

Electrical Properties

Dielectric materials

Electric insulators

Used in capacitors and electrical insulators.

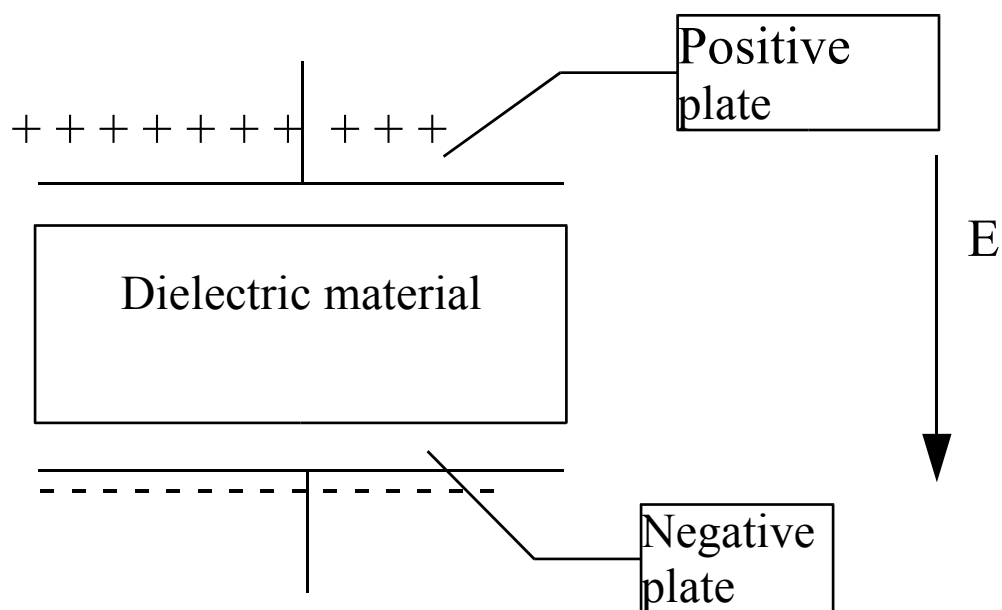
Required properties:

- high dielectric strength
- low dielectric loss

Application of a potential difference across a dielectric leads to polarisation but no long range motion of ions or electrons.

Polarisation disappears on removing the voltage.

Define by behaviour of material in a parallel plate capacitor:



The relative permittivity is defined by

$$\epsilon' = \frac{C_1}{C_0}$$

C_1 charge in the presence of the dielectric, C_0 the charge in a vacuum

ϵ' depends on the degree of polarisation or charge displacement that can occur in a material.

Air	$\epsilon' \sim 1$;
most ionic solids	$\epsilon' \sim 5-10$;
ferroelectric BaTiO ₃	$\epsilon' \sim 10^3-10^4$

Four factors influence the polarisability

1. Electronic polarisability

- electron/nucleus

2. Ionic polarisability

- displacement/separation of ions

3. Dipolar polarisability

- alignment of dipoles

4. Space charge polarisability

- imperfect dielectrics, long range charge migration

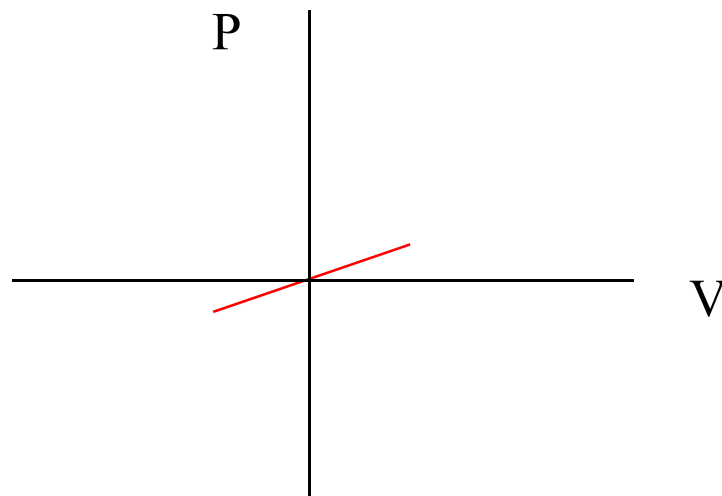
Ferroelectricity

Characterised by

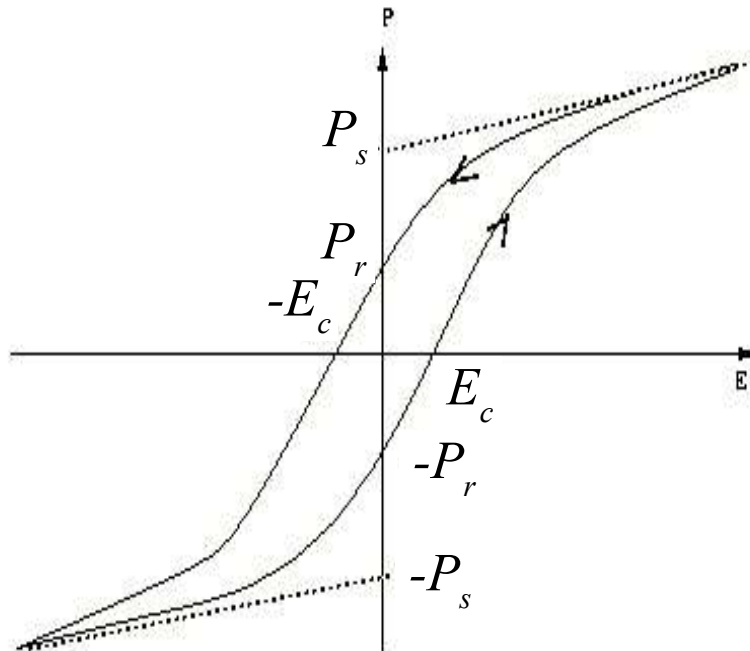
1. Extremely large relative permittivities
2. Possibility that some residual polarisation will remain after the applied voltage has been switched off.

Variation in induced polarisation (P), or stored charge show a complicated hysteresis.

Normally there is a simple linear relation between the polarisation and voltage.



Polarisation behaviour (Hysteresis Loop)



Features

- different behaviour on increasing/decreasing the voltage
- saturation polarisation, BaTiO_3 , $P_s = 0.26 \text{ Cm}^{-2}$ at 23°C
- remanent polarisation,
- coercive field, E_c , to return polarisation to zero

Explanation for hysteresis

Characteristic feature:

- one type of cation present ,e.g. Ti^{4+} in BaTiO_3 , able to undergo significant displacement, e.g. $0.1 \text{ \AA}$, relative to its anionic neighbours

Structure of BaTiO_3 :

Above 120°C normal perovskite. TiO_6

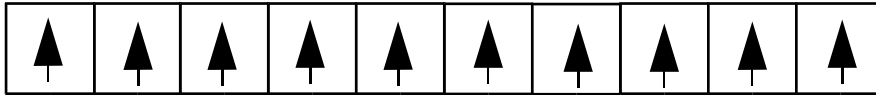
- symmetric charges, normal dielectric

Below 120°C .

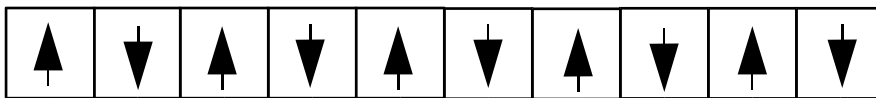
Ti are displaced towards one of the apical oxygens.

- Spontaneous polarisation.
- In the absence of an electric field no net polarisation
- applied field aligns the individual dipoles
- Saturation polarisation occurs when all the dipoles are aligned.
- thermal motion destroys alignment
- Remanent polarisation results from remaining alignment caused by the internal electric field of the dipoles
- Coercive field overcomes the internal field

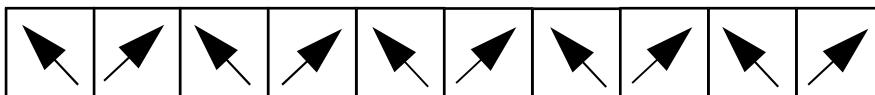
Possible alignments:



ferroelectric



antiferroelectric



ferrielectric

Domain structure

- adjacent TiO_6 dipoles tend to align parallel to each other.
- variable size $\sim 10\text{-}100\text{ s \AA}$.
- within a domain the net polarisation of the dipoles has a common crystallographic direction.
- net polarisation vector resultant.

Electric field changes net polarisation:

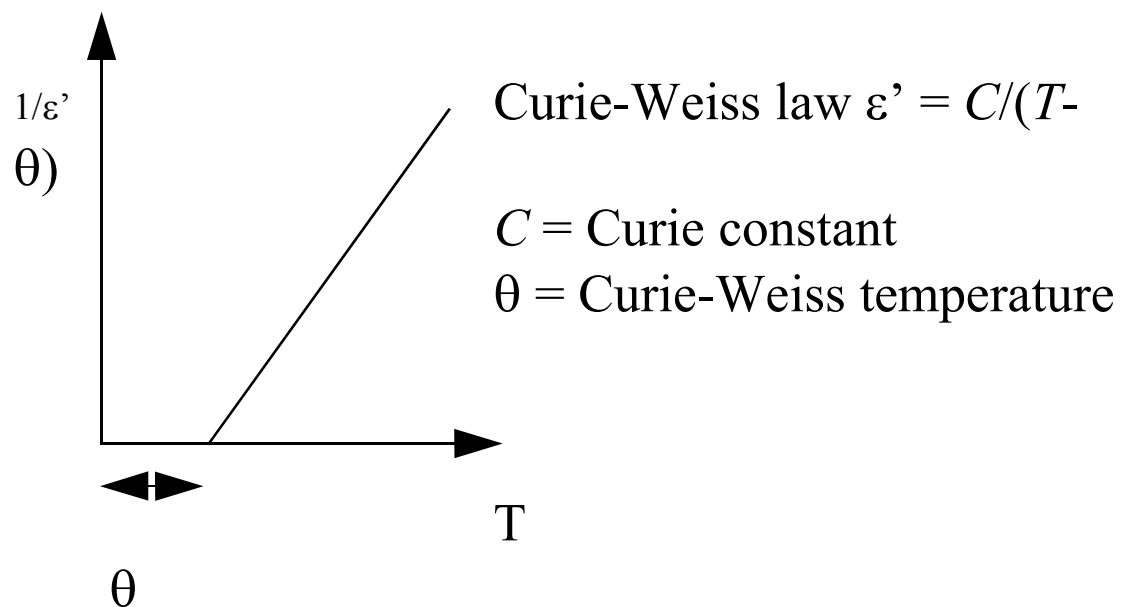
1. Domain polarisation may change
2. Magnitude of P within a domain increases
3. Domain wall migration - domains increase in size

Curie-Weiss Law

Ferroelectric state is a low temperature one
- thermal motion destroys the common displacement in adjacent octahedra.

The temperature at which this breakdown occurs is called the ferroelectric Curie temperature, T_c .

Above, T_c , the material is paraelectric cf paramagnetic, possessing individual dipoles but no preferential alignment, no net residual polarisation.



ferroelectric-paraelectric transition
= order-disorder phase transition.

Ordering is based on preferential distortion or tilting of polyhedra - example of a displacive phase transition.

Condition for spontaneous polarisation:
space group non-centrosymmetric.

Ferroelectric oxides used in capacitors because of high dielectric constants. But these are found near T_c .

To maximise for BaTiO_3 must displace the Curie point closer to room temperature.

How is this done:

1. Substitute Sr for Ba - unit cell contraction, less freedom for Ti ions to move in TiO_6 octahedra
2. Replace smaller Ti by the larger Zr, rapid decrease in T_c

Ferroelectric materials

	T_c (°C)
barium titanate BaTiO_3	120
potassium niobate, KNbO_3	434
lead titanate, PbTiO_3	490
lithium niobate, LiNbO_3	1210
lead zirconate titanate, PZT $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$	Depends on x
Potassium dihydrogen phosphate KDP, KH_2PO_4	-150

KDP

Example with hydrogen bonding

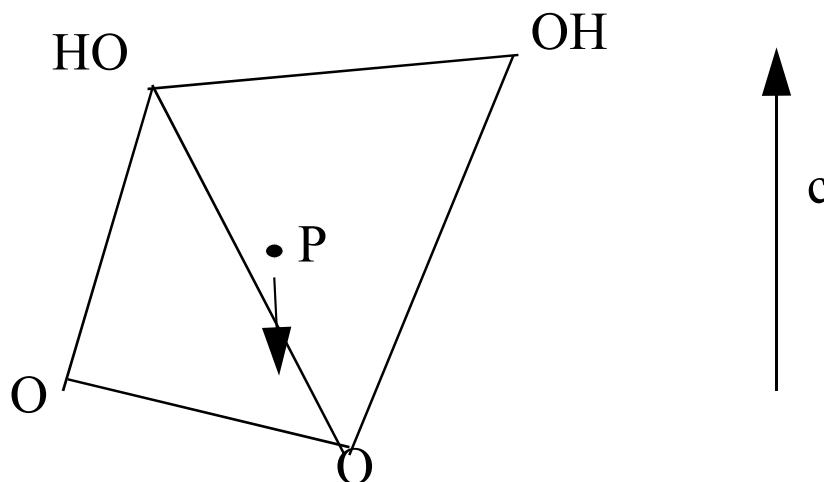
Isolated PO_4 tetrahedra, linked by K^+ and hydrogen bonds .

In each H bond the hydrogens are displaced so as to be nearer to one oxygen or the other.

For each PO_4 tetrahedron, there are two close H and two distant H.

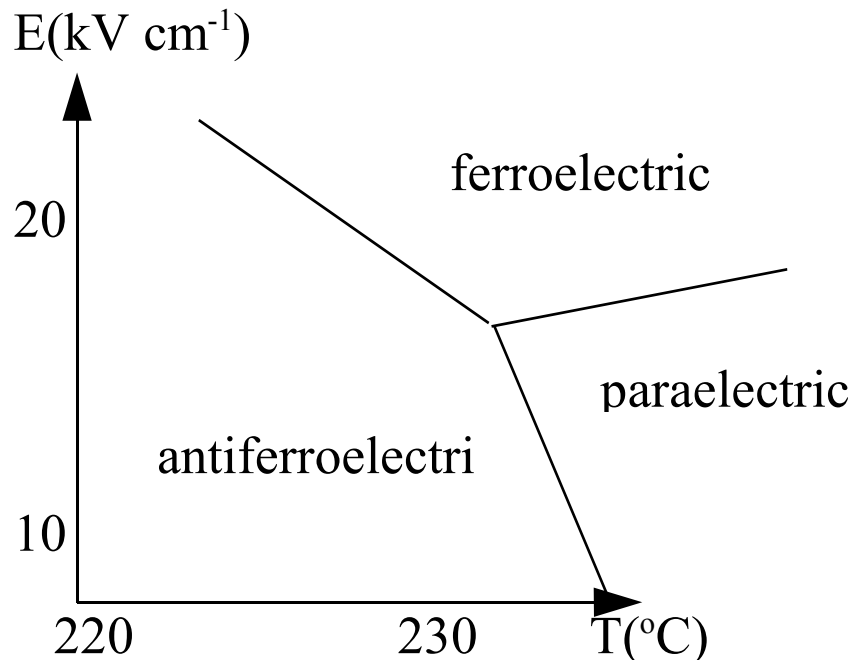
Paraelectric forms the H positions are randomised over the two positions.

Ferroelectric KDP the H's order themselves so that both are associated with the upper edge of each PO_4 tetrahedron. H's responsible for the spontaneous polarisation, since P are displaced downwards away from the H atoms.





more complex behaviour



Individual dipoles align anti-parallel.

Net spontaneous polarisation is zero.

Above T_c , normal paraelectric.

Energy difference between anti/ferro is small so if E large become ferroelectric. Antiferro is a non-polar state so no hysteresis loop.

But in this case when the field increases above a certain limit then becomes ferro and we will see a hysteresis loop (NB only at the high positive and negative fields.)