

Ferroelectricity: The Foundation of a Field from Form to Function

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Abstract

This article highlights the major role Arthur von Hippel and the Laboratory for Insulation Research at the Massachusetts Institute of Technology played in the early development of the field of ferroelectricity in mixed oxides with the perovskite structure and, in particular, in the identification of ferroelectricity in barium titanate following its discovery in industrial laboratories in the United States during World War II. Very early optical and x-ray studies highlighted the characteristics of the ferroelectric domain structures in both ceramic and single-crystal BaTiO₃, the elimination of domains at the Curie temperature T_C , and the salient characteristics of the two low-temperature phase transitions. Perhaps the culmination of this work was the detailed studies of lamella 90° domains by Peter Forsbergh and the gorgeous patterns these could generate. This article also traces the manner in which the early studies contributed to whole industries based on perovskite ferroelectrics. The ceramic capacitor industry is now fabricating sophisticated, cofired multilayer capacitors (MLCs) with up to a thousand 1- μm -thick dielectric layers interleaved with base metal electrodes, addressing a market for some 10¹³ capacitors per year.

Manufacturers of large piezoelectric transducers depend almost exclusively on perovskite-structure oxide ceramics. Navy sonar systems are major customers, but spinoff has occurred into a wide range of commercial and medical ultrasound systems. The capability of current materials has improved more than tenfold over the original BaTiO₃ ceramics as a result of the effective application of molecular engineering, a strong testament to the insight of the founder of this area of study.

Keywords: Arthur von Hippel, barium titanate, BaTiO₃, capacitors, ferroelectric, interdisciplinary, Massachusetts Institute of Technology, materials research, MIT, perovskite, transducers.

Ferroelectricity

Ferroelectricity is perhaps even today almost as much an art as it is a science. During the last 60 years, ceramists have identified hundreds of new ferroelectric oxides with many important applications. Ferroelectricity involves a complex interplay of electrical, mechanical, and thermal effects near a displacive phase transformation. On cooling through the phase transition, the symmetry is lowered and beautiful polar domain patterns are observed in the low-temperature ferroelectric state.

Ferroelectricity is defined as a physical phenomenon in which a spontaneous electric dipole moment can be reoriented from one crystallographic direction to another by an applied electric field. The reorientation process involves two or more domain states within the crystal (or within individual grains in a ceramic). The key experiment is the existence of a hysteresis loop between polarization and electric field, analogous to the ferromagnetic hysteresis loop between magnetization and magnetic field. Much of the terminology

in the field of ferroelectricity was developed in analogy with ferromagnetism, including the very name ferroelectricity.

Most useful ferroelectrics possess high dielectric constants and follow Curie–Weiss behavior near the Curie point where the material transforms from the ferroelectric state to a high-temperature paraelectric state. All ferroelectrics are also piezoelectric, pyroelectric, and electro-optic. It is these five phenomena, dielectric hysteresis, electric permittivity, piezoelectricity, pyroelectricity, and electro-optic behavior, that make ferroelectric materials useful. High permittivity is used in capacitors, piezoelectricity in electromechanical transducers, pyroelectricity in infrared imaging systems, electro-optics in photonic communication, and dielectric hysteresis in nonvolatile memories. Doped ferroelectrics are also excellent semiconductors that are widely used as PTC (positive temperature coefficient) thermistors.

Discovery of Ferroelectricity in BaTiO₃

One of the major turning points in ferroelectricity came during the 1940s with the discovery of a number of simple mixed oxides that crystallize with the perovskite structure. Prior to the perovskite era, ferroelectricity was mostly a scientific curiosity unique to two rather friable water-soluble crystals, Rochelle salt (sodium potassium tartrate tetrahydrate) and KDP (potassium dihydrogen phosphate), and at that time was thought to be an order–disorder phenomenon associated with the hydrogen bonds.

Arthur von Hippel's discovery of ferroelectricity in barium titanate ceramics changed all that. The first indications of unusual dielectric behavior in mixed oxide ceramics came from work carried out in industrial laboratories. Probably the first dielectric measurements were by Thurnauer and Deaderick at American Lava Co. (later acquired by 3M) in 1941.^{1,2} Their high permittivity value of 1100 was confirmed by measurements at Erie Resistor Corp. A more detailed study by Wainer and Salomon³ at National Lead Co. (now NL Industries) was the first to show the dielectric constant peak near 125°C and also to demonstrate that the peak could be shifted to room temperature by solid solution with strontium titanate, making the ceramic more useful as a capacitor. Although hampered by wartime secrecy, the information reached Europe by 1944. Wainer's work was submitted for publication in January 1943, but was not released for publication until 1946.⁴ At about this time, first publication of the discovery was also appearing in Britain.⁵ Independent

discovery was also reported from Russia in 1946⁶ and from Japan in 1946.⁷

Structurally, barium titanate has long been recognized as a member of the cubic perovskite family.⁸ The most important ferroelectric materials crystallize in the perovskite structure. This structure may be described as a simple cubic unit cell with a large cation (A) on the corners, a smaller cation (B) in the body center, and oxygens (O) in the centers of the faces. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral positions at the corners of the unit cell (Figure 1).

The presence of a tetragonal distortion at room temperature was first reported by Rooksby⁹ and Megaw.¹⁰ As with many important discoveries, the huge dielectric permittivity of BaTiO₃ ceramic stimulated interest throughout the world. The key measurements which established its ferroelectric character, however, were those of Arthur von Hippel and his group.

During World War II, von Hippel and his co-workers in the Laboratory for Insulation Research at the Massachusetts Institute of Technology were engaged in the study of ceramic dielectrics for use in military microwave systems. Beginning with the empirical data of Wainer and Salomon,³ a systematic investigation of BaTiO₃ ceramics was carried out at the laboratory. Dielectric hysteresis measurements immediately established the existence of ferroelectricity below 120°C, as well as the existence of two additional phase changes below room temperature.^{11,12} Dielectric data collected at five different field strengths are shown in Figure 2.

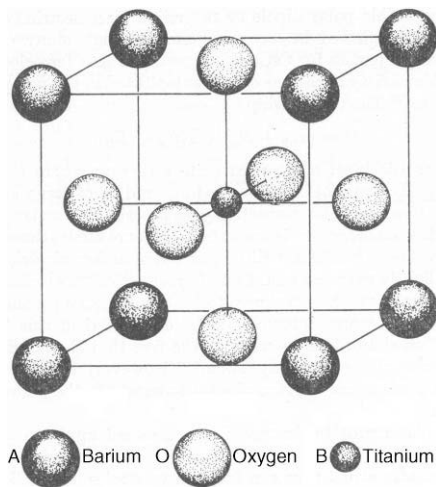


Figure 1. The perovskite structure, as typified by BaTiO₃ above its Curie point.

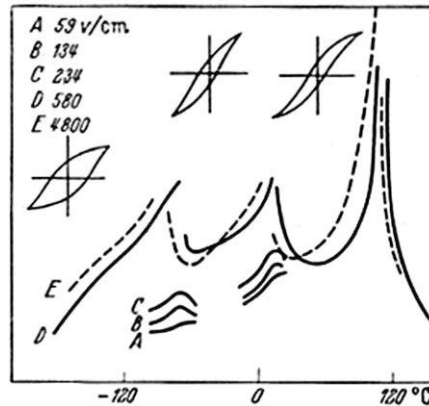


Figure 2. Dielectric constant measurements on ceramic BaTiO₃ carried out by von Hippel and co-workers in 1945.¹² Dielectric hysteresis established the existence of ferroelectricity in the tetragonal, orthorhombic, and rhombohedral states of BaTiO₃. The three peaks in the permittivity correspond to the transition temperatures. The dependence of the dielectric constant on applied field is associated with domain wall motion.

The MIT results were rapidly confirmed by Wul and Goldman in Russia.¹³ Von Hippel published this great discovery after the war¹⁴ and then went on to study the piezoelectric properties of electrically poled BaTiO₃.

The first publication on poled barium titanate ceramics was by Roberts,¹⁵ a graduate student working with von Hippel at MIT, and the first reduction to practice was a piezoelectric BaTiO₃ phonograph pickup by Gray¹⁶ of Erie Technological Products (now Murata Erie North Amer-

ica Inc.). The idea of piezoelectricity in a randomly oriented polycrystal was at that time so incomprehensible that the great Hans Jaffe, father of the later lead zirconate titanate family (today the dominant piezoceramic), testified at the legal hearing which established priority of the Gray patent that it was only after discussion with von Hippel that he understood how ferroelectric BaTiO₃ ceramic could be piezoelectric without a continuous biasing electric field.

Matthias and von Hippel¹⁷ were the first to study the effects of electric fields on the ferroelectric domain patterns, as shown in Figure 3. Optical microscope images in polarized light revealed the symmetry changes in the BaTiO₃ single crystal with decreasing temperature as the spontaneous electric polarization changed from one of the fourfold $\langle 001 \rangle$ axes to one of the twofold $\langle 110 \rangle$ axes to one of the threefold $\langle 111 \rangle$ axes. The corresponding point group symmetries are $m\bar{3}m$ to $4mm$ to $3m$. It is the presence of the three ferroelectric phase transformations that make BaTiO₃ such a useful capacitor dielectric over a wide temperature range. Another very important observation by Matthias and von Hippel was the much higher dielectric constant perpendicular to the spontaneous polarization, just the opposite to that in Rochelle salt and KDP and critical for the high piezoelectric response in the ceramic.

Peter Forsbergh, another of von Hippel's graduate students, measured the birefringence in BaTiO₃ crystals and made extensive observations of the domain structure.¹⁸ Under changes in external conditions, domain patterns often change principally by the appearance and growth

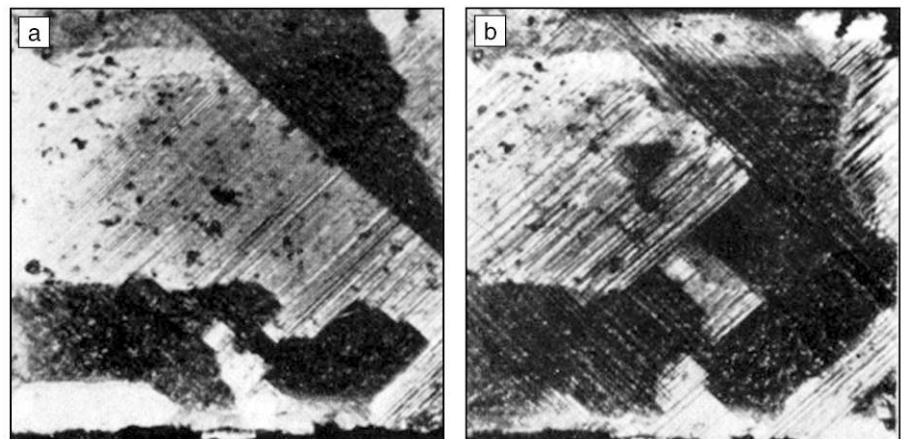


Figure 3. A multidomain crystal of BaTiO₃ (a) before and (b) after the temporary application of a dc electric poling field. Variations in the pattern under ac fields were also observed using stroboscopic illumination.¹⁷ (No scale given in original figure.)

of thin laminar wedges, the length of which changes smoothly with the applied field or mechanical stress. These 90° walls are both ferroelectric and ferroelastic, whereas antiparallel domains separated by 180° walls are only ferroelectric and the co-joining domains require the presence of a transverse field to become optically distinguishable. Thin, wedge-shaped domains are illustrated in Figure 4.

Comprehensive accounts describing the properties of barium titanate ceramics and single crystals were published by von Hippel¹⁹ and by Forsbergh.²⁰

The atomistic origin of ferroelectricity involves the movements of ions in the perovskite unit cell of BaTiO_3 . Working in von Hippel's laboratory, Howard Evans was probably the first to determine the motions by x-ray diffraction.²¹ The crystal structure of the high-temperature hexagonal phase was also determined in the Laboratory for Insulation Research,²² and von Hippel's group was among the first to recognize the importance of infrared lattice modes and their relation to ferroelectricity.²³ The "soft mode" model for ferroelectricity followed a few years later.²⁴

Much of the early history of BaTiO_3 is described in von Hippel's books *Dielectric Materials and Applications*²⁵ and *Dielectrics and Waves*.²⁶ More recent updates are in *Molecular Science and Molecular Engineering*²⁷ and *The Molecular Design of Materials and Devices*.²⁸

Ferroelectric Products

It is interesting to note the massive developments in electronic ceramics that have stemmed from the early work on ferroelectricity in barium titanate. Now, more than 60 years after its discovery, bar-

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presently available materials,
we are free to dream and
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—Arthur von Hippel

ium titanate still dominates the ceramic capacitor market, which has expanded to some 10^{13} units per year. Developing an understanding of the dielectric, the control of its ferroelectric characteristics by the microstructure, and its defect structure have led to the modern multilayer ceramic capacitor (MLC), a technological tour-de-force incorporating up to a thousand $1\text{-}\mu\text{m}$ -thick layers cofired with interleaving base metal electrodes. Units covering the capacitance range from picofarads to millifarads with temperature-controlled permittivity, very low electrical series resistance (ESR), and incredible reliability are now widely available.

The second major area of application in ceramic piezoelectric transducers has contributed in no small measure to the current U.S. dominance of the marine environment. Piezoelectric ultrasonic transducers provide the eyes and ears for the U.S. submarine fleet and early warning of any intruders in the world's shipping lanes. Over time, a huge range of spinoffs has occurred into commercial and medical products so that ultrasonic tomography has become a preferred technique in non-destructive medical diagnostics. Currently,

new ferroelectric single crystals developed for the Office of Naval Research are providing tremendously improved performance in sensing and actuation for both Navy and medical ultrasound systems and are moving effectively into commercial production.

Many other areas of application draw on the unusual properties and property combinations in ferroelectric oxide systems. Currently, there is substantial activity in pyroelectric properties for long-wavelength infrared thermal imaging, in electro-optics for modulation and switching in guided wave structures, and in nonlinear optics for quasi-phase-matched optical harmonic generation. Thin ferroelectric films have reawakened interest in ferroelectric random-access memories, and smart cards that incorporate limited memory capability are already in production in Asia.

Conclusion

As a professor of electrical engineering, Arthur von Hippel was heavily involved in the optimization of capacitor and transducer compositions, but he also took a broad view of the role of ferroelectric studies in the development of materials science: the understanding of solid-state phase transitions, the evolution of soft lattice mode behavior, and the emergence of new evidence for substantial order-disorder in barium titanate. Developing a detailed understanding of the domain structure so elegantly displayed in the early MIT optical studies is a continuing problem, with new evidence that the 90° wall itself may be an origin for enhanced dielectric permittivity.

Many of these recent ideas and applications were anticipated by von Hippel. In 1962, he wrote:

We begin to design materials with prescribed properties, to understand the molecular causes of their failings, to build into them safeguards against such failure, and to arrive at true yardsticks of ultimate performance. No longer shackled to presently available materials, we are free to dream and find answers to unprecedented challenges. It is this revolutionary situation which makes scientists and engineers true allies in a great adventure of the human mind.²⁹

Arthur von Hippel was a true molecular engineer.

Acknowledgments

Arthur von Hippel was a pioneer in the history of ferroelectric materials and devices. Robert Newnham has fond memo-

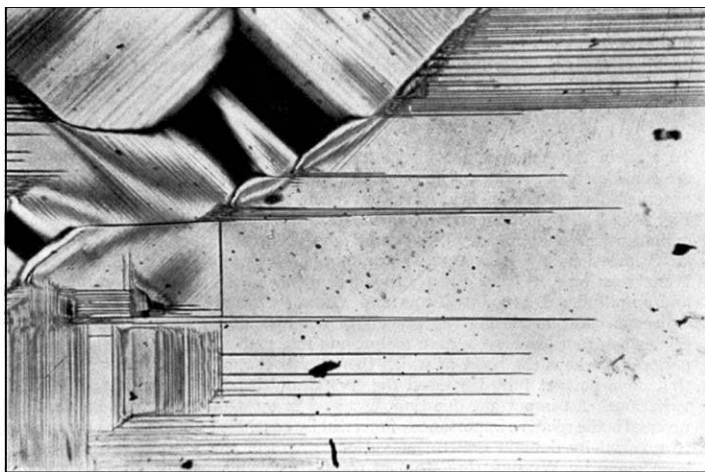


Figure 4. A photomicrograph of 90° wedge domains in a single crystal of barium titanate viewed in polarized light.¹⁸ (No scale given in original figure.)

ries of many happy days at MIT. The Laboratory for Insulation Research was the prototype of a materials science center, with engineers, chemists, physicists, and ceramists working together on problems of mutual interest. Few of the modern interdisciplinary laboratories have achieved a comparable degree of scientific integration. Professor von Hippel supplied the enthusiasm and breadth of understanding which made it work. His students will remember the round-table discussions on molecular engineering in which we met with experts from many fields and together outlined a vision of the future.

Many scientists converse fluently on their own specialty—but few show an equal interest in the work of others. It takes a big mind and a big heart.

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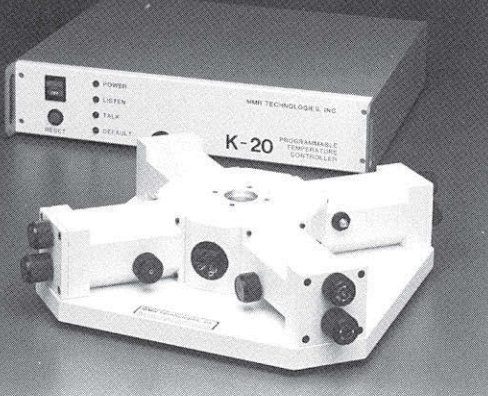
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