Electrical and optical properties of materials
John JL Morton

Part 3: Piezo- pryo- and ferro-electricity

We have already seen in the discussion of dielectric properties of materials that (apart from the absence of *dia*-electricity), electrical and magnetic properties are closely analogous with each other. In this part of the course, we shall consider a further analogy: *ferro-electricity* and ferromagnetism[1]. We shall also investigate related phenomena of piezo- and pyro-electricity.

In ferromagnetism, a necessary condition is that the materials should consist of alignable magnetic dipole moments. Similarly, ferroelectric materials require some electric dipole, which in turn means they must *lack a centre of symmetry*. Electric dipoles, arising from charge, can exert strong influences on the structure of the material, in contrast to magnetic dipoles, which arise from spin.

	32 crystal classes	
	↓	
of which	21 lack centre of symmetry	and 11 are centro-symmetric
	↓	
of which	20 exhibit piezo-electricity (piezoelectric classes)	and 1 (class 43) which is too symmetric and doesn't
	↓	
of which	10 exhibit pyro-electricity (polar classes)	and 10 don't (non-polar classes)
	↓	
of which	some are ferro-electric	and some are not ferro-electric

Table 3.1: Piezo-, pyro- and ferro-electric crystal classes

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[1]The *ferro* in ferro-electricity arises purely because of the analogy to ferromagnetism, and not because of any link to iron!

3.1 Piezo-electricity

Piezo-electricity is the property of a crystal to exhibit electric polarisation P under the influence of an applied mechanical strain S, or (vice versa) to exhibit a mechanical strain under the influence of an applied electric field E. Formally:

$$(3.1)$$

where d_p is the piezoelectric coefficient and sT is the standard elastic compliance term, given compliance s and applied stress T. The additional strain $d_p E$ arises from the piezo-electric effect. We can also express the converse case in terms of the polarisation:

$$(3.2)$$

In addition to $\chi_e \epsilon_0 E$, the polarisation arising from some external electric field E, we have $d_p T$ the additional polarisation arising from the piezo-electric effect.

Note that other definitions for the piezoelectric coefficient are also used (e.g. the electric field generated per unit strain). In each case, looking at the units should tell you how the coefficient is being defined if it isn't stated explicitly.

Study of simple 2D structures will convince you that a necessary condition is that the structure should lack a centre of symmetry (see Figure 3.1 for an example). Of the 32 crystal classes, or point groups, 21 lack a centre of symmetry (see Table 3.1), but of these only 20 exhibit piezo-electricity [2]. All crystals in these 20 classes are piezo-electric to some extent.
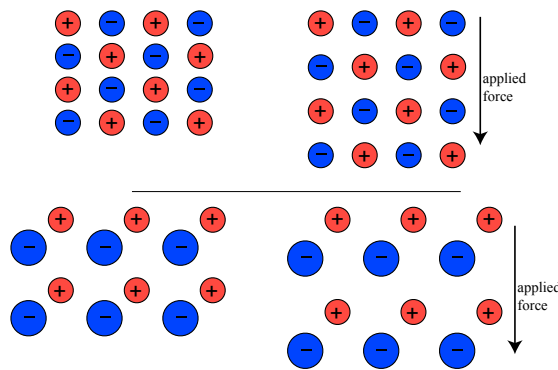

Figure 3.1: The importance of a lack of centre of symmetry for piezo-electricity

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[2]The odd one out is cubic class 43 which has high symmetry in other respects

3.1.1 Applications for piezo-electrics

Transducers

The relationship between mechanical strain and electric field found in piezo-electric materials can be exploited in transducers. For example:

a) mechanical $\rightarrow$ electrical	record player "crystal" pick-up, strain gauges, cigarette lighters
b) electrical $\rightarrow$ mechanical	production of ultrasonic waves, earphones

Oscillators

In general, the polarisation either lags or leads with respect to the applied field, but when the frequency is right (matching the natural frequency of the crystal), standing waves are set up. This resonance is very sharp and stable and is exploited in quartz oscillators, crystal clocks and buzzers. A cube of quartz, for example, has a series of mechanical resonances when its physical length L is an integer number of half-wavelengths: $L = n\lambda/2$. We can relate this to a frequency using the speed of sound v_s in the material ($v_s = f\lambda$). Hence, the lowest frequency resonance will occur at $f = v_s/2L$. By placing the crystal between two plates, in a capacitor-like arrangement, it is possible to create an electrical component with a very stable resonant frequency (about a part in 10^{8-9}), much higher than a typical RC circuit. The resonance frequency will only depend on the crystal geometry — the crystal may then be placed in a temperature-controlled environment for greater accuracy.

3.2 Pyro-electricity

From the Greek *pyr* (fire), and known by the Ancient Greeks[3], pyro-electricity refers to the generation of (often temporary) polarisation in a material on heating or cooling. Ten of the twenty piezo-electric classes exhibit pyro-electricity and in general must be those classes which contain permanent dipoles — i.e. the ten polar classes. It would, however, be very strange indeed if room temperature were to be the exact temperature at which the dipoles cancelled out internally. The explanation of the general case is that the crystals are always spontaneously polarised to some extent, but resulting surface charges are cancelled out by charges absorbed from the surroundings. On heating or cooling, the internal anisotropy changes, causing the internal

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[3]The first reference to the pyroelectric effect is in writings by Theophrastus in 314 BC, who noted that tourmaline attracted bits of straw and ash when heated.

polarisations to change in ways with which the external compensating charges do not keep pace.

3.2.1 Applications for pyro-electrics

In principle the materials are useful for thermometry, but they are largely unreliable when in air. As a result, they are not often used for *absolute* measurements of temperature, but rather sudden (and possibly small) changes. This time-temperature dependence is made use of in television cameras (e.g. plumbicon detectors), as well as passive infrared detectors capable of detecting human body radiation. The figure-of-merit for pyro-electrics in such applications is the (vector) *pyro-electric coefficient* $\mathcal{P} = \partial P/\partial T$ — the rate of change of polarisation with temperature.

One more recent potential application is the generation of large (temporary) polarisations by quickly changing the temperature of a pyro-electric material. Such fields can then be used to accelerate ions or other charged particles.

3.3 Ferro-electricity

Ferro-electrics are in a sub-group of the pyro-electrics in which the direction of spontaneous polarisation may be reversed by the application of an electric field. This last property is not determined by crystal class: usually it is only an experimentally determined parameter for a given material.

As in the case of ferromagnetism (to be discussed in much greater detail in the coming course on Magnetic Properties of Materials), there exists a temperature, the ferro-electric Curie temperature, above which the material is not ferro-electric (it is then just para-electric). Associated with this temperature are anomalies in i) specific heat, ii) perhaps a latent heat and, because of electrostrictive effects (dimensional changes brought about by the basic piezo-electricity of the material) changes in iii) lattice parameters and iv) symmetry. The high-temperature phase will in general have the higher symmetry — the necessary loss of symmetry occuring spontaneously on cooling through the Curie temperature. However, the situation in the ferro-electric is rather more complicated that that of the ferromagnetic as certain materials are only ferro-electric over a fixed range of temperatures (rather than just below a certain temperature). For example, Rochelle salt ($NaKC_4H_4O_6.4H_2O$) is ferro-electric only between $-18°$ and $+23°$.

A satisfactory explanation of ferro-electricity is still the subject of active research — a simple dipole theory (analogous to the Weiss theory of ferromagnetism) is not correct, and the other models put forward lie beyond
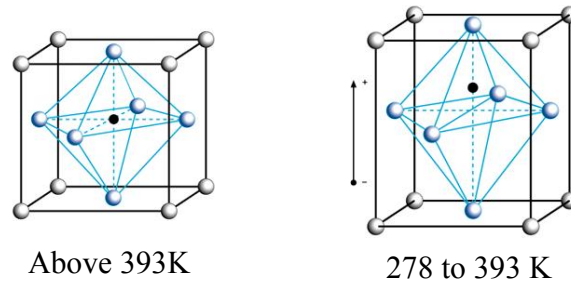
Above 393K   278 to 393 K

Figure 3.2: Barium titanate is ferroelectric in the range 298-393 K

the scope of this course. That said, one indication of the origin of the phenomenon comes from the so-called *ferro-electric catastrophe*. Consider two ions A & B separated by a distance a (see Figure 3.3). If A has an instantaneous electric dipole moment p, then this will tend to polarise B and vice versa. The field at B from the dipole A is:

$$(3.3)$$

If the polarisability of B is α_B then the dipole:

$$(3.4)$$

If this dipole p_B is greater than the dipole which is producing it, p_A then the system will escalate to complete polarisation, i.e. the ferro-electric state. The condition $p_B > p_A$ is satisfied when:
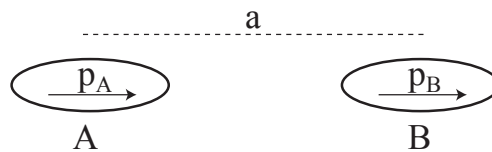
$$(3.5)$$

Figure 3.3: The ferro-electric effect

3.4   Ferro-electric domains and hysteresis loops

As in the ferromagnetic case, a *domain* is a region in which the direction of spontaneous polarisation is uniform. The domains are separated by domain

walls. Under the influence of an applied field, a piece of material of ideal geometry (needle-shaped with field applied parallel to its length) will polarise in an hysteretic way, as shown in Figure 3.4. There are some differences between this and the ferromagnetic case:

a. Polarisation rotation cannot occur as the direction of polarisation is fixed by the structure — there are a fixed number of crystallographic directions along which polarisation may occur. In the orthorhombic structure of Rochelle salt, for example, only one direction (+ and −) is possible, analogous to a uniaxial ferromagnet such as cobalt. In tetragonal barium titanate there are three possible directions (each + or −) resulting from the higher temperature cubic structure, which leads to a more complicated domain structure.

b. In general, domain growth is favoured in the 'forward' direction, i.e. long domains tend to grow even longer. This indicates that, unlike the ferromagnetic case, the 'head-to-tail' coupling is stronger than the 'sideways' interaction. As a result, domains and domain walls can be very narrow, leading to applications in computer memories.
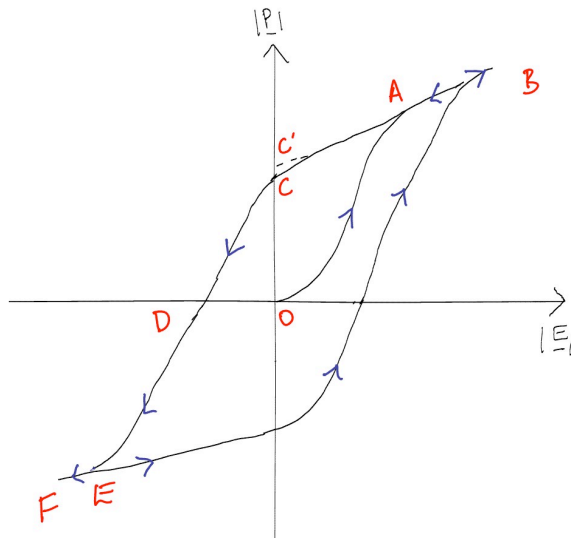

Figure 3.4: Hysteresis loop of a typical ferro-electric

Despite these differences, the resulting hysteresis loop is similar. On applying an increasing electric field near a principal polarisation direction, the polarisation path OAB is traced to saturation (the residual slope comes from an addition para-electric term $P_{para} = \chi\epsilon_0 E$). Reduction of the electric

field along BAC is almost a straight line (P_{para} is reduced back to 0). The deviation from the linear case (BAC') to the actual case (BAC) is due to a suppression of free poles at $E \approx 0$. The coercive field OD is then required to reduce the polarisation to zero. As in the ferromagnetic case, the area enclosed within the hysteresis curve is a measure of the energy less per cycle under AC conditions — smaller loops are traversed if the field is lower than required for saturation.

As an example, barium titanate $BaTiO_3$ (perovskite structure at a high temperature and tetragonal below T_c) has values:

$$\begin{array}{ll} \text{Remnant polarisation } OC & 6 \times 10^{-2} \text{ Cm}^{-2} \\ \text{Coercive field } OD & -8 \times 10^4 \text{ Vm}^{-1} \end{array}$$

Liquid crystal displays, described later on, have a typical coercive field of 150kV/m.

3.5   Applications of ferro-electrics

Uniaxial materials in particular have appeal as potential computer memory elements, with 0 and 1 represented by the $+$ and $-$ polarisations in each domain. The reduced 'sideways' coupling between adjacent domains means that one piece of single crystal could potentially carry a large number of bits without significant cross-talk. Electrodes for the digits can be on the scale of 10s to 100s of nm.

In 2004 Fujitisu released a 1Mbit FeRAM (Ferroelectric random access memory) using 350 nm process technology), claiming 10^4 faster write times with an order of magnitude less power, compared to EEPROM. The number of re-write cycles in FeRAM chips is also claimed to be several orders of magnitudes greater.

More recently in 2009, Toshiba announced the prototype of FeRAM with 128Mbits (16MBytes) with read/write speeds of 1.6GB/s, claiming the record for highest-bandwith, highest-density non-volatile memory.

Examples of materials used in FeRAM production are lead zirconate titanate (PZT or $Pb(Zr,Ti)O_3$) and bismuth ferrite ($BiFeO_3$, or BFO). PZT has lower charge storage capability (polarisation versus applied electric field, per unit volume), and hence the lower limit on useful cell dimensions is predicted to be $\sim$130 nm. Materials such as BFO have greater polarisability and are being actively pursued for the next generations of FeRAM devices.
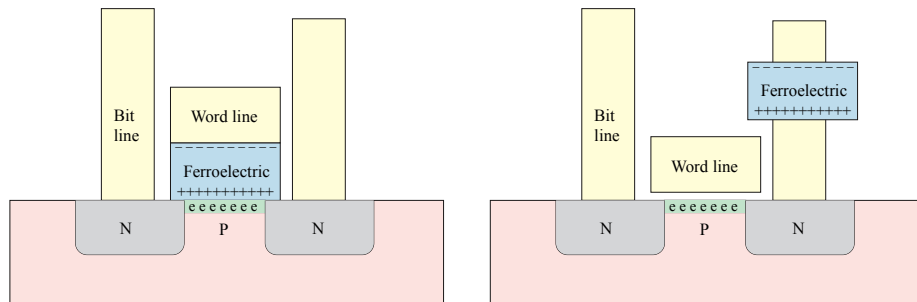
Figure 3.5: Schematic of two FeRAM cells, showing how the word and bit lines are used to address a particular cell. The scheme on the left incorporates the ferroelectric into the transistor structure, as employed in Figure 3.6
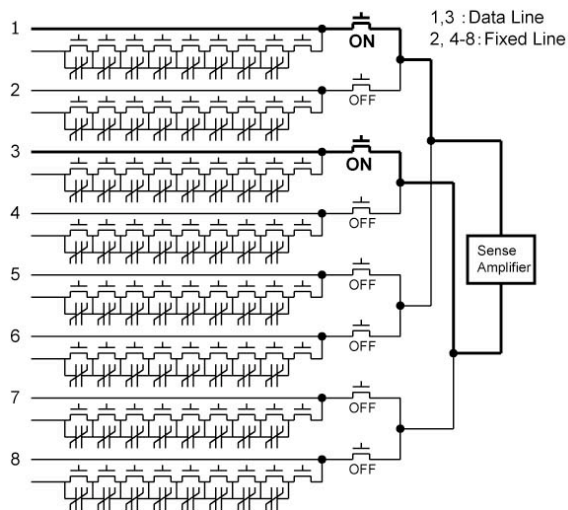

Figure 3.6: Schematic of Toshiba's 2009 FeRAM prototype. Neighbouring data lines are operating in sequence (one on, one off) in order to reduce noise between the lines