Kap. 11
Insulating solids

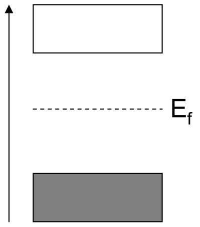
Conductors	Ag, Au, Fe, Ni, Cr
Semiconductors	Si, Ge, FeS_2, MnO_2
Insulators	MgO, Al_2O_3, TiO_2, polyethylene

Dielectrics

Insulators

-Localized electrons, bonds or on atoms

Dielectric constant, ε_r



$$q = \frac{\varepsilon_0 AV}{d}$$

$$q' = \frac{\varepsilon_r \varepsilon_0 AV}{d}$$

Capacitor

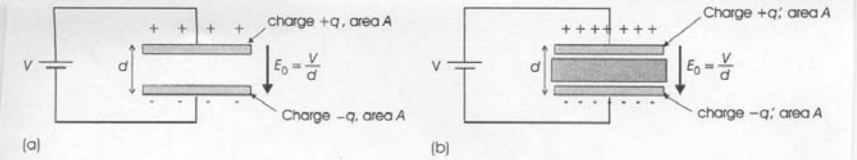


Figure 11.1 (a) Charges will accumulate on metal plates as a result of an applied voltage, V; the field between the plates, E_0, is equal to V/d. (b) A slab of dielectric (insulator) inserted between the plates will cause the charges on the plates to increase in proportion to its relative permittivity

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Dielectrics

The relative permittivity (dielectric constant, ε_r) describes the response of a solid to an electric field. -> Polarizability.

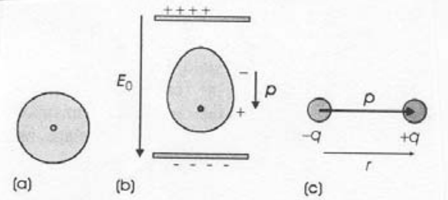


Figure 11.2 (a) For an atom in the absence of an electric field, the centres of gravity of the positive (nucleus) and negative (electrons) charges are coincident. (b) In an electric field these become separated to create a dipole. (c) An electric dipole consists of two equal and opposite charges separated by a distance r. The dipole moment is given by the vector $\boldsymbol{p}$, which points from negative to positive. The dipole gives rise to an electric field, $\boldsymbol{E}$, in the surrounding volume

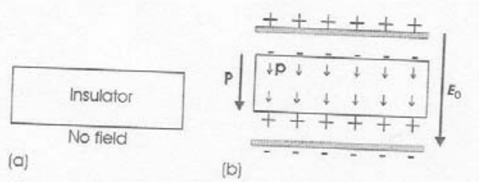


Figure 11.3 (a) In the absence of an applied electric field a dielectric has no surface charge. (b) In an electric field, $\boldsymbol{E}_0$, the material has a surface charge as a result of the formation of internal dipoles, $\boldsymbol{p}$, that induce an observable polarisation, $\boldsymbol{P}$

$$P = \varepsilon_0 \chi E_0$$

$$\chi = (\varepsilon_r\text{-}1)$$

$$P = \varepsilon_0(\varepsilon_r\text{-}1)E_0$$

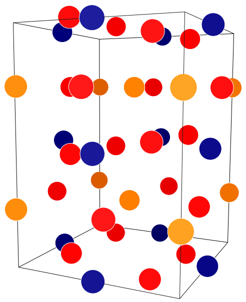
Dielectrics

The polarization of a material depends on the polarisability of a range of different effects.

Each constituent will be acted upon by a local electrical field.

$p = \alpha E_{loc}$ where E_{loc} is not necessarily the same as E_0

$$P = N \alpha E_{loc}$$



Dielectrics

Electronic polarisability, α_e

Ionic polarisability, α_i

Orientational polarisability, α_d

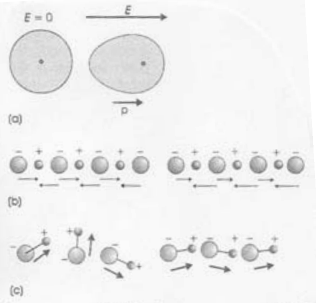
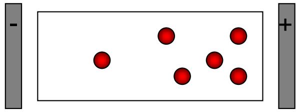


Figure 11.4 The effects of an electric field: (a) Electronic polarisation, (b) ionic polarisation and (c) orientational polarisation; dipoles are shown as arrows

Space charge polarisability, α_e



Bulk polarisability, α_e

$$\alpha_{tot} = \alpha_e + \alpha_i + \alpha_d + \alpha_s$$

Dielectrics

The different types of polarisation are frequency dependent

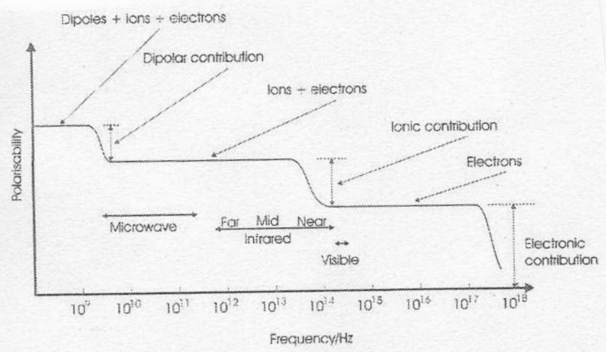


Figure 11.5 The contribution of electronic, dipole, ionic and orientation polarisability to the overall polarisability of a solid

$$n^2 = \varepsilon_r$$

Dielectrics

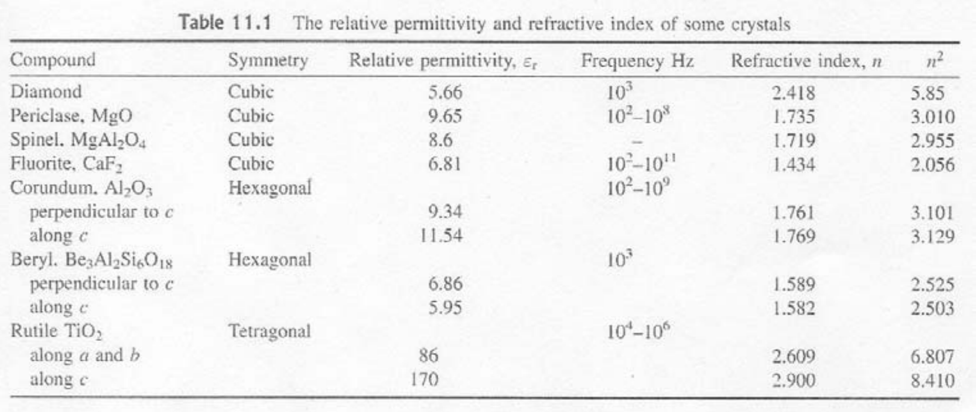


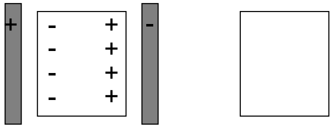
Table 11.1 The relative permittivity and refractive index of some crystals

Compound	Symmetry	Relative permittivity, ε_r	Frequency Hz	Refractive index, n	n^2
Diamond	Cubic	5.66	10^3	2.418	5.85
Periclase, MgO	Cubic	9.65	10^2–10^8	1.735	3.010
Spinel, $MgAl_2O_4$	Cubic	8.6	–	1.719	2.955
Fluorite, CaF_2	Cubic	6.81	10^2–10^{11}	1.434	2.056
Corundum, Al_2O_3	Hexagonal		10^2–10^9		
perpendicular to *c*		9.34		1.761	3.101
along *c*		11.54		1.769	3.129
Beryl, $Be_3Al_2Si_6O_{18}$	Hexagonal		10^3		
perpendicular to *c*		6.86		1.589	2.525
along *c*		5.95		1.582	2.503
Rutile TiO_2	Tetragonal		10^4–10^6		
along *a* and *b*		86		2.609	6.807
along *c*		170		2.900	8.410

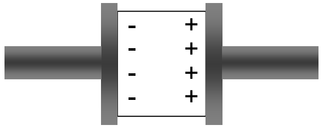
The polarization is not always isotropic

-electric

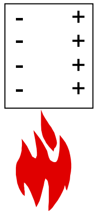
For normal dielectrics, the observed polarisation is zero in absence of an electric field.



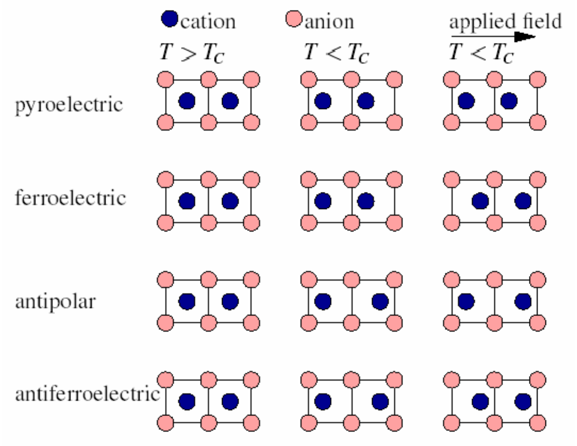
Piezoelectric materials develop a surface electric charge when subjected to mechanical stress.



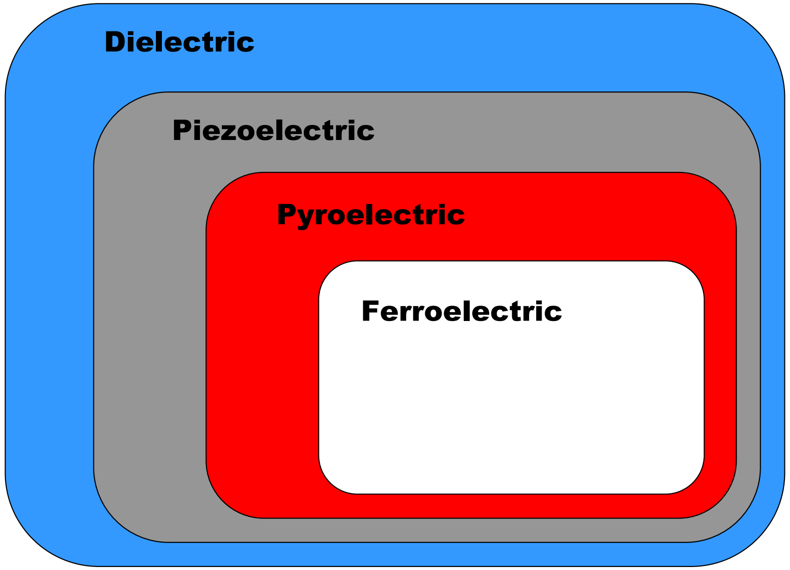
Pyroelectric materials develop surface charge when the temperature is changed.



-electric



-electric



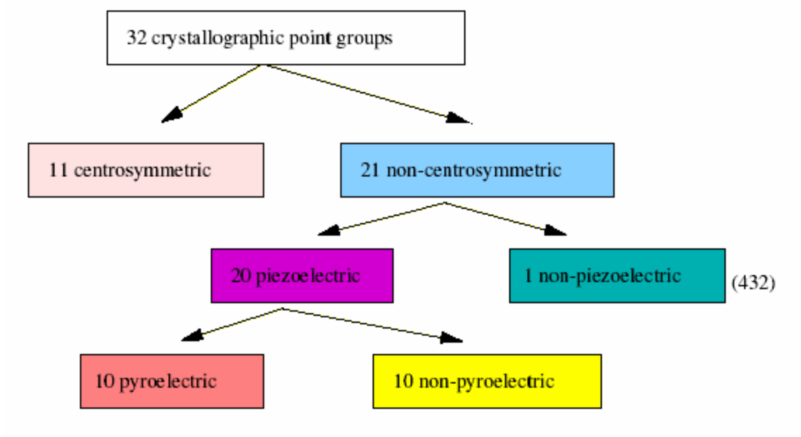
Dielectric

Piezoelectric

Pyroelectric

Ferroelectric

-electric



32 crystallographic point groups

11 centrosymmetric

21 non-centrosymmetric

20 piezoelectric

1 non-piezoelectric (432)

10 pyroelectric

10 non-pyroelectric

Piezoelectric, Metal-oxygen tetrahedra

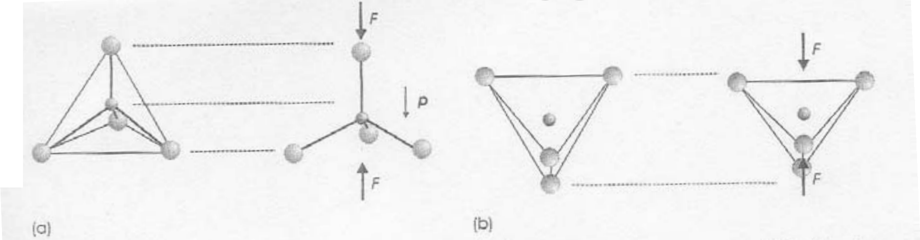
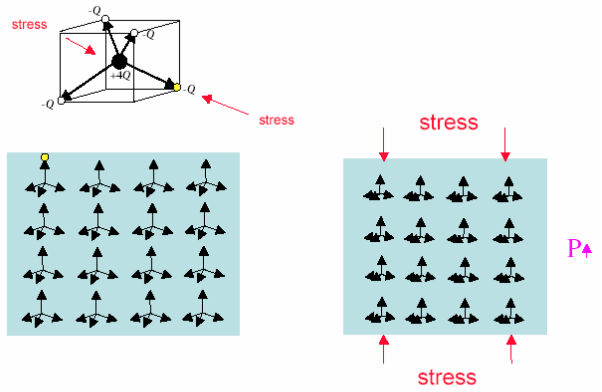


Figure 11.7 (a) A load, F, applied to a tetrahedron along a bond gives rise to a dipole as a result of distortion. (b) A load, F, applied perpendicular to a tetrahedron edge does not



Piezoelectric, dipole containing crystals

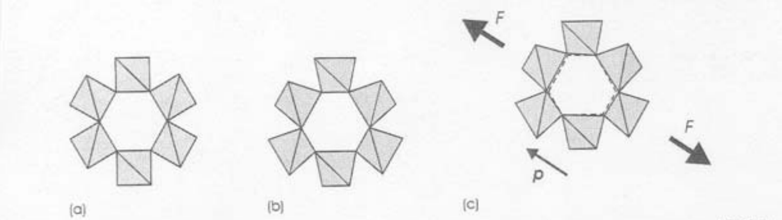


Figure 11.8 (a) Part of the idealised structure of high-temperature (β) quartz drawn as corner-connected [SiO_4] tetrahedra, projected down the c axis (note that the tetrahedra are arranged in a helix, not in rings). (b) Part of the structure of room-temperature (α) quartz; the tetrahedra are distorted and each gives rise to an electric dipole, but these add to zero in the unit shown and over a unit cell. (c) Application of a load, F, to the structure in the direction drawn distorts the structure from the unstressed form, shown as dotted lines, so that the dipoles no longer cancel. This leads to the overall dipole, p. Similar diagrams can be drawn for other directions; not all give rise to observable dipoles

Piezoelectric, Polymers

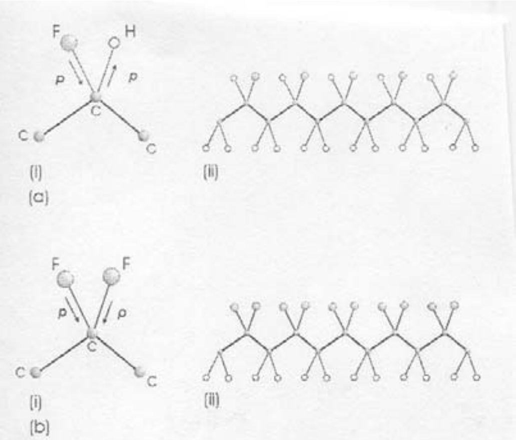
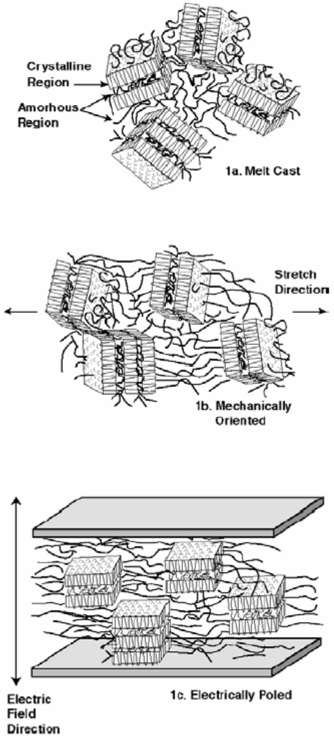


Figure 11.9 (a) Poly(vinyl fluoride), PVF, $[CH_2{-}CHF]_n$: (i) dipoles present in a tetrahedral unit of PVF and (ii) isotactic structure of a polymer chain of PVF. (b) Poly(vinylidene fluoride), PVF_2, $[CH_2{-}CF_2]_n$: (i) dipoles present in a tetrahedral unit of PVF_2 and (ii) isotactic structure of a polymer chain of PVF_2



Piezoelectric, Polymers

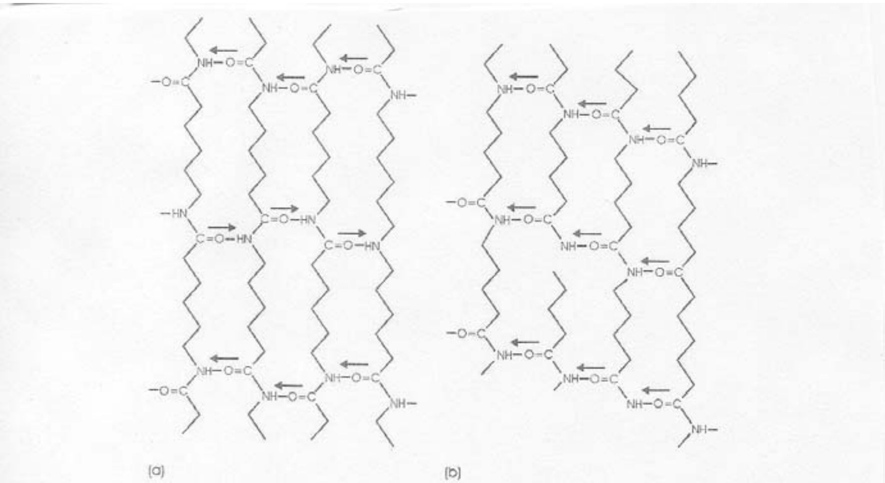


Figure 11.10 (a) The electric dipoles present in chains of an even nylon, nylon 6; no overall dipole moment is observed. (b) The electric dipoles present in chains of an odd nylon, nylon 5; the dipoles add to produce an observed dipole moment

Piezoelectric, Polymers

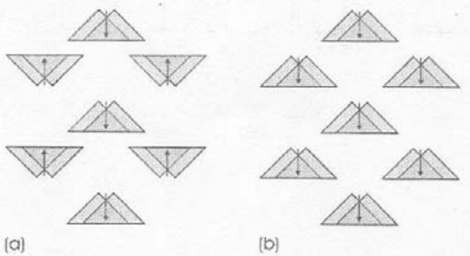
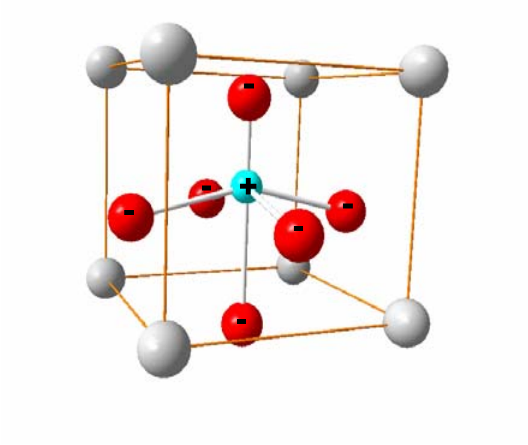


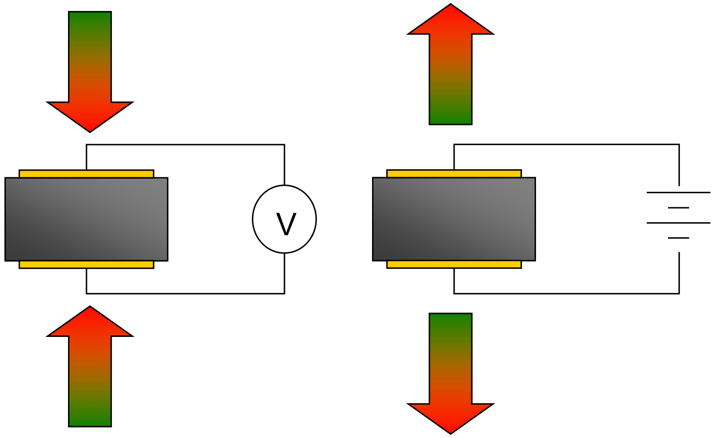
Figure 11.11 The schematic crystal structure of two forms of poly(vinylidene fluoride), PVF_2, viewed down the polymer chains, shown as double triangles; the electric dipoles in the chains are drawn as arrows. (a) The dipoles cancel in a centrosymmetric structure and the material is a nonpiezoelectric. (b) The dipoles add together in a noncentrosymmetric structure and the material is piezoelectric

Piezoelectric effect

$PbTiO_3$

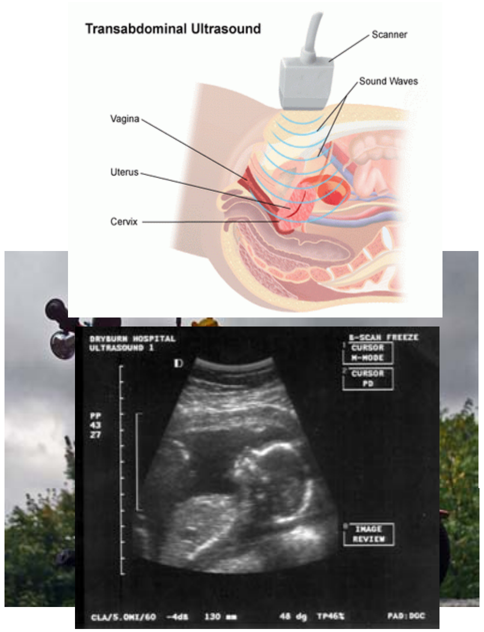


Piezoelectric effect



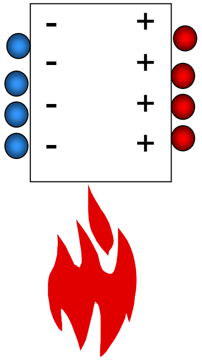
Piezoelectric effect

Piezoelectric effect



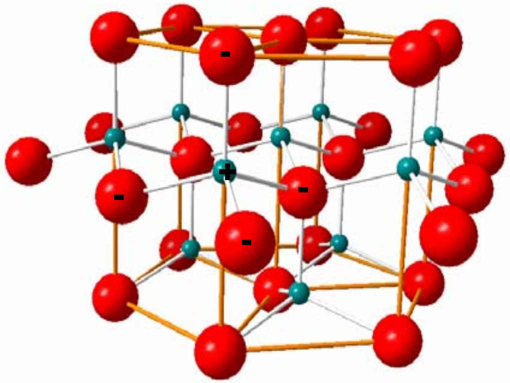
Pyroelectric effect

PVDF (polyvinylidene fluoride)
$LiTaO_3$
$BaTiO_3$
$PbTiO_3$
$Pb(Zr,Ti)O_3$



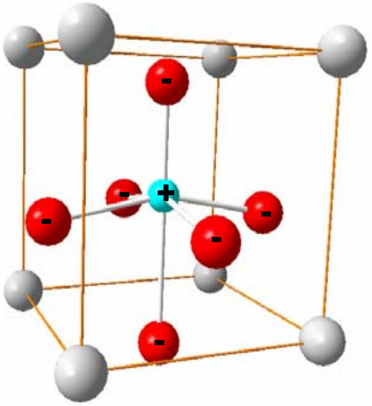
Pyroelectric effect

ZnO

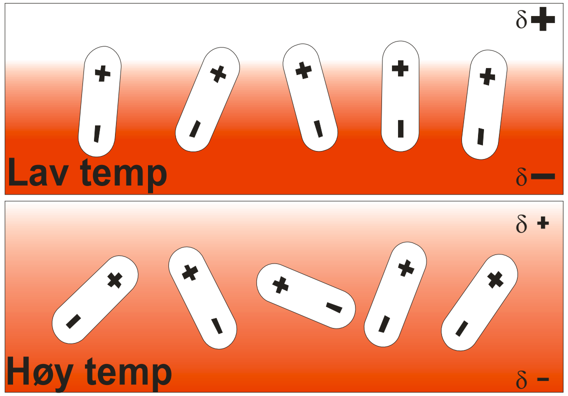


Pyroelectric effect

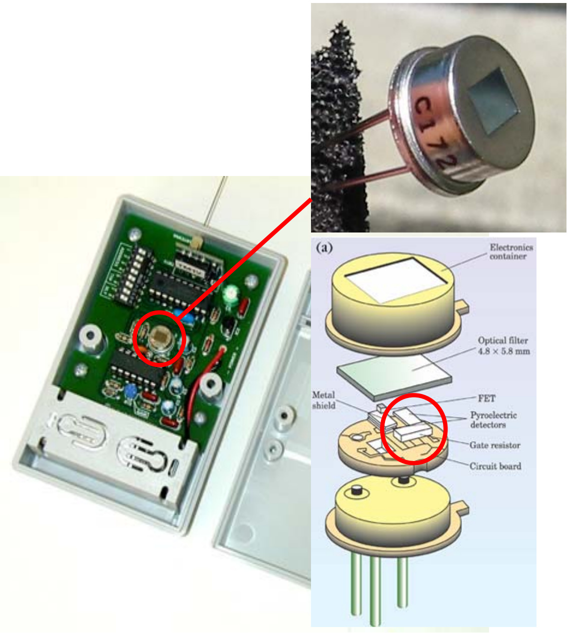
$PbTiO_3$



Pyroelectric effect

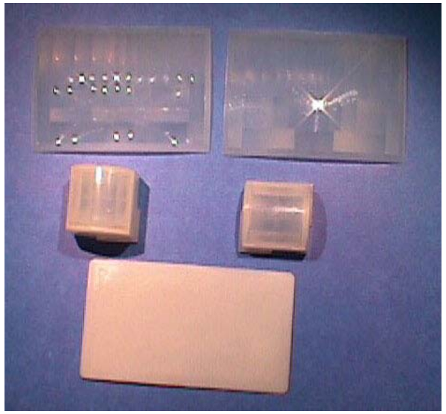


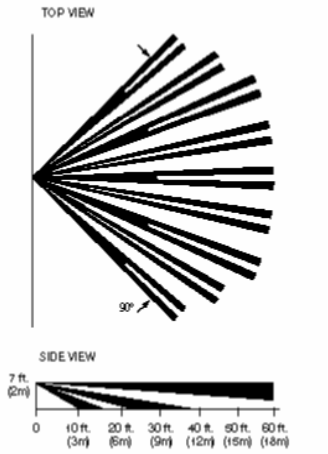
Pyroelectric effect



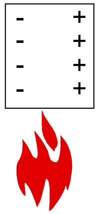
Pyroelectric effect

Segmented lense

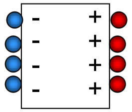




Pyroelectric



Pyroelectric crystals do not usually show an external charge since surface charges are neutralised by ions or other charged particles in the air.



The buildup of spontaneous polarisation can be written:

$$(\Delta P_s)_i = \pi_i \Delta T$$

The pyroelectric effect is composed of two effects:

-The primary effect is measured for crystals with constant size

-The secondary effect is due to strains that develop due to temperature difference

Pyroelectric

Important that the crystal structures does not have centre of symmetry.
Requires also unique polarization axis.

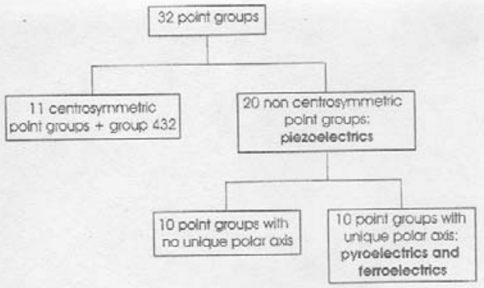


Figure 11.12 The relationship between point group and piezoelectric and pyroelectric properties

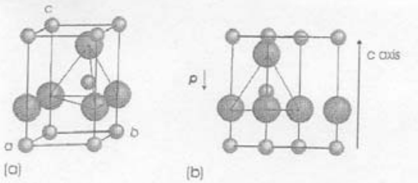


Figure 11.13 (a) The structure of hexagonal ZnO (zincite); a ZnO_4 tetrahedron is outlined. (b) An electric dipole, *p*, parallel to the *c* axis, arises in the unsymmetrical ZnO_4 tetrahedron; the wurtzite form of ZnS is isostructural

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Ferroelectrics

In ferroelectric materials, the spontaneous polarisation can be switched.

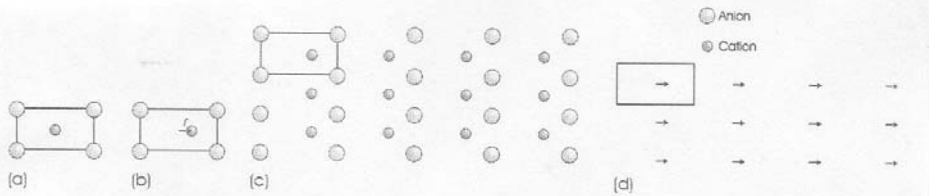

Figure 11.14 (a) A cation-centred unit cell; (b) cation displacement, *r*, creating an electric dipole in each cell; (c) an array of unit cells; and (d) an array of electric dipoles

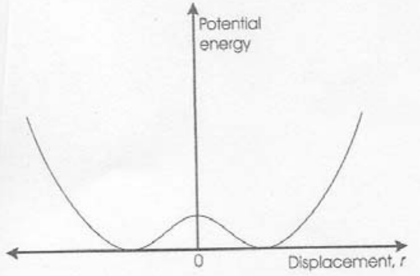

Figure 11.15 The variation of potential energy with cation displacement, ±*r*, from the centre of a surrounding anion polyhedron

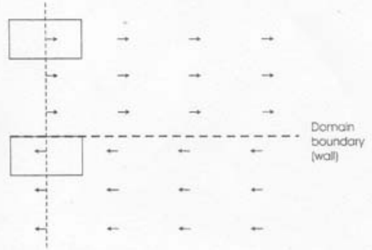

Figure 11.16 Domains due to the differing alignment of dipoles in adjacent regions of a crystal. The regions are separated by a domain wall, which extends over several tens of nanometres in practice

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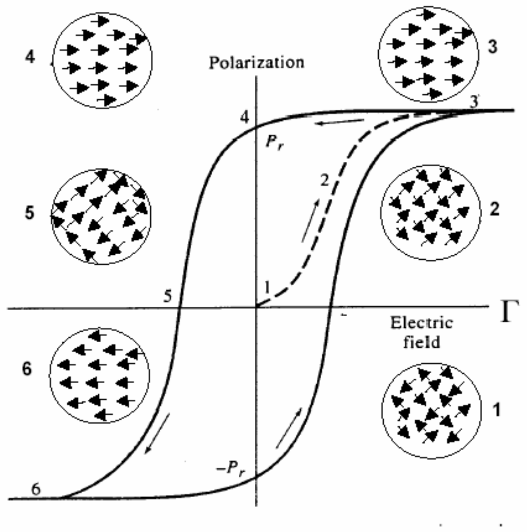
Ferroelectrics, hysteresis



Ferroelectrics, temperature dependence

Temperature will affect the relative permitivity, ε_r.

$$\varepsilon_r = \frac{C}{T - T_c}$$

T_c = Curie temperature
C = constant

$$\frac{1}{\varepsilon_r} = \frac{T}{C} - \frac{T_c}{C}$$

$$\varepsilon_r = \frac{C}{T - T_0}$$

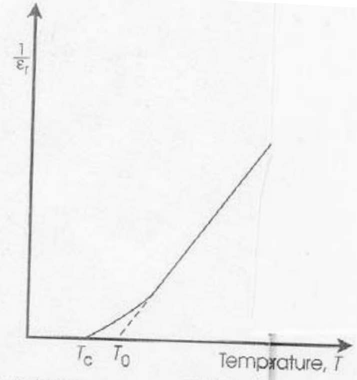
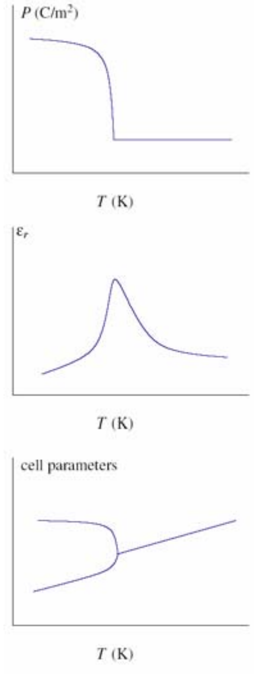
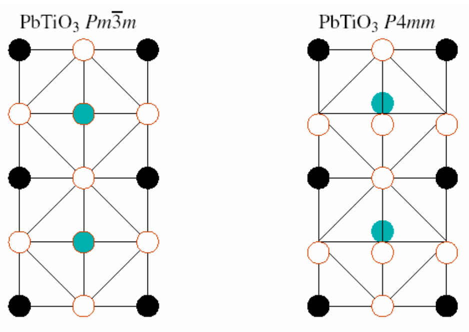


Figure 11.18 The Curie–Weiss behaviour of a ferroelectric solid above the Curie temperature T_c. Note: ε_r, relative permittivity; *T*, absolute temperature

T_c notes the transition from paraelectric to ferroelectric

Ferroelectrics, PbTiO$_3$





Ferroelectrics, hydrogen bonds

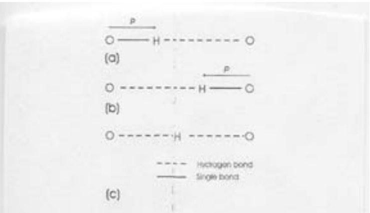


Figure 11.19 (a) and (b) Below the ferroelectric transition temperature, T_c, hydrogen atoms in hydrogen bonds lie to one side or the other of the centre. (c) Above T_c the hydrogen atoms are, on average, central. Hydrogen bonds are shown as broken lines, and normal covalent bonds are shown as continuous lines

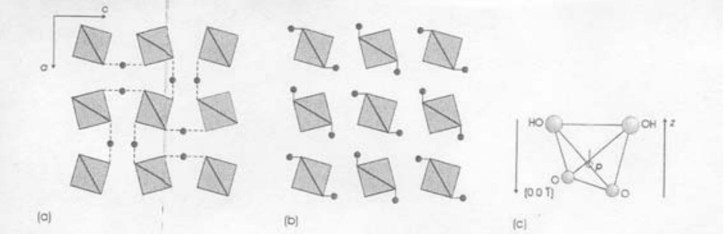


Figure 11.20 Potassium dihydrogen phosphate, KH$_2$PO$_4$: (a) skeleton of the structure of KH$_2$PO$_4$ projected down the [0 0 1] direction (the PO$_4$ tetrahedra are shown in projection as squares; the hydrogen bonds are shown as broken lines; the potassium atoms are omitted); (b) low-temperature structure showing ordered H atoms (black circles). (c) The displacement of the P atoms in the PO$_4$ tetrahedra as a result of the H-atom ordering, and the subsequent formation of (OH) groups, induces an electric dipole, p, parallel to the c axis

Ferroelectrics, Polar groups

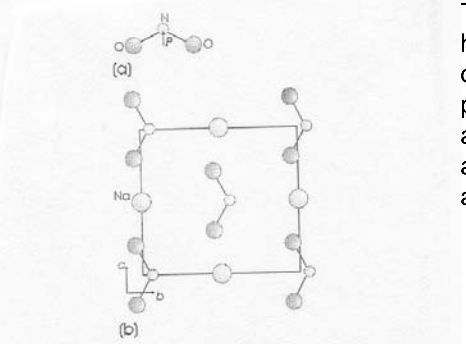


Figure 11.21 (a) The structure of a planar nitrite, (NO$_2^-$) group; the electric dipole, p, in each unit points towards the nitrogen (N) atom. (b) The low-temperature structure of sodium nitrite, NaNO$_2$, projected down the [1 0 0] direction; the dipoles are aligned along the b axis. In the high-temperature paraelectric form the dipoles are arranged at random along $+b$ and $-b$

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.

Ferroelectrics, Medium sized cations

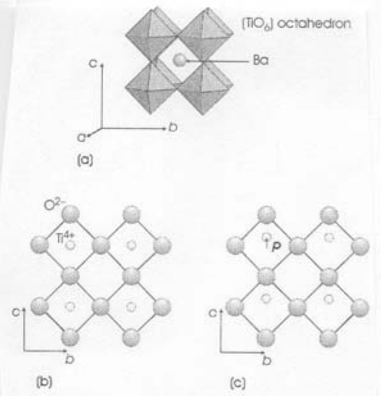
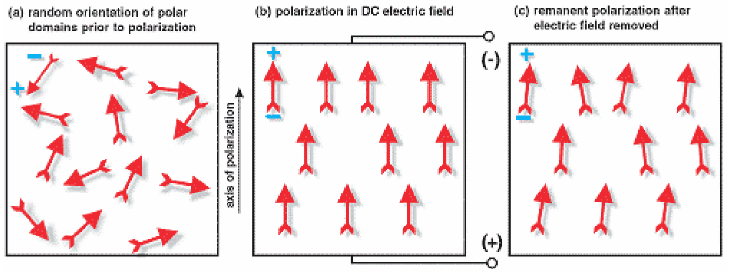


Figure 11.22 (a) The cubic perovskite structure of high-temperature cubic barium titanate, BaTiO$_3$, drawn as corner-shared TiO$_6$ octahedra; the Ba^{2+} ions occupy the unit cell centre. (b) Projection of the structure down the [1 0 0] direction, with the Ba^{2+} ions omitted. (c) Schematic view of the low-temperature tetragonal form, with the displacements of the Ti^{4+} ions exaggerated and the Ba^{2+} ions omitted. The electric dipoles, p, generated by the off-centre displacement of the Ti^{4+} ions, point along the c axis of the tetragonal unit cell

Ferroelectrics, poling

Figure 1.2 Polarizing (poling) a piezoelectric ceramic*



(a) random orientation of polar domains prior to polarization

(b) polarization in DC electric field

(c) remanent polarization after electric field removed