 0.57$ °C with constant $c = 1.0030 \pm 0.0068 \times 10^8$ F K/m. We took a least squares best fit for the 100 hottest data points, since these were the most linear and least interrupted by the first order transition. Error bars are smaller than the line width.

which using our data predict a divergence of the dielectric constant at a critical temperature of 89.96 ± 0.57 °C.

Error Analysis

The determination of frequency ω and resistance R were measured to five significant figures with only small fluctuations around their values. Similarly, the voltages V_Q and V_{IP} were determined to four significant figures with only small fluctuations around their values. Meanwhile, C_{stray} was determined to four significant figures, but may have fluctuated during the experiment due to wire movements and environmental factors. The least accurate measurements we took were of the area and mass of the crystal which were measured to two significant figures. These less accurate values were limited by the optical resolution of a photo of the sample and the precision of a scale measuring the crystal's mass. The impact of these rough values is to introduce some systematic error into the determination of the dielectric constant: viz, the entire graph is a linear scaling of the true graph.

Discussion

While mean field theory and second order phase transitions predict a divergence of the dielectric constant at a critical temperature, no such divergence is observed: see Fig. 7. Rather, a discontinuity in the dielectric constant occurs, indicating a first order phase transition. We believe that this phase transition is a transition from cubic to tetragonal symmetry where inversion symmetry is broken and a polarized domains appear.

CONCLUSIONS

$BaTiO_3$ has a very large dielectric constant, and this dielectric constant is dependent on temperature. In particular at around 119.45 °C the dielectric constant is discontinuous and undergoes a first order phase transition. If we were to repeat the experiment, we would have taken more accurate measurements of the crystal's mass and dimensions.

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