Functional Inorganic Materials
Lecture 7:
Piezo-, pyro-, and ferroelectrics

Fall 2020

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Lecture Assignment 7 is a MyCourses Quiz

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School of Chemical
Engineering

Contents

- General overview of **non-centrosymmetric materials**
  - Piezo-, pyro- and ferroelectrics are limited to crystals with certain symmetry properties
- **Piezoelectric** materials
  - Electric polarization from mechanical force
  - Mechanical deformation due to electric field
- **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)

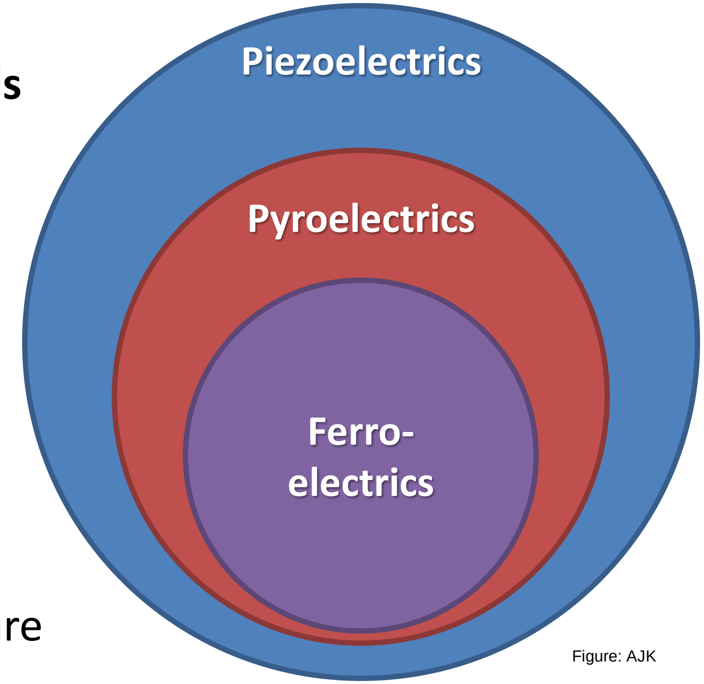


Figure: AJK

Literature on non-centrosymmetric materials

Chem. Mater. **1998**, *10*, 2753−2769

Noncentrosymmetric Oxides

P. Shiv Halasyamani[†] and Kenneth R. Poeppelmeier*

TUTORIAL REVIEW www.rsc.org/csr | Chemical Society Reviews

Bulk characterization methods for non-centrosymmetric materials: second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity

Kang Min Ok, Eun Ok Chi and P. Shiv Halasyamani*

Received 17th January 2006
First published as an Advance Article on the web 28th April 2006
DOI: 10.1039/b511119f

Let's start with a brief review of crystal systems and crystal classes, because crystal symmetry is very important for understanding non-centrosymmetric functional materials

Crystal systems

Figure 1.3 *(a) The seven crystal systems and their unit cell shapes;* ***a, b, c, α, β, γ = Lattice parameters***

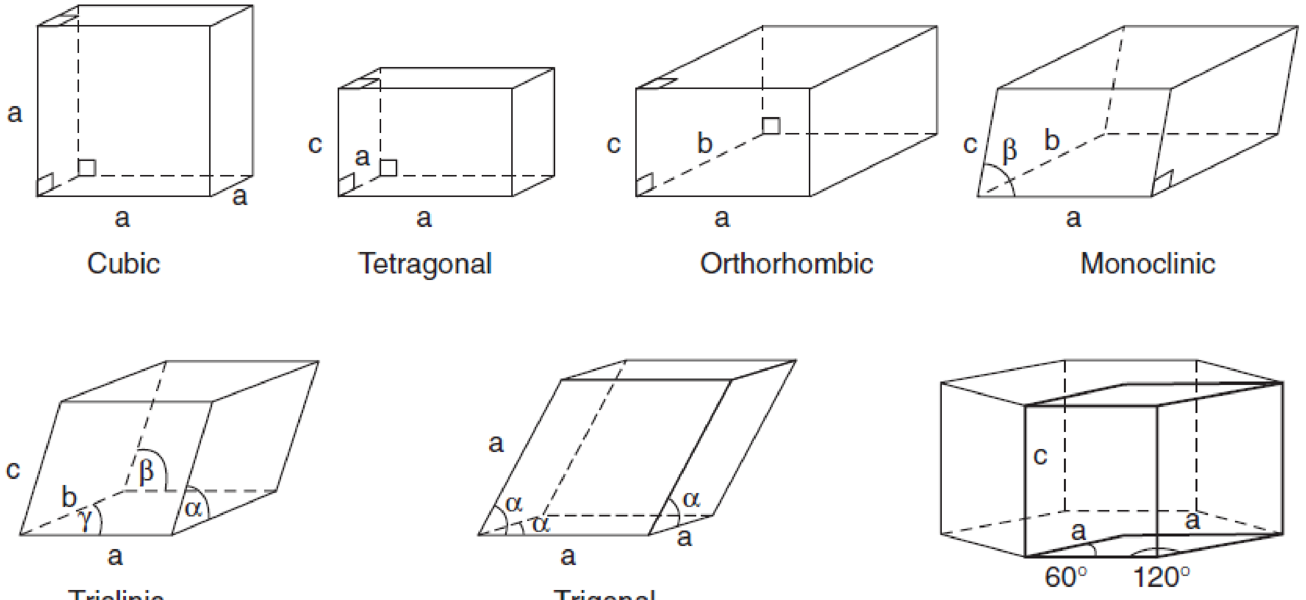


Table 1.1 ***The seven crystal systems***

Crystal system	Unit cell shape[b]	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
Trigonal (b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic[a]	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P

Ref: West p. 3-4

Crystal classes

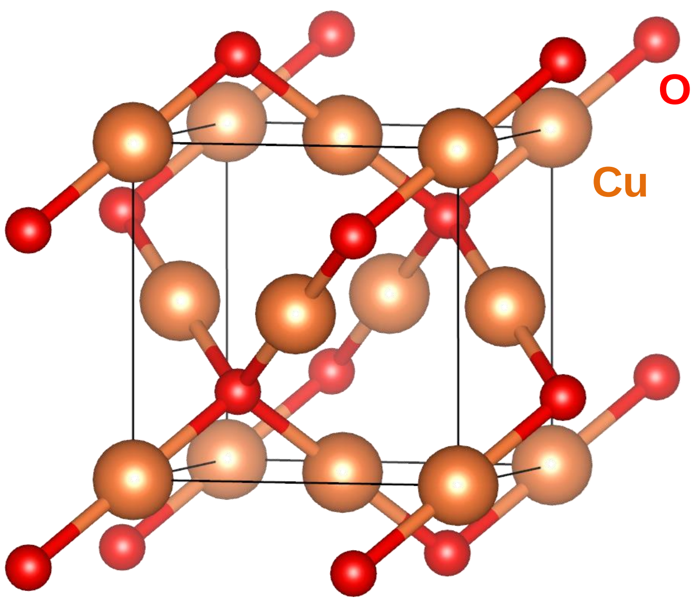
- The seven crystal systems consist of 32 crystal classes corresponding to the 32 crystallographic point groups

Crystal system	Crystal classes (point groups) in Hermann-Mauguin notation	Crystal classes (point groups) in Schönflies notation
Triclinic	$1, \bar{1}$	C_1, C_i
Monoclinic	$2, m, 2/m$	C_2, C_s, C_{2h}
Orthorhombic	$222, mm2, mmm$	D_2, C_{2v}, D_{2h}
Tetragonal	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$
Trigonal	$3, \bar{3}, 32, 3m, \bar{3}m$	$C_3, S_6\ (C_{3i}), D_3, C_{3v}, D_{3d}$
Hexagonal	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$	$C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}$
Cubic	$23, \bar{4}3m, m\bar{3}, 432, m\bar{3}m$	T, T_d, T_h, O, O_h

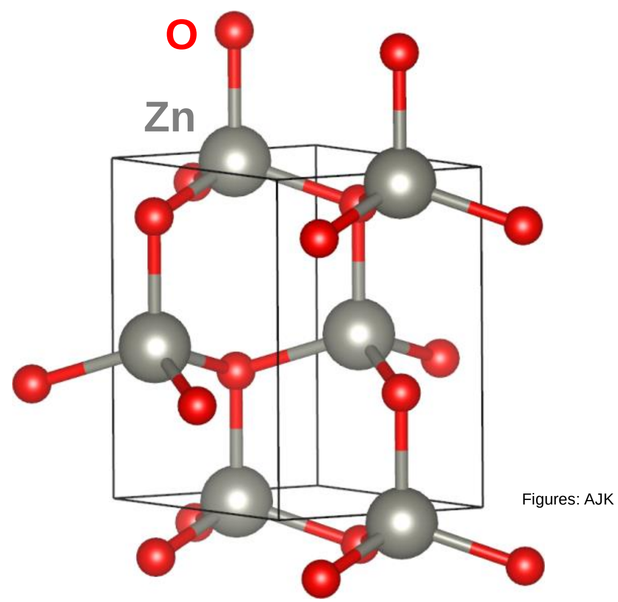
Ref: *Inorganic Structural Chemistry* (2nd ed.), Ulrich Müller, **2006**, Wiley p. 24 and Wikipedia

Centrosymmetric and non-centrosymmetric materials

- Centrosymmetric crystal classes possess an ***inversion center***: for every point (*x*, *y*, *z*) in the unit cell there is an indistinguishable point (-*x*, -*y*, -*z*)
- Non-centrosymmetric crystal classes ***do not possess an inversion center***
- Piezo-, pyro-, and ferroelectricity only possible for ***non-centrosymmetric materials***



Cu_2O (space group *Pn*-3*m*)
Centrosymmetric oxide with **inversion center**

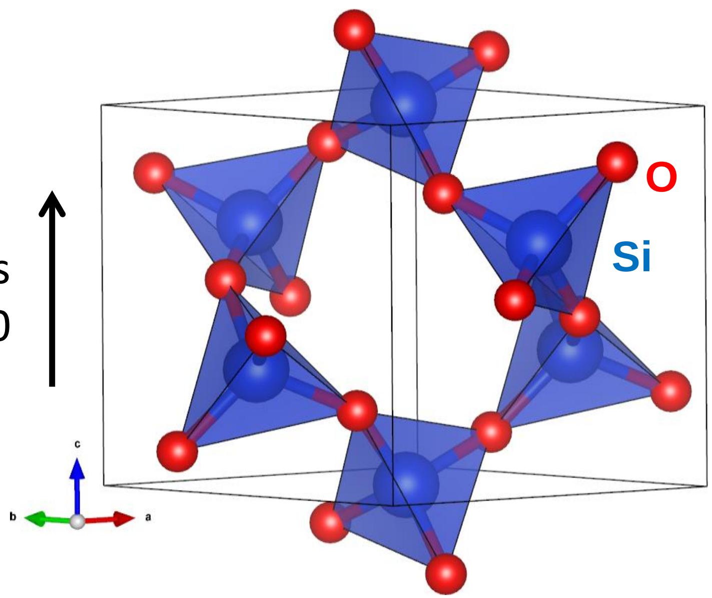


ZnO (space group $P6_3mc$)
Non-centrosymmetric oxide with **no inversion center**

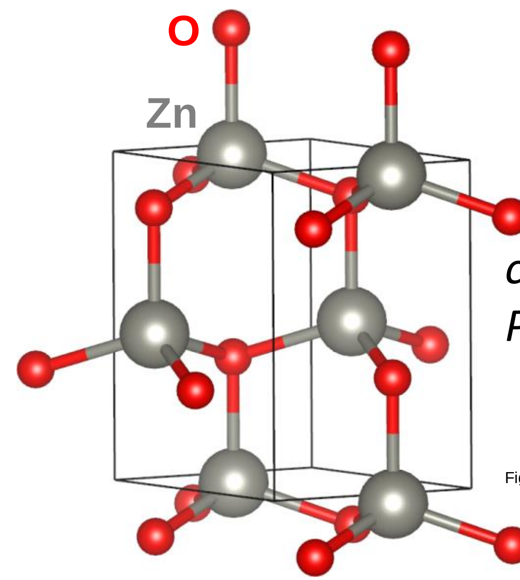
Polar and non-polar materials

- 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*** $\boldsymbol{P_s}$

c-axis
$P_s = 0$



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



c-axis
$P_s \neq 0$

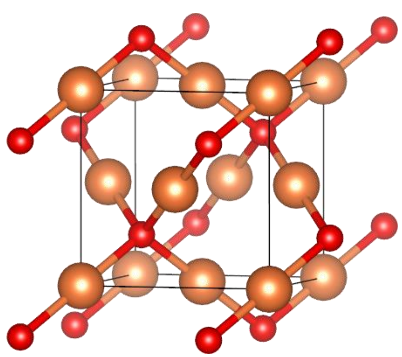
Figures: AJK

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

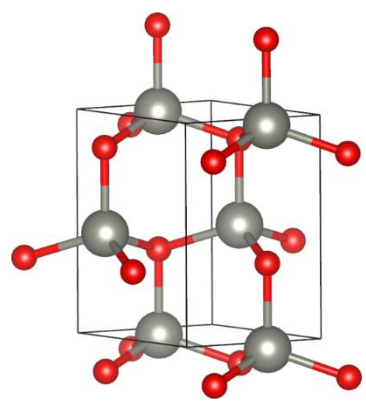
Classification of crystal classes

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,

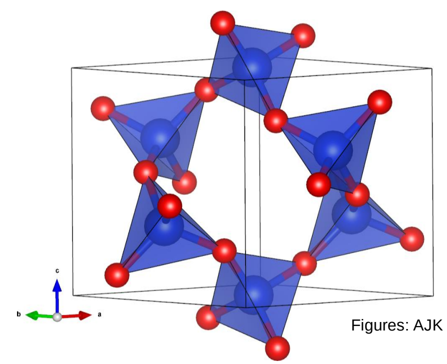
Refs: *Chem. Mater.* **1998**, *10*, 2753 and Wikipedia



Cu_2O (*Pn*-3*m*)



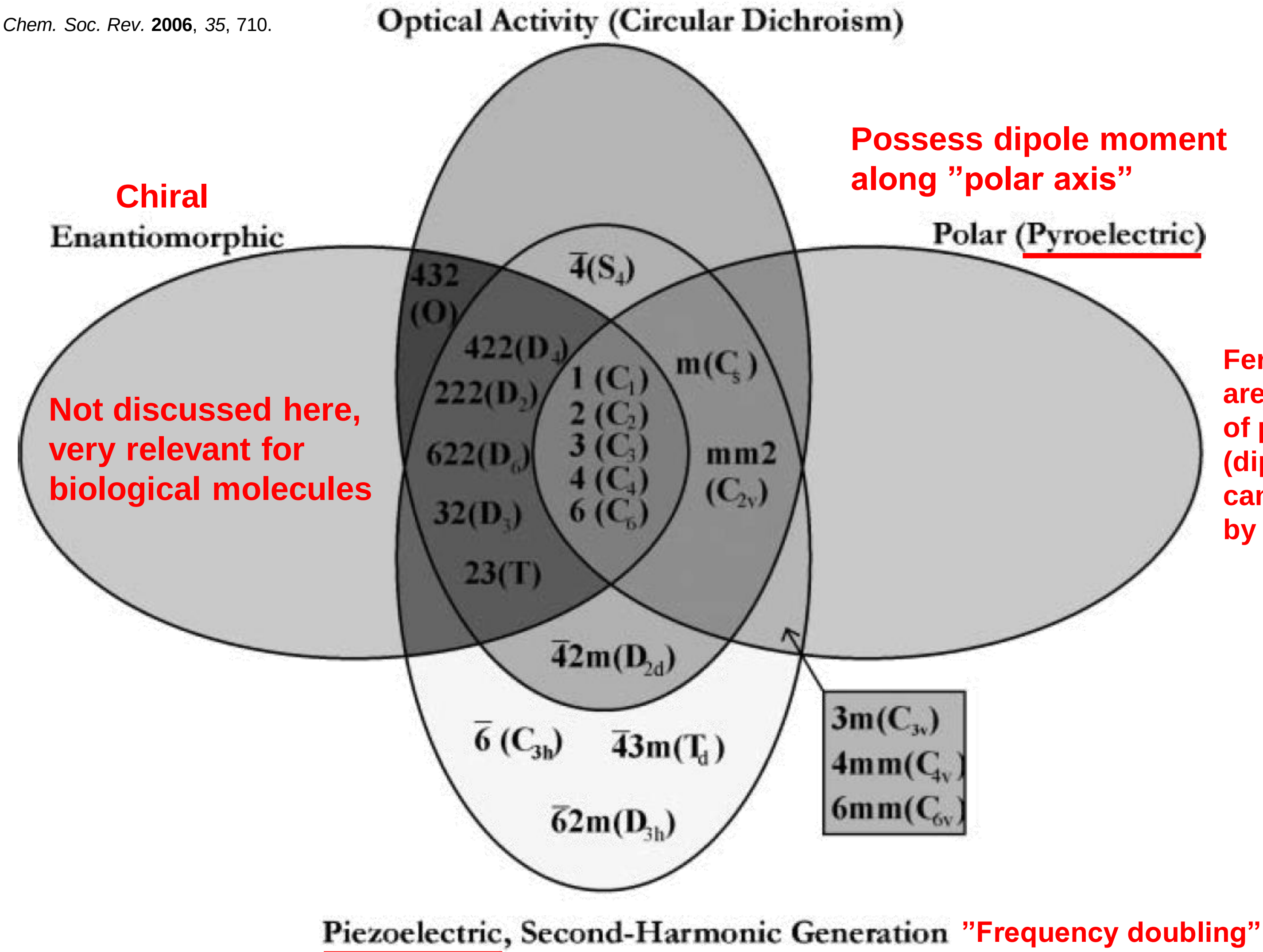
ZnO ($P6_3mc$)



α-SiO_2 ($P3_221$)

Non-centrosymmetric crystal classes and functionality

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



Ferroelectrics are a subgroup of pyroelectrics (dipole moment can be reversed by external field)

Piezo- and pyroelectric coefficients

Direct piezoelectric effect

$P = d\sigma$, where

- σ = applied tensile **stress** (N m^{-2})
- d = piezoelectric modulus (C N^{-1})
- P = resulting polarization (C m^{-2})

Converse piezoelectric effect

$\varepsilon = dE$, where

- E = applied electric field (N C^{-1})
- d = piezoelectric modulus (C N^{-1})
- ε = resulting **strain** in the crystal

(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)

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

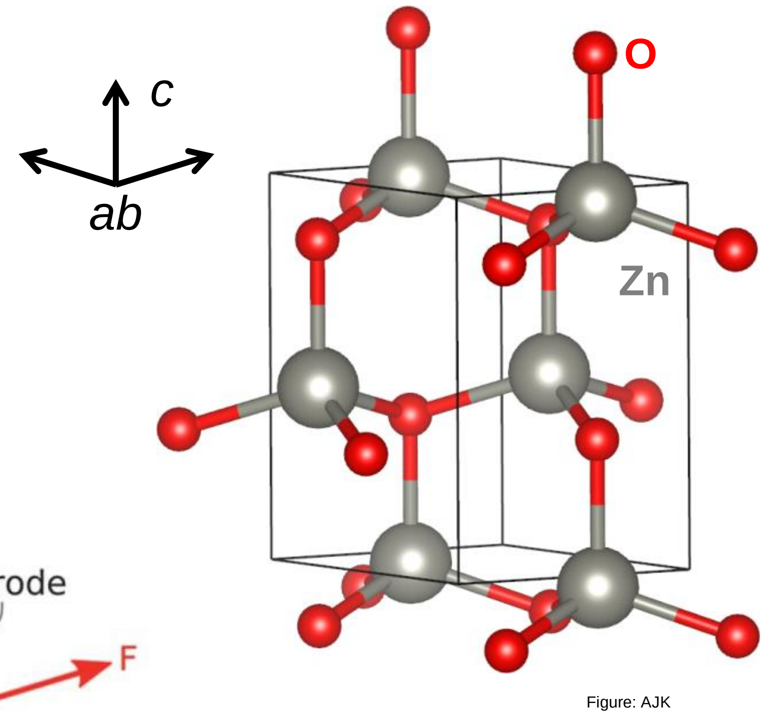
where T is the temperature, P is the polarization, ρ is the mass density, and C is the heat capacity under constant electric field.

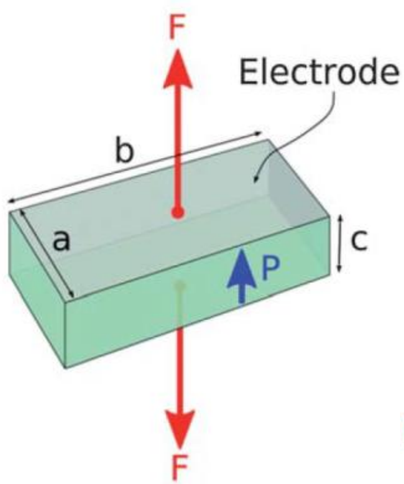
Often piezo- and pyroelectricity are discussed using just scalar coefficients *d* and *p*.
In reality they are *tensors* d_{ijk} and p_i and can be specified more accurately with the help of crystal symmetry.

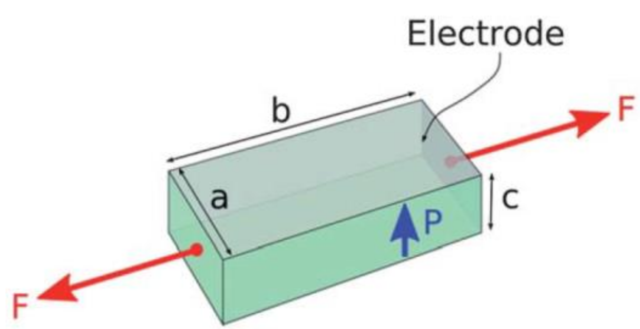
Piezoelectricity in ZnO

Let's use ZnO as an example.

ZnO (*P*6$_3$*mc*) has three symmetry-allowed distortions that lead to a piezoelectric response







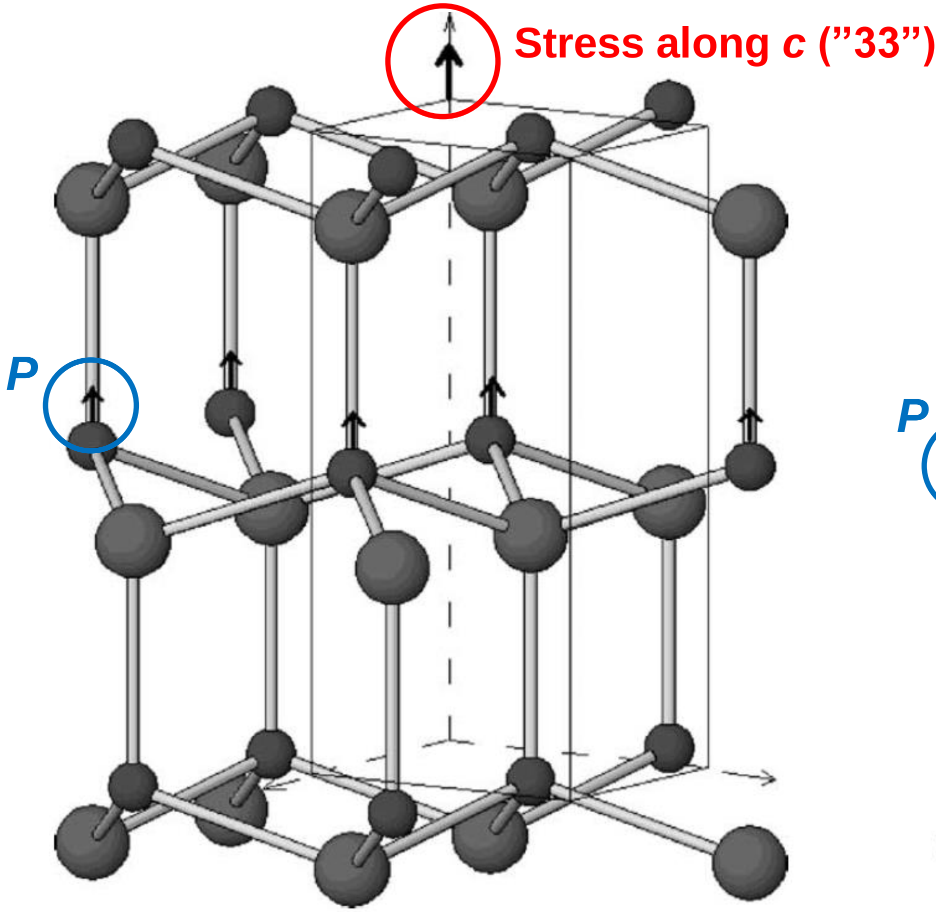
1. Stress along *c*, polarization along *c*

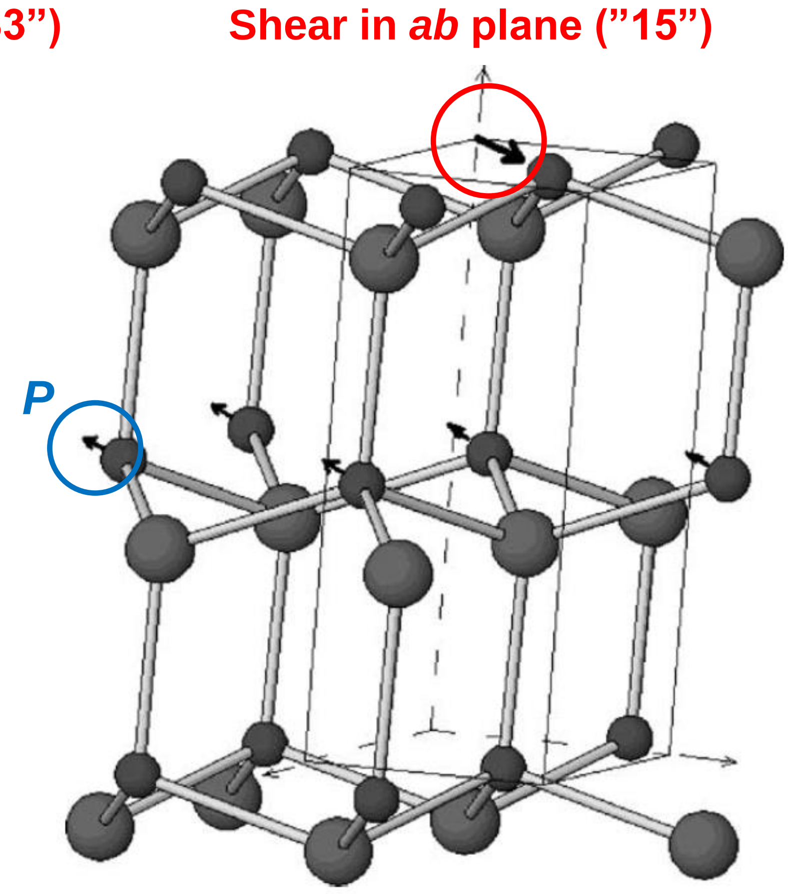
2. Stress in *ab*-plane, Polarization along *c*

3. Shear in *ab*-plane (*next slide*)

Bowen *et al. Energy Environ. Sci.* **2014**, *7*, 25.

Piezoresponse to shear in ZnO

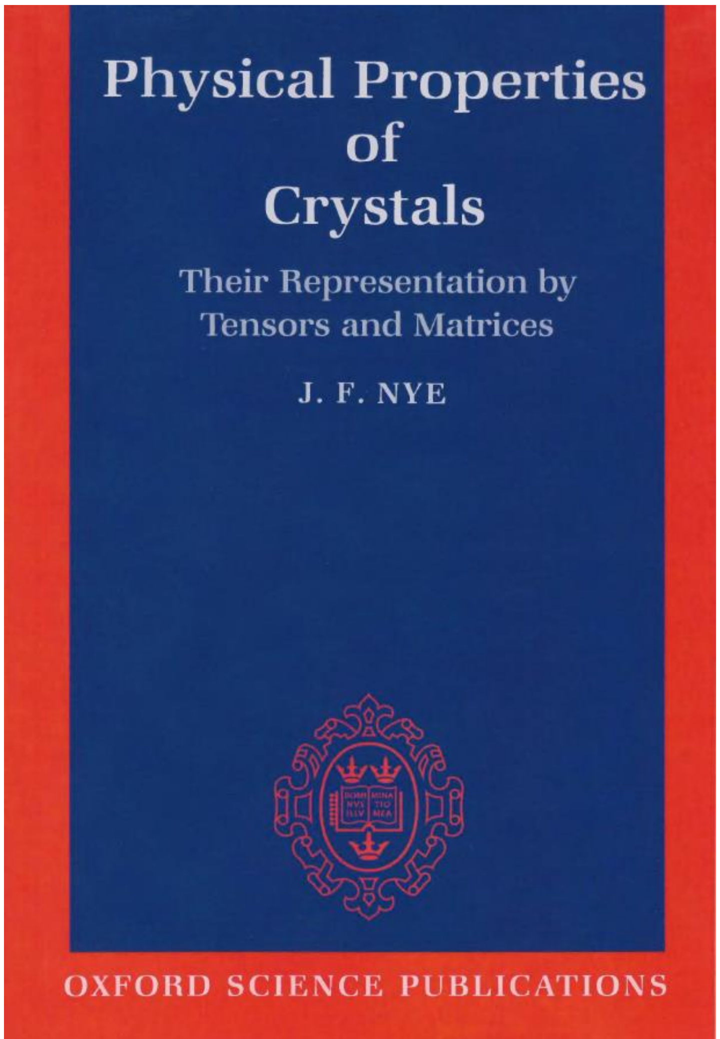




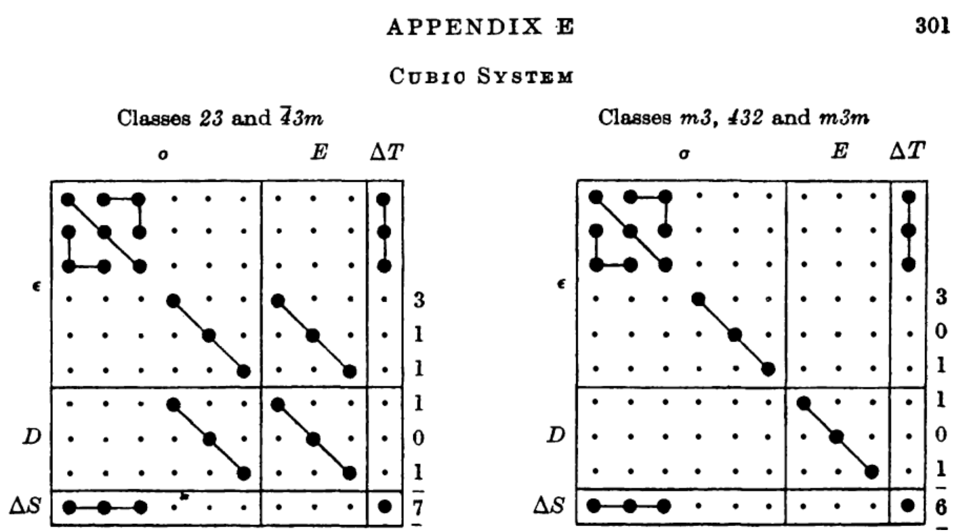
M. Catti *et al.* J. Phys. Chem. Solids **2003**, *64* 2183.

The number of symmetry-allowed distortions depends on the crystal class. Listings of these are available in textbooks (*next slide*).

Tensors (and matrices) for equilibrium properties



- 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)



Quantifying the functionalities with physical property tensors (Nye)

APPENDIX E

MATRICES FOR EQUILIBRIUM PROPERTIES IN THE 32 CRYSTAL CLASSES

	σ	E	ΔT
ϵ	$\mathbf{s}$	$\mathbf{d}_t$	$\boldsymbol{\alpha}$
D	$\mathbf{d}$	$\boldsymbol{\kappa}$	$\mathbf{p}$
ΔS	$\boldsymbol{\alpha}_t$	$\mathbf{p}_t$	C/T

$\mathbf{s}$ = 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

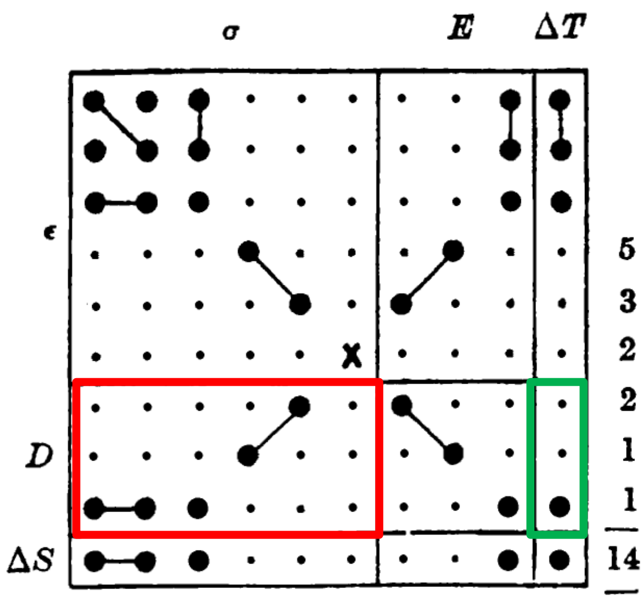
◉ a component equal to twice the heavy dot component to which it is joined

◎ a component equal to minus 2 times the heavy dot component to which it is joined

✕ $2(s_{11} - s_{12})$

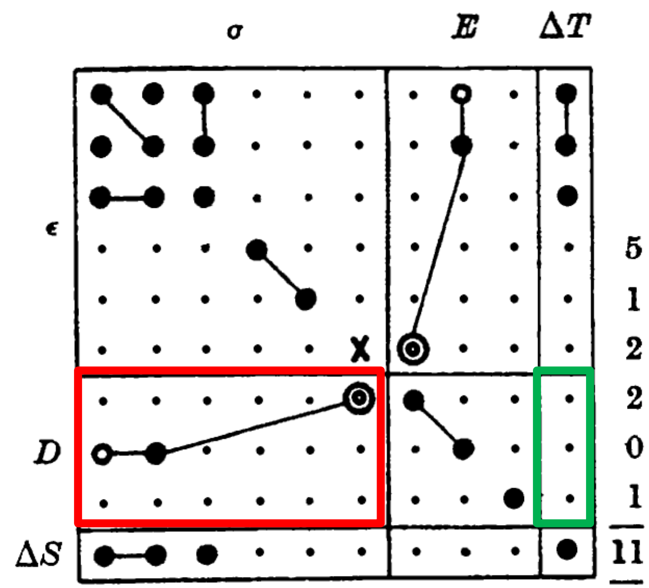
Polar (e.g. ZnO, $P6_3mc$)

Class *6mm*



Non-polar (e.g. $P\text{-}6m2$)

Class $\bar{6}m2$



No pyroelectricity

ZnO piezoelectricity tensor

ZnO (space group $P6_3mc$)

Three independent non-zero components in the piezoelectric tensor

What do they actually mean:

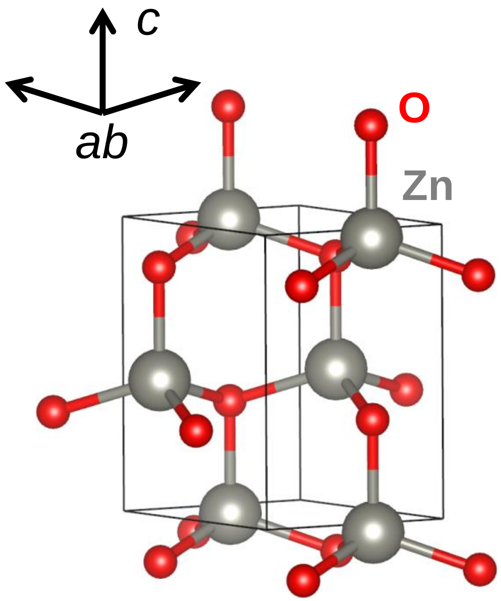
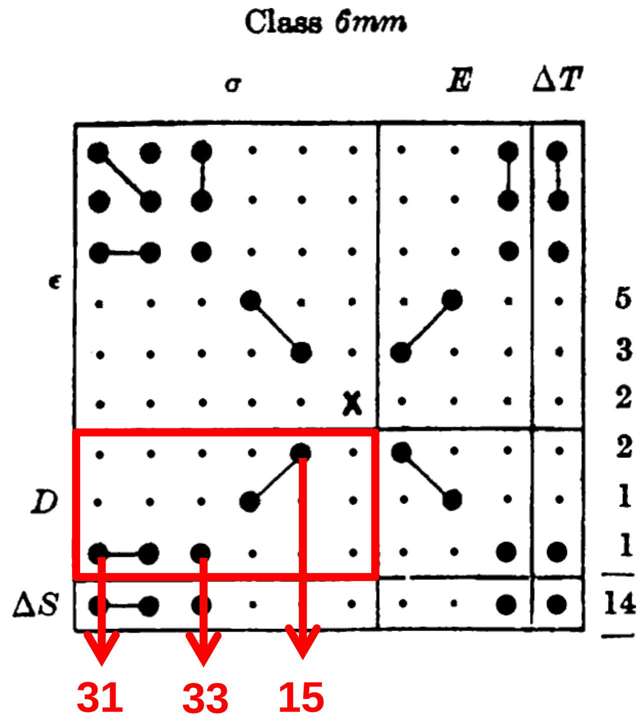
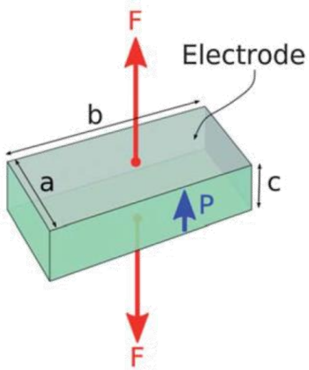
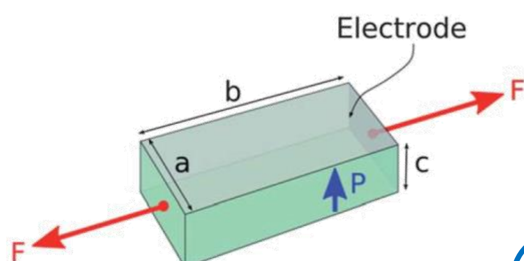


Figure: AJK

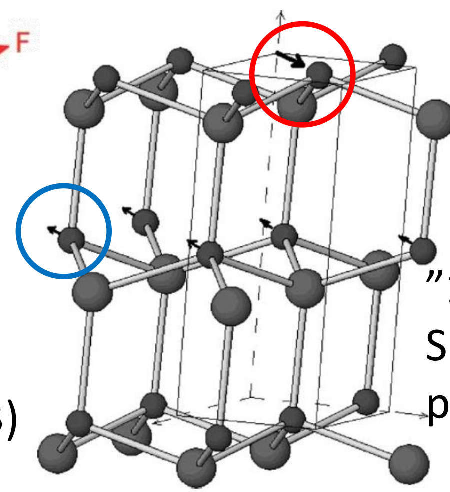




”33” component: Stress along *c* (3), polarization along *c* (3)



”31” component: Stress along *a* (1) polarization along *c* (3)



”15” component: Shear in *ab*-plane (5), polarization along *a* (1)

Bowen *et al. Energy Environ. Sci.* **2014**, *7*, 25.

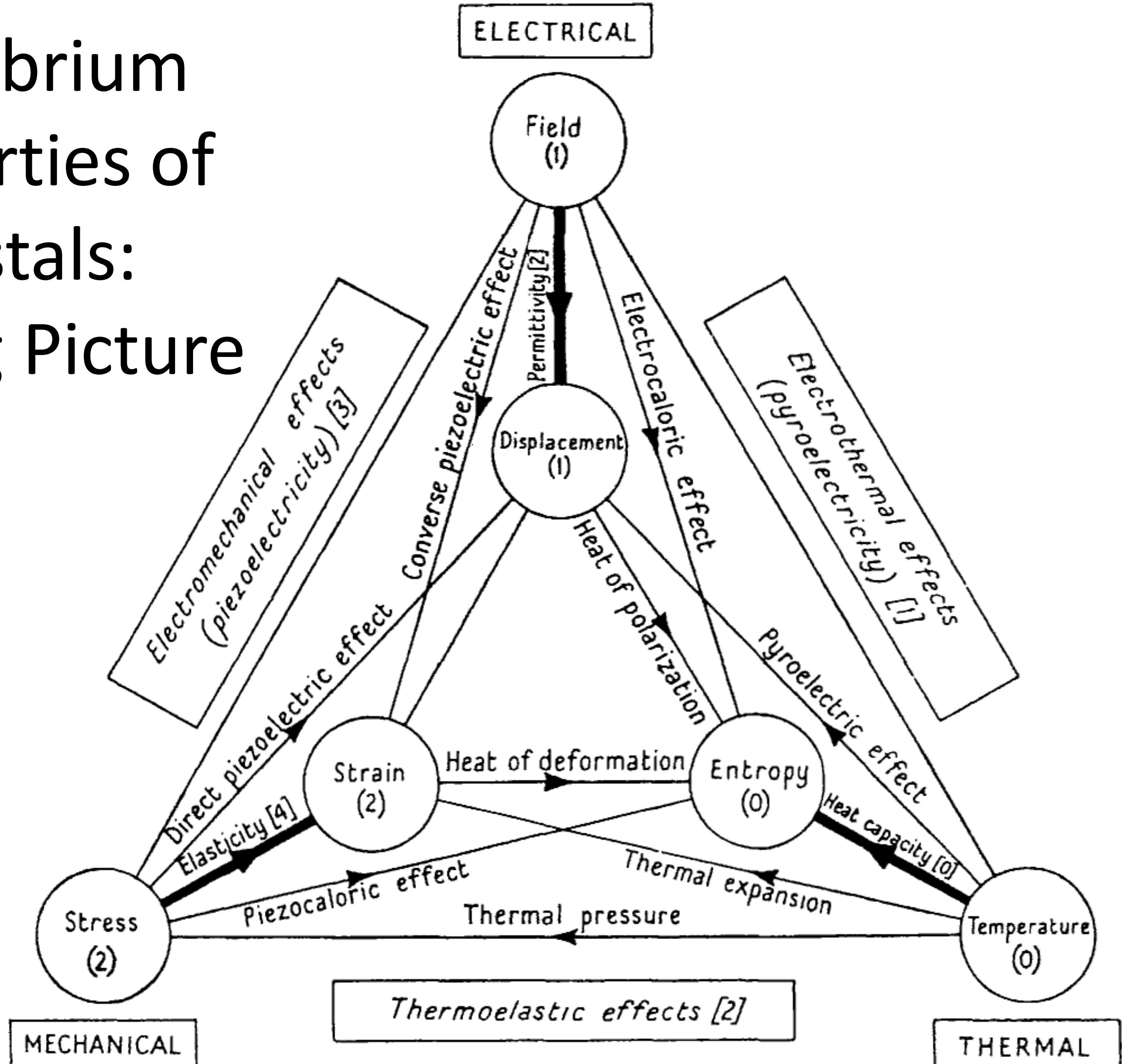
Piezo- and pyroelectricity are equilibrium properties

- Equilibrium properties may be described by reference to ***thermodynamic equilibrium states*** and ***thermodynamically <u>reversible</u> changes***
  - Example: isothermal expansion of ideal gas confined by external pressure
- The ***thermal***, ***electrical***, and ***mechanical*** properties of a crystal are all related
  - They may be measured when the crystal is in equilibrium with its surroundings

- Compare the equilibrium properties with ***transport properties***, which are concerned with ***transport processes*** and ***thermodynamically <u>irreversible</u> phenomena***
  - Example of an irreversible phenomenon: release gas into vacuum
  - Example properties: thermal and electrical conductivity and thermoelectricity
  - A temperature difference in different parts of a solid leads to a heat flow as the system tries to reach equilibrium

J. F. Nye, Physical Properties of Crystals, Oxford University Press **1957**, **1985**

Equilibrium properties of crystals: The Big Picture



J. F. Nye, Physical Properties of Crystals, Oxford University Press **1957**, **1985**

Piezoelectricity: applications (1)

- Piezoelectricity was discovered in 1880 by Jacques and Pierre Curie (direct effect)
- Converse piezoelectric effect predicted mathematically by Gabriel Lippmann (1881) and immediately confirmed by Curies
- It only took until 1917 when piezoelectrics were already used in warfare
- Ultrasonic submarine detector created by Paul Langevin and coworkers
  - Ultrasound-generating transducer made out of quartz crystals (transducer = converts one form of energy to another)
  - Hydrophone to detect the returned echo
- The success of piezoelectric sonar resulted in huge boom for discovering new materials
- Discovery of ferroelectric piezoelectrics such as $BaTiO_3$ during WW2 -> radios

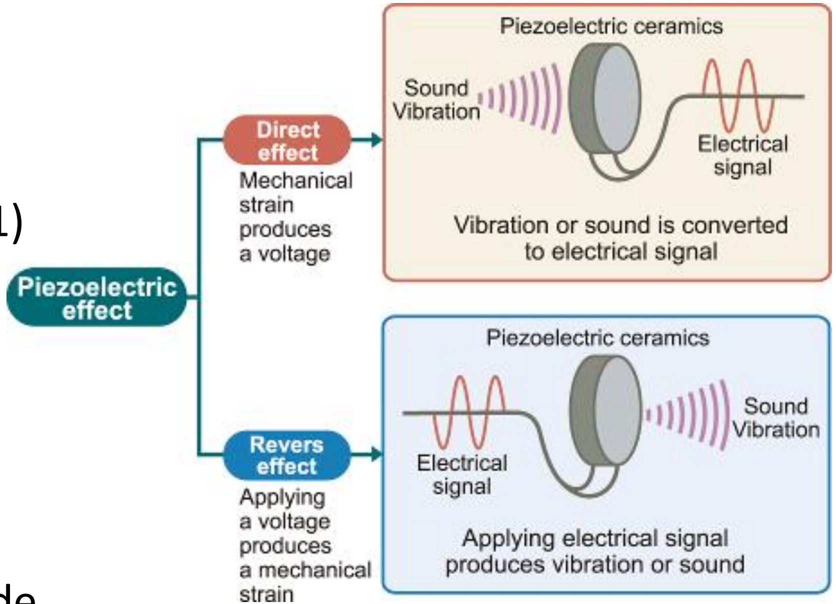


Figure: Honda

Piezoelectric transducer

Refs: *J. Micromech. Microeng.* **2000**, *10,* 136, Wikipedia

Piezoelectricity: applications (2)

- Generation of high voltages
- Spark-ignition (gas stoves, cigarette lighters)
  - Piezoelectric voltages can be thousands of volts
- Generation of electronic frequencies (*e.g.* for radio equipment)
- Microbalances
- Vibration sensors
- Actuators (precise positioning, piezomotors)
  - Scanning probe microscopies like AFM and STM
  - Atomic level accuracy of positioning with piezoelectric crystals

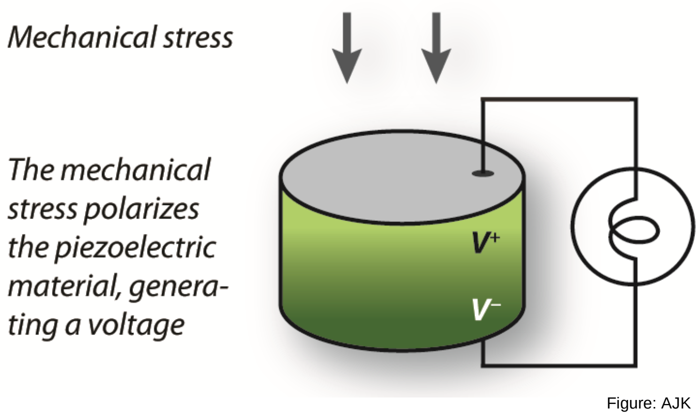


Figure: AJK

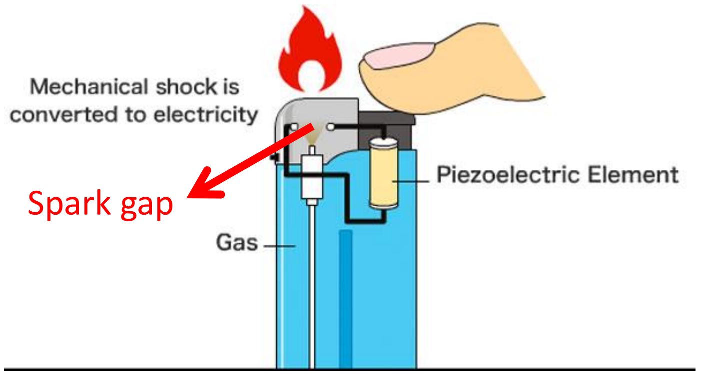


Figure: www

Piezoelectric lighter

Refs: *J. Micromech. Microeng.* **2000**, *10,* 136, Wikipedia

Property data for piezoelectrics

REVIEW

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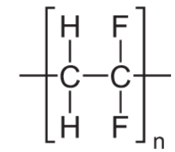
Cite this: *Energy Environ. Sci.*, 2014, 7, 25

Piezoelectric and ferroelectric materials and structures for energy harvesting applications

C. R. Bowen,*[a] H. A. Kim,[a] P. M. Weaver[b] and S. Dunn[c]

Polyvinylidene fluoride

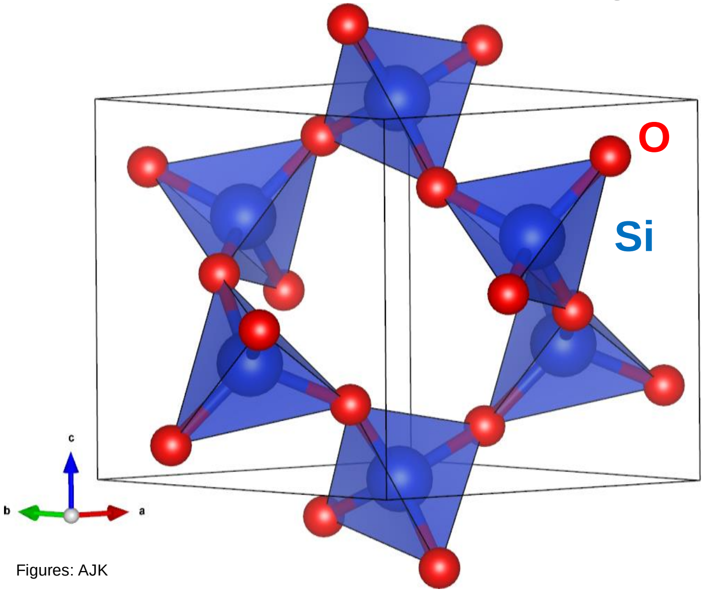


	GaN	ZnO	SiO_2	$BaTiO_3$	PZT-5H ("soft")	PMN-PT	$LiNbO_3$	PVDF
Structure	Wurzite	Wurzite	α-quartz	Perovsk.	Perovsk.	Perovsk.	$LiNbO_3$	Polymer
Piezoelectric	X	X	X	X	X	X	X	X
Pyroelectric	X	X	-	X	X	X	X	X
Ferroelectric	-	-	-	X	X	X	X	X
d_{33} (pC N^{-1})	3.7	12.4	-2.3 (d_{11})	149	593	2820	6	-33
d_{31} (pC N^{-1})	-1.9	-5.0		-58	-274	-1330	-1.0	21
d_{15} (pC N^{-1})	3.1	-8.3	0.67 (d_{14})	242	741	146	69	-27

$Pb[Zr_xTi_{1-x}]O_3$

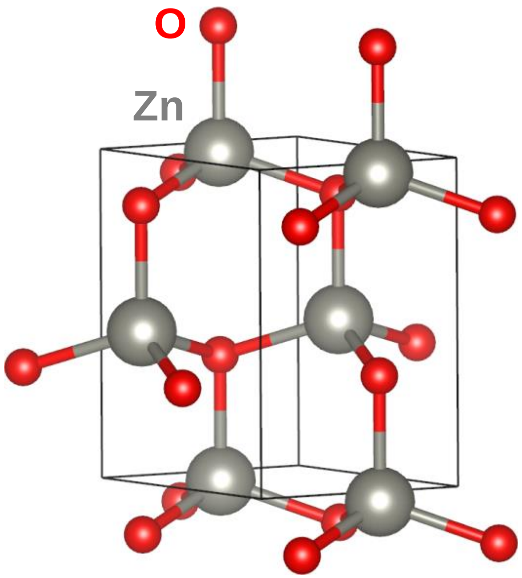
$(1-x)Pb[Mg_yNb_{1-y}]O_3 - xPbTiO_3$

Important crystal structures for piezoelectrics

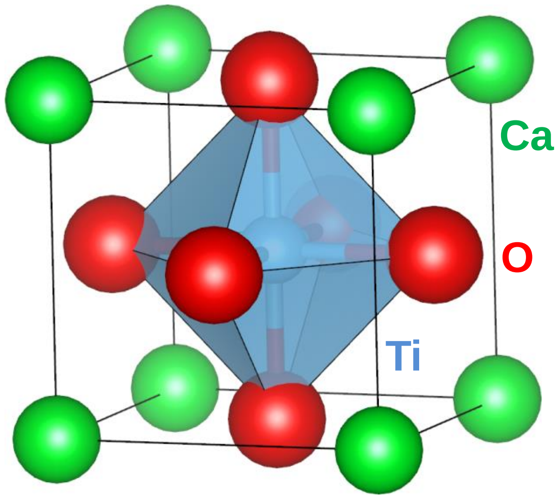


Figures: AJK

Quartz
α-SiO_2 ($P3_221$)



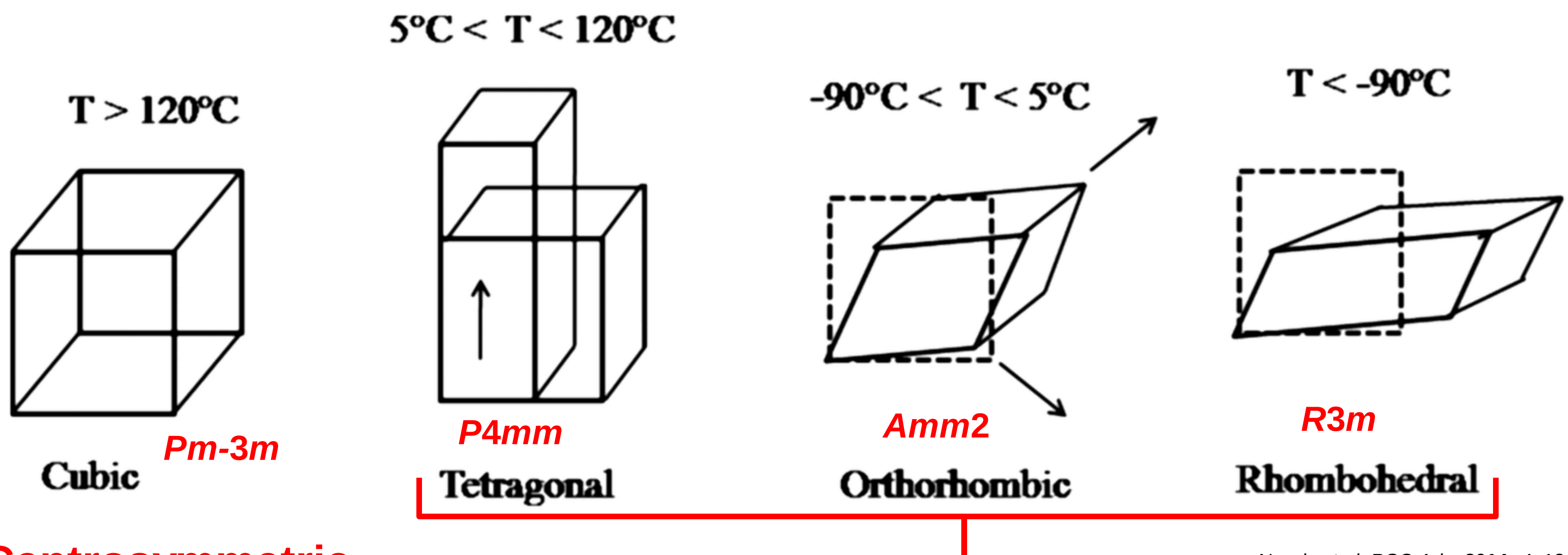
Wurtzite
ZnO ($P6_3mc$)



Perovskite
$CaTiO_3$ (Pm-$3m$)

The ideal cubic structure is centrosymmetric and not piezoelectric, see the next slide

$BaTiO_3$ phases (perovskite structure)



Centrosymmetric, no piezoelectric effect

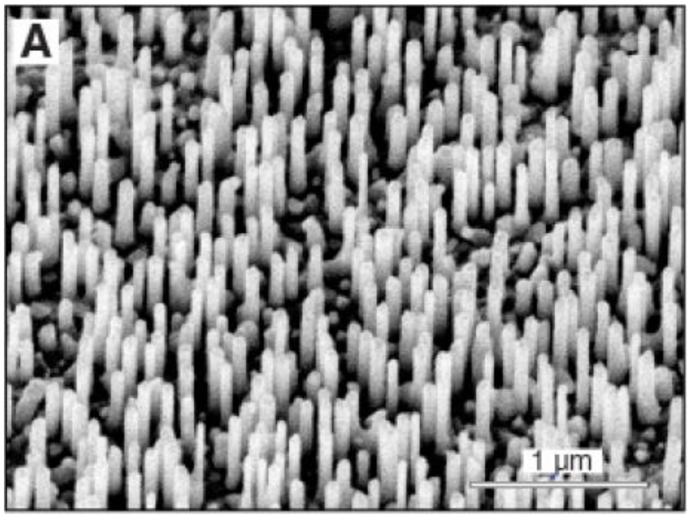
Non-centrosymmetric, piezoelectric effect

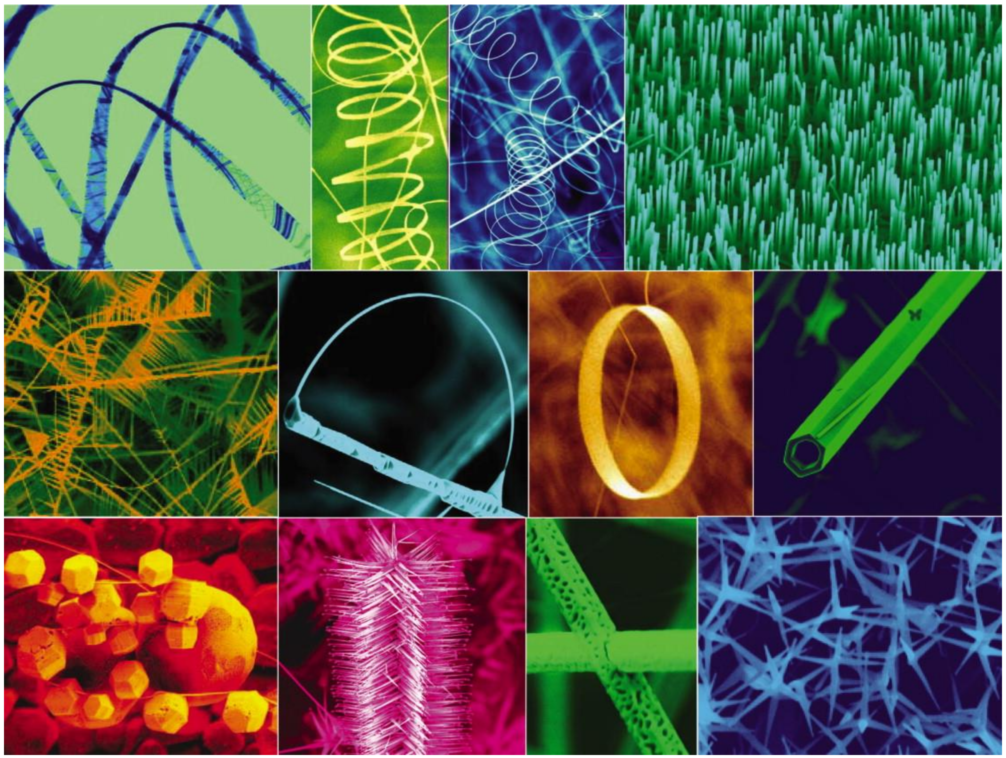
Nayak *et al. RSC Adv*. **2014**, *4*, 1212.

Nanostructured piezoelectrics

Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays

Zhong Lin Wang[1,2,3]* and Jinhui Song[1]   SCIENCE VOL 312 14 APRIL 2006

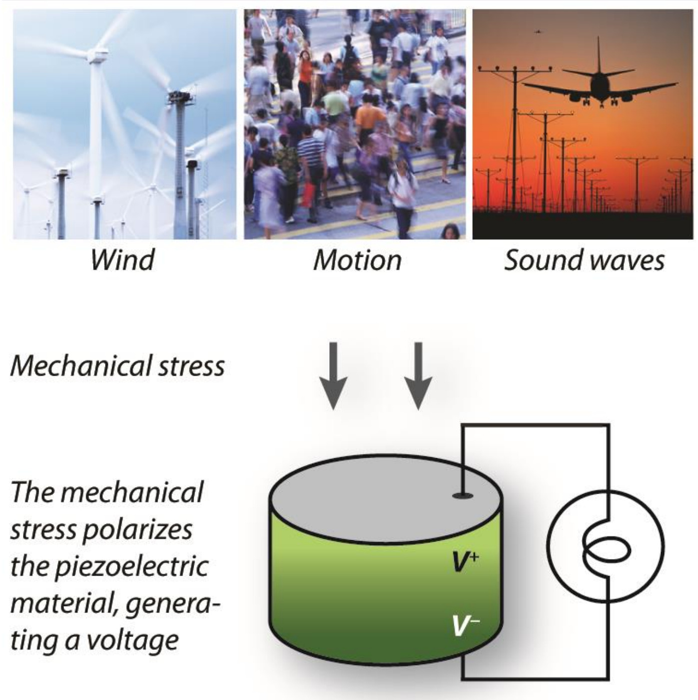




ZnO nanostructures synthesized under controlled conditions by thermal evaporation of solid powders (Wang, *Materials Today*, **2004**, *7*, 26).

Piezoelectricity: prospective applications

- Nanostructured piezoelectrics are being investigated for several applications
  - Piezotronics (piezo-electronics, e.g. piezopotential-based transistors)
  - Energy harvesting (convert mechanical energy to electricity)



Super-Flexible Nanogenerator for Energy Harvesting from Gentle Wind and as an Active Deformation Sensor

*Sangmin Lee, Sung-Hwan Bae, Long Lin, Ya Yang, Chan Park, Sang-Woo Kim, Seung Nam Cha, Hyunjin Kim, Young Jun Park, and Zhong Lin Wang**

Adv. Funct. Mater. **2012**, DOI: 10.1002/adfm.201202867

Energy harvesting

Nanotechnology-Enabled Energy Harvesting for Self-Powered Micro-/Nanosystems

Zhong Lin Wang and Wenzhuo Wu* *Angew. Chem. Int. Ed.* **2012**, 51, 11700–11721

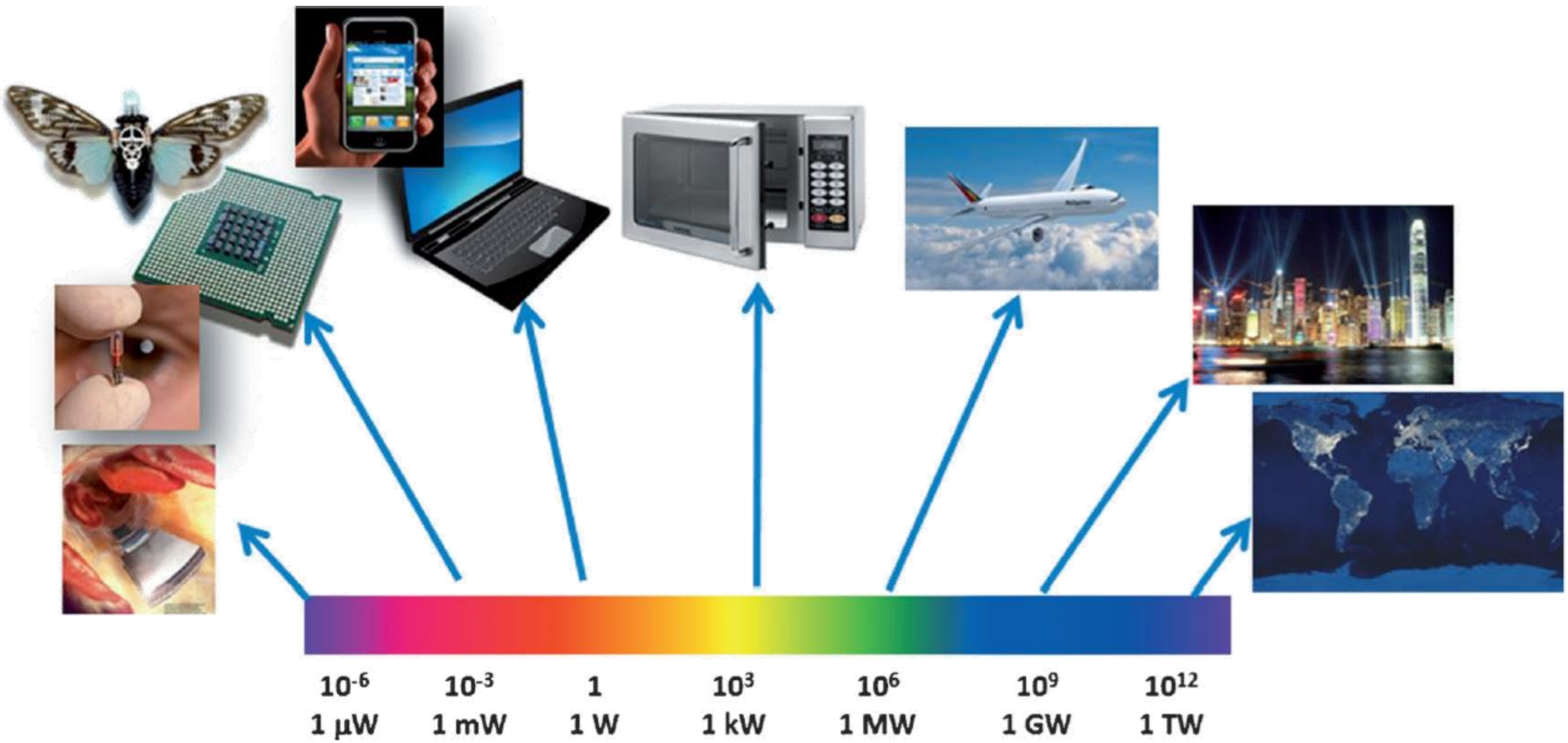


Figure 1. Power requirements for different applications: In the future there will be a great demand for mobile/implantable electronics with extremely low power consumption.

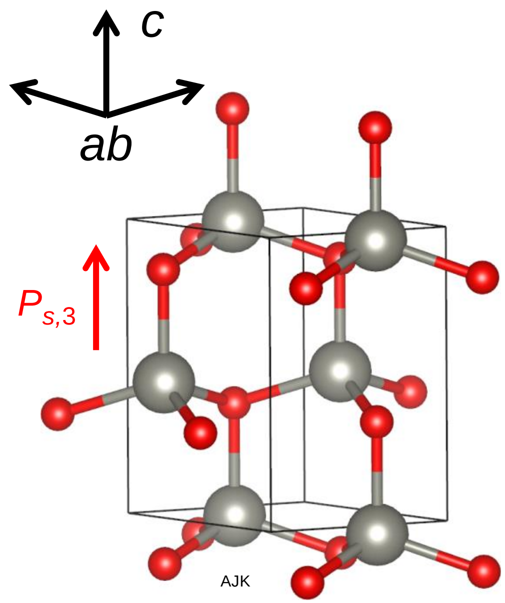
Free book: Z. L. Wang, Nanogenerators for Self-powered Devices and Systems, 2011 (Link)

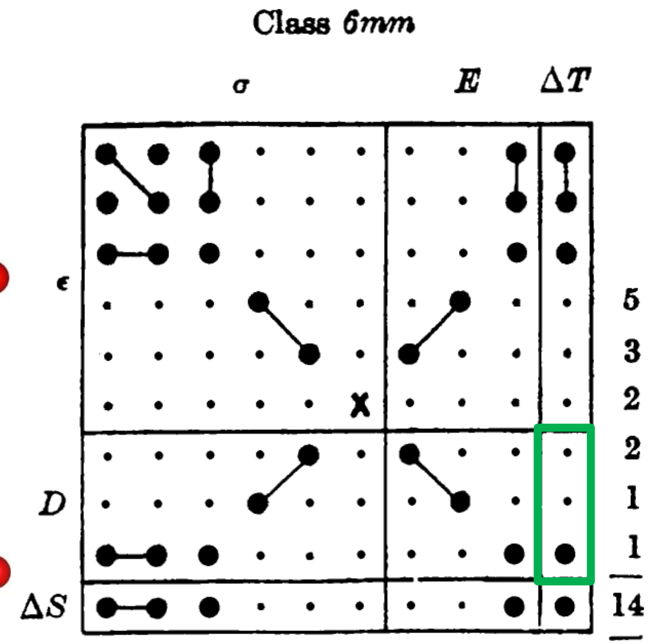
Pyroelectricity

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

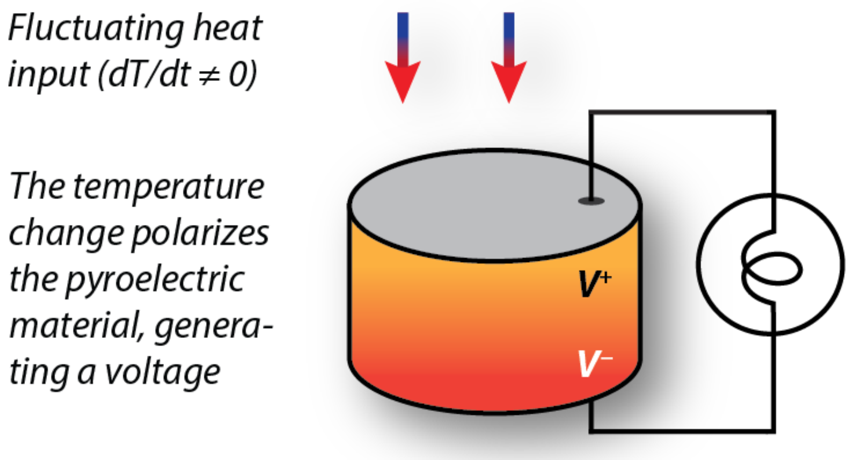


Figure: AJK

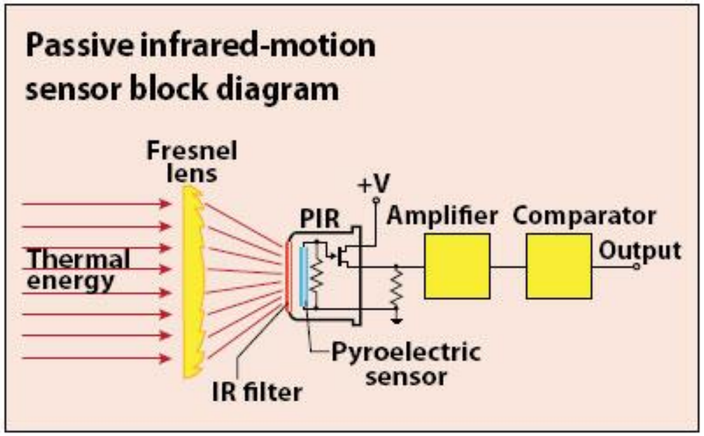


Figure: www

Property data for pyroelectrics

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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}

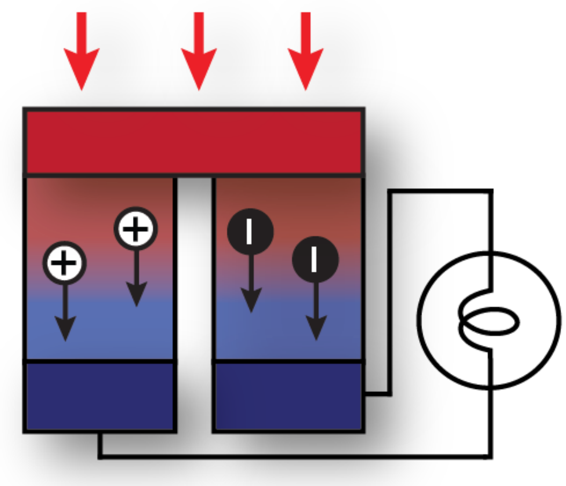
Thermoelectrics vs. pyroelectrics

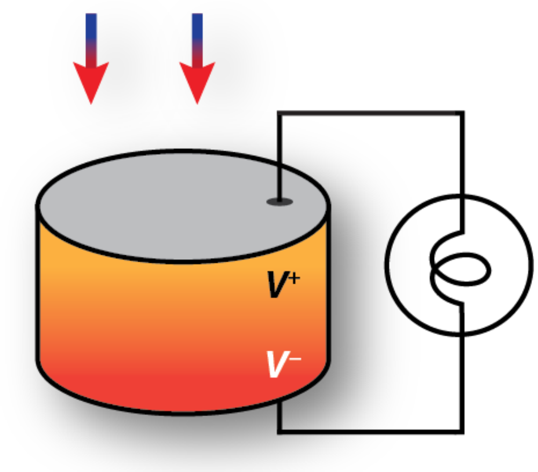
Thermoelectric generator

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

Pyroelectric generator

- Fluctuating heat input required for optimal operation

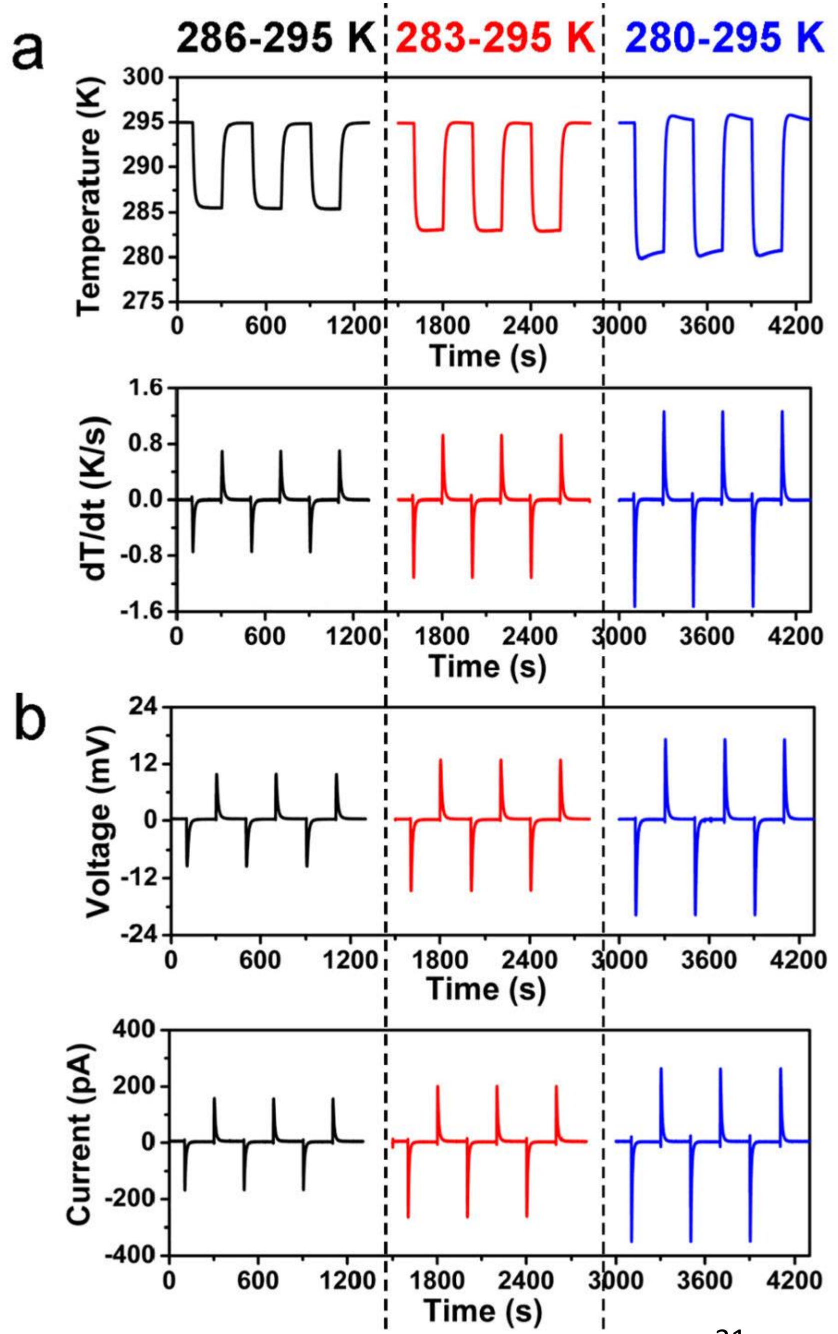




Figures: AJK

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

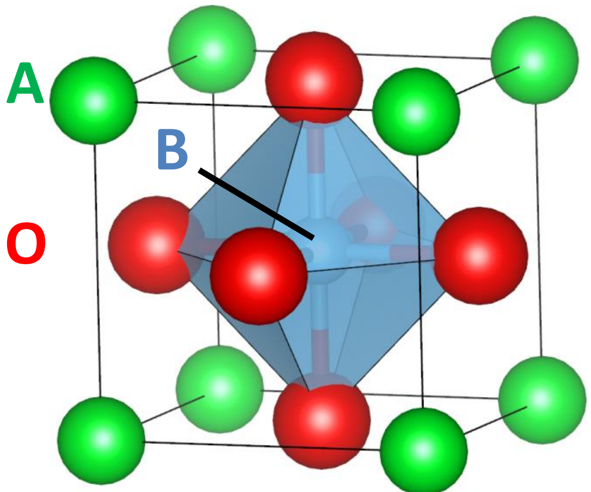
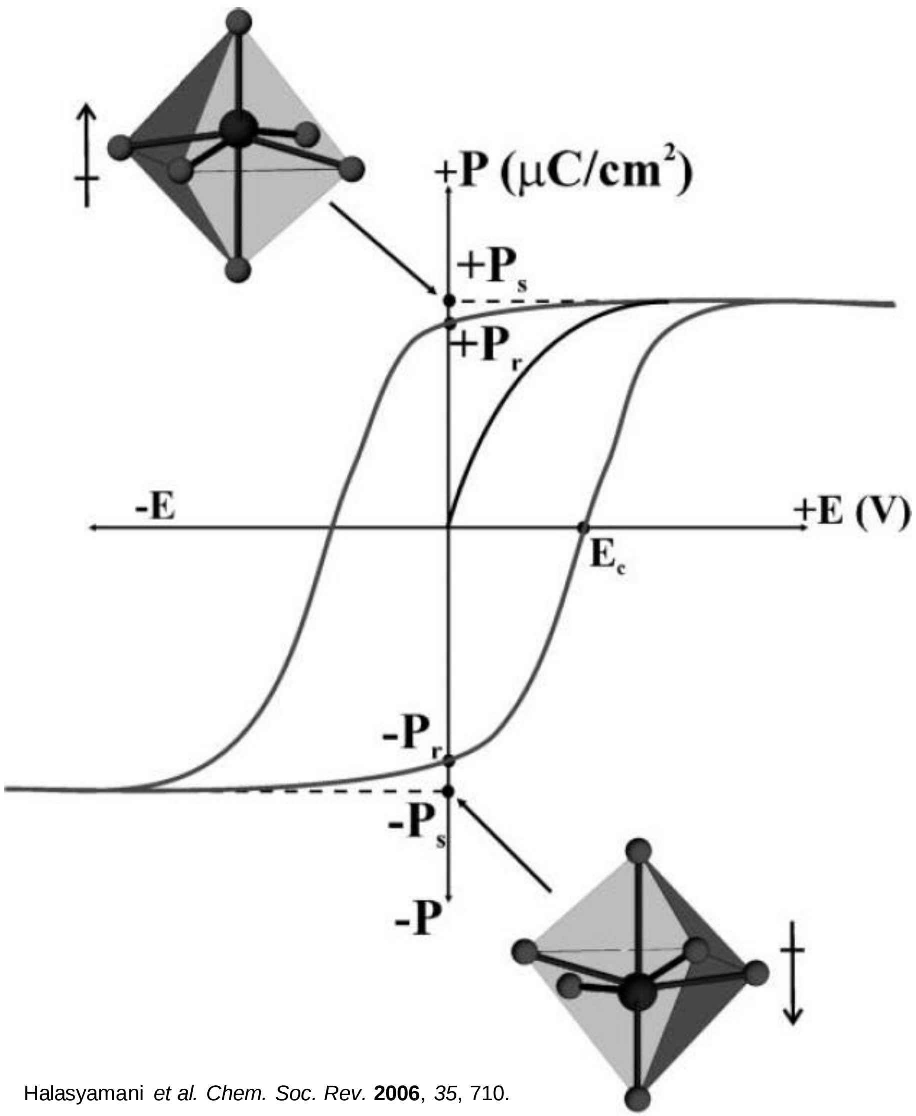


Figure: AJK

Ideal perovskite structure (ABO_3, e.g. $BaTiO_3$)

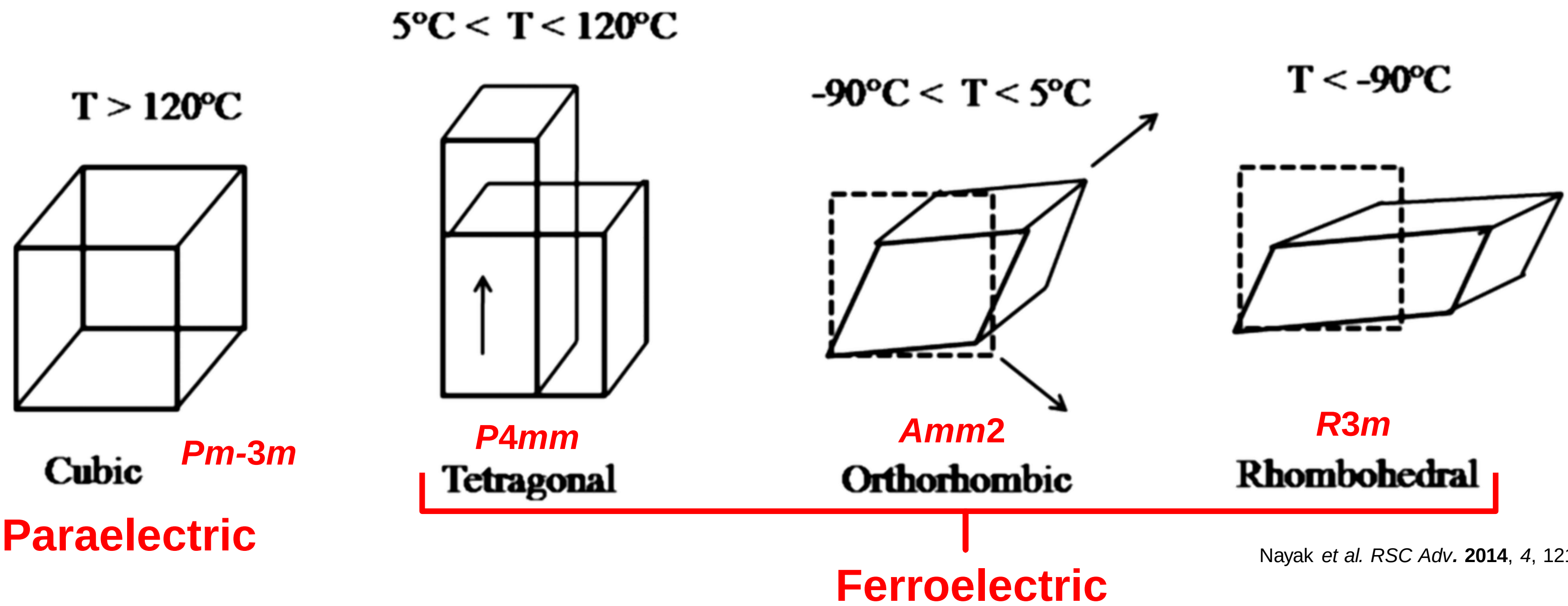
Non-cubic perovskites can possess switchable polarization *P*

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



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

$BaTiO_3$ phases



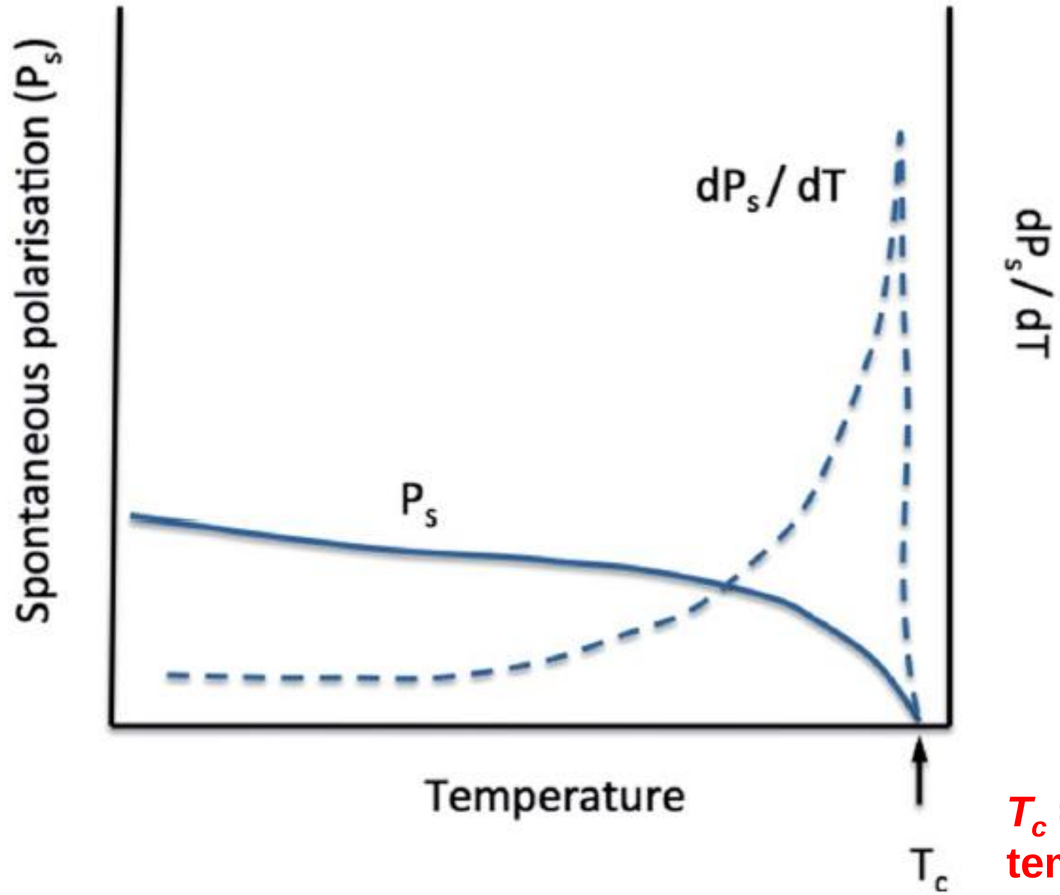
Nayak *et al.* *RSC Adv.* **2014**, *4*, 1212.

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

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

Ferroelectric pyroelectrics



***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 (not that competitive with DRAM)
  - Capacitors with tunable capacitance
  - Ferroelectric field-effect transistors (rather hypothetical at the moment)