

Dielectric Spectroscopy of De Vries Smectic Liquid Crystals

Clayton Thatch

Bachelors of Science in Physics

California Polytechnic State University

San Luis Obispo, CA

For: Dr. Jonathan Fernsler

June 19, 2014

Abstract

In this experiment we used dielectric spectroscopy to observe the dielectric response of two De Vries liquid crystals; W-652 and W-751. A frequency sweep was run for each sample with various electric fields applied using an AC current. The samples demonstrated opposing effects at the SmA to SmC as the electric fields were increased. The W-751 showed an increased response with an increased electric field and a resonance peak in high frequencies that shifted through the transition, although there were no clear results in the low frequency range so there is no conclusive trend. The W-652 sample opposed the expected results of a DeVries liquid crystal and decreased response with an increased voltage. This effect is a unique property of the sample and further analysis is out of the scope of this experiment.

1. Introduction

Traditionally we are taught that the primary states of matter are the solid, liquid, gas, and plasma phases. In 1888 Friedrich Reinitzer, an Austrian botanical physiologist, discovered a second melting point between the solid and liquid phases in a cholesterol compound [6]. This phase would become beneficial in understanding biological systems and electro-optical sciences, later given the name liquid crystalline phase. These substances maintain the positional order of a solid structure with the “flow” of molecules in the liquid phase. The balance of these properties allow us to accurately model the bi-layer membrane in biological systems, create fast digital displays, and many more possibilities.

Liquid crystals can be modeled as long rod shaped molecules caused by their shape which causes the molecule to be rigid along its long axis. Due to the shape of the liquid crystal molecules, they are able to obtain some orientational order similar to a solid, yet lose some of the positional order of a solid allowing it to “flow” more like a liquid. Unlike ferromagnetic phases where each molecule points in a certain direction the liquid crystal samples have equal numbers of molecules pointing in opposite directions. This means that direction \mathbf{n} is equal to director $-\mathbf{n}$ and the molecules are aligned on the axis between them. The most common phases within the liquid crystal state are; isotropic, nematic, smectic A (SmA), and smectic C (SmC) but there are many more.

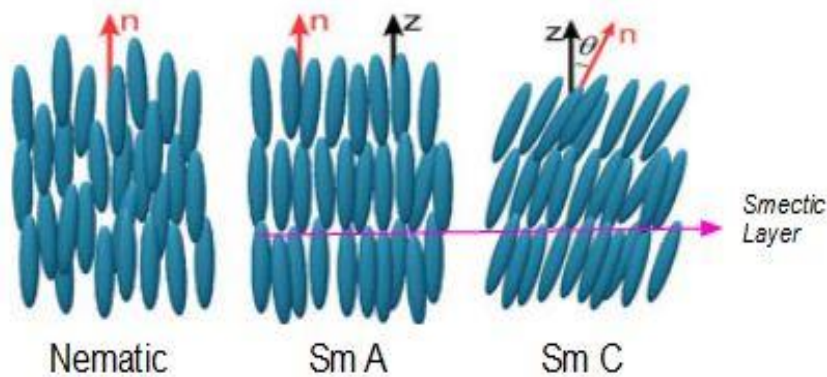


Figure 1. Three phases of liquid crystals; nematic, Smectic A, and Smectic C. \mathbf{n} represents the director of the sample and \mathbf{z} the axis perpendicular to the layers.

When a liquid crystal is in the nematic phase there is only orientational order due to the rod shape. The shape of the molecules will cause them to point in an average direction, \mathbf{n} , the molecules will not form layers as we will see in the smectic phases. (see Figure 1). The molecules have a symmetry about the director where $\mathbf{n} = -\mathbf{n}$, implying that an equal number of molecules point in either direction and not polarization is allowed along the director.

Another common phase a liquid crystal can have is the smectic phase, which is broken into smectic A and smectic C and other subphases. This phase comes from the early discoveries of this phase representing the mechanical properties of soap. Liquid crystals in this phase have orientational order and positional order in one dimension. Contrary to the nematic phase form layers. The center of mass of the molecules form a density modulation in the direction of the layer normal \mathbf{z} , which creates positional order. In the smectic A phase the director \mathbf{n} of the molecules is normal to smectic layer and parallel to \mathbf{z} (see Figure 1). This phase is similar to the nematic phase except the molecules form layers instead of being randomly oriented. The smectic C phase has properties very similar to the smectic A phase where molecules form layers and point along a director. The director makes a spontaneous tilt angle Θ with respect to the layer normal \mathbf{z} meaning there is no preferred direction with the smectic layer (see Figure 1).

1.1 Properties of Liquid Crystals

Now that we know the basic phases of a liquid crystal we can explore the properties associated with these phases and the transitions between them. In the smectic C phase we saw that the molecules had a tilt θ with respect to the layer normal \mathbf{z} . If you rotate the tilt of the SmC phase you can see that they form what is called a tilt cone along the director, see Figure 2. In chiral molecules this tilt induces a polarization in the direction of $\hat{\mathbf{z}} \times \hat{\mathbf{n}}$ due to the symmetry of the phase. The reason there is polarization in this direction is that there can be no special direction along \mathbf{n} , since $\mathbf{n} = -\mathbf{n}$ and there can be no polarization along \mathbf{z} , because the layers look the same in the \mathbf{z} and $-\mathbf{z}$ directions, so the only direction that could be unique and has polarization is in the direction perpendicular to \mathbf{z} and \mathbf{n} . This abstract concept was predicted by Noel Clark at the University of Colorado Boulder in the mid-

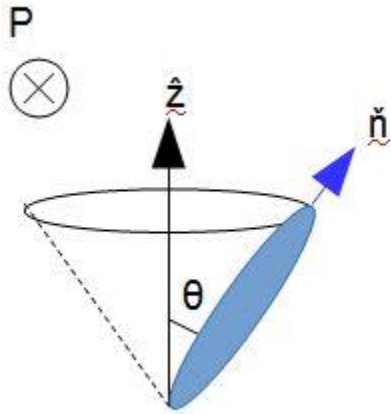


Figure 2. Crystals in the SmC phase experience a tilt, with angle θ , and are free to revolve around a cone.

1970's. In Figure 2 you can see that this cross product results in a polarization that is directed into the page. When we apply an electric field to our sample the molecule will revolve around the tilt cone until the polarization is aligned with the direction of the field.

When we consider the smectic A phase we can conclude that there is no polarization. Since the polarization is $\hat{z} \times \hat{n}$ then there is zero polarization because the molecules are aligned with the director and the cross product must then be zero. In our experiment we will see the effect of the induced polarization due to the transition into SmC* with an applied electric field. This *electroclinic effect* causes the molecules to tilt their axes in the plane perpendicular to the applied electric field. In the SmC* phase the electroclinic effect creates not only a tilt but a non-zero polarization due to the tilt making $\hat{z} \times \hat{n}$ not parallel

Liquid crystals also possess a level of chirality that describes their asymmetry. This term can apply to specific molecules or a bulk of LC, if a bulk is not symmetrical then it is considered chiral. If a molecule is not mirror symmetric then it is considered chiral. Otherwise the molecule or bulk can be considered achiral which shows symmetry. Commonly liquid crystals will form in helical structures when they are in a ferroelectric phase so they have no net polarization which lowers their free energy. In these samples when the layers are formed they tilt and each layer has a different polarization direction, it usually takes about 100-1000 layers to make the complete rotation around the tilt cone which creates a net polarization of zero.

Ferroelectricity is important to understand the SmC* phase. The * in the SmC* phase is used when you have chiral molecules (achiral molecules have a SmC phase). Only chiral molecules with their SmC* phase can be ferroelectric. Otherwise you have equal polarization in the $\mathbf{z} \times \mathbf{n}$ direction and the $-\mathbf{z} \times \mathbf{n}$ direction. Ferroelectricity describes a phase where the bulk of the material has a permanent electric polarization without an electric field. From before we know that molecules in the SmC* phase have a polarization due their tilt in each layer. The sample is ferroelectric if all of the layers point in the same direction. If the layers point in opposite directions then there is zero net polarization, this effect is called antiferroelectricity.

1.2 De Vries Liquid Crystals

In our tests we will use a specific type of liquid crystal called De Vries smectic LC's. This class of liquid crystals do not experience any layer shrinkage during the SmA-SmC phase transition [8]. In other liquid crystals the layers shrink during the transition because in

smectic C the molecules tilt away from the director which effectively shortens the distance between layers by $\sim l \cos\theta$, where l is the molecular length and θ is the tilt angle. De Vries proposed a model for this behavior where these liquid crystals have a spontaneous tilt with random azimuthal directions in each layer. This causes the molecules to essentially cancel each other out so that the SmA phase still has a common average director that is perpendicular to the layers along \mathbf{z} . Once in the SmC phase they maintain this common tilt but they tilt in a common azimuthal direction. Therefore, they do not have any shrinkage between SmA and SmC.

2. Theory

The concepts behind dielectric spectroscopy are based on the fundamental physics of a capacitor. Following from our explanation of the smectic phases, our sample forms distinct layers upon one another effectively creating “shelves” of molecules. Within these shelves the director is perpendicular to the shelf layers. By placing the sample in between two glass slides we create the sides of this metaphorical bookshelf and the molecules are standing upright like books (see Figure 3). For our experiments the samples are created using two glass slides coated with Indium Tin Oxide or ITO so the cell can conduct electric charge at the surface of the glass. By placing the liquid crystal material between two conducting plates we are able to effectively treat our sample as a capacitor with dielectric material discussed further in Section 2.1 [9].

In order to align the molecules of the liquid crystal we add a separate nylon coating and use a brush to lightly scratch into this layer. The grooves from the brush help align the molecules on our bookshelves. The thickness of our sample is an important property of our measurements and before we apply the liquid crystal material we use an Ocean Optics spectrometer for a precise thickness measurement. Then with the material applied and the slides containing the sample two wire leads are attached using conducting epoxy. This allows us to polarize the material by applying electric fields across the slides, Figure 3 shows a basic schematic of the material in between slides in the SmA and SmC phases.

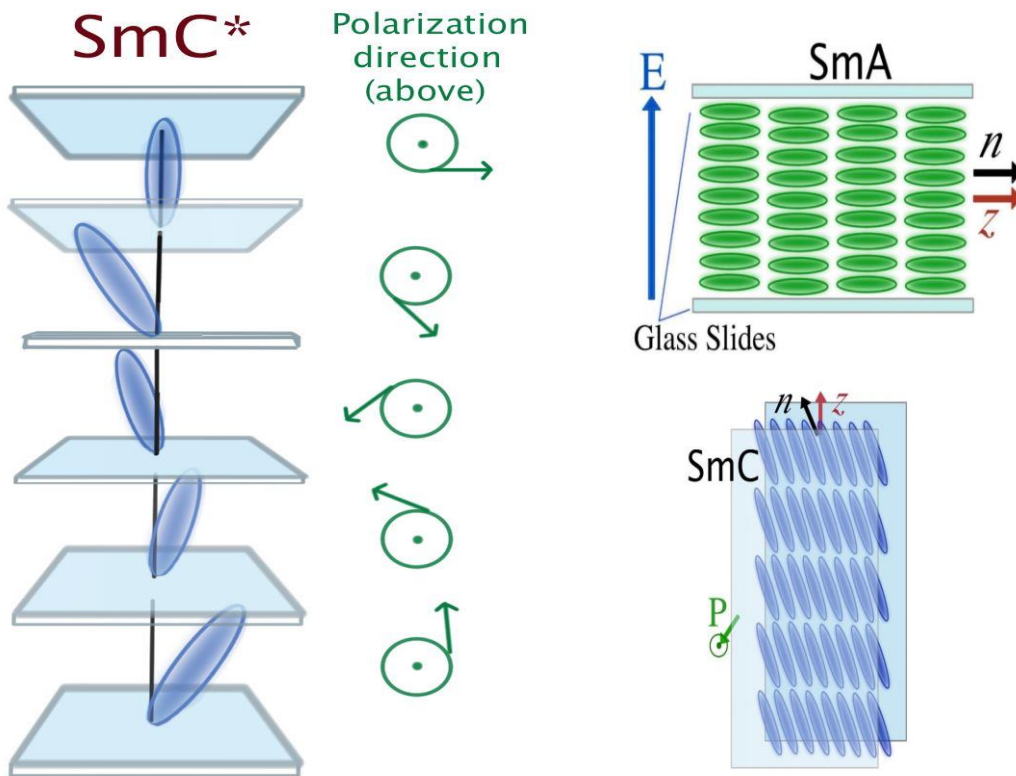


Figure 3. Basic schematic of our liquid crystal samples between two conductive glass slides. The samples can be treated as a capacitor with dielectric material.

By applying an alternating power source we are able to observe the response of the capacitor with an applied potential. The constant changing potential between the plates (glass slides in our tests) causes a time delay between the current phase angle and applied voltage as shown in Figure 4.

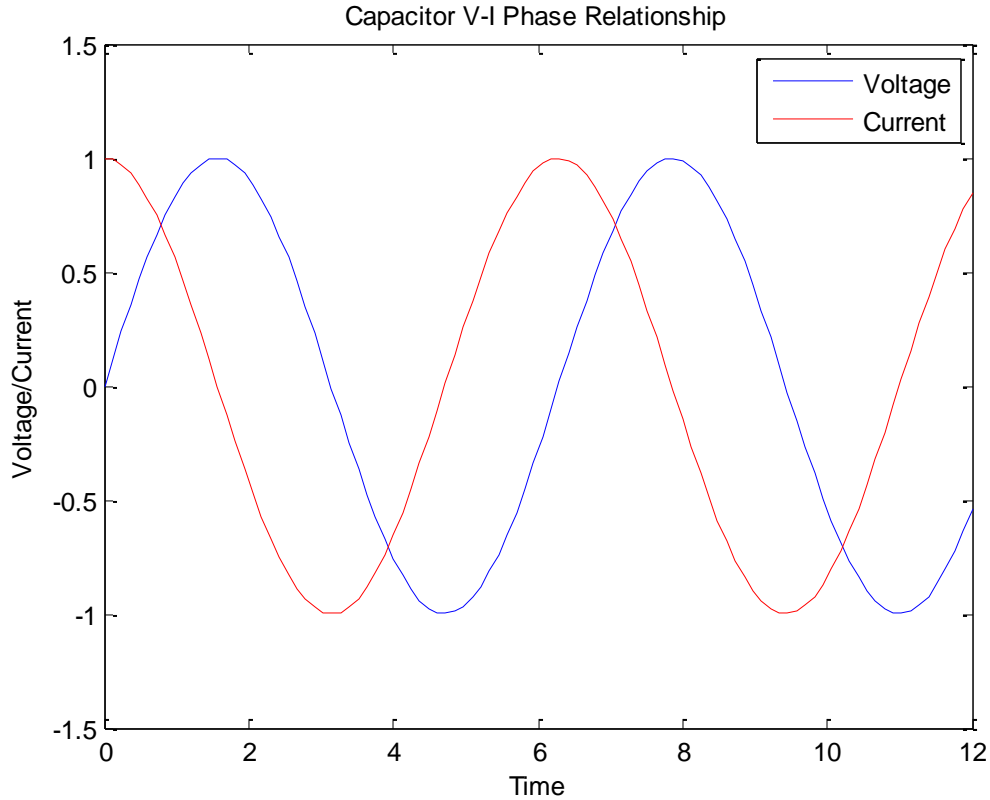


Figure 4. A demonstration of the phase angle between current (red) and applied voltage (blue)

Since current is the charge over time and the potential of a capacitor is total charge over capacitance, Q/C . This means that the current is the derivative of the potential across the capacitor, this ratio of the potential to the current is the impedance. The impedance is a major characteristic of a capacitor and the focus of this experiment it can be defined as:

$$Z = \frac{1}{\omega C} e^{-j\frac{\pi}{2}} = \frac{1}{j\omega C}$$

As shown in the above equation, the impedance is dependent on the frequency applied and we will measure the effect of the frequency on our impedance over a range of temperatures. Although the impedance here is imaginary we do not treat our sample as such because it is not an empty capacitor, it will follow the capacitance and impedance of a dielectric capacitor.

2.1 Capacitors

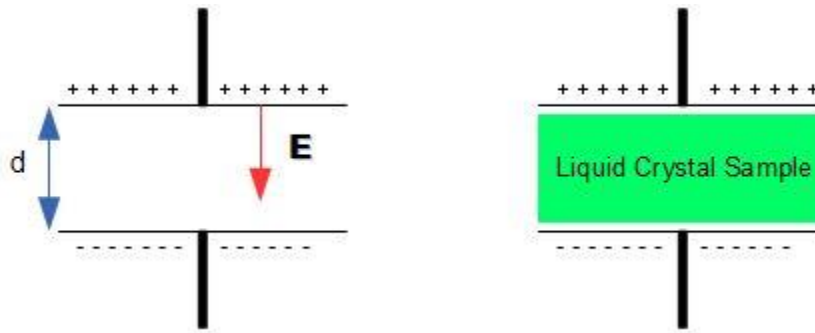


Figure 5. The capacitor consists of two plates separated by a distance, d . When a dielectric material is between the two plates (such as liquid crystals), the properties of the capacitor changes

The slides act as parallel conducting plates that each hold equal and opposite charges and separated by a distance, d . The capacitance or ratio of charge on each plate is given by:

$$C = \frac{Q}{V}$$

Where Q is the total charge, and V is the potential across the plates. With separation between the plates, d , which in the experiment is the thickness of our sample we can define the potential between the two plates:

$$V = \int_0^d E dz = \int_0^d \frac{p}{\epsilon} dz = \frac{pd}{\epsilon} = \frac{Qd}{\epsilon A}$$

Where p is the free charge, and ϵ is the permittivity of free space. The total surface charge can then be expressed as:

$$\frac{Q}{A} = \epsilon E \rightarrow Q = \epsilon EA$$

In this equation E is the effective electric field through the sample and by putting this relationship back into our first equation for the capacitance we find that:

$$C = \frac{\epsilon A}{d} = \frac{Q}{Ed}$$

2.2 Dielectric Capacitors

In our experiment we can treat the sample as a capacitor with dielectric material between the plates because liquid crystals are a dielectric material. Dielectric material, or dielectric

for short, is an electrical insulator that when placed under an applied electric field can be polarized. When there is an applied voltage the electric charges do not flow through the material (like a conductor) but only shift slightly from their equilibrium position. This shift causes dielectric polarization, where positive charges are displaced in the direction of the electric field. When composed of weakly bonded molecules, they will become polarized and orient their axis to align with the field. This effect known as polarization in an electric field can be described as the density of dipole moments between two plates of a capacitor:

$$\mathbf{P} = \epsilon\chi\mathbf{E}$$

In this equation, \mathbf{P} is the polarization density, ϵ is the permittivity, χ is the electric susceptibility, and \mathbf{E} is the applied electric field. The susceptibility factor shows how sensitive the dielectric material is to the environment including the temperature, density, and pressure. In our measurements it will behave linearly because of the small alternating electric field. Including this polarization density into the charge on the surface of our capacitors plates allows us to describe the surface charge as:

$$\frac{Q}{A} = \epsilon\mathbf{E} - \mathbf{P} \rightarrow Q = (\epsilon\mathbf{E} - \mathbf{P})A$$

By the same method we used to find the capacitance of a standard capacitor we can plug in the surface charge:

$$C = \frac{Q}{V} \rightarrow C = \frac{Q}{dE}$$

Because the voltage across our sample is due to the change in the electric field we can then solve for the electric field to determine an expression for the capacitance of the dielectric from the above equation.

$$\mathbf{E} = \frac{1}{\epsilon} \left(\frac{Q}{A} + \mathbf{P} \right) \rightarrow \mathbf{E} = \frac{Q}{A\epsilon_0\epsilon_r}$$

Where $\epsilon_r = \chi + 1$, using this relationship we can then find the new capacitance of our dielectric material:

$$C = \frac{Q}{\mathbf{E}d} = \frac{Q}{\frac{Qd}{A\epsilon_0\epsilon_r}} = \frac{A\epsilon_0\epsilon_r}{d} = C_0\epsilon_r$$

The expression ϵ_r is due to the dielectric material in our sample and is related to the polarization susceptibility of our liquid crystal. This factor will be affected when we use an alternating electric field with varying frequencies to measure the samples impedance.

2.3 How does this relate to our experiment?

We used a HP 4192 LF Impedance Analyzer to measure the impedance of a sample. The device applies an AC voltage across the liquid crystal sample then measures the magnitude

of the impedance, the utility of this specific machine is its' ability to measure the phase delay between the current and voltage as described previously. By measuring the phase angle we can then separate the impedance into its real and imaginary components which can be described as:

$$R = |Z|\cos\theta \text{ (real)} \quad X = |Z|\sin\theta \text{ (imaginary)}$$

In these equations Z is the total magnitude of the impedance and θ is the phase angle. The real part, R, is called the resistance and the imaginary part, X is considered the reactance of the sample. Although we know the impedance of the liquid crystal samples should be entirely imaginary, there is resistance in our measurements due to the electrodes across the slides. The combination of these components give us the complex impedance given by:

$$Z = R + iX$$

Using this equation we can determine the admittance, Y, of our sample which is the reciprocal of the complex impedance:

$$Y = \frac{1}{Z} = G + iwC$$

This allows us to describe the conductance, G, and the capacitance, C. Note that the capacitance is an imaginary value. We will use our measurements to determine experimental values of the conductance and capacitance:

$$G = \frac{R}{R^2+X^2} \quad C = -\frac{X}{w(R^2+X^2)}$$

From these values we can then derive dielectric properties: the complex dielectric variable, ϵ_r , which also has real and imaginary components, ϵ' and ϵ'' respectively, as shown by:

$$\epsilon_r = \epsilon' + i\epsilon''$$

If we treat the liquid crystal sample as a dielectric capacitor then the admittance of our sample becomes:

$$Y_{LC} = \frac{1}{Z_{LC}} = jwC = jwC_0\epsilon_r$$

We can then solve this equation to get our complex dielectric variable in terms of the conductance and capacitance:

$$\epsilon_r = \frac{Y_{LC}}{jwC_0} = \frac{G}{jwC_0} + \frac{jwC}{jwC_0} = \frac{C}{C_0} + \frac{G}{jwC_0}$$

Therefore we can describe the components of ϵ_r , as:

$$\epsilon' = \frac{C}{C_0} \text{ and } \epsilon'' = \frac{G}{wC_0}$$

We will use the HP 4192 LF Impedance Analyzer to determine these values and measure their changes over a range of frequencies and temperatures.

3. Results and Discussion

These experiments measured the dielectric response of de Vries liquid crystal samples; W-652 and W-751. For the W-652 sample we swept the frequency from 10^3 Hz to 10^6 Hz in steps of 1 kHz. The W-751 was run more precise at lower frequencies; 5 to 250 Hz in step sizes of 5 Hz, then 300 to 1.2×10^5 Hz in steps of 100 Hz. These varying step sizes allowed the results to give more concise data in the lower frequencies where we expect to see a peak. Appendix B displays all of the dielectric measurements made for the two samples over various voltages and frequency ranges. We measured the dielectric spectrum across two applied voltages for each sample (see Figures 7 & 9); 10 mV and 1V. Each sample has a width of approximately 4 micrometers which means our applied voltages are 2.5 mV/micron and 0.25 V/micron, respectively.

From Figure 6 we see that the W-652 sample does not show a SmC* helix, this demonstrates that the helix is unwound. This is likely due to the helix pitch, width of the molecules to make one complete helix turn, being larger than the width of the sample. Since the helix width is larger, the helix is then forced to unwind in order to accommodate the space of our sample. If we created a thicker sample it is possible that we would see a helix in Figure 6. The helix would be evident by small lines running perpendicular to the direction of our molecules in the sample. When the helix is unwound in this fashion it suppresses the phason mode and ideally would allow us to observe the soft-mode peak of the sample. This soft-mode peak is primarily in lower frequency ranges about 0-50 Hz and we were unable to accurately observe or measure this peak in our measurements.

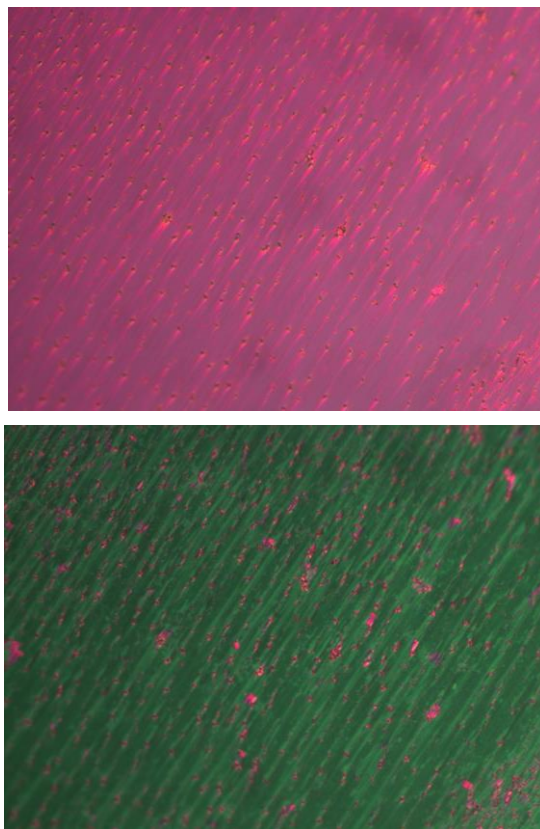


Figure 6. Images of the W-652 sample in SmA* (top) and SmC* (bottom) phases.

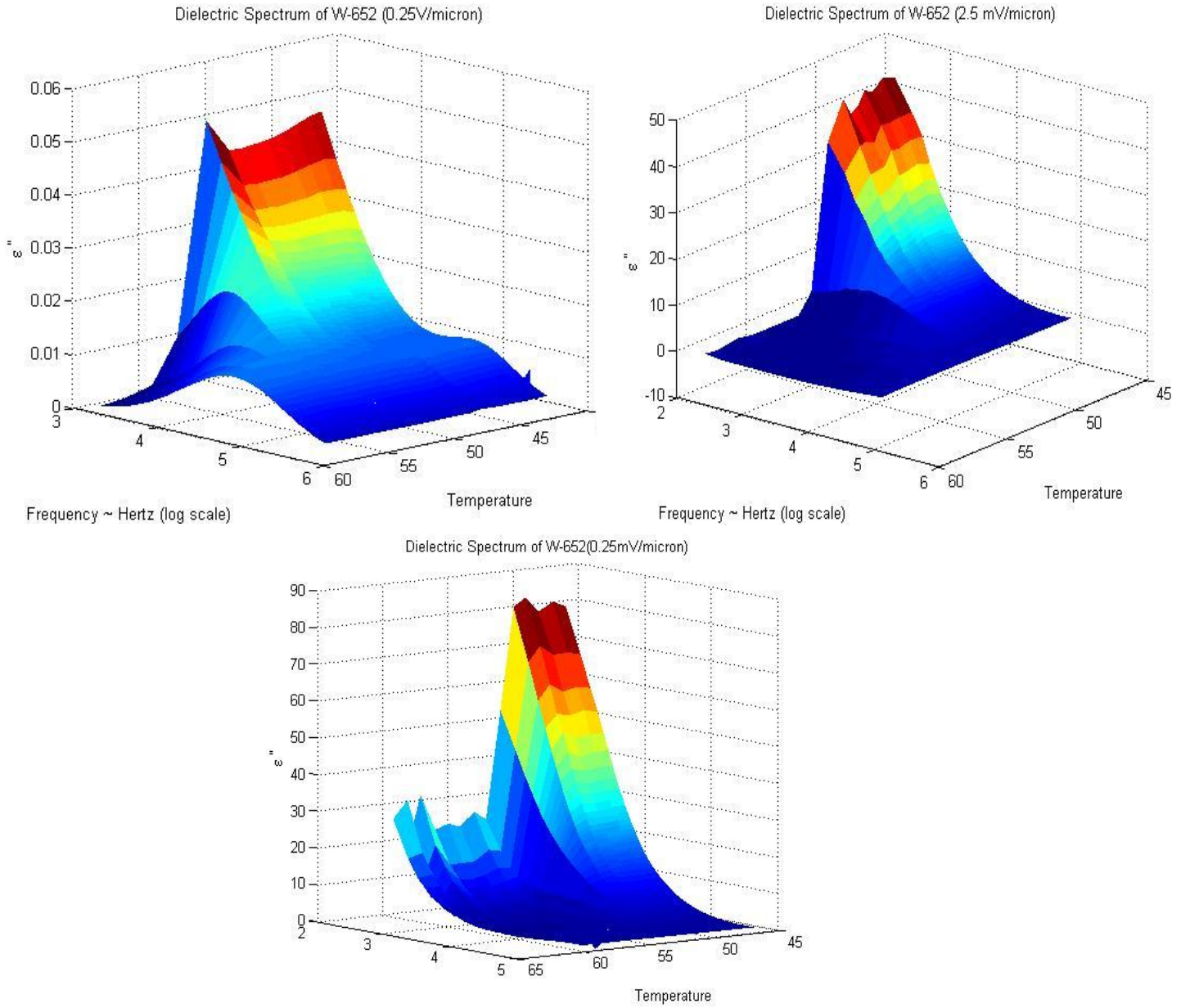


Figure 7. Dielectric spectrum of W-652 sample swept with applied voltages of 0.25 V/micron (left), 2.5 mV/micron (right), and 0.25mV/micron (bottom)

In the same W-652 sample we see that across different applied voltages in the same frequency range that the magnitude of the dielectric response changes drastically with the electric field. From our results we see that an increase in electric field shows a decreased dielectric response at the transition temperature. However, in De Vries samples we expect

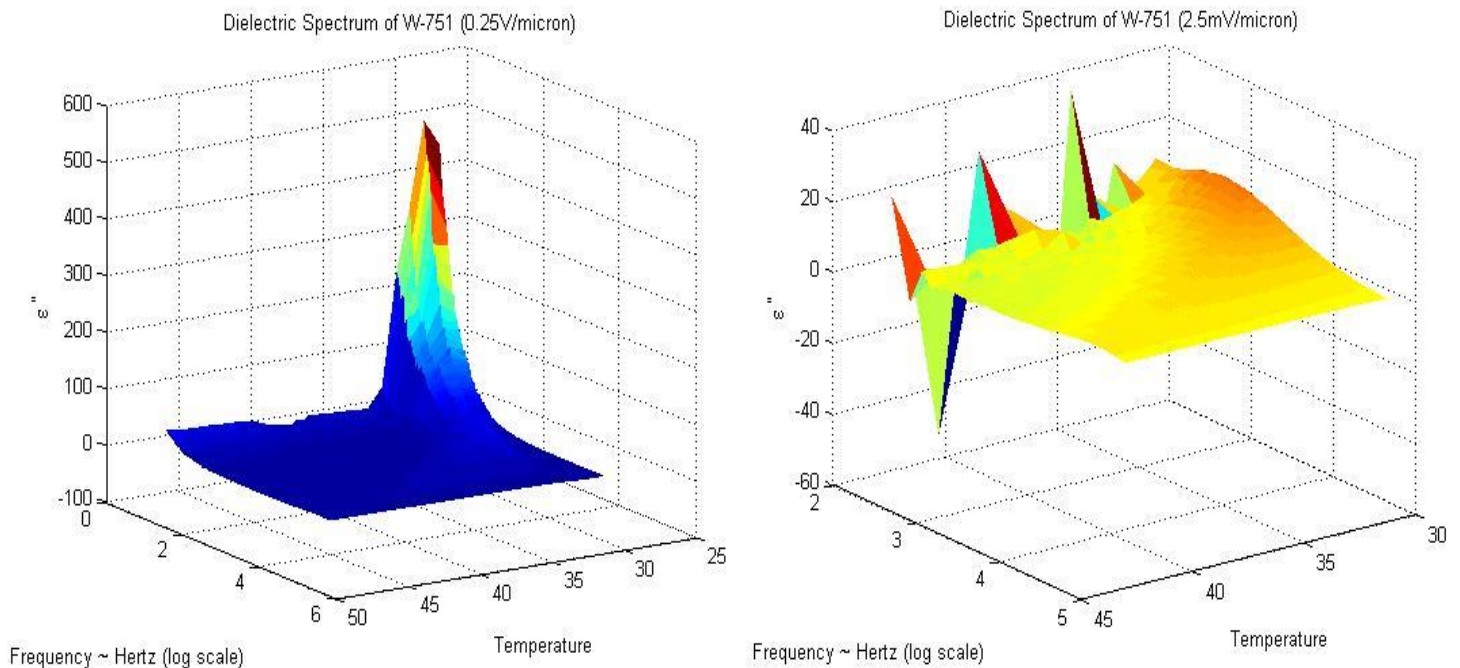


Figure 8. Dielectric spectrum of W-751 sample swept with applied voltages of 0.25 V/micron (left) and 2.5 mV/micron (right)

a larger applied electric field to cause an increase in the dielectric response because it unwinds the helix of the sample. [3]. Our data (see Figure 7) demonstrates the opposite result which could be attributed to the thickness of our sample. The W-652 sample we used in our measurements does not appear to have helix-cone that we would expect to see (see Figure 6), which could discredit the explanation of a larger response due to unwinding the helix. This relationship of an increasing dielectric response with a decreasing applied electric field is an interesting result but the explanation is complex and out of the scope of this experiment.

The W-751 sample is similar to our W-652 sample because both are too thin to show a helix cone (see Figure 9). In Figure 9 we see the dielectric spectrum for the W-751 has a much larger response with a larger applied voltage. Similar to the W-652 results we are unable to observe the soft-mode peak due to large amounts of noise in our measurements at lower frequencies (see Figure 8). However, there is consistently a high frequency peak that migrates from approximately 50kHz at 50°C to 1kHz at 30°C. This peak grows larger as it approaches the SmA to SmC transition which would imply an association with the transition although the reason for this effect is unclear. It is possible that this effect is related to dipole relaxation, ionic relaxation, or dielectric relaxation, and would require further testing for a conclusive result.

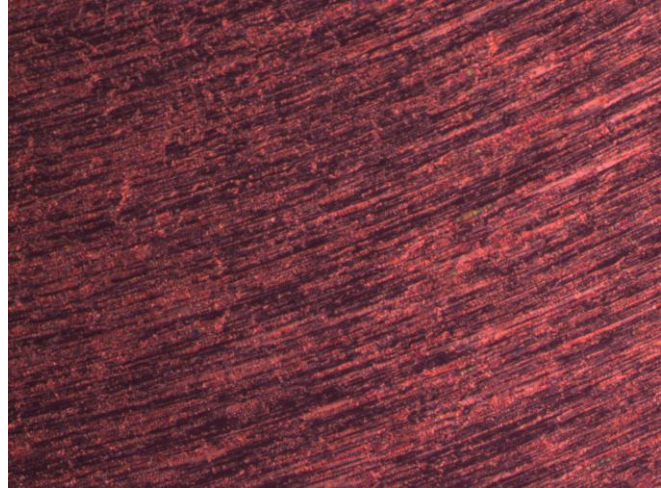


Figure 9. Real image of the W-751 sample in the SmA* unfortunately our sample is not thick enough to display a helix cone.

References:

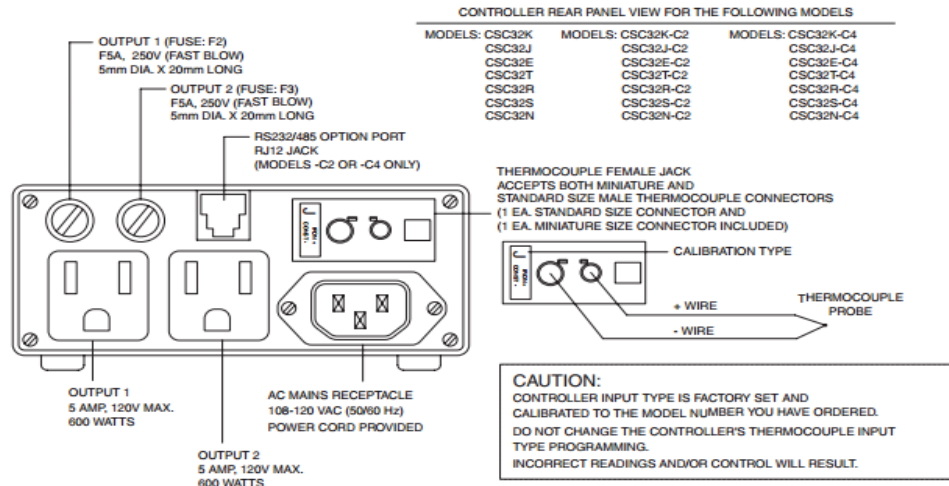
- [1] A. Ferrarini and C. Greco. Electroclinic effect in nematic liquid crystals: The role of molecular and environmental chirality. *Physics Review*, 2013.
- [2] D. Coleman, N. Clark, F. Giesselman, E. Korblova, J. Lagerwall, J. Oton, R. Shao, and D. Walba. The peculiar optic, dielectric and x-ray diffraction properties of a fluorinated de Vries asymmetric-diffuse-cone-model ferroelectric liquid crystal. 2005.
- [3] M. Krueger and F. Giesselmann. Dielectric spectroscopy of de vries-type smectic a - smectic c transitions. *Physical Review*, 71, 2005
- [4] Z. Sailer. *Dielectric Behaviour of de Vries Liquid Crystals*. 2013.
- [5] Deblal Das, Tanmoy Lahiri, and Tapas Pal Majumder. Theoretical investigation of helix distortion and dielectric spectrum of antiferroelectric liquid crystals. *Physica B*, February 2011.
- [6] Shri Singh, Avanish Singh Parmar, and Abhilasha Singh. Phase transitions in ferroelectric liquid crystals. *Phase Transitions*, Vol. 81(9), September 2008.
- [7] U Manna, Jang-Kun Song, Yu P Panarin, Atsuo Fukuda, and J K Vij. Electro-optic and dielectric study of the de vries-type smectic-a* phase exhibiting transitions to smectic-c phase. *Physical Review*, Vol. 77, 2008
- [8] P Malik, K K Raina, A Bubnov, A Chaudhary, and R Singh. Electro-optic switching and dielectric spectroscopy studies of ferroelectric liquid crystals with low and high spontaneous polarization. *Thin Solid Films*, August 2010.
- [9] P Perkowski. Dielectric spectroscopy of liquid crystals. electrodes resistivity and connecting wires inductance influence on dielectric measurements. *Opto-Electronics Review*, Vol. 20(1):pg. 79–86, 2012.

Appendix A

Running the Impedance Analyzer

1. Connections

- HP 4192A LF Impedance Analyzer: A thick white cable exiting the back from the left side should then be routed into the first USB slot of the PC, this cables allows the Impedance Analyzer to properly communicate with the LabView Program. On the front of the device the L/H potentials and currents should be connected to their corresponding spots on the connection box with the silver side facing down. Make sure the cable length switch is directed up to 1 meter.



- The Omega Benchtop Temperature Controller: A yellow jack connected to a white cord with a blue line connects the thermocouple female jack. The end of this wire needs to be as close to the middle of the oven as possible; **DO NOT LET THIS FALL OUT**. From the Output 1 slot a white power cord will separate into two pairs of red cables, these are the heating pads connected to the underside of the oven, make sure the pads do not block the center hole of the oven.

2. Initializing

- From the desktop open the LabView Program “HP4192A Impedance Analyzer”, if the icon is not on the desktop then go to “Documents” > “Impedance Analyzer” > “HP4192A Impedance Analyzer”
- With the program displayed, turn on the HP 4192A LF Impedance Analyzer (Note: this is the only button you will use on the machine, the rest controlled by the program).
- Turn on the Omega Benchtop Temperature Controller (See Manual for description of using the Temperature Controller)

3. Running LabView

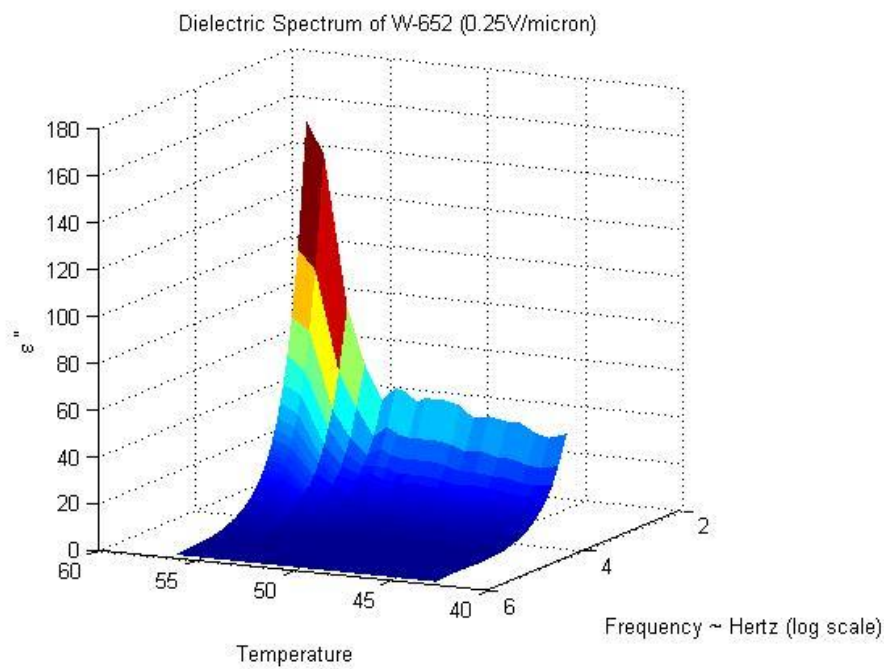
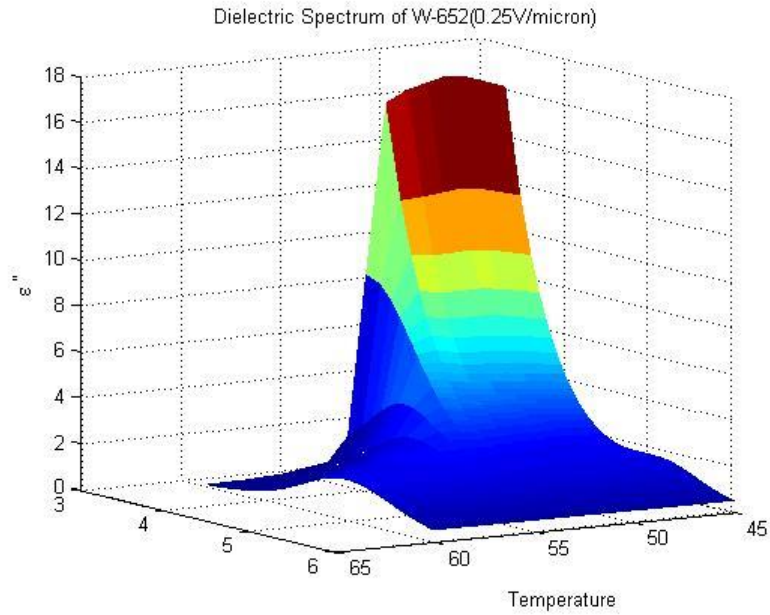
- Set the Device Address to “GPIB1::17::INSTR”
- Set Function A (z/y:0) to “Z/Y”
- Set Function B (deg q:0) to “RAD D”
- Set Trigger (internal:0) to “INTERNAL” and Circuit mode (auto:0) to “SERIES (R,Z)”
- Change Auto Sweep from “Off” to “On” and make sure the Last Sweep is aborted
- Then set your parameters for the start frequency, end frequency, and step size (Note: the device range is 5 Hz – 13MHz, and can run voltages up to 35 V)
- Turn on the option for “Write to Excel” if you want the device to save the data for later use
- Start the test by pressing the run button in the upper left

Troubleshooting

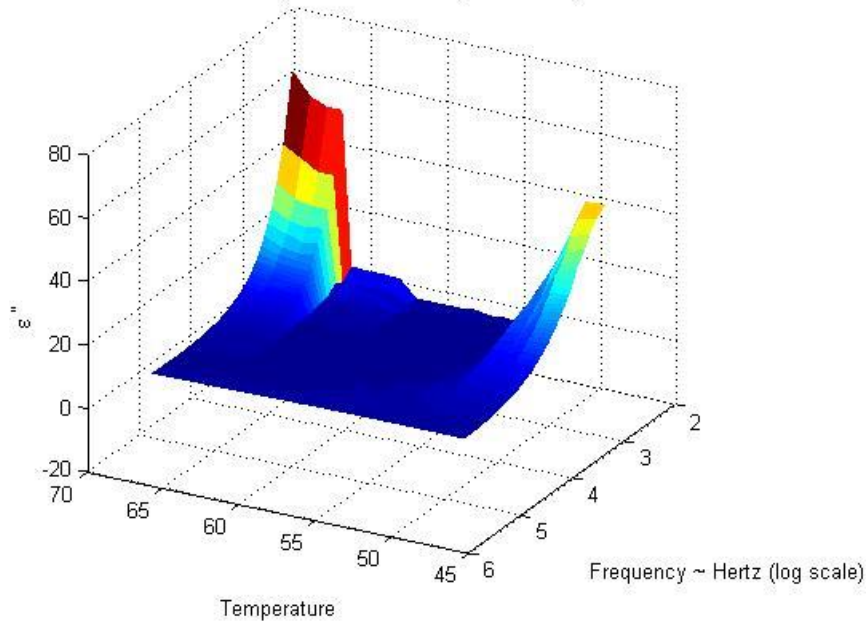
- Especially common at low frequencies the device will return an error looking like Figure A. It is due to a timing issue with the device at these low frequencies. It will then send you to the block diagram of the LabView program, re-run the test from this window and the test will work. Generally the error only happens once but you may need to re-run multiple times.

Appendix B : Dielectric Measurements

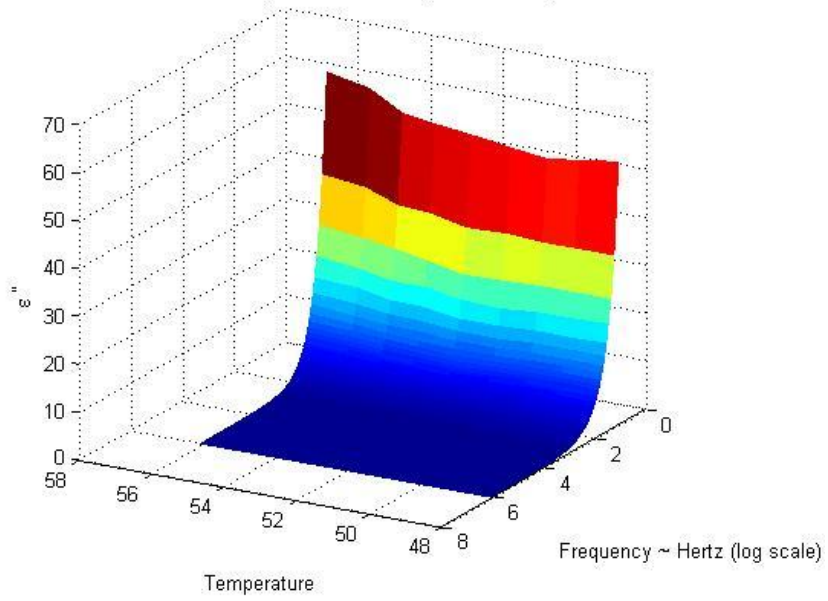
- W-652 sample (4 micron thick cell)



Dielectric Spectrum of W-652 (0.5V/micron)

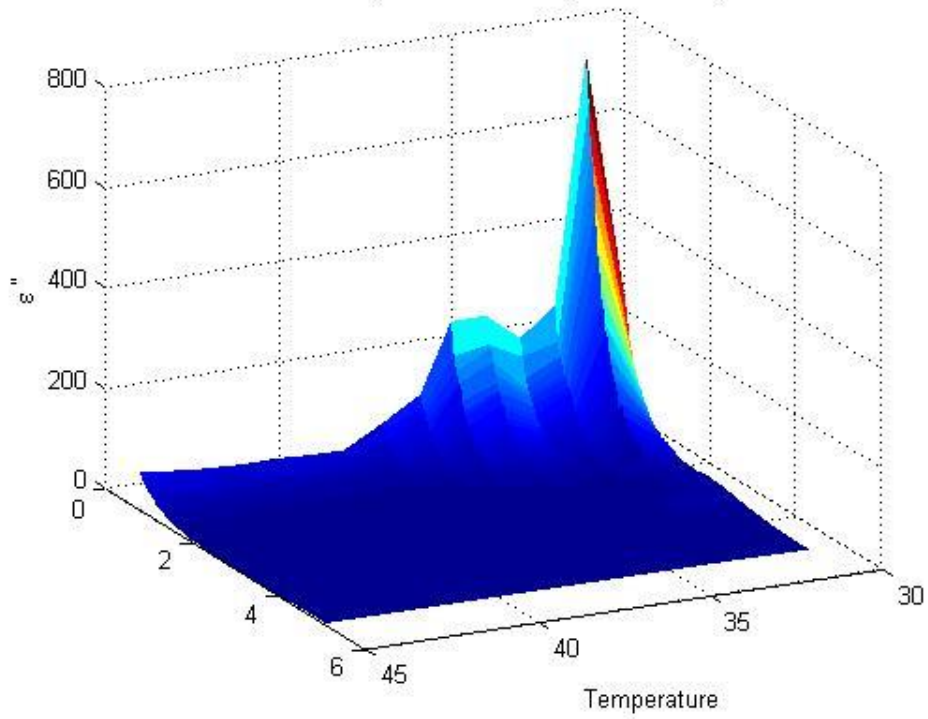


Dielectric Spectrum of W-652 (1.25V/micron)

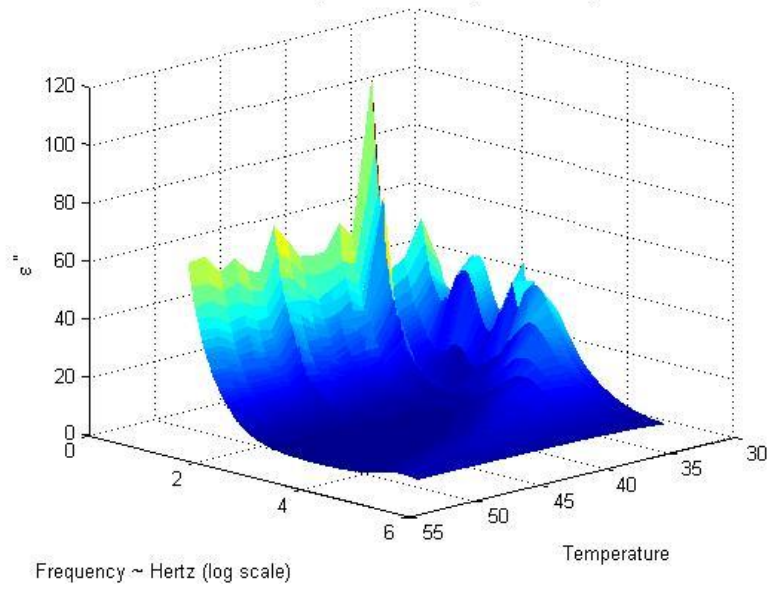


- W-751 sample (4 micron thick cell)

Dielectric Spectrum of W-751(0.25V/micron)



Dielectric Spectrum of W-751(0.25V/micron)



Frequency ~ Hertz (log scale)