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Capacitance and Ferroelectrics

A voltage V applied across a capacitor of caacitance C allows a quantity Q of charge to be stored. Then

$$C = \frac{Q}{V}$$

The units are Coulombs/Volt or Farad (F).

In a parallel plate capacitor, if the area of the plates in A, the separation between them l, then if there is a vacuum in the capacitor (between the plates) the capacitance is obtained from:

$$C = \epsilon_0 \frac{A}{l}$$

where ϵ_0 is the permittivity of vacuum, a constant having the value 8.85×10^{-12} F/m. If a dielectric material is inserted into this region, then the equation modifies to:

$$C = \epsilon \frac{A}{l}$$

where ϵ is the dielectric constant of the medium. It is convenient to consider the relative dielectric constant

$$\epsilon = \epsilon_r \epsilon_0$$

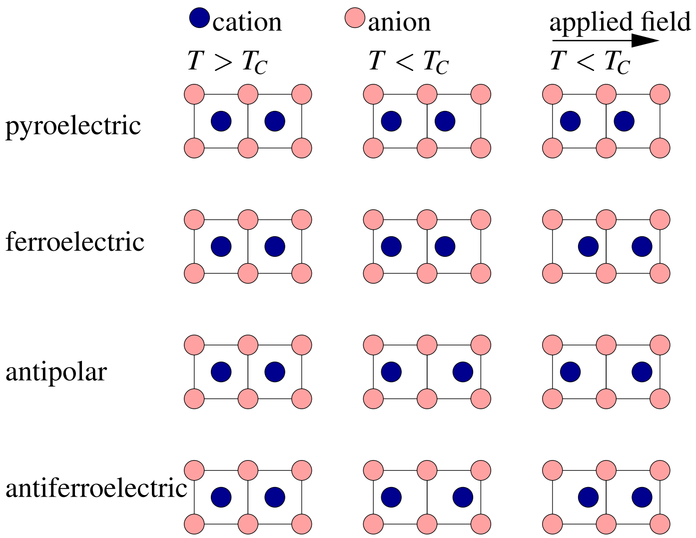
The relative dielectric constants of different media typically vary between 1 and 100. Water is about 80. Certain special materials (such as relaxor ferroelectrics) have ϵ_r running into the 1000s. The dielectric constant is usually frequency dependent (see Callister).

If an electric field $\mathcal{E}$ is applied on a sphere of dielectric constant ϵ, then the surface charge density D of the sphere is

$$D = \epsilon_0 \mathcal{E} + \mathcal{P}$$

Where P is the electric polarization — the number of electric dipoles per unit volume.

Crystals comprising cations and anions can be classified into four types, according to their *polar* behavior:

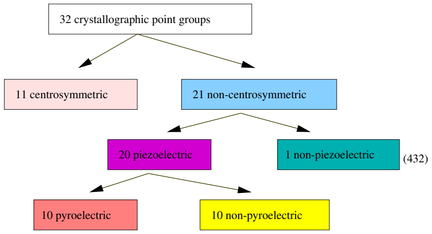


Piezoelectric materials: There is coupling between electrical and mechanical energies. For example, an applied stress results in the generation of polarization.

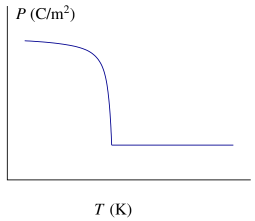
Pyroelectric materials: A material with a temperature dependent polarization. This requires a unique polar axis.

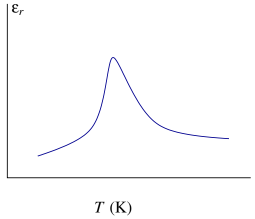
Ferroelectrics: A subgroup of pyroelectric materials in which the spontaneous polarization can be reoriented between "equilibrium" states by applying an electric field. All ferroelectrics are both pyroelectric and piezoelectric.

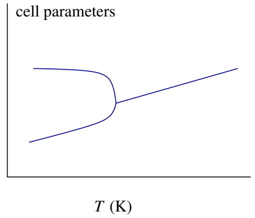
The possibility of inorganic crystals being polar (pyroelectric or piezoelectric) is strictly a function of their point group symmetry:



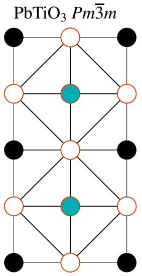
The ferroelectric phase transition (for example, in $PbTiO_3$) is characterized by the development of a spontaneous (zero field) polarization, changes in the dielectric constant, and crystal structural changes.:

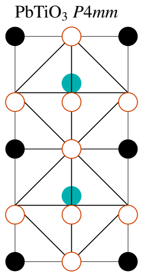




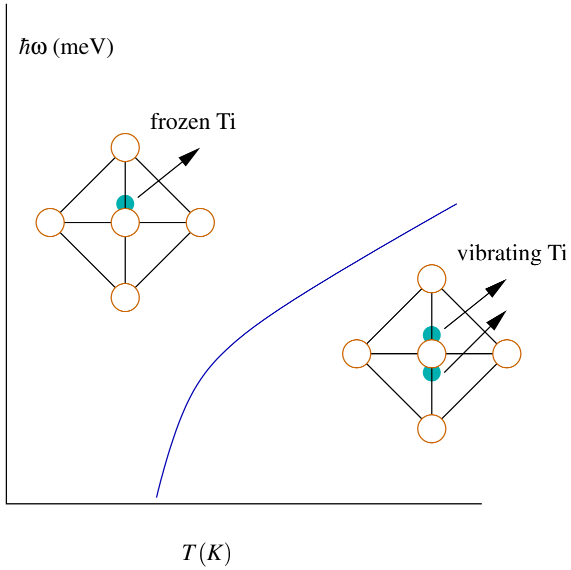


At the origins of such a phase transition are developments of a dipole within the unit cell, due to the centers of positive and negative charges not coinciding:



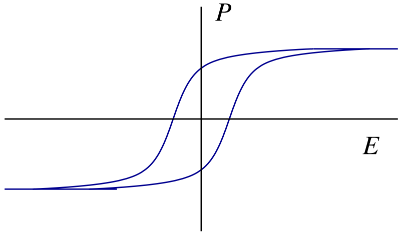


In the particular case of $PbTiO_3$, the phase transition from the cubic, paraelectric phase to the tetragonal ferroelectric phase (a displacive phase transition) is associated with the freezing of a phonon mode that is referred to as the "soft mode". Phonon modes are specific vibrational modes of the crystal lattice. In the case of $PbTiO_3$, this phonon mode is associated with the Ti atom in the center of the octahedron:



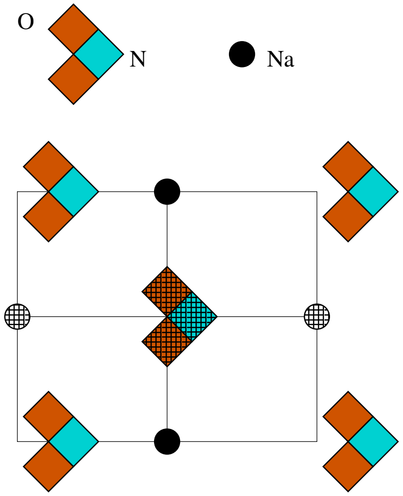
The frequency (energy) of the soft mode goes to zero as the phase transition is approached.

Ferroelectric materials are also characterized by hysteresis of the polarization below the ferroelectric T_C, just as are ferromagnets are characterized by a hysteresis of the magnetization:



As is true for ferromagnets, the hysteretic behavior is a consequence of the presence of domains in the material.

Some materials undergo an *order-disorder* phase transition from the paraelectric phase to the ferroelectric phase. An example is $NaNO_2$ (sodium nitrite):

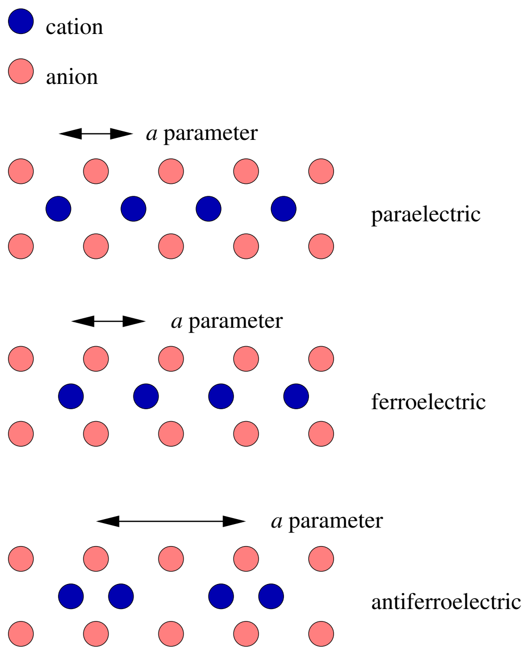


Room temperature ferroelectric structure of $NaNO_2$ projected on (001). The rigid NO_2^- groups have been shown as little chevrons, and the Na^+ ions as circles. Hatching indicates that the atoms are at a height of -1/2.

Above the phase transition at 438 K, the structure is non-polar and has the $Immm$ space group. Below this temperature, the material is ferroelectric and has the space group $Im2m$; the ferroelectric structure is displayed.

The dipole moment is lost in the high temperature structure because of disorder. Half the chevrons point to the left and half to the right, and correspondingly, the Na ions also occupy two different sites at random.

Antiferroelectrics: These are usually characterized by antiparallel dipole moments in the unit cell. The formation of antiparallel moments (as in antiferromagnetic systems) results in the formation of larger unit cells.



An example of an antiferroelectric is $PbZrO_3$, which is cubic ($Pm\overline{3}m$), paraelectric above 503 K. Below this temperature, a combination of *two* effects, the tendency of the ZrO_6 octahedra to tilt as a consequence of the tolerance factor being less than 1, and the tendency of the Pb^{2+} ions to go off-center, result in the antiferroelectric, orthorhombic crystal structure.

Antiferroelectrics do not display hysteresis, except at high fields, where they develop separate loops at positive and negative fields. A similar dependence of magnetization on the magnetic fields is seen in *metamagnets*.