A Short History of Ferroelectricity

Arne Lüker, Instituto Superior Técnico
Departamento de Física
Av. Rovisco Pais 1
P-1049-001 LISBOA
Portugal

It all began with a salt in La Rochelle, a small but important city at the south-west coast of France. Jehan Seignette, born in 1592, a militant protestant, succeded to run a pharmacy in spite of serious obstacles opposed to him by the clerics. One of his sons, Pierre, born in 1623, became a medical doctor at the University of Montpellier and his younger brother Elie, born in 1632, took over his father's business. In these years pharmacy consisted mainly in extracting plants and distilling essences. Apparently purgatives such as "folia sennae" introduced to Europe by Arab medical men in the early middle age, played an important role. Because of unpleasent side effects patients were very reluctant to take them. This was the reason Dr. Seignette suggested to his brother to look for some mineral drugs or to make some. Although "mineralia" were in use for curing various diseases in eastern countries already 2000 years B.C., Pierres idea was decisive. As the result of hard work Elie came out with a salt in approximately 1665, which he called "sel polychreste" derived from the greek $\pi o \lambda \nu \chi \rho \eta \sigma \tau o \sigma$, which means a salt of various utilities. It was a real creation and the way he produced the salt was kept secret for ever it seems [1].

Fig. 1: David Brewster

Only 65 years later the French pharmacist and chemist Simon Boulduc in Paris found out by analysis that sel polychreste must be "some soda" [2]. It is likely that Elie Seignette started from crème of tartrate (potassium hydrogen tartrate) he obtained from wines – so famous and abound in the Bordeaux region – and soda which makes the tartrate soluble in water. The "sel polychreste" – or Rochelle salt as we know it today - conquered the market in France, especially in Paris and it was in widespread use for more than two centuries as a mild drug.

Fig. 2: Jacques and Pierre Curie with parents

In the nineteenth century – nearly 200 years after its discovery - the physical properties of Rochelle salt began to excite interest. In 1824 David Brewster had observed the phenomenon of pyroelectricity in various crystals, among which was Rochelle Salt [3] but perhaps the first systematic studies were those of the brothers Pierre and Paul-Jacques Curie in 1880 [4]. 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. They also noticed that Rochelle salt was by far more active than quartz for instance and all the rest of the crystals they investigated. But the fascinating dielectric features of Rochelle salt escaped them.

Fig. 3: Thomas Alva Edison with his phonograph, 1899

Thomas Alva Edison was maybe the first who used its piezoelectrical effect in a commercial application in 1899 – the phonograph. However, his invention was just a curiosity and far too expensive. At this time Rochelle salt was of pure academic significance.

During World War I, however, physicists and electrical engineers showed an increasing interest in its physical properties mainly because of its unusually high piezoelectric moduli. At the beginning of the war 1914-18 A.M. Nicholson in the USA [5] and Paul Langevin in France [6] began to perfect independently an ultrasonic submarine detector. Their transducers were very similar: a mosaic of thin quartz crystals glued between two steel plates (the composite having a resonant frequency of about 50 KHz), mounted in a housing suitable for submersion. Working on past the end of the war, they did achieve their goal of emitting a high frequency "chirp" underwater and measuring depth by timing the return echo. The strategic importance of their achievement was not overlooked by any industrial nation, however, and since that time the development of sonar transducers, circuits, systems, and materials has never ceased.

Fig. 4 Paul Langevin

Petrus Josephus Wilhelmus Debye, or Peter Debye as we know him today, professor of theoretical Physics at the University of Zürich had carefully observed the work on piezoelectricity and in 1912 he came up with an idea. To explain the results he knew he brought forth the hypothesis that a certain class of molecules carry a *permanent electric dipole moment* in analogy to the magnetic

moment of the atoms of paramagnetic substances. Following Langevin's theory of paramagnetism Debye gave the equation *(ε-1)/(ε+2)=a+b/T*, where *a* is proportional to the density of the substance and *b* to the square of the electric dipole moment [7]. This relation was perfectly confirmed later in many cases.

Debye came to a further conclusion. According to his relation for a critical temperature $T_K=b/(1-a)$ the dielectric constant reaches infinity. Therefore, he proposed T_K to be the analogue to the Curie temperature of a ferromagnet. For temperatures lower than T_K a *permanent dielectric* polarisation ought to be expected even in the absence of an electric field. To his knowledge, he said, no such a phenomenon had been observed so far. The basic feature of *ferroelectricity* was anticipated, however!

Erwin Schrödinger in his "Habilitations-Schrift" submitted at the University of Vienna late in 1912, the year Debye published his „Vorläufige Mitteilung", went a step further. He elaborated on Debye's simple model and tried to extend it to solids. If this could be done successfully, Schrödinger speculated, then all solids should become "ferroelektrisch" at a sufficiently low temperature [8]. So, in fact, the term ferroelectric or ferroelectricity was coined by Schrödinger as early as 1912!

Fig. 5: Peter Debye

Another major contributor to the early Rochelle Salt period was Joseph Valasek. Born on April 27, 1897 in Cleveland, Ohio, he got his bachelor's degree in physics at Case Institute of Technology where Prof. D. C. Miller started him on a career in physics. His first employment was at the National Bureau of Standards in Washington D.C., where he got familiar with various methods of pyrometry applied in steel industry. In this connection he learned about the phenomenon of ferromagnetism both theoretically and experimentally. In 1919 he came to the University of Minnesota in Minneapolis as a graduate teaching assistant.

Fig. 6: Erwin Schrödinger 1933

Under the supervision of Prof. W. F. G. Swann, a physisist known by his theoretical work in cosmic rays physics but also known to have a wide overview in many other directions, Valasek began a systematic study of the analogy between the magnetic properties of ferromagnetics and the dielectric properties of Rochelle Salt.

Joseph Valasek presented his first paper on "Piezoelectric and allied Phenomena in Rochelle salt" at the meeting of the American Physical Society in Washington in April 1920. He stated: *"... the dielectric displacement D, electric intensity E, and polarisation P ... are analogous to B, H and I in case of magnetism."* The data *..."is due to a hysteresis in P analogous to magnetic hysteresis. This would suggest a parrallelism between the behavior of Rochelle salt as a dielectric and steel, for example, as a ferromagnetic substance. Bearing out this idea, typical hysteresis curves were obtained for Rochelle salt, analogous to the B, H curves of magnetism."* The full version of his presentation was submitted to Physical Review in December 1920 [9]. It marks two milestones. Here Valasek stated for the first time that "*pe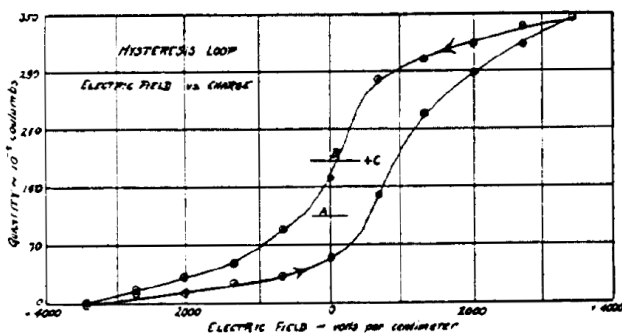rmanent polarisation is the natural state*" of Rochelle salt and published the first hysteresis curve of a ferroelectric material (Fig. 8). In the same year he became Master of Arts.

Valaseks Ph.D Thesis "Piezo-electric activity of Rochelle salt under various conditions" is dated 1922 [10]. Perhaps the most history-making graph is that of the temperature dependence of piezoelectric response, indicating the existance of a relatively narrow temperature range of high piezoelectric activity, in fact indicating the existence of two phase 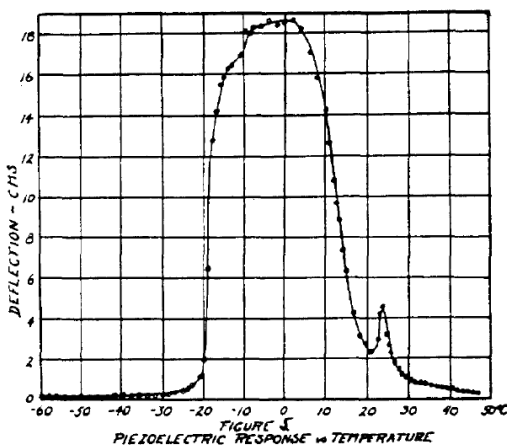transitions (Fig. 9). Indeed Valasek speaks here for the first time about the existance of two Curie points in Rochelle salt.

Valaseks studies were to lead later to the firm establishment of the term *ferroelectricity* to describe this set of phenonema. Yet it is interesting to observe that he never used the word ferroelectricity. Maybe he never heard about Erwin Schrödingers proposal. Who knows?

Until now Rochelle salt was the only known material with ferroelectric characteristics and scientist all over

Fig. 7: Joseph Valasek 1922

Fig. 8: The first published hysteresis curve [9]

Fig. 9: Piezoelectric activity of Rochelle salt vs. temperature indicates the existence of two phase transitions [10]

4

the world began to ask, if there are more. Among them Paul Scherrer, who is well known in the material science community for his formula to calculate the grain size from the rocking curve of x-ray diffraction measurements (XRD). Together with Peter Debye he worked at the "Physikalisches Institut" at the "Eidgenössische Technische Hochschule" (ETH) in Zürich on dielectrics. Scherrer believed in the molecules of water of crystallisation to be essential for a material to be ferroelectric. Together with his student Georg Busch he searched the literature which was still scare and came across a paper by Gert Steulmann at the "Institut für allgemeine Elektrotechnik" of the "Technische Hochschule" in Dresden [11]. The average dielectric constants of various potassium salts had been measured by an immersion method, amongst others K_3PO_4, K_2HPO_4 and KH_2PO_4! Quite normal values of 7.75 and 9.05 respectively for the first two salts were observed, but for KH_2PO_4 a value higher than 30 was found. In view of the orthorhombic symmetry of potassium-dihydrogen

Fig. 10: Paul Scherrer

phosphate this was surprising and it supported Busch's vague idea, that mobile hydrogen atoms might be responsible for ferroelectricity, rather than the water molecules – the hypothesis of his supervisor. That indeed O-H-O bonds do exist in KH_2PO_4 was shown by J. West at Bragg's laboratory in Manchester by a quantitative x-ray analysis of its structure [12]. It was Steulmann also who speculated about the existance of some sort of dipoles in these crystals without elaborating further on his conjecture, however. These ideas proved to be true and early in March 1935 KH_2PO_4 was found to be ferroelectric with a critical temperature of about 123 K by Busch and Scherrer [13].

This discovery was a breakthrough in the field of ferroelectricity and KH_2PO_4 has become a model substance up to the present. Furthermore in his thesis, which appeared in 1938 [14], Busch suggested the *hydrogen bonds* between adjacent oxygen atoms to be responsible for ferroelectricity. The same idea was applied by Slater [15] in 1941, who gave the first significant molecular theory of ferroelectricity based on the mdel of hydrogen bonds.

After having finished his thesis Busch suggested to investigate $NH_4H_3IO_6$, a material in which hydrogen bonds were known to exist also. It was shown much later that ammonium iodate is antiferroelectric. Today many substances exhibiting hydrogen-bond-ferroelectricity are known and ferroelectricity is no longer a singularity of Rochelle salt.

September 1st 1939: Germany invaded Poland, the beginning of the Second World War. This triggered the interest in ferroelectrics, mainly for sonar systems to detect submarines and other military applications. Barium Titanate, $BaTiO_3$, the first man-made perovskite ferroelectric was discovered in 1942 and 1944 in the United States, Russia and Japan. At least in the USA the research was accelerated because 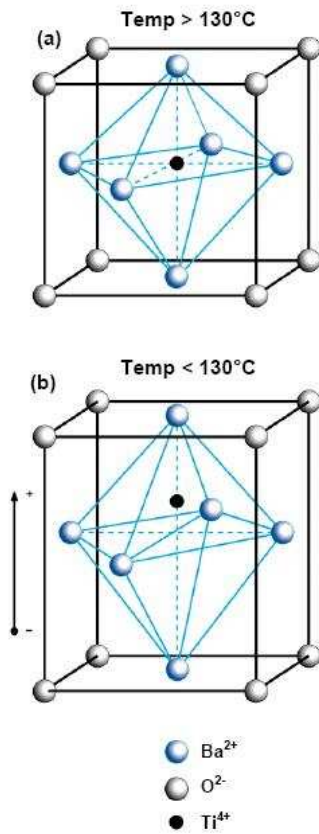of the war. At that time, mica was used in most capacitors, but U-boats threatened the supplies of mica to the USA from South America. The initial reports were based on doping studies of TiO_2 with BaO, which produced ceramic materials with enhanced dielectric permittivities. The mixed oxides were made by Thurnmaurer and Deaderick at the American Lava Corporation as early as 1941, the filing date of U.S. Patent No. 2,429,588 [16]. The high permittivities were found by measurements made at the Erie Resistor Company, with dielectric constants exceeding 1000, ten times greater than any other ceramic known at that time, such as TiO_2 (ε_r=110).

Fig. 11:The BaTiO₃ crystal structure above (a) and below (b) the phase transition between cubic and tetragonal

The race to understand the nature of the dielectric anomaly in BaO-TiO_2 ceramics continued, and in 1945 and 1946, von Hippel (USA), and Wul and Goldman (Russia) demonstrated ferroelectric switching in these ceramics [17, 18]. The discovery of ferroelectricity in BaO-TiO_2 ceramics was extremely important, as it demonstrated for the first time that ferroelectricity could exist in simple oxide materials, and it was not always associated with hydrogen bonding. $BaTiO_3$ is a member of the perovskite family named after the naturally occurring mineral perovskite $CaTiO_3$. The simplicity of the structure of $BaTiO_3$ (Fig. 11) seduced several investigations to undertake x-ray diffraction studies of the structural changes occurring at the phase transitions [19] and it enabled the investigation of the most important theoretical backgrounds of these materials. A.F. Devonshire developed his phenomenological model of ferroelectrics on the basis of the electromechanical, structural and thermal properties of $BaTiO_3$ in 1951 [20]. This approach built upon the earlier ideas of Landau and Ginzberg and invoked the point group symmetry and nonlinear elasto-dielectric coupled interactions with electrostriction and piezoelectric coefficients. The resulting Landau-Devonshire-Ginzberg Theory (LDGT) of ferroelectrics is still the most powerful tool for the understanding of ferroelectrics.

At the end of the war, public disclosure led to intense interest not only in academic circles, but in practical markets, in particular high capacitance, small volume capacitors in early television and radio circuits, as well as active elements for phonograph pick-ups, accelerometers, and ultrasonic generators. The British Navy, for instance, used some underwater sonar devices based on the piezoelectric response of $BaTiO_3$ ceramics until the end of the last century. Lately, the $BaTiO_3$ piezoelectric properties have been revisited in the form of single crystals and textured ceramics because of environmental concerns with the lead-based perovskites based on the perovskite $PbZrO_3$-$PbTiO_3$ system (PZT).

The next significant perovskite with ferroelectric properties was Barium-Strontium Titanate, (Ba,Sr)TiO_3 or BST. In this system the A site of $BaTiO_3$ is doped with Sr. This alters the Curie temperature of $BaTiO_3$ (Fig. 12). Below the Curie temperature a ferroelectric material behaves like a "normal" ferroelectric; e.g. it has a hysteresis like Valasek observed in Rochelle Salt. But above the Curie temperature the material becomes *paraelectric*, the hysteresis can not be observed anymore. In terms of tunability (the change of the permittivity with an applied voltage) the paraelectric state offers the opportunity for varactors (variable capacitors) and phase shifters with a linear change of the permittivity in a certain voltage region.
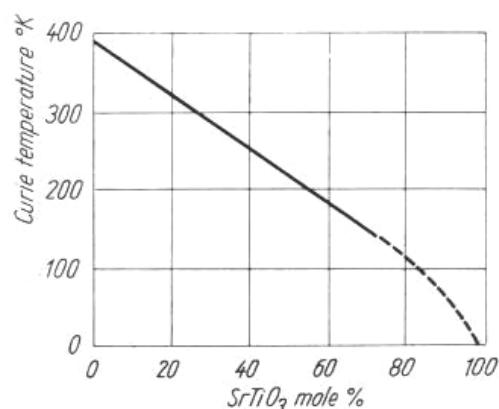

Fig. 12:Temperature of phase transition in solid solution of (Ba, Sr)TiO_3 vs. composition [21]

Despite the fact that BST was (and still is) a matter of investigation for over 60 years now, there are problems with this material. High growth temperatures (700 – 1000°C) and large leakage current densities ars some of the major obstacles for these material to be used in e.g. dynamic random eccess memories (DRAM) or microwave dielectric applications. The high growth temperature is detrimental for the integration to semiconductor devices and large leakage current densities limit the use of thinner films.

In recent years a new perovskite material, namely Lead Strontium Titanate, (Pb, Sr)TiO_3 or PST, has attracted the interest of researchers. Although there are health and environmental concerns with lead-based materials, this material has remarkable advantages compared to BST. It is easy to deposit crack-free, has relatively low loss and a high tunability (~80%), and a comparable low growth temperature (<700°C). Therefore (Pb,Sr)TiO_3 is an attractive candidate to replace (Ba,Sr)TiO_3 in future applications.

Coming back to Seignette Salt and the term *ferroelectric*, Helen D. Megaw from the United Kingdom said in 1957: "… perhaps the real reason for its [i.e. of the name Seignette-electricity] rejection … is its failure to fit comfortably into the English language. As an adjective, *ferroelectric* is euphonious, while *Seignette-electric* grates on the ear" [22].

References

1. Maurice Soenen, La Pharmacie à La Rochelle. Les Seignettes et le sel polychreste. Thèse de doctorat de l'Université de Bordeaux, 1910

2. Simon Boulduc, Compt. rendus Acad. Roy. des Sciences 1731

3. David Brewster, *Edinbg. J. of Science*, Vol. 1, No. II. 208-218 (1824). Observation on the Pyro-Electricity in Minerals

4. Jacques et Pierre Curie, *Compt. rend.* **91**, 294-295, 383-387 (1880). Développement par pression de l'électricité polaire dans des crystaux hémiédriques à faces inclinées.

5. A.M. Nicholson, Piezophony. U.S. Patent 1, 495, 429. Filed April 10, 1918. Patentd May 27, 1924. A.M. Nicholson, Generating and Transmitting electric Currents , U.S. Patent 2, 212, 845. Filed April 10, 1918. Patented August 27, 1940

6. Paul Langevin, Procédé et appareils d'émission et de réception des ondes élastiques sous-marines à l'aide des propriétés piézoélectriques du quartz. Brevet d'Invention No. 505,703. Demandé le 17 septembre 1918. Délivré le 14 mai 1920

7. P. Debye, Physik. Zeitschr. XIII, 97-100 (1912). Einige Resultate einer kinetischen Theorie der Isolatoren (Vorläufige Mitteilung).

8. Erwin Schrödinger, Aus sen Sitzungsberichten der Kaiserl. Akademie der Wissenschaften in Wien. Mathem.-Naturw. Klasse; Bd. CXXI, Abt. Iia, November 1912. Studien üder Kinetik der Dielektrika, dam Schmelzpunkt, Pyro-und Piezoelekrizität.

9. J. Valasek, Phys. Rev. **15**, 537 (1920); **17**, 475-481 (1920). Piezoelectric and allied phenomena in Rochelle salt.

10. J. Valasek, Phys. Rev. **19**, 478-491 (1922); Piezo-electric activity of Rochelle salt under various conditions.

11. G. Steulmann, Z. Phys. **77**, 114-116 (1932). Die Dielektrizitätskonstante einer Anzahl von Kaliumsalzen und Alkalihalogeniden.

12. J. West, Z. Krist. **74**, 306 (1930). A quantitative X-Ray Analysis of the Structure of Potassium-Dihydrogen-Phasphate (KH_2PO_4)

13. G. Busch and P. Scherrer, Naturwiss. **23**, 737 (1935). Eine neue Seignetteelektrische Substanz

14. G. Busch, Helv. Phys. Acta **11**, 269-298 (1938). Neue Seignette-Elektrika.

15. J.C. Slater, J. Chem. Phys. **9**, 16-33 (1941). Theory of the Transition of KH_2PO_4.

16. H. Thurnaurer and J. Deaderick, U.S. Patent 2,429,588, Oct. 21, 1947, filed Oct. 2 1941

17. A. von Hippel, R.G. Breckenbridge, F.G. Chesley, and L. Tisza, Ind. Eng. Chem. **38**, 1097 (1946)

18. B. Wul and J.M. Goldman, C.R. Acad. Sci. URSS **51**, 21 (1946)

19. W. Känzig, Helv. Phys. Acta **24**, 175 (1951)

20. A.F. Devonshire, Phil. Mag. **40**, 1040 (1949), Phil. Mag. **42**, 1065 (1951)

21. Rushman and Srivens, Trans. Farad., A, **42**, 231 (1946)

22. H.D. Megaw, Ferroelectricity in Crystals. London: Methuen & Co., Ltd., 1957, p. 2