Ferroelectricity

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field.\textsuperscript{[1][2]}

The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek\textsuperscript{[3]}. Thus, the prefix ferro, meaning iron, was used to describe the property despite the fact that most ferroelectric materials do not have iron in their lattice.

Polarization

Most materials are polarized linearly with external electric field; nonlinearities are insignificant. This is called dielectric polarization (see figure). Some materials, known as paraelectric materials, demonstrate a more pronounced nonlinear polarization (see figure). The electric permittivity, corresponding to the slope of the polarization curve, is thereby a function of the external electric field. In addition to being nonlinear, ferroelectric materials demonstrate a spontaneous polarization (see figure). Such materials are generally called pyroelectrics. The distinguishing feature of ferroelectrics is that the direction of the spontaneous polarization can be reversed by an applied electric field, yielding a hysteresis loop.

Typically, materials demonstrate ferroelectricity only below a certain phase transition temperature, called the Curie temperature, $T_c$, and are paraelectric above this temperature.

Applications

The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. This fact makes ferroelectric capacitors smaller compared to dielectric (non-tunable) capacitors of similar capacitance.

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function. Indeed, ferroelectric capacitors are used to make ferroelectric RAM\textsuperscript{[4]} for computers and RFID cards. These applications usually thin films of ferroelectric materials as this allows the high coercive field required to switch the polarization to be achieved with a moderate voltage, though side effect of this is that a great deal of attention needs to be paid to the...
Ferroelectric polarisation

interfaces, electrodes and sample quality for devices to work reliably.[5]

All ferroelectrics are required by symmetry considerations to be also piezoelectric and pyroelectric. The combined properties of memory, piezoelectricity, and pyroelectricity make ferroelectric capacitors very useful, e.g., for sensor applications. Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. Also, the electro-optic modulators that form the backbone of the Internet are made with ferroelectric materials.

One new idea of recent interest is the ferroelectric tunnel junction (FTJ) in which a contact made up by nanometer-thick ferroelectric film placed between metal electrodes. The thickness of the ferroelectric layer is thin enough to allow tunneling of electrons. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electroresistance (GER) switching effect.

Another hot topic is multiferroics, where researchers are looking for ways to couple magnetic and ferroelectric ordering within a material or heterostructure; there are several recent reviews on this topic[6].

Materials

The internal electric dipoles of a ferroelectric material are coupled to the material lattice so anything that changes the lattice will change the strength of the dipoles (in other words, a change in the spontaneous polarization). The change in the spontaneous polarization results in a change in the surface charge. This can cause current flow in the case of a ferroelectric capacitor even without the presence of an external voltage across the capacitor. Two stimuli that will change the lattice dimensions of a material are force and temperature. The generation of a surface charge in response to the application of an external stress to a material is called piezoelectricity. A change in the spontaneous polarization of a material in response to a change in temperature is called pyroelectricity.

Ferroelectric phase transitions are often characterized as either displacive (such as BaTiO₃) and order-disorder such as NaNO₂), though often phase transitions will have behavior that contains elements of both behaviors. In barium titanate, a typical ferroelectric of the displacive type, the transition can be understood in terms of a polarization catastrophe, in which, if an ion is displaced from equilibrium slightly, the force from the local electric fields due to the ions in the crystal increases faster than the elastic-restoring forces. This leads to an symmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment. The ionic displacement in barium titanate concerns the relative position of the titanium ion within the oxygen octahedral cage. In lead titanate, another key ferroelectric material, although the structure is rather similar to barium titanate the driving force for ferroelectricity is more complex with interactions between the lead and oxygen ions also laying an important role. In an order-disorder ferroelectric, there is a dipole moment in each unit cell, but at high temperatures they are pointing in random directions. Upon lowering the temperature and going through the phase transition, the dipoles order, all pointing in the same direction within a domain.

An important ferroelectric material for applications is lead zirconate titanate (PZT), which is part of the solid solution formed between ferroelectric lead titanate and anti-ferroelectric lead zirconate. Different compositions are used for different applications, for memory application PZT closer in composition to lead titanate is referred, whereas piezoelectric applications make use of the diverging piezoelectric coefficients associated with
The morphotropic phase boundary that is found close to 50/50 composition.

In 1979 Swedish Sven Torbjörn Lagerwall discovered ferroelectric liquid crystals in collaboration with Noel Clark. The technology allows the building of flat-screen monitors. Mass production began in 1994 by Canon, who bought the license.

Ferroelectric crystals often show several transition temperatures and domain structure hysteresis, much as do ferromagnetic crystals. The nature of the phase transition in some ferroelectric crystals is still not well understood.

The ferroelectric effect also finds use in liquid crystal physics by incorporation of a chiral dopant into an achiral nematic C matrix. These liquid crystals exhibit the Clark-Lagerwall effect\textsuperscript{[7]} that causes a change from one istable state to another upon switching of electric field direction.
Barium titanate

From Wikipedia, the free encyclopedia

Barium titanate is an oxide of barium and titanium with the chemical formula BaTiO₃. It is a ferroelectric ceramic material, with a photorefractive effect and piezoelectric properties. It has five phases as a solid, listing from high temperature to low temperature: hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral crystal structure. All of the structures exhibit the ferroelectric effect except cubic. Barioperovskite is a very rare natural analogue of BaTiO₃, found as microinclusions in benitoite.

Properties

Barium titanate has the appearance of a white powder or transparent crystals. It is insoluble in water and soluble in concentrated sulfuric acid.

Manufacture

Barium titanate can be manufactured by liquid phase sintering of barium carbonate and titanium dioxide, optionally with other materials for doping.

High purity barium titanate powder is reported to be a key component of new barium titanate capacitor energy storage systems for use in electric vehicles.¹

Uses
Barium titanate is used as a dielectric material for ceramic capacitors, and as a piezoelectric material for microphones and other transducers. The Curie point of barium titanate is 120 °C. As a piezoelectric material, it was largely replaced by lead zirconate titanate, also known as PZT.

Polycrystalline barium titanate displays positive temperature coefficient, making it a useful material for thermistors and self-regulating electric heating systems.

Fully-dense nanocrystalline barium titanate has 40% higher permittivity than the same material prepared in classic ways.[2]

Barium titanate crystals find use in nonlinear optics. The material has high beam-coupling gain, and can be operated at visible and near-infrared wavelengths. It has the highest reflectivity of the materials used for self-pumped phase conjugation (SPPC) applications. It can be used for continuous-wave four-wave mixing with milliwatt-range optical power. For photorefractive applications, barium titanate can be doped by various other elements, e.g. iron.[3]

The addition of inclusions of barium titanate to tin has been shown to create a bulk material with a higher viscoelastic stiffness than that of diamonds. Barium titanate goes through two phase transitions that change the crystal shape and volume. This leads to composites where the barium titanates have a negative bulk modulus (Young's modulus), meaning that when a force acts on the inclusions, there is displacement in the opposite direction, further stiffening the composite.[4]

Thin films of barium titanate display electrooptic modulation to frequencies over 40 GHz.[5]

The pyroelectric and ferroelectric properties of barium titanate are used in some types of uncooled sensors for thermal cameras.

See also

- Strontium titanate
- Lead zirconate titanate

References

Question

How are ceramic capacitors constructed?

Answer

**Dipped Ceramic Capacitors.** The simplest ceramic capacitor consists of a square or circular shaped ceramic with electrodes attached (see figure). The capacitance is given by

\[ C = \frac{\varepsilon_0 K_d A}{d} \]

where \( A \) is the area of the two plates, \( \varepsilon_0 \) is the dielectric permittivity of vacuum, \( K_d \) is the dielectric's dielectric constant and \( d \) is the distance between the two plates.

Manufacturing starts with finely powdered base ceramic material that are pressed into dies and fired at high temperatures. Individual capacitors may be cut from large sheets of ceramic material. The capacitor electrodes (i.e. the plates) are attached by screen printing a mixture of silver, finely powdered glass, and a binder on both sides of the disk, and firing the ceramic element again. This evaporates the binder, and the melted glass binds the silver to the ceramic surface. Next, hairpin wires are clipped onto the capacitor and it is dipped in solder. Once cooled the capacitor is dipped into paint, marked, and the lower ends of the hairpin cut off. Clearly the whole process lends itself to automation, and dipped ceramic capacitors are very inexpensive. Capacitor characteristics depend on the type of ceramic used.

![Dipped ceramic capacitor construction](image)

Dipped ceramic capacitor construction. (a) Capacitor after electrode and hairpin attachment. (b) Capacitor after dipping and marking.

**Monolithic/Multilayer Ceramic Capacitors.** MLC capacitors are marvels of modern material science. Manufacturing MLC capacitors is considerably more complicated than manufacturing dipped ceramic capacitors. First, the base ceramic material is mixed with a binder and fashioned into thin sheets. Electrodes are painted onto one side of the sheets using a paint that consists of a liquid binder with fine metal particles in suspension. The metals that are used include gold, palladium, platinum, and silver alloys. The reason for using these metals is that when the base ceramic is fired, oxygen is required for the ceramic proper to form. If one uses a metal such as iron, for example, it would oxidize completely during the firing process. Precious metals do not have this problem, but is a
major cost component of monolithic ceramic capacitors. However, recently some manufacturers have reported using nickel and copper for the electrodes. This promises to reduce the cost of the raw materials, but at the expense of more elaborate manufacturing processes.

Once the ink is dry, the sheets are stacked on top of each other. The painted electrodes are arranged so that alternate electrodes exit from opposite ends. The top- and bottom-most layers do not have painted electrodes. The laminated layers are then compressed and fired, which sinters them into one monolithic structure.

Next, the ends are terminated, often using silver. For leaded capacitors, wires are attached, and finally the capacitor is encapsulated in plastic and marked. In the case of chip capacitors, the silver end terminations are covered with tin to aid soldering. The whole capacitor may be covered with lacquer.

References

- **Kemet.** A major manufacturer of MLC capacitors. The site has several good technical articles, including electron microscope photographs of cross sections of MLC capacitors.
- **Panasonic.** A major manufacturer of a wide array of electronic products and components, including MLC capacitors.
- **AVX** is a major capacitor manufacturer and has an extensive line of MLC chip capacitors.