Novel ferroelectrics

While ferromagnetic materials have a long history, the first ferroelectric crystal[1], Rochelle salt, was identified as such as recently as 1922. The name itself is a misnomer since Rochelle salt (sodium potassium tartrate tetrahydrate) or other ferroelectrics for that matter do not contain iron. Many of them are water-soluble organic or inorganic compounds or oxides.

It is interesting to note that the closely-related properties of piezoelectricity and pyroelectricity in tourmaline (calcium aluminium silicate) were, according to Cady[2], 'recognized in Ceylon and India from time immemorial'. They were known as 'Ceylon magnets' when they were first brought to Europe around 1703 by Dutch merchants Canton in 1759 observed opposite polarizations on the freshly-exposed surface of a fractured tourmaline crystal and Brewster introduced the term 'pyroelectricity' in 1829.

The analogy with ferromagnets that led to the term 'ferroelectricity' is because of the observed spontaneous polarization which is reversible in nature. Thus, both classes are characterized by hysteresis loops, between dielectric displacement (D) and applied electric field (E) for ferroelectrics and between magnetization (B) and applied magnetic field (H) for ferromagnets. The work done in reversing the polarization (magnetization) is given, in both cases, by the area enclosed by the hysteresis curve, while the field required to reduce the polarization to zero is called the coercive field.

Another phenomenological similarity is that both types of materials have characteristic Curie temperatures T_c beyond which the spontaneous alignment of electric or magnetic dipoles vanishes, resulting in a paraelectric or a paramagnetic phase. The phase transition can be termed first- or second-order depending upon whether a characteristic parameter such as polarization goes to zero discontinuously as in the case of barium titanate or continuously as for triglycine sulphate (TGS). In the case of ferroelectrics the crystal structure often changes at the Curie temperature, e g. from tetragonal to cubic for barium titanate. One indication of such a phase transition is that the frequency of a lattice vibration in the crystal becomes 'soft', i e goes to zero as T_c is approached. Although this was demonstrated for the ferroelectric strontium titanate in the sixties, Raman and Nedungadi[3] had discovered this phenomenon while studying a phase transition in quartz using the Raman effect as far back as 1940!

Domain formation is again common to both ferroelectrics and ferromagnets These are regions of unidirectional polarization which arise spontaneously and can be made to grow by 'poling' in an external electric field, preferably at elevated temperatures. Domain walls in ferroelectrics are however much narrower, a few unit cells thick, due to the much weaker elastic forces compared with magnetic exchange energies Antiferroelectricity analogous to antiferromagnetism arises due to oppositely directed polarizations resulting in zero net polarization These similarities have led to the coining of the term 'ferroic' to describe both classes[4] and also to include a new class of 'ferroelastic' materials.

This is where the similarity ends because the physical origins of the two phenomena are quite different Ferromagnetism is due to the coupling between the magnetic moments of unpaired electrons, while ferroelectricity involves lattice distortion due to the interaction between ionic charges and vibrational modes. In both cases the ordered state arises because it is energetically favourable, i e. the energy of the system is lowered. Thus, classical macroscopic theories deal with calculation of the free energies of these systems.

Ferroelectrics are naturally expected to be ionic compounds in which separation between the centres of positive and negative charges in the polarized state gives rise to spontaneous dipole moment. They have high resistivity since residual electronic conductivity would result in internal charge neutralization. In fact, they do not manifest their properties like a lodestone because the bulk polarization is neutralized by free surface charges. Normally, one uses small 'keepers' between the magnet pole pieces to prevent demagnetization. Freshly exposed surfaces of fractured crystals are required to display electrostatic attraction and repulsion at opposite faces.

Piezoelectrics, pyroelectrics and ferroelectrics

Ferroelectricity is related to piezoelectricity[3], discovered in quartz (crystalline silica) by the brothers Pierre and Jacque Curie in 1880. From the point of view of crystal structure, absence of a centre of symmetry is obviously a prerequisite for both. Of the 32 crystal classes, it is now known that 20 show piezoelectricity – a change in electric polarization proportional to applied stress or its inverse, a change in dimensions due to an applied electric field Of these a subgroup of 10 classes are polar and show pyroelectricity – a change in polarization due to a change in temperature. Typical pyroelectrics are ZnS, ZnO and tourmaline. Among the pyroelectrics are some whose polarization can be reversed due to an applied electric field. These are the ferroelectrics such as ADP and KDP (ammonium and potassium dihydrogen phosphates), TGS (triglycine sulphate) as well as oxides such as barium titanate, lithium niobate and lithium tantalate. Thus, all ferroelectrics are pyroelectric and piezoelectric but not vice versa.

Piezoelectrics such as quartz are extensively used as transducers and highly stable oscillators. In fact, they are still the best time-keepers in electronic watches. More recent applications are as surface acoustic wave (SAW) devices, which can be used as filters, delay lines and signal correlators. Colour TV sets as well as cellular telephones contain SAW filters fabricated on lithium niobate.

The high dielectric constants, up to a few thousand or more, of ferroelectrics such as barium titanate have led to applications as small-area chip capacitors, which are, however, rather lossy compared to alumina and polymeric capacitors. Pyroelectrics such as TGS have started replacing conventional thermopiles as infrared (IR) detectors due to their higher responsivity and speed. The principle is simple – a small change in detector temperature due to absorbed radiation results in change in polarization, which can be detected across an output resistor. These detectors can operate at room temperature and have wide spectral range from the UV to the IR.

The optical properties of ferroelectrics are also unusual The highly nonlinear optical properties of transparent ferroelectrics such as KDP, ADP and the recently discovered barium betaborate (BBO) result in the efficient generation of second and higher harmonics of laser beams, permitting frequency conversion from the IR and red to the blue–green region. They can be used as electrooptic switches and modulators for modulating high-power solid-state lasers. They can also be used for mixing two optical signals, generating sum and difference frequencies such that a weak signal in the far IR can be frequency-shifted into the visible or near IR, where sensitive detectors are available.

Magnetic materials formed the basis of the first memory elements in computers. The two directions of magnetization are well suited for representing the binary digits 1 and 0. This is the principle of magnetic cores, tapes and discs. Ferroelectric memories were expected to be their natural counterparts. However, in spite of extensive research efforts, such memories could not be realized because of slow and irreversible depolarization. It was found that electric fields much less than the coercive field applied over a long period of time could switch the polarization, causing loss of information. Thus, although ferroelectrics with high dielectric constants can be used to store charge in a capacitor, as memory elements their performance cannot compare with magnetic and the now ubiquitous semiconductor memories.

Semiconducting ferroelectrics

Some ferroelectrics such as barium titanate are strictly not insulators since its energy band gap is ≈ 3 eV. The first semiconducting ferroelectric discovered in 1950 was the V–VI–VII compound SbSI, which has an indirect band gap of 1.4 eV and which shows photoconductivity. It has a Curie temperature of only 20°C and grows as thin dendrites. Another well-known example is GeTe, which belongs to the GeTe–SnTe family. However, since it has a low energy band gap of < 0.5 eV, the low resistivity makes it unsuitable for device applications.

Recently, Weil *et al.*[5] reported ferroelectric behaviour in $Cd_{1-x}Zn_xTe$ for $x = 0.04$–$0\,45$ – a member of the CdTe–ZnTe system – both the end members of which are not ferroelectric. However, the dielectric constants were relatively small, varying from 10.8 to 11.4 between 20 and 180°C in the ⟨1 1 0⟩ direction and reaching a maximum of 50 in the ⟨1 1 1⟩ direction for $x = 0.1$. The hysteresis loops were also not very rectangular in nature.

While examining the properties of anisotropic layer-type III–VI chalcogenides InTe and GaTe, Bose and Pal[6] attempted to dope p-GaTe using Ge. It was found that the resistivity in the $Ga_{1-x}Ge_xTe$ system increased rapidly, showing a maximum of $10^5\ \Omega$ cm at $x = 0\,1$. The relative dielectric constants in two orthogonal directions also increased monotonically, reaching 255 and 360, respectively, perpendicular and parallel to the layer planes at 300 K. A maximum value of 2510 was reached for $x = 0.49$ at the Curie point of 428°C. The Curie–Weiss law was obeyed and the phase transition shown to be of second order.

GaTe is a semiconductor with a direct band gap of 1.66 eV and shows photoconductivity. It has a monoclinic structure but does not show ferroelectric behaviour. Due to difficulties in crystal growth it has been little studied, unlike GaSe, which has a direct band gap of 2 eV, has shown laser action and is also a well-known nonlinear dielectric used for second harmonic generation. In the mixed phase GaTe–GeTe system, increase in Ge resulted in the band gap decreasing uniformly to 0 62 eV for $x = 0\,49$ The ferroelectric nature of the material was confirmed from $x = 0\,20$ to $x = 0.49$ through well-defined square hysteresis loops. At 300 K, for $x = 0.35$ the saturation polarization was found to be 5.75 $\mu C/cm^2$, twice that of TGS. This is equivalent to 3.6×10^5 electrons in a 1 μm^2 area of a memory device, which can be read with high signal-to-noise ratio. The coercive field of 85 kV/cm is equivalent to 8.5 V across a 1 μm film, which is adequate for device applications. One advantage of this new material is the much higher Curie temperature $T_c = 450$°C for $x = 0\,35$ compared to $T_c = 49$°C for TGS and 135°C for barium titanate, which may result in slower depolarization if the resistivity can be raised further by compensatory doping The composition also lends itself to deposition in thin-film form by techniques such as molecular beam epitaxy (MBE) on GaAs to form small-area chip capacitors or memory elements.

The nonlinear optical properties of GaTe and its alloys are yet to be evaluated but are expected to be superior to those of GaSe in the infrared because of the higher polarizability of Te compared to Se. Thus, it appears that these ferroelectric materials may show the way to interesting new applications

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