

Synthesis and Ferroelectric Properties of KNO_3 films

Shahid Ramay and Muhammad Sabieh Anwar

LUMS School of Science and Engineering

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Potassium nitrate (KNO_3) shows ferroelectric behavior at temperatures between -152°C and 120°C due to change in its crystal structure and phase. In the current experiment, we will study the ferroelectric behavior of this material as a function of temperature with a homemade Sawyer Tower circuit. Through this experiment, we will explore phase transitions, and will appreciate how these transition lead to different physical properties. The take home lesson is that these properties are intimately connected to the underlying crystal structure.

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

APPROXIMATE PERFORMANCE TIME: One week

References and Essential Reading

- [1] M. Dawber, I. Farnan, and J.F. Scott, “A classroom experiment to demonstrate ferroelectric hysteresis”, *Am. J. Phys.*, 71(8), 2003.
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- [3] C.B. Sawyer and C.H. Tower, “Rochelle Salt as a dielectric”, *Phys.Rev.* 35, 269 1930.
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- [5] Evelyn J. Freney, Laurence A.J. Garvie, Thomas L. Groy and Peter R. Buseck, “Growth and single crystal refinement of phase-III potassium nitrate, KNO_3 ”, *Acta Cryst. B* 65, 659, 2009.
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1 List of Equipment

1. Dual channel oscilloscope
2. Variac
3. Microwave oven
4. Hot plate up to 400°C
5. Thermocouple
6. Al sheet
7. KNO₃ powder
8. Iron oxide thin films (optional, for investigating ferroelectric behaviour of nanosized thin films)
9. High wattage resistors
10. High voltage capacitor
11. Thumb pins
12. Insulated gloves
13. Connecting wires
14. Crocodile clips
15. Glass microscope slides

2 Objectives

In this experiment students will learn,

1. to make a thin layer of KNO₃ with the melt technique
2. how moisture affects the ferroelectric properties of KNO₃,
3. how temperatures affects the coercive field and spontaneous polarization of KNO₃, and
4. the role of crystal structure in determining the material properties.

3 Theoretical background

The ferroelectric effect was first discovered by Valasek in 1921, in Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_5 \cdot \text{H}_2\text{O}$.

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 ,

$$\mu = q\mathbf{r}. \quad (1)$$

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. 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.

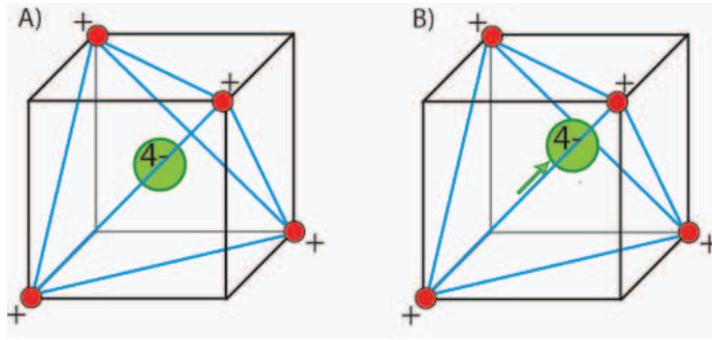


Figure 1: In (A) the structure is said to be non-polar. There is no displacement of the central atom, and no net dipole moment. In (B), however, the central atom is displaced and the structure is polar, possessing a spontaneous electric dipole moment.

3.4 Ferroelectricity in BaTiO_3

Barium titanate BaTiO_3 is a classic example used for demonstration the role of crystal structure in determining the ferroelectric properties. BaTiO_3 is a ferroelectric material having 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.

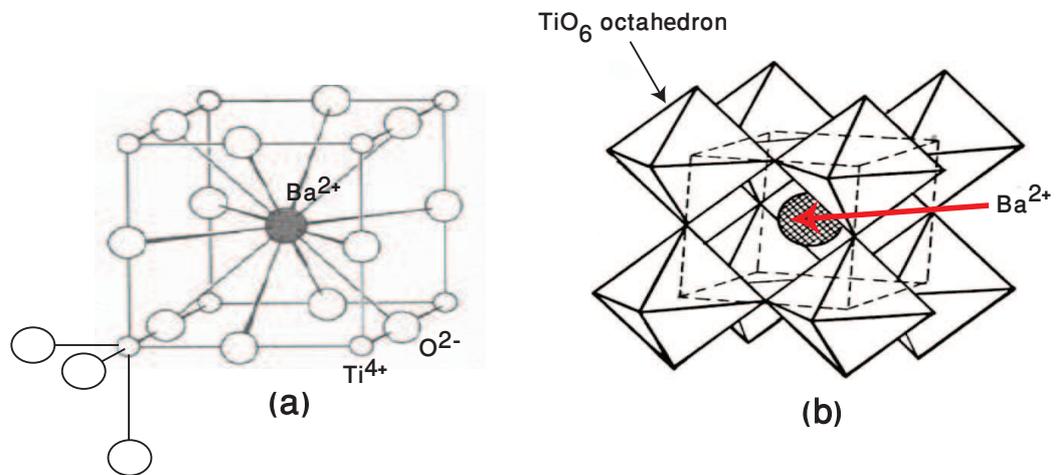


Figure 2: (a) Shows the perovskite structure of BaTiO_3 with the TiO_6 environment depicted for one of the corner Ti^{4+} ion. (b) shows a space filling model of the perovskite structure: the TiO_6 octehedra full up the volume, sharing their corners with one another. In this model, the large Ba^{2+}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

3.4.1 Cubic BaTiO₃

Above 120°C, BaTiO₃ has cubic crystal lattice. The unit cell comprises a Ba²⁺ ion in the center, Ti⁴⁺ ions at the cube corners and O²⁻ ions at the centres 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 carefully, each Ti ion is in fact surrounded by a octahedron of O²⁻ ions. Since the ionic radius of Ti⁴⁺ 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 BaTiO₃ non-ferroelectric?

3.4.2 Tetragonal BaTiO₃

As the material is cooled, the cubic lattice undergoes transformations. For example, it changes into tetragonal at 120°C. In the tetragonal phase, the cube distorts. As a result the octahedral TiO₆ group also distorts and the Ti⁴⁺ ion displaces along a Ti-O bond axis. The displacement of the Ti⁴⁺ ion causes a non-overlap of the positive and negative charge centres, 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.

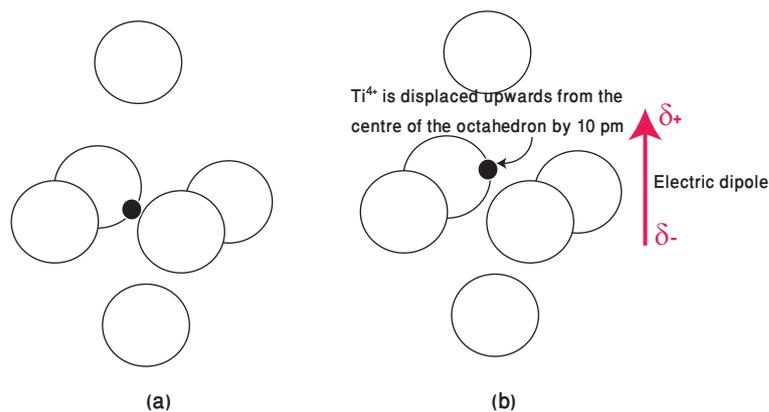


Figure 3: Displacement of a Ti⁴⁺ ion within the octahedral oxygen cage, conferring ferroelectric properties.

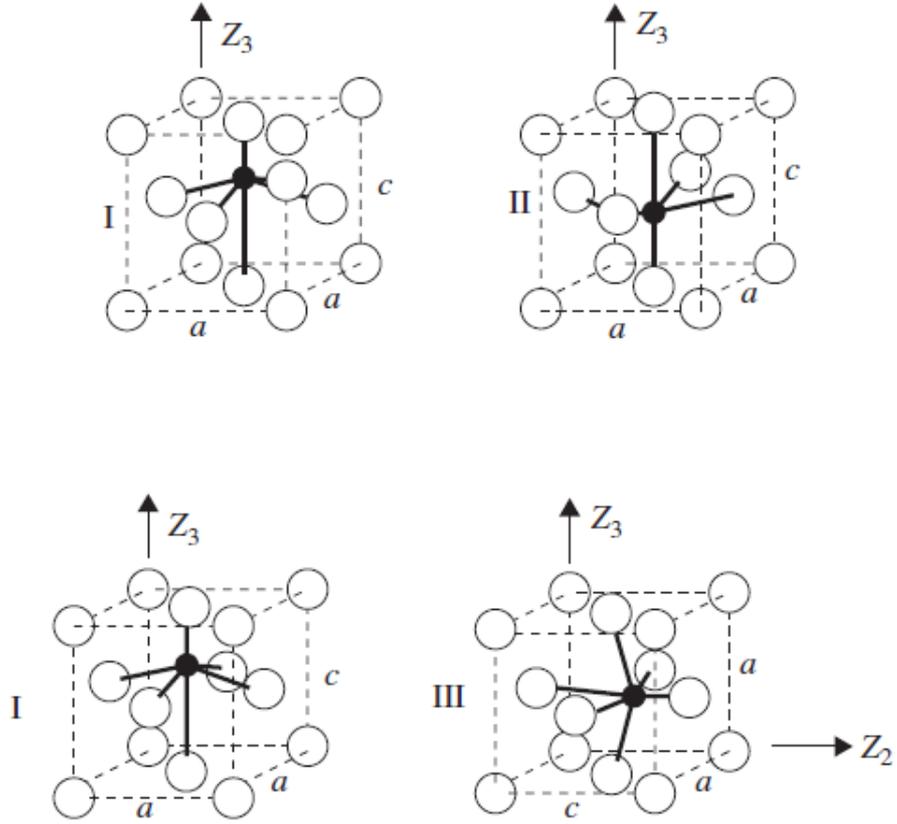


Figure 4: I and II show electric dipoles that are 180° with respect to each other whereas I and III depict dipoles that are aligned at 90° with respect to each other. (This figure is reproduced from [7].)

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 . The Polarization and electric displacement D become non-linear functions of the electric field. They are related to each other through the constitutive relationship,

$$\mathbf{D} = \mathbf{P} + \epsilon\mathbf{E}. \quad (2)$$

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 and a loop is shown in Figure 5.

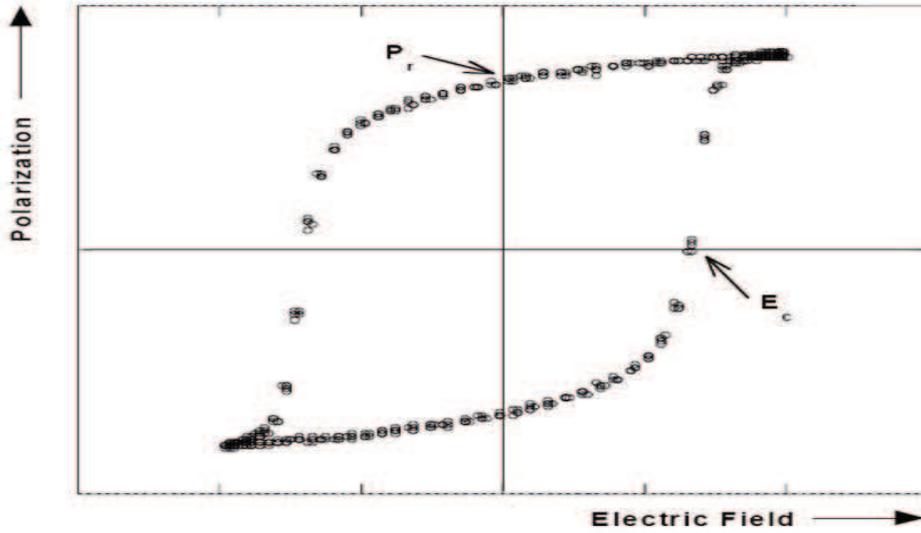


Figure 5: Hysteresis loop of a typical ferroelectric material.

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

Polarization can be measured with the help of a standard Sawyer-Tower circuit, shown in Figure 6. An a.c. field applied across the sample is attenuated by a resistive divider, and the current is integrated into charge by virtue of a large capacitor C_{ref} in series with the sample. Both these voltages are fed into the X and Y channels of an oscilloscope operating in the dual mode to generate the P - E loop. In our case, we use high wattage resistors $R_1 = R_2 = 100$ and a reference capacitor of $C_{\text{ref}} = 0.4 \mu\text{F}$ with a high voltage rating. The applied a.c voltage is 25 V.

Q 4. Based on simple circuit analysis arguments, explain the working of the Sawyer-Tower circuit with the assumption $C_{\text{ref}} > C_{\text{sample}}$?

4 The Experiment

In the present experiment, we will investigate the ferroelectric behavior of KNO_3 instead of BaTiO_3 . Even though KNO_3 has a rather complicated structure [7], but

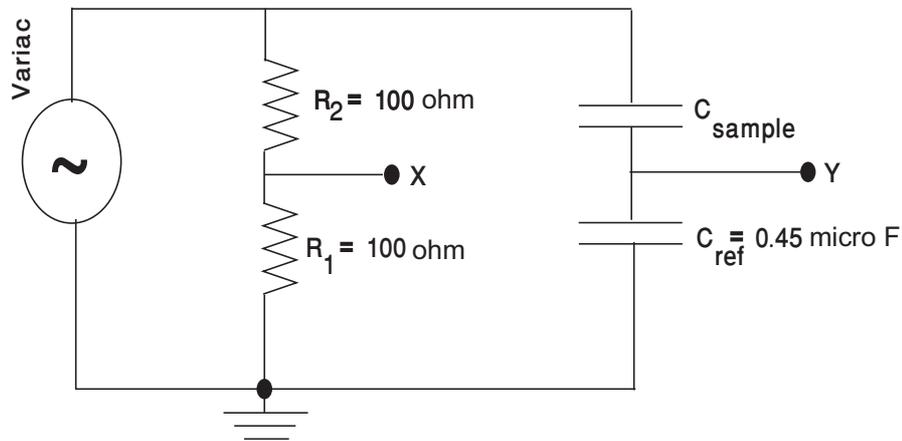


Figure 6: The Sawyer-Tower circuit.

its film is easier to synthesize in the short time period allocated for the present experiment. The description of BaTiO₃ serves as a useful reminder that the crystal structure determines the ferroelectric properties of the material!

BaTiO₃ has a melting point of 1650°C while KNO₃ melts at 330°C. It is easy to make thin film of KNO₃ by melting as compared to BaTiO₃. Be warned that KNO₃ is a strong hydrophilic and water kills the ferroelectricity of the material, so before use the nitrate must be dried in a conventional microwave oven for about two minutes. KNO₃ is highly conductive in the molten state, so extreme care must be taken when it is dried in the microwave oven. Do not overheat, as arcing may occur in the molten conductive state of the salt.



Figure 7: (a) Heat KNO₃ powder in a conventional microwave oven, then (b) melt KNO₃ powder on Al sheet to make thin film with inverted thumbpins acting as electrodes.

KNO₃ is applied on the surface of an Al sheet. The KNO₃ is melted while the Al sheet is clamped to a hotplate. Inverted thumbpins are placed on the KNO₃ layer. Upon melting the thumbpins automatically adhere to the KNO₃ form a capacitor of some thickness. At 330°C, KNO₃ is fully melted and the heater is turned off. The thermometer is being constantly monitored by a multimeter equipped with a

thermocouple

Now apply a 25 volts amplitude a.c signal with the help of the variac, as the coercive voltage is about 17-20 volts, the precise depending on the thickness of the sample. As the capacitor goes through the phase transition, the loop will change dramatically and become very square.

- Q 5.** Record temperature dependent hysteresis loops for your KNO_3 films.
- Q 6.** Replace your sample with a conventional capacitor. What do you observe on the oscilloscope screen and why?