

# Kap. 11

## Insulating solids

Ag, Au, Fe, Ni, Cr

**Conductors**

Si, Ge, FeS<sub>2</sub>, MnO<sub>2</sub>

**Semiconductors**

MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, polyethylene

**Insulators**

### Dielectrics

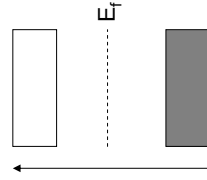
-Localized electrons, bonds or on atoms

Dielectric constant,  $\epsilon_r$

$$q = \frac{\epsilon_0 A V}{d}$$

$$q' = \frac{\epsilon_r \epsilon_0 A V}{d}$$

**Insulators**



### Capacitor

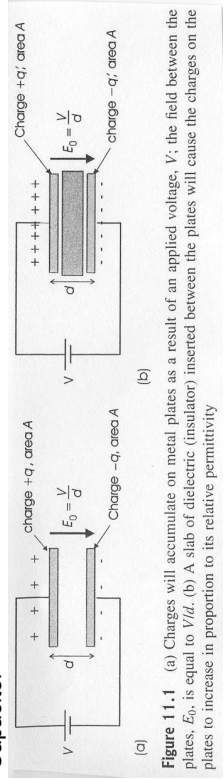


Figure 11.1 (a) Charges will accumulate on metal plates as a result of an applied voltage,  $V$ ; the field between the plates,  $E_0$ , is equal to  $V/d$ . (b) A slab of dielectric (insulator) inserted between the plates will cause the charges on the plates to increase in proportion to its relative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

### Dielectrics

The relative permittivity (dielectric constant,  $\epsilon_r$ ) describes the response of a solid to an electric field.  $\rightarrow$  Polarizability.

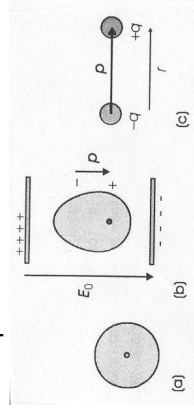


Figure 11.2 (a) For an atom in the absence of an electric field, the centres of gravity of the positive (nucleus) and negative (electrons) charges are coincident. (b) In an electric field these become separated to create a dipole. (c) An electric dipole consists of two equal and opposite charges separated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

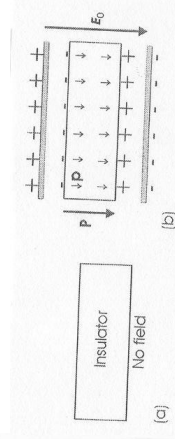


Figure 11.3 (a) In the absence of an applied electric field a dielectric has no surface charge. (b) In an electric field,  $E_0$ , the material has a surface charge as a result of the formation of internal dipoles,  $p$ , that induce an observable polarisation,  $P$

$$P = \epsilon_0 \chi E_0$$

$$\chi = (\epsilon_r - 1)$$

$$P = \epsilon_0 (\epsilon_r - 1) E_0$$

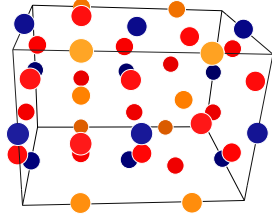
# Dielectrics

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.

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

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



# Dielectrics

Electronic polarisability,  $\alpha_e$

Ionic polarisability,  $\alpha_i$

Orientalional polarisability,  $\alpha_d$

Space charge polarisability,  $\alpha_e$

Bulk polarisability,  $\alpha_e$

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

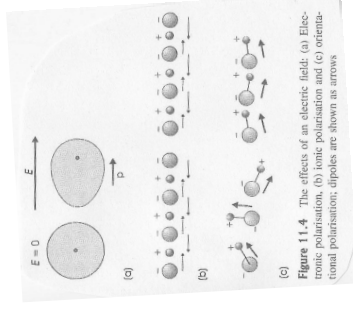
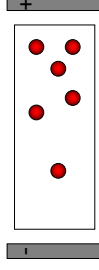


Figure 11.4 The effects of an electric field: (a) Electronic polarisation, (b) ionic polarisation and (c) orientational polarisation; dipoles are shown as arrows



# Dielectrics

The different types of polarisation are frequency dependent

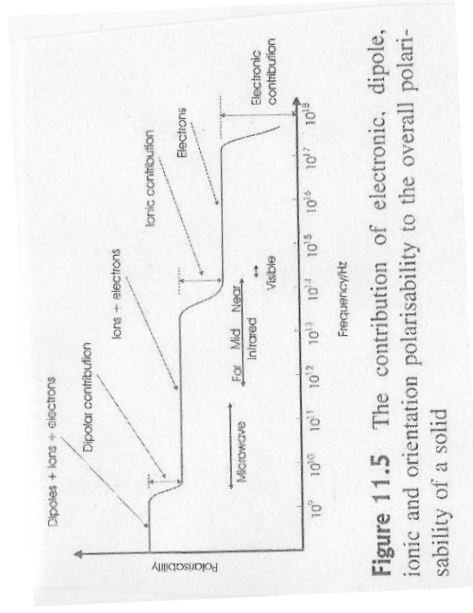


Figure 11.5 The contribution of electronic, dipole, ionic and orientation polarisability to the overall polarisability of a solid

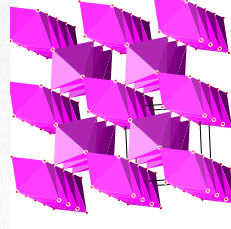
$$n^2 = \epsilon_r$$

# Dielectrics

Table 11.1 The relative permittivity and refractive index of some crystals

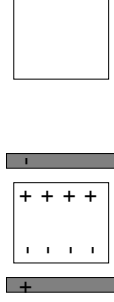
Compound	Symmetry	Relative permittivity, $\epsilon_r$	Frequency Hz	Refractive index, $n$	$n^2$
Diamond	Cubic	5.66	$10^3$	2.418	5.85
Periclase, MgO	Cubic	9.65	$10^2-10^8$	1.735	3.010
Spinel, Mg-Al <sub>2</sub> O <sub>4</sub>	Cubic	8.6	—	1.719	2.955
Fluorite, CaF <sub>2</sub>	Cubic	6.81	$10^2-10^{11}$	1.434	2.056
Corundum, Al <sub>2</sub> O <sub>3</sub>	Hexagonal	9.34	$10^2-10^9$	1.761	3.101
along <i>c</i>		11.54		1.769	3.129
Beryl, Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub>	Hexagonal	6.86	$10^3$	1.589	2.525
perpendicular to <i>c</i>		5.95		1.582	2.503
along <i>c</i>					
Rutile TiO <sub>2</sub>	Tetragonal	86	$10^4-10^6$	2.609	6.807
along <i>a</i> and <i>b</i>		170		2.900	8.410
along <i>c</i>					

The polarization is not always isotropic

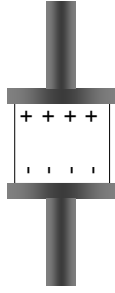


## -electric

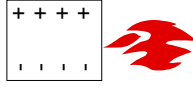
For normal dielectrics, the observed polarisation is zero in absence of an electric field.



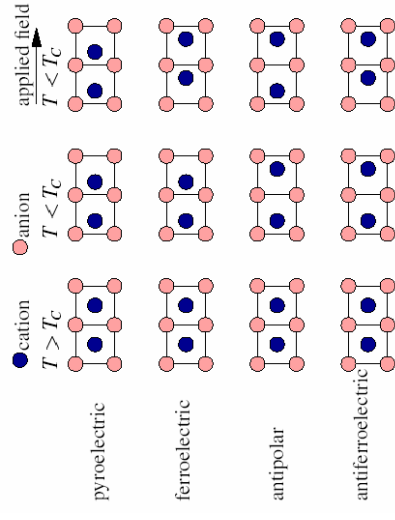
Piezoelectric materials develop a surface electric charge when subjected to mechanical stress.



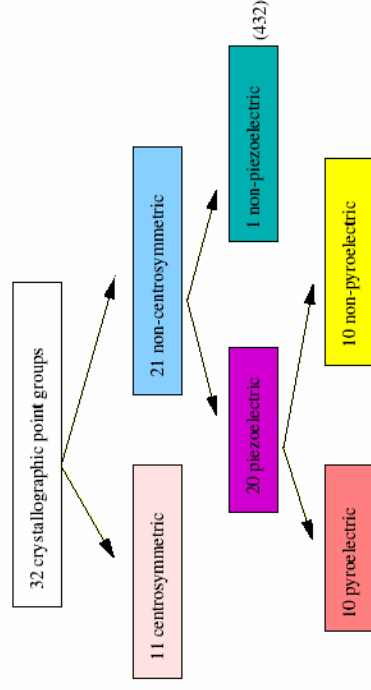
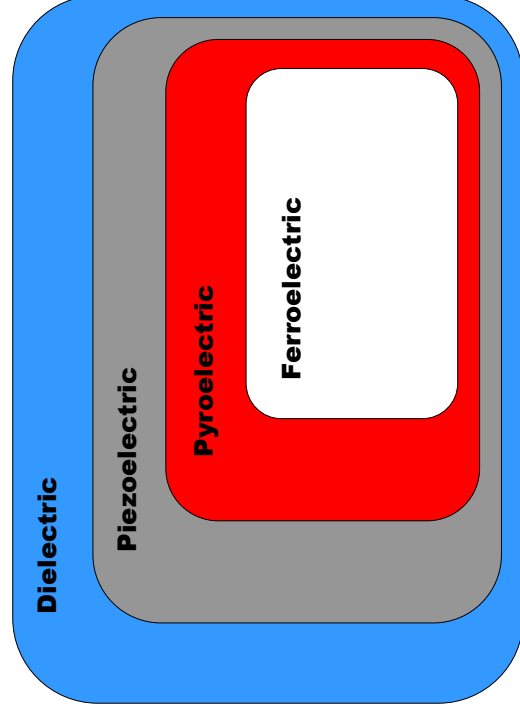
Pyroelectric materials develop surface charge when the temperature is changed.



## -electric



## -electric



# Piezoelectric, Metal-oxovan tetrahedra

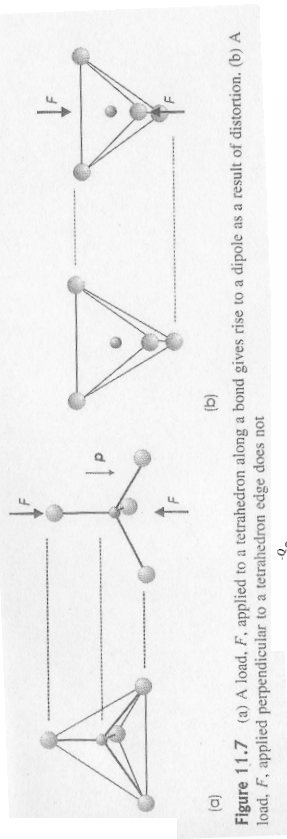


Figure 11.7 (a) A load,  $F$ , applied to a tetrahedron along a bond gives rise to a dipole as a result of distortion. (b) A load,  $F$ , applied perpendicular to a tetrahedron edge does not.

# Piezoelectric, dipole containing crystals

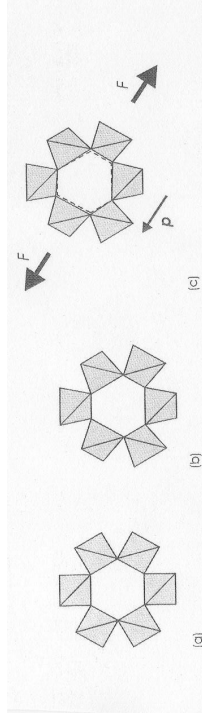
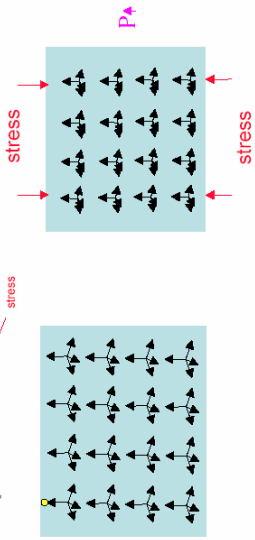


Figure 11.8 (a) Part of the idealised structure of high-temperature quartz drawn as corner-connected tetrahedra, projected down the  $c$  axis (note that the tetrahedra are arranged in a helix, not in rings). (b) Part of the structure of room-temperature quartz; the tetrahedra are distorted and each 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

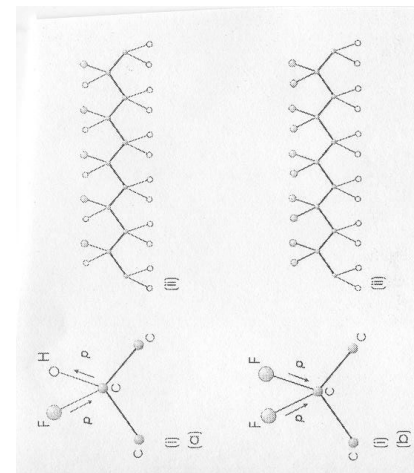


Figure 11.9 (a) Poly(vinyl fluoride), PVF,  $[\text{CH}_2-\text{CHF}]_n$ ; (i) dipoles present in a tetrahedral unit of PVF and (ii) isotactic structure of a polymer chain of PVF. (b) Poly(vinylidene fluoride),  $\text{PVF}_2$ ,  $[\text{CH}_2-\text{CF}_2]_n$ ; (i) dipoles present in a tetrahedral unit of  $\text{PVF}_2$  and (ii) isotactic structure of a polymer chain of  $\text{PVF}_2$ .

# Piezoelectric, Polymers

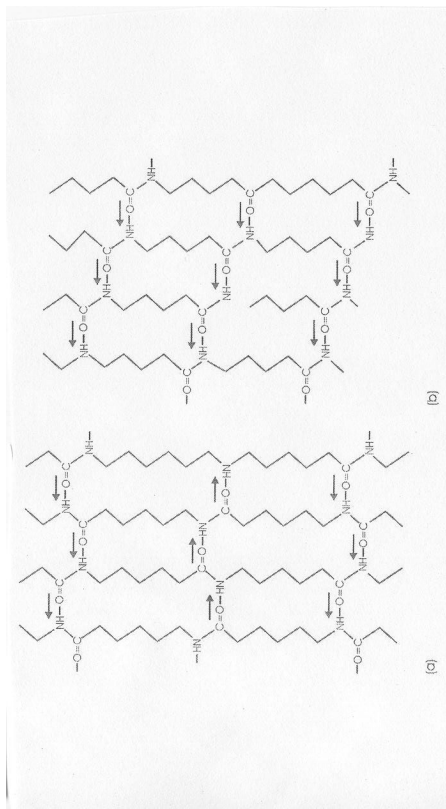
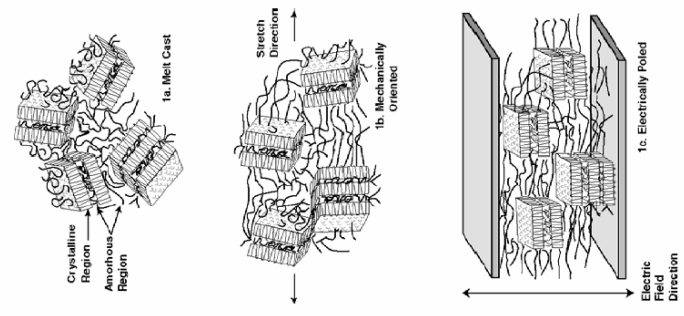
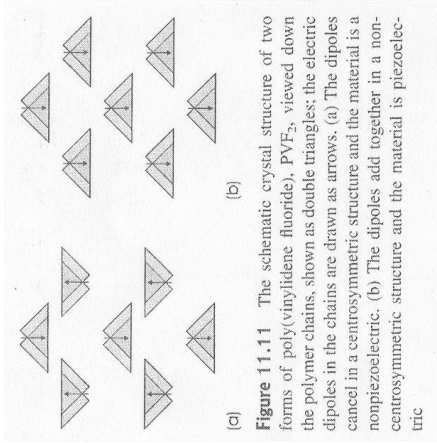


Figure 11.10 (a) The electric dipoles present in chains of an even nylon, nylon 6; no overall dipole moment is observed. (b) The electric dipoles present in chains of an odd nylon, nylon 5; the dipoles add to produce an observed dipole moment.



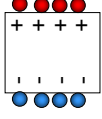
# Piezoelectric, Polymers



**Figure 11.11** The schematic crystal structure of two forms of poly(vinylidene fluoride), PVF<sub>2</sub>, 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 non-centrosymmetric structure and the material is piezoelectric

# 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:

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

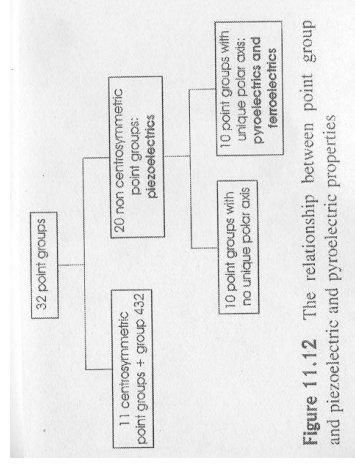
The pyroelectric effect is composed of two effects:

- The primary effect is measured for crystals with constant size
- The secondary effect is due to strains that develop due to temperature difference



# Pyroelectric

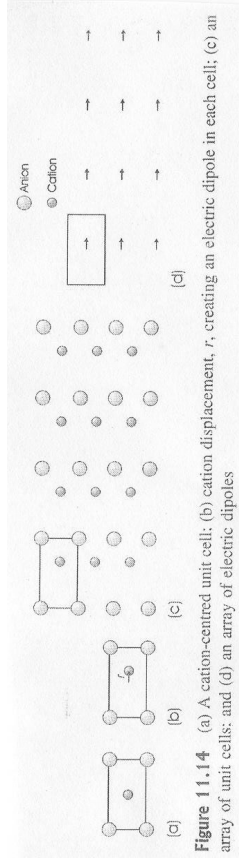
Important that the crystal structures does not have centre of symmetry. Requires also unique polarization axis.



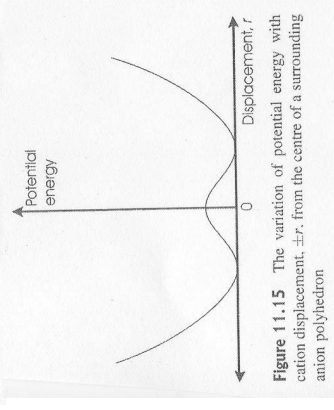
**Figure 11.12** The relationship between point group and piezoelectric and pyroelectric properties

# Ferroelectrics

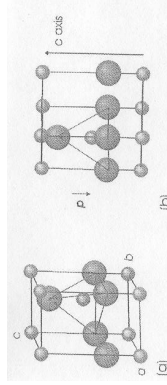
In ferroelectric materials, the spontaneous polarisation can be switched.



**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

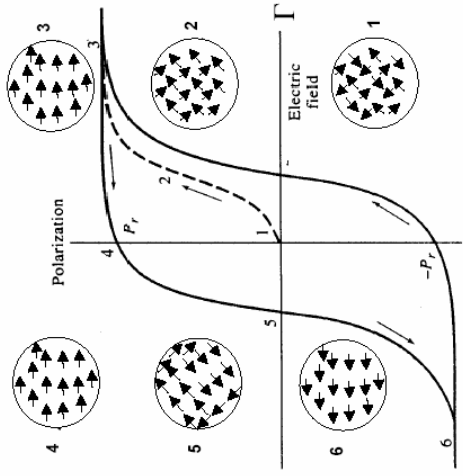


**Figure 11.16** Domains due to the differing alignment of dipoles in adjacent regions of a crystal. The regions are separated by a domain wall, which extends over several tens of nanometres in practice



**Figure 11.13** (a) The structure of hexagonal ZnO (zincite); a ZnO<sub>4</sub> tetrahedron is outlined. (b) An electric dipole,  $P$ , parallel to the  $c$  axis, arises in the unsymmetrical ZnO<sub>4</sub> tetrahedron; the wurtzite form of ZnS is isostructural

## Ferroelectrics, hysteresis



## Ferroelectrics, temperature dependence

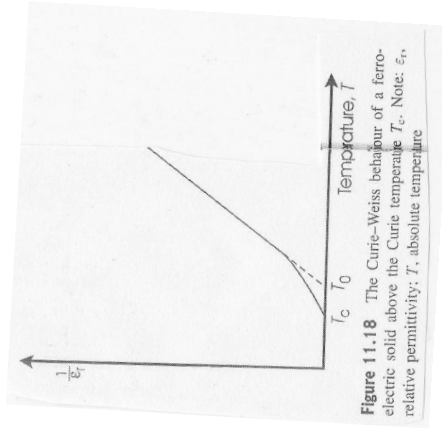
Temperature will affect the relative permittivity,  $\epsilon_r$ .

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

$T_c$  = Curie temperature  
C = constant

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

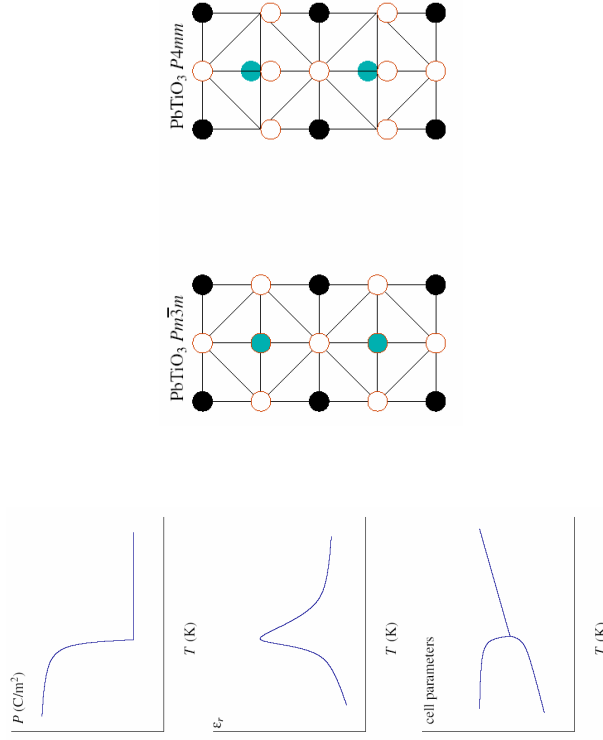
$$\epsilon_r = \frac{C}{T - T_0}$$



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

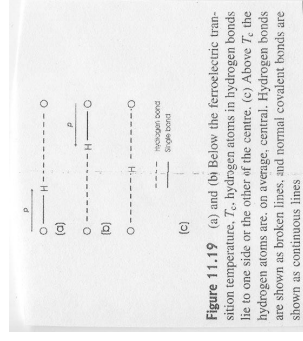
$T_c$  notes the transition from paraelectric to ferroelectric

## Ferroelectrics, PbTiO3

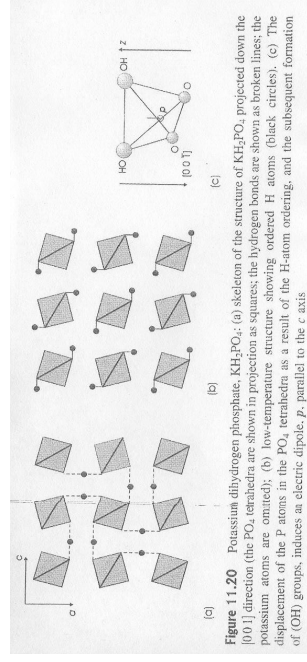


## Ferroelectrics, PbTiO3

## Ferroelectrics, hydrogen bonds

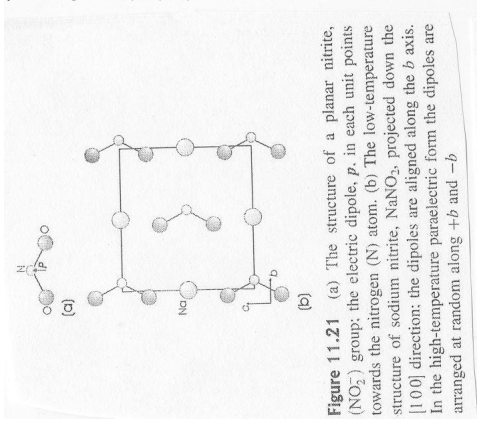


**Figure 11.19** (a) and (b) Below the ferroelectric transition temperature,  $T_c$ , hydrogen atoms in hydrogen bonds lie to one side or the other of the centre. (c) Above  $T_c$ , the hydrogen atoms are, on average, central. Hydrogen bonds are shown as broken lines, and normal covalent bonds are shown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



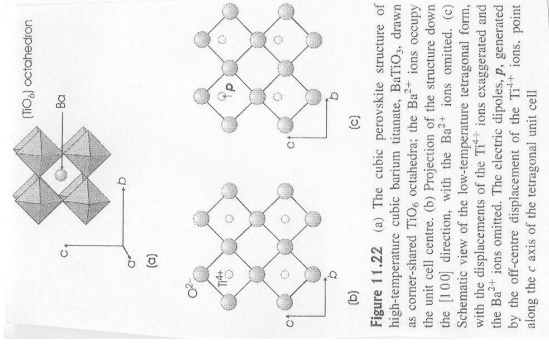
**Figure 11.20** Potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ : (a) skeleton of the structure of  $\text{KH}_2\text{PO}_4$ , projected down the  $[001]$  direction (the  $\text{PO}_4$  tetrahedra are shown in projection as squares; the hydrogen bonds are shown as broken lines; the potassium atoms are omitted); (b) low-temperature structure showing ordered H atoms (black circles); (c) The displacement of the P atoms in the  $\text{PO}_4$  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



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



## Ferroelectrics, poling

