Electrical Properties of Ferroelectric materials

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March 23, 2022

1 Introduction

Ferroelectric materials are dielectric materials whose spontaneous polarization has at least a couple of equilibrium states. The macroscopic polarization of these materials is switchable by applying an external electric field. They are a special type of polar material. Not all materials having molecular dipole moment are ferroelectric materials. For instance, individual water molecules possess effective electric dipole moments, but they are randomly oriented in space and these molecular dipole moments do not spontaneously polarize so water is not a ferroelectric material.

Keywords Ferroelectricity, phase transition, coercive field, spontaneous electric polarization, hysteresis

APPROXIMATE PERFORMANCE TIME: Two week

References

[1] J. Fousek, "Joseph Valasek and the discovery of ferroelectricity", IEEE, p. 1-5, 1994.

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

[3] R.E. Newnham, "Properties of Materials: Anisotropy, Symmetry, Structure", Oxford, p. 174.

[4] M. Stewart and M.G. Cain, "Ferroelectric hysteresis measurement and analysis", National Physical Laboratory, University of Manchester, 1999.

[5] M. Dawber, I. Farnan, and J.F. Scott, "A classroom experiment to demonstrate ferroelectric hysteresis", Am. J. Phys., 71(8), 2003.

2 List of Equipment

1. Ferroelectric samples
2. Dual channel oscilloscope
3. Ferroelectric measurement probe station
4. Screwdriver
5. Banana to crocodile cables (3)

3 Theoretical background

The ferroelectric effect was first discovered by Valasek in 1921, in Rochelle salt, $KNaC_4H_4O_5.H_2O$ [1].

3.1 Electric dipole moment

A ferroelectric material must possess a spontaneous electric dipole moment that can be switched in an applied electric field. This effect is found when two particles of charge q are separated by a distance r,

$$\mu = q\mathbf{r}. \tag{1}$$

Here μ is the dipole moment, q is the charge and $\mathbf{r}$ is the vectorial distance between the two charges.

3.2 Electric polarization

All solids consist of charged particles (nuclei and electrons) but overall they are neutral. For most solids, there is also no net separation of positive and negative charges; there is no net dipole moment. Even if a solid is composed of molecules with permanent dipole moments (e.g ice), the molecules are generally arranged in such a way that the unit cell of the crystal and the bulk solid have no net dipole moment. If this solid is placed in an electric field then a field is induced in the solid which opposes the applied field. This field arises from two sources:

1. a distortion of the electron cloud of the atoms or molecules, and
2. slight movement of the atoms themselves.

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.

3.3 Ferroelectricity and crystal structure

Ferroelectricity is exhibited only in materials with a specific crystal structure. Ferroelectricity does not exist in centrosymmetric materials because any dipole moment generated in one direction would be forced by symmetry to be zero [2]. Besides non-centrosymmetry, there must also be a spontaneous local dipole moment. This means that the central atom must be in a non-equilibrium position, leading to a non-overlap of the centers of gravity of the positive and negative charges. This concept is illustrated in Figure 1.

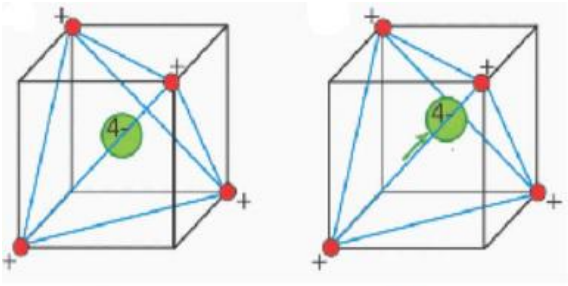

Figure 1: In (a) the structure is said to be non-polar. There is no displacement of the central atom and no net dipole moment. In (b), however, the central atom is displaced and the structure is polar, possessing a spontaneous electric dipole moment.

3.4 Ferroelectricity in $BaTiO_3$

Barium titanate $BaTiO_3$ is a classic example used to demonstrate the role of crystal structure in determining the ferroelectric properties. $BaTiO_3$ is a ferroelectric material having a very large dielectric constant ($\gtrsim 1000$) and is widely used in making ceramic capacitors. This material has the following phases with each phase being a unique crystal structure.

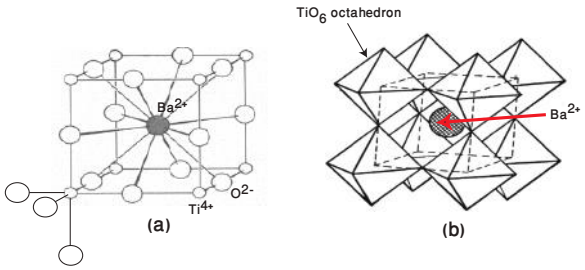

Figure 2: (a) Shows the perovskite structure of $BaTiO_3$ with the TiO_6 environment depicted for one of the corners Ti^{4+} ion. (b) shows a space-filling model of the perovskite structure: the TiO_6 octahedra full up the volume, sharing their corners. In this model, the large Ba^{2+} ions snugly fit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

3.4.1 Cubic $BaTiO_3$

Above 120°C, $BaTiO_3$ has cubic crystal lattice. The unit cell comprises a Ba^{2+} ion in the center, Ti^{4+} ions at the cube corners, and O^{2-} ions at the centers of the cube edges. The structure, called a perovskite structure, is shown in Figure 2. Several important ceramics and high-temperature superconductors possess perovskite structures. In the language of crystallography, the fractional coordinates of the ions are Ti: $(0, 0, 0)$, Ba: $(1/2, 1/2, 1/2)$ and O: $(1/2, 0, 0), (0, 1/2, 0), (0, 0, 1/2)$. If you observe, each Ti ion is surrounded by an octahedron of O^{2-} ions. Since the ionic radius of Ti^{4+} is very small (75 pm) as compared to oxygen, there is plenty of room for it to move inside the oxygen cage. The cubic phase is non-ferroelectric.

Q 1. The Ti−O bond length is 1.953 Å. What is the Ti−Ba bond length? In the cubic crystal system, all edges of the unit cell are of equal length.

Q 2. Why is cubic $BaTiO_3$ non-ferroelectric?

3.4.2 Tetragonal $BaTiO_3$

As the material is cooled, the cubic lattice undergoes transformations. For example, it changes into tetragonal at 120°C [3]. In the tetragonal phase, the cube distorts. As a result the octahedral TiO_6 group also distorts and the Ti^{4+} ion displaces along a Ti-O bond axis. The displacement of the Ti^{4+} ion causes a non-overlap of the positive and negative charge centers, resulting in a permanent electric dipole moment, a concept that is illustrated in Figure 3, conferring ferroelectric properties to the structure. The ion can be off-center in six possible directions (six O's surround an individual Ti). Due to these possibilities, neighboring domains have electric polarizations that are either 90 or 180 degrees with respect to each other. The possibilities of dipole

moments that are 180 and 90 degrees with respect to each other are illustrated in Figure 4.

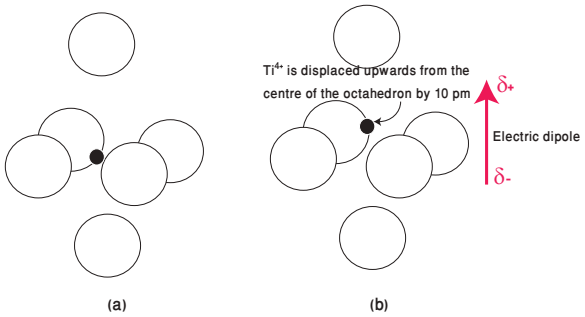

Figure 3: Displacement of a Ti^{4+} ion within the octahedral oxygen cage, conferring ferroelectric properties.

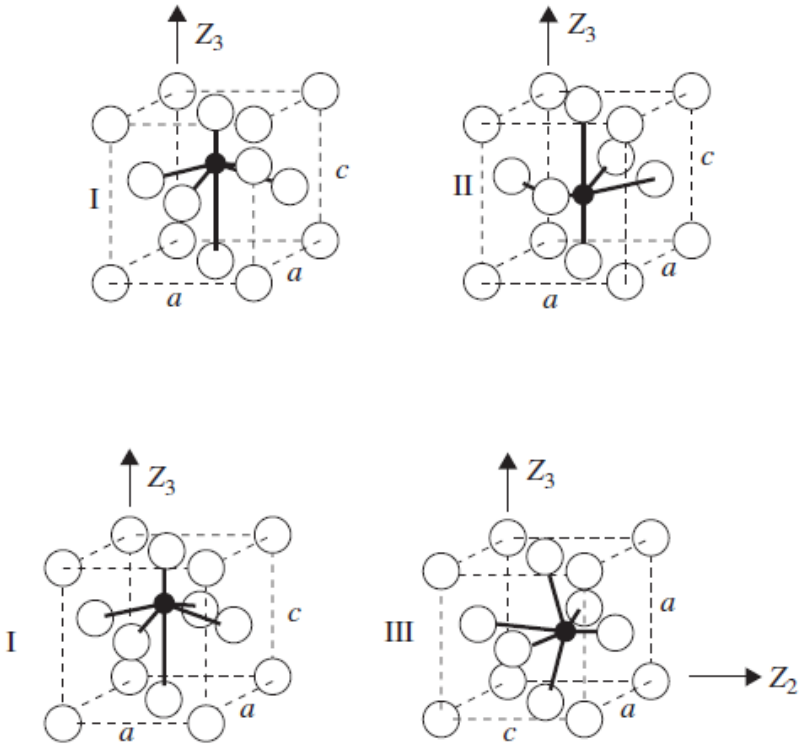

Figure 4: I and II show electric dipoles that are 180° with respect to each other whereas I and III depict dipoles that are aligned at 90° with respect to each other. (This figure is reproduced from [3].)

3.4.3 Orthorhombic or Rhombohedral $BaTiO_3$

Upon further cooling of $BaTiO_3$, Ti^{4+} starts to move along a diagonal between two Ti-O bonds, and at $-90°C$, a complete rhombohedral or orthorhombic ferroelectric phase is formed.

3.5 Ferroelectric hysteresis

Polarization can be reversed by applying a large alternating field and this produces a hysteresis loop between the electric field E and polarization P [4]. The polarization P and electric displacement D become non-linear functions of the electric field. They are related to each other through the constitutive relationship,

$$\mathbf{D} = \mathbf{P} + \varepsilon \mathbf{E}. \tag{2}$$

Usually in ferroelectric materials, the second term is negligible and a D-E becomes interchangeable with a P-E loop. From the saturated P-E loop, we can also measure coercive field (E_c) and remanent polarization (P_r). A ferroelectric hysteresis loop is both frequency and temperature-dependent. Figure 5 displays the hysteresis loop $BaTiO_3$ measured at 22 °C and the source frequency of 50 Hz.

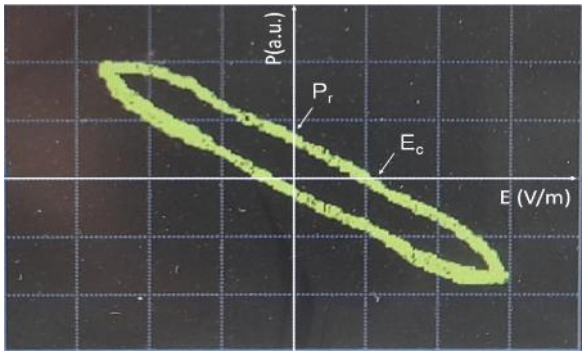

Figure 5: Hysteresis loop of $BaTiO_3$ at 22 °C.

Q 3. What are the differences and similarities between (a) dielectric and ferroelectric, (b) ferroelectric and ferromagnetic materials?

3.6 Measurement of polarization with a Sawyer-Tower circuit

The standard circuit used to measure a ferroelectric hysteresis loop is the Sawyer-Tower circuit (Figure 6a) [5]. The field applied across the sample is attenuated using

the resistor divider network consisting of R_1 and R_2. This voltage is applied to the x-channel of the oscilloscope. The current through the sample is converted into charge by the capacitor connected in series to the sample. This voltage is connected to the y-channel of the oscilloscope. These two voltages generate the P-E loop of the sample.

Q 4. Based on simple circuit analysis arguments, explain the working of the current to voltage converter circuit?

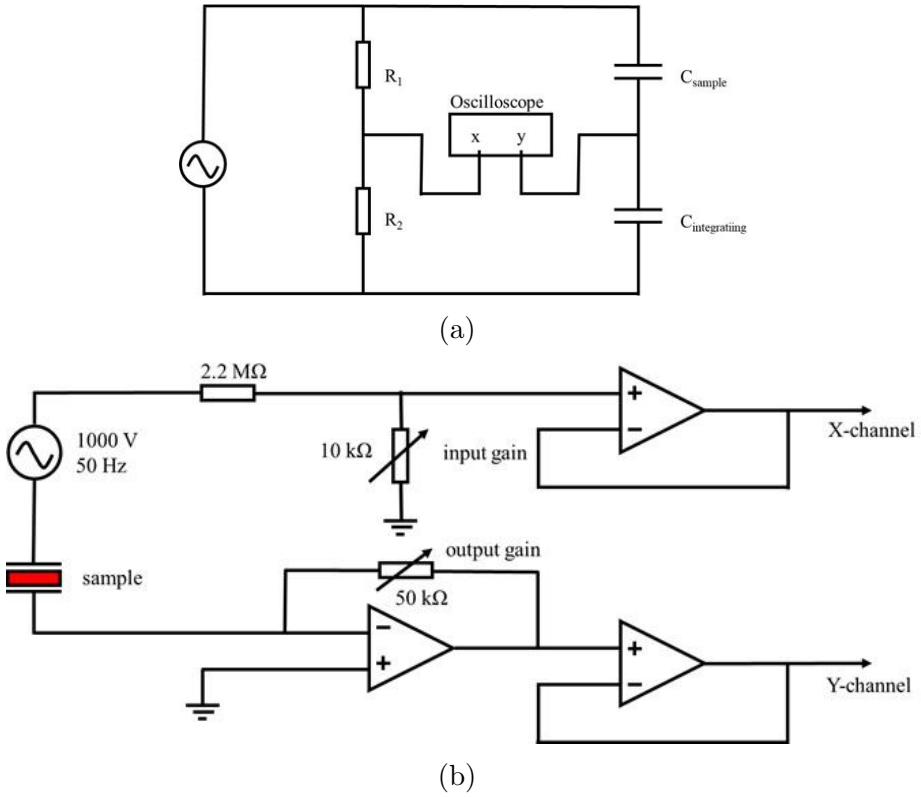

Figure 6: (a) Schematic of a Sawyer-Tower circuit and (b) circuit diagram for ferroelectric P-E loop measurements as implemented in the experimental setup.

4 The Experiment

This experiment gives students a hands-on experience with ferroelectric phenomena. In the present experiment, we will investigate the ferroelectric behavior of various ferroelectric materials. The schematic diagram of the experimental setup is shown in Figure 6b.

Q 5. Based on explanation in previous section, explain the working of the circuit shown in Figure 6b?

Q 6. Explain the Lissajous pattern of an ideal capacitor? How is the pattern different from that of an ideal resistor? How do we obtain these curves on an oscilloscope?

Q 7. In this experiment, we are interested in finding the P-E hysteresis loop of the ferroelectric materials. The circuit diagram (Figure 6b) shows that we get voltages at the output. Derive the P-E loop from these voltages.

4.1 Setting up the apparatus

This experiment involves high voltages. For safety, we have placed a plastic casing on top of the probe station (Figure 8). The following steps are performed to run this experiment:

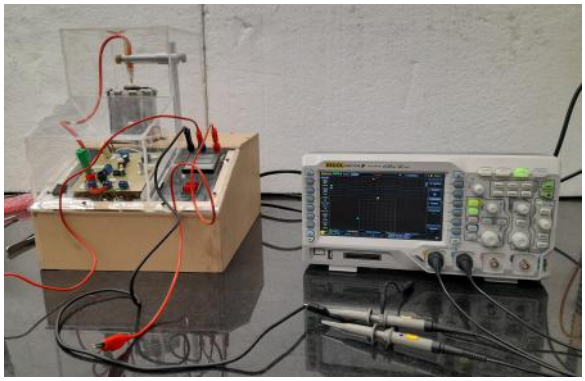

Figure 7: Ferroelectric probe station with plastic top.

1. Making sure that the main power is not connected, remove the plastic top.
2. Place the sample pellet at the material point using the tweezers (Figure 8).
3. Put back the plastic top. Now connect channel 1 of the oscilloscope to the blue connector (x-channel) and channel 2 to the red connector (y-channel) as shown in the Figure 8.
4. Connect the black connector (ground terminal) to the ground of the oscilloscope.
5. Turn on the power supply
6. Turn on the AC input.
7. By using a screwdriver, change the input signal gain and output signal gain. At this point, the oscilloscope will show a plot as shown in Figure 5.
8. Now turn on the temperature controller to increase the temperature of the sample to 50 °C. Observe the changes in the hysteresis loop.

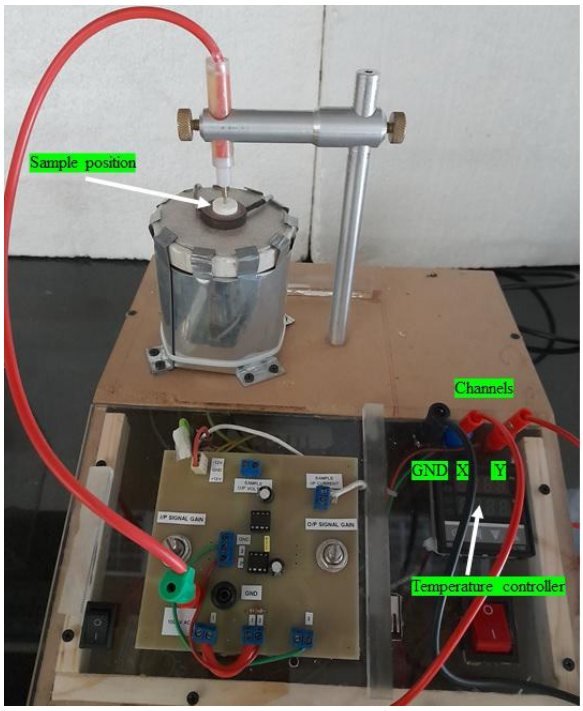

Figure 8: Assembled setup with ferroelectric sample in its position.

Repeat the above-mentioned procedure for various ferroelectric samples. Analyze the P-E loops of the samples and explain how they differ from that of linear devices such as capacitors and resistors.