

# 1

## Foreword

*B. Jiménez, J. A. Gonzalo*

The prehistory of **ferroelectricity**, or rather, the early history of ferroelectricity, begins, as pointed out by Prof. Sidney B. Lang (Ben-Gurion University, Beer Sheva, Israel) with the early-recorded observation of **pyroelectricity** more than twenty-three centuries ago. The Greek author Teophrastus wrote that the mineral “lyngourion” (probably tourmaline) showed the property of being able to attract little bits of wood. This property must have had something to do with the heating/cooling of the mineral in question. More recently, in the 18<sup>th</sup> century, investigations of the phenomenon of pyroelectricity made a significant contribution to early researches in electrostatics. In the following century this contributions were extended to other researches in mineralogy, thermodynamics, crystal physics, etc. Piezoelectric effects were intimately connected also with the discovery of **piezoelectricity** in 1880 by the Curie brothers in France, and forty years later, with the discovery of **ferroelectricity** in 1921 by Valasek in the US.

In the second half of the 20<sup>th</sup> century research in pyroelectric, piezoelectric and ferroelectric effects of materials has flourished and has found a very large number of varied applications.

Amongst the thirty-two crystal classes (point groups), as it is well known, eleven

of them are characterized by having a center of symmetry, and, being centrosymmetric they cannot have a polar character, cannot be ferroelectrics. The application of an external electric field will produce displacements of the positively and negatively charged atoms in the unit cell. The resulting strain of the cell will be the same upon reversal of the electric field, showing its electrostrictive character.

The twenty-one remaining crystal classes lack a center of symmetry, they may have one or more polar axes, and (with the exception of the cubic class 4.32) show piezoelectric effects, i.e. the application of pressure causes an electric current to flow in a –certain direction, and the application of a contrary tensile stress gives rise to a flow of charge in the opposite direction. If an electric field is applied the crystal will be stretched. This makes piezoelectric crystals extremely versatile as electromechanic transducers. Such modern new tools as the Tunneling Microscope and the Atomic Force Microscope, which make possible the investigation of actual microscopic processes in crystal surfaces are allowed just by the availability of excellent piezoelectric materials.

Of the twenty piezoelectric classes, as it is well known, ten have a single polar axis and they are spontaneously polarized. This

spontaneous polarization is temperature dependent, resulting in the pyroelectric effect.

All ferroelectric crystals belong to one or another pyroelectric class and have the property that an external field can reverse their polarization. Sometimes, however, the field must be extremely high to achieve in practice polarization reversal.

There are many analogies between ferroelectricity and ferromagnetism as pointed out by Valasek, but there are also important differences, which set apart one physical phenomenon and the other, as might be expected.

There are several criteria to classify ferroelectric crystals and the main ones were established early in the game. For many years the phenomenon of ferroelectricity was known to occur only in Rochelle Salt. Later potassium dihydrogen phosphate and a number of its isomorphs were recognized as ferroelectrics. Then during the Second World War, barium titanate, the prototype of many oxide ferroelectric perovskites to come was discovered. After this discovery and due to efforts of Matthias, Pepinsky, Smolenski and others, the number of ferroelectric materials increased in a spectacular way. The need of a classification scheme for ferroelectrics was recognized and several criteria were proposed: (i) Chemical classification: ferroelectrics were classified in two groups: hydrogen-bonded ( $\text{KH}_2\text{PO}_4$ , or KDP, triglycine sulfate, or TGS, etc) and double oxides ( $\text{BaTiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ , etc). (ii) Number of allowed directions for the spontaneous polarization: uniaxial ferroelectrics, like triglycine sulfate or Rochelle Salt, and multiaxial ferroelectrics, polarizable along several crystallographic directions, which become equivalent in the high temperature paraelectric phase, like  $\text{BaTiO}_3$ , and many perovskites. (iii) Ferroelectrics with a non-centrosymmetric high tempera-

ture phase (like KDP, which is piezoelectric above  $T_c$ , the ferroelectric Curie temperature) and ferroelectrics with a centrosymmetric high temperature phase (like  $\text{BaTiO}_3$  and many other perovskites, TGS and its isomorphs, etc). (iv) Order-disorder ferroelectrics, in which permanent dipoles which are randomly oriented above the transition temperature become spontaneously ordered below  $T_c$  (potassium dihydrogen phosphate, triglycine sulfate) and displacive ferroelectrics, such as many perovskites, in which reorientable dipoles in the paraelectric high temperature phase are not clearly recognizable. (Recent investigations however tend to soften the strict separation between both groups, i.e. between the order-disorder and the so called displacive ferroelectrics, stressing the coexistence in practice of order-disorder and displacive features in many or even in most ferroelectrics. It is pointed out that in a rigid lattice, almost undeformable dipoles may show a predominantly order-disorder transition, while in a more deformable lattice, deformable dipoles, in which the constituent ions show clear temperature dependent displacements, can be taken as a displacive transition). Usually typical order-disorder transitions show Curie constants of the order of  $C \approx 10^3$  K while typical displacive transitions show much larger Curie constants, with  $C \approx 10^5$  K. An effective field approach to ferroelectric transitions (which may be generalized to include deformable dipoles) gives  $C$  in terms of the number of unit dipoles per unit volume ( $N$ ), the elementary dipole moment ( $\mu$ ) and Boltzmann's constant ( $k_B$ ) as  $C \approx 4 \pi N \mu^2 / k_B$ . This suggests larger values for  $N$  and  $\mu$  in the ferroelectrics usually considered as prototypically displacive like  $\text{BaTiO}_3$ .

The history of the theoretical understanding of the phenomenon of ferroelectricity is one of slow progress over the years in the both fronts, the microscopic structural, lat-

tice dynamical front, and, to a lesser extent, also in the thermodynamic, phenomenological front. The crystal structure of the first known ferroelectric, Rochelle Salt, is so complicated that the chances of success of a microscopic theory, first attempted by Kurchatov (1933), along a line similar to that of the theory of Weiss for ferromagnetism, were very small. The statistical theory of Slater (1941), in which the arrangement of dipolar units ( $\text{H}_2\text{PO}_4$ ) is linked by H-bonds, depicting KDP, was somewhat more successful, but only qualitatively. About twenty years later, Blinc would introduce quantum tunneling to describe the huge isotope effect in this ferroelectric. But it was the discovery by Wul and Goldman of ferroelectricity in  $\text{BaTiO}_3$  (1945, 1946) followed by other perovskites, such as  $\text{KNbO}_3$  and  $\text{KtaO}_3$  (Matthias 1949),  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  (Matthias and Remeika, 1949 and  $\text{PbTiO}_3$  (Shirane, Hoshima and Suzuki, 1950), as well as the almost simultaneous discovery of antiferroelectricity in  $\text{ZrTiO}_3$ , which shifted attention to the theoretical description of ferroelectric and antiferroelectric phenomena in a really much simpler structure, the perovskite structure, much more amenable to microscopic investigation. Mason and Matthias (1950) did propose a simple microscopic model to describe Ferroelectricity in  $\text{BaTiO}_3$ , in which the small  $\text{Ti}^{4+}$  ion surrounded by six oxygen ions is depicted as being in an off center six fold potential well minimum, giving rise to a unit dipole, capable of undergoing order-disorder changes under the influence of both thermal energy and the electrostatic energy of the effective local field in which the cooperative influence of all other neighboring unit dipoles predominates. This model was then strongly criticized by Jaynes, using arguments apparently plausible but, not too well founded and it was used latter as starting point for improved statistical models.

Independently, Slater (1950) pointed that the ferroelectric behavior of  $\text{BaTiO}_3$  could be caused by long-range dipolar forces (via the Lorentz local effective field) competing with local short-range forces. Latter this provided the basic framework to describe the phase transition in displacive type ferroelectrics.

Mueller (1940), and later Ginzburg (1945, 1949) and Devonshire (1949, 1951, 1954) were the first to propose macroscopic, thermodynamical theories of ferroelectricity. Devonshire's theory, which described in detail the successive phase transitions in  $\text{BaTiO}_3$ , (from cubic to tetragonal, from tetragonal to orthorhombic and from orthorhombic to rhombohedral) became the paradigm of a phenomenological theory for ferroelectricity, and has remained so through several decades.

In 1960 Anderson and Cochran recasted the microscopic theory in terms of crystal lattice dynamics, and predicted successfully the existence of "soft-modes", later observed by neutron, infrared and Raman scattering.

A selection of representative papers from Valasek to Cochran is given in the first section of this book. Then from the first historic International Meeting on Ferroelectricity in 1966, one can follow better the ups and downs of research in ferroelectric materials and ferroelectric transitions, through the series of International and European Meetings of which the last one was, for the moment, the 10<sup>th</sup> International Meeting on Ferroelectricity, held in Madrid in September 3 to 7, 2001. The Organizing Committee was happy to count on such distinguished speakers as Profs. Blinc, Ginzburg, Müller for the Opening Session, which was inaugurated by the Minister of Education, Culture and Sports of Spain Dr. Pilar del Castillo, accompanied by the Chancellors of the main Universities in Madrid.

To understand the impressive developments which have taken place since the discovery of Rochelle salt and then Barium Titanate to our days it is necessary to take account of the great variety and large amount of materials discovered since then presenting ferroelectric properties, from the oxides and inorganic salts to the polymers, liquid crystals and biological tissues.

This large variety of materials has made possible numerous applications of linear and non-linear dielectric properties so that ferroelectrics constitute now a large section in the field of advanced functional materials with an important share in the market. The possibility of presenting the ferroelectric material in various forms: mono and polycrystalline, meso and nano structured, massive and thin film, allows the use of ferroelectrics in the most diverse technology applications, from devices to transform high power energy to integration in silicon electronic devices in the new technologies. In this respect it is not an exaggeration to say

that ferroelectric materials make up now a strong and well defined chapter of the Science and Technology of Materials.

At the same time the ease of preparation has allowed that, not only in advanced countries but in developing countries also, competitive scientific research in these materials has been possible contributing substantially to their technologic and social development.

The importance of ferroelectric materials is well attested by the series of current scientific meetings: the ISAF in the USA, the ECADP in Europe, the monographic ones regularly held in Japan and Russia. In all of them the number of contributors grows steadily.

All of this foretells a promising future for Ferroelectricity and ferroelectric materials.

Madrid, September 2004

*Julio A. Gonzalo*  
UAM, Madrid

*Basilio Jiménez*  
CSIC, Madrid