

History of the First Ferroelectric Oxide, BaTiO₃

C.A. Randall, R.E. Newnham, and L.E. Cross
Materials Research Institute
The Pennsylvania State University
University Park, PA 16802 USA

BaTiO₃ is the most widely used ferroelectric material, and even sixty years after its discovery, it is the most important multilayer ceramic dielectric. The objective of this short paper is to indicate some of the chronologically important scientific contributions enhancing the understanding and use of BaTiO₃. BaTiO₃ was discovered during World War II in 1941 and 1944 in the United States, Russia, and Japan. At least in the U.S.A., the research was accelerated because of the war. At that time, mica was used in most capacitors, but U-boats threatened the supplies of mica to the U.S.A. from South America. The initial reports were based on doping studies of TiO₂ with BaO, which produced ceramic materials with enhanced dielectric permittivities. The mixed oxides were made by Thurnauer and Deaderick at the American Lava Co. as early as 1941, the filing date of U.S. Patent No. 2,429,588.⁽¹⁾ The high permittivities were found by measurements made at the Erie Resistor Company, with dielectric constant exceeding 1000, ten times greater than any other ceramic known at that time, such as TiO₂ ($\epsilon_r=110$). Later, more precise studies were reported by Wainer and Solomon in the United States, Ogawa and Waku in Japan, and Wul and Goldman in Russia.^(2,3,4) It has been speculated that German scientists failed to identify BaTiO₃ because of space charge polarization caused by differences in ore extraction methods for TiO₂. The chloride methods used in Russia, Japan, and the U.S.A. led to a lower Nb content and therefore less conduction than in the sulfuric acid route method used in Germany.⁽⁵⁾

The race to understand the nature of the dielectric anomaly in ceramic BaO–TiO₂ ceramics continued, and in 1945 and 1946, von Hippel (USA), and Wul and Goldman (Russia) demonstrated ferroelectric switching in the ceramics.^(6,7) The discovery of ferroelectricity in BaO–TiO₂ ceramics was extremely important, as it demonstrated for the first time that ferroelectricity could exist in simple oxide materials, and it was not always associated with hydrogen bonding. BaTiO₃ is a member of the perovskite family based on the mineral CaTiO₃, as predicted from fundamental crystal chemical principles described much earlier by

Goldschmidt (1926).⁽⁸⁾ The first detailed description of the crystal structure of BaTiO₃ in the high temperature ferroelectric phase was proposed by Helen D. Megaw (1945) in the United Kingdom and confirmed soon after with the work of Miyake and Ueda (1946).^(9,10) Figure 1 shows the basic structure of barium titanate with the titanium ion occupying the octahedrally coordinated site and the Ba ion in the twelve coordinated site in a high temperature Pm3m cubic symmetry. The ferroelectric phase at room temperature is tetragonal with oxygen and titanium ions shifting to produce a spontaneous polarization. Later, Kay and Vousden (1949) showed that BaTiO₃ had a series of ferroelectric-ferroelectric transitions from tetragonal (P4mm)→orthorhombic (Bmm2), at 5°C and at -90°C a transition from orthorhombic to rhombohedral (R3m), Figure 2.⁽¹¹⁾ These data indicated coexisting regions and hysteresis consistent with first order behavior in the transition that was earlier detected by Wul (1946) and also Harwood, Popper, and Rushman (1949) with humps in the specific heat data at the transition temperatures.^(7,12) Precise refinements for tetragonal BaTiO₃ were performed later by Pepinsky and Shirane and compared with the tetragonal phase of PbTiO₃.⁽¹³⁾

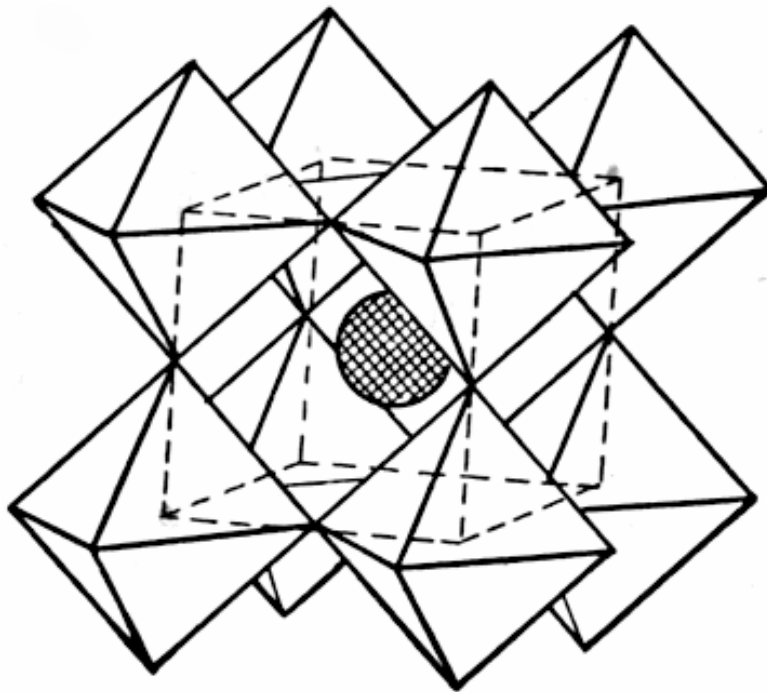


Figure 1. Basic perovskite structure of BaTiO₃ with the Ba ion in the center of the cell and Ti ions inside the oxygen octahedra.

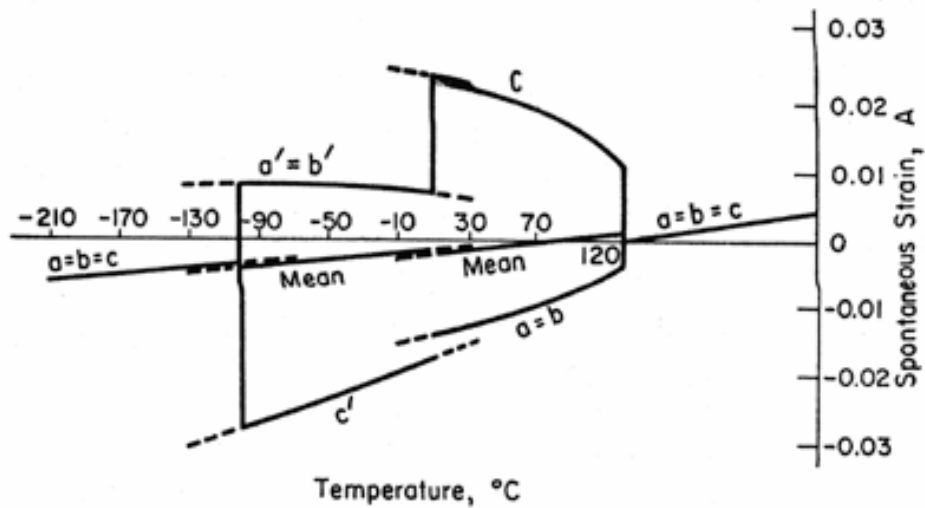


Figure 2. Variation in lattice parameter through the various polymorphic structures of BaTiO_3 .⁽¹⁷⁾

Better understanding of the nature of the phase transitions came with the growth of BaTiO_3 crystals. The first crystals were produced in and around 1947; however, these were small. Later in 1954, Remeika produced larger crystals that enabled the ferroelectrics community to extend the fundamental understanding of the dielectric anisotropy, domain switching, and electro-optical and electromechanical properties of ferroelectric BaTiO_3 .⁽¹⁴⁾ Merz produced some classical polarization and permittivity data back in 1949 that are often used in textbooks to illustrate dielectric anisotropy in the ferroelectric phases of BaTiO_3 . Later, Cross revisited the BaTiO_3 crystals for polarization data and dielectric anisotropy in the lower temperature ferroelectric phases, as the Merz data were plagued by multidomain effects.^(15,16) With the increased availability of BaTiO_3 single crystals, understanding of the ferroelectric domain structures was improved through consideration of the low energy configurations and size effects in both the tetragonal and orthorhombic ferroelectric phases. At that time, these observations were made with optical microscopes, Kay (1948), Matthias and von Hippel (1948) and Blättner, Kanzig and Merz (1949).⁽¹⁷⁻¹⁹⁾ Figure 3 shows a photomicrograph with 90° domains in a single crystal BaTiO_3 using a polarized light microscope (after Forsbergh (1949)).²⁵ The low temperature orthorhombic domain observations were often made outside the laboratory

on cold winter days. In later years, domain observations were made with electron microscopy techniques, such as the classic work of Tanaka and Honjo (1964)⁽²⁰⁾, and more recently, observations with Atomic Force Microscopy.⁽²¹⁻²²⁾

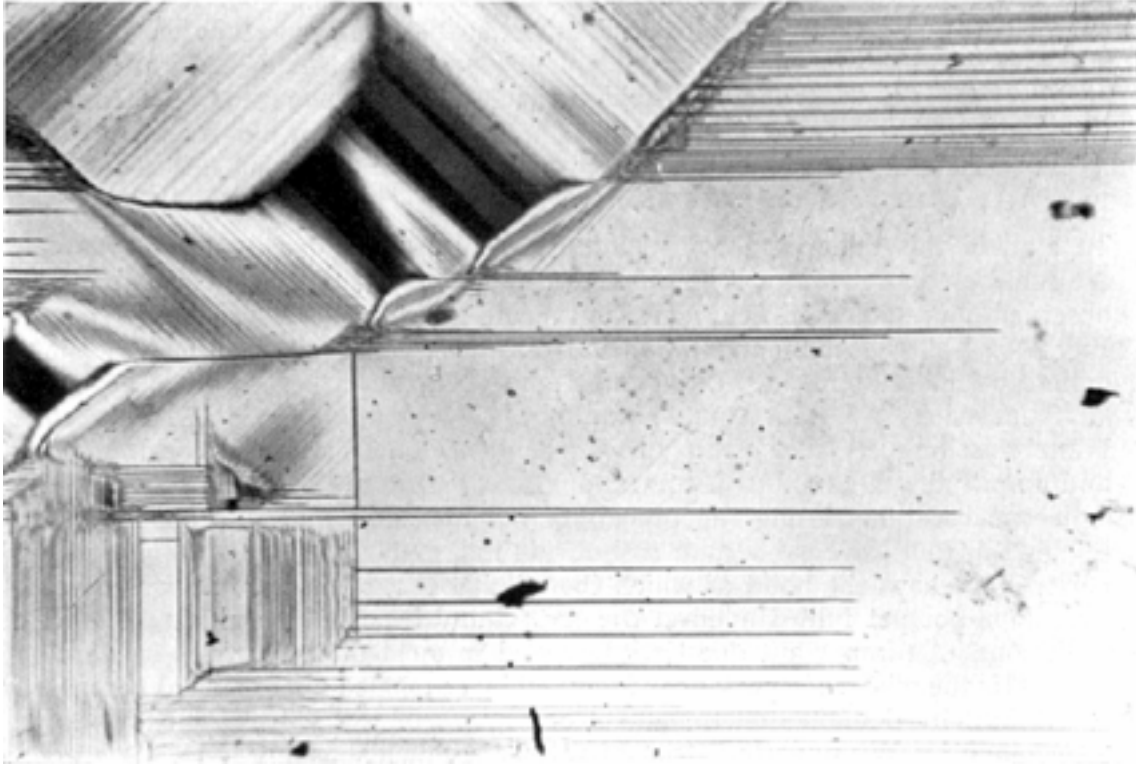


Figure 3. Optical micrograph of 90° domains in a single crystal of barium titanate.(After Forsbergh Jr. (1949)).

Merz et al. and Miller et al., amongst others, looked into the details of the domain switching in BaTiO_3 crystals,^(23,24) separating contributions to the switching current from domain nucleation and domain wall motion under different field strengths. The effects of mechanical stresses on ferroelastic switching of the 90° domains were observed by Forsbergh.⁽²⁵⁾ Many of these early observations underpin the more sophisticated models of domain switching we have today.^(26,27)

The interrelationship between the anomalous electromechanical, structural, and thermal properties of BaTiO_3 was modeled phenomenologically by A.F. Devonshire.⁽²⁸⁾ This approach built upon the earlier ideas of Landau and Ginzberg and invoked the point group symmetry and nonlinear elasto-dielectric coupled interactions with electrostriction and piezoelectric

coefficients.^(29,30) With such a model, the basic interrelationships in single domain BaTiO₃ could be described using the general form of the Devonshire theory:

$$\Delta G = \frac{1}{2}\alpha_{ij}P_iP_j + \frac{1}{4}\alpha_{ijk\ell}P_iP_jP_kP_\ell + \frac{1}{6}\alpha_{ijk\ell mn}P_iP_jP_kP_\ell P_mP_n \\ + \frac{1}{2}c_{ijk\ell}x_{ij}x_{k\ell} + a_{ijk}x_{ij}P_k + \frac{1}{2}q_{ijk\ell}x_{ij}P_kP_\ell$$

- where ΔG – the free energy of crystal expressed in terms of polarization and strain
 i,j,k,ℓ,m,n – 1,2,3, indicating directional indices
 P_i – polarization coefficients
 α_{ij} – reciprocal dielectric susceptibility
 $\alpha_{ijk\ell}$ – fourth order coefficient
 $\alpha_{ijk\ell mn}$ – sixth order coefficient
 x_{ij} – strain tensor coefficient
 $c_{ijk\ell}$ – stiffness coefficient
 a_{ijk} – piezoelectric coefficient
 $q_{ijk\ell}$ – electrostrictive coefficient

From experimental data, a self-consistent set of coefficients can be obtained to generate the energy function. Then through thermodynamic relations, temperature, stress, and electric field dependences can be readily determined and predicted. In later years, more microscopic models were developed to explain the dielectric and structural properties of the ferroelectric oxides. However, BaTiO₃ itself has challenged the theorists with the experimental evidence of local dipole components existing above the Curie temperature, as detected by diffuse x-ray scattering, Raman spectroscopy, inelastic neutron scattering, and second harmonic generation. It is now accepted that BaTiO₃ has elements of both displacive soft-mode phonons and order-disorder behavior.⁽³¹⁻³³⁾ The debate on the true microscopic nature of the BaTiO₃ phase transition continues to challenge each new generation of ferroelectricians.

As mentioned earlier, the initial discovery of barium titanate came from government-sponsored programs during the World War II. But at the end of the war, public disclosure led to intense interest not only in academic circles, but in practical markets, in particular high capacitance, small volume capacitors in early television and radio circuits, as well as active

elements for phonograph pick-ups, accelerometers, and ultrasonic generators.⁽³⁴⁾ Prior to the discovery of BaTiO₃, ceramic materials were rarely encountered in capacitor technology. The only applications were in the form of an insulator at the base of a mica compression condenser or as the insulating case of a high voltage capacitor. To aid in the processing of ceramics for capacitor applications, the BaO-TiO₂ phase diagram was investigated by Rase and Roy.⁽³⁵⁾ Important solubility regions in the Ti-rich side of the phase diagram were identified, along with transition temperatures between cubic and hexagonal forms of the perovskite and the eutectic temperature of $\approx 1320^\circ\text{C}$ on the Ti-rich side of the diagram. Many years later, more detailed investigations with chemical precursors were used to refine the phase diagram on the Ti-rich side and overcome problems with a metastable Ba₂Ti₂O₅ phase that cursed the earlier phase diagram studies. From the phase diagram studies, new microwave dielectrics were discovered, such as Ba₂Ti₉O₂₀.^(36,37) Based on such phase diagrams, scientists have been able to better understand the microstructural and phase development of BaTiO₃ ceramics for both capacitor and transducers applications. With the widespread use of BaTiO₃ ceramics in multilayer capacitors came a need to better understand compositional, defect chemistry, and powder processing of BaTiO₃. Composition studies researched the temperature shift of the phase transitions. It was noted that through controlling concentrations and compositional distributions, the temperature dependence variations of dielectric properties could be engineered for different application areas. Donor and acceptor effects were understood through extensive defect chemistry work. One of the best, and arguably the most comprehensive, studies was performed by Seuter in a Ph.D thesis carried out at Philips Laboratories.⁽³⁸⁾ Work of this type and from others helps explain many key factors, such as dielectric aging (time dependent variation of dielectric permittivity), insulation resistance, and failure mechanisms in capacitors. Modern-day capacitors are fabricated to dielectric layers $\sim 1.5 \mu\text{m}$, using reducing atmospheres with nickel internal electrodes. An example of such a multilayer device is shown in Figure 4(a) and (b).

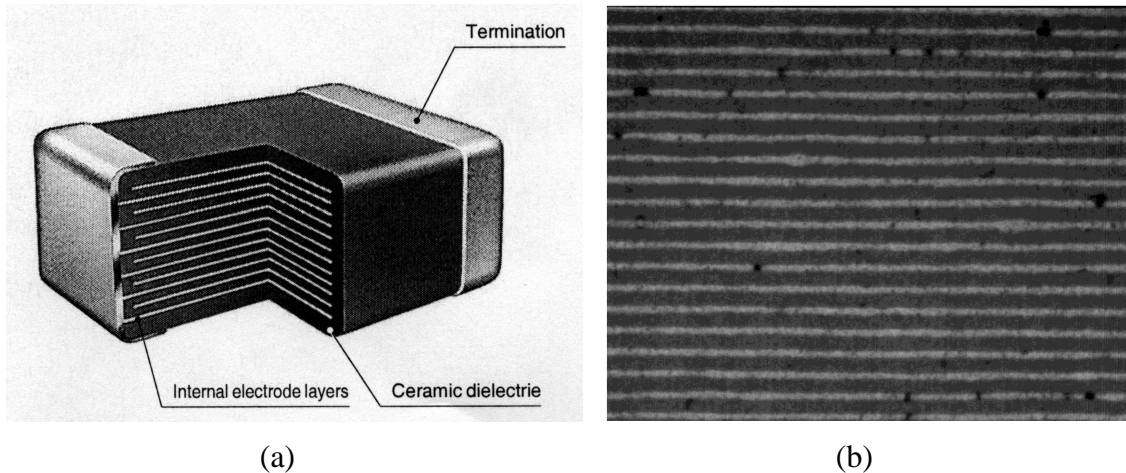


Figure 4. (a) Basic structure of a surface mount multilayer capacitor, and (b) micron-scaled layers made from laminating doped barium titanate layers and printed nickel electrode layers, and then cofiring in reducing atmospheres for the capacitor structure.

Polycrystalline BaTiO_3 appropriately doped with an excess of donors and TiO_2 can lead to unusual nonlinear resistors known as positive temperature coefficients resistors (PTCRs). This phenomenon involves an enhanced resistivity at the Curie transition temperature at 125°C . A schematic representation of this PTCR phenomenon is shown in Figure 5. First discovered by Subari in 1959⁽³⁹⁾, the semiconductor properties are strongly influenced by the ferroelectric transition, with up to 6–7 orders of magnitude change in resistivity in the best BaTiO_3 PTCR thermistors. This phenomenon is only observed in polycrystalline BaTiO_3 , with the spontaneous polarization of the ferroelectric domains modifying the band-bending and, therefore, the electronic transport across the grain boundary.⁽⁴⁰⁾

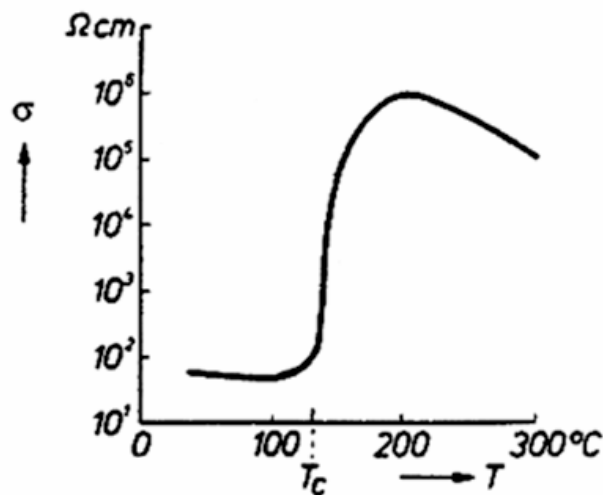


Figure 5. Anomaly of the conductivity in a semiconducting BaTiO_3 ceramic.

BaTiO₃ was the very first ceramic transducer. To establish piezoelectric activity from the BaTiO₃ ceramics, the domains had to be aligned to induce a macroscopic polarization. Once induced, the BaTiO₃ ceramics were employed for a variety of transducers, which control current, either electrical or mechanical energy, and the conversion of one into the other. It was as early as September 1946 that an engineer (R.B. Gray) at the Erie Resistor Company, working on the D.C. degradation of the first BaTiO₃ capacitors, recognized that the “hum” was the result of an induced piezoelectric effect.⁽⁴¹⁾ Later, S. Roberts recognized the poling effect in his publication in 1947.⁽⁴²⁾ Some of the early work was discussed by Hans Jaffe (1950).⁽⁴³⁾ BaTiO₃ phonographic pickups were the first use of piezoelectric ceramics. The British Navy until very recently used some underwater sonar devices based on the piezoelectric response of BaTiO₃ ceramics. Lately, the BaTiO₃ piezoelectric properties have been revisited in the form of single crystals and textured ceramics because of environmental concerns with the lead-based perovskites based on the perovskite PbZrO₃–PbTiO₃ system.⁽⁴⁴⁾

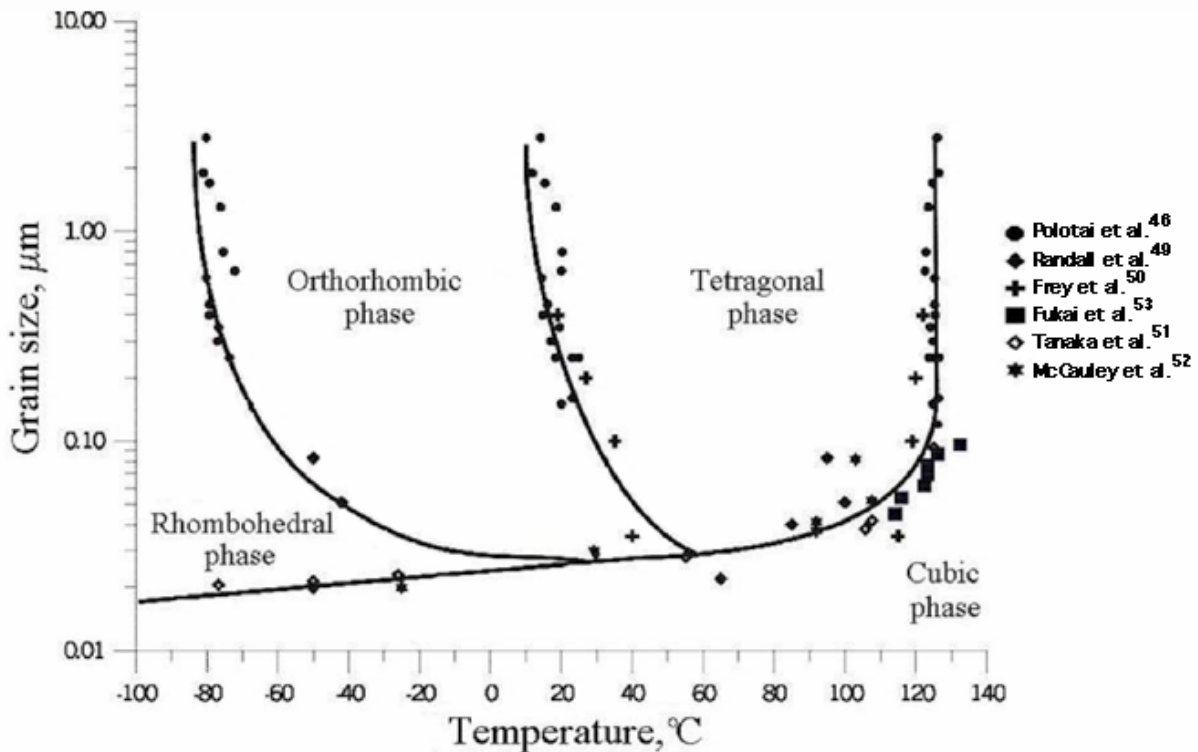


Figure 6. Grain size variations affecting the transition behavior of pure barium titanate.

Over the years, BaTiO₃ has been used in a wide variety of applications in various forms of crystals, bulk ceramics, multilayers, and thin films.⁽⁴⁵⁾ The ability to be used in so many different applications is a consequence of the complex coupling and the various interactions associated with ferroelectric phenomena. As for the future of BaTiO₃, there is at the time of writing a lot of interest in producing nanoparticles for future multilayer dielectrics.^(45,46,47) These are fundamental and experimental studies to understand the size effects that control interfacial and surface phenomena in greater detail than ever before in the history of BaTiO₃, see Figure 6.⁽⁴⁶⁻⁵⁴⁾

Acknowledgements

The authors wish to thank K. Wakino and W. Cook for their useful input. Also thanks to J. Aller for typing this manuscript.

References

- (1) H. Thurnaurer and J. Deaderick, U.S. Patent No. 2,429,588, Oct. 21, 1947; filed (1941).
- (2) E. Wainer and A.N. Solomon, Titanium Alloy Manufacturing Co. Report No. 8 (September 1942) and No. 9 (January 1943).
- (3) T. Ogawa and S. Waku (discovered 1944); T. Ogawa, Busseiron, Kenkyu No. 6 1 (1947).
- (4) B. Wul and J.M. Goldman, C.R. Acad. Sci URSS 46 139 (1945).
- (5) K. Wakino (private communication).
- (6) A. Von Hippel, R.G. Breckenridge, F.G. Chesley, and L. Tisza, Ind. Eng. Chem. 38 1097 (1946).
- (7) B. Wul and J.M. Goldman, C.R. Acad. Sci. URSS 51 21 (1946).
- (8) V.M. Goldschmidt. Shrifter Nofke Videnskaps-Akad. Oslo I: mat-Naturv. Kl. No. 2, 8 (1926).
- (9) H.D. Megaw, Nature 155 484 (1945).
- (10) S. Miyake and R. Ueda, J. Phys. Soc. Jap. 1 32 (1946).
- (11) H.F. Kay and P. Vousden, Phil. Mag. 40 1019 (1949).
- (12) M.G. Harwood, P. Popper, and D.F. Rushman, Nature 160 58 (1950).
- (13) G. Shirane and R. Pepinsky, Phys. Rev. 91 812 (1953).
- (14) J.P. Remeika, J. Am. Ceram. Soc. 76 940 (1954).

- (15) W.J. Merz, Phys. Rev. 76 1221 (1949).
- (16) L.E. Cross, Phil. Mag. 44 1161 (1953).
- (17) H.F. Kay, Acta Cryst. 1 229 (1948).
- (18) B.T. Matthias and A. Von Hippel, Phys. Rev. 73 1378 (1948).
- (19) H. Blattner, W. Kanzig, and W.J. Merz, Helv. Phys. Acta 22 35 (1949).
- (20) H. Tanaka and G. Honjo, J. Phys. Soc. Jap. 19 954 (1964).
- (21) L.M. Eng, M. Bammerlin, C.H. Loppacher, M. Guggisberg, R. Bennewitz, E. Lüthi, E. Meyer, T.M. Huseir, H Heizelmann, and H.J. Günterdobt, Ferroelectrics 222 153 (1999).
- (22) A.L. Gruverman, Nanotechnology 8 (3A) 38 (1997).
- (23) W.J. Merz, Phys. Rev. 95 690 (1954).
- (24) R.C. Miller and A. Savage, J. Appl. Phys. 30 808 (1959).
- (25) P.W. Forsbergh, Jr., Phys. Rev. 76 1187 (1949).
- (26) J. Fousek and B. Brezina, Czechoslov. J. Phys. 9 265 (1959).
- (27) J. Kobayashi, Phys. 21 151 (1967).
- (28) A.F. Devonshire, Phil. Mag. 40 1040 (1949), Phil. Mag. 42 1065 (1951).
- (29) V.L. Ginzberg, J. Phys. USSR 10 107 (1946).
- (30) L.D. Landau and L.M. Lifshitz, Physik Z. Sowjetanion 8 153 (1935).
- (31) R. Comes, M. Lambert, and A. Guinier, Comm. Solid State Phys. 6 715 (1968).
- (32) D. Heimann and S. Ushioda, Phys. Rev. B9 2122 (1974).
- (33) J. Harada, J.D. Axe, and G. Shirane, Phys. Rev. B4 155 (1971).
- (34) A.E. Dranetz, G.N. Howatt, and J.W. Crownover, Tele-Tech 8 [4] 29 (1949).
- (35) D.E. Rase and R. Roy, J. Am. Ceram. Soc. 38 102 (1955).
- (36) R.S. Roth, C.J. Rawn, C.G. Lindsay, W. Wong, J. Sol. State Chem. 104(1) 99 (1993).
- (37) H.M. O'Bryan and J. Thomson, J. Am. Ceram. Soc. 66(1) 66 (1983).
- (38) A.M. J.H. Seuter, Philips Res. Reports, Suppl. No. 3 (1974).
- (39) O. Subari, J. Am. Ceram. Soc. 44 54 (1961).
- (40) W. Heywang, J. Am. Ceram. Soc. 47 484 (1964).
- (41) R.B. Gray, U.S. Patent No. 2,486,560, Nov. 1 (1949); filed in 1946.
- (42) S. Roberts, Phys. Rev., 890–5 (1947).
- (43) H. Jaffe, Ind. Eng. Chem. 42 [2] 264–68 (1950).
- (44) S.E. Park, S. Wada, L.E. Cross, and T.R. Shrout, J. Appl. Phys. 86 (5) 2746 (1999).

- (45) H. Chazono and H. Kishi, *Jap. J. Appl. Phys.* 40 (9B) 5624 (2001).
- (46) A.V. Polotai, A.V. Ragulya, C.A. Randall, *Ferroelectrics* 288, 93–102 (2003).
- (47) S. O'Brien, L. Brus, and C.B. Murray, *J. Am. Chem. Soc.* 123 (48) 12085 (2001).
- (48) A.V. Polotai, A.V. Ragulya, T.V. Tomila, and C.A. Randall, *Ferroelectrics* 298, 243–251 (2004).
- (49) C.A. Randall, *J. Chem. Soc. Jap.* 109(1), S2-S6 (2001).
- (50) M.H. Frey, Z. Xu, P. Han, and D.A. Payne, *Ferroelectrics* 206 (1–4) 337–353 (1998).
- (51) M. Tanaka and Y. Makino, *Ferroelectrics Letters* 24 (1–2) 13–23 (1998).
- (52) D. McCauley, R.E. Newnham, and C.A. Randall, *J. Am. Ceramics Soc.* 81 (4) 979–987 (1998).
- (53) Y. Fukai, *Ferroelectrics* 203 227–231 (1997).
- (54) L. Mitoserin, C. Harnagea, P. Nanni, A. Testino, M.T. Buscaglia, V. Buscaglia, M. Viviani, Z. Zhao, and M. Nygren, *Appl. Phys. Letts.* 84 (13) 2418–2420 (2004).