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# Memories of The Early Days of $\text{BaTiO}_3$

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In this chapter, we trace some of the early history of ferroelectric ceramics in the Western world and present first-hand accounts of this period written by Helen Megaw, William Cook, Jr., Nello Coda, and Wilhelm Buessem. These four pioneers were involved with different aspects of the discovery of perovskite ferroelectrics in the United States and Western Europe.

## Introduction

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, we can identify pre-perovskite and post-perovskite periods of activity (Table I).

Certainly, one of the major "turning points" in ferroelectricity came in the very early 1940s with the discovery of the unusual dielectric properties of a number of simple mixed oxides which crystallize with the perovskite structure. In the "pre-perovskite 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 a rapidly deepening fundamental understanding.

**Table I.** Important Periods in the Evolution of Freeelectricity

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-K 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, dipoles and thin films

**Table II.** Pioneering Studies of Barium Titanate

1940	Wainer and Salomon (Ref. 1)	Discovery of BaTiO <sub>3</sub>
	to Ogawa (Ref. 2)	
1943	Wul and Goldman (Ref. 3)	
1945	B. Gray (Ref. 4)	First operating poled BaTiO <sub>3</sub> transducer
1945	A. von Hippel (Ref. 5)	Ferroelectricity in BaTiO <sub>3</sub>
1946	Ginsburg (Ref. 6)	
1946	H. Megaw (Ref. 7)	Crystal structure
1947	Matthias and Merz	Single crystals
1948	Matthias, von Hippel Blattner, (Ref. 9) Kanzig, Merz, Sutter, (Ref. 10) Cross, Dennison, and Nicholson (Ref. 11)	Optical domain structure
1949	A.F. Devonshire (Ref. 12)	Phenomenology
1949	H.F. Kay, P. Vousden (Ref. 13)	Structure changes
1952	Merz (Refs. 14-16)	Single crystal
1954		Switching studies
1953	Fraser, Danner, Pepinsky (Ref. 17)	Neutron diffraction study of BaTiO <sub>3</sub>

## Perovskite Era

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 ceramic perovskite dielectrics in the 1940 s. 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 1950 s. 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 relevant to the early development of capacitors and transducers. References to some of the important scientific studies are given in Table II.

## Evolution of Multilayer Capacitors

Harold Stetson recently traced the early history of multilayer ceramic technology in the United States.<sup>18</sup> During World War II, the Army Signal Corps contracted Remington Arms Company and the duPont Company to find replacements for capacitor-grade mica, which was in short supply. A process was developed in which layers of vitreous enamel were deposited by spraying. These layers of dielectric enamel were alternated with silver paste electrodes deposited by silk-screen printing. The process was made public in 1947 by C. I. Bradford and B. L. Weller of Remington Arms and S. A. McNeight of duPont.<sup>19</sup> Brad Weller later formed Vitramon and exploited the technology with great success. The Signal Corps equipment was later transferred to Sprague Electric Company in North Adams, Massachusetts. Sprague went on to develop formulations based on BaTiO<sub>3</sub> and metallizations other than silver.<sup>20</sup> Another important wartime development took place at the M.I.T. Laboratory for Insulation Research. Howatt, Breckenridge and Brownlow described this work in

1947.<sup>21</sup> The purpose of the work project was to devise a way of fabricating thin sheets of titanate ceramics in multilayer form. Howatt and his colleagues invented the doctor-blade method of forming thin ceramic layers from fluid slips using a scraping blade over a substrate. After drying, the thin sheets were electroded, stacked and fired. Glen Howatt recognized the commercial value of this process, and went on to found the Glenco Corporation.

## Evolution of the Ceramic Piezoelectric Transducer

### BaTiO<sub>3</sub>-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 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. Gray<sup>22</sup> of Erie should be credited with having the first working piezoelectric ceramic 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 III.

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 not surprising that for some time controversy raged as to whether the effect was electrostrictive<sup>23</sup> or piezoelectric.<sup>24,25</sup>

**Table III.** Evolution of BaTiO<sub>3</sub>-Based Transducers

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

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 Merz<sup>26</sup> that the controversy was effectively resolved.

In the earliest studies the ceramics used were largely BaTiO<sub>3</sub>, processed so as to maintain a rather coarse grain size. Poling was usually 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.<sup>27</sup>

By the early 1950s, ceramic piezoelectric transducers based on BaTiO<sub>3</sub> 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 BaTiO<sub>3</sub> 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<sup>28,29</sup> still in use are listed in Table IV.

### Lead Zirconate : Lead Titanate Ceramics

It was rather natural in the early 1950s, following the wide success of the simple  $\text{BaTiO}_3$ -based ceramic transducer, that people should examine other ferroelectric perovskite compounds for potential applicability. Some of the very early basic work on pure  $\text{PbTiO}_3$  and on the  $\text{PbTiO}_3 : \text{PbZrO}_3$  solid solution system, which established the useful high Curie temperature of lead titanate and the outline of the phase diagram for this system, was carried out in Japan by Shirane and Takeda,<sup>30</sup> Shirane et al.,<sup>31</sup> and Sawaguchi.<sup>32</sup> The development of PZT transducers is traced in Table IV.

**Table IV.** Evolution of Piezoelectric Ceramic Transducers

1950	G. Shirane, S. Hoshino, K. Suzuki	$\text{PbTiO}_3$
1952	G. Shirane, K. Suzuki	$\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ solid solutions
1952	G. Goodman	$\text{PbNb}_2\text{O}_6$
1953	Sawaguchi	AF and F in $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$
1954	B. Jaffe, R.S. Roth, S. Marzullo	Morphotropic boundary
1955	H. Jaffe, B. Jaffe, W.R. Cook, Jr., D. Berlincourt, R.R. Gerson	Evolution of modified PZT formulations
1959	L. Egerton, D.M. Dillon	$(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$
1971	H. Jaffe, W.R. Cook, Jr., B. Jaffe	Piezoelectric Ceramics

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 (refs. 33, 34) at the National Bureau of standards. These studies clearly discerned the importance 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.<sup>35</sup> 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.<sup>36,37</sup> 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 (an offshoot 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 the work has been given in the book *Piezoelectric Ceramics*.<sup>38</sup> This text is essential reading for any serious student of ceramic piezoelectrics.

One interesting fact of the system  $\text{PbTiO}_3 : \text{PbZrO}_3$  is that the high vapor pressure of  $\text{PbO}$  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  $\text{PbO}$  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  $\text{BaTiO}_3$  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.<sup>39</sup>

### Appendix

To conclude this chapter, we append reminiscences written by four of the pioneers of perovskite ferroelectrics.

**Dr. Helen Megaw** was a Fellow of Girton College and Associate Director of Crystallographic Research at the Cavendish Laboratory, Cambridge University. In her article, she recounts the early crystallographic studies of  $\text{BaTiO}_3$  in Great Britain. Many of these events took place during the hectic days of World War II when barium titanate was discovered.

**Dr. Wilhelm Buessem** was in charge of dielectrics research at Siemens Laboratory in Germany during this period. After the war, he emigrated to the United States and became a Professor of Electroceramics at Penn State. He also served as a longtime consultant to Sprague Electric, a major manufacturer of multilayer ceramic capacitors.

**Mr. Nello Coda** was chief engineer at Erie Technological Products (now Murata-Erie) for almost fifty years. He participated in the development of BaTiO<sub>3</sub> capacitors and piezoelectric ceramic transducers, and is now living in retirement in Erie, Pennsylvania.

**Dr. William Cook, Jr.** is co-author the widely read book *Piezoelectric Ceramics* which summarizes much of the technology and materials development of electromechanical transducers. His co-authors, Hans Jaffe and Bernard Jaffe are now deceased, but Dr. Cook describes their contributions to optimization of PZT transducers.

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## Early Work on Ferroelectricity in Great Britain

Helen D. Megaw

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In September 1936, I had completed 2 years of post-doctoral work. As no university posts seemed to be available, I thought it was time I turned to my second choice for a career, which was school-teaching. (I was not attracted by the idea of industrial research.) So I took a teaching post in September 1939. In September 1939, at the outbreak of the war, I had just moved to another school post in Bradford (much further north), which had been evacuated. There was a Central Scientific Register which was supposed to assign scientists where they would be most useful. I registered, but said I thought I was needed where I was, at least until the evacuation had settled down. Nothing happened; I did stay where I was, very happily, and I never heard again from them.

Early in 1943 or sometime then, there were notices in the papers that scientists were wanted. So I consulted an adviser I could trust, to ask would this apply to me—he said it would (it was all very hush-hush, but I could do what was wanted). So I sent in my notice to the school for July, and waited. But after some time my adviser told me that it was doubtful if I would be wanted then, that I would not be, because they had decided to recruit for the project in America. I therefore ought to look for other openings. Later, I was very thankful I had been wanted, when I realized (years afterwards) that it had been the atom bomb!

About April of 1943, I wrote again to the Scientific Central Register, who sent me notice of a vacancy for an x-ray crystallographer at Mitcham Works Ltd. I applied, had an interview, and in due course was appointed, and took up work about July or August of 1943. Mitcham Works Ltd. was somehow associated with Mullards' and either was or belonged to a small subsidiary company of Philips of Eindhoven. It had been Philips' policy not to allow any research to be done in their English laboratories. But when Holland was over-run, the

British government took them over, and tried to build them up into places of useful research. With this background, the staffing of the lab was rather curious. The head of the lab was a Mr. van Moll, of no obvious scientific standing. Under him were one or two quite good people, who gave me a friendly welcome, encouragement and support, but who had otherwise nothing to do with the ferroelectric story—their own lines of work were quite different. A high proportion of the staff consisted of young graduates, either B. Sc's or Ph.D's, who had taken very much shortened crash courses (war-time ones) in London University. They were lively and interested, but inexperienced.

Having appointed me, Mr. van Moll did not know what to do with me. They had no x-ray tube, nor was it possible to buy one. However, I had worked with a gas tube at Cambridge for my Ph.D., and plans were available, and it was decided to build one in the workshop. But mechanical facilities were scanty, and materials were difficult to obtain, and progress was slow.

About October of 1943, while waiting for an x-ray tube, I spent much time reading, trying to catch up on as much as possible of what I had missed from 1936 onwards, when I had been almost completely out of touch with the scientific world. I remember at this time first becoming aware of Bragg's first work on the AlNiCo alloys.

Early in 1944, I asked for and obtained an invitation on the Cavendish in Cambridge, the Crystallography Department being run for Bragg by Henry Lipson. I also obtained permission from Mitcham Works to go there. The idea was that I should work on some small problem of interest to Lipson, and in doing so, refresh my knowledge and bring it more up-to-date, learn more modern techniques and renew my contacts with the scientific world. All this succeeded very well. The problem (concerned with grain size and distortion in cold-worked metals) had no connection with any work I had done before, or was to do afterwards, but it fitted in well with what Lipson was engaged in, and was publishing as a short note.

In summer 1944, I went back to London, to Mitcham Works. I think the x-ray tube was ready to work, and there was a powder camera, but my recollection of the detailed sequence of events is not clear. All my notebooks were left with the lab when I moved on, and though I may have some odd lists of diaries or papers, I do not know where to find them. However, I was obviously getting to know my colleagues better, and it must have been sometime about now that the

critical conversation took place, as follows. (I do not report verbatim, but give the gist).

In early autumn 1944, one of my young colleagues, Dr. D. F. Rushman, said he had some material whose crystal structure he would like me to study. The story is this. Some condensers of very high capacity were sent to this country from America. The government allocated them, and the relevant information, to a number of specific laboratories and individuals, to be kept secret and we were *not* among them! However, I got hold of some, pulled them to pieces, and found this material. It is barium titanate,  $\text{BaTiO}_3$ . It has an extremely high dielectric constant.

Either then or in a second conversation, he said, "The dielectric constant depends on temperature and has peaks." He showed me his plots of  $E$  vs.  $T$  which showed the peaks—I think two of them, or perhaps all three. He said he thought they were transitions—and I remember being very surprised that a material with a melting point of about  $1400^\circ\text{C}$  could possibly have a phase change near  $120^\circ\text{C}$ .

There was no mention then of the word "ferroelectric". I do not know if I even know of it. That came much later.

I went ahead and did the structure. It came out absolutely straightforwardly from a powder photograph, but I cannot remember whether the photograph was taken at Mitcham, or on a later visit to Cambridge.

Autumn 1944. I soon accepted that the  $120^\circ\text{C}$  peak must mean a phase change, but to test it I needed another visit to Cambridge, where there was a very suitable high temperature camera. I can still remember my thrill of pleasure in the dark room when I looked at the photo and saw that the lines were those of a simple cubic material!

I wanted to publish, but Mr. van Moll would not allow it. (I sometimes wonder whether the Phillips Organization had a lingering memory of the way they had made patents for some very profitable magnetic materials from work published by Bragg! I went on with powder work on other perovskites, and also with some studies at other temperatures, back-reflection powder photos on flat plates, taken with a rather primitive set-up at Mitcham. I continued without success to press for publication.

Either in late 1944 or very early 1945, I was again at Cambridge, and there was some kind of conference. Bragg was there, and in conversation I told him something of my work. He was horrified to learn

that work done at Cavendish was to be treated as secret—this was entirely against his principles, and he would not have given permission for it. He told me that the research on the material had been officially allocated to Willis Jackson (who I did not know except by name). Of course I did not want to keep it secret, and found Bragg's comment a useful argument when I renewed pressure—whether Bragg also put on pressure directly I don't know—but permission was granted, provided I only wrote about the structure and said nothing of the electrical properties. The restriction didn't worry me—they weren't my business.

My letter on the structure of  $\text{BaTiO}_3$  at room temperature, mentioning the transition to cubic, was written, and sent to Nature on February 24, 1945. It was published on April 21, 1945, side by side with a letter from Rooksby of G.E. Co., also reporting a determination of the structure, but undated. I was never told by anyone, nor did ask, how this came about, but I guessed that what happened was as follows:

When my letter reached the Editor of Nature, or his referee, he realized that the same work had been done independently by Rooksby, but he had been forbidden to publish by secrecy requirements. They then got to work, lifted the ban, and encouraged Rooksby to write it up, but decided that since the two pieces of work were independent, simultaneous publication was fair (only they couldn't put a date on Rooksby's).

I was *very happy with the solution*. I liked and respected Rooksby, and would not like to have seen him done out of credit that was his due; nor would I have liked to have been deprived of any credit due to me for priority.

From this time onward, ideas of "ferroelectricity" were coming out into the open, in connection not only with perovskites, but with KDP and Roshelle salt. I think my own contributions over the next few years are best summarised by noting my papers:

1945 "Crystal Structure of Barium Titanate" (*Nature*, **155**, 484)

1946 "Changes in polycrystalline Barium-Strontium Titanate at its Transition Temperature" (*Nature*, **157**, 20)

1946 "Crystal Structure of Doble Oxides of the Perovskite Type" (*Proc. Phys. Soc.* **58**, 133-152)

1946 "Crystal Structure of Barium Titanium Oxide and Other Double Oxides of the Perovskite Type" (*Trans. Faraday Soc.* **42A**, 224-231)

1946 "Crystal Structure of Barium Titanium Oxide at Different Temperatures" (*Experientia*, **2**, 183-184)

1947 "Temperature Changes in the Crystal Structure of Barium Titanium Oxide" (*Proc. Roy. Soc. A*, **189**, 261-283)

In August or September of 1945, I left Mitcham Works for a post at Birkbeck under Bernal. My experimental work there was quite different. I began to study some clay minerals. After I had recorded the work on perovskites, my notebooks were returned to Mitcham, and for the next few years I was thinking and discussing as shown in my papers.

My experimental demonstration of a below-room temperature transition in  $\text{BaTiO}_3$  or  $(\text{Ba},\text{Sr})\text{TiO}_3$  is recorded in the 1947 paper. My methods were very string-and-sealing ways. I have a very clear recollection of inspecting the photographs at Mitcham Works and making the deduction, but I did not remember that I had at first thought the transition took it back to cubic. I was obviously well aware of the twinning effects. I think now on looking at the photos that one can distinguish the complex of lines due to the orthorhombic and rhombohedral phases at  $-78^\circ\text{C}$  and  $-183^\circ\text{C}$  respectively, but I do not know at all whether I had read or heard anything on the subject except what I mentioned earlier. I was at this time, more interested in explaining the cause of the transitions, than the detail of their twinning, which seemed to me a quite obvious consequences of the geometry—there was a lot of good work about that in  $\text{KH}_2\text{PO}_4$ , by Ubbelohde and Woodward, which I read.

I think it may be relevant to give some of my background and general approach, which influenced me, not only in 1945-46, but has continued to do so all my working life.

During my time in Cambridge, I was deeply imbued with the ideas of Bragg's "Atomic Structure of Minerals" as communicated and partly supplemented by Bernal (also Vol. 1 and 2 of the *Stukturberichte*). This reinforced a natural tendency to visualize. A crystal structure



was to me an array of atoms with size, specific interatomic distances and angles. It could be thought of as a model, with spokes for the interatomic distances, representing forces—something that could be built, except for the difficulty of continuing the pattern to infinity.

I did not need to theorize about the forces, except where they were simple electrostatic, but considered they should be assessed empirically from their repeated occurrence in different building blocks in all sorts of different structures. Again, neither the bond lengths nor the bond angles were to be regarded as rigid, but given some elasticity, to be assessed empirically in their different contexts. This was a wholly static picture, but I considered it valuable as a first approximation; the effects of thermal vibrations could be added as a later approximation when desirable.

The other big influence was Bernal's work on water and the hydrogen bond—his first paper, jointly with R. H. Fowler, and the second written up in a paper in which I was joint author, "The Function of Hydrogen in Intermolecular Forces", *Proc. Roy. Soc. A.* **151**, 384-420 (1935). I should explain about this paper. All the ideas were Bernal's. My contribution—apart from my share in the writing, was in finding examples of structures to illustrate his ideas, and in describing them. For structures where the positions of all atoms other than hydrogen had not been directly determined with reasonable accuracy, I made some rather wild guesses, which could not be substantiated or accepted later. But where all the O atom positions and interatomic distances were known, the approach proved very fruitful. Notably for  $\text{Al}(\text{OH})_3$  (hydrargillite) whose structure I myself had determined, I was able to predict the positions of the H atoms, which were confirmed years later, when it became possible to detect H's directly by diffraction methods.

I therefore, had very clear ideas, derived from Bernal, about hydrogen bonds and hydroxyl bonds which were not the conventional ones of the time. These were consistent and easily combined with my assumptions about the structures of oxides and other inorganic structures, where the forces leading to cohesion were ionic or partly homopolar.

A structure was stable if the placing of its atoms (including symmetry conditions) allowed the bond lengths, bond angles, and non-bonding contact distances of them all to be fitted together without greatly straining any. If this was not possible, the structure was

modified by small displacement of atoms—one could not be displaced individually, without effecting its neighbors, and their neighbors, and hence the whole continuous framework. If this destroyed some of the symmetry, it was geometrically obvious that a second permissible structure of equal energy existed related to the first by operation of the symmetry element which had been lost.

In 1945, when I determined the structure of  $\text{BaTiO}_3$ , I knew that Ti might be displaced from what was in ideal perovskite a center of symmetry, but the displacement (if any) was too small to be measured by any means at my disposal. It was only made possible by the reduction of symmetry from cubic to tetragonal, for which there was no explanation yet. However, as it did seem to be linked with the question of atomic radius, I tried studying other perovskites with different atoms, but was restricted to powder methods which meant I could not get much if at all beyond lattice dimensions and crystal system (whether cubic, tetragonal, orthorhombic, or possibly rhombohedral).

In September of 1945 (as I said above), I moved from Mitcham Works to Birkbeck. I had to break off all my experimental work on perovskites, though I still had some writing up to do. My work in Birkbeck was to be concerned with hydrated calcium silicates, but I did widen my reading, though how and when I became aware of "ferroelectrics" as such—perhaps not till much later—or of the other materials such as  $\text{KH}_2\text{PO}_4$  and Rochelle salt.

Certainly I was aware of the work of Ubbelohde and Woodward on  $\text{KH}_2\text{PO}_4$ . They were very much concerned with the twins observed at the transition (e.g. *Nature* **156** 20 (1945)) which they called "hybrids". To me however, it was obvious that if you had pseudosymmetric structures, differing very slightly from the "aristotype" (though I had not yet introduced that word), then one could easily be converted to another by various environmental factors, e.g. temperature, local stresses or electric fields, and one would expect an original single crystal to be a mosaic of "domains", whose choice of orientation and or actual structure, would be determined by, possibly, the clamping stresses of its neighbors or temperature gradients at particular points. The variants were so alike that they fitted together with only small stresses to give a "mosaic crystal".

Detailed studies could be very helpful towards clarifying what the possible structures were on either side of the transition. But they neither explained the reason for the occurrence of pseudosymmetric

structures nor their physical properties. The same applied to all the studies of twinning in  $\text{BaTiO}_3$ , which soon became current. Physical properties of twins were all averages which needed further analysis.

About this time too, perhaps in 1946, I became aware of the thermodynamic work of involving the formulation of the free energy as a power series in the Polarization  $P$ . (I do not know whether I first read it in papers by Devonshire in *Phil Mag*—but they seem later than I remember, 1949 and 1951.) Anyway, I thought the work was elegant, and useful in connecting up various experimentally measured physical properties. But to me, it was fundamentally inadequate for two reasons—firstly, because none of the work got round to giving satisfactory account of the origin of polarization, and secondly because they were always using derived, macroscopic quantities, as if they were fundamental.

I mean, for example, that lattice parameters and their changes cannot be given as an explanation, unless you explain how the particular interatomic forces in the unit cell average themselves out to give these lattice parameters. Also, a dipole is the product of changing distance—but the distance must be fixed by some forces other than electric ones emanating from the charge, and to specify it as the displacement of an ion from where it used to be is about as meaningful as saying it is the length of a short piece of string! In the expression for the free energy, what are the coefficients of the powers of  $P$ ? They are derived only by working backwards from other physical properties measured for the materials as a whole. They are all ‘macroscopic’. It was clear to me in fact that however useful thermodynamics was in relating properties to each other, it was no use at all in explaining them, because its fundamental assumptions were of randomness, and the unimportance of direction. It never got back beyond energies to the distribution, the localization and directions of the array of forces and elasticities of atoms or atom groups, which gave rise to potential energy, even before one tried to consider kinetic energy.

About  $\text{KH}_2\text{PO}_4$ , the geometry of the transition was quite unambiguous. The structure of the room temperature form was well known, and the existence of the short, symmetrical hydrogen bond. Geometrically, the H was either at the center of the bond, or statistically on either side. If one H was off-center, the neighboring atoms were so displaced as to pull the others off-centre in a pattern which made a piece of perfect pseudosymmetric structure in a small domain -

how large, one did not know, but with a mosaic of domains in which the alternative off-center position was chosen.

In years after, there was much argument among physicists, concerned with lattice modes, whether the “order parameter” was the hydrogen bond, the displacement of P or the axial ratio. It seemed to me almost entirely meaningless, since the choice of one alternative for one, fixed the choice for the others. The only useful question was, “which could be regarded as the trigger?”. Another possibility considered by me, but not by others, I think, was the requirements of the K-O polyhedron. Very much more recently, about 1986 or so, this was confirmed in a paper by R. Nelmes, one of the last of a series of beautiful papers on very careful and elegant work on  $\text{KH}_2\text{PO}_4$ , and all its isomorphs by Nelmes, Thornton, and other collaborators.

To return to earlier days, a very good account of the transition was given in 1944 by Quervain (*Helv. Phys. Acta*, **17**, 509). This was clear and correct about the geometry of the transition, while dealing also with the physics. Direct evidence about the placing of the H or P atoms did not come until 1953-55 with a pair of beautiful papers, using neutron diffraction analysis, by G.E. Bacon and R. S. Pease, in *Proc. Roy. Soc. A.*, **220**, 397 (1953) and **230**, 359 (1955). Even so, more work was needed to establish finer details, but the papers mentioned above by Nelmes et al. confirmed their essential results, while adding very important refinements.

The state of affairs was quite different for Rochelle salt. This was a much more complex structure of lower symmetry with far more atoms to be located, most with arbitrary parameters not fixed by symmetry. The structure had been done in 1941, but the techniques of the time did not allow great precision even for the non-hydrogen atoms, and there was no certainty about all the O-O bond lengths. It turned out afterwards that the one identified as the H bond in the 1940's and 50's was not! Even if it had been, the attempt to link it with ferroelectricity by analogy with  $\text{KH}_2\text{PO}_4$  was wholly fallacious. This bond was a longer bond, and unsymmetrical. To move the H from one end (one minimum of a double potential well) to the other would have completely changed the environment of the two oxygens at the ends, and hence the structure. We would no longer have had two domains differing only in orientation, but unpredictably different structures.

In September of 1946, I moved again, this time to Cambridge to the Cavendish. My experimental work here was still completely uncon-

nected with ferroelectricity. I started work to determine the structure of a calcium aluminum silicate, a willite. But I went on thinking about ferroelectrics.

At some date, I cannot remember, but probably somewhere around 1951 or very early 1952, I was invited to a conference in London, organized by Professor Ubbelohde, dealing with phase transitions. I gave a contribution, whether as a prepared paper, or just joining in the discussion, I cannot now remember. However, the questions I was asked, or comments by other speakers, made me aware that I was thinking along quite different lines from the others, and from Professor Ubbelohde. (I rather think they were assuming that twinning was the cause of transitions—but I may be misremembering). Anyhow, as I went home on the train and then into my room in the Cavendish, I began to clarify my own thoughts, and tried to work it out coherently. It was really quite a revelation—I remember the excitement of it. It covered some of the aspects mentioned above. I went on and wrote it up, and it turned into a paper presented in March 1952 (“Origin of Ferroelectricity in Barium Titanate and other Perovskite-Type Crystals” *Acta Cryst.* 5, 739 (1952)).

I regard that paper as the real starting point of the publication of my original thinking. Later that year I extended my work to cover  $\text{KH}_2\text{PO}_4$ , Rochelle salt and a reference to  $\text{LiNbO}_3$ . This was sent in on May 21, 1953, and published as “Ferroelectricity and Crystal Structure II” *Acta Cryst.* 7, 187 (1954) in February 1954. This complemented the 1952 paper.

A note about my source of information about  $\text{LiNbO}_3$  may not be amiss. A paper by P. Bailey came to me, I think as reference. I recognized it as excellent work, but very confusingly written up. I thought readers in general would not understand it as it stood, and suggested to the Editor that while it was not acceptable, it could be made so. I told him that I would like him to come and talk to me about it, help him edit it, and that it would make a good and important paper. Unfortunately, though I wrote several times to him and his senior colleague, he never came—and I could do no more in my references than quote his thesis, from which it had been drawn. Later, in 1966, very much more refined work by Abrahams and colleagues confirmed Bailey’s structure, as described by Megaw in 1954, though because of difficulties arising from different choices of axes of reference, it needed an explanatory note Megaw, *Acta Cryst. A*, 24, 583 (1968).

In 1958, I received an invitation from Pepinsky (I spent the summer in his lab in State College, PA), which I accepted with great pleasure. On my first landing in America, I went straight to a meeting of the A.C.A. in Ann Arbor. I there gave a paper about  $\text{KH}_2\text{PO}_4$  based on the one submitted to *Acta Cryst.* in May of 1953. After it, Pepinsky, in the discussion, made a criticism so fierce that the chairman said he thought I should have the right to reply at the end of the session. Though very grateful to the chairman, I was not seriously worried. I was confident that my own ideas were right, and thought Pepinsky was quite wrong. But I remember that later someone in the audience said to me, “Are you still going to State College?” Well I went to State College, and spent a very enjoyable summer. It was worth the opportunities it gave me to travel, see something of America, meet people and see other labs, rather than for any work I actually did there!

I was trying to do something about clearing up the problem of Rochelle salt. But in my work on the actual crystals, I was baffled by the problems of its almost universal twinning, and got nowhere. Again, my attempts to do a structure determination using Pepinsky’s machine gave no results. It was not nearly sensitive enough, and I doubt if I had good enough data. I just abandoned it, and did not worry. The structure of Rochelle salt has proved very difficult. An attempt, published years later, was somewhat indeterminate, and I doubt if there is a reliable one yet.

Meanwhile, I had travelled in America, met many people, and learned a lot, but about facts and about new points—there was nothing that did anything appreciable to change mine.

Some time before 1951, my attention was called to the interesting character of  $\text{NaNbO}_3$  by a note from E. A. Wood at Bell Telephone Laboratory. In 1951, there was a preliminary note on its structure in *Acta Cryst.* 4, 373, 345 by P. Vousden, but I was not able to start work on it until some years later.

Meanwhile, in parallel with work on  $\text{NaNbO}_3$  by Shirane, Newnham and Pepinsky (*Phys. Rev.* 96, 981 (1954)), work was being done in England on it by Cross and Nicholson, *Phil. Mag.* 7, 536 (Research Supplement) and *Phil. Mag. Series 7*, 46, 453, and Cross, L. E. *Phil. Mag. series 8*, 1, 76. Apart from Devonshire’s theoretical papers in *Phil. Mag.* in 1949 and 1954, this is the only work I know of being done in the U. K. on ferroelectricity.

About this time, I was invited to write a book about fer-

roelectricity, with a free hand as to what I should include. I was, I think, rather slow, but the book was finished in February 1956, and published in 1957 by Methuen ("Ferroelectricity in Crystals"). (Much, though of course not all, of what I have written so far in this note can be found in or deduced from that book.)

About 1957, I started work on the structure of  $\text{NaNbO}_3$ , but it was tricky, and took a long time. The first two papers were with M. Wells: *Acta Cryst.* **11**, 858 (1958) and *Proc. Phys. Soc.* **78**, 1258 (1961). Other papers on this material lie outside the period of interest.

My later experimental work on ferroelectric materials has been concerned with two aspects only:

- (1) Structure determinations.
- (2) Measurement of lattice parameters and their temperature dependence, and the evidence they provide for the temperature and nature of transitions.

I have written a number of other discussion papers; and also there is a good deal about ferroelectrics in my 1973 book, "Crystal Structures; A Working Approach".

To conclude, these notes are written in March 1989, and I find my memory a bit patchy in places. I do not think it misleads me, but there are details I can't fill in—especially as to dates. However, the dates on my published papers provide a very good framework.

I might mention this: When I gave a paper to any meeting, it was my habit to write it out in full, making the final draft just the day before. I took it in the meeting, but did not either read or recite it, just had it there to refer to if needed, but I actually had a set of headings as notes, from which I reconstructed it as I went. I kept these final drafts, and filed them, and when I was clearing out my office, I arranged for them to be kept with other papers in the Library of Girton College Cambridge. Any diaries or papers that I thought worth keeping would be there too.

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## The Early History of Piezoelectric Ceramics

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William R. Cook Jr.

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There were several independent threads to the discovery and development of piezoelectric ceramics of  $\text{BaTiO}_3$  and later  $\text{Pb}(\text{Ti,Zr})\text{O}_3$  ("PZT"). The early days were summarized by Hans Jaffe in Chapter one of *Piezoelectric Ceramics* by B. Jaffe, W. R. Cook Jr. and H. Jaffe.

Hans had been hired in 1940 by Brush Development Company to develop a substitute for rochelle salt, which, while a very efficient piezoelectric material (coupling coefficient near 100% at the 24°C Curie point), was chemically unstable because of dehydration, and dielectrically highly variable with temperature. His first material was  $\text{NH}_4\text{H}_2\text{PO}_4$  (ADP). When  $\text{BaTiO}_3$  came along, he shifted much of the research to it, and later to  $\text{Pb}(\text{Ti,Zr})\text{O}_3$ .

The highlights of the *American* discoveries (and there were nearly simultaneous discoveries in other countries) were:

- (1) The discovery by Hans Thurnauer of American Lava Company of the high dielectric constant of barium titanate ( $\text{BaTiO}_3$ ) in 1941, published in an intentionally obscure journal during the war years in 1942;
- (2) The extensive work of Eugene Wainer and associates at TAMCO, especially Reports 8 and 9 in September 1942 and January 1943, which were widely circulated in American laboratories under security clearance;
- (3) The work at the MIT Laboratory for Insulation Research of von Hippel which discovered the reason for the high dielectric constant: ferroelectricity;
- (4) The independent discoveries by R. B. Gray of Erie Resistor in 1941 (because of the war, patent applied for in 1946) and by Shepard Roberts of MIT (published in 1947) that the polar axes of the individual ceramic grains could be aligned to yield a piezoelectric body. Gray was working on material originally supplied by Hans Thurnauer; and,

(5) The realization by Bernard Jaffe, then at NBS, that there could be other ceramic piezoelectric bodies, based upon the phase studies and dielectric and ferroelectric work in the  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  system by Shirane, Hoshino, Nomura, Suzuki, and others, and particularly by the  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  phase diagram by Sawaguchi.

There were several interesting observations concerning those days that may not have been emphasized before. Around 1951 or earlier, Charles Gravley of the Brush Development Company (The predecessor company to Clevite Corporation—where the prolific group under Hans Jaffe was located) developed a sponge ceramic of  $\text{BaTiO}_3$ , made by mixing up a powder and a binder, beating it with an egg beater, drying it and then firing it. I believe a U.S. patent was issued on the material. It was an early crude version of the more sophisticated composites developed at Penn State, and had the aim of lowering some of the piezoelectric constants and thus increasing markedly the hydrostatic piezoelectric effect. Due to its inherent weakness to loads, it never became a product.

When I went to work at Brush Development Company in February 1951, one of my first projects was to survey the literature on perovskites and other possible oxide ceramics. The result was issued as an internal company report. One conclusion that I reached was that the quadrangle  $\text{BaTiO}_3$ - $\text{BaZrO}_3$ - $\text{PbZrO}_3$ - $\text{PbTiO}_3$  looked interesting, and I made several ceramic compositions in the quadrangle in 1951-52. I was not a trained ceramist, however, and the compositions were not very well done. They did not pole to show significant piezoelectric effects, and the work was abandoned.

Bernard Jaffe, at NBS, tried the straight  $\text{PbTiO}_3$ - $\text{PbZrO}_3$  diagram (and also included substantial substitution of Sn for Ti, Zr). He succeeded where I had failed for several reasons:

1. He had a more complete familiarity with the Japanese work;
2. He zeroed in on the phase boundary near 53% Zr;
3. He was a ceramist, and made better ceramics;
4. He developed a means of compensating for the potential loss of PbO during firing by providing a source of PbO, to control the atmosphere.

This last reason was probably the factor that made the biggest

difference, and also, in spite of his many later important contributions to the field of piezoelectric ceramics, was probably the most important commercially. Berny gave a paper on the work in Orlando, Florida, I believe in early 1954. Hans Jaffe heard it and was enthusiastic. By 1955 Berny was part of our group.

The developments came thick and fast. Even before Berny joined us, Frank Kulcsar was busy trying additives; the highly piezoelectric low coercive force niobium and lanthanum additives (two patents and later, and American Ceramic Society article) were developed then as well as the more obvious strontium additive. Why Frank tried either of these additives was a mystery even then, since they were known to have a poor effect in  $\text{BaTiO}_3$ , but he just went his own way. It was not until 1960 that Robert Gerson of our laboratory properly explained the phenomenon of the off-valent additive, whereupon the reverse characteristic, the "hardening" or high coercive force additives, was also explained, by me (see a mid-1960's patent covering those elements not already patented by others, as well as *Piezoelectric Ceramics*, chapter seven). At the time, and in our book, we did not emphasize the role that substitution of  $\text{F}^-$  for  $\text{O}^{2-}$  played in also creating the low coercivity highly piezoelectric body similar to Nb, La, Sb, W, etc., but we knew about it. It was probably initially pointed out by Berny Jaffe. Unfortunately, it had already been mentioned in the patent literature by others, so we felt from a business point of view that it was unwise to point out the way around our patents. Since they have long since expired, this is no longer a problem to anyone, and I recently sent a note to the Journal of the American Ceramic Society pointing out that this was the explanation for some published results involving fluorine that had been given a different interpretation.

The other type of additive that was of interest involved such substitutions as uranium, chromium or manganese, elements that had at least two stable valences, and which were associated with ultralow aging of dielectric and piezoelectric properties. Our explanation at the time was that a small percentage of the additive was gradually changing valence with time, which was counteracting the natural aging of properties. I do not know if anyone had ever confirmed this explanation.

People noticing two Jaffes at our laboratory were forever asking if they were related. They were not. Berny was short, plump, and dark-haired with Russian ancestry; whereas Hans was tall, lean, and

sandy-haired and had grown up in pre-Hitler Germany. Each was brilliant in his own way, and each contributed greatly to the science of piezoelectricity.

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## Ceramic Capacitor Development at Erie Technological Products

Nello Coda

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After obtaining a degree in Electrical Engineering I joined the Erie Resistor Corp. in Erie, Pa., later called Erie Technological Products, Inc., on Dec. 2, 1942. The main products of the company were insulated and non-insulated composition resistors (1/4 W to 4 W rating), molded mica and button mica capacitors, and a new line of tubular ceramic capacitors which were sold mainly for their stability or their predictable and reproducible temperature characteristic.

The ceramic capacitor line was started in 1936 when American Lava Corp. of Chattanooga, Tenn. tried to exploit a new ceramic product. The idea was brought over from Germany by Dr. Hans Thurnauer when he joined his father at American Lava years earlier. Ceramic capacitors were first made in Germany in the early 1930's or before.

The first series of dielectrics was made by blending MgO or CaO and TiO<sub>2</sub> and it became known as the TC series, going from P120K16 through NPOK16 to N750K85. Shortly thereafter (1943 or 1944), a new series was made available by American Lava in which the NPO member was a blend of BaTiO<sub>3</sub> and TiO<sub>2</sub> with a K of 30 and the N750 remained TiO<sub>2</sub>. For very low capacitance application there was also a P120K6 dielectric, the composition of which I do not recall. The dissipation factor (DF) in all of these series was usually well below 0.1 % and remained low up to the highest frequencies in use at the time.

The next development in dielectric materials that was already underway in 1942 when I joined the company, was the exploitation of BaTiO<sub>3</sub>. The first of these compositions had a dielectric constant well above 1200, and it became known as K1200. I well remember the surprise at discovering the Curie peak at about 115°C when I tested one of the early samples submitted by American Lava in 1943. By this time the company realized that we were severely handicapped in not having a ceramic operation of our own, so in 1943 or 1944 we hired Paul

Siegriest, a ceramist, to set up a small ceramic laboratory, and eventually a pilot production facility with extruders, presses and kilns. With few exceptions, all ceramic capacitors at the time were of the tubular variety. The major exception was the line of trimmer capacitors which, at first, were sent to our plant in England for use in military radar and similar high frequency applications. The electroding paints were developed in our chemistry lab under the direction of John Toppari, and AgO was used for the pigment. Later we brought in duPont, which preferred to work with finely divided silver for pigment, and in time we also adopted it wherever possible because it did not present the fire hazard of the oxide. Silver oxide paints continue to be used in "Paint to Capacity" applications to this day I believe.

In the early years as I recall there were only two companies making ceramic capacitors: Erie Resistor Corp. and the Centralab Div. of Globe Union, which also made a line of composition resistors, as well as switches, and steatite and alumina parts. The ceramic composition development there was done by Roland Roup, who much later founded Solid State Dielectrics which is now a part of duPont. When we began to produce ceramic dielectrics ourselves, American Lava offered their dielectrics for sale to two other companies: Muter, which never grew very large, and Electrical Reactance, which eventually became part of Aerovox, now AVX, and is today a large supplier in the business.

The development of the K1200 dielectric composition in time expanded into a full series of high K dielectrics with dielectric constants up to 10,000, as well as an intermediate temperature compensating series that started at N1400 and went up to N5600. This latter series was called "extended TC", but with the exception perhaps, of N1400, was never in great use as there was very little need for large temperature coefficients and these dielectrics exhibited instability and aging similar to high K dielectrics. By the late 40's the high K series was expanded by adding K250 and K600, and a new composition with a dielectric constant of about 1500 was developed based on Coffeen's work on BiSn. This composition had excellent life characteristics (high V/m rating at high temperature), and had very low aging, but suffered from a high dissipation factor at radio frequencies (1MHz and up). In practice, I don't think the higher loss really mattered much, but some customers refused to use it by specifying "frequency stable" bodies.

In the late 1940's we began to expand production of dielectrics, and we hired Bobbie L. Joyner, a ceramic engineer, to manage the operation, and in time he hired Larry Kopell, a ceramist, to speed up composition development work. By this time Paul Siegreest had left.

In the early or mid 1940's while evaluating and characterizing BaTiO<sub>3</sub> dielectrics, Robert Gray, a physicist, discovered that when this dielectric was cooled through the Curie point with a direct voltage applied to it, it acquired piezoelectric properties. Bob Gray spent a great deal of time in the study of the phenomenon, including x-ray studies at a laboratory in Buffalo, N.Y., which convinced him that the material was truly piezoelectric. While doing the theoretical work, he also made a phonograph pick-up using a polarized BaTiO<sub>3</sub> tube, and made very few friends in the lab when he played his children's records again and again. He also applied for a patent which was eventually issued in 1949 or 1950. Unfortunately, he never published or even wrote any papers on the subject, which made it difficult to prove the validity of the patent when the government challenged it in the early 1950's. With the end of the war, business at Erie Resistor dropped dramatically, and as Bob Gray left the company, no further research work was done on piezoelectric materials after 1946. As mentioned earlier, the Gray patent was issued in 1949 or 1950, and Erie Resistor gave an exclusive license to Brush Development Co.—later Clevite—including the right to grant sublicences. Starting in the mid 40's applications developed for piezoelectric devices, including proximity fuse applications and, in time, I believe, phonograph pick-ups and microphones. I think many of the latter applications had to await the development of PZT formulations, which exhibited properties similar to BaTiO<sub>3</sub>, but were more stable with temperature. There was also some reluctance on the part of makers of phonograph pick-ups and microphones to replace Rochelle Salt elements with a finite life with long lasting transducers made of ceramic. In time Erie Resistor made phonograph pick-up elements which were called bimorphs, but we did not have a good process to make thin films and we eventually discontinued the line. At this time, the most successful maker of bimorphs, and later, thin plate capacitors was Gulton Mfg. Co., which used a casting technique to produce their ceramic films (0.8 mils and up).

After the Gray patent was issued, Erie Resistor offered to negotiate a licence agreement with the U.S. Government since most of the use was for military equipment. Unable to succeed, the company, along

with Brush Development Co., brought suit for infringement and eventually won a substantial monetary settlement in the late 1950's.

In late 1949 the Engineering Department was divided into an Engineering and Product Development group under my direction, and an R&D group under J. H. Heibel, my former boss. We both reported to B. B. Minnium, Vice President of Engineering.

Most of my time in the 1950's and 1960's was devoted to finding new applications for our ceramic products, including a full line of disc capacitors, high voltage capacitors, trimmer capacitors and special application units. In the R&D group they continued to do work on improving dielectric composition capacitors. I recall the following:

1. Reduced titanate capacitors wherein a  $BaTiO_3$  ceramic disc was reduced when fired under special conditions, then electroded with a specially doped silver paint and fired under precisely controlled conditions in a clean, oxidizing atmosphere. High capacitance rectifying junctions developed between the electroded areas and the reduced titanate core, which, when connected in series, produced a useful low voltage, high value capacitor. By this process, Erie Resistor produced fairly linear capacitors rated 12V, 18V, and 25V; but Centralab, who first marketed this type of capacitor, also produced a 3V unit, which we found difficult to duplicate. Both Erie and CRL had patent positions on this type of capacitor, but the claims were not sufficiently explicit to bar either one from making the unit, so we both agreed not to interfere with each other.

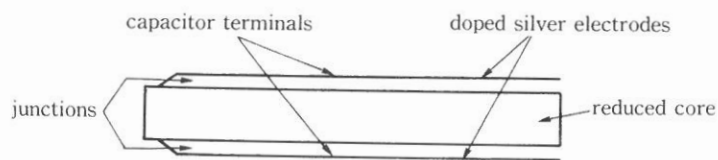


Illustration: Reduced Core Capacitor

2. The Slip Dip Capacitor was perhaps the forerunner of the multilayer capacitor. The unit started out as a green ceramic rod which was first coated with a palladium paint, and then coated again by dipping it into a ceramic slip and withdrawing it slowly to produce a dielectric layer a few mils thick. The unit was then fired at ceramic firing temperature, subsequently electroded with silver paint, and fired at a suitably lower silver firing temperature. The voltage rating of

these units was of the order of 25 to 50 V.

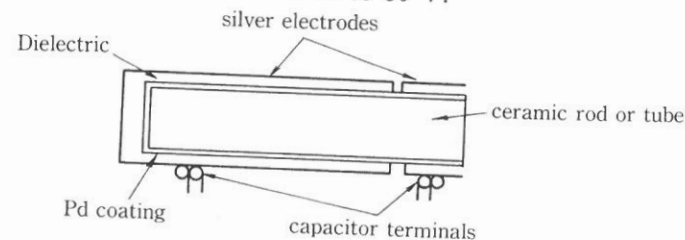


Illustration: Slip Dip Capacitor

3. The success with the Slip Dip capacitor spurred work on a multiple layer plate version in which we tried to work with both green and fired ceramic plates as thin as 10 mils, electroded with Pd or Pt paints and fired into a solid block. One version of this capacitor, up to seven layers thick, seemed so promising that we assigned it a part number (890 Series), and advertized it. However it turned out to be too difficult to reproduce, and it had to be taken out of production.

During the 1950's, Erie Resistor Corp expanded considerably. In 1954, a new plant was built in Trenton, Ontario to expand the very small assembly plant we had had in Toronto for many years. Consequently, good relations were developed with the Canadian government agencies, and in time we obtained financial support to expand production of button mica capacitors and later develop new ceramic products. To staff this laboratory, we employed technical people from England, among them James Walsh and Geoff Robinson, who would later move to the United States. In 1956, a ceramic plant was opened in State College, Pa. with Bobby Joyner in charge, and Larry Ruffner and Larry Kopell to do the ceramic engineering. Later, a Material Research Laboratory was added with Don Hamer in charge.

Starting in the early 1960's, there was also considerable restructuring in Erie. Mr. G. Richard Fryling, who had been president, retired and became chairman of the board, and brought in Marion Pettegrew as interim president while his son, George Fryling, was being groomed for the job. Mr. Pettegrew in turn brought in a new second layer of management in Marketing, Finance and Research. The new Director of Research was Ivan Brandt, but I remained associated with product development and engineering, and continued to report to Byron Mininum.

With the failure of the 890 lines due mainly to our inability to produce a thin ceramic film, we welcomed the opportunity to offer



financial assistance to a small company in LaJolla, CA run by Joseph Crownover in exchange for know-how on their products. This company manufactured a line of thin plate, 2 mil, ceramic capacitors, and also very small multilayer capacitors made in the same manner we had tried to make the 890 line. The technique developed was simple, but very well thought out, and in time we adopted it to produce a line of multilayer capacitors in Erie which we called Monobloc. I personally took a very active part in this early work, and worked with John Toppari, Senior Chemist in the R&D group during the transition and in the early stages of production.

Meanwhile in Canada, they were very actively working on electrical filters (simple T, L and Pi designs), but were severely handicapped by the lack of high value capacitance units. To solve this problem, they obtained a contract with the Canadian government to develop a rolled multilayer capacitor by screening high temperature electrodes on thin green ceramic strips, rolling them in pairs as wound paper capacitors are made, and sintering them at ceramic firing temperatures. While originally the ceramic film may have been made by casting, as was being done in Erie, eventually they developed a process in which a thin mylar strip was dipped into a ceramic slip and slowly withdrawn, coating both sides with ceramic. The coated mylar was then dried, electroded, rolled on a mandrel, slowly baked and fired. Surprisingly, the mylar film burned out completely, leaving no trace of its former presence. This method of making ceramic film lent itself beautifully to mechanization not only in the film making, but also in film processing, and was eventually used to make all rolled capacitors, and later, the newly developed discoidal ceramic capacitors for Canadian-made filters. The quality of these capacitors was never totally satisfactory, the biggest problem being delamination between ceramic layers, although there was never any evidence of delamination where the mylar film had been.

In Erie, film for multilayer capacitors at first was made by casting on and stripping from a glass plate, but eventually we developed a process in which a coated mylar film was made as in Canada, but the ceramic layer was stripped from the mylar and edge bonded to a paper carrier, stored in rolls, and then processed through the mechanized electroding, drying, and stacking machines. As time passed, the mechanization was improved, but we still had occasional problems with delaminations which, while not always greatly detrimental, caused

customer complaints, nevertheless.

Other subjects for study were the compatibility between the electrode material and the dielectric composition. Certain compositions—the better ones, it seemed—would only tolerate expensive platinum electrodes while others accepted additions of palladium, including only palladium, and even silver palladium mixtures. The method of deposition was also studied, but screening remained the only practical way as long as I was there. On the theory that the green electrode binder created problems in bake-out and firing, we signed a one-year contract with A.D. Little to explore a transfer printing technique, but the process yielded no improvement as it used essentially the same amount of binder as the screening compositions did. Later, I discussed a similar contract with Batelle to explore electrostatic deposition of metal powder only, but the management of the company did not support me on this and nothing ever came of it.

In the late 1960's or early 1970's the manager of our Nuremberg plant in Germany reported that Siemens of Munich had developed a ceramic material with a dielectric constant of 50,000. This seemed very attractive, so after some preliminary discussions, I traveled to Munich to explore details, and while I had many misgivings about the practicality of the system, we eventually signed a license agreement. The dielectric in their case was  $\text{BaTiO}_3$ , which was doubly-doped to produce a barrier layer at each grain upon a single firing. The effective dielectric constant was strongly dependent on grain size, which had to be  $50\mu\text{m}$  or larger, and was also affected greatly by the binder (frit) content of the electrode material. Unlike Siemens, which made this capacitor in tubular form, we had to produce it in disc form, and could only effectively compete against ordinary thick discs (say 20 mil), which were much cheaper to produce. The temperature characteristic of this dielectric was rather poor, and Japanese company eventually put an end to the product by producing a version using a titanate other than barium, which had a much better temperature characteristic, and, I believe, an even higher dielectric constant. In time the ingredients for this body became available from a supplier in California, and I think David Payne worked on it also, but I have no clear recollection of this.

By the late 1970's, the operation in Erie became very small, and I gradually assumed a role of adviser, eventually retiring in 1982.

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# Capacitor Studies at Siemens and Sprague

Wilhelm R. Buessem

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From October 1938 until February 1947, I was in charge of the Siemens Ceramic Research Laboratory in Neuhaus (Thuringia). Siemens had neglected the area of Ceramic Dielectrics completely both in regard to research and especially patents. They tried to make up for it by establishing a good size, well-equipped and well-staffed research laboratory as they had done in other areas and they might well have succeeded, if it had not been for one factor: eleven months later, on September 1, 1939 World War II broke out in Europe, which changed everything, especially the direction of our research. Of course, we might not have found BaTiO<sub>3</sub> going in the old direction, but in any case, Siemens did not invent BaTiO<sub>3</sub> dielectrics! The credit for that belongs to Wainer, Salomon and von Hippel for their work in 1942-1944.

There is a good chance, however, that the high-K of BaTiO<sub>3</sub> was detected by another laboratory in Germany at the same time or even earlier. Dr. Erich W. Rath was the head of the laboratory of the Hermsorf-Schomburg Isolatoren Gesellschaft (abbreviated Hescho) from 1924 to 1945; he was an ingenious inventor and created the field of titante ceramic in the early thirties almost singlehandedly. The Hescho laboratory was like the Siemens laboratory in the Russian Zone. After the war Dr. Rath escaped like most of the Siemens people into the American Zone. The American Military Government asked scientists in their Zone to write about their work during the war; this was published under the title: *Naturforschung und Medizin in Deutschland 1939-1945*. In volume XXVI, chapter six, Dr. Rath wrote his story under the title: "Dielectricische Untersuchungen an titandioxyd haltigen Systemen." I noted the extensive bibliography—19 pages—on BaTiO<sub>3</sub> in Gmelin's Handbook of Inorganic Chemistry volume 41, Titanium; although it contains papers and patents of American English, Dutch, Russian, Swiss and Japanese authors published 1945-1949,

I could not find Dr. Rath's report cited. Either Dr. Rath did not mention BaTiO<sub>3</sub> or the Gmelin people did not consider the Military report a scientific publication. Dr. Rath died January 19, 1987.

In 1944, during the war, the German Air Ministry had organized a conference, to discuss the possibility of developing ceramic turbine blades for jet engines. The ceramic material most suitable seemed to be dense Al<sub>2</sub>O<sub>3</sub> (Sinterkorund) because of its remarkable high-temperature strength. Siemens had developed this material and was producing it in large quantities for aircraft sparkplug insulators. This accounted for my presence at this meeting. The report of this meeting landed in due time in the "German Intelligence Office" at the Headquarters of the Air Force in Wright Field, where next door in the Materials Laboratory a large program to develop ceramic materials for turbine blades was under way. As a consequence all participants of this meeting were invited to the United States and all those, who were not in Russian hands, accepted. I came to Dayton in March 1947 and developed a new method to measure "Thermal Shock Resistivity"; poor performance under practical thermal shock conditions eliminated Al<sub>2</sub>O<sub>3</sub> and other oxides very quickly: no great scientific testing was needed for that!

The government had biographies of the German scientists sent to interested industries; the research and development people of some of them came to talk to us, usually very pleasant conversations. Among those visitors was Dr. Preston Robinson, co-founder and scientific director of the new Sprague Electric Company in North Adams, Massachusetts. (The old Sprague Electric Company had been renamed 'General Electric Company' and is located in Schenectady, New York.) We talked a lot about BaTiO<sub>3</sub> and other dielectrics, which had recently become known. When I became a professor at Penn State in September 1950, we made contact very soon and in February 1951, I became Consultant to Sprague Electric, a job which I held for twenty-five years: on February 1976 I made my last trip to North Adams! In the mean-time, Siemens in Germany had built new facilities for research and fabrication in the American Sector (Munich) and also started working on BaTiO<sub>3</sub> and other dielectrics. An interesting result of this development was the invention of the high-K fine-grained BaTiO<sub>3</sub> in 1954.

After some promising experiments, Sprague became interested in this material and contacted Siemens about a license. It turned out that

Siemens was interested in a capacitor line which Sprague manufactured and a meeting was arranged. In October 1957, on Sputnik day to be exact, Dr. Lazier, Dr. Brown, and myself flew to Munich, where after two days of discussions, Sprague and Siemens came to an agreement about licenses and exchange of knowledge about certain types of capacitors, BaTiO<sub>3</sub> capacitors among them. A few weeks later, a team from Siemens came to North Adams to inspect the facilities and procedures there.

Two experiments which Sprague performed with the new material at that time were later helpful when Penn State developed the theory of the high-K of the fine-grained material. Prokopowicz found that thin platelets coated with a shrinking plastic coat, i.e. subjected to a two-dimensional compression had an increased capacitance contrary to a decrease in large-grain material, and Dr. (Mrs.) Hutchins found with the electron microscope, that the fine-grained material had practically on 90° domain walls.

Sprague soon established the Sprague Fellowship at Penn State. The first fellow was A. K. Goswami, whose Doctor Thesis on the subject of high-K of fine-grained BaTiO<sub>3</sub> published with Dr. L. E. Cross in the Journal of the American Ceramic Society **49**, p. 33-36, 1966, won the "Outstanding Paper of 1957-1967 Award" in 1968.

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## 「特別寄稿」邦訳

丸竹正一, 脇野喜久男

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