COMMONWEALTH OF AUSTRALIA

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First On-Line Test

- **Worth:** 5% of overall grade
- **How to complete:** Online via "Assignments" in Canvas
- **Due:** The test is open for 1 week and closes 11:59 pm Sunday at the end of Week 5
- **Duration:** You have one hour to complete the test. You can have one attempt only (i.e., not like weekly quizzes)
- **Description:** The test contains 15 multiple choice questions.
- **Content:** Material from lectures 2 to 11, including pre-lecture videos 1-3, all worksheets, and tutorials 1 and 2
- **Specific things that will be tested:** ability to identify molecules with the same point group symmetry (note that this can often be done visually without needing to work out all of the symmetry operations and assignment of point group symbols); definitions of the various types of symmetry operations (including those that incorporate translation); Miller indices; application of the Bragg Equation; information that can be extracted from diffraction patterns; structural descriptions of various ionic lattices; Born-Mayer and lattice enthalpy trends; understandings of the nature of electron delocalisation and therefore mechanism for electron conduction in various materials we've encountered (1D/2D/3D); understanding of key parameters in the measurement of dielectric and magnetic materials.

Dielectric Properties of Materials

Lecture 9

Electronic Properties of Materials

Lecture 10

Dielectric Properties of Materials

Lecture 11

Magnetic Properties of Materials

Outline

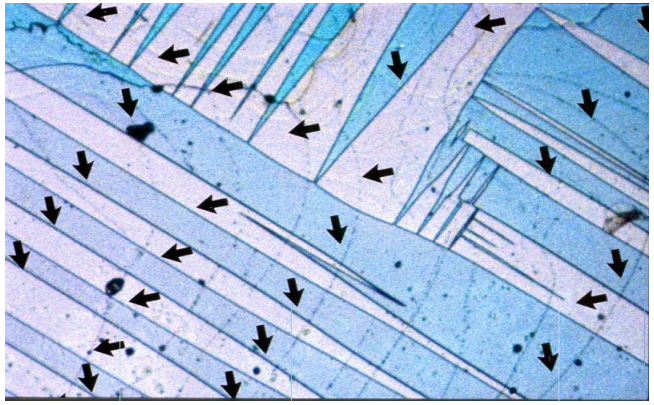
- Defining dielectric materials
- Structural features
  - Non-centrosymmetry
  - Atomic displacements
- Behaviour in an electric field
  - Paraelectricity
  - Ferroelectricity
- Structural features (cont.)
  - Non-bonding electrons
- Material properties
  - Piezoelectric materials
  - Second harmonic generation/ non-linear optical materials

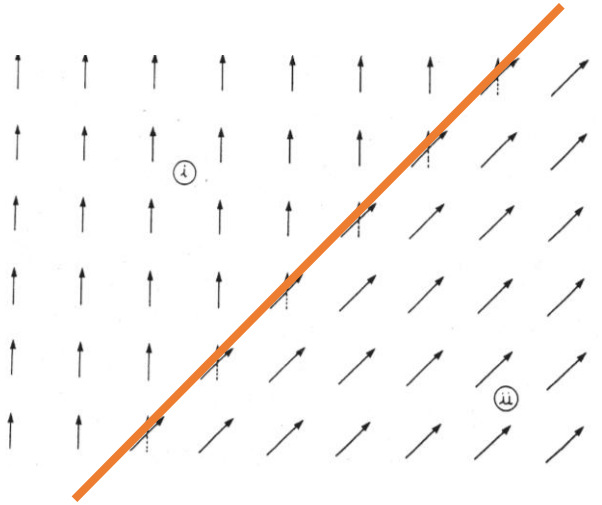
Dielectric Materials

- A **dielectric** is an electrical insulator that can be polarised by an applied electric field.
- When a dielectric is placed in an electric field, electric charges slightly shift from their average equilibrium positions, causing **dielectric polarisation**.
- Mechanisms of polarisation include:
  - Electronic polarisation – displacement of electron density relative to the nucleus it surrounds.
  - Ionic polarisation – relative motions of cations and anions.
  - Orientation polarisation – rotation of molecular dipoles.
  - Space charge polarisation – diffusion of ions over several interatomic distances.

Types of Dielectric Materials

- Dielectric materials are classified by how they behave in an applied electric field.
- **Paraelectric** materials generates dielectric polarisation when an electric field is applied to the material but loses the polarization when the field is removed.
- **Ferroelectric** materials have spontaneous polarisation that is retained when the electric field is removed.





A polar crystal with domain boundaries where the polarity is pointing in different directions

Application of Dielectrics: Plate Capacitor

A **capacitor** is made up of two conductors, called plates, of surface area *A*, separated by a distance *d*, carrying charges of equal magnitude and opposite sign.

The **capacitance**, C, is the ratio of the charge on either plate, Q, to the magnitude of the potential difference between the places, ΔV:

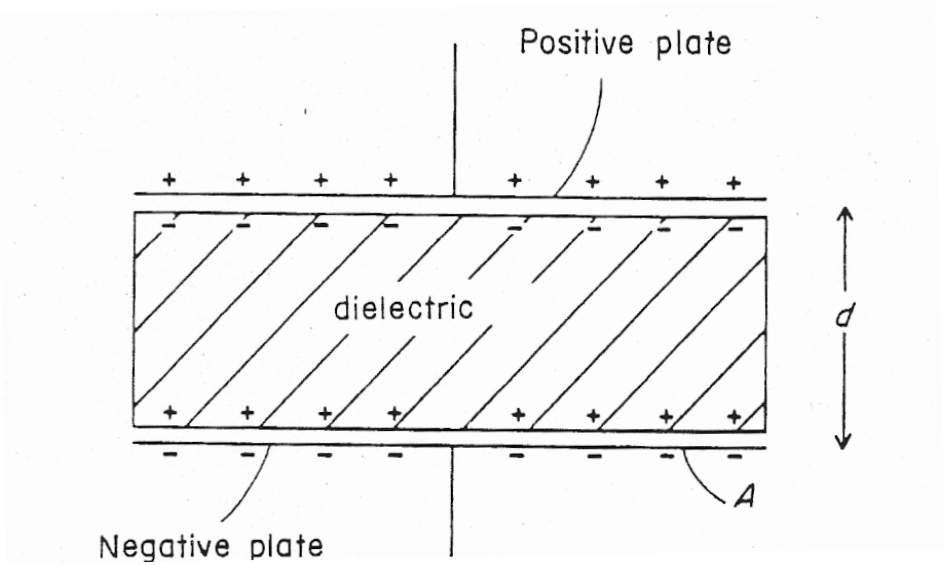
$$C = Q / \Delta V \quad \text{also} \quad C = \varepsilon_0 A / d$$

The electric potential energy, *U*, of a capacitor is given by:

$$U = \tfrac{1}{2} C(\Delta V)^2$$

When a dielectric material is inserted between the plates of a parallel plate capacitor **the capacitance increases by a factor ε_r , the relative permittivity:**

$$C = \varepsilon_r \varepsilon_0 A / d$$



Relative Permittivity (Dielectric Constant)

The **relative permittivity**, ε_r, is a measure of how readily a material becomes polarised in an electric field.

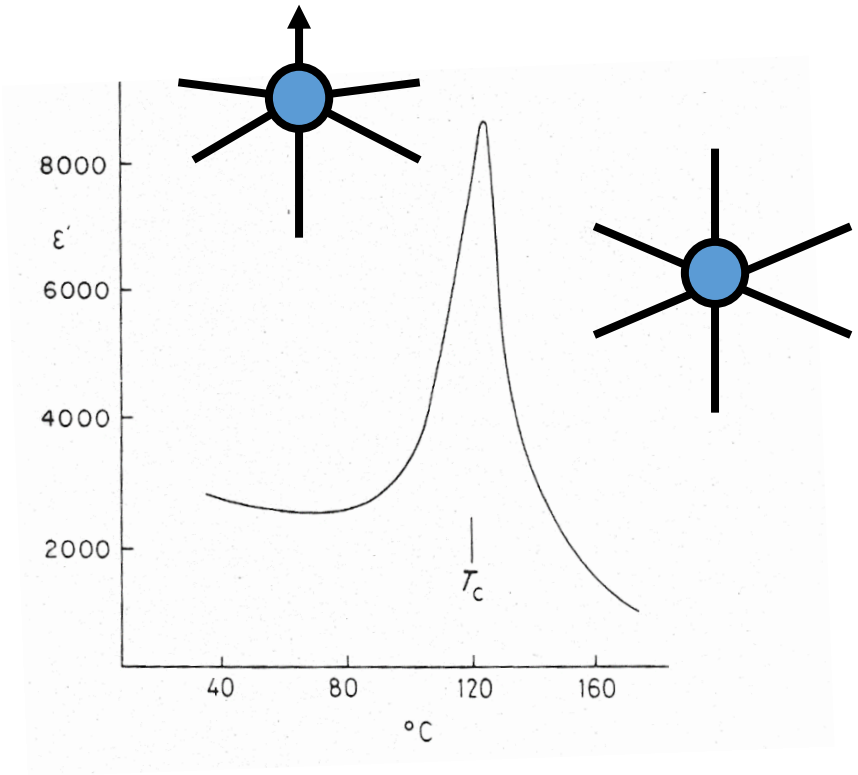
It is a unitless parameter that provides the permittivity relative to that of a vacuum which, by definition, has $\varepsilon_r = 1$.

Aside: ε_0, the absolute permittivity of a vacuum, appears in the Born-Mayer equation (Lecture 7) and in Maxwell's equations (Lecture 1).

Material	**Relative permittivity, ε_r**
Vacuum	1 (by definition)
Air	1.00058986
Teflon	2.1
Polyethylene	2.25
Carbon disulfide	2.6
Silicon dioxide	3.9
Concrete	4.5
Rubber	7
Diamond	5.5–10
Salt	3–15
Graphite	10–15
Silicon	11.68
Ammonia	17
Methanol	30
Ethylene glycol	37
Water	80
Sulfuric acid	84
Strontium titanate	310
Barium strontium titanate	500
Barium titanate	1200–10,000 (20–120 °C)
Lead zirconate titanate	500–6000
Calcium copper titanate	>250,000

Relative Permittivity of Barium Titanate

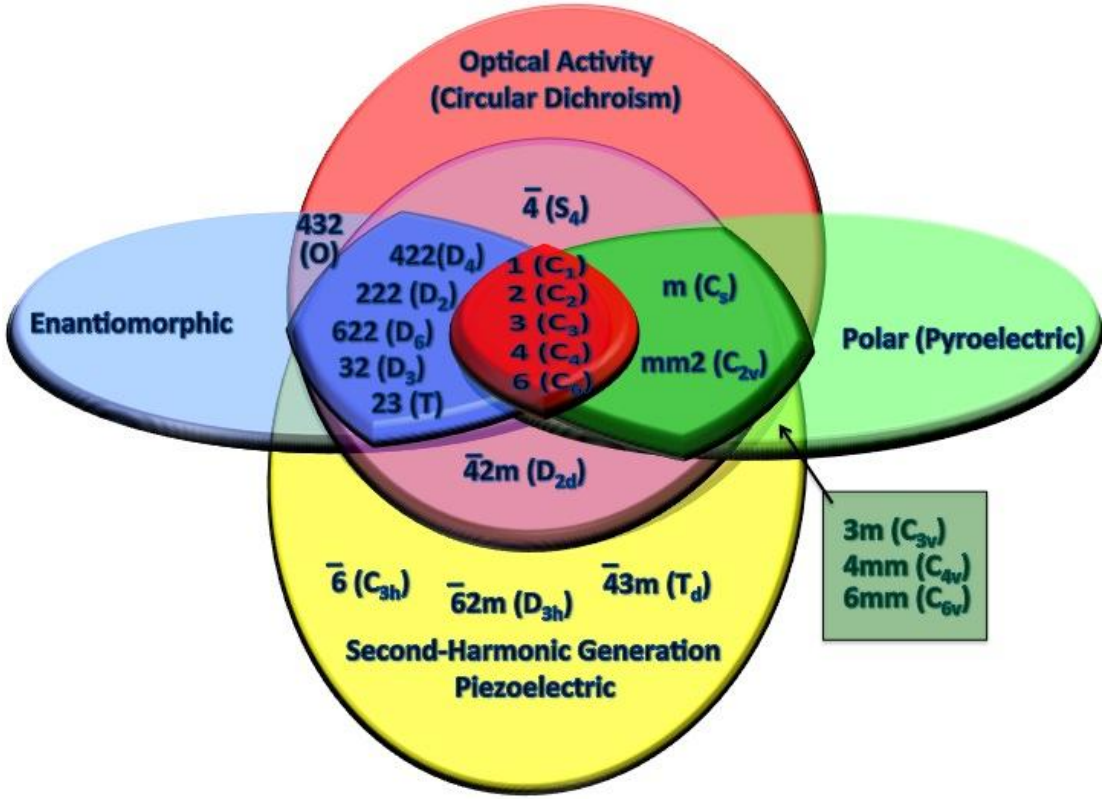
The relative permittivity of barium titanate, $BaTiO_3$, is dependent on tempareture and reaches very high values (compared to 'normal' dielectrics, ε_r ~5–10) with a maximum at 120 °C.



Q: Why do we need to understand crystal symmetry?

A: So we can work out and describe the structures of materials.

A: Materials properties depend on symmetry.



Non-centrosymmetric symmetries (those that don't contain inversion centres)

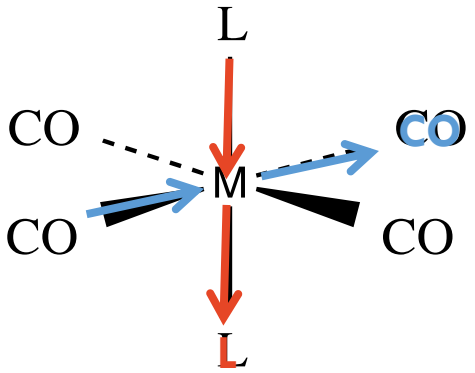
doi: 10.1021/cm980140w

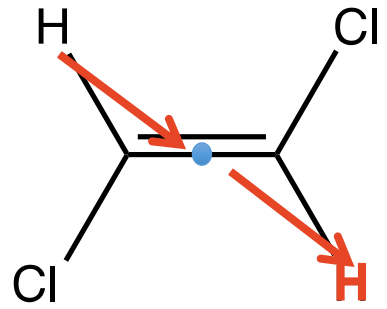
Revision: Inversion (i)

A point of inversion, or a Centre of Symmetry (i), is a point through which every atom can move in a straight line to an identical atom on the other side of the point at the same distance.

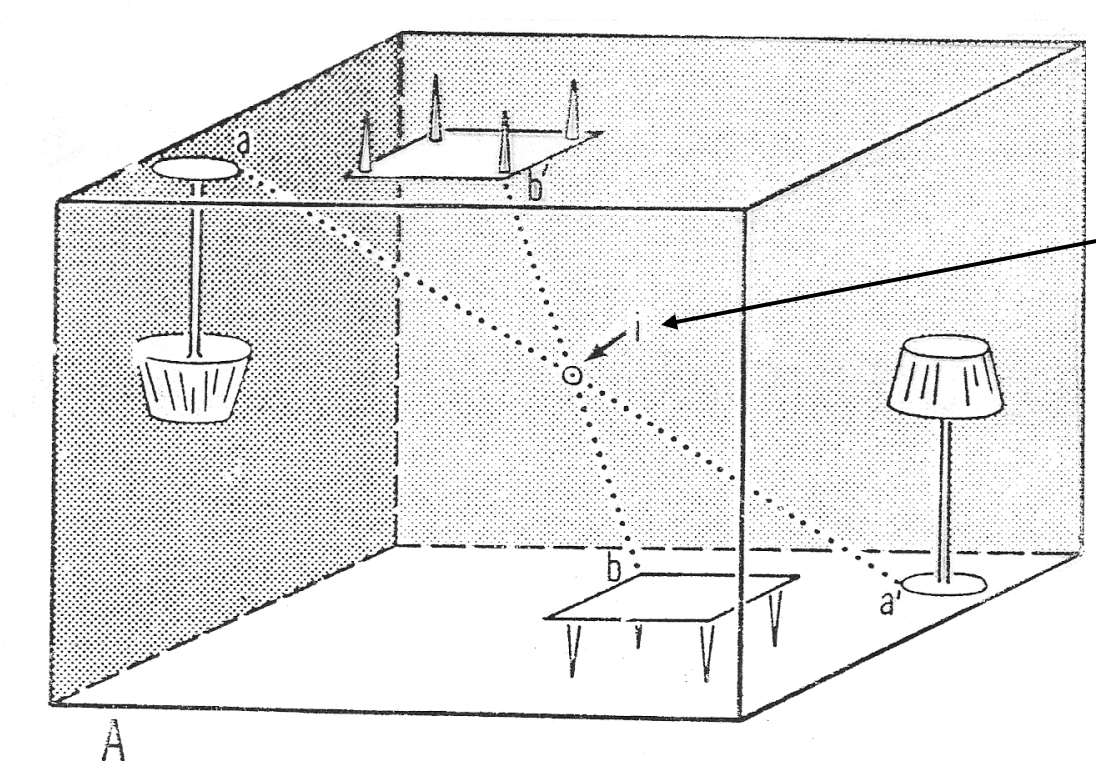
Inversion occurs through a point, called the inversion centre

The inversion centre can be on an atom or on a bond.





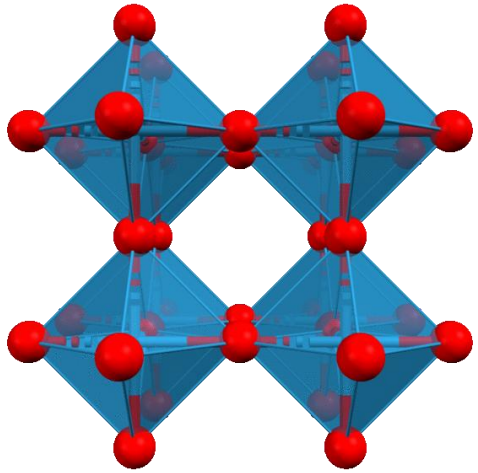
Revision: Inversion (i)



inversion centre

Revision: Structure of ReO_3

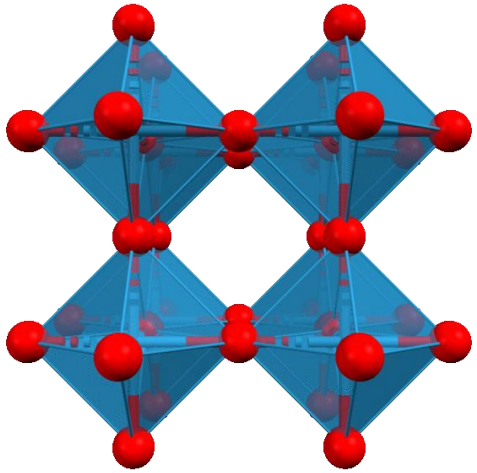
Transition Metal Oxides: Rhenium vs. Tungsten



ReO_3

$5d^1$

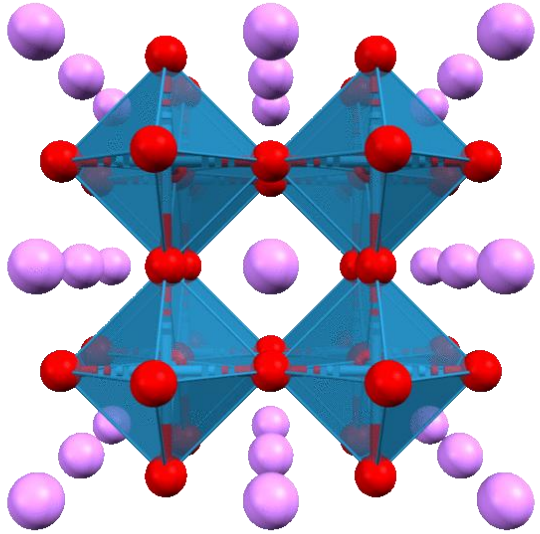
metallic



WO_3

$5d^0$

insulating



$NaWO_3$

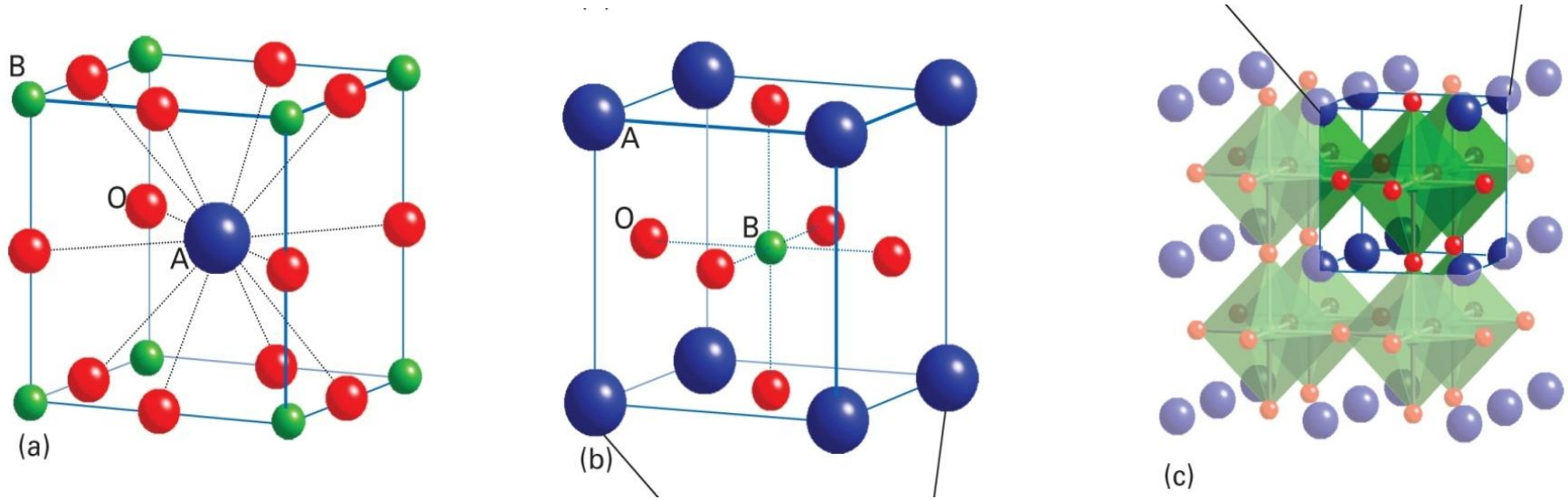
$5d^1$

metallic

Structure of Barium Titanate

Perovskite-type structures have the general formula ABX_3 (where the BX_3 atoms form the ReO_3 lattice)

- A = cation in 12-fold coordination (by X)
- B = cation in octahedral coordination (by X)
- X = anion (O^{2-}, F^-, etc.)

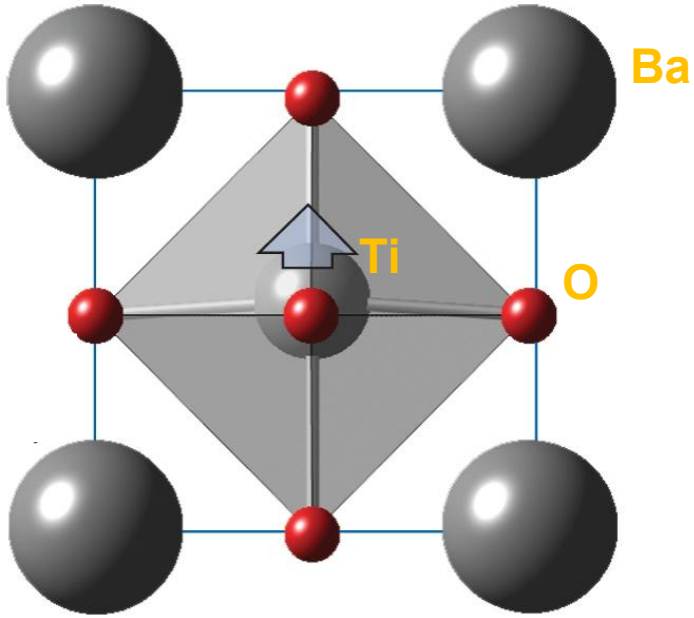


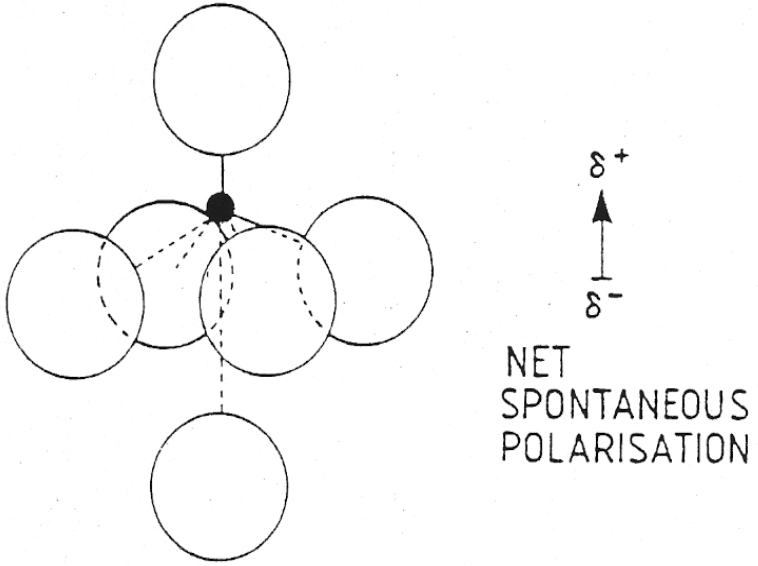
Mechanism of Polarisation in $BaTiO_3$

Spontaneous polarisation of a TiO_6 octahedron in $BaTiO_3$.

The polarisation is caused by the titanium ions moving off the centre of the octahedron (i.e., ionic polarisation) – i.e., **non-centrosymmetric symmetry**.

In principle there are **six equivalent orientations** in which this can occur, giving rise to domains in the structure with the polarity in different orientations.

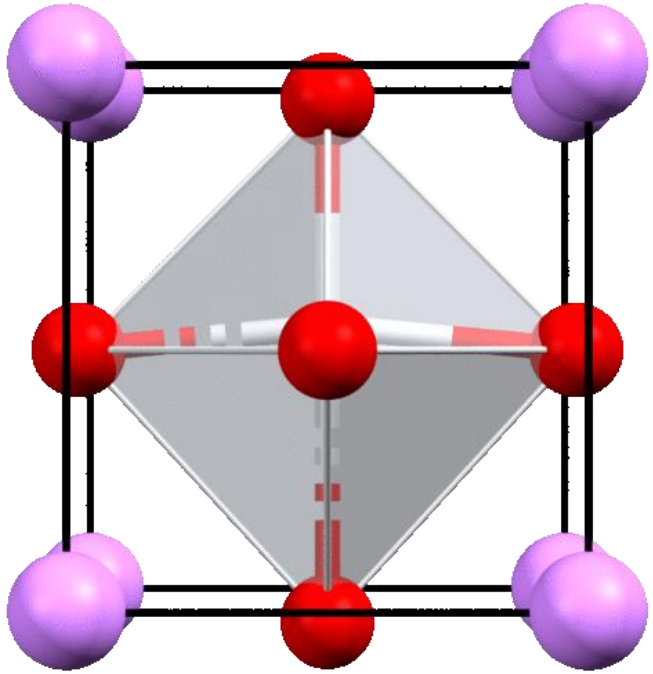




Polar and Non-Polar Forms of $BaTiO_3$

Polar form of $BaTiO_3$:

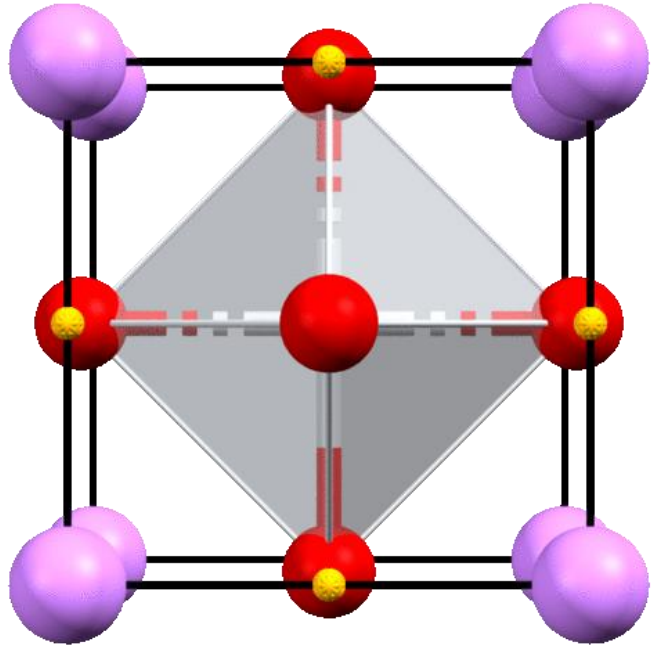
- space group *P4mm* (no inversion symmetry)
- Ferroelectric behaviour



https://materialsproject.org/materials/mp-5986/#

Non-polar form of $BaTiO_3$:

- space group *Pm*-3*m* (inversion symmetry)
- Paraelectric behaviour



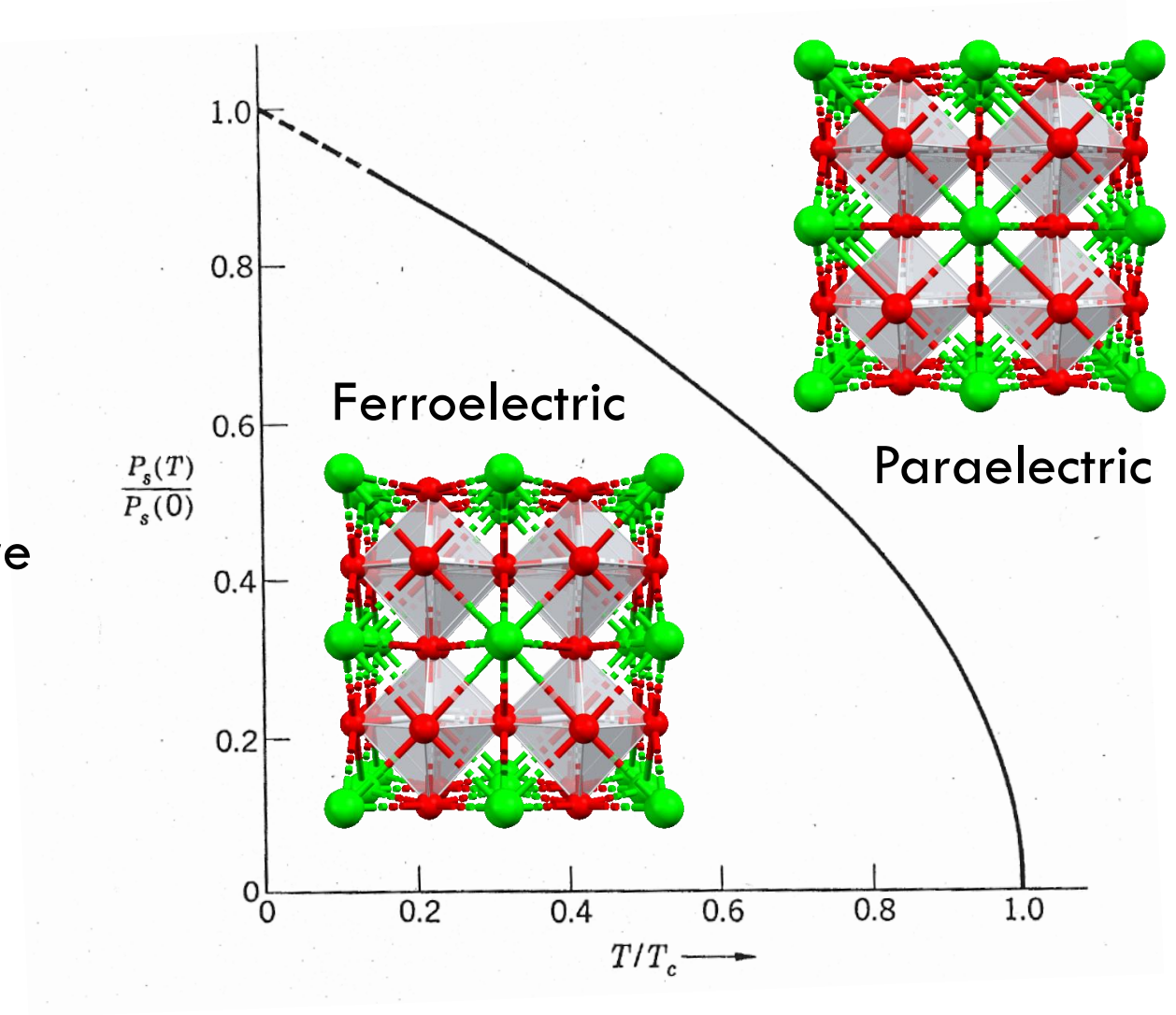
https://materialsproject.org/materials/mp-2998/#

Phase Transition at the Curie Temperature

A solid-solid **phase transition** is the transformation of one crystalline solid into another.

With increasing temperature, phase transitions generally lead to a higher symmetry structure.

The change from a low-temperature ferroelectric state to a high-temperature paraelectric state occurs at the **Curie temperature,** T_C.



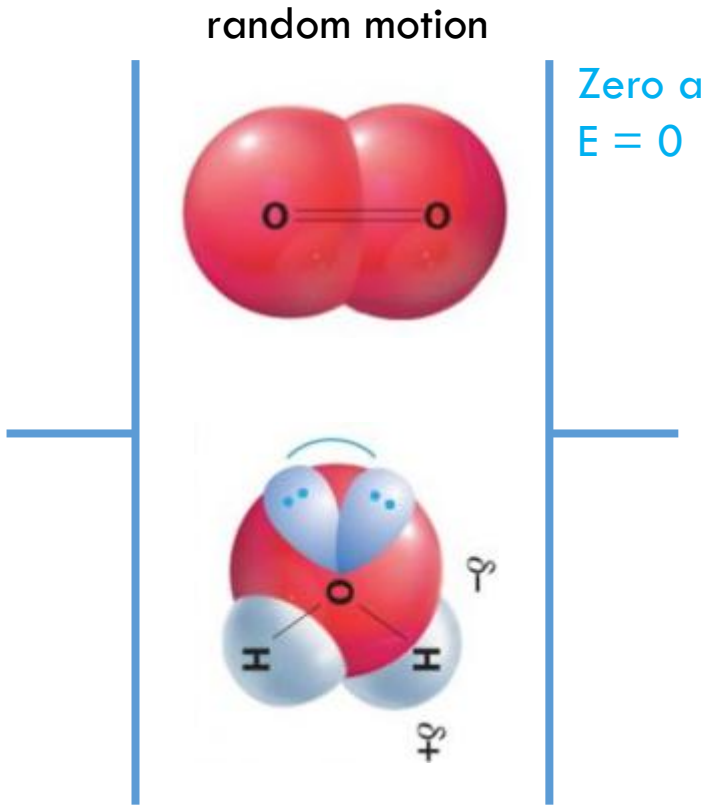
Phase Transition at the Curie Temperature

The Curie temperature varies depending on structure and composition, which can be tailored for specific applications.

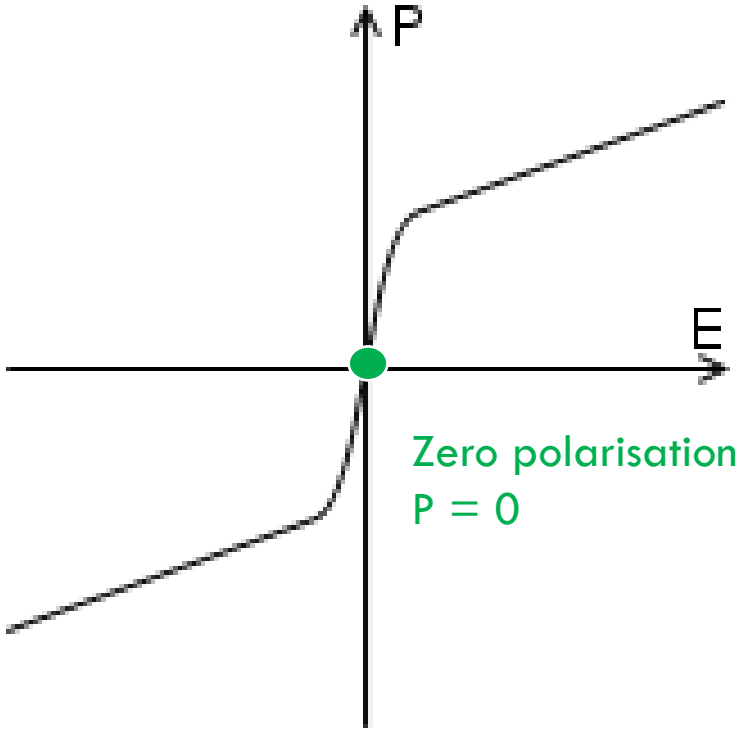
Material	T_C (°C)
Barium titanate, $BaTiO_3$	120
Lithium niobate, $LiNbO_3$	1210
Lead titanate, $PbTiO_3$	490
Lead zirconate titanate, $Pb(Zr_{1-x}Ti_x)O_3$	depends on *x*
Bismuth titanate, $Bi_4Ti_3O_{12}$	159
Potassium dihydrogen phosphate	-150
Rochelle salt, $KNaC_4H_4O_6.4H_2O$	-18 to +24

Polarisation (P) in an Electric Field (E)

Paraelectric Behaviour



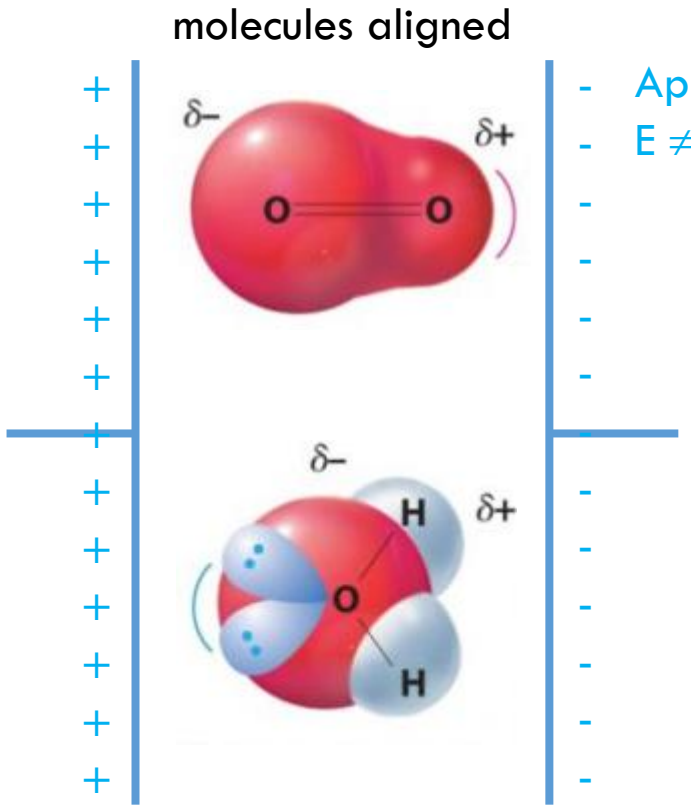
Polarisation



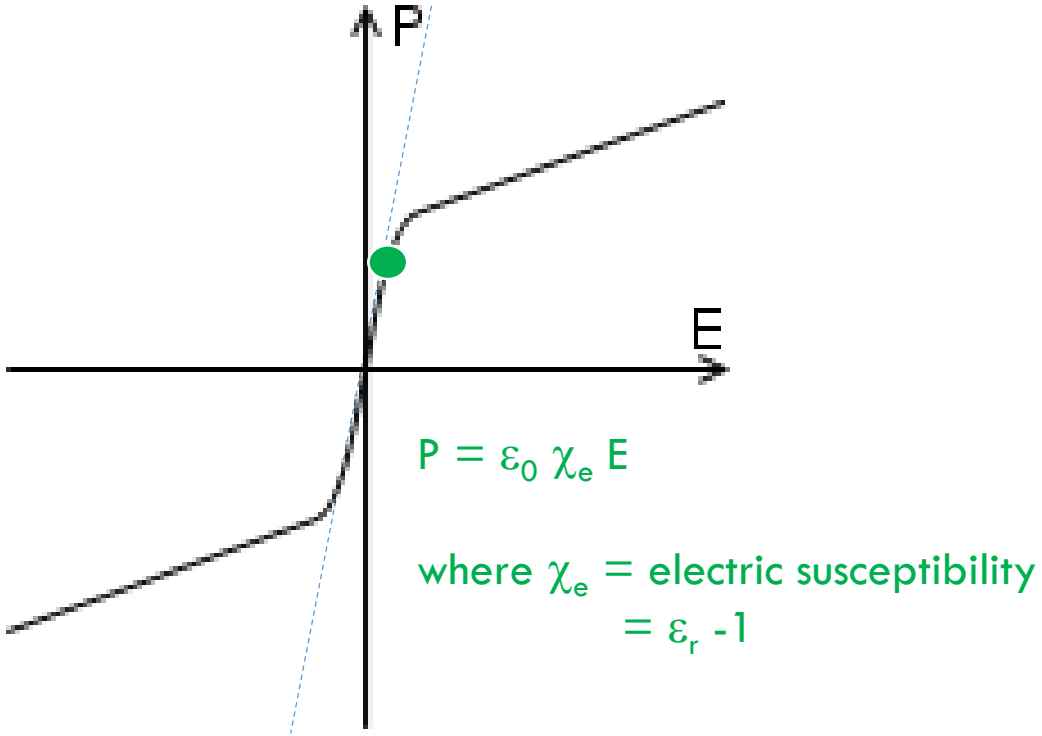
Paraelectric loop

Polarisation (P) in an Electric Field (E)

Paraelectric Behaviour



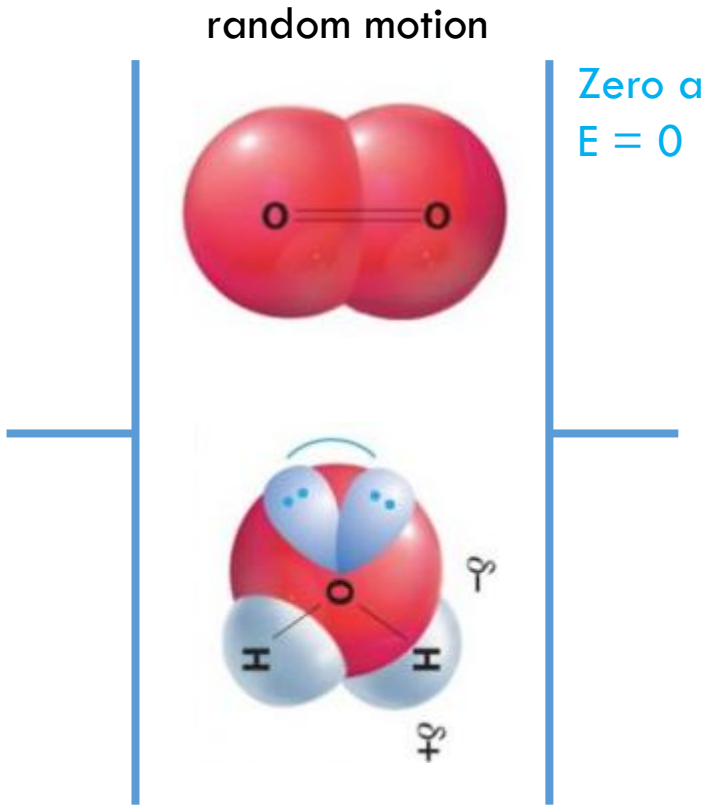
Polarisation



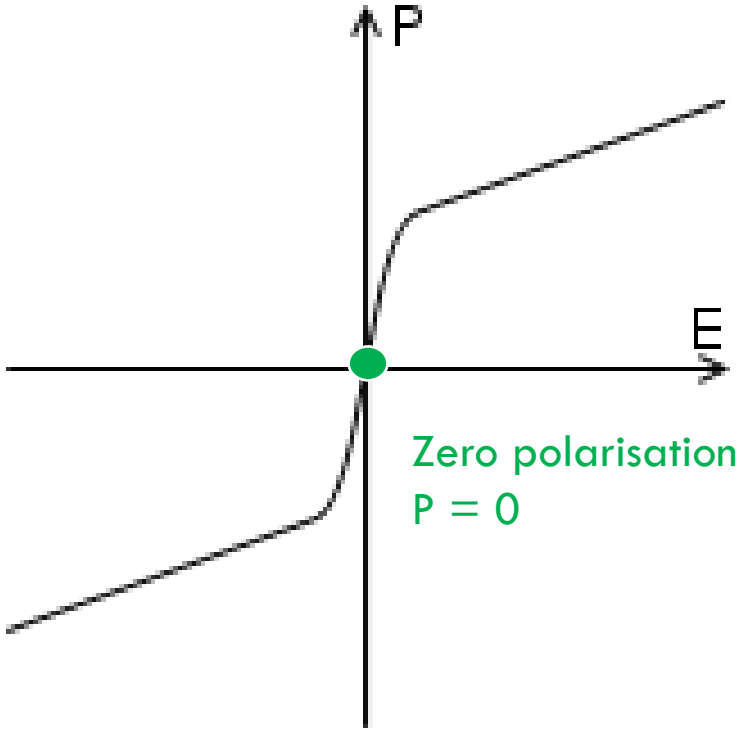
Paraelectric loop

Polarisation (P) in an Electric Field (E)

Paraelectric Behaviour



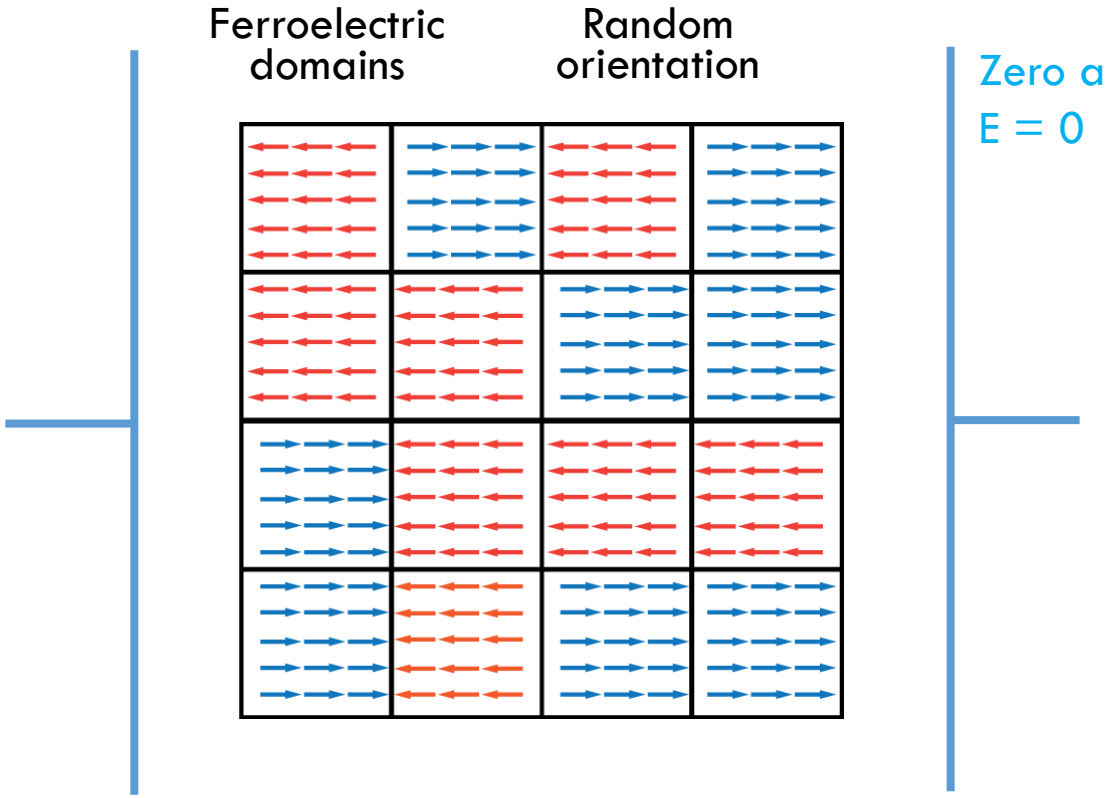
Polarisation



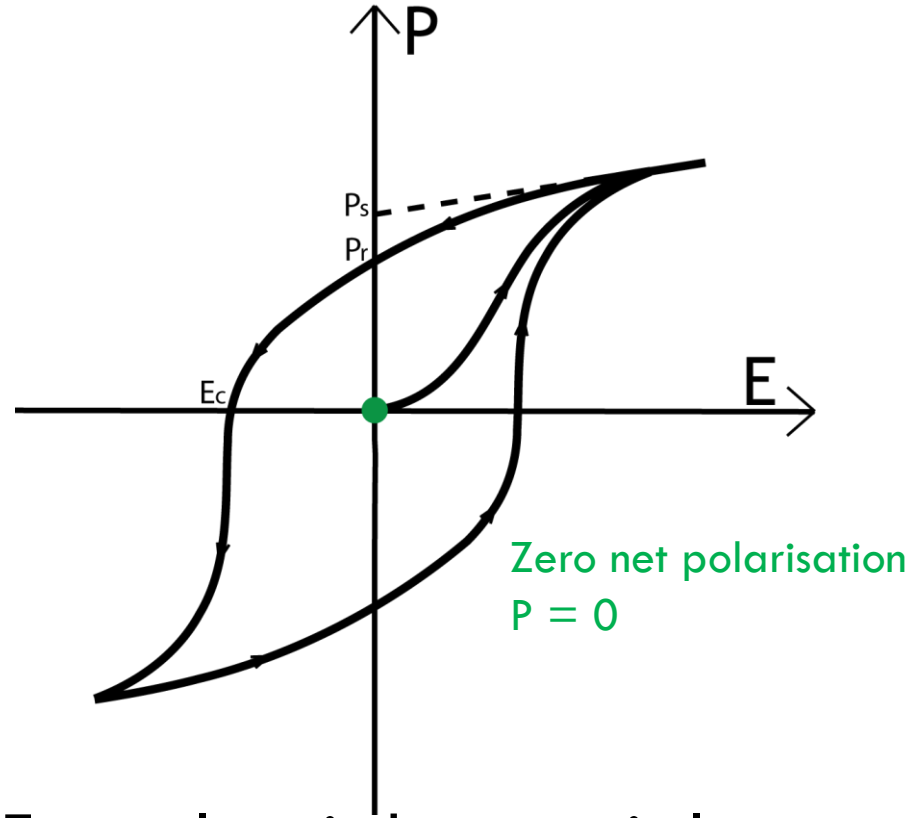
Paraelectric loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



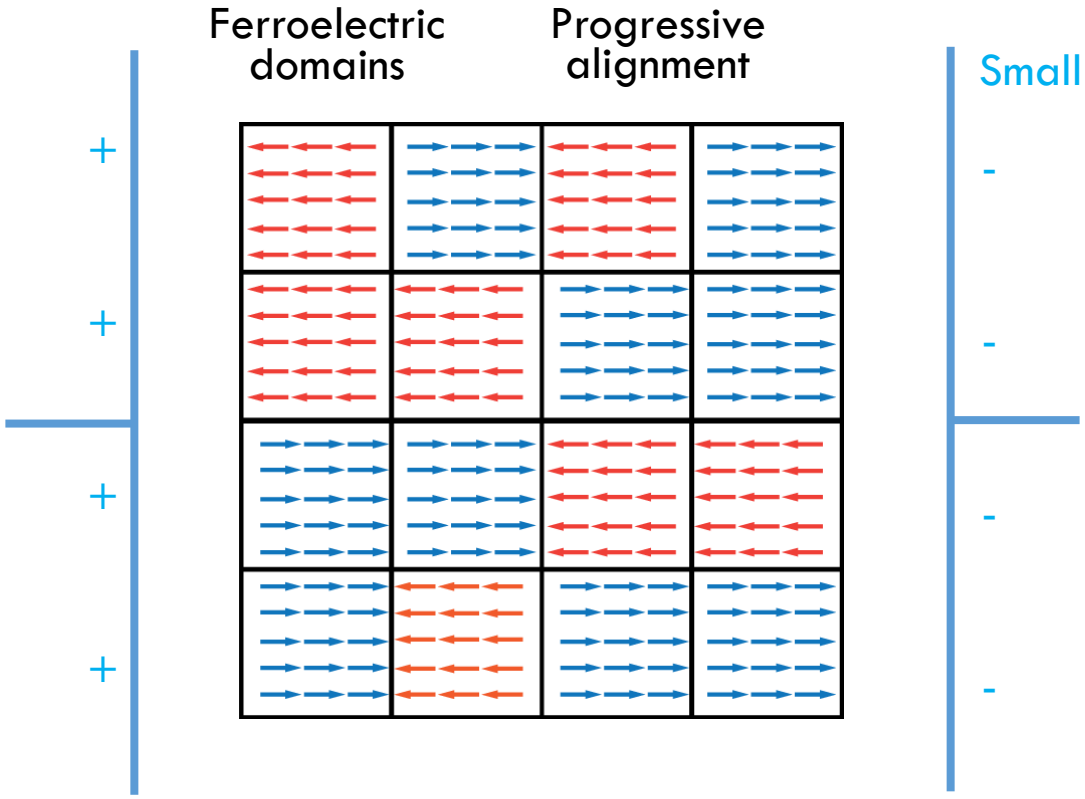
Polarisation



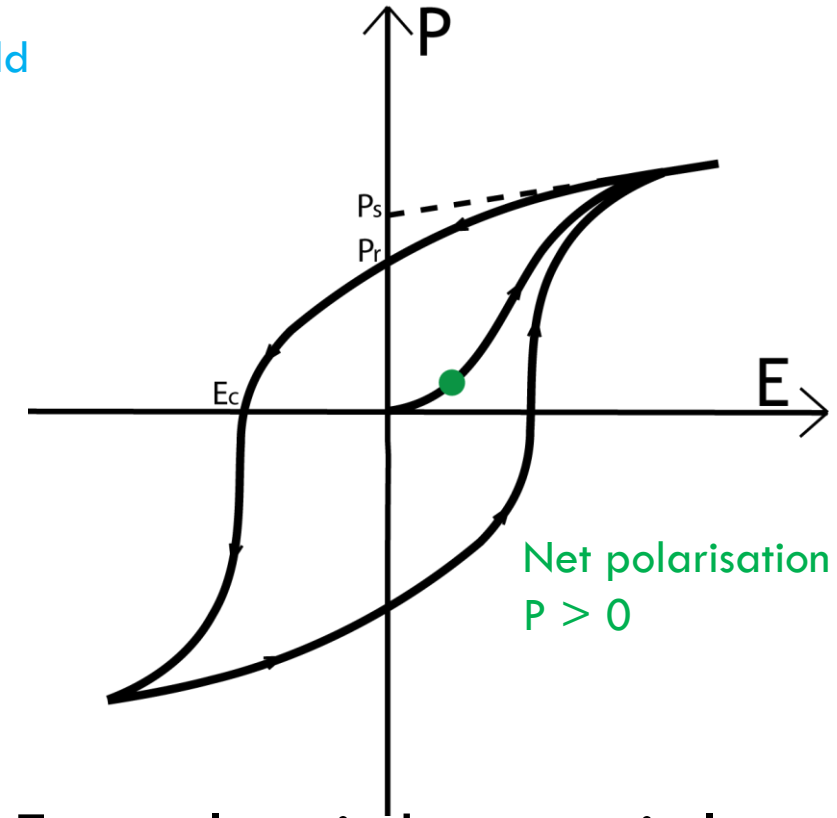
Ferroelectric hysteresis loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



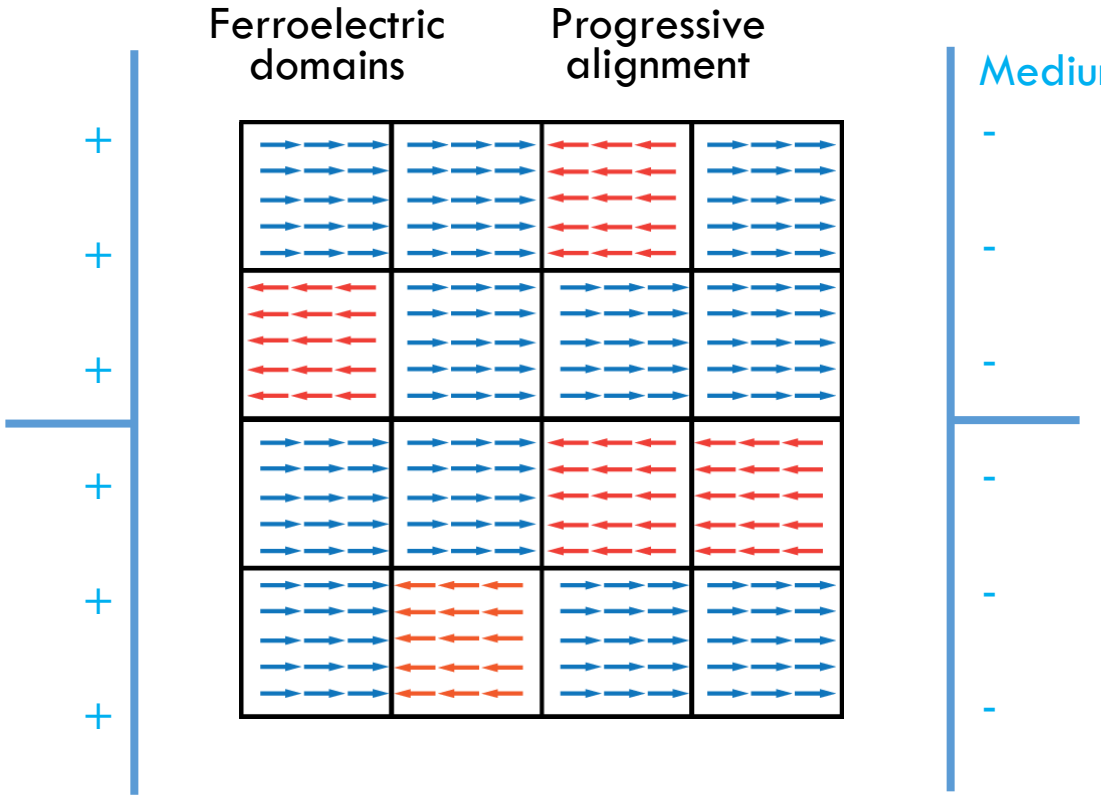
Polarisation



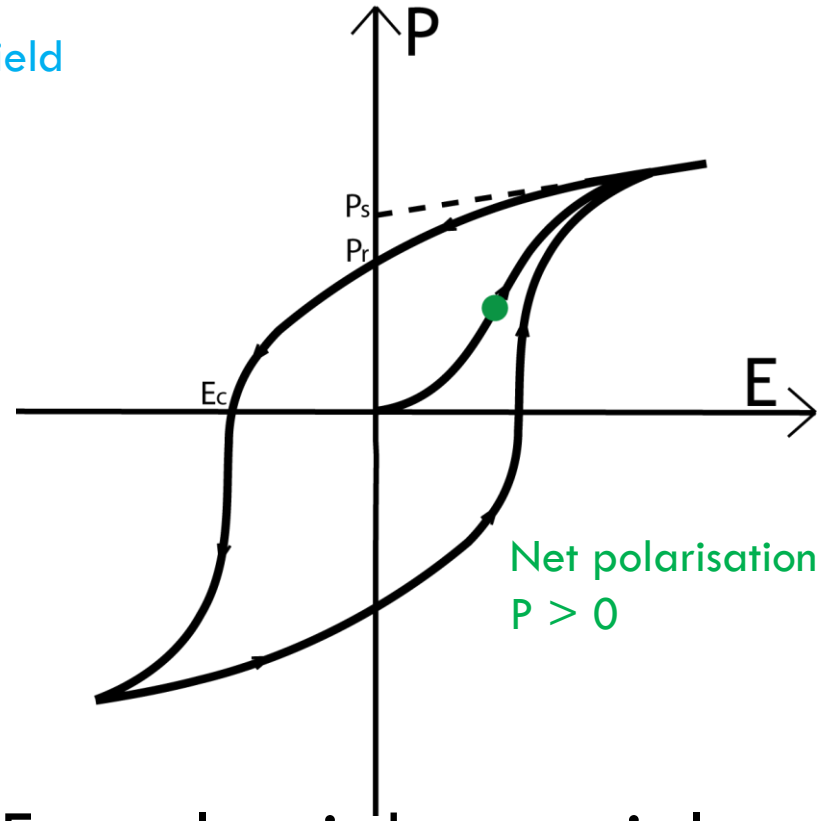
Ferroelectric hysteresis loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



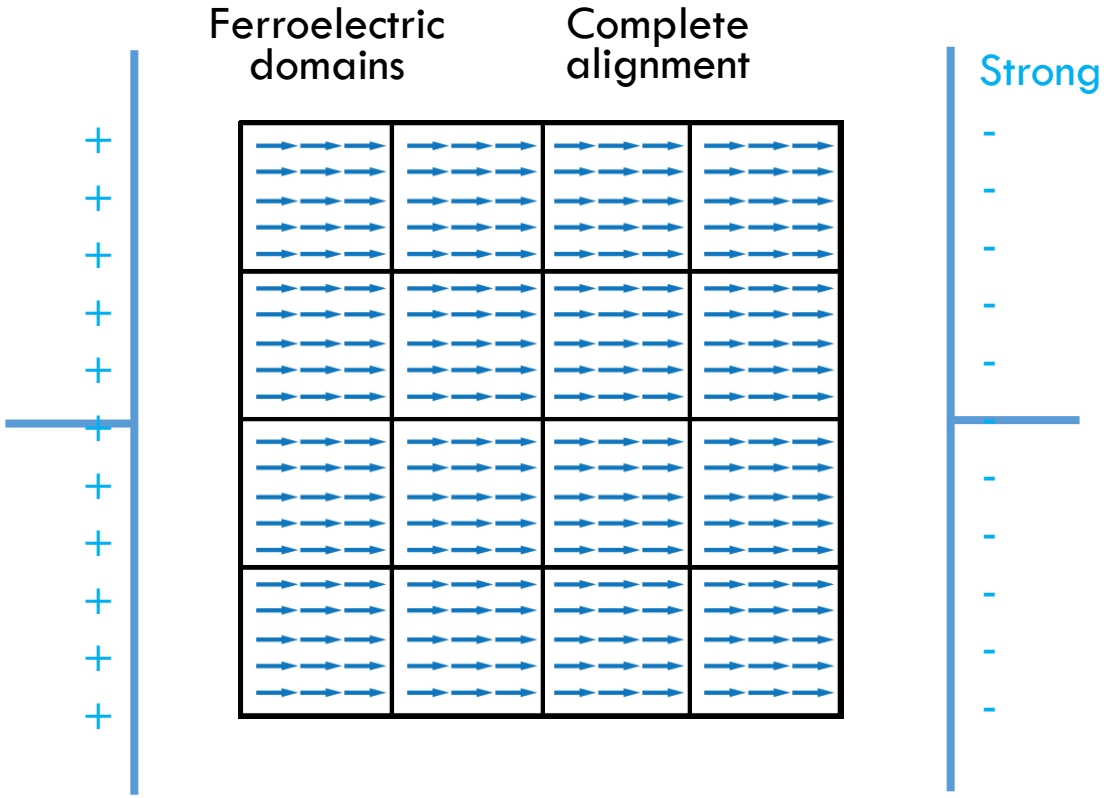
Polarisation



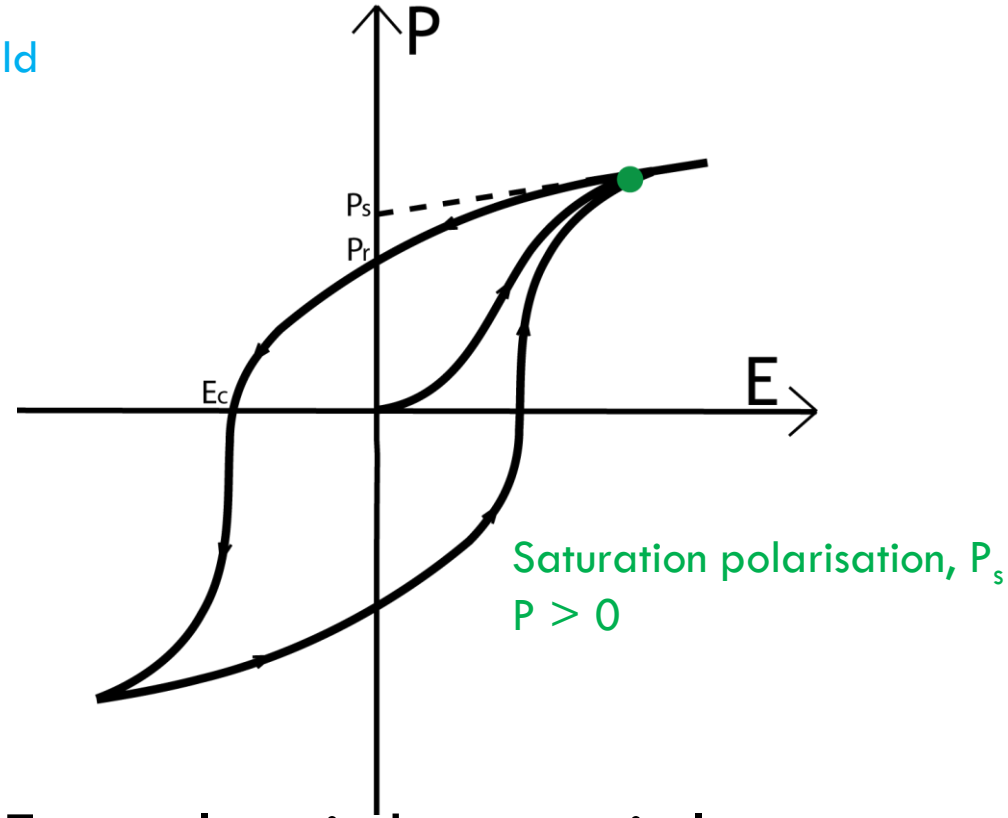
Ferroelectric hysteresis loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



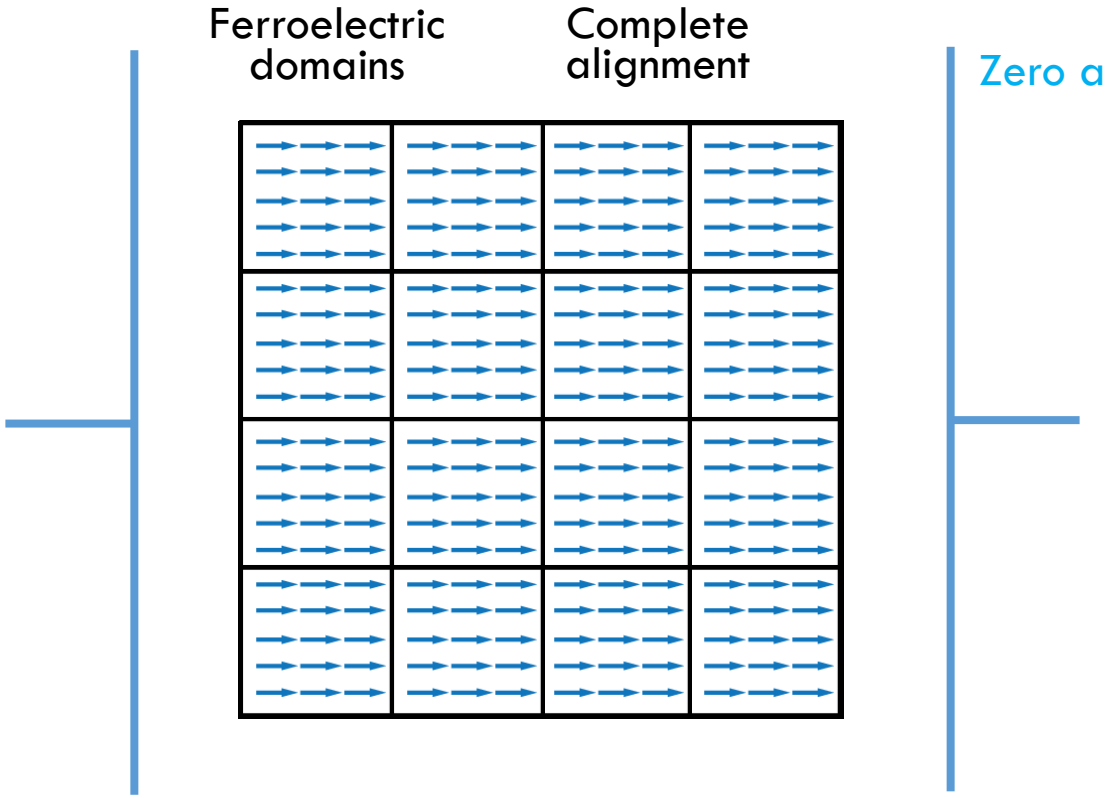
Polarisation



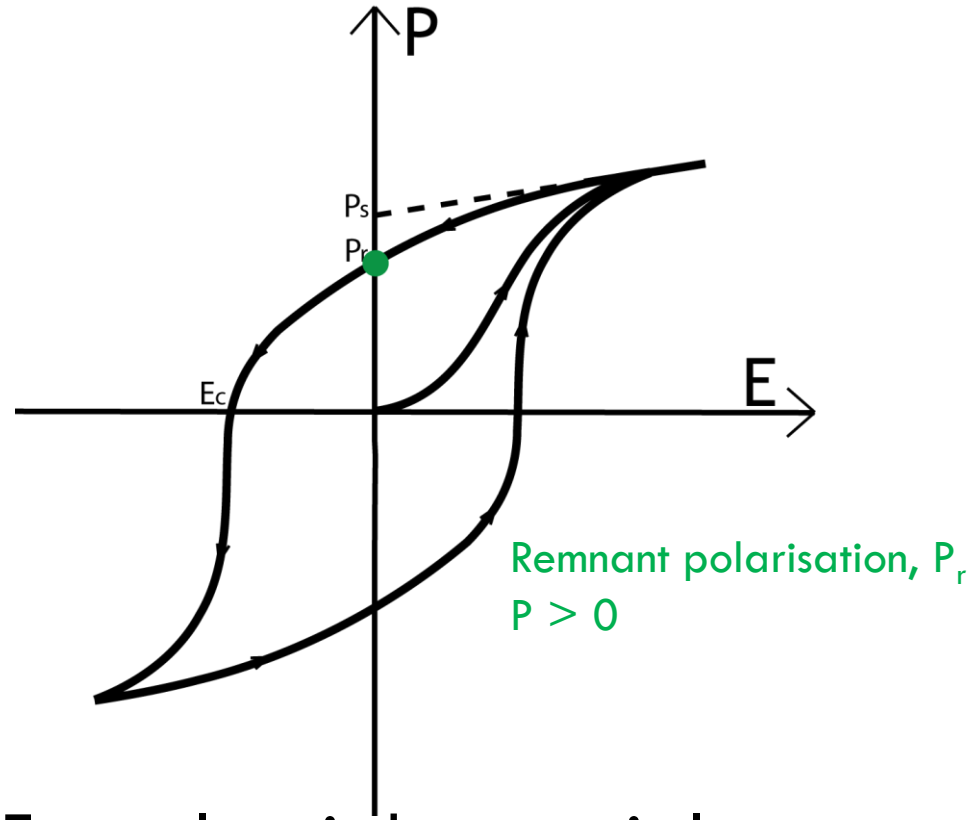
Ferroelectric hysteresis loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



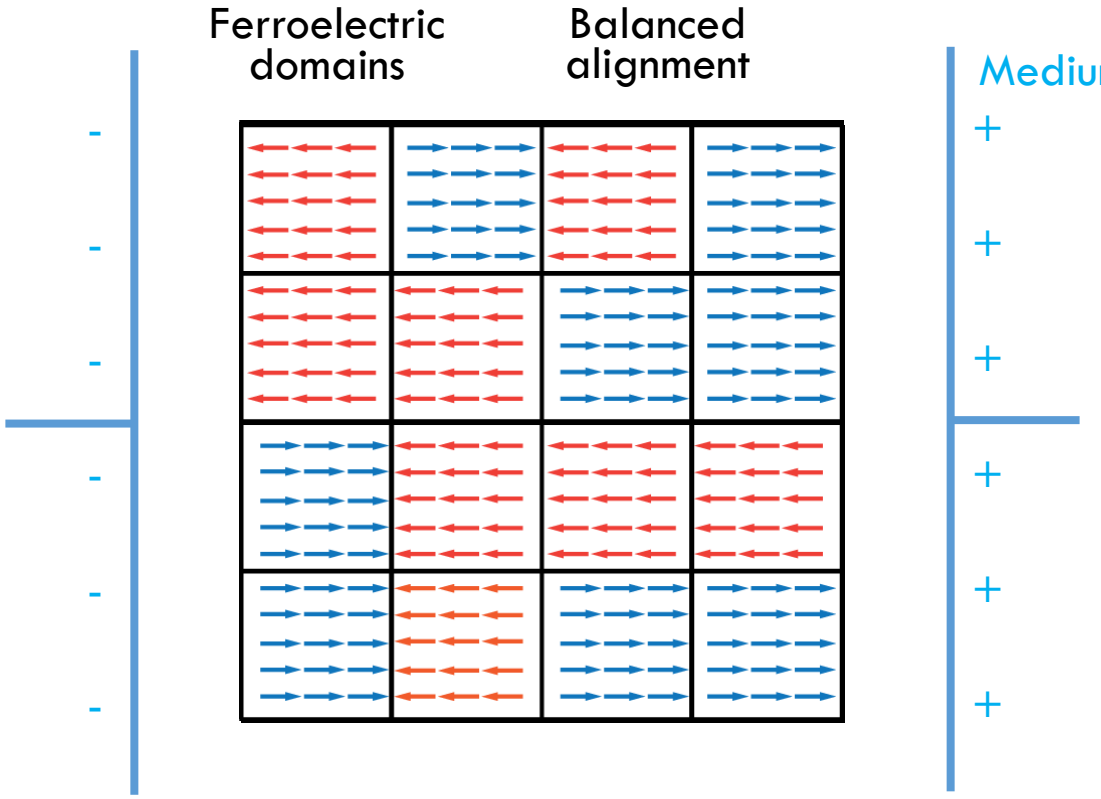
Polarisation



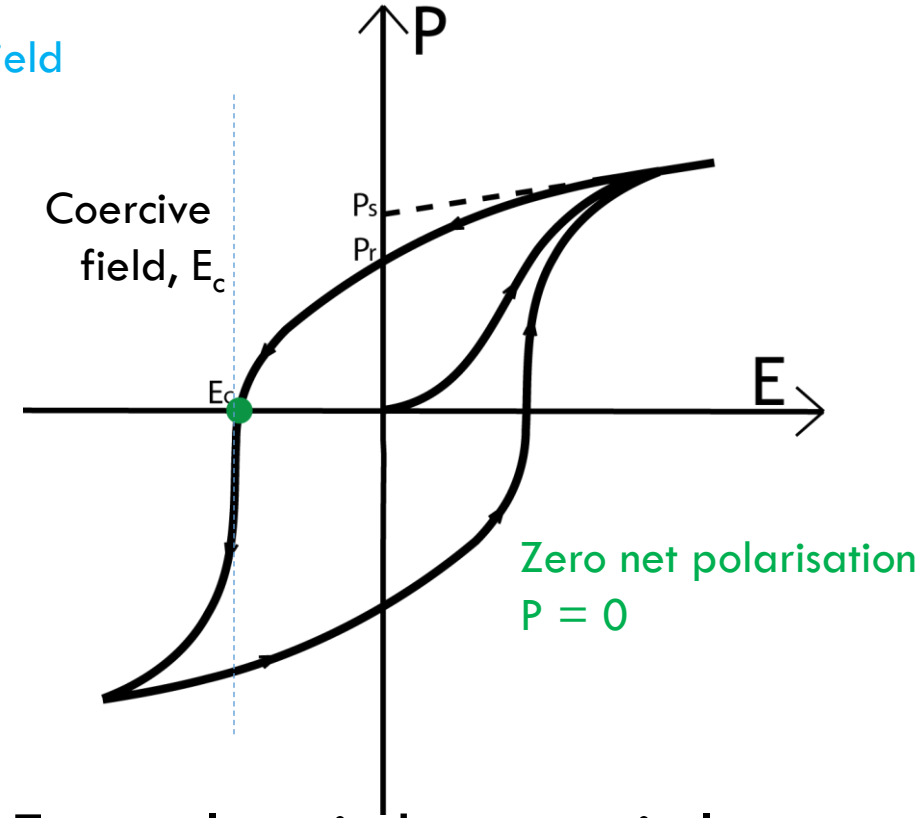
Ferroelectric hysteresis loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



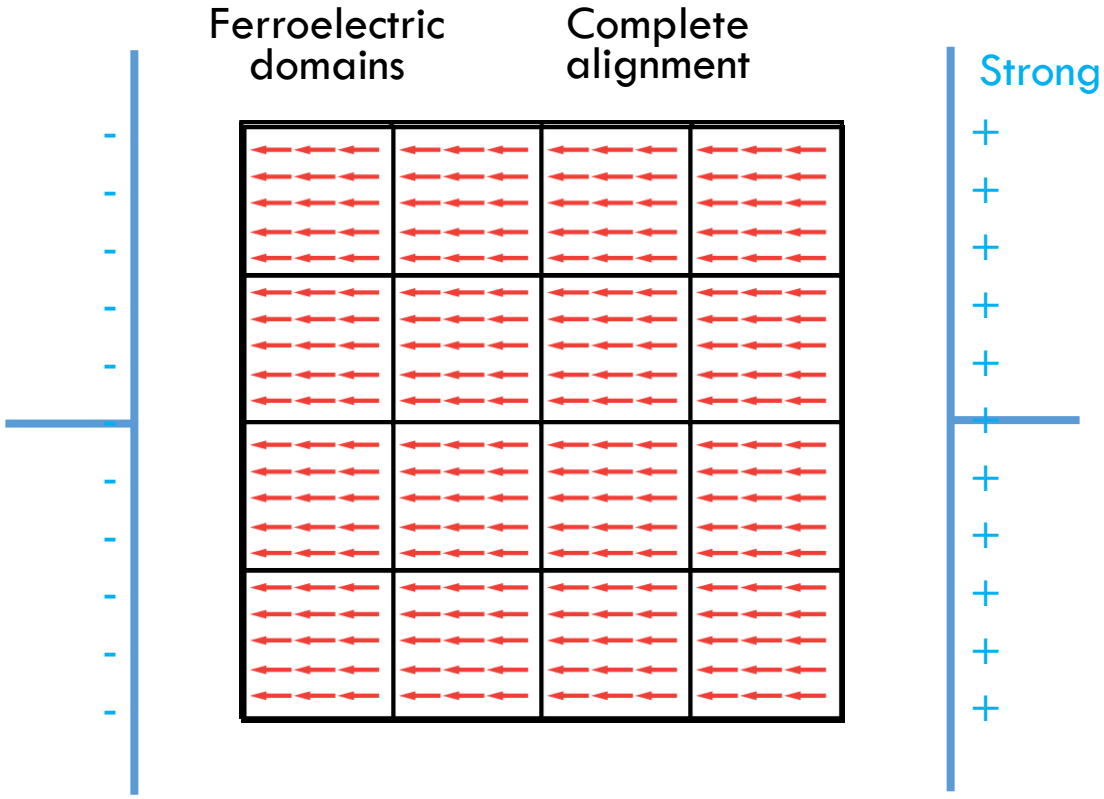
Polarisation



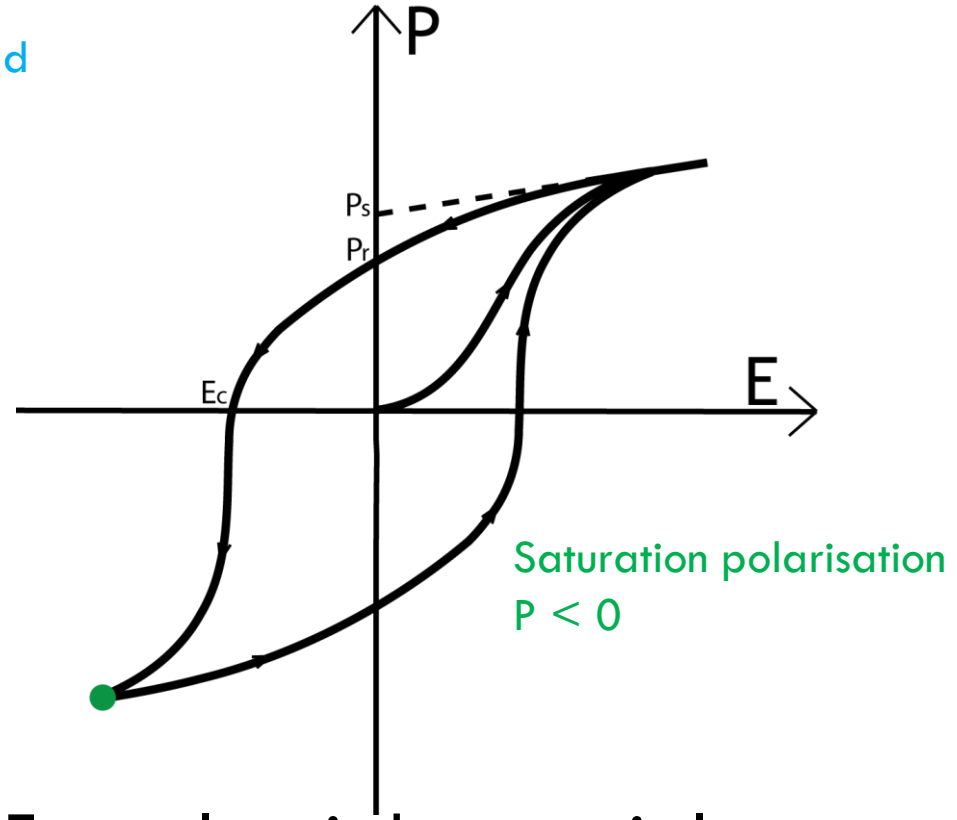
Ferroelectric hysteresis loop

Polarisation (P) in an Electric Field (E)

Ferroelectric Behaviour



Polarisation



Ferroelectric hysteresis loop

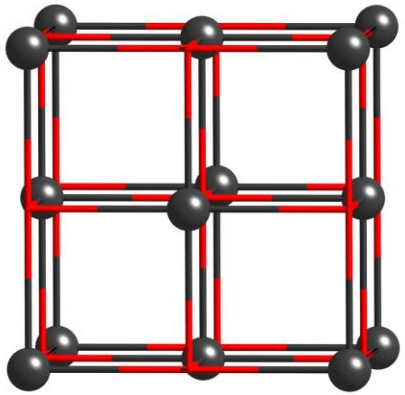
Polarisation from Non-bonding Electrons

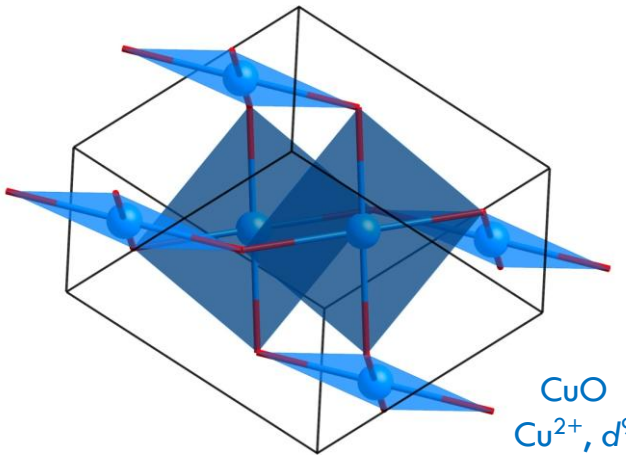
d-Electron Effects

d-electrons do not generally participate in bond formation, but they do influence coordination environments and can cause structural distortions.

- Crystal-field splitting → smaller radii
- Jahn-Teller distortions → symmetry-lowering
  - E.g.,

MnO
Mn^{2+}, d^5
Ideal NaCl-type





CuO
Cu^{2+}, d^9
Distorted NaCl-type

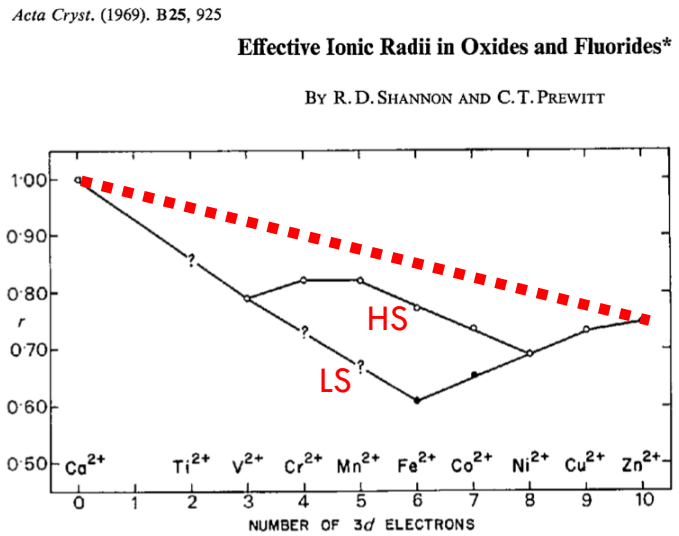


Fig. 3. 'Effective' ionic radius *vs.* number of 3*d* electrons for divalent transition-metal ions.

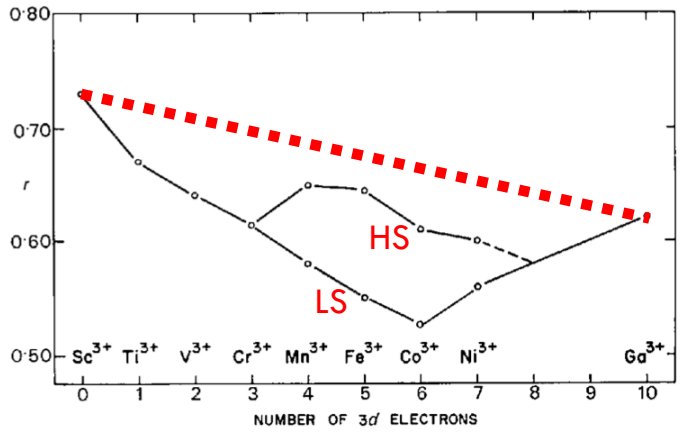


Fig. 4. 'Effective' ionic radius *vs.* number of 3*d* electrons for trivalent transition-metal ions.

Polarisation from Non-bonding Electrons

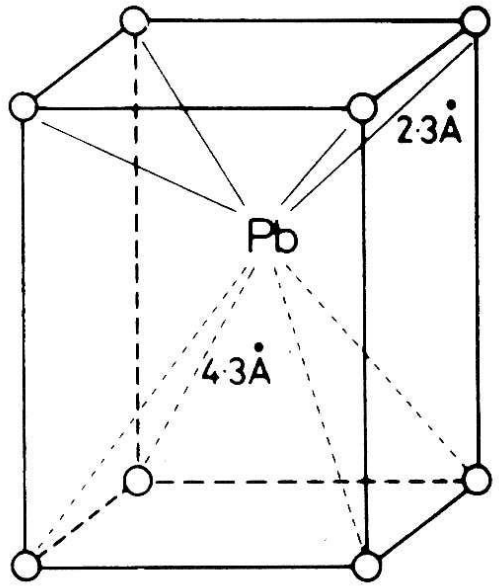
Inert Pair Effect

Heavy metal cations with valences 2 less than the group valence often have stereochemically active electron lone pairs. E.g.,

Sn^{2+}, Sb^{3+}, Te^{4+} : $[Kr]4d^{10}5s^2$

Tl^{+}, Pb^{2+}, Bi^{3+} : $[Xe]4f^{14}5d^{10}6s^2$

These non-binding lone pairs are not spherically symmetric (due to sp-hybridisation) leading to asymmetry in the structure.



α-PbO

Figure from West "Basic Solid State Chemistry"

Polarisation from Non-bonding Electrons

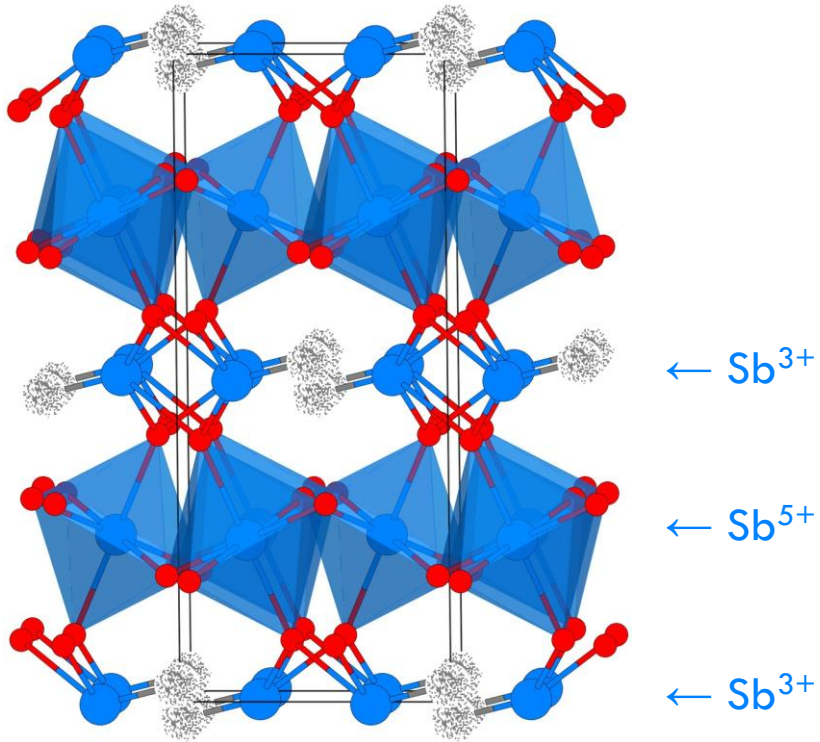
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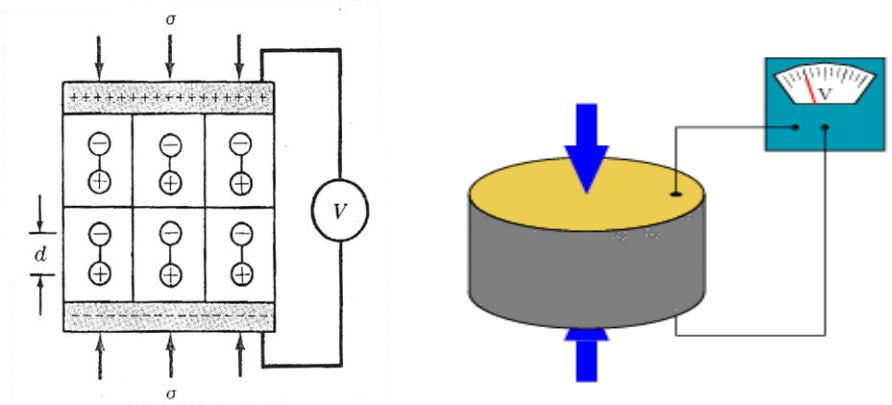
α-Sb_2O_4

Ordered layers of Sb^{3+} and Sb^{5+} sites gives rise to a locaslised polar structure

Piezoelectric Materials

Piezoelectric effect

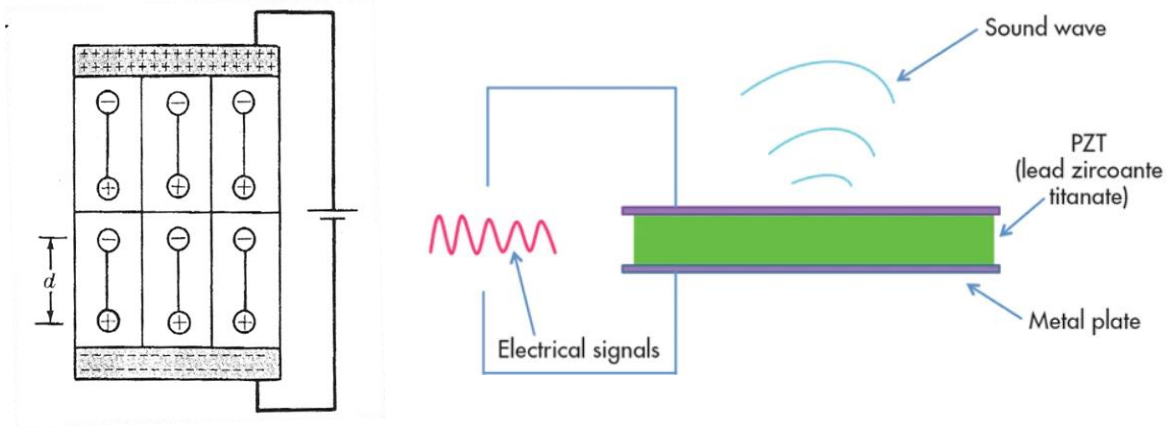
Applied stress on material causes a voltage difference to develop



Applications in microphones, tilt-sensors, strain gauges, ignition devices (e.g., bbq), quartz crystal microbalances, scanning probe microscopes, etc.

Reverse piezoelectric effect

Applied voltage across a materials causes a dimensional change

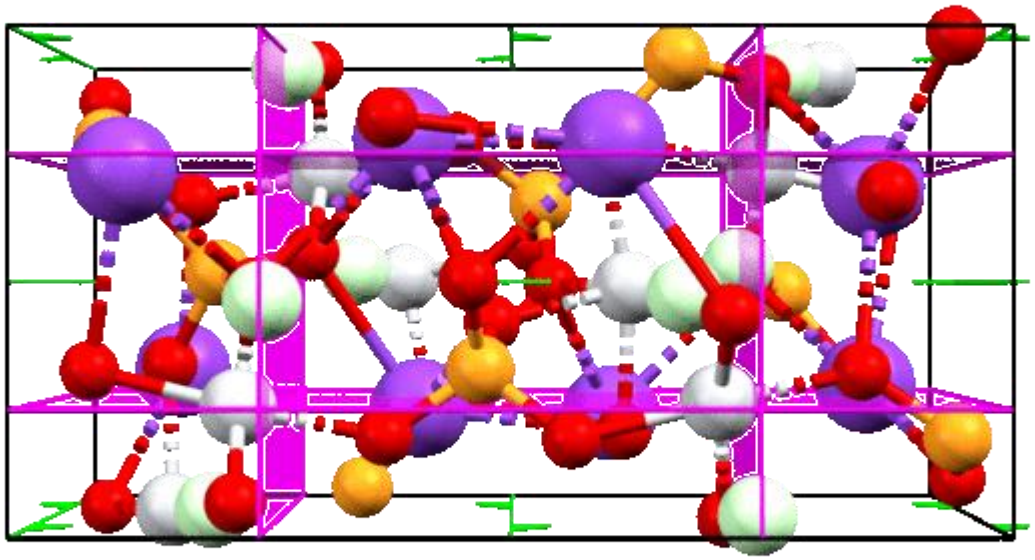


Applications in crystal oscillator timing devices, speakers, inkjet printing, actuators, vibrational damping, scanning probe microscopes (to control needle position), etc.

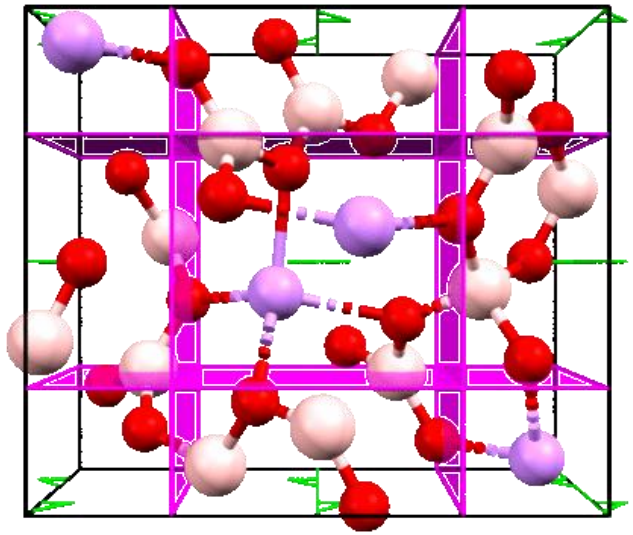
Non-Linear Optical Materials

Second-harmonic generation (SHG)

$KTiOPO_4$ and LiB_3O_5 are technologically important SHG materials.
Both have space group symmetry $Pna2_1$, which lacks a centre of inversion.



$KTiOPO_4$ ('KTP')

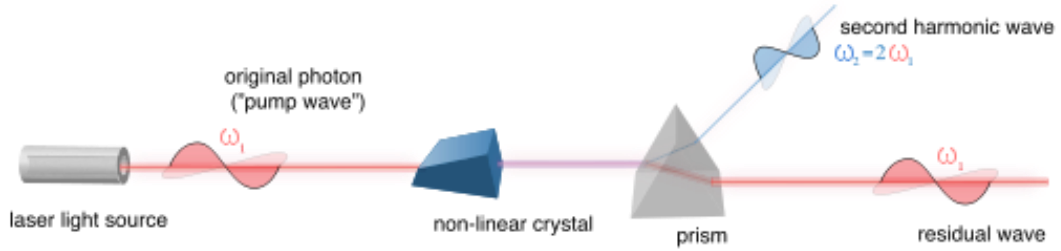


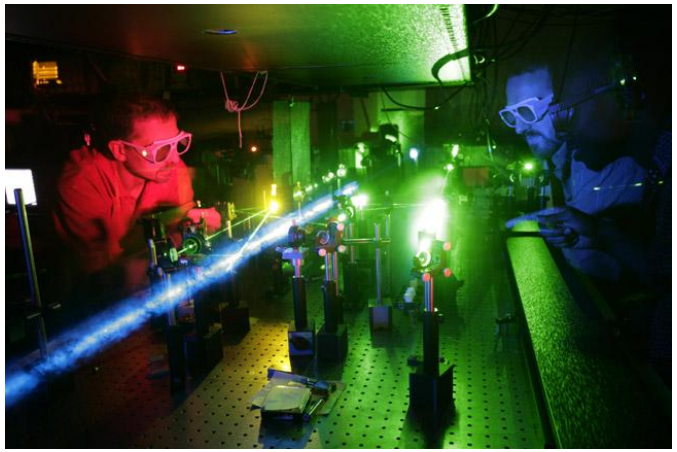
LiB_3O_5 ('LBO')

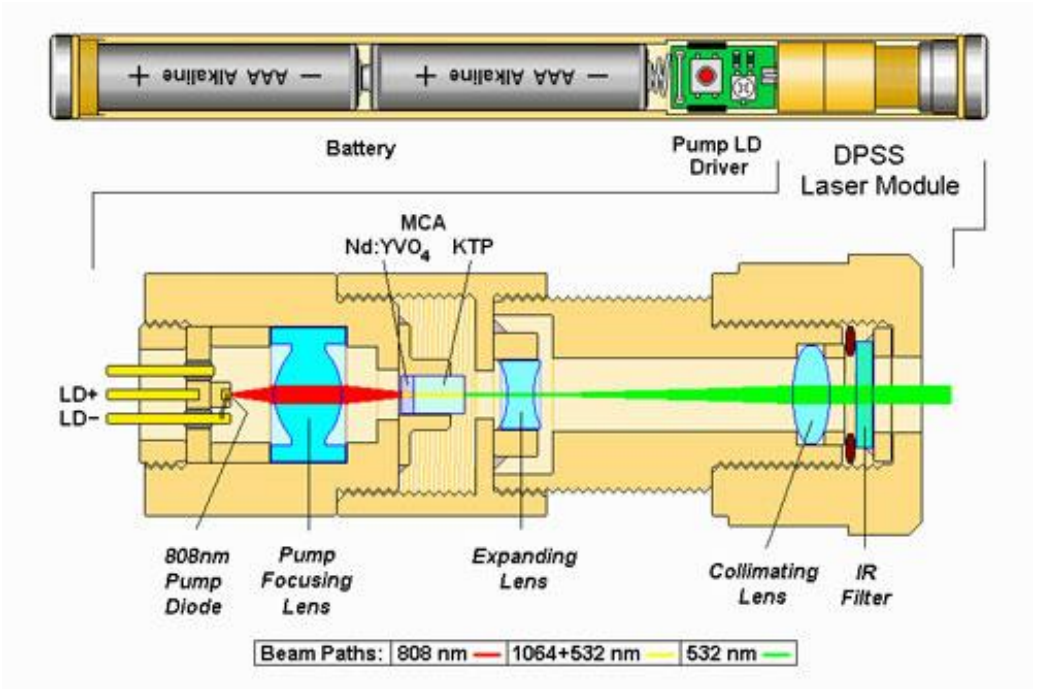
Non-Linear Optical Materials

Second-harmonic generation (SHG)

Application in green lasers: As red light passes through KTP, two photons interact and are combined to create a new photon with twice the energy, i.e., green light.







Learning Outcomes

After this lecture you should be able to

- Understand how local atomic displacement leads to lowered crystal symmetry.
- Name and explain different types of dielectric materials/properties, including the features of a ferroelectric hysteresis loop.
- Predict the effect of temperature on dielectric properties.
- Recognise non-bonding electron effects that can cause structural distortions.
- Complete the lecture worksheet and start preparing for the in-semester test to be held in week 5 (covering content from lectures 2 to 11).

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 24.