Aalto University
School of Chemical
Engineering

Functional Inorganic Materials
Lecture 11:
Pyroelectricity and ferroelectricity

Fall 2021

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Lecture Assignment 11 is a MyCourses Quiz

Contents

- Brief overview of **polar materials**
  - Pyro- and ferroelectrics are limited to crystals with certain symmetry properties
- **Pyroelectric** materials
  - Electric polarization from fluctuating temperature
  - Temperature change due to electric current (***electrocaloric effect***)
  - Pyroelectric effect is **not** related to thermoelectric Seebeck and Peltier effects!
- **Ferroelectric** materials
  - Subgroup of pyroelectric materials: reversible electric polarization (dipole moment)

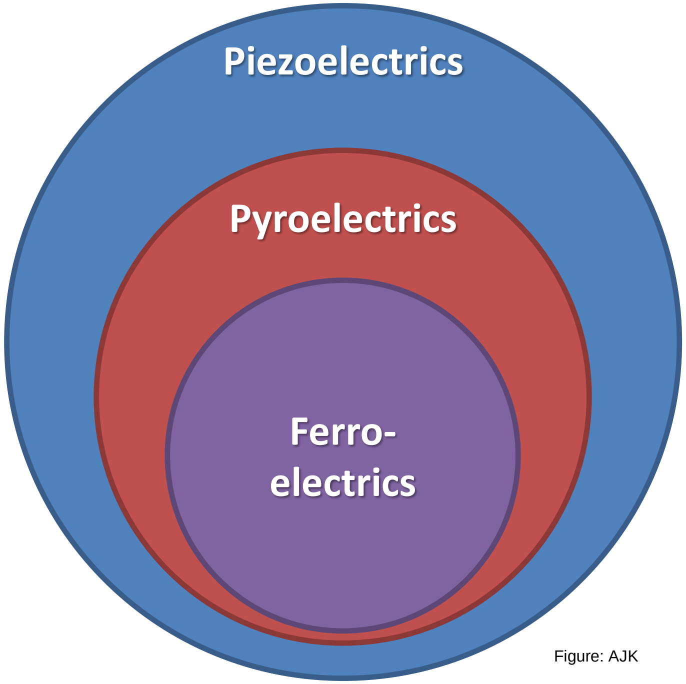


Figure: AJK

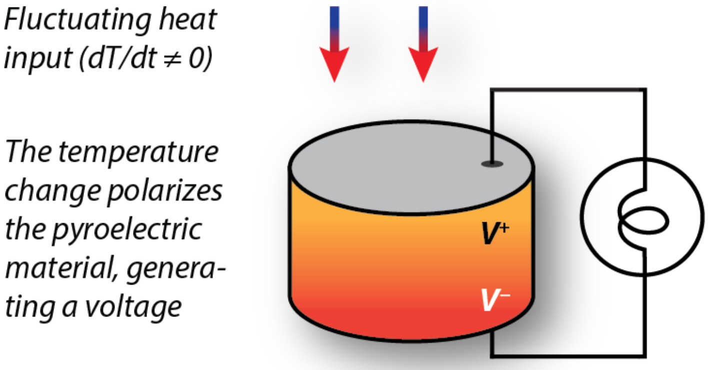
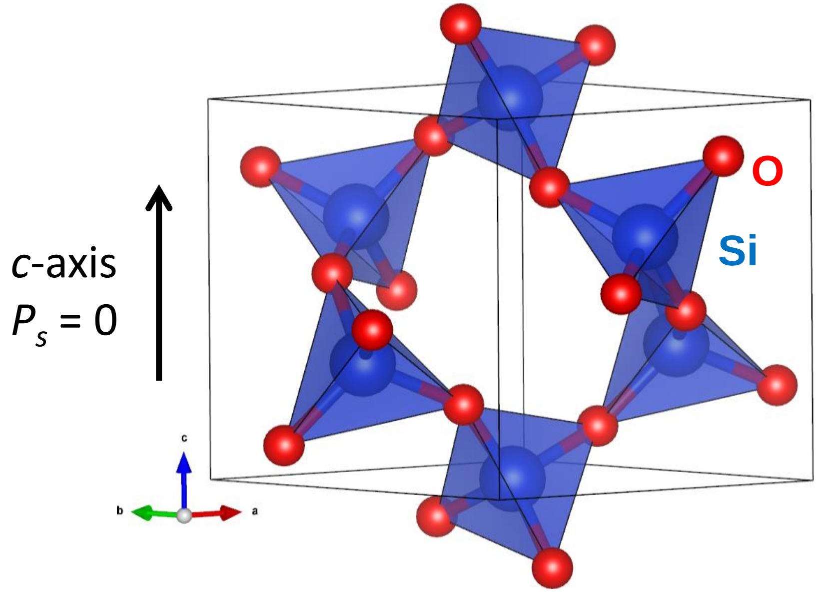


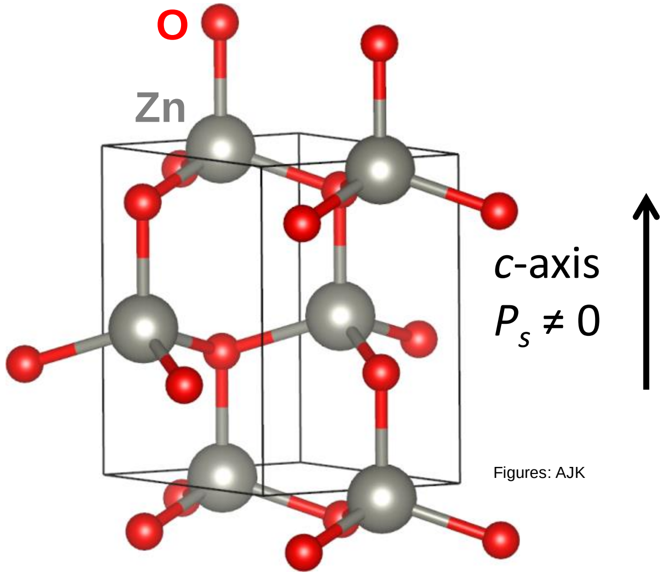
Figure: AJK

Polar and non-polar materials

- Non-centrosymmetric materials can be ***polar*** or ***non-polar***
  - A polar crystal has more than one point that every symmetry operation leaves unmoved
  - For example, a ”**polar axis**”, with no mirror plane or twofold axis perpendicular to it
  - Physical property (e.g. ***dipole moment***) can differ at the two ends of the axis
- Pyro- and ferroelectricity is only possible for ***polar materials***
  - Polar materials show ***spontaneous polarization*** $\boldsymbol{P_s}$



α-SiO_2, α-quartz (space group $P3_221$)
Non-centrosymmetric oxide with
no polar axis (*c* has perpendicular C_2 axis)



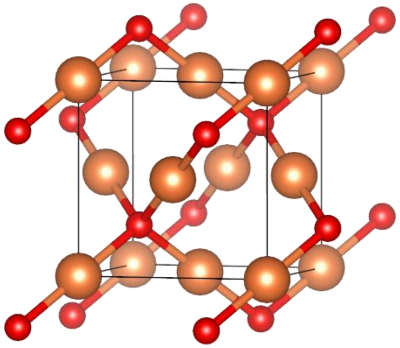
Figures: AJK

ZnO (space group $P6_3mc$)
Non-centrosymmetric oxide with
a **polar axis** (*c*-axis)

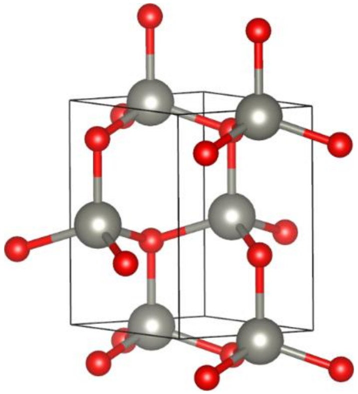
Classification of crystal classes

Crystal system	Centrosymmetric crystal classes (11)	Non-centrosymmetric crystal classes (21)	
		Polar (10)	Non-polar (11)
Triclinic	$\bar{1}$	1	–
Monoclinic	$2/m$	$2, m$	–
Orthorhombic	mmm	$mm2$	222
Tetragonal	$4/m, 4/mmm$	$4, 4mm$	$\bar{4}, 422, \bar{4}2m$
Trigonal	$\bar{3}, \bar{3}m$	$3, 3m$	32
Hexagonal	$6/m, 6/mmm$	$6, 6mm$	$\bar{6}, 622, \bar{6}m2$
Cubic	$m\bar{3}, m\bar{3}m$	–	$23, \bar{4}3m, 432,$

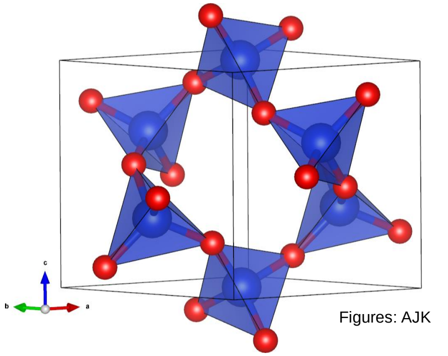
Refs: *Chem. Mater.* **1998**, *10*, 2753 and Wikipedia



Cu_2O ($Pn\text{-}3m$)



ZnO ($P6_3mc$)



Figures: AJK

α-SiO_2 ($P3_221$)

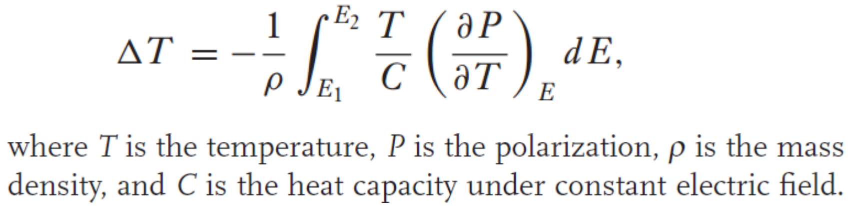
Pyroelectric coefficients

(Primary) **pyroelectric effect**

$\Delta P_s = p\Delta T$, where

- ΔT = temperature **change** (K)
- p = pyroelectric coefficient (C $m^{-2}K^{-1}$)
- ΔP_s = change of **spontaneous polarization** (C m^{-2})

Electrocaloric effect (not discussed here)

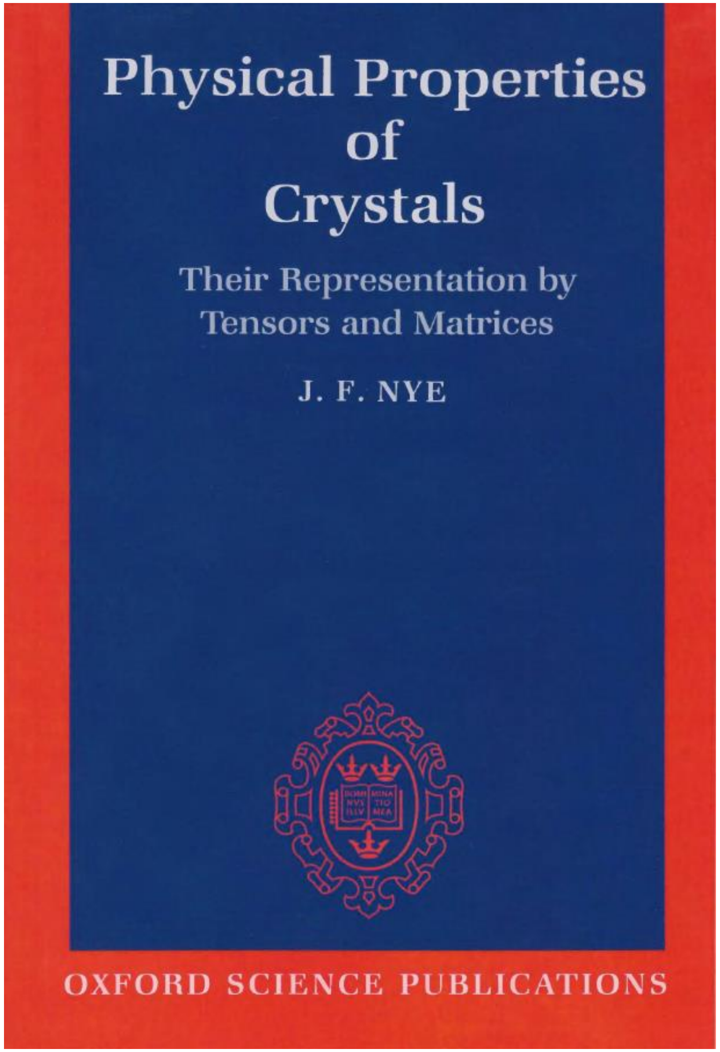


$$\Delta T = -\frac{1}{\rho}\int_{E_1}^{E_2} \frac{T}{C}\left(\frac{\partial P}{\partial T}\right)_E dE,$$

where T is the temperature, P is the polarization, ρ is the mass density, and C is the heat capacity under constant electric field.

Often pyroelectricity is discussed using just scalar coefficient *p*.
In reality, it is a *tensor* p_i and can be described more accurately with the help of crystal symmetry.

Tensors (and matrices) for equilibrium properties



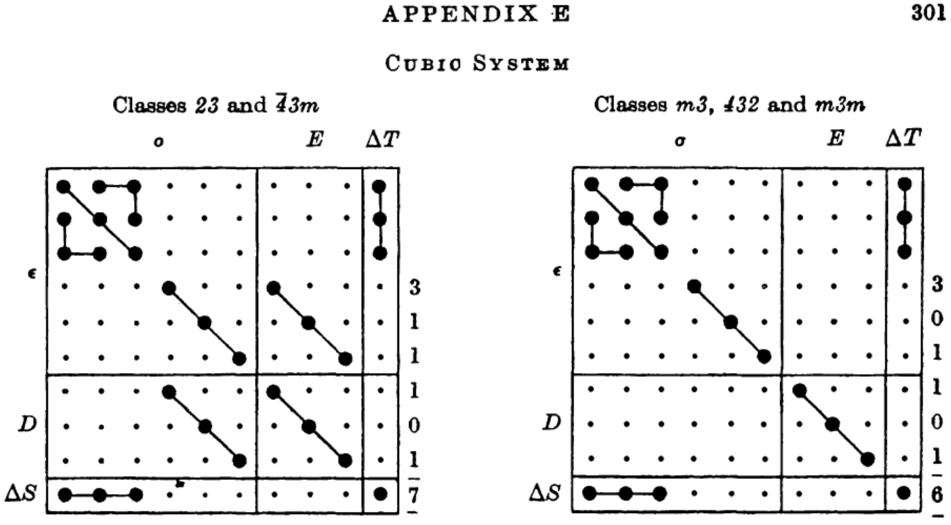
Physical Properties of Crystals

Their Representation by Tensors and Matrices

J. F. NYE

OXFORD SCIENCE PUBLICATIONS

- Physical properties of crystals can be formulated systematically in ***tensor notation***
- Piezoelectricity, pyroelectricity, elastic properties, *etc*.
- J. F. Nye: Equilibrium property matrices for all crystal classes (Appendix E)



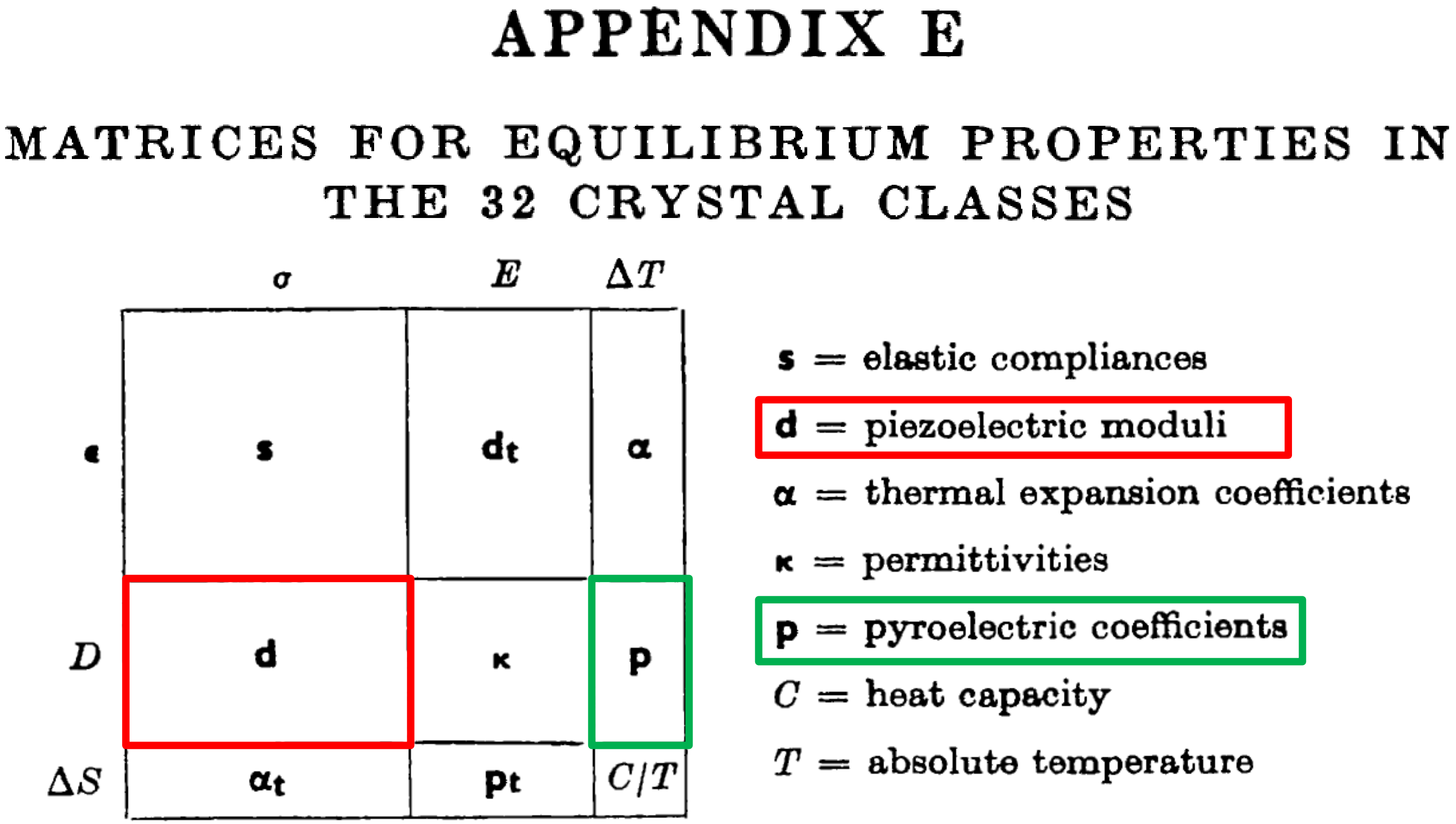
APPENDIX E 301

CUBIC SYSTEM

Classes 23 and $\bar{4}3m$

Classes $m3$, 432 and $m3m$

Quantifying the functionalities with physical property tensors (Nye)



APPENDIX E

MATRICES FOR EQUILIBRIUM PROPERTIES IN THE 32 CRYSTAL CLASSES

$$\begin{array}{c|c|c|c|}
 & \sigma & E & \Delta T \\
\hline
\epsilon & \mathbf{s} & \mathbf{d}_t & \boldsymbol{\alpha} \\
\hline
D & \boxed{\mathbf{d}} & \boldsymbol{\kappa} & \boxed{\mathbf{p}} \\
\hline
\Delta S & \boldsymbol{\alpha}_t & \mathbf{p}_t & C/T \\
\hline
\end{array}$$

$\mathbf{s}$ = elastic compliances

$\mathbf{d}$ = piezoelectric moduli

$\boldsymbol{\alpha}$ = thermal expansion coefficients

$\boldsymbol{\kappa}$ = permittivities

$\mathbf{p}$ = pyroelectric coefficients

C = heat capacity

T = absolute temperature

Physical property tensors (Nye)

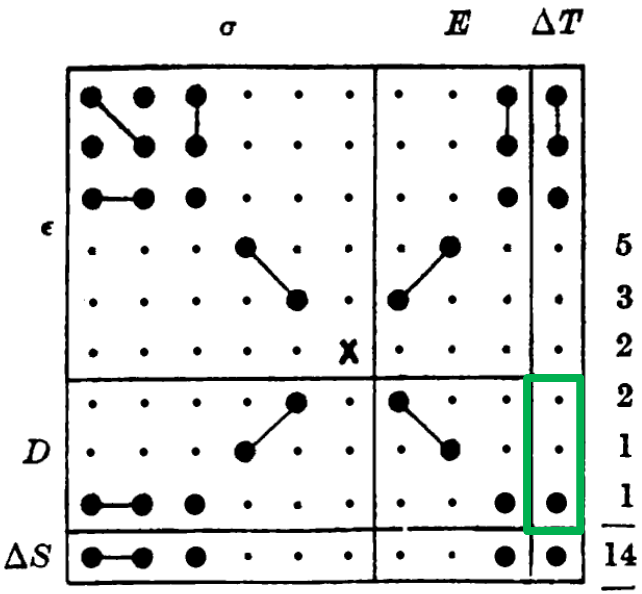
Matrices for equilibrium properties in the 32 crystal classes

KEY TO NOTATION

- • zero component
- ● non-zero component
- ●—● equal components
- ●—○ components numerically equal, but opposite in sign
- ◉ a component equal to twice the heavy dot component to which it is joined
- ◎ a component equal to minus 2 times the heavy dot component to which it is joined
- × $2(s_{11}-s_{12})$

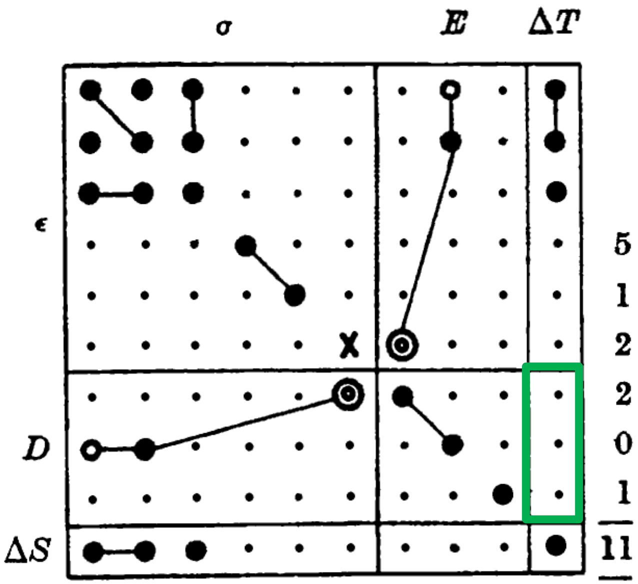
Polar (e.g. ZnO, *P*6_3*mc*)

Class 6*mm*



Non-polar (e.g. *P*-6*m*2)

Class $\bar{6}m2$



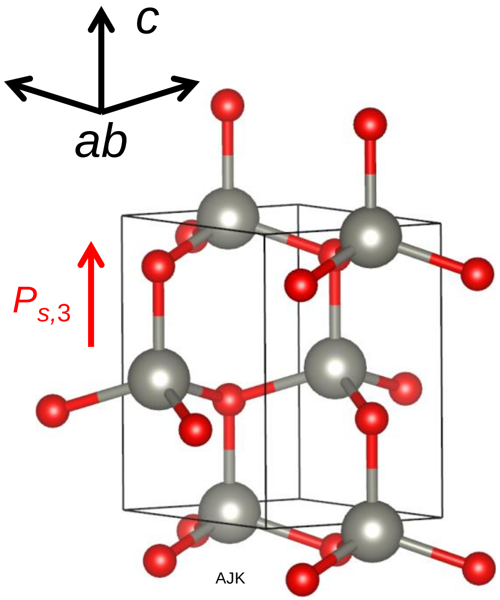
No pyroelectricity

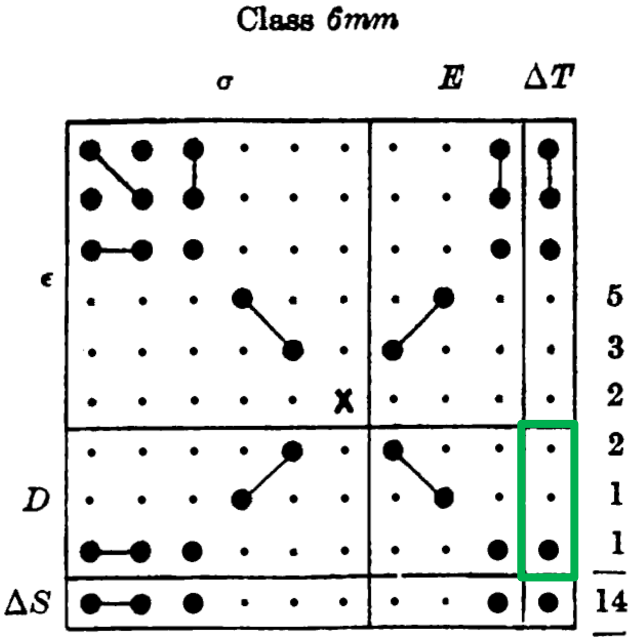
Pyroelectricity in ZnO

ZnO (space group $P6_3mc$)

One non-zero component in the pyroelectric tensor:

Spontaneous polarization along *c*-axis ($P_{s,3}$) changes when *T* changes





Pyroelectricy actually comprises of several effects: primary, secondary, and tertiary.

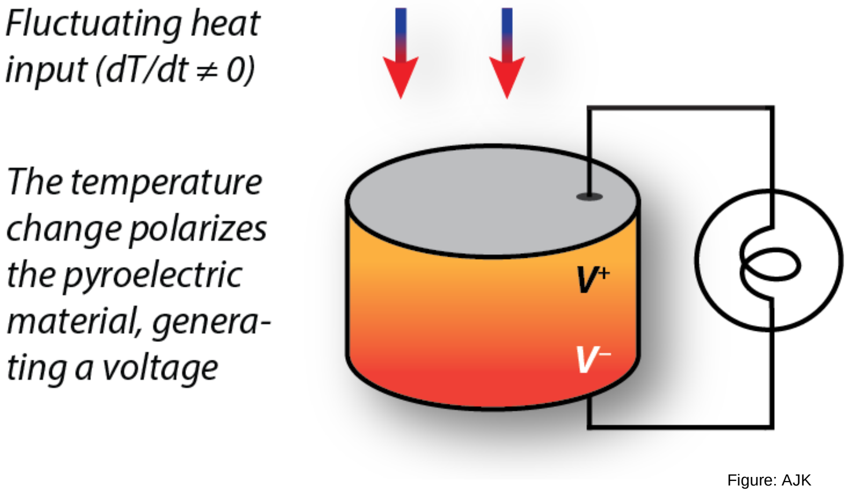
The **secondary** effect is actually piezoelectric effect arising from thermal expansion

The **tertiary** effect is also piezoelectric effect, arising from uneven heating (temperature gradients -> non-uniform thermal stress / strain).

The converse effect of pyroelectricity is called the **electrocaloric effect**.

Pyroelectricity: applications

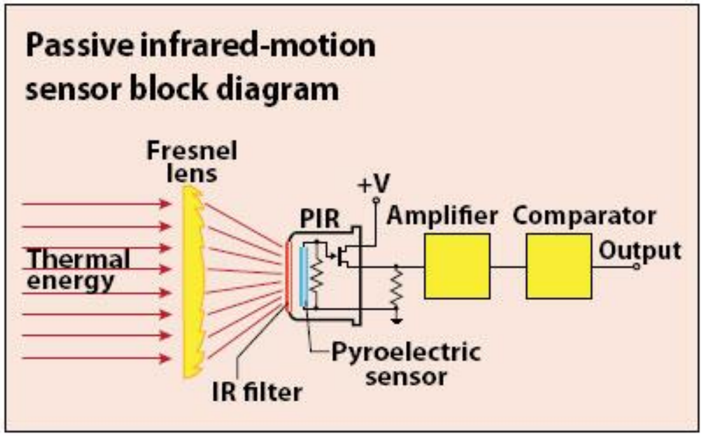
- In principle the effect was already discussed by the ancient Greeks
- Theophrastus noted in 314 BC that *lyngourion* (perhaps mineral *tourmaline*) could attract sawdust or bits of straw
- Re-discovered in 1707 by Johann Georg Schmidt
- Name coined by Sir David Brewster in 1824
- Studies of pyroelectricity led to the discovery of piezoelectricity
- Sensor applications (already existing since 1970s)
  - Heat-sensing
  - Infra-red detection
  - Thermal imaging
  - Fire alarms



Fluctuating heat input ($dT/dt \neq 0$)

The temperature change polarizes the pyroelectric material, generating a voltage

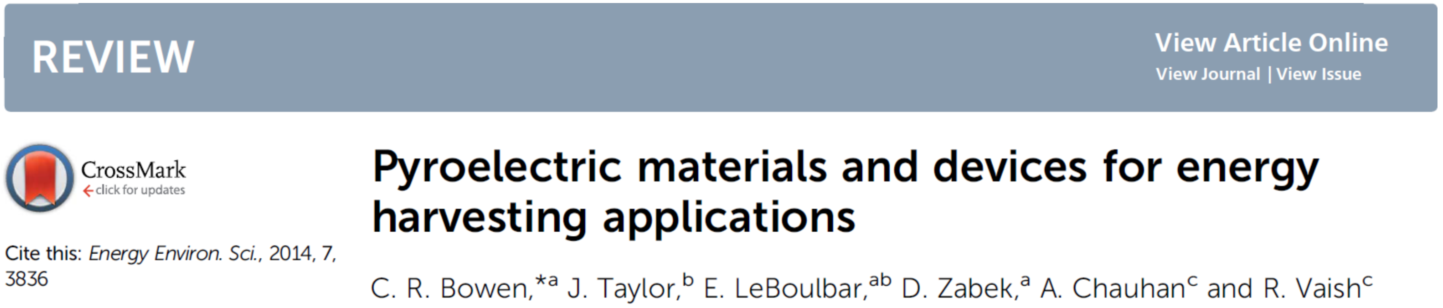
Figure: AJK



Passive infrared-motion sensor block diagram

Figure: www

Property data for pyroelectrics



REVIEW

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Cite this: *Energy Environ. Sci.*, 2014, 7, 3836

Pyroelectric materials and devices for energy harvesting applications

C. R. Bowen,*[a] J. Taylor,[b] E. LeBoulbar,[ab] D. Zabek,[a] A. Chauhan[c] and R. Vaish[c]

	GaN	ZnO	$BaTiO_3$	PZT-5H ("soft")	PMN-0.25PT	$LiNbO_3$	PVDF
Structure	Wurzite	Wurzite	Perovsk.	Perovsk.	Perovsk.	$LiNbO_3$	Polymer
Piezoelectric	X	X	X	X	X	X	X
Pyroelectric	X	X	X	X	X	X	X
Ferroelectric	-	-	X	X	X	X	X
p_3 (μC m^{-2} K^{-1})	-4.8	-9.4	-200	-380	-746	-83	-27

Primary / secondary pyroelectricity for ZnO: -6.9 / -2.5 μC m^{-2} K^{-1}
Primary / secondary pyroelectricity for $BaTiO_3$: -260 / **+60** μC m^{-2} K^{-1}

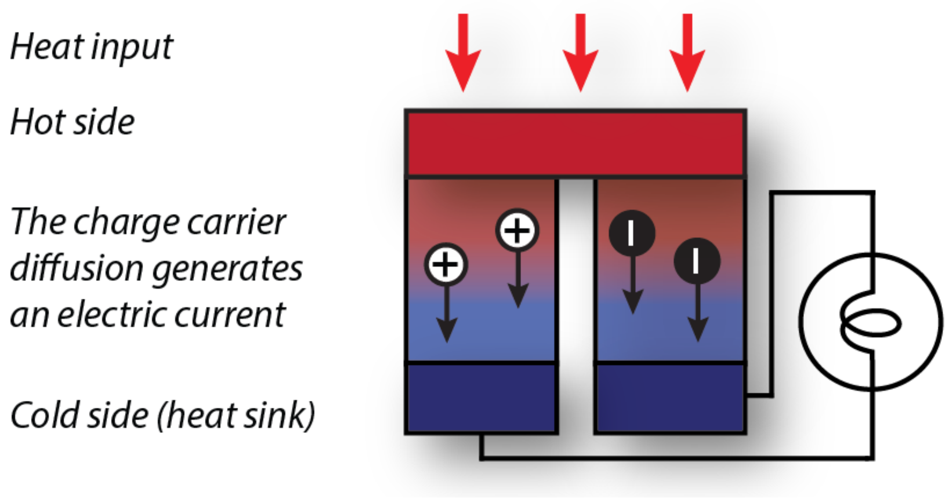
Thermoelectrics vs. pyroelectrics

Thermoelectric generator

- Constant temperature difference required for optimal operation (temperature gradient)

Pyroelectric generator

- Fluctuating heat input required for optimal operation

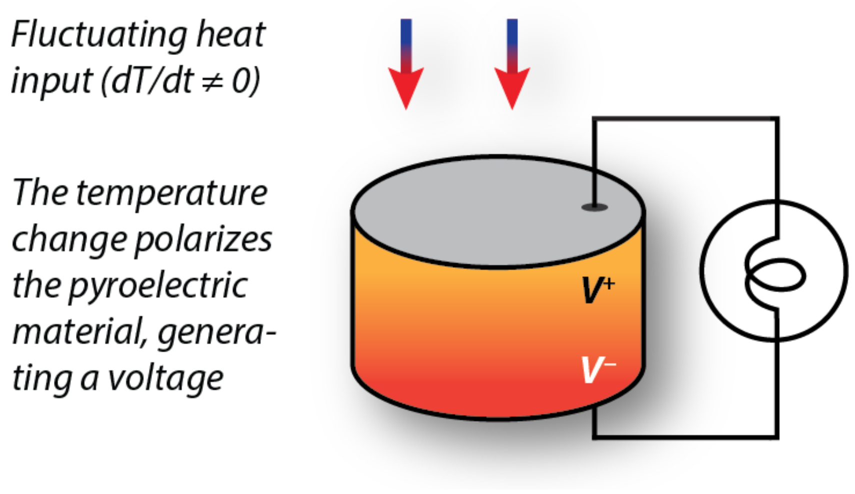


Heat input

Hot side

The charge carrier diffusion generates an electric current

Cold side (heat sink)



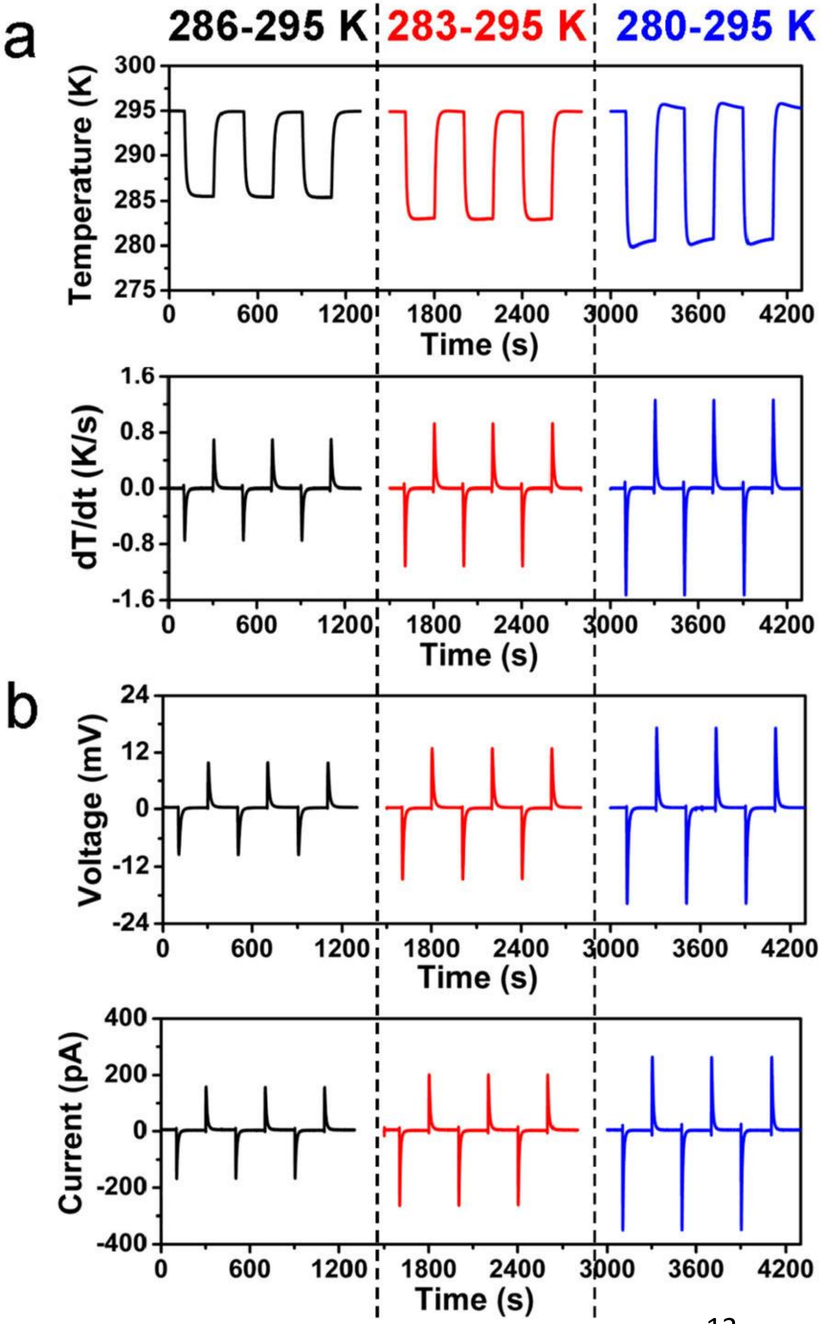
Fluctuating heat input ($dT/dt \neq 0$)

The temperature change polarizes the pyroelectric material, generating a voltage

Figures: AJK

Pyroelectricity: Prospective applications

- Energy harvesting (convert heat fluctuations into electricity)
  - Pyroelectric generators have been suggested to have **higher Carnot efficiency** in comparison to thermoelectrics
  - Sebald *et al. Smart Mater. Struct.* **2009**, *18*, 125006
- Cooling applications via the electrocaloric effect (poorly understood, much research required)



Ferroelectricity

- A ferroelectric is an insulating material with two or more discrete states of different **nonzero electric polarization** in **zero applied electric field**.
  - This polarization is referred to as **spontaneous polarization**.
- For a system to be considered ferroelectric, it must be possible to **switch** between these states with an applied electric field
- Materials are typically ferroelectric only below a certain phase transition temperature, called the **Curie temperature** (T_C)
  - Above T_c, ferroelectric becomes **paraelectric**

- A small, interactive learning package on ferroelectricity is available at DoITPoMS: https://www.doitpoms.ac.uk/tlplib/ferroelectrics/index.php

K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): Physics of Ferroelectrics: A Modern Perspective, *Topics Appl. Physics* **2007**, *105*, 1–30.

Hysteresis in ferroelectricity

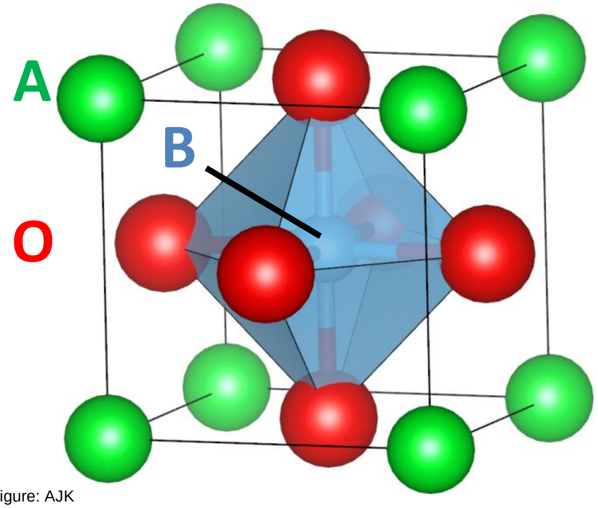
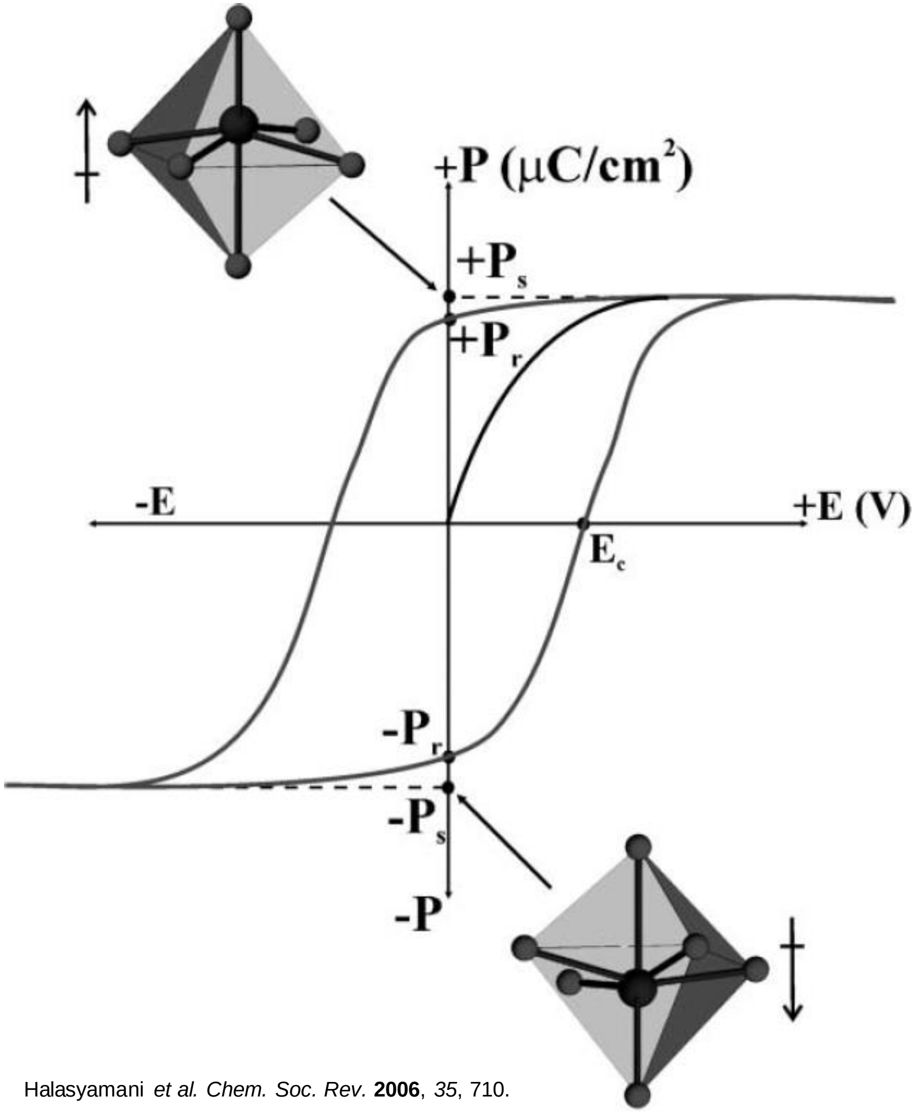


Figure: AJK

Ideal perovskite structure (**ABO$_3$**, e.g. **BaTiO$_3$**)

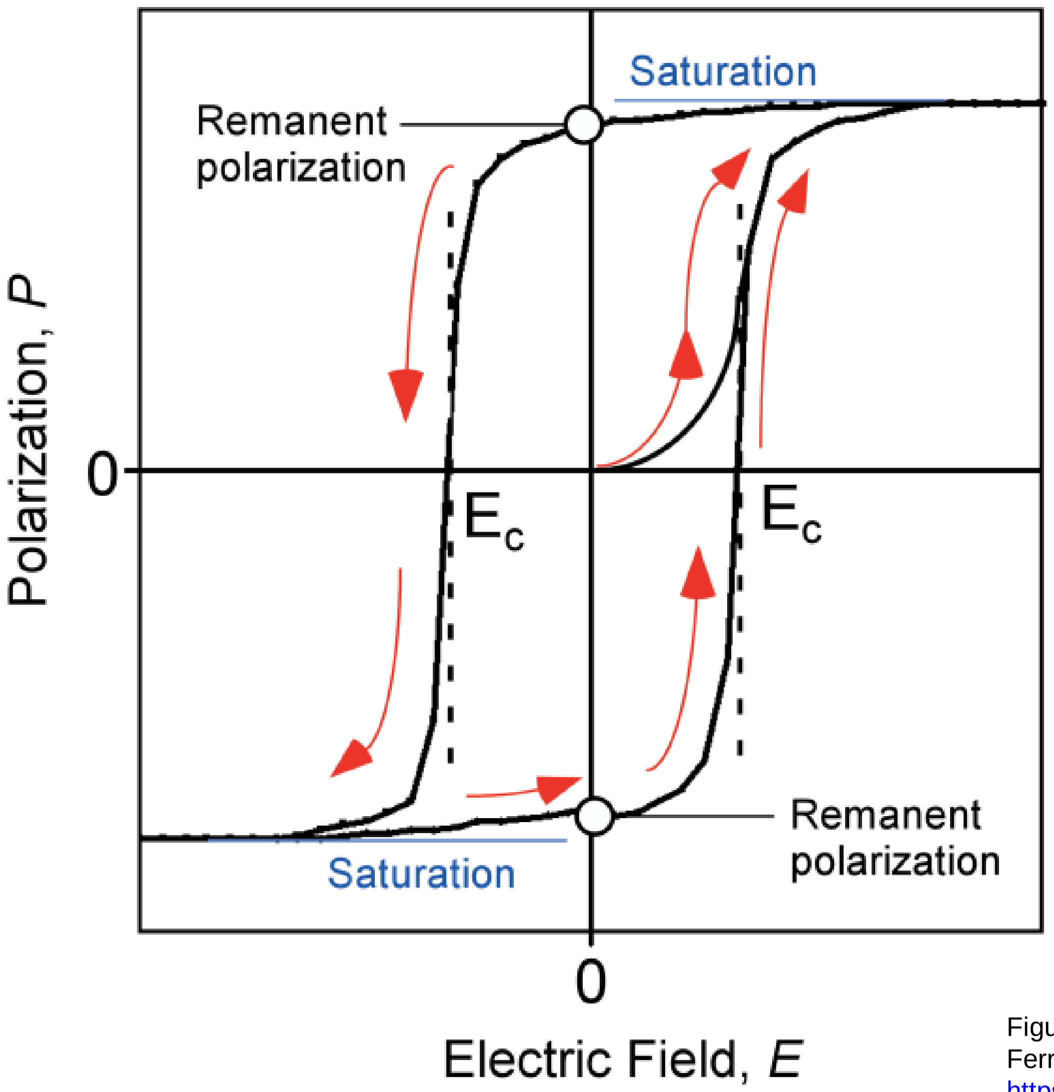
Non-cubic perovskites can possess switchable polarization *P*

Spontaneous polarization P_s is related to the displacement of the **B** atom (Ti)



Halasyamani *et al. Chem. Soc. Rev.* **2006**, *35*, 710.

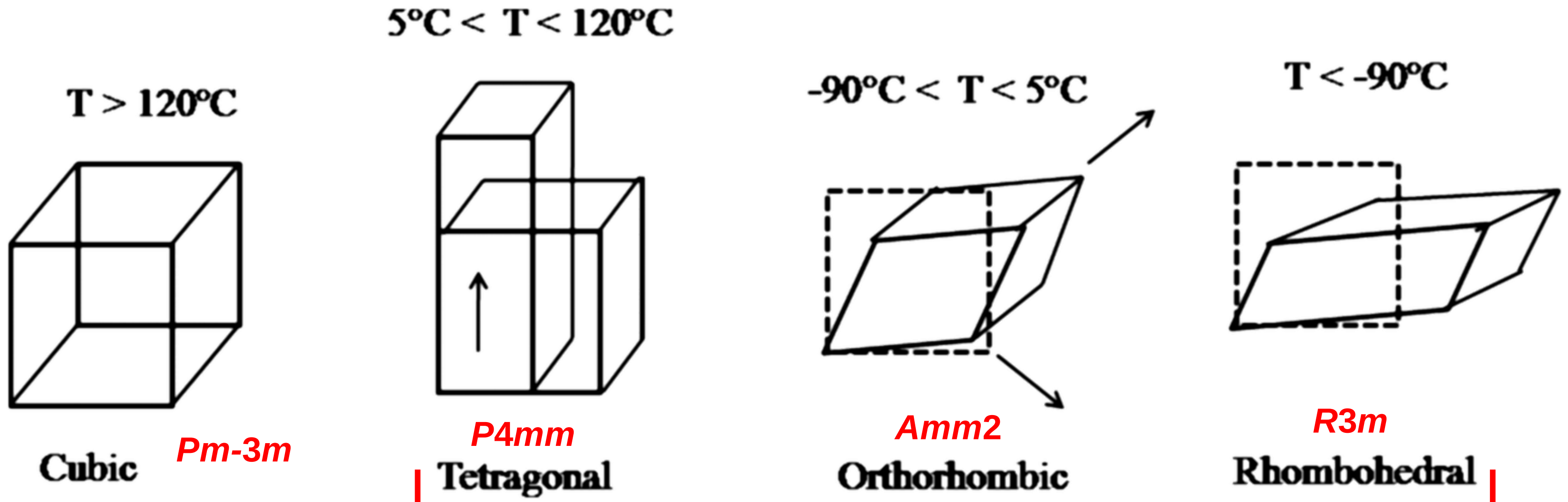
Electric field–Polarization curve



E_c = Coercive field

Figure: Shkuratov, Explosive Ferroelectric Generators, https://doi.org/10.1142/10958

$BaTiO_3$ phases



Pm-3m

P4mm

Amm2

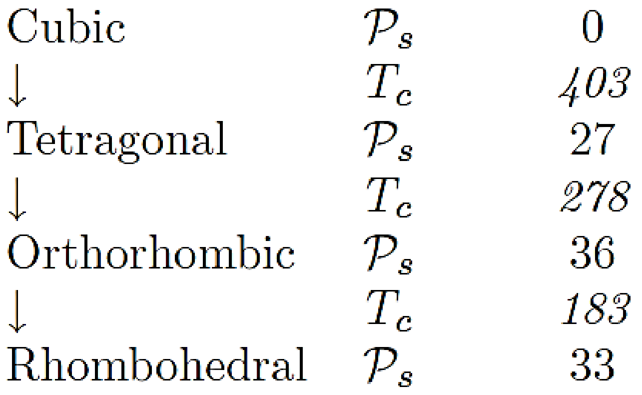
R3m

Paraelectric

Ferroelectric

Nayak *et al.* *RSC Adv*. **2014**, *4*, 1212.

Spontaneous polarization P_s (μC cm^{-2}):



Cubic	$\mathcal{P}_s$	0
↓	T_c	*403*
Tetragonal	$\mathcal{P}_s$	27
↓	T_c	*278*
Orthorhombic	$\mathcal{P}_s$	36
↓	T_c	*183*
Rhombohedral	$\mathcal{P}_s$	33

Curie temperature

Vanderbilt *et al.* *Phys. Rev. Lett.* **1994**, *73*, 1861.

Ferroelectric domains (1)

- Ferroelectric materials have a **domain** structure
- A ferroelectric domain is an area of oriented spontaneous polarization
- Within each domain, the polarization is aligned, but unless the material is in the *saturation condition*, different domains can have different polarization orientations.

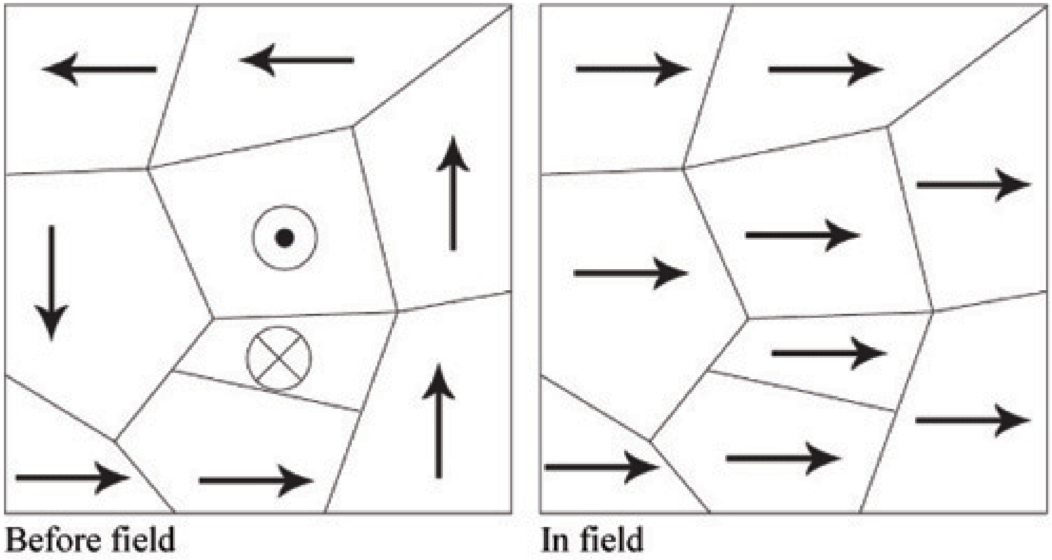
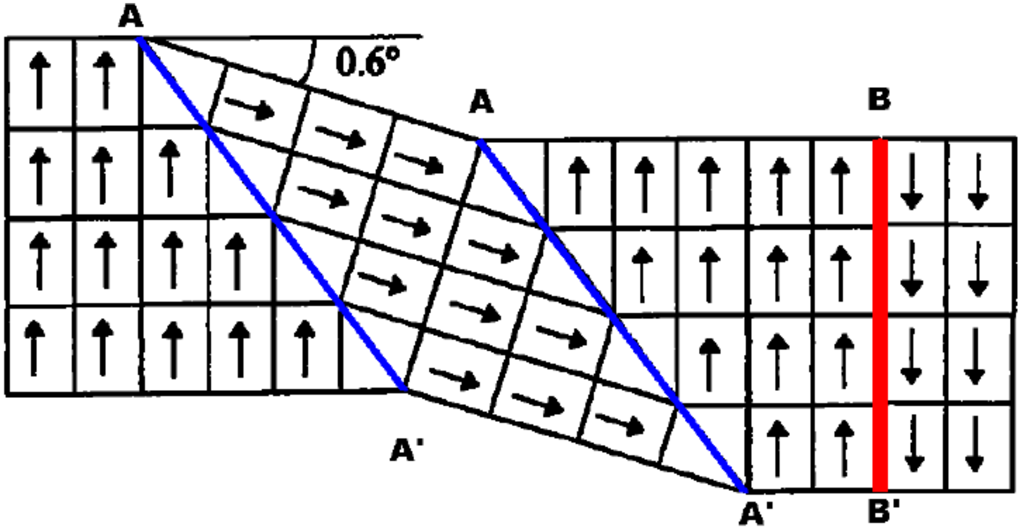


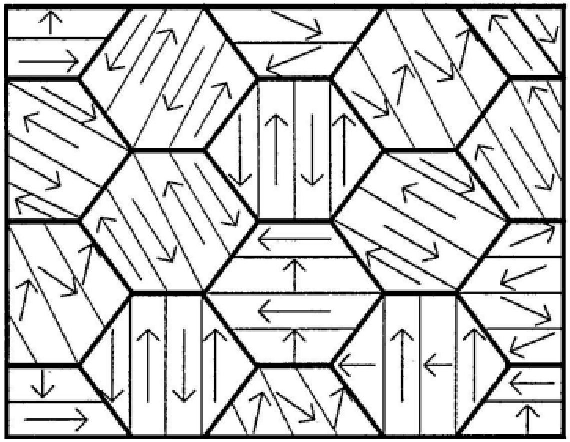
Figure: University of Cambridge / DoITPoMS
(CC-BY-NC-SA 2.0 UK)

Ferroelectric domains (2)



Ferroelectric domain walls in a perovskite ferroelectric. A-A’ lines represent 90° domain walls, and the B-B’ line a 180° domain wall (the tetragonality is highly exaggerated).

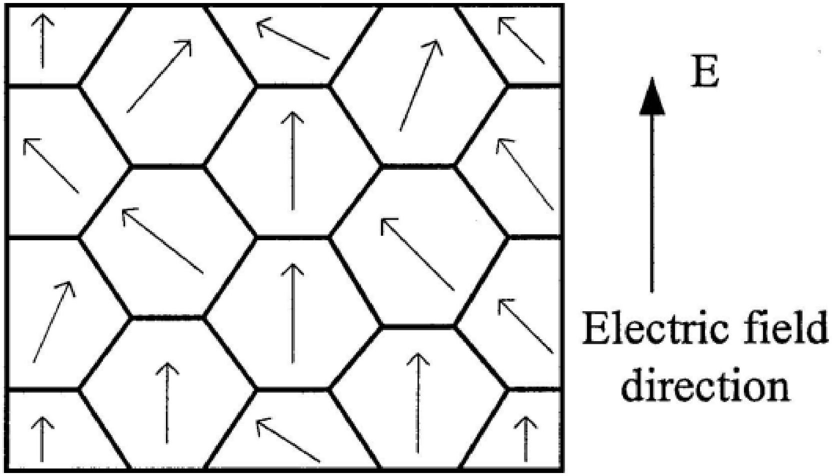
Domains and grains



Ferroelectric domains (thin lines) inside grains of a **polycrystal** (thick lines)

Poling with electric field

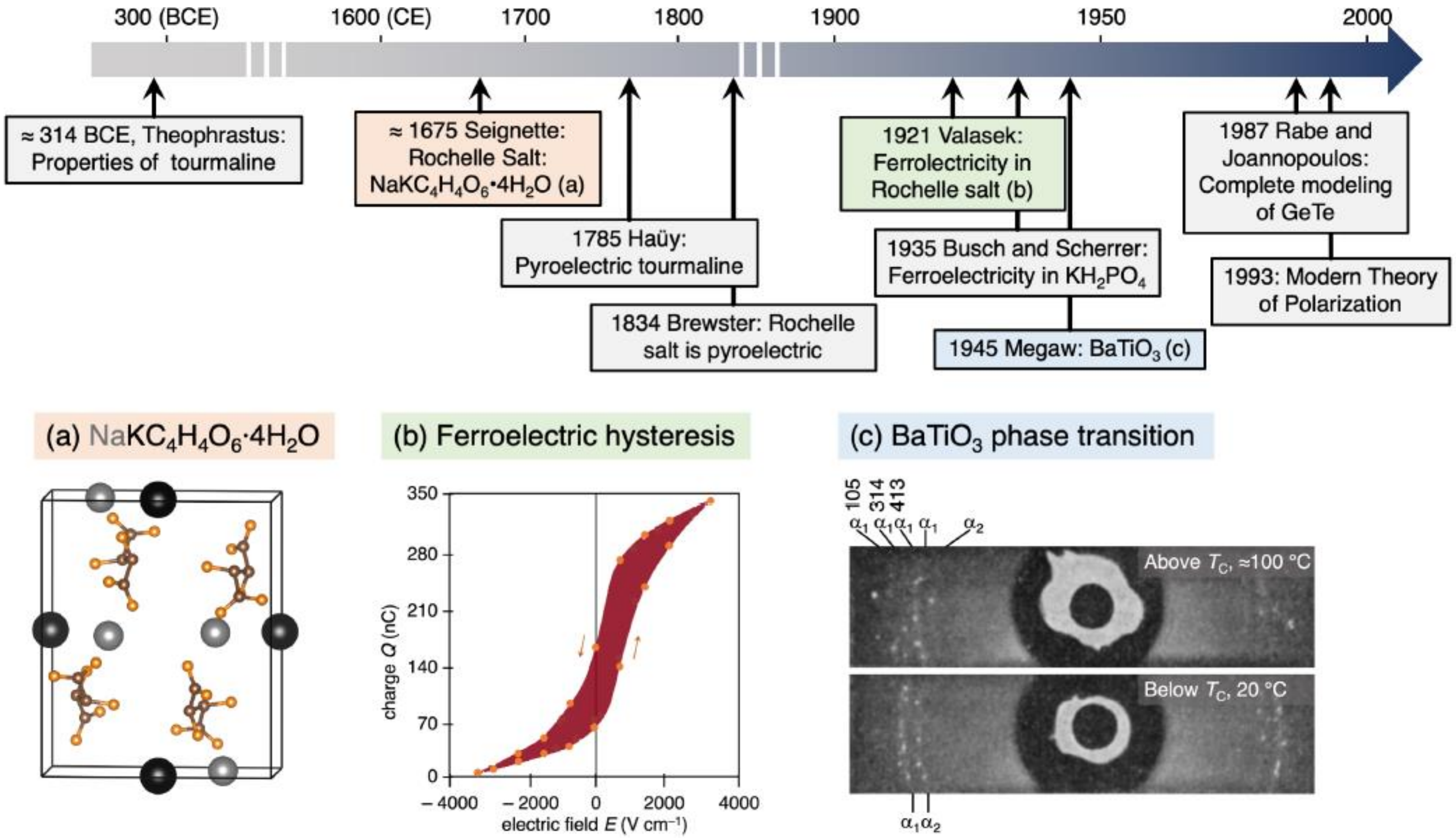
→



Domains have become aligned in the saturation condition, but grains remain to have different orientation

Figure: Journal of Materials Science: Materials in Electronics **2005**, *16*, 507–515.

Key events for ferroelectrics



≈ 314 BCE, Theophrastus: Properties of tourmaline

≈ 1675 Seignette: Rochelle Salt: $NaKC_4H_4O_6{\cdot}4H_2O$ (a)

1785 Haüy: Pyroelectric tourmaline

1834 Brewster: Rochelle salt is pyroelectric

1921 Valasek: Ferroelectricity in Rochelle salt (b)

1935 Busch and Scherrer: Ferroelectricity in KH_2PO_4

1945 Megaw: $BaTiO_3$ (c)

1987 Rabe and Joannopoulos: Complete modeling of GeTe

1993: Modern Theory of Polarization

(a) $NaKC_4H_4O_6{\cdot}4H_2O$

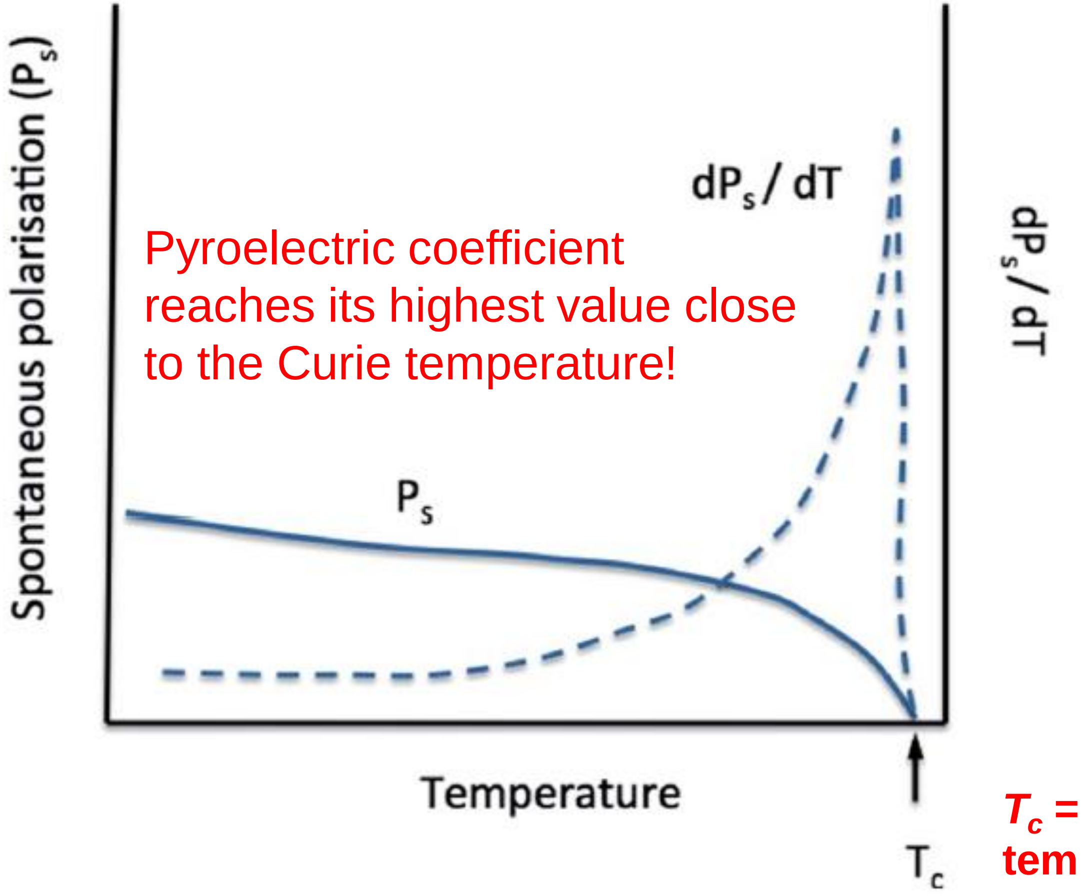
(b) Ferroelectric hysteresis

(c) $BaTiO_3$ phase transition

FIG. 1: Upper panel: Timeline of some key events in the history of ferroelectrics, from 300 BCE to the present time. (a) Crystal structure of the paraelectric phase of Rochelle salt. Hydrogen atoms and water molecules are omitted for clarity. (b) The ferroelectric hysteresis loop of Rochelle salt recorded by Valasek in 1921 (data from reference [1]). (c) A reproduction of the X-ray images recorded by Megaw with Cu $K\alpha_1$ and $K\alpha_2$ radiation [2] of high-angle reflections in $BaTiO_3$ powders above and below the ferroelectric phase transition.

Figure: Spaldin and Seshadari, IUCr newsletter, 2021, 29(3) (link)

Ferroelectric pyroelectrics



Pyroelectric coefficient reaches its highest value close to the Curie temperature!

***T_c* = Curie temperature**

Fig. 1 Temperature dependence of spontaneous polarisation P_s and pyroelectric coefficient dP_s/dT of a ferroelectric material, adapted from.[14]

Bowen *et al. Energy Environ. Sci.* **2014**, *7*, 3836.

Ferroelectricity: Applications

- Obviously, all **piezoelectric** and **pyroelectric** applications discussed above

- In addition, some new applications arise from the switchable polarization
  - Ferroelectric random-access-memory (RAM)
    - Not affected by power disruption or magnetic interference
  - Capacitors with tunable capacitance
  - Ferroelectric field-effect transistors (rather hypothetical at the moment)