Ferro-electric Capacitors

Introduction

The ability of a substance to retain electric polarization in absence of external field bias, is called ferro-electricity (FE). Although this phenomenon, first reported in Potassium Sodium Tartrate or Rochelle salt (by J. Valasek \(^a\) in 1920), does not manifest in iron related compounds, it has been named ‘ferro’ due to the close resemblance to its magnetic counterpart ferro-magnetism. The most notable features of a FE compound are the polarization hysteresis and the existence of a critical temperature (T\(_c\)), above which it loses its retentivity to become para-electric (PE). A ferro-electric capacitor (FEC) is made by placing a FE material between two conducting plates. FECs find application in memory devices and field/pressure/temperature sensors.

Theory

Electric capacitance is the ability of a substance (usually an insulator) to contain electrostatic energy by the induction of an intrinsic polarization \( \vec{P} \), resulting from the alignment of its polar bonds under external electric field \( \vec{E} \).

A small potential difference \( V \) (producing the \( \vec{E} \) field) perturbs the dipole orientations linearly, causing the accumulation of charge \( Q \) \(^b\), through the proportionality constant \( C \) (defined capacitance). In this regime, the capacitance depends solely on system geometry.

\[
C \equiv \frac{Q}{V}
\]

It is in this region that most of the regular capacitors function. However, if the field strength is increased enormously the alignment continues to increase upto a saturation value, beyond which the capacitance becomes zero. At this point, the system deviates strongly from linear behavior, urging a new definition of capacitance in a differential form:

\[
C = \frac{dQ}{dV}
\]

\(^a\) J. Valasek Physical Review 17, 475 (1921).

\(^b\) The charge on capacitor plates and the intrinsic polarization \( \vec{P} \) are related by surface area \( \vec{A} \):

\[
\vec{A} Q = -\vec{P} \cdot \vec{A}
\]
When the external voltage is decreased, the stored charge continues to reduce, until it becomes zero (when \( \overline{E} \) is zero). These nonlinear capacitors do not show any hysteresis or remnant polarization, as in Figure 1 (a), hence they are called *para-electric* (PE) capacitors.

![Figure 1](image1.png)

**Figure 1**: Evolution of Induced Charge with changing voltage for (a) PE and (b) FE capacitors.

On the other hand, if the material does possess these features, it is entitled as *ferro-electric* (FE); the charge response of an FE, to modulated voltage is sketched in Figure 1 (b). This phenomenon ensues from a strong coupling between their structural and dielectric properties; one of such cases is explicated in the following.

Certain materials undergo a *solid-solid* structural transition (akin to the better known *liquid-solid* structural transition from water to ice), for example in Barium Titanate (BaTiO₃) transforms from *cubic* at high temperatures to *tetragonal* structure at lower temperatures; arising from a crossover in the free energies of the two structures at 120 °C (also called a critical

![Figure 2](image2.png)

**Figure 2**: Cubic and Tetragonal structures of BaTiO₃

---

\(^c\) This difference could depend on the energy spectra of the allowed electronic and phononic modes.
temperature, $T_c$). Due to this structural transition, a non-vanishing dipole is formed in the unit cell, which results in a macroscopic polarization (which is present even in absence of any external field). Consequently, BaTiO$_3$ shows massive remnant polarization and hysteresis phenomena, owing to which it is often used in FE based devices. A similar FE material is *Lead Zirconate Titanate* (PbZr$_{1-x}$Ti$_x$O$_3$), also fondly called PZT; it is this compound that shall be employed in the present experiment.

In the case of ferro-electric behavior below the critical temperature, $T_c$, the amount of ‘crystallinity’ of the substance strongly affects the long range correlations between the dipoles. Consider for e.g. *Figure 3*, where the field responses of mono-crystalline and poly-crystalline samples have been sketched. It is observed that where polarization switching happens suddenly for the single crystal at a particular ‘critical’ electric field, its counterpart in a polycrystal is distributed over a wider range of electric field. This trend is then justified by invoking a domain model in polycrystals, whereby the work done by electric field not elongates the dipolar correlations but also gradually move the domain walls, resulting in a much smoother hysteresis curve. The PZT samples being used in the experiment are polycrystals.

---

\[ A \] The total dipolar response at time $t_0$, which is $P_{in}(t = t_0)$ comes from two contributions – the external field $E(t_0)$ at that moment, and the spontaneous polarization $P_{in}(t < t_0)$, at the previous instant. It is the latter which makes $P_{in}$ a path dependent variable, resulting in hysteresis.

\[ B \] A domain is region where all the dipoles contained therein are aligned in one direction. However, dipolar correlations in two different domains are vanishingly small, resulting in non-parallel alignment of two domains. The shrinking of the correlation length emerges due to surface strains and boundary mismatch between different grains of a poly-crystal.
Experimental Details

The study of FE properties shall be done using the EDU module of RADIANT Technologies. The setup is a self-contained system which consists of a power supply and a microprocessor to interface with the circuit with a computer. For performing tests a waveform generator (to supply the input field), along with an oscilloscope and an electrometer to measure the field and charge, have also been integrated into the system.

The general procedure followed is:

a) A Digital-to-Analog converter transforms the user signal command into an actual output to the sample via a voltage driver.

b) The response current signal, retrieved from the sample, is then amplified and sent to the integrator circuit (this device counts the total electron flow on the basis of current signal).

c) This data is then converted into a digital command using an Analog-to-Digital convertor, and sent to the computer.

The details of the circuitry can be found in Chapter 6 of the system manual. The EDU package comes with two AB type ² 20/80 PZT based FE capacitors colored black and white.

The parameters which can be controlled within the EDU setup are the magnitude of the maximum voltage (called $V_{max}$ in the program), the type of the waveform (called Drive profile type), and the duration/frequency thereof (called Hysteresis Period). Since the capacitors are AB-type, one can also make a choice of the capacitor (controlled through Capacitor to Measure). Exploiting these features, the following experiments shall try to probe few properties of hysteresis and ferro-electric materials. The details about these program functions and other capacitor related issues (such as imprinting, capacitor recovery etc.) can be found in the manual.

---

² An AB type capacitor contains two identical capacitors (named A and B), with one of their terminals connected to a common ground (and the other electrode free). The specific PZT compound packaged therein is PbZr<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>. 

Figure 4: EDU module of Radiant Technologies (marked along with the electronic devices therein).
Experimental Problems

Problem 1: Introduction to hysteresis

The aim of this experiment shall be to characterize the hysteresis related properties \(^8\) of the PZT based FE capacitor. A comparison between the two capacitors (encased with \textit{white} and \textit{black} markings respectively) should be presented. The Para-electric and the Ferro-electric regions should be identified.

The details given in \textit{Expt I01} of the \textit{EDU manual} can be helpful. Moreover, the specifications to be adopted while performing these experiments are as follows:

- \textbf{Waveform:} \textit{Standard Bipolar} (Corresponding to a voltage sweep: \(0\text{V} \rightarrow V_{\text{max}} \rightarrow -V_{\text{max}} \rightarrow 0\text{V}\))
- Choice of \(V_{\text{max}}\): \(9\text{V}\)

Problem 2: Dependence on system history

Consider a particular capacitor and scan different bipolar waveforms with the voltage maxima sequenced in the following order:

- Path 1: \(9\text{V} \rightarrow -9\text{V} \rightarrow 9\text{V} \rightarrow 9\text{V}\)
- Path 2: \(9\text{V} \rightarrow -5\text{V} \rightarrow 9\text{V} \rightarrow 9\text{V}\)
- Path 3: \(9\text{V} \rightarrow 5\text{V} \rightarrow 9\text{V} \rightarrow 9\text{V}\)

Plot the curves in a regular (non-centered) style. The details given in \textit{Expt F01} of the \textit{EDU manual} can be helpful.

Justify the similarities and differences between the results of Paths 1, 2 and 3. Suggest an experimental scheme, comprising of a certain voltage scanning pattern, which can \textit{effectively remove} the impact of the sample’s history.

\(^8\) The hysteresis characterization is usually done using properties such as \textit{Saturation Polarization}, \textit{Remanence}, \textit{Coercivity} and \textit{Work done} to do polarization reversal.
Problem 3: Effect of Electric field

Study the hysteresis-related properties (of any one of the capacitors) as a function of different electric biases (i.e. different external voltages). The use of standard bipolar waveforms, with the parameter Vmax (in EDU configure panel) adjusted between the values 1V and 9V is recommended.

Discuss the observed trends. Also suggest the potential applications of this phenomenon.

Problem 4: Effect of Time

Study the effect of time on the saturation polarization and remnant polarization of a capacitor. Usage of square pulses, with different time-widths controlled using the Hysteresis period option in EDU, is recommended.

Make inferences from the time dependent plots of the polarization. Discuss the underlying physics.

Further details of the experiment can be found in

1. The EDU help manual and the references therein.