

History of Ferroelectrics

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Ferroelectric ceramics are widely used as capacitors, transducers, and thermistors, accounting for about one-half the sales of electroceramic components. The historical roots leading to the discovery of ferroelectricity can be traced back to the last century and the work of the famous crystal physicists Weiss, Pasteur, Pockels, Hooke, Groth, Voigt, and the brothers Curie. Beginning with the pioneering work on Rochelle salt and potassium dihydrogen phosphate, the study of ferroelectrics accelerated rapidly during World War II with the discovery of barium titanate. Then came a period of rapid proliferation with more than 100 new ferroelectrics identified in the next decade, including lead zirconate titanate, the most widely used piezoelectric transducer. In the following decade, the concepts of soft modes and order parameters led to the age of "high science" in the sixties. Neutron experiments authenticated the soft-mode concept and led to the discovery of a number of peculiar improper ferroelectrics such as gadolinium molybdate. In the seventies came the age of diversification in which the electrooptic properties, defect chemistry, and electronic conduction phenomena in ferroelectric ceramics were explored. In the present decade we are witnessing the beginnings of electroceramic integration: Ferroelectric transducers and capacitors are being integrated into multilayer packages along with ceramic substrates, metallic interconnect circuitry, and ceramic resistors. Further integration and miniaturization will take place in the years ahead as electroceramic technology follows the pathways of the semiconductor industry.

Ferroelectricity, involving as it does the complex interplay of dielectric and elastic behavior in highly nonlinear, anisotropic, polarizable, deformable crystals, is perhaps even now almost as much an art as a science. Like both these types of human endeavor, it has passed through a number of well-marked "phases" when specific materials, techniques, or models for study were particularly in vogue. Following the art historian, one might try to identify and name these major periods of activity and our own attempt along these lines is summarized in Table I.

Certainly one of the major "turning points" in ferroelectricity came in the very early 1940s with discovery of the unusual dielectric properties of a number of simple mixed oxides which crystallize with the perovskite structure. In the "preperovskite era," ferroelectricity was something of a scientific curiosity, unique to two rather friable water-soluble crystal families with complex crystal structures. After the 1940 discoveries, the robust, stable ceramic oxides with very simple structures and obviously exploitable properties led to significantly greater involvement with the topic, a steadily broadening base of practical applications, and rapidly deepening fundamental understanding.

To further subdivide about this early period, one may note that, for a long time, from the late 1890s to 1935, a single interesting crystal was the

Table I. Important Events in Ferroelectricity

1920–1930	Rochelle Salt period: discovery of ferroelectricity
1930–1940	KDP age: Thermodynamic and atomistic models of ferroelectricity
1940–1950	Early barium titanate era: High- <i>K</i> capacitors developed
1950–1960	Period of proliferation: Many new ferroelectrics discovered
1960–1970	Age of high science: Soft modes and order parameters
1970–1980	Age of diversification: Ferroics, electrooptics, thermistors
1980–1990	Age of integration: Packages, composites, and integrated optics
1990–2000	Age of miniaturization: Size effects, manipulated modes and dipoles

sole object for study. It seems perhaps reasonable to term this the early Rochelle Salt period. In 1935 the agonies of working with this unstable complex crystal were partially relieved by the discovery of ferroelectricity in the potassium dihydrogen phosphate family. These were easier, more symmetric crystals to work with, but with ferroelectricity confined to temperatures below -150°C . We have termed the decade from 1930 to 1940 the intermediate KDP period.

After 1940, in the postperovskite era, it appears that the developments fall rather neatly into four decade-long periods. The barium titanate period, 1940 to 1950, occurred when the major experimental features of this fascinating crystal were first studied, and the capacitor and transducer applications for ceramic BaTiO_3 were firmly established. The years 1950 to 1960 were a period of rapid proliferation in the number of known ferroelectrics. Over this period, the number of known ferroelectrics grew from Rochelle Salt, KDP, and three or four ferroelectric perovskites in 1950 to twenty-five firmly established families of ferroelectrics, more than twenty definite perovskite compounds, and innumerable solid solutions in the early 1960s.

Perhaps the most significant theoretical development in ferroelectricity occurred in 1960 with the formulation of the elegant soft-mode description of the ferroelectric transition made almost simultaneously and independently by Cochran and Anderson. This dynamical phenomenological description provided the vital link whereby the static phenomenologies of Mueller and Devonshire could be interconnected with tractable atomistic descriptions through the elementary excitations of the crystal lattice.

Over the 1960 to 1970 period the full weight of the information from inelastic neutron, Raman, Brillouin, and Rayleigh scattering, together with NMR, NQR, and EPR wherever appropriate, was brought to bear in verifying and extending the soft-mode description. Truly an era of “high” scientific endeavor during which ferroelectrics evolved in the

solid state physics community from crystallographers' toys to the pivotal prototypes for the description of displacive solid-solid phase transitions.

Subsequent problems associated with central peaks in the Raman and neutron scattering data and the escalating interest in critical phenomena and scaling indices, tempts one flippantly to term the era of the 70s that of "hardening of the modes." This would, however, be a gross injustice to what continues to be a primary tool for studying phase transitions. Rather, we believe that the decade of the 70s may turn out to be a key period of diversification in which the thinking which evolved with considerable refinement for simple proper ferroelectrics was applied to other mimetically twinned ferroic crystals, and the concept of dynamical mode instabilities, which have proved so fruitful in understanding the onset of the static displacement systems in ferroelectric domain structures, were applied to an ever-widening spectrum of solid state phase transitions.

During the age of diversification, a number of interesting practical developments took place as well. Investigations of doped BaTiO_3 led to the discovery of a remarkable change in resistance at the Curie point. PTCR thermistors are now used widely as self-regulating heating devices.

At present we are in the midst of the age of integration, in which many electroceramic components are being incorporated into thick-film circuits, thin-film circuits, or multilayer packages. Capacitors, transducers, and electrooptic switches made from ferroelectric ceramics and crystals are among these circuit elements. Looking ahead, it seems obvious that further miniaturization will take place. Many of the techniques developed for semiconductor crystals will be applied to ferroelectrics.

Clearly, in a short paper of this type it is not at all possible to do justice to the many scientists and engineers who contributed to the development of ferroelectrics. Only major highlights can be touched on and, in drawing out these highlights, personal bias is hard to avoid. However, for the basic science, the published record is generally available and the credit already properly apportioned.

The second goal in this presentation is to predict the future of ferroelectric ceramics, and to unravel an evolving technology of this type; an even more difficult task. But, as Lincoln once said, "The world will little note nor long remember what we said here."

The Early Rochelle Salt Period

Some of the more important people and events in this earliest period, which formed the basis for all later ferroelectric activities, are summarized in Table II. The object of this period of study was first separated in 1655 by Elie Seignette, an apothecary in the town of La Rochelle, France. Sodium potassium tartrate tetrahydrate (Rochelle Salt) was used for over 200 years for its mild purgative medicinal properties. Late in the nineteenth century its physical properties began to excite interest. In 1824 Brewster¹ had observed the phenomenon of pyroelectricity in various crystals, among which was Rochelle Salt, but perhaps the first systematic studies were those of the brothers Pierre and Paul-Jacques Curie² in 1880. This classic work established unequivocally the existence of the piezoelectric effect and correctly identified Rochelle Salt and a number of other crystals as being piezoelectric.

Table II. Early Rochelle Salt Period $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$

1655	Elie Seignette	La Rochelle First recorded synthesis of Rochelle Salt
1880	P. Curie, J. Curie	Piezoelectric properties
1894	F. Pockels	Dielectric anomalies Kerr E.O. effect
1917	J. A. Anderson, A. M. Nicolson, W. G. Cady	Piezoelectric effects practical applications
1921 to 1924	J. Valasek W. F. G. Swann	Analogy to magnetism Origin of ferroelectricity
1930	C. B. Sawyer	Rochelle Salt bimorphs "benders" and "twisters"
1937	H. Jaffe	Symmetry change at T_c
1940	H. Mueller	First complete phenomenological theory

It appears that one of the first studies to identify the anomalous dielectric response in Rochelle Salt was by Pockels.³ Such studies were later to become one of the major diagnostic techniques for finding new ferroelectrics. Unfortunately, some incorrect work by an equally eminent German colleague led Pockels to doubt his original measurements and he did not proceed with the work. Pockels did, however, go on to establish the large quadratic electrooptic Kerr effect in Rochelle Salt.⁴

One of the earliest U.S. involvements with Rochelle Salt appears to have occurred as a response to the urgent demands of submarine warfare in World War I. Sidney Lang,⁵ in his dialogue with Walter G. Cady, drew out the importance of a historic meeting in 1917 with French scientists, which became a turning point in Cady's career, leading to the establishment of one of the most important programs on piezoelectricity in this country. Perhaps more than anyone, Walter Cady deserves credit for melding science and technology in the unique way which led to the development of the piezoelectrically stabilized resonator. His massive contribution to the science of piezoelectricity is admirably summarized in his book *Piezoelectricity*, first published in 1946, and still a classic in the field.

Cady's career is a direct negation of the hypothesis by the young and arrogant that a scientist's productive life is over by age thirty. He did not begin work on piezoelectrics until late in his forties and was still a lively experimenter into his 90th year. It was a real sorrow for both piezoelectric and ferroelectric communities that on December 9, 1974, Walter Cady died only one day short of his 100th birthday, and of the many tributes which were being formulated to mark that auspicious occasion. Early

observations on Rochelle Salt by Cady and coworkers included measurements of elastic properties, dielectric constant, piezoelectric effects (including the first observation of the Curie point at 23°C), and the anomalously high d_{14} value in this crystal.

Unfortunately, it is difficult to estimate the full extent of Cady's early work on Rochelle Salt, since much of it was conducted under a U.S. Navy contract for sonar applications and was consequently classified and remained unpublished. Certainly, however, the work must have been rather well known to the small inner circle of workers in this field, and was no doubt most helpful in forwarding understanding of this material.

Another major U.S. contributor to the early Rochelle Salt period was Joseph Valasek. Born in this country, of Czech parents. Valasek studied at the University of Wisconsin from 1921 to 1924. Following a suggestion from his supervisor, W. F. G. Swann, he began a systematic study of the analogy between the magnetic properties of ferromagnetics and the dielectric properties of Rochelle Salt.⁶⁻⁹ These studies were to lead later to the firm establishment of the term *ferroelectricity* to describe this set of phenomena. His ballistic galvanometer studies of the charge and discharge of carefully prepared X-cut Rochelle Salt crystals clearly demonstrated for the first time the hysteretic nature of the polarization and its marked dependence on temperature. Dielectric constant measurements for fields along the X axis established the Curie-Weiss form for the permittivity, and the occurrence of two Curie temperatures.

Of very significant practical importance for the whole subject was the origination by C. B. Sawyer¹⁰ of the bimorph configuration for nonresonant transducer applications of Rochelle Salt. With the entrepreneurial skill of Sawyer, and the engineering expertise of Williams, the Rochelle Salt bimorph "benders and twistors" were to evolve into one of the most profitable product lines for the Brush Development Company. By the late 1940s, almost every inexpensive phonograph had a Rochelle Salt bimorph pickup head.

Perhaps an appropriate culmination for the Rochelle Salt period came with a series of four papers by H. Mueller¹¹⁻¹⁴ of M.I.T. Appearing from 1935 to 1940, they effectively summarized the experimental information of the early period and clearly propounded the static phenomenology which became the basis for Devonshire's later treatment in barium titanate. Mueller for the first time distinguished the three possible origins for proper ferroelectricity in Rochelle Salt, namely the possibility of a dielectric-, an elastic-, or a piezoelectric-dominated instability and, from the experimental information, showed that the driving force in Rochelle Salt was a softening of the clamped dielectric stiffness χ_{11} .

In highlighting the Rochelle Salt era, we have of course emphasized the very important role of studies here in the United States during this formative period. One should also mention the superb work at the Physical-Technical Institute in Leningrad under the direction of Shulvas-Sorokina, and later I. Kurchatov and coworkers.¹⁵ This group was responsible for one of the first realistic microscopic theories for the origin of spontaneous polarization.

Before leaving the early Rochelle Salt work, it would perhaps be as well to review briefly some of the major difficulties which Rochelle Salt presented to these early studies.

First, Rochelle Salt is not stable against dehydration either in vacuum or in dry air. It is thus a difficult material to electrode for reliable electrical measurement. Second, over most of the early period, the crystal symmetry, based on morphological assessments, was incorrectly assigned. The occurrence of spontaneous polarization was a fearsome violation of the by-then sacred Neumann's principle, and it was not until Jaffe's¹⁶ suggestion of the necessary occurrence of phase change at T_c that this seeming conflict was resolved.

Third, we may recognize the very marked structural complexity. With 112 atoms unit cell, it was not until 1941 that Beevers and Hughes in England¹⁷ made the first X-ray structure analysis and it was not until 1954 that the detailed neutron diffraction data of Fraser et al.¹⁸ was finally able to pin down the troublesome water molecules.

Fourth, the strong ferroelastic bias in most small crystals made them almost always unipolar and even the larger samples were often spontaneously biased. It is interesting to note that the domain structure was on a scale entirely unexpected by the original investigators and, though it is quite obvious when the (100) surface is viewed in polarized light, it was not until considerably later, after the methods had been well established for the perovskites, that domain structures were observed optically in Rochelle Salt.

Last, we may note that Rochelle Salt remains one of the few ferroelectric crystals with such a limited ferroelectric range and two clear Curie points. It should therefore not be surprising that the first microscopic theory which even attempted an explanation of this limited range did not evolve until Mason's work in 1950.¹⁹

In view of these many special problems, one must conclude that the early workers were in many ways highly unlucky in being presented with Rochelle Salt as their only model material, and that under the circumstances their work was truly outstanding.

Intermediate KDP Age

The horizon for workers in ferroelectrics was significantly broadened in 1935 by Busch and Scherer's^{20,21} report of the occurrence of ferroelectricity in potassium dihydrogen phosphate and the isostructural dihydrogen arsenate. Here the crystal structure was significantly simpler, the symmetry of the paraelectric phase higher ($\bar{4}2m$), and the basis of the structural arrangement of phosphate or arsenate tetrahedra linked by hydrogen bonding at the corners had already been hypothesized from earlier structural studies by West.²² It is interesting to note that in the first dielectric studies²⁰ two Curie points were recorded (this was expected for ferroelectrics) but very quickly the lower "change" was shown to be a domain effect and the polarization P_s to persist down to very low temperatures.

Perhaps the major U.S. contribution to this short KDP period was the brilliant theoretical paper by Slater,²³ which traced the "trigger" for the onset of ferroelectricity to an ordering of the hydrogen bonds (which are almost orthogonal to the X axis) into an antipolar array. This theory was conceived long before the neutron studies of Bacon and Pease,²⁴ which completely confirmed the basic hypothesis.

It is perhaps interesting to note that, as in Rochelle Salt, the finer points of the kinetics of the changes at T_c remained puzzling for a long pe-

riod. In KDP, however, Raman and NMR spectra later revealed the fascinating interconnection between the proton ordering and the soft mode in the motion of the potassium and phosphate ions which is the dominant carrier of spontaneous polarization.

The most important applications of the KDP family, which occurred in this preperovskite era (Table III), were not strictly ferroelectric: The strong piezoelectric activity in the paraelectric phase of antiferroelectric ammonium dihydrogen phosphate proved extremely useful for higher power sonar transducers, another activity of the Brush Development Company.²⁵

Perovskite Era

Unfortunately, it is impossible to provide a detailed discussion of all the developments since the perovskite families appeared on the scene in the early 1940s. To justify to some extent the categorization used earlier, Tables IV, V, and VI catalog a few of the highlights of the three ten-year periods 1940 to 1950, 1950 to 1960, and 1960 to 1970.

The very important contributions to the field in this country in each of these periods may be noted. The pioneering work at National Lead Company by Wainer, Solomon, and their coworkers firmly established the ceramic perovskite dielectrics in the 1940s. The stimulating competition between Ray Pepinsky and his group at Penn State and Berndt Matthias and his coworkers at Bell Telephone did much to enlarge the number of known ferroelectric families in the 1950s. During the decade the number of ferroelectric families increased from three to twenty-five. The simultaneous but independent realization of the soft-modes description of ferroelectricity in the perovskite by Anderson in the United States and Cochran in the United Kingdom provided the avenue for coupling ferroelectric studies into the mainstream of solid state research and provided just the right framework with which to exploit the full power of the emerging new techniques of laser Raman spectroscopy and neutron inelastic scattering for the study of phonon spectra.

Much more could and should be said about the many important contributions to the exciting developments in ferroelectricity over these times, but the primary task here is to trace a few of the central ideas and applications. References have been inserted in the three tables for a number of the key papers.

Table III. Potassium Dihydrogen Phosphate Group KH_2PO_4

1930	J. West	Crystal structure
1935	G. Busch, P. Scherrer	First report of ferroelectricity
1941	J. C. Slater	Proton ordering theory
1953	G. E. Bacon, R. S. Pease	Neutron diffraction locating hydrogen
1944	B. Zwicker, P. Scherrer	Large longitudinal E.O. effect

Table IV. Perovskite Era (Early BaTiO₃ Period)

1940 to 1943	Wainer and Salomon (Ref. 26) Ogawa (Ref. 27) Wul and Goldman (Ref. 28)	Discovery of BaTiO ₃
1945	B. Gray (Ref. 29)	First operating poled BaTiO ₃ transducer
1945	A. von Hippel (Ref. 30)	Ferroelectricity in
1946	Ginsburg (Ref. 31)	BaTiO ₃
1946	H. Megaw (Ref. 32)	Crystal structure
1947	Matthias and Merz (Ref. 33)	Single crystals
1948	Matthias, von Hippel, Blattner, (Ref. 34) Kanzig, Merz, Sutter, (Ref. 35) Cross, Dennison, and Nicholson (Ref. 36)	Optical domain structure
1949	A. F. Devonshire (Ref. 37)	Phenomenology
1949	H. F. Kay, P. Vousden (Ref. 38)	Structure changes
1952	W. Merz (Refs. 39–41)	Single crystal
1954		Switching studies
1953	Fraser, Danner, Pepinsky (Ref. 42)	Neutron diffraction study of BaTiO ₃

Evolution of the Ceramic Piezoelectric Transducer

BaTiO₃-Based Transducers

Before discussing the evolution of the technology of piezoelectric ceramics, it is important to reiterate the difficulty of establishing clearly the priorities, and to apologize if someone who had a key but largely “concealed” role because of the proprietary nature of commercial development has been inadvertently omitted from consideration.

The difficulty is perhaps rather well illustrated by the considerable legal effort which was required to establish the true patent position in this field. The authors are indeed greatly indebted to Nello Coda, Chief of Engineering of Erie Technological Products, for making available the transcripts of those original proceedings, which now make fascinating reading.

On the basis of this evidence, it appears clear that R. B. Gray⁹⁵ of Erie should be credited with having the first working piezoelectric ce-

Table V. Period of Proliferation

1949 to 1960	20 Perovskite compounds	WO ₃ to Pb ₃ MgNb ₂ O ₉	Matthias (Refs. 43–45) Smolenskii (Refs. 46–48)
1949	LiNbO ₃ family		Matthias (Ref. 49)
1951	LiTiC ₄ H ₄ O ₆ ·H ₂ O		Matthias (Ref. 50)
1952	Cd ₂ Nb ₂ O ₇ pyrochlore family		Cook, Jaffe (Ref. 51)
1953	PbNb ₂ O ₆ tungsten bronze		Goodman (Ref. 52)
1955	G.A.S.H. family		Holden (Ref. 53)
1956	Sn(NH ₂) ₂ thiourea		Soloman (Ref. 54)
1956	TGS family		Matthias (Ref. 55)
1956	(NH ₄) ₂ SO ₄ family		Matthias (Ref. 56)
1956	Colemanite		Goldsmith (Ref. 57)
1956	(NH ₄) ₂ Cd ₂ (SO ₄) ₃ family		Jona, Pepinsky (Ref. 58)
1957	Alums		Jona (Ref. 59)
1957	Dicalcium strontium propionate		Matthias (Ref. 60)
1957	Boracite family		Le Corre (Ref. 61)
1958	(NH ₄)HSO ₄		Pepinsky (Ref. 62)
1958	NaNO ₂ family		Sawada (Ref. 63)
1958	KNO ₃		Sawada (Ref. 64)
1959	LiH ₃ (SeO ₃) ₂ family		Pepinsky (Ref. 65)
1959	(NH ₄)NaSO ₄		Pepinsky (Ref. 66)
1960	N(CH ₃) ₄ ·HgCl ₃ family		Fatuzzo, Merz (Ref. 67)
1960	K ₄ Fe(CN) ₆ ·3H ₂ O family		Waku (Ref. 68)
1962	SbSI family		Fatuzzo (Ref. 69)
1963	YMnO ₃ family		Bertaut (Ref. 70)

ramic transducer (about 1945) and that it was he who had the first clear understanding of the importance of electrical poling in establishing a remnant polar domain configuration in the ceramic and consequent strong piezo response. It is also clear, however, from the hard-fought legal case that many other scientists and engineers, both in the United States and abroad, were poised on the brink of, or had actually realized but not effectively reported, somewhat similar findings. The dates associated with some of these early studies are summarized in Table VII.

It is perhaps difficult now to realize the absolutely revolutionary thinking which was required at that time to accept even the possibility of piezoelectric response in a randomly axed polycrystal, and it is perhaps

Table VI. The Age of "High" Science

1959	W. Cochran (Refs. 71,72)	The soft mode
1960	L. Anderson (Ref. 73)	Description of BaTiO ₃
1962	R. Cowley (Ref. 74)	Confirmation in SrTiO ₃ by inelastic neutron scattering
1962	Barker, Tinkham, (Ref. 75) Spitzer, Miller, Kleinman, Howarth (Ref. 76)	Confirmation in BaTiO ₃ , SrTiO ₃ by ir reflectance
1963	R. C. Miller (Ref. 77) Miller, Kleinman, Savage (Ref. 78)	Optical SHG KDP, BaTiO ₃
1967	Kaminow, Damon (Ref. 79)	Raman spectra in KDP
1967	Fleury, Worlock (Ref. 80)	Raman spectra in SrTiO ₃ , KTaO ₃
1967	Johnston, Kaminow (Ref. 81)	Raman spectra in LiNbO ₃ , LiTaO ₃
1968	Fleury (Ref. 82)	Soft modes and 106 K transition in SrTiO ₃
1968	Cross, Fouskova, Cummins (Ref. 83)	"Peculiar" ferroelectricity in Gd ₂ (MoO ₄) ₃
1967 to 1969	Aizu (Refs. 84–86) Shuvalov (Ref. 87)	Complete symmetry classification of all ferroelectrics
1970	Pytte (Ref. 88) Sanikov (Ref. 89) Aizu (Refs. 90–91)	Improper ferroelectricity in Gd ₂ (MoO ₄) ₃
1970	Shirane (Ref. 92)	Inelastic neutron PbTiO ₃
1971	Nunes (Ref. 93)	Studies of soft KNbO ₃
1971	Harada (Ref. 94)	Modes in BaTiO ₃

not surprising that for some time controversy raged as to whether the effect was electrostrictive⁹⁶ or piezoelectric.^{97,98}

From our present perspective, one can see that there was much merit to both points of view, and that really the phenomena are adequately described either as spontaneous polarization-biased electrostriction of the prototypic phase, or true piezoelectricity of the ferroelectric phase. It was not, however, until the very clear demonstration of pure piezoelectricity in untwinned barium titanate single crystals by Caspari and Merz⁹⁹ that the controversy was effectively resolved.

In the earliest studies the ceramics used were largely BaTiO₃, processed so as to maintain a rather coarse grain size. Poling was usually

Table VII. Evolution of BaTiO₃-Based Transducers

1945	R. B. Gray	First "working" transducer
1946	Rushman, Strivens	Piezoelectricity in (Pb _x Ba _{1-x})TiO ₃
1947	S. Roberts	Dielectric and piezoelectric properties of barium titanate
1947	W. L. Cherry, R. Adler	Piezoelectric effect in polycrystalline BaTiO ₃
1948	W. P. Mason	Electrostrictive effect in BaTiO ₃ ceramics
1949	A. V. Rzhanov	Piezoelectric effect in barium titanate
1950	Caspari, Merz	Demonstration of "pure" piezoelectricity in single-crystal BaTiO ₃
1952	Berlincourt, Kulcsar	BaTiO ₃ + CaTiO ₃
1954	W. P. Mason	BaTiO ₃ + PbTiO ₃ + CaTiO ₃

carried out by cooling electroded samples through the Curie temperature at 120°C under a substantial biasing potential, the optimum conditions for individual formulation being established by trial-and-error methods.¹⁰⁰

By the early 1950s, ceramic piezoelectric transducers based on BaTiO₃ were becoming well established in a number of both civil and military applications. There was a real need to improve the stability against depoling which accompanied traversing the 0°C phase transition in pure BaTiO₃ and the stability against depoling associated with the low coercivity of the pure titanate ceramics. A number of composition manipulations have been tried to alleviate these problems, and two of the more successful^{101,102} still in use are listed in Table VIII.

Evolution of the Lead Zirconate-Lead Titanate and Other Piezoelectric Ceramic Systems

It was rather natural in the early 1950s, following the wide success of the simple BaTiO₃-based ceramic transducer, that people should examine other ferroelectric perovskite compounds for potential applicability. Some of the very early basic work on pure PbTiO₃ and on the PbTiO₃:PbZrO₃ solid solution system, which established the useful high Curie temperature of lead zirconate and the outline of the phase diagram for this system, was carried out in Japan by Shirane and Takeda,¹⁰³ Shirane et al.,¹⁰⁴ and Sawaguchi.¹⁰⁵ The development of PZT transducers is traced in Table VIII.

The key studies, however, which established the PZT system as exceptionally suitable for the formulation of piezoelectrics in this composition system were carried through by Jaffe and coworkers^{106,107} at the National Bureau of Standards. These studies clearly discerned the im-

Table VIII. Evolution of Piezoelectric Ceramic Transducers

1950	G. Shirane, S. Hoshino, K. Suzuki	PbTiO ₃
1952	G. Shirane, K. Suzuki	Pb(Zr,Ti)O ₃ solid solutions
1953	E. Sawaguchi	AF and F in Pb(Zr,Ti)O ₃
1954	B. Jaffe, R. S. Roth, S. Marzullo	Morphotropic boundary
1955 on	H. Jaffe, B. Jaffe, W. R. Cook, Jr., D. Berlincourt, R. R. Gerson	Evolution of modified PZT formulations
1952	G. Goodman	PbNb ₂ O ₆
1959	L. Egerton, D. M. Dillon	(Na _{0.5} K _{0.5})NbO ₃
1971	H. Jaffe, W. R. Cook, Jr., B. Jaffe	Piezoelectric ceramics

portance of the composition-dependent rhombohedral-tetragonal ferroelectric-ferroelectric phase change near the 52:48 mole fraction composition and initiated a whole new emphasis in piezoceramic research. There was at that time clear realization of the value of proximity to a phase change in facilitating poling.¹⁰⁸ However it was Jaffe's recognition that the temperature-independent morphotropic boundary in PZT allowed one to stay close to the phase change over the whole temperature course of the poling process which was of vital importance.

The earliest measurements show a clear maximum in response for PZT compositions near the morphotropic boundary, and more recent studies have amply confirmed its importance for poling.^{109,110} Over the next ten years, the major developmental emphasis was with the lead zirconate-lead titanate solid solution ceramics, and the major center for this activity was certainly the Clevite Company (a development from the old Brush group). Studies associated with the names of H. Jaffe, B. Jaffe, W. R. Cook, Jr., D. Berlincourt, R. R. Gerson, F. Kulscar, and H. A. Kreuger in that group were at the heart of the development. An excellent account of much of this work has been given in the book *Piezoelectric Ceramics*.¹¹¹ This text is essential reading for any serious student of ceramic piezoelectrics.

One interesting facet of the system PbTiO₃:PbZrO₃ is that the high vapor pressure of PbO at the forming temperature, which was originally believed to be a curse in dealing with these ceramics, has in later studies turned out to be a major blessing. The "fugitive" nature of the PbO provides a measure of autocompensation in the semiconductor properties, and high-resistivity samples can be made with a much wider range of aliovalent dopant ions than would ever be possible in the BaTiO₃ family.

It is just this "docility" and flexibility for chemical manipulation to modify the ferroelectric properties which was so effectively exploited at first by the Clevite group, and later by all other transducer manufacturers to tailor the original advantageous properties for specific application

areas. The basis for many of the modifier ion schemes was provided by Jaffe.¹¹²

Studies by Smolenskii and Agronovskaya¹¹³ in the 1950s provided a large family of lead-containing perovskite compounds of complex composition. It was perhaps natural that a number of these $\text{Pb}(X_\alpha Y_{1-\alpha})\text{O}_3$ materials should be tried as third components to modify the system $\text{PbTiO}_3\text{:PbZrO}_3$. Much recent work in Japan has been concerned with the exploration of such systems. Although some of these new bodies do show practical advantages in specific devices, in general the properties are not markedly different from those of PZT.

Undoubtedly, the PZT family is the most important and versatile composition base for ceramic piezoelectric elements, but two other developments in the materials field are also of major interest. In 1952, studies by Goodman¹¹⁴ at Globe Union uncovered the interesting and strong ferroelectric properties in the "Goodmanite" phase of PbNb_2O_6 . Studies by Goodman and by Lewis and coworkers¹¹⁵⁻¹¹⁷ at General Electric in Great Britain showed that ceramic lead metaniobate could be poled to a strongly piezoelectric state, and that in the system $\text{PbNb}_2\text{O}_6\text{:BaNb}_2\text{O}_6$ a morphotropic boundary did occur. Unfortunately, the metaniobate is a tough ceramic to process, and though it has been the subject of considerable research because of its high hydrostatic sensitivity and low mechanical Q , it has found only specialized application.

A later development was the demonstration by Egerton and Dillon at Bell Laboratories of a morphotropic boundary in the $\text{NaNbO}_3\text{:KNbO}_3$ solid solution system and piezoelectrics with compositions near the $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ boundary are still hot-pressed by Bausch and Lomb for specialized applications.

Summary

Ferroelectric ceramics are used in multilayer capacitors, PTC thermistors, piezoelectric transducers, and electrooptic devices. Along with packaging materials and magnetic ferrites, they account for a major portion of the electroceramics market.

The early history of ferroelectrics can be traced to pioneering studies on Rochelle Salt and potassium dihydrogen phosphate, two water-soluble crystals. But the major impetus in ferroelectric ceramics came near the end of World War II, when BaTiO_3 and other perovskite-family oxides were discovered.

The number of applications expanded steadily during the next three decades and is now entering an age of integration and miniaturization in which three-dimensional ceramic circuitry is being developed. Multilayer structures on a submillimeter scale incorporate resistors, capacitors, dielectrics, metal interconnects, and piezoelectric transducers. Further advances will undoubtedly occur in the years ahead as the field of electroceramics follows in the footsteps of the semiconductor industry.

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