Synthesis and Ferroelectric Properties of KNO_3 Film

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Introduction:

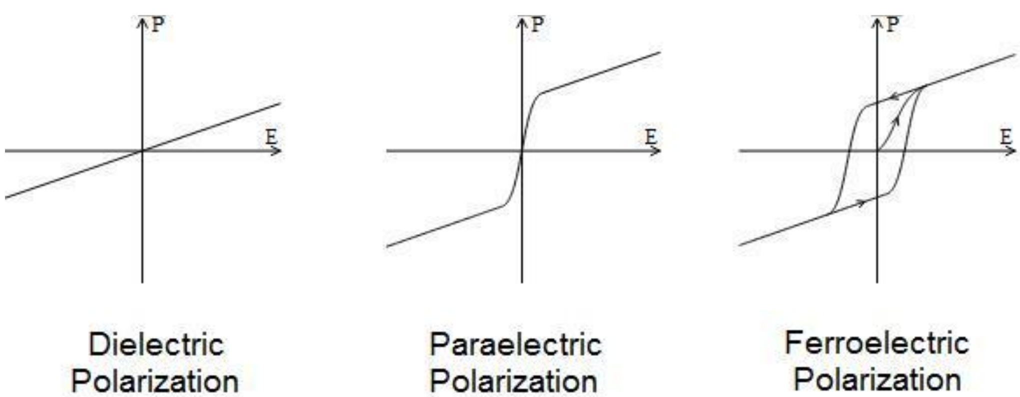
In this experiment, we will observe Ferroelectric behavior of Potassium Nitrate film using a Sawyer Tower Circuit.

Theoretical Background:

The phenomenon of ferroelectricity was discovered in 1921 by J. Valasek who was investigating the dielectric properties of Rochelle salt ($NaKC_4H_4O_6.4H_2O$). [1]

Ferro electricity is the property of certain materials in which they possess a spontaneous electric polarization that can be reversed by the application of external electric field yielding a hysteresis loop. Typically materials demonstrate Ferro electricity only below a certain phase transition temperature known as Curie temperature.

Most materials are linearly polarized by an external electric field. This is called Dielectric Polarization. Paraelectric materials demonstrate a nonlinear polarization and Ferroelectric materials demonstrate a spontaneous polarization that can be reversed by an applied electric field. [2]



When an electric field is applied, a ferroelectric material possesses a spontaneous electric dipole moment which is given by:

$$\mu = qr$$

where μ is dipole moment, q is the charge and r is distance between two charges.

Mathematically, the average dipole moment per unit volume induced in the solid is called the electrical polarization and is denoted as P. Ferroelectric materials are preferably polarized in certain crystallographic directions. This polarization arises due to distortion of the electronic cloud or slight movement of the atoms themselves. For ferroelectricity to be exhibited materials should be non-centro symmetric and have spontaneous local dipole moment.

As an example, we will closely look at the structure of Barium Titanate which is a ferroelectric material.

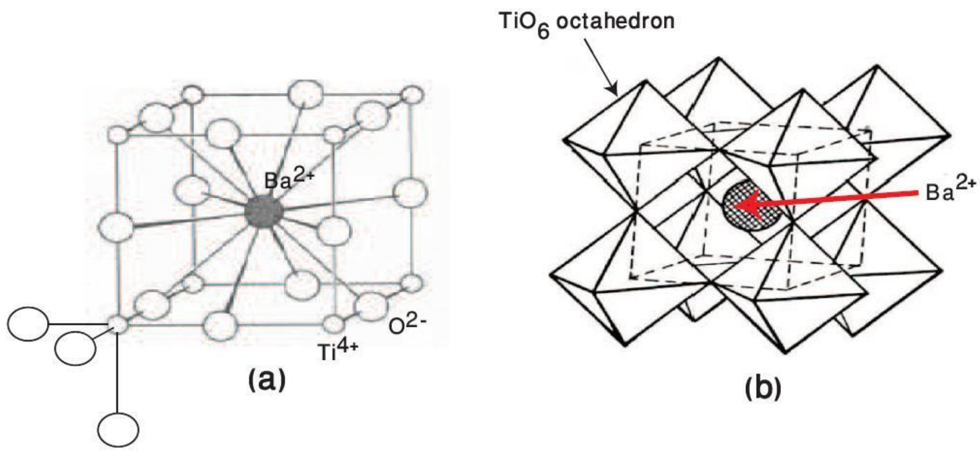


Figure: (a) Shows the perovskite structure of $BaTiO_3$ with the TiO_6 environment depicted for one of the corner Ti^{4+} ion. (b) shows a space filling model of the perovskite structure: the TiO_6 octehedra full up the volume, sharing their corners with one another. In this model, the large Ba^{2+} ions snugly fit into the interstices between the octahedra.

Above 120°C, $BaTiO_3$ has cubic crystal lattice with each unit cell comprising Ba^{2+}ion in the centre, Ti^{4+}at the cube corners and O^{2-}ions at the centre of the cube edges. The cubic phase of $BaTiO_3$ is not ferroelectric. As the material is cooled, cubic lattice undergoes transformations. At 120°C, it changes into tetragonal. In that phase the cube distorts. As a result TiO_6 group also distorts and Ti^{4+}ion gets displaced along $Ti - O$ bond axis. Such displacement causes a non-overlap of positive and negative centers creating a permanent electric dipole moment. This gives ferroelectric properties to $BaTiO_3$. [3]

A hysteresis loop between electric field E and polarization P is formed when polarization is reversed by applying a large alternating field. The Polarization and electric displacement D become non-linear functions of the electric field satisfying the relation:

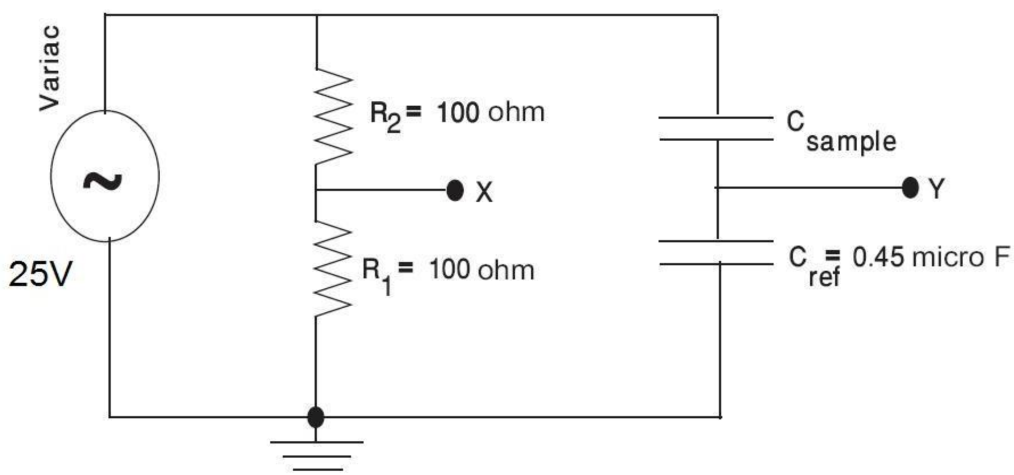
$$D = P + \varepsilon E$$

Usually in ferroelectric materials, the second term is negligible and a D-E loop becomes interchangeable with a P-E loop.

We will do our experiment with Potassium nitrate (KNO_3) which shows ferroelectric behavior at temperatures between 152℃ and 120℃ due to change in its crystal structure and phase. $BaTiO_3$ has a melting point of 1650°C while KNO_3 melts at 330°C . When KNO_3 is made as a thin film, the lower temperature limit of the ferroelectric phase is lowered, and it can be stable at room temperature. In bulk the phase transition can be reached only on cooling and not by heating. This is because the ferroelectric phase is narrower than the thermal hysteresis.

Experimental Procedure:

- A Sawyer-Tower Circuit is made whose circuit diagram is shown below:



The Sawyer Tower Circuit

By measuring the potential V across a standard capacitor in series with KNO_3 film, we can determine the charge Q on KNO_3capacitor using the relation:

$$Q = CV$$

We display the signal applied to the material as X signal of an X-Y trace on an oscilloscope. Most of the voltage drop is across KNO_3 capacitor so we can consider X-signal to represent voltage across the sample which is proportional to Electric Field E. When two capacitors are in series, the charge on each capacitor must be the same. In an ideal capacitive circuit, no current flows, so the charge on the standard capacitor and KNO_3 capacitor are the same. As the capacitance of standard capacitor is known we are able to determine Q from the magnitude of voltage signal we measure at the standard capacitor. The Y-signal is proportional to charge on KNO_3capacitor which gives us polarization.
Hence an X-Y curve on the oscilloscope is proportional to a P-E curve.

For dielectrics, we get a straight line between P and E while in Ferro electrics there is a remnant polarization hence it would display hysteresis.

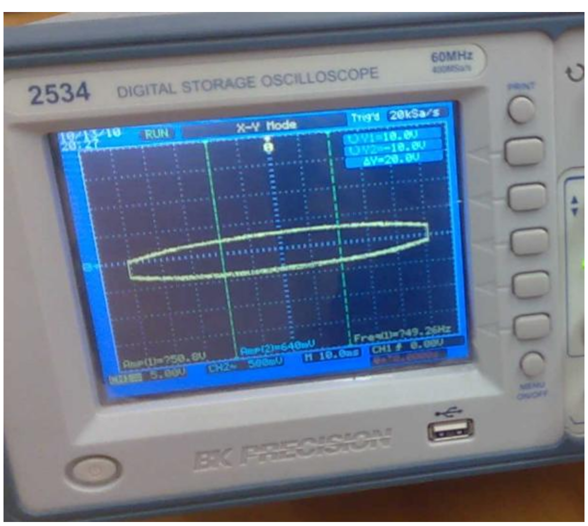
- KNO_3 is highly hydrophilic dried in a microwave oven for 2 minutes because Ferro electricity is degraded when materials absorb water.

- An aluminium sheet is clamped to hotplate and is insulated from it by glass pieces.
- KNO_3powder is placed inside the aluminium sheet and 3-4 thumb pins are placed in the powder.
- Heater is turned on until the powder is completely molten and temperature is constantly determined by a thermocouple.
- Heater is turned off when KNO_3 is completely molten and sample is allowed to cool.
- At about 170°C, the alligator clips are attached, one to the capacitor (thumb pin forms the capacitor itself when KNO_3 is in molten state)
- 25 volt signal is provided to the circuit from the variac.
- Sample capacitor is connected to the Sawyer Tower circuit and result is observed on the oscilloscope.

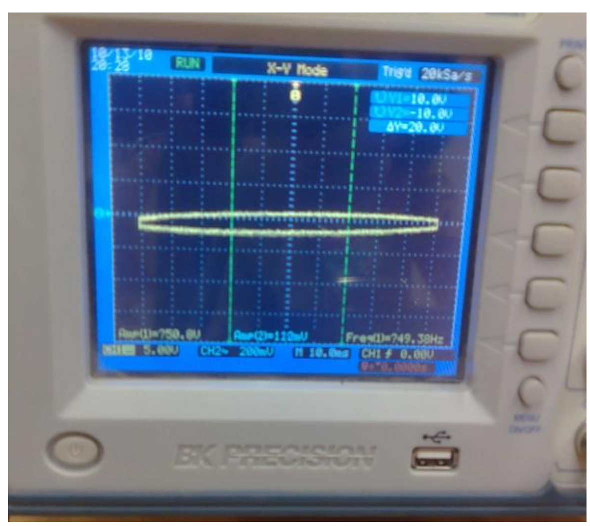
RESULTS:

The P-E loop observed at different temperatures on the oscilloscope is recorded as shown below:

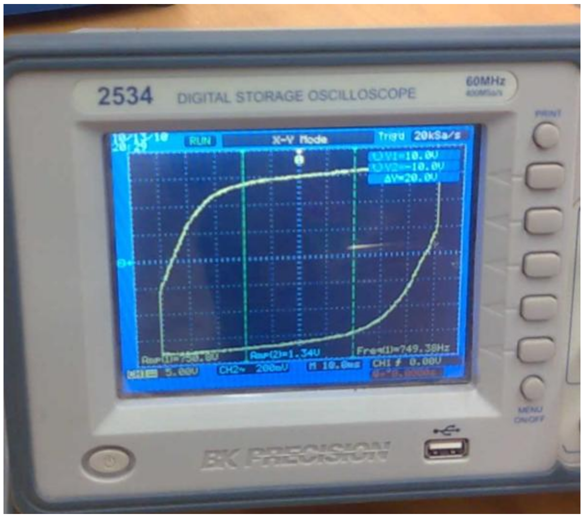
At 160°C



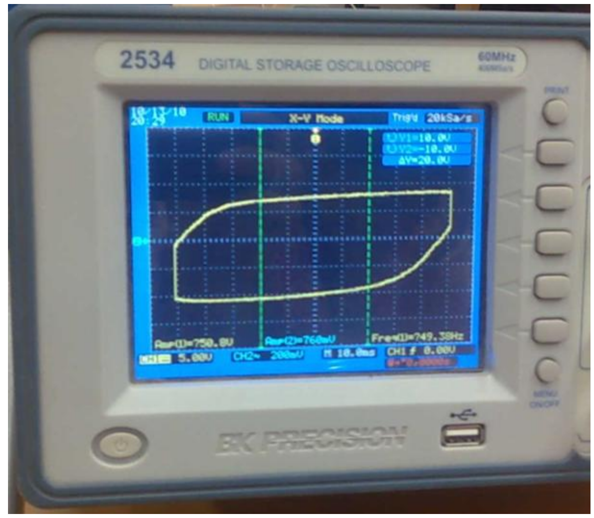
At 136°C



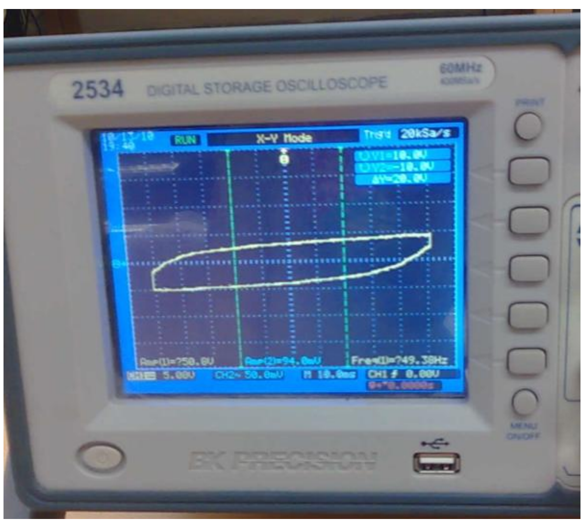
At 120°C



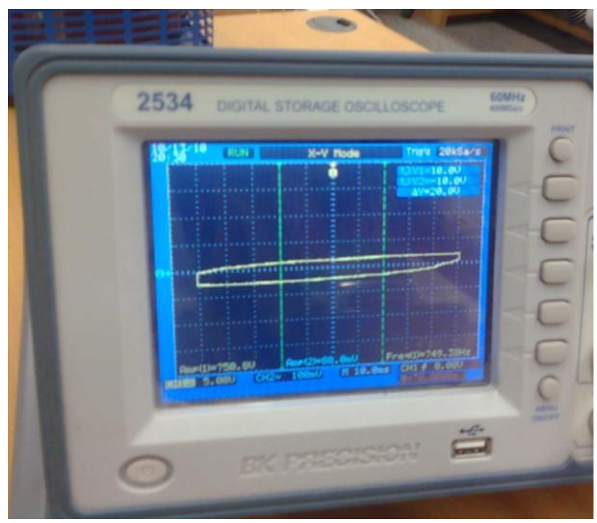
At 108°C



At 98°C



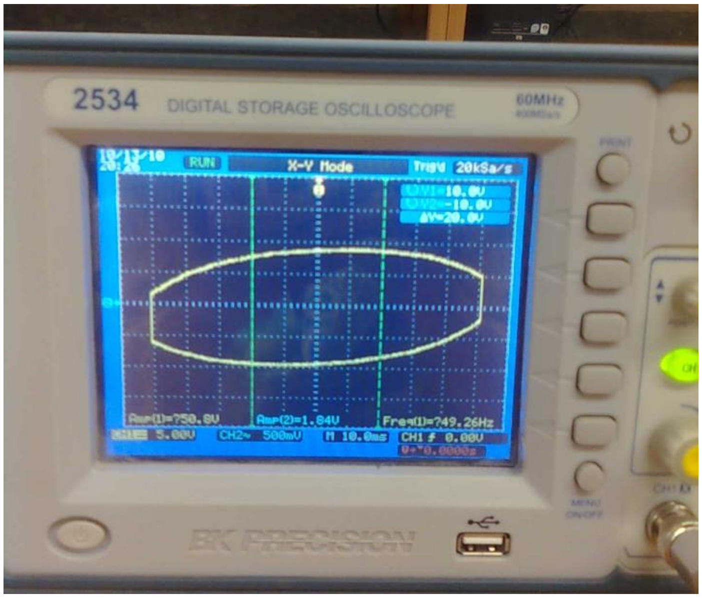
At 80°C



At 120°C we can clearly see the hysteresis loop showing Ferro electric behavior of KNO_3.

Conclusion and Discussion:

We observed a P-E hysteresis loop at around 120°C for Potassium Nitrate. If we replace our KNO_3 capacitor by some conventional capacitor the X-Y graph shown by oscilloscope would be an ellipse depending on the amplitude. This shows a 90° phase difference between voltage and capacitance for a non-ferroelectric material instead of hysteresis loop for Ferroelectric ones.



The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. Because of this, ferroelectric capacitors are small in physical size compared to non-tunable dielectric capacitors of similar capacitance.

The hysteresis effect shown by of ferroelectric materials can be used as a memory function, and ferroelectric capacitors are indeed used to make ferroelectric RAM for computers. In these applications thin films of ferroelectric materials are typically used, as this allows the field required to switch the polarization to be achieved with a moderate voltage. [4]

The basic idea of the experiment is to analyze and determine the characteristics of a Ferroelectric material. The next step would be to predict the properties of other ferroelectric substances, synthesize them and finally characterize them.

References:

[1] http://www.ieee-uffc.org/ferroelectrics/teaching/articles/e003/e0030291.pdf

[2] www.wikipedia.com

[3] Anthony R. West, \Basic Solid State Chemistry", John Wiley and Sons, p. 53-56, 331-338, 1996.

[4] J.F. Scott (2000). *Ferroelectric Memories*. Springer.