Experiment 1: Observing $BaTiO_3$ transition from Para-electric to Ferroelectric properties

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ABSTRACT

To gain a better understanding of phase transitions, we observed a high temperature phase transition for $BaTiO_3$ where it transitions from from Ferroelectric to Para-electric. The principal measurement we made for this experiment was measuring the capacitance of $BaTiO_3$, as it shows the phase transition of the materials structure as temperature increases, specifically the structure of the $BaTiO_3$ changes such that it becomes a cubic structure when above the Curie Temperature and tetragonal below. Upon cooling we can observe the lowering of symmetry of the $BaTiO_3$ crystal, which causes its capacitance to decay. To conduct the experiment we used a lock-in Amplifier with a low-pass filter to collect the response signals of the $BaTiO_3$ as it was heated, which lead us to see that the Capacitance of the material drastically increases once we heat passed the Curie Temperature.

I. BACKGROUND INFORMATION

The main objective of this experiment was to observe the phase transition of Barium Titanate $BaTiO_3$ by heating it to the Curie Temperature. Not only is $BaTiO_3$ a natural Ferroelectric it has many uses in industry making it optimal to experiment on to observe phase transitions. $BaTiO_3$ has 3 phase transitions one below 183 Kelvin with an associated rhombohedral structure and below 278 Kelvin with orthohombic structure, when above 120 Celsius it is a high-symmetry crystal known as a perovskite having chemical formula ABO_3, and having a cubic FCC structure where A is centered, B is the corners. When cooled the structure undergoes a set of phase transitions lowering the symmetry with the lattice constant a decreases and C which increases. The transition has 6 oxygen ions around the Ti atom that elongate but don't remain symmetric causing the dipole moment to be aligned along the positive or negative based on the elongation and the dipole moment scales with distortion describing the phase transition from parraelectric to ferrorelectric.

$$\varphi = \frac{c-a}{a} \qquad [1]$$

where the polarization P can be defined as $P \sim \frac{\varphi}{v}$ where v is the volume of the cell. For our experiment we focus on the highest temperature transition from parraelectric to ferroelectric. Ferroelectric material is identified when the electric charges exhibit instantaneous polarization. Ferroelectric material has low symmetry, the $BaTiO_3$ material above 120 Celsius has high symmetry to get to the lower symmetry you must cool below the Curie Temperature of 120 Celsius T_c where the $BaTiO_3$ will be a Ferroelectric. When the material is parraelectric it becomes a dielectric , in these states the dielectric constant greatly increases and decreases as Temperature falls below the Curie temperature.

$$\epsilon(T) = K(T)\epsilon_0 \qquad [2]$$

The value of K is the main focus of this experiment, specifically it effects the permitivity of free space with a temperature dependence allowing us to see how the Capacitor value changes with temperature.

A phenomenological theory about temperature dependant ferroelectrics was made by L.D. Landau in the 1930's, where he described the dielectric constant x(T) increases with temperature till the Curie Temperature where divergence occurs. A factor to consider in our experiment is that the dielectric constant also depends on frequency, though to simplify this we used a stable frequency that aligned our in and out of phase voltages to be a factor of π, as well as keeping the overall frequency below 1kHz, and applying a low-pass filter.

To begin our experiment, we first tested a sample chamber which will house the sample and then ran the experiment with the sample $BaTiO_3$ itself. The exact setup we used had us use a Sample chamber with heater coil, a wired sample of material used in the actual experiment and a Pt resistive thermometer to measure the temperature as a voltage all inside the sample chamber. To properly measure the impedance in the system we used a Lock-In Amplifier as well as a DVM to read the voltages throughout the experiment. To feed the system a voltage to heat the sample we had a power supply generator directly connected to the heating coil which we turned on to around 50 volts when measuring the sample.

The principle of the measurement was the capacitance caused by the change in phase and temperature for this experiment. To measure the capacitance we placed the sample of $BaTiO_3$ in the test chamber that heats and connected it to a circuit by using two conducting prongs connected by conductive silver paint on the sample. The Crystal must be securely placed and the phase transitions start to occur around 120 Celsius. The capacitance can be measured by equation 3 where the A is area of capacitor, d is its distance, and the $K\epsilon_0$ is the thing being observed changing in the experiment.

$$C = K\epsilon_0 A/d \qquad [3]$$

The first part of the experiment had us analyze the equipment we are using and gather some preliminary data. The sample chamber we used has a platinum resistor for temperature measurement. To avoid heating the sample we had to make sure the inputted voltage through the capacitor did not exceed 10 mVolts and we verify that the current does not influence the sample by measuring various voltage and currents across it but seeing the same resistance which we did and saw. To heat the system properly, the heating coil is wrapped around the aluminum block in the sample chamber. To properly receive measurements you must use the aluminum cap, we did this once without and the data came out horribly.

The next step in our set up was to properly calibrate our thermometer. Our thermometer was a Pt thermometer probe. The thermometer we received was uncalibrated, but given a guideline equation of 4 we were able to calibrate the thermometer our-self, where A in the equation is used as a constant to capture the growth in resistance in the thermometer itself due to temperature. Industry standard value is $\alpha = .3851/C\Omega$, but ours varied slightly from this value but overall; the way we tested the thermometer was first varying the current to see how it reacts but it maintains a constant resistance but when we heated the system the resistance grew with temperature changing the results despite the current remaining constant. Though the equation has some systematic error as derivative of R of T varies about 2% at higher temperatures. We are also asked a question, if a 1Ω resistor is added to the measurement of Pt how much systematic error would that introduce in the temperature measurement. The answer considering the rest of the system is unaffected, the systematic error would be minimal about 1%, specifically the resistance we measured was 109Ω and this would not effect the alpha measurement seen in equation 5 as the resistance at 100 is subtracted by the one at 0 so the 1Ω added would cancel itself out.

$$R(T) = R_0 + AT \qquad [4]$$

$$\alpha = \frac{R_{100} - R_0}{100CR_0} \qquad [5]$$

After making sure our set up was acting properly and testing the components , we began measurement of the capacitance. The main object allowing us to test this measurement was the lock-in amplifier, which collects response signals from the frequency it drives them also. A signal source supplies the drive frequency at ω_r, and a synchronous reference as a second input to lock-in. The amplifier releases a dc output that is proportional to a Fourier component of the signal input with a reference. Since we use a low pass filter to receive all the measurements the dc is filtered out. We receive two output channels from which we receive our in phase voltage as well as our quadrature voltage. The lock-in signal input will be the potential difference across the capacitor. we are also given 4 equations to work from. We measure between 100Hz and 10 kHz but only choose 1 frequency in that range so we can see how the capacitance changes.

$$tan(\phi) = \frac{V_Q}{V_{ip}} \qquad [6]$$

$$V_s = [V_{ip}^2 + V_Q^2]^{1/2} \qquad [7]$$

$$V_{ip} \sim V_0 \qquad [8]$$

$$V_Q = -V_0\omega(RC) \qquad [9]$$

We are also asked a question to work out the in-phase and out-of phase components of the potential across the capacitor and they go as follows with the real and imaginary components respectively,.

$$V_{out} = \frac{Z_C}{Z_R + Z_C} V_{In} = \frac{\frac{-i}{wC}}{R - \frac{i}{wC}} V_{in} = -\frac{i}{RwC - i} V_{in} = \frac{1 - iRwC}{(RwC)^2 + 1}$$

$$V_{ip} = \frac{V_0}{1 + C^2R^2\omega^2} \qquad [10]$$

$$V_Q = \frac{-CRV_0\omega}{1 + C^2R^2\omega^2} \qquad [11]$$

The final results of our experiment were the following, for the α measurement for the thermometer we got a α close to industry standard with a value of $\alpha = .3871/C\Omega$, so equation 4 for the temperature worked and the thermometer was properly calibrated with a resistance of 109 Ω. Then we tested the voltages for in-phase and out of phase with various frequencies on a 1042 picoFarad capacitor where the frequency for equilibrium was 296.5 Hz. The last and most important measurement we made was for the capacitor, first we measured it theoretically getting a area of 6mm and a distance between plates of about 3cm we get that the capacitance is around 177 picoFarad which is around the initial capacitance of 135 picoFarad from the actual experiment with frequency 524 Hz, initial voltage .6008 volts, Amplitude of .995 volts, using a $1M\Omega$ resistor and using the capacitance formulas above to solve. The end result was that we were aligned with what our capacitor should be and followed it well within the temperature change.

II. TABLES AND GRAPHS

The first measurement in the lab we made, was to check the resistance through the thermometer by varying the current and seeing how the voltage reacts, the purpose of which was to show the resistance remains stable, then we proceeded by keeping a stable current and measuring temperatures with our thermometer at very cold and very hot regimes by putting it in boiling or ice water allowing us to see the resistance change with temperature allowing us to find a value for the resistance as a function of temperature. We received a 109Ω resistance at room temperature which is around 294 Kelvin (we found 100Ω at 273 Kelvin). Using equation 4 we can simply use 100Ω as our resistance and the α term that follows is multiplied by 294 Kelvin and it all equals 109Ω thus we can use simple math to find $\alpha = .3871/C\Omega$ which is close to industry standards. It also follows this method for the cold and hot thermometer where a slight change in resistance occurs, for a cold at 273 Kelvin the Resistance we 100.745, and for a hot 273 Kelvin we had a Resistance of 138.75, since this a 100 Kelvin increase and resistance increases 38.75 which can show $\alpha = .3875$.

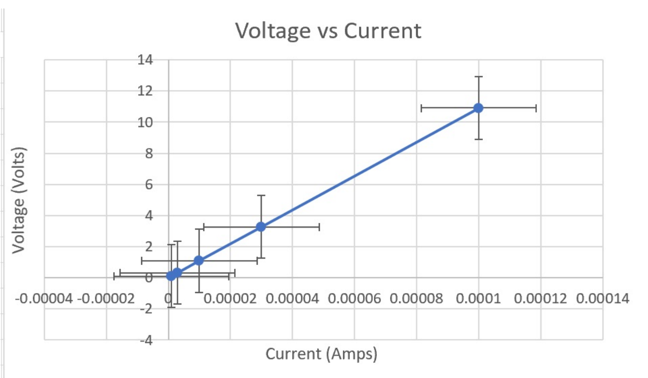

Figure 1: This graph shows the change in current corresponding the the change in voltage, it is completely linear signifying the resistance is a stable term.

The next item on our agenda was to verify the voltage across a 1042 picoFarad capacitor across an AC circuit and lock-in amplifier that we will use with the $BaTiO_3$ sample to make sure it provides accurate readings. To conduct this we simply attached a capacitor to the future place of the sample, specifically the wiring, and then connected it to the low pass circuit and the lock-in amplifier. The resistor we used in the circuit had an error, despite reading 422.7 $k\Omega$ it had a value of 464Ω, we factored that into our ωRC time which we wanted to have a value of 1 to make the in phase voltage and out of phase voltage to have phase of $\pi/2$, though our predicted value was 225 Hz to follow this, though the measured value we received was 296.5 Hz is where stability lay, which in the low frequency regime is an acceptable value. The next thing we did was the same methodology but instead of changing the capacitor and keeping a stable frequency at 150Hz.

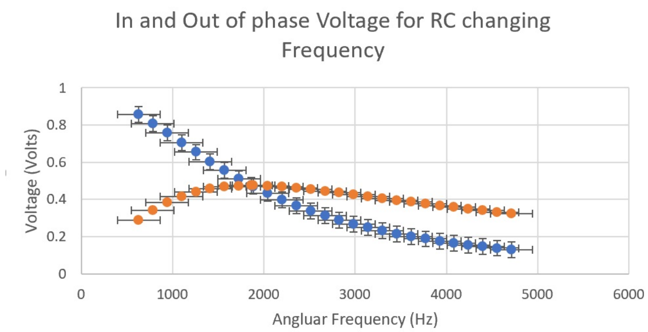

Figure 2: This graph corresponds to the varying in frequency for RC circuit, and seeing how the voltages align and work in this range for a 1042 pF capacitor.

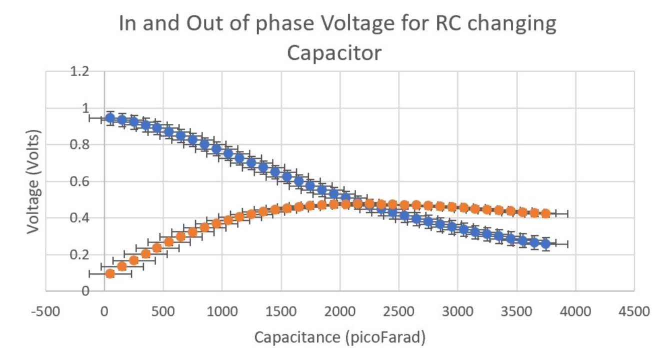

Figure 3: This graph corresponds to the varying in capacitor for RC circuit, and seeing how the voltages align and work in this range at 150Hz.

To make sure the resultant capcitance is following our standards we measure the voltage phase difference because the capacitance is calculated from equation 12 and we must make the the voltages work perfectly.

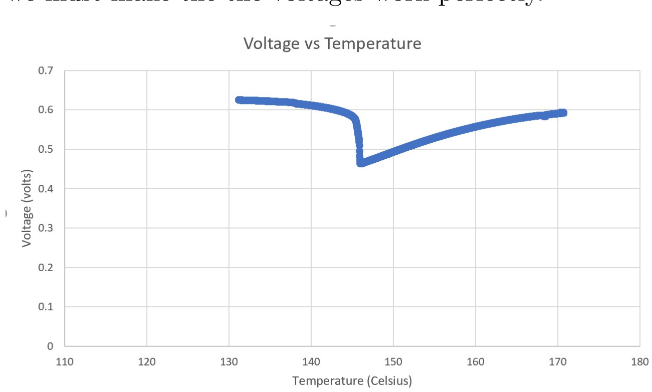

Figure 4: This graph corresponds to the varying in the total Voltage across the capacitor over a temperature regime.

The decisive experiment in this laboratory was measuring the actual capacitance change with time, in our case we look at how the permitivity of free space changes with temperature in both cases and then an anomalous case where the capacitance has a large spike. In our measurements we used a 1.07 $M\Omega$ resistor, 524Hz driving frequency, with a resulting V_{in} = .6008 Volts and V_{tot} = .995 Volts, which can allow us to have a capacitance value, but as temperature increases the resistance and voltages change also allowing us to see how the capacitance changes, using a formula seen in equation 12, and you can see the resultant capacitance's in figures 5 and 6 for the heating and cooling data on capacitance respectively.

$$C = \frac{1}{R\omega}(\frac{V_{tot}}{V_{in}} - 1)^{1/2} \qquad [12]$$

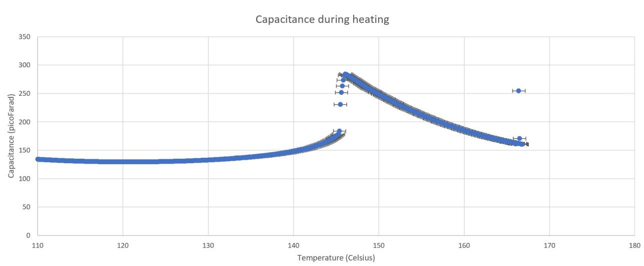

Figure 5: This graph shows the capacitor evolve with temperature heating.

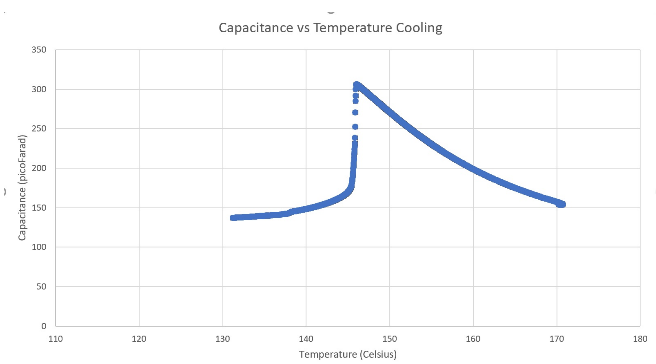

Figure 6: This graph shows the capacitor evolve with temperature cooling.

III. ANALYSIS

The results of the initial measurements of the resistance of the thermometer was simple, just using equation 4 we were able to match the expectations of the the thermometer and receive an $\alpha = .3875$ which was close matching the actual industry value.Though we also calculated an error showing us the temperature would vary about $T \pm 2.6311C$ which again was close to the 2% error in industry We were also able to properly align the in and out of phase voltages a 1042 picoFaraad capacitor which had a error of $\pm 2.464pF$ with a 464 $k\Omega$ resistor with a 296.5 ±.1 Hz frequency.

The data that we got was good, it covers the 1st phase transition of the $BaTiO_3$ effectively. We get that the temperature was moving appropriately and matches the transition of the $BaTiO_3$ which we predicted with the Curie Temperature. The quadrature and inphase voltages began to decouple as the temperature became higher indicating a change in the RC circuit we initially constructed with the unheated sample of $BaTiO_3$. Our initial capacitance was 135 picoFarad which at the peak of the phase transition became a Capacitance of 285 heating and 302 cooling ±3.26 picoFarad, with a dielectric constant of about 1600. We had a stray capacitance of about 182.599 ± 1.995 that we subtracted out of our measurements and, to measure the capacitance's error we used the following formula

$$\sigma C = C_{Best}((\sigma V_0/2V_{0beset})^2 + (\sigma V_{ip}/2V_{ibeset})^2$$

$$+(\sigma R/R_{beset})^2 + (\sigma f 2\pi/f_{beset})^2 + (\sigma C_{signal})^2)[13]$$

To get the dielectric we simply use our initial capacitance without the dielectric as our base value, and then apply the ϵ_0 multiplied by a constant to get the resultant capacitance's at heat change and we effectively get the change in dielectric constant, this can be seen with K ϵ_0 in equation 3. One expectation we expect from this is that after reaching the Curie temperature the capacitance again begins to form a 1/T ratio, this is what was expected and this is what is shown in the data. The resultant voltages we received from the circuit plotted against temperature show us that the voltage receives a big dip around the Curie temperature where the resultant phase transition takes place again this parameter is what we expect.

The last note on the phase transitions is the molecular and mathematical reasons why the everything occurs. The initial phenomenology was established by Landau's theory of phase transitions, where he analyzed how the free energy of a system reacts when heater. Specifically he shows that lattice distortions form when the energy of the system increases and that the application of magnetism to the free energy model with a perturbation. This eventually leads to the magnetic susceptibility being dependent on temperature, specifically the curie temperature and a phenomenological constant. The resultant equations are show below.

$$f = f_0 + am^2 + \frac{b}{2}m^4 \qquad [14]$$

$$\frac{df}{dm^2} = a + bm^2 = 0 \qquad [15]$$

$$x = m/B = \frac{1}{2a_0(T - T_c)} \qquad [16]$$

IV. CONCLUSION

In this lab we sought to observe the 1st phase transition due to cooling of the $BaTiO_3$ structure which changes from cubic to tetragonal during the transition. To cause this transition we simply heated a $BaTiO_3$ sample and then let it cool. The way we were able to observe this phase transition was by observing the capacitance or more succinctly the magnetic susceptibility change throughout the experiment. Specifically the susceptibility of a ferromagnetic is dependant on temperature and below the Curie Temperature the susceptibility becomes small shown by Landau theory of phase transitions. In our particular experiment we observed the capacitor have a spike at the Curie temperature and that the equipment we are using are within physical ranges after testing. In our particular experiment we had some issues, we were not able to gather data initially as the top of the heater was not placed severing our connection with the Op-Amp, also the lock-in amplifier had noise that had to be removed, and overall error with received values, though all can be mitigated with carefulness and repeated measurements in the overall experiment. The final results we have left with though match the theoretical expectations of what $BaTiO_3$ can achieve in this temperature range and our results were not effected by sources of error from equipment or systematically, allowing us to have a clear understanding of phase transitions for this crystal.