Impact of ferroelectricity

By Susan Trolier-McKinstry

Since the discovery of ferroelectricity 100 years ago, ferroelectric materials are everywhere in our electronics-based society. Learn how they drive a $7 billion industry.

Ferroelectric materials are ubiquitous in electrical and electromechanical components and systems. Ferroelectricity is associated with large dielectric and piezoelectric coefficients, particularly when the composition is adjusted to position the solid near a phase boundary. This characteristic allows high volumetric efficiency dielectric charge storage, as well as high displacement actuators at modest voltages. The ability to reorient the spontaneous polarization between crystallographically-defined states is essential in allowing poling of ceramic materials to obtain net piezoelectric or pyroelectric responses.

Capacitors

The largest industrial use of ferroelectric materials is in multilayer ceramic capacitors. The poor availability of mica-based crystals during World War II spurred development of air- and moisture-stable, high volumetric efficiency dielectrics. The subsequent dawn of the electronics age led to production of several trillion $BaTiO_3$-based capacitors around the world on an annual basis, with hundreds to thousands used in each current generation smart phone or computer. The size of this market is approximately $6 billion. Among the major capacitor suppliers around the world are Murata, Taiyo Yuden, Samsung Electromechanics, Kyocera (AVX), TDK, Yageo, and Kemet.

Medical ultrasound is the second most widely adopted imaging modality in medicine. It works thanks to ferroelectric materials.

The relatively closely-spaced ferroelectric phase transitions in $BaTiO_3$ enable a high relative permittivity over a broad temperature range. Equally important is the processing science that fostered progressive miniaturization of the dielectric layers thickness over the last several decades—the so-called Moore's law of capacitors—which has helped enable miniaturization of many electronic devices, including cellular phones.

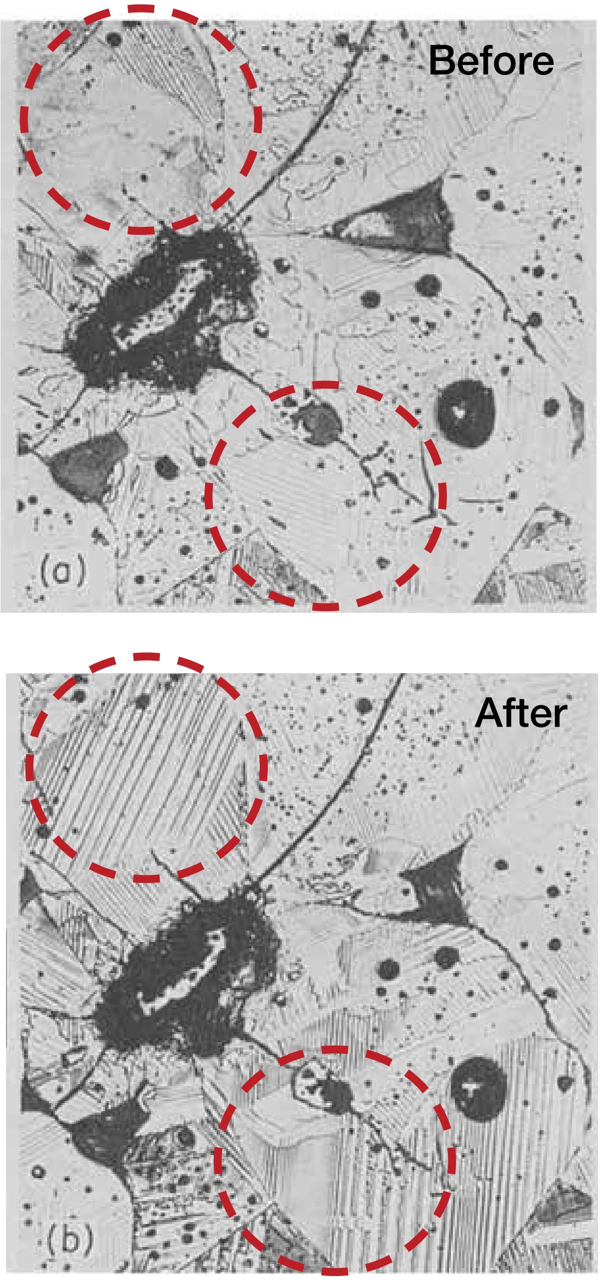
Industrial production is dominated by tape casting, electroding, and lamination to produce multilayer components at progressively decreasing case sizes. At present, commercial parts with layer thicknesses less than one micron with thin, highly-conductive nickel metal layers are readily available, with projected future miniaturization down to dielectric thicknesses of about 0.3 micron. The rich defect chemistry of these systems allows production of high reliability parts, even in the case where low oxygen partial pressure firing induces a high concentration of oxygen vacancies.

Piezoelectric applications

A second major use of ferroelectric materials is in piezoelectric ceramics, single crystals, and composites for actuators, sensors, and transducers. In the future, it is possible that ferroelectric piezoelectrics will also be widely adopted for kinetic energy harvesting systems for distributed low-power systems, including emplaced sensors for the Internet of Things. The world-wide piezoelectric ceramics market is approximately $1B annually. This market is dominated by lead zirconate titanate-based (PZT) materials; numerous formulations are utilized to tailor the piezoelectric responses, the coupling coefficients, and the field-induced hysteresis.

Among the main uses of these piezoelectrics are precise positioners, sonar systems, fish finders, medical ultrasound transducers, fluid flow meters, ultrasound systems for nondestructive testing, high precision accelerometers, transformers, and many other applications. Of these, medical ultrasound is the second most widely adopted imaging modality in medicine and offers tremendous capability in high resolution imaging of subsurface features without necessitating ionizing radiation (see image of infant). At this point, an enormous number of lives have been saved through the use of medical ultrasound employing ferroelectric–polymer composite transducers. Notably, the diversity of form factors and compositions needed for this range of applications of piezoelectric materials means that production for any given component in the piezoelectrics markets tend to be smaller. There are numerous suppliers of piezoelectric ceramics, including Channel Technologies, Murata, American Piezoceramics, Piezo Kinetics, Meggitt (Ferroperm), Morgan Electroceramics, TDK, PI Ceramics, Sinocera, and many others. In other cases, ferroelectric single crystals are used for domain engineered high strain piezoelectrics, or for surface acoustic wave devices.

While capacitors and piezoelectrics comprise two of the largest uses of ferroelectric materials, many other electrooptic components are also of commercial importance, e.g., $LiNbO_3$ for frequency doublers, optical modulators, and more; positive temperature coefficient of resistance thermistors for self-limiting heaters; pyroelectric based room occupancy sensors and fire detectors; and computing memory elements (including PZT and $SrBi_2Ta_2O_9$).



Microstructure of barium titanate (a) before and (b) after application of an electric field. The ferroelectric response of barium titanate causes reorientation of its domain structure, most easily seen in the circled areas.

Credit: DeVRIES, R.C. and BURKE, J.E. (1957), Microstructure of barium titanate ceramics. *Journal of the American Ceramic Society*, 40: 200-206. doi:10.1111/j.1151-2916.1957.tb12603.x

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Prenatal ultrasound (left) and cardiac ultrasound (above).

Ferroelectricity—A revolutionary century of discovery

By Geoff Brennecka, Rachel Sherbondy, Robert Schwartz, and Jon Ihlefeld

A century after the discovery of ferroelectricity, we look at the physics that makes ferroelectric materials so useful and the research that got us here.

Imagine a young couple that has just "seen" their infant still in the womb for the first time after a routine ultrasound scan. What joy! This news is worth sharing, so they click an image of the monitor on their smartphones and send it to grandparents, family, friends, and their entire social media networks.

Meanwhile, across the medical campus, a recent retiree undergoes a cardiac procedure guided with real-time ultrasound scans to repair a blockage discovered, also with ultrasound. What relief! This patient just found out he will be a grandfather and now confidently awaits that day with anticipation.

Capsule summary

A SALTY START

University of Minnesota graduate student Joseph Valasek gave the first presentation on ferroelectricity in Rochelle salt in 1920. He could scarcely have predicted how his careful measurements would end up playing a fundamental role in many of today's technologies.

VERSATILE USES

The switchable spontaneous polarization that defines ferroelectricity directly enables applications such as nonvolatile ferroelectric random access memory, but many other applications, such as multilayer ceramic capacitors, are enabled by ferroelectric materials even without directly using the switchable polarization.

FUTURE FERRO

In the past 10 years, two new structural classes—including fluorite-structured HfO_2 and wurtzite-structured (Al,Sc)N—joined the ferroelectric family and bring with them some potential technological superiority to traditional materials.

These routine activities of modern life are possible because of piezoelectric ultrasound transducers, many thousands of ferroelectric multilayer ceramic capacitors, and a host of other electronics, sensors, actuators, and devices based on ferroelectric materials.

Ferroelectrics have intrigued materials scientists since their first report in 1920 and first publication the following year.[1] The label "ferroelectric" can be slightly misleading, as only a small fraction of ferroelectric compositions contain iron. Rather, the nomenclature was adopted in recognition of the parallels between the newly discovered phenomenon of ferroelectricity and the already-familiar ferromagnetism, which originally was thought to be tied exclusively to iron.

The defining characteristic of a ferroelectric material is the existence of spontaneous dipoles within its crystal structure whose direction can be reoriented by the application of an electric field. In other words, all materials belonging to a polar point group are potentially ferroelectric, but it takes a demonstrated polarization reversal for the material to earn the title.[2] (See sidebar, "Genesis of hysteresis…"). This strict definition highlights an important conundrum: a variety of phenomena can produce polarization-vs-field measurements that suggest ferroelectricity, but they are instead artifacts masquerading as polarization reversal.[3] At the same time, only a small fraction of the applications enabled by ferroelectric materials directly take advantage of the switchable polarization. Instead, as summarized here, the tremendous utility of ferroelectric materials in modern life typically arises from phenomena associated with, but not necessarily directly leveraging, the full reorientation of this spontaneous dipole.

Discovery and early developments

In 1919, Joseph Valasek began his Ph.D. work at the University of Minnesota under professor W.F.G. Swan, who suggested that Valasek investigate the curious crystals of Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$). These crystals were relatively straightforward to grow and were already known to be piezoelectric, pyroelectric, and optically active. Annoyingly, they were also very sensitive to humidity, and nearly all of their interesting properties seemed to depend on everything, including temperature, electric field, and previous history.

Valasek's first task was to develop sensitive measurements that could finally pin down the properties of this mischievous Rochelle salt. Valasek's thesis and the associated publications are a veritable treatise on crystal physics and careful measurements. It is interesting to note that of Valasek's five papers in *Physical Review* on Rochelle salt, he is the sole author on four of them, and the seminal paper[1] reporting the first ever ferroelectric hysteresis loop received just over 200 citations in the ensuing century. The scientific enterprise certainly has changed!

Reading Valasek's papers, it is clear he imagined this new phenomenon would lead to new functionality and new devices, but he could scarcely have predicted how his care-

FERROELECTRIC TIMELINE

In the ferroelectrics community

1912
THE PREDICTION
Erwin Schroedinger proposes the word "ferroelectric" ("ferroelektrisch" in German) as the analogy of ferromagnetism for spontaneous electrifying of liquids when cooling

1920
THE DISCOVERY
Joseph Valasek, graduate student at the University of Minnesota, gives first presentation on ferroelectricity in Rochelle salt at the Meeting of the American Physical Society on April 23

1944–1946
PEROVSKITES ENTER
T. Ogawa and S. Waku (Japan, 1944), B. Wul and J.M. Goldman (Russia, 1945), and A. von Hippel (U.S., 1946) investigate ferroelectricity in $BaTiO_3$; R.B. Gray (U.S., 1945) showcases first operating poled $BaTiO_3$ transducer

1950–1955
PZT
Groups, including those of Shirane, Takeda, and Sawaguchi in Japan, explore the $PbTiO_3$:$PbZrO_3$ solid solution system

1952
FERAM PROPOSED
Ferroelectric random access memory (FeRAM) is proposed in Dudley Allen Buck's master's thesis

1971
HIGH VALUE PZT
B. Jaffe's group explains the importance of phase transitions in $PbTiO_3$:$PbZrO_3$

2000s
LEAD-FREE
Interest in identifying lead-free piezoelectric materials increases across the globe

In the world

1900
COMMERCIAL RADIO
Radio receivers become more practical and radio becomes a household item

1914–1918
WWI
World War I stretches from July 28, 1914, to Nov. 11, 1918

1939–1945
WWII
World War II stretches from Sept. 1, 1939, to Sept. 2, 1945, stimulating spending for the military sector

1942
DIGITAL COMPUTERS
The first digital computer (as recognized by the U.S. Patent office) is completed. The Atanasoff-Berry computer (ABC) is started in 1937 and work continues until 1942

1947
TRANSISTORS
Bell Laboratories successfully demonstrates the first transistor on December 23

1969
ARPANET DEBUT
The Advanced Research Projects Agency Network (ARPANET) debuted in the United States and made the technical foundation for the internet. Thus began the race for semiconductors and optics technology

1996
HANDHELD COMPUTERS
The first handheld computer (Palm Pilot) is available for purchase

2000
FLASH DRIVES
USB flash drives become an alternative to the floppy disc and CD for portable data storage

Figure 1. Timeline presenting development of ferroelectric materials alongside global advances at the time.

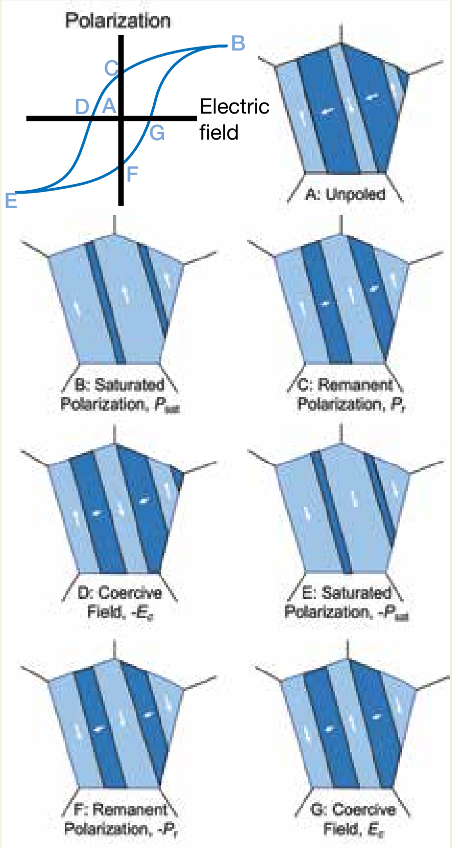
ful measurements of nonlinear dielectric response of finicky Rochelle salt crystals would end up playing such a fundamental role in so many technologies a century later. Figure 1 presents an approximate timeline of the development of ferroelectric materials from prediction in 1912 to discovery in 1920 to the first ceramic transducer in 1945 through to the present time's search for eco-friendly compositions. This history, juxtaposed against global advances at the time, gives interesting context to the significance of ferroelectric devices to the evolution of digital technology.

One thing that has not changed significantly since Valasek's time is that much of the funding devoted to development of new materials is driven by potential military applications. In Valasek's case, the interest was in detection of submarines. To this day, needs for improved materials for sonar remain a strong driver of ferroelectric and piezoelectric materials development. In fact, World War II spurred development of $BaTiO_3$, $Pb(Zr,Ti)O_3$, and $Bi_4Ti_3O_{12}$ based ferroelectrics roughly simultaneously in isolated groups in the United States, Japan, and Russia. This development, discussed in more detail below, is an excellent example of how the phenomenon of ferroelectricity enables otherwise unachievable performance even when the switchable polarization itself is only indirectly related to the application.

In the century since Valasek first discovered the ferroelectric effect, enormous research effort went into understanding these extraordinary materials and how to make them better, controlling their properties precisely, shrinking the size of components, and deploying them in new and novel applications. Much of that research was—and continues to be—reported in ACerS publications. The sidebar "Historically significant ferroelectrics papers" highlights key papers over the years that advanced the science and art that led to the implementation of ferroelectric components in devices we enjoy today.

It is worth noting that ferroelectric polymers, most notably polyvinylidene fluoride, do exist and find significant application. However, in this article we focus on inorganic, nonmetallic (i.e., ceramic) ferroelectrics, which are both more numerous and more widely used than their squishier counterparts.

Genesis of hysteresis in ferroelectric materials



Credit: Ihlefed

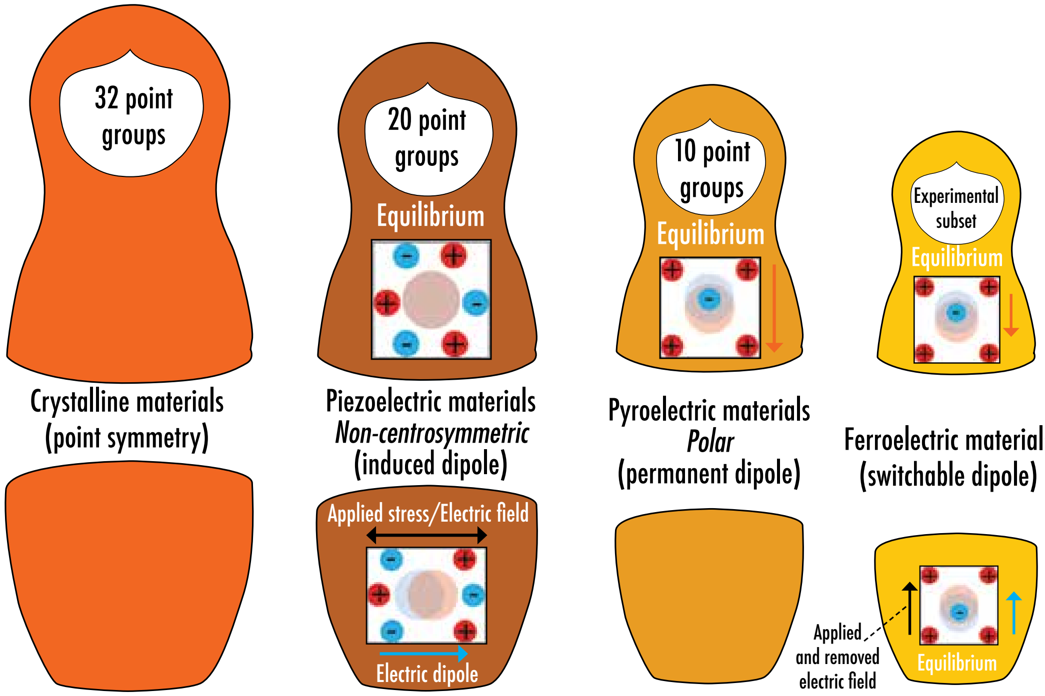
Polarization reversal is the defining characteristic of ferroelectric materials, and the hysteretic response is often represented as a plot of polarization vs. electric field, as shown schematically here. Diagrams A-G show how the domain structure responds to applied field in a single grain at different stages on the hysteresis loop. The colored regions represent domains in which all of the unit cells are collectively polarized in the direction of the arrow. In the initial unpoled state (A), the domain structure forms to minimize total energy, balancing charge, strain, and the energy penalty associated with formation of domain walls themselves. Application of an electric field gradually aligns domains (B) via the motion of domain walls to increase the volume of material polarized along with the external field; this maximum polarization is known as the saturated polarization (P_{sat}). When the external field is removed, the material relaxes (C) and some of the domain volume reorients to minimize strain and charge, but some residual net polarization is retained and is referred to as the remanent polarization (P_r). When an external field of the opposite polarity is applied, some volume of the domains reorient accordingly.The point at which the net polarization on the sample is zero (D) is the coercive cield, E_c, referring to the field required to coerce the sample into switching. Further increases in this polarity of field lead to a P_{sat}, and removal of the applied field lands the polarization at a value of $-P_r$. Subsequent field reversal will trace out an approximately symmetric hysteresis loop without ever returning to a stable net zero polarization unless, or until, the sample is 'depoled,' for example, by heating above the Curie temperature.

Fundamentals of ferroelectric ceramics

One of the most significant characteristics of ferroelectric ceramics is their ability to exhibit single crystal-like behavior even when fabricated as polycrystalline ceramics. In addition to typically being significantly less costly and easier to produce than single crystals, fabrication of polycrystalline ceramics also introduces opportunities for microstructure engineering and formation of complex shapes. Use of polycrystalline ceramics as piezoelectrics depends upon the ability to break full isotropic symmetry through the application of a poling field and thus relies on extrinsic effects (domain wall motion) in ferroelectrics. The sidebar "What does symmetry have to do with it" reviews the importance of crystallographic symmetry to piezoelectricity and ferroelectricity.

Intrinsic piezoelectricity is linear under small fields, so applying a +5 V field in one direction will produce equal and opposite strain to applying –5 V in the same direction. In a typical sintered polycrystalline ceramic, even if each of the billions of individual grains is piezoelectric, they all collectively cancel out their neighbors, and the net result is zero macroscopic piezoelectric response. This fact is why quartz piezoelectrics, such as those used for timekeeping in watches, must be single crystals.

Therefore, to use polycrystalline materials as piezoelectrics, the macroscopic



Credit: Sherbondy

Figure 2. Of the crystalline or polycrystalline materials that exhibit piezoelectric behavior, some are pyroelectric, and of those, some are ferroelectric. Materials are classified into these categories based on the symmetry of their unit cell, which in turn dictates how they interact with thermal, electrical, and mechanical energies.

random symmetry of the grains must be broken in some way. One option is to force the grains to all (or at least mostly) grow in a coordinated direction. This approach is used for AlN thin films in MEMS resonators and clever ceramic processing approaches such as templated grain growth.[4] Another option is to start with a crystallographically random polycrystalline ceramic sample and break the macroscopic symmetry in some way, such as with the application of a large electric field. The applied field aligns crystallographic dipoles, and this "poling" process is enabled by the field-induced alignment of spontaneous dipoles, in other words, ferroelectricity (Fig. 2).

The outstanding properties of ferroelectric materials for piezoelectric and charge storage applications arise from a combination of intrinsic and extrinsic contributions. Ceramics based on barium titanate ($BaTiO_3$) dominate the capacitor market while lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT) based ceramics are the most widely used piezoelectric ceramic for more than six decades, finding applications in medical ultrasound transducers, sonar, micropositioners, and more. These materials are cubic and thus nonferroelectric at temperatures above T_C (the Curie temperature) and transform to a lower symmetry polar state below this temperature. Figure 3 shows how the ferroelectric phase transition occurs in the prototypic ferroelectric, $BaTiO_3$ (Fig. 3).

Historically significant ferroelectrics papers

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R.B. Atkin and R.M. Fulrath, (1971) Point defects and sintering of lead zirconate titanate, *JACerS*, **54**(5), 265–270.

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S.L. Swartz, T.R. Shrout, W.A. Schulze, and L.E. Cross, (1984) Dielectric properties of lead-magnesium niobate ceramics, *JACerS*, **67**(5), 311–315.

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C.A. Randall, N. Kim, J.P. Kucera, W.W. Cao, and T.R. Shrout, (1998) Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics *JACerS*, **81**(3), 677–688.

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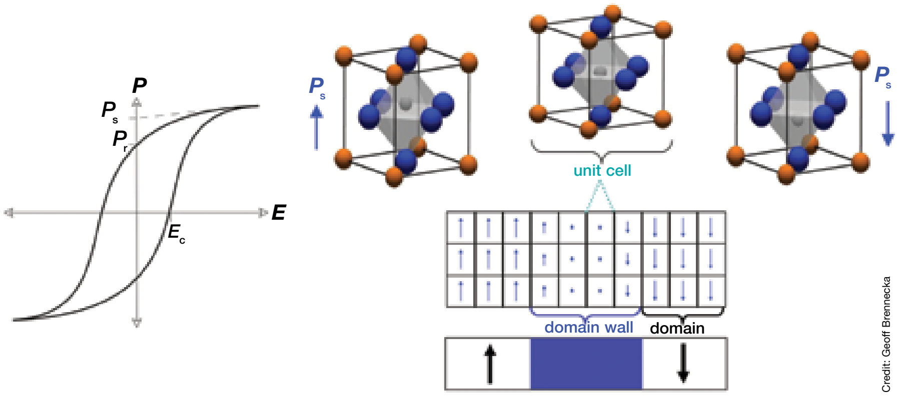


Credit: Geoff Brennecka

Figure 3. During the phase transition that results upon cooling through the Curie temperature, the BaTiO$_3$ unit cell expands by roughly 1% in the polar direction while shrinking accordingly in the two perpendicular directions. Displacement of the cation species (the Ba^{2+} and Ti^{4+}) and anion species (O^{2-}) in opposing directions results in a polar (tetragonal) crystal structure and the presence of a small electrical dipole, a spontaneous polarization, within each unit cell. While the dimensional changes associated with this phase transition are relatively small (about 0.1 Å), the lower symmetry is the key to enabling ferroelectricity and its derivative properties.

What does symmetry have to do with it?

Differences in atomic packing and bonding in different crystallographic directions influence a material's mechanical, thermal, electrical, magnetic, and optical properties, all of which can be direction-dependent. The symmetry principles that govern the categorization of crystalline materials into seven crystal systems and 32 point groups also reflect in the symmetry of the material's properties. This simple but powerful concept that the properties of a crystalline material must exhibit at least the same symmetry as the underlying crystal structure is Neumann's principle.[S1]

All crystalline substances, neglecting quasicrystals, belong to one of 32 crystallographic point groups. Eleven of those point groups possess an inversion center, which means that for any point (*x*,*y*,*z*) in the crystal, the corresponding point (-*x*,-*y*, -*z*) is completely identical. In other words, if you pick any point in space and turn the crystal "inside out" through that point, it will look and behave exactly the same as when you started. Of the remaining 21 point groups, 20 are piezoelectric (the combination of other symmetry operators prohibits piezoelectricity in point group 432), which simply means that applying a stress to the crystal will create a net separation of positive and negative charges in the crystal, hence the name piezoelectric, which translates simply to pressure-electric. This polarization results in the buildup of charges at the crystal surface. The converse is also true: applying an electric field to pull the positive and negative charges apart will produce a net strain in a piezoelectric material. It is this intrinsic coupling of electrical and mechanical energies that makes piezoelectricity such a useful phenomenon.

Of the 20 piezoelectric point groups, 10 are spontaneously polarized, meaning they have a built-in (spontaneous) dipole even without the presence of an applied field. These are the polar point groups, and because the magnitude of the spontaneous dipole changes with temperature, such polar materials are also known as pyroelectric (temperature-electric) materials. If the direction of this spontaneous dipole can be reoriented through the application of an electric field, the material is a ferroelectric. This fact means that ferroelectrics are an experimental subset of pyroelectric materials. If a material undergoes dielectric breakdown (essentially a lightning bolt) before the applied electric field is sufficient to reverse its polarization, it is not ferroelectric, or at least it was not, before you and your lightning bolt destroyed it.

Therefore, all ferroelectric materials are pyroelectrics, and all pyroelectrics are piezoelectric, but not all piezoelectric materials are pyroelectric, and not all pyroelectrics are ferroelectric. If that is confusing, just remember that all squares are rectangles, but not all rectangles are squares.

S1. Neumann's principle. Online Dictionary of Crystallography. http://reference.iucr.org/dictionary/Neumann's_principle. Accessed Dec. 2, 2019.

The change in shape and the resulting spontaneous polarization along the (by definition) *c*-axis occurs in every unit cell in the sample, and of course each unit cell is influenced by those around it. Having all of the unit cells transition in the same direction would be both a tremendous coincidence and a higher energy state than having some disorder. Thermodynamic free energy minimization drives the formation of domains to reduce both elastic (strain) and electrostatic (charge) energies. Domain sizes and distributions depend on boundary conditions and defects, but the ability to configure and reconfigure these domains by applying electric fields is both the defining property of ferroelectrics and the source of extrinsic contributions that often dominate the properties.

It is worth noting that in recent decades, researchers have found that electrically driving single crystal piezoelectrics along nonpolar directions can produce very large extrinsic contributions to electromechanical strain, taking advantage of similar mechanisms to those described here for polycrystalline ceramics.

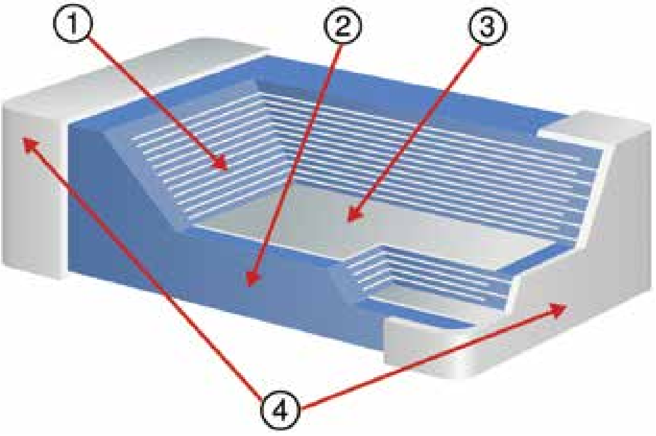
Some of the same factors that enable large piezoelectric responses in ferroelectrics also contribute to large permittivities, which is of great importance for charge storage in capacitors. Relative permittivity (also referred to as dielectric constant, though it is anything but constant in the materials discussed here) is proportional to the change in polarization with an applied electric field. When a small electric field is applied to a ferroelectric, the intrinsic response discussed above results in a change in polarization that is typically much larger than in linear dielectrics, such as silica or alumina. This change in polarization leads to a large relative permittivity and a high volumetric capacitance. Additional extrinsic effects, small motions of domain walls, lead to even larger changes in polarization and even higher relative permittivities. These attributes make ferroelectrics well-suited for many capacitor applications. For example, the relative permittivity of BaTiO$_3$-based dielectrics in the multilayer ceramic capacitors (MLCC, Fig. 4) that are present in our cell phones, computers, and other electronics, is greater (often much greater) than 1,000. For comparison, silica has a relative permittivity value of just 3.9.

Abundant applications

Sophisticated ceramic processing and microstructure engineering enabled scaling of ferroelectric-containing MLCCs, such that today our electronics operate with dielectric layer thicknesses far less than one micron packaged into capacitors with more than 100 active layers. Packaged MLCC devices today can be many times smaller than a grain of salt. In fact, MLCC scaling over the past 50 years rivaled—and often outpaced—the aggressive transistor scaling of the semiconductor industry known as Moore's Law.

As discussed in the sidebar "What does symmetry…", polar crystals exhibit the pyroelectric effect, or a change in polarization magnitude with a change in temperature. While all polar materials possess this property, ferroelectrics may have pyroelectric coefficients that are much larger than their nonferroelectric counterparts, often in the proximity of a ferroelectric phase transition. This property makes ferroelectric pyroelectrics particularly well-suited for thermal sensors. A wide variety of ferroelectrics are used for pyroelectric sensors, but some of the most common are single crystal $LiNbO_3$ or $LiTaO_3$ owing to their combination of high pyroelectric coefficient, low losses, and low relative permittivity, which increases the measurable voltage for a given amount of charge produced.

$LiNbO_3$ and $LiTaO_3$ single crystals also find tremendous use in the optics sector, often in the form of periodically poled lithium niobate (PPLN) and periodically poled lithium tantalate (PPLT), structures for waveguides, phase matching, difference frequency generation, and many others. This periodic poling takes advantage of the nearly strain-free 180-degree domain walls in these crystals as well as their large coercive fields. In fact, the coercive fields of as-grown $LiNbO_3$ and $LiTaO_3$ crystals at room temperature are often very close to the breakdown strengths of the crystals, so the pure materials are often poled as they are pulled from a melt or at temperatures approaching their Curie temperature where the coercive fields are lower. Doping with magnesium reduces the coercive field and increases the laser damage threshold of $LiNbO_3$ and $LiTaO_3$ by compensating for the lithium deficiency inherent in melt-grown $LiNbO_3$ and $LiTaO_3$ crystals. Creating an array of inverted domains with periodicity related to the wavelength of an incident laser beam enables a variety of clever manipulations of the beam as it passes through the PPLN or PPLT crystal, and the high coercive fields ensure that once the material is poled, it will stay that way during operation, even under large optical powers and occasionally large applied electric fields.



Credit: Wikimedia, Jens Both Elcap, CC BY-SA 3.0

Figure 4. Schematic structure of a multilayer ceramic capacitor. Layers are (1) dielectric ceramic, (2) outer ceramic layer, (3) electrode, and (4) contact surface.

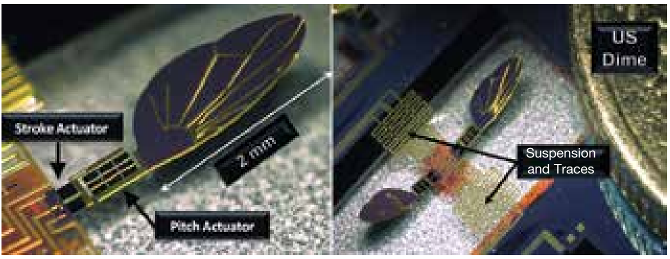
One technology that utilizes the full switching of polarization, the very hallmark of ferroelectricity, is ferroelectric random access memory, FeRAM. In this technology, the polarization of the ferroelectric represents a binary bit of information (i.e., 1 or 0). When coupled in series with a transistor, the amount of current flowing through the channel when the transistor is activated allows differentiation of the positive or negative polarization (memory) state of the ferroelectric capacitor. A voltage pulse is then used to set the polarization of the ferroelectric for the next stored bit. The result is a nonvolatile memory that can maintain its state for timescales up to 45 years.[5] FeRAM has advantages over other memory technologies in terms of the number of read/write cycles possible and the energy required for each switching event, though its physical scaling into the tens of nanometer range remains a significant challenge.

While ferroelectric and related materials dominate the high strain piezoelectric technologies of sonar, ultrasound, and micro- and nano-positioners, these technologies rely on bulk ceramics or single crystals fabricated into specific geometries for best performance. To affect technologies at smaller size scales, such as millimeter-scale robotics, RF switches, and actuators for inkjet printers, the device sizes must also decrease. This requirement has driven significant efforts into development of ferroelectric piezoelectric thin films and micro-electro-mechanical systems (MEMS) devices that can perform at reduced dimensions—a field known as piezoMEMS. Figure 5 shows an example piezoMEMS device designed to imitate dragonfly flight.[6] The most broadly studied material for piezoMEMS is PZT. In approximately 30 years of piezoMEMS study, the piezoelectric performance of PZT thin films substantially improved through advances in processing and understanding of the roles of mechanical boundary conditions.

While PZT and other lead-based ferroelectric piezoelectrics demonstrate the most utility for electro-mechanical applications, the looming European Union Restriction on Hazardous Substances (ROHS) requirements drive the search for reduced lead in materials and has also led to the study of lead-free piezoelectric ceramics and films. The piezoelectric coefficients of the lead-free materials, such as $(K,Nb)NbO_3$ and $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ to date lag behind those of lead-based systems and represent a large area of current and future study and growth.

Frontiers of ferroelectricity

In the first 90 years of ferroelectrics research, attention focused on a few



Credit: U.S. Army Research Laboratory

Figure 5. U.S. Army Research Laboratory's prototype PZT piezoMEMS dragonfly with stroke and pitch actuated wing design. The image on the right shows a platform suspended on the dragonfly between individually controllable wings.[7]

primary crystal structures and materials populating those structures at the forefront for commercial applications. These include the perovskite ferroelectrics $LiNbO_3$ and $LiTaO_3$ described previously; layered structures, such as $SrBi_2Ta_2O_9$; and dihydrogen phosphates, such as KH_2PO_4. However, in the past 10 years, two new structural classes have joined the ferroelectric family and bring with them some potential technological superiority to traditional materials on the basis of chemical compatibility with dominant semiconductor technologies. These include fluorite-structured HfO_2 and wurzite-structured (Al,Sc)N.

In 2011, Boscke et al. first reported ferroelectricity in fluorite-structured silicon-doped HfO_2 thin films.[7] The observation of a switchable polarization in this material surprised the community and generated a great deal of excitement. This excitement was driven largely by the inherent silicon compatibility of hafnia and the fact that the first observation of ferroelectric response in HfO_2 occurred in films that were only 10 nm thick just shortly after HfO_2-based gate dielectrics emerged in commercial integrated circuits. HfO_2-based ferroelectrics are poised to enable scaling of existing ferroelectrics-based technologies, such as FeRAM, to even smaller dimensions. In addition to demonstrated and commercialized ferroelectric thin film technologies, the integrated circuit process compatibility of HfO_2 positions it to enable other new devices, such as negative differential capacitance field effect transistors (NC-FETs) and ferroelectric-FETs, which may offer continued performance increases to silicon based integrated circuits.

All of the commercially relevant ferroelectric ceramics discussed so far are oxides, but recent efforts have identified promising nitride ferroelectrics. Primary among them is (Al,Sc)N.[8] MEMS resonators based on AlN thin films dominate the wireless communications market since the early 2000s, and in recent years, such resonators showed improved piezoelectric response via alloying with ScN or other transition metal nitrides. Increasing the concentration of scandium in (Al,Sc)N reduces the *c/a* ratio of the polar AlN wurtzite structure, gradually pushing the unit cell closer to the nonpolar hexagonal BN-type structure in which the cation sits in the same plane as the anions. At sufficiently high scandium contents, the amount of electric field required to switch the polarity of this structure can be less than the breakdown strength of the sample, and the material is ferroelectric. In large part due to the size of the MEMS industry already established around AlN thin films for radio frequency communications, ferroelectric (Al,Sc)N films and their derivatives have attracted tremendous attention for a number of integrated devices, but the enormous driving force for phase separation makes reliable fabrication rather challenging.

Recent predictions suggest ferroelectric behavior in nitride perovskites, including $LaWN_3$.[9] Calculations point to a polar structure with a sufficiently low energy barrier between anti-aligned polarities to make it a strong candidate for ferroelectricity,[10] but these await experimental confirmation. Similarly, ferroelectricity reported in several of hybrid halide perovskites took the photovoltaic world by storm, though the veracity of the genuine ferroelectric nature and the potential role(s) of the spontaneous polarization on the properties of these materials remains controversial.

We will not pretend to know exactly what lies ahead for the second century of ferroelectricity, but it is a safe bet that ferroelectrics will continue to play the role of enabler, quietly operating behind the scenes, facilitating critical functions and systems.

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