Aalto University
School of Chemical
Engineering

Functional Inorganic Materials
Lecture 9:
Piezoelectricity

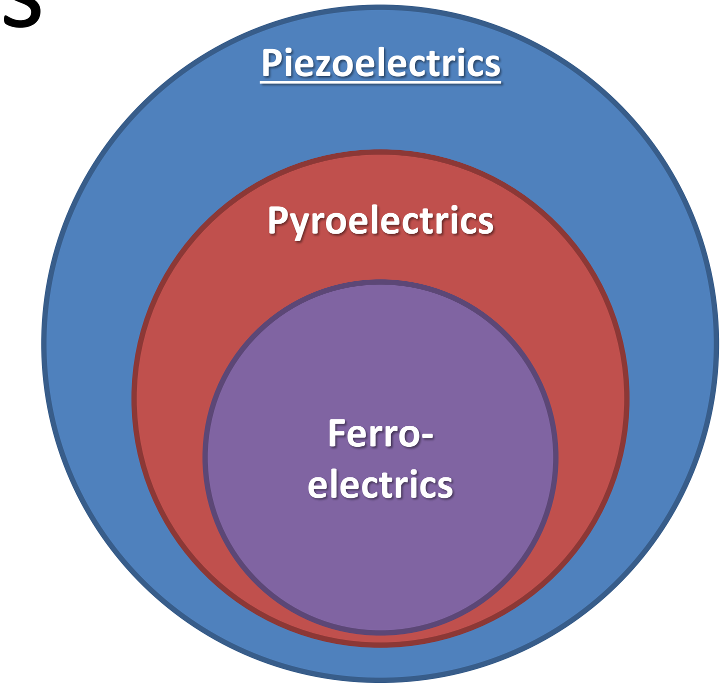
Fall 2022

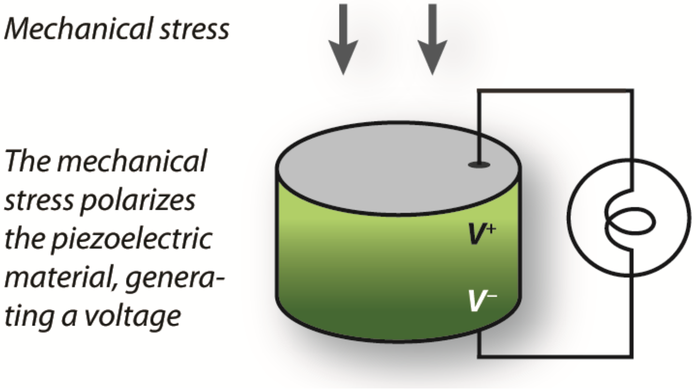
Antti Karttunen (antti.karttunen@aalto.fi)
Department of Chemistry and Materials Science

Lecture Exercise 9 is a MyCourses Quiz

Contents

- General overview of **non-centrosymmetric materials**
  - Piezoelectricity is limited to crystals with certain symmetry properties
- **Piezoelectricity**
  - Electric polarization from mechanical force
  - Mechanical deformation due to electric field
- Applications of piezoelectricity in various fields of technology
  - Energy harvesting as a potential future application





The mechanical stress polarizes the piezoelectric material, generating a voltage

Figures: AJK

Literature on non-centrosymmetric materials

P. Shiv Halasyamani and Kenneth R. Poeppelmeier, Noncentrosymmetric Oxides, *Chem. Mater.* **1998**, *10*, 2753–2769. DOI: https://doi.org/10.1021/cm980140w

Kang Min Ok, Eun Ok Chi and P. Shiv Halasyamani, Bulk characterization methods for non-centrosymmetric materials: second harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity, *Chem. Soc. Rev.*, **2006**, *35*, 710–717. DOI: https://doi.org/10.1039/B511119F

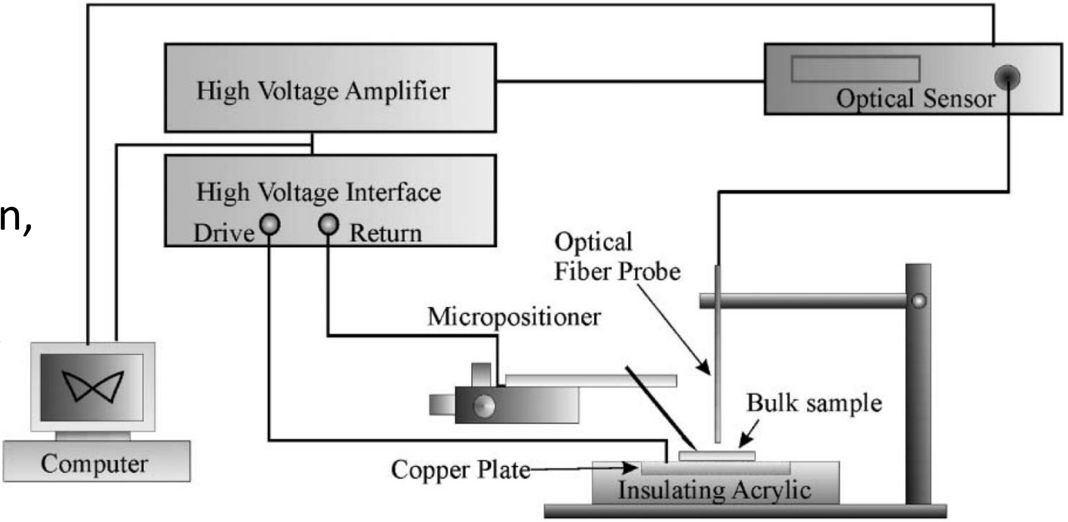


Fig. 3 Experimental system to measure converse piezoelectric effects.

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

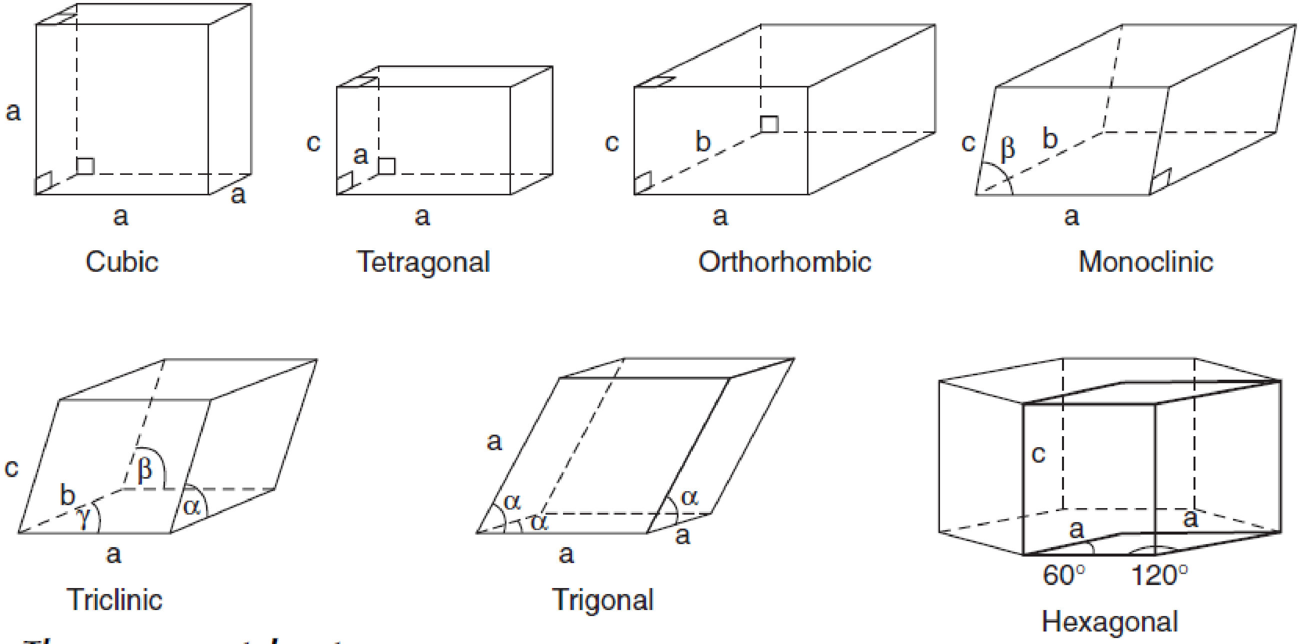


Table 1.1 ***The seven crystal systems***

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

Ref: West p. 3-4

Crystal classes

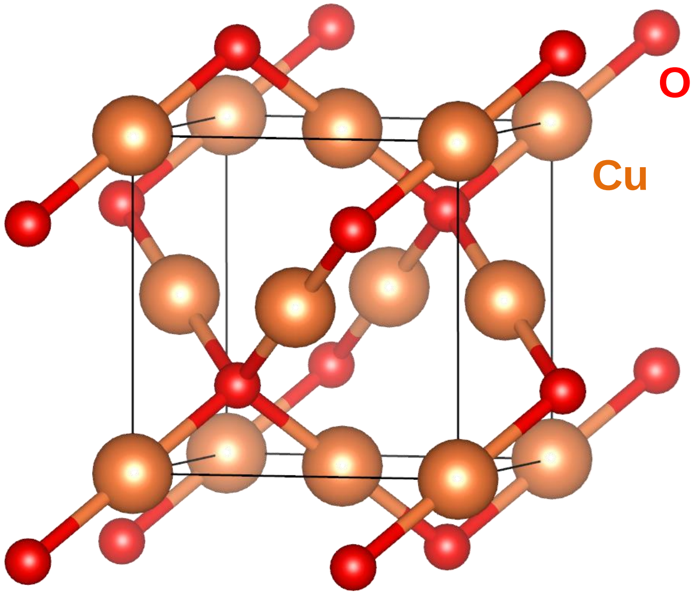
- The seven crystal systems consist of 32 crystal classes corresponding to the 32 crystallographic point groups

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

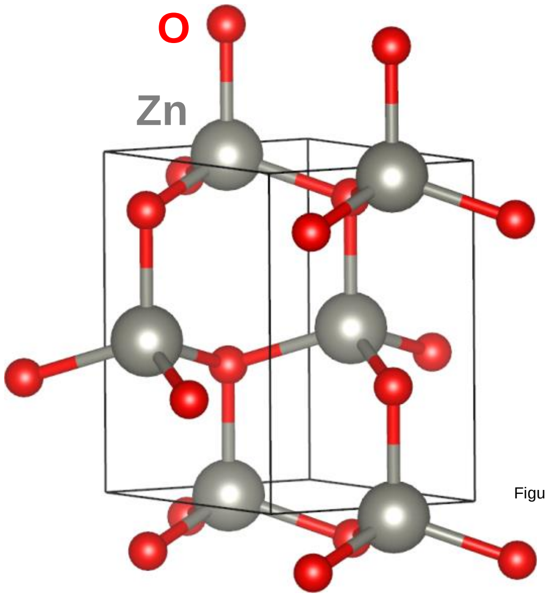
Ref: *Inorganic Structural Chemistry* (2nd ed.), Ulrich Müller, **2006**, Wiley p. 24 and Wikipedia

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 are possible only for ***non-centrosymmetric materials***



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

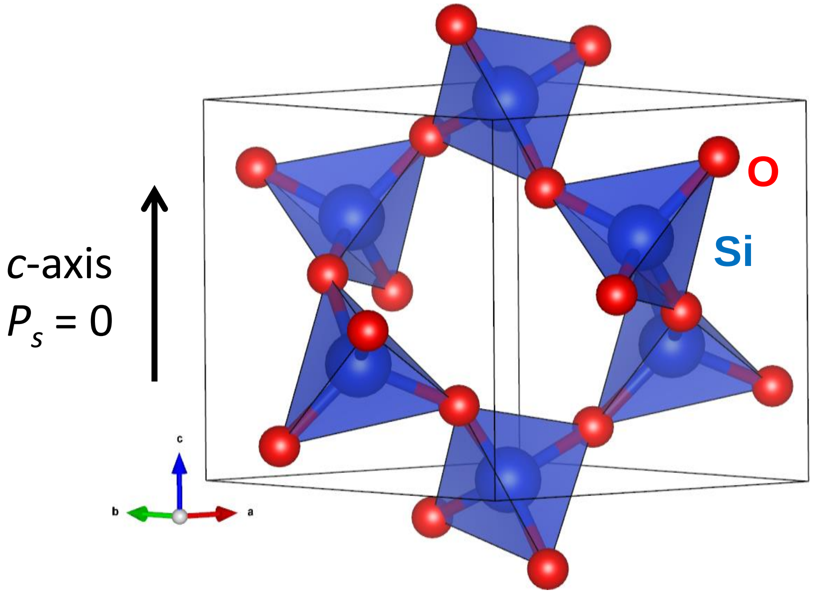


Figures: AJK

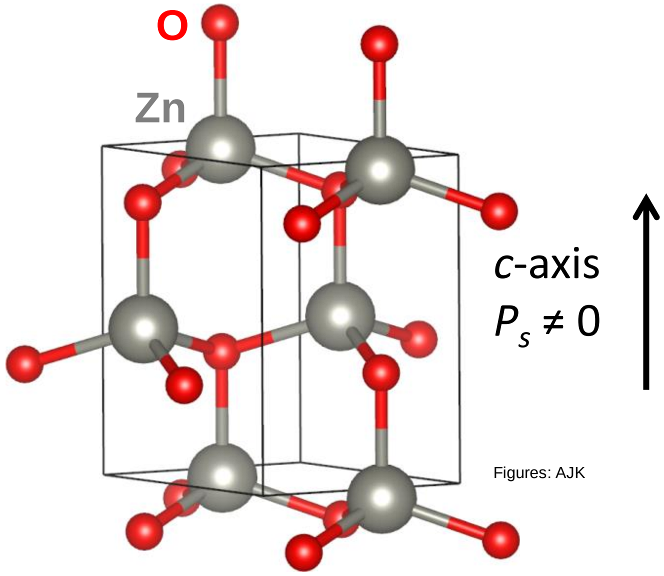
ZnO (space group $P6_3mc$)
Non-centrosymmetric oxide with
no inversion center

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*** P_s



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



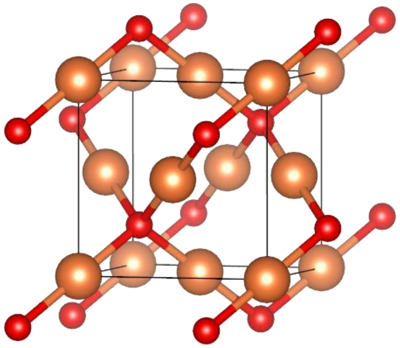
Figures: AJK

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

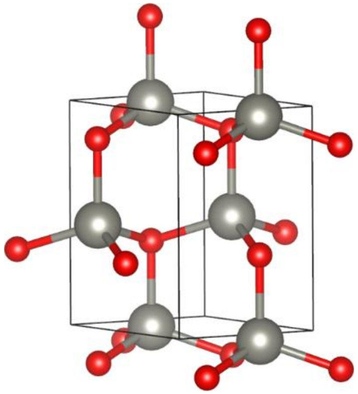
Classification of crystal classes

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	$m\bar{3}, m\bar{3}m$	–	$23, \bar{4}3m, 432,$

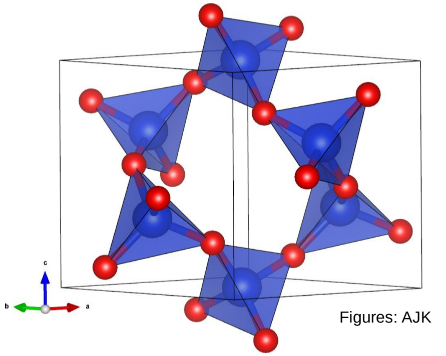
Refs: *Chem. Mater.* **1998**, *10*, 2753 and Wikipedia



Cu_2O (Pn-$3m$)



ZnO ($P6_3mc$)

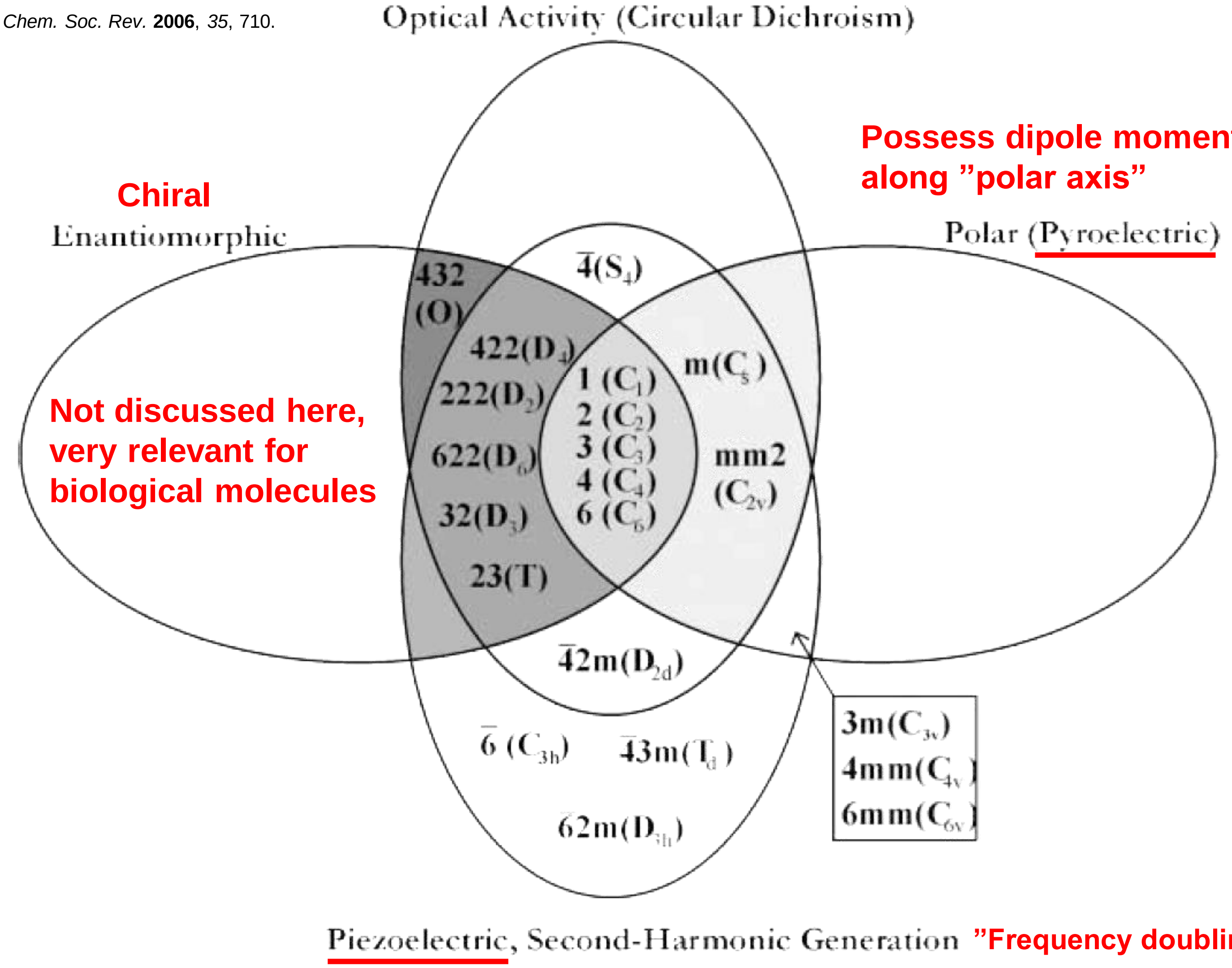


Figures: AJK

α-SiO_2 ($P3_221$)

Non-centrosymmetric crystal classes and functionality

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



Chiral

Not discussed here, very relevant for biological molecules

Possess dipole moment along ”polar axis”

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

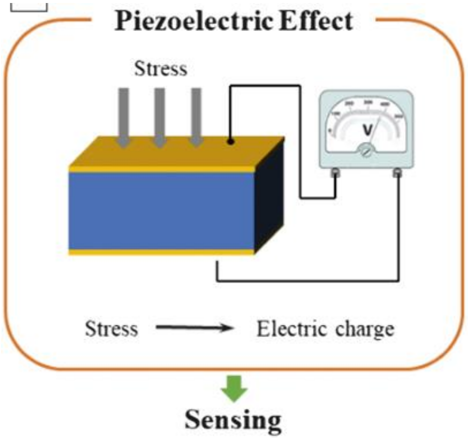
”Frequency doubling”

Piezoelectric coefficients

Direct piezoelectric effect

$P = d\sigma$, where

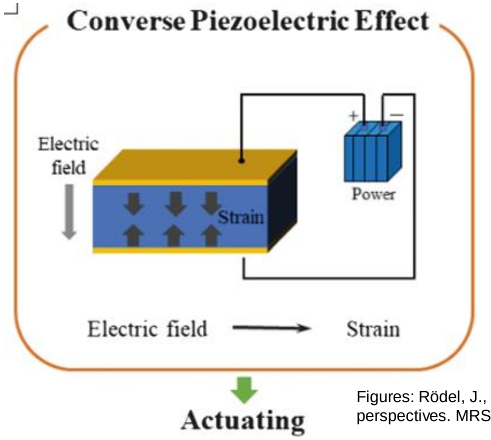
- σ = applied tensile **stress** ($\mathrm{N\,m^{-2}}$)
- d = piezoelectric modulus ($\mathrm{C\,N^{-1}}$)
- P = resulting polarization ($\mathrm{C\,m^{-2}}$)



Converse piezoelectric effect

$\varepsilon = dE$, where

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



Figures: Rödel, J., & Li, J. (2018). Lead-free piezoceramics: Status and perspectives. MRS Bulletin, 43(8), 576-580. doi:10.1557/mrs.2018.181

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

Piezoelectricity in ZnO

Let’s use ZnO as an example.

ZnO (*$P6_3mc$*) has three symmetry-allowed distortions that lead to a piezoelectric response

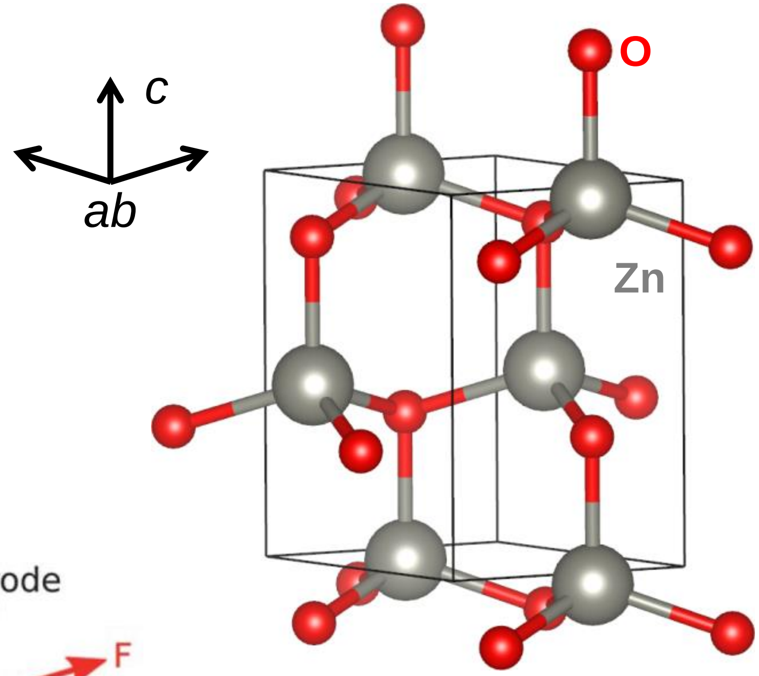
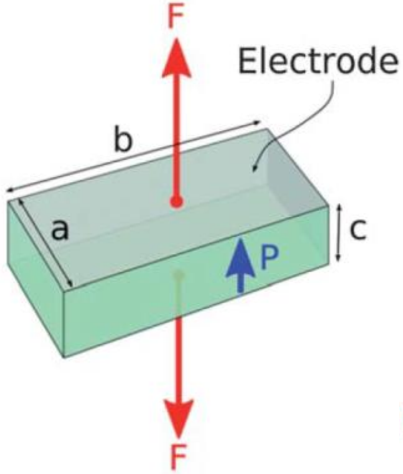
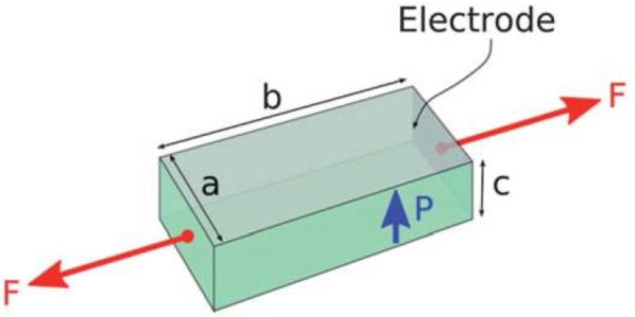


Figure: AJK



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

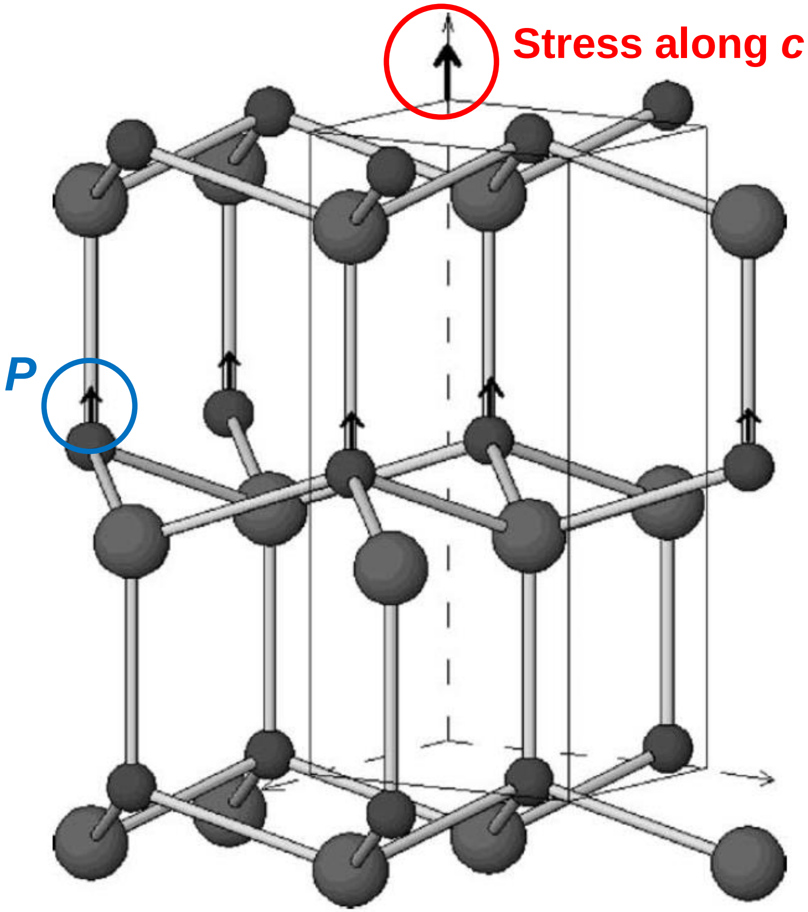


2. Stress in *ab*-plane, Polarization along *c*

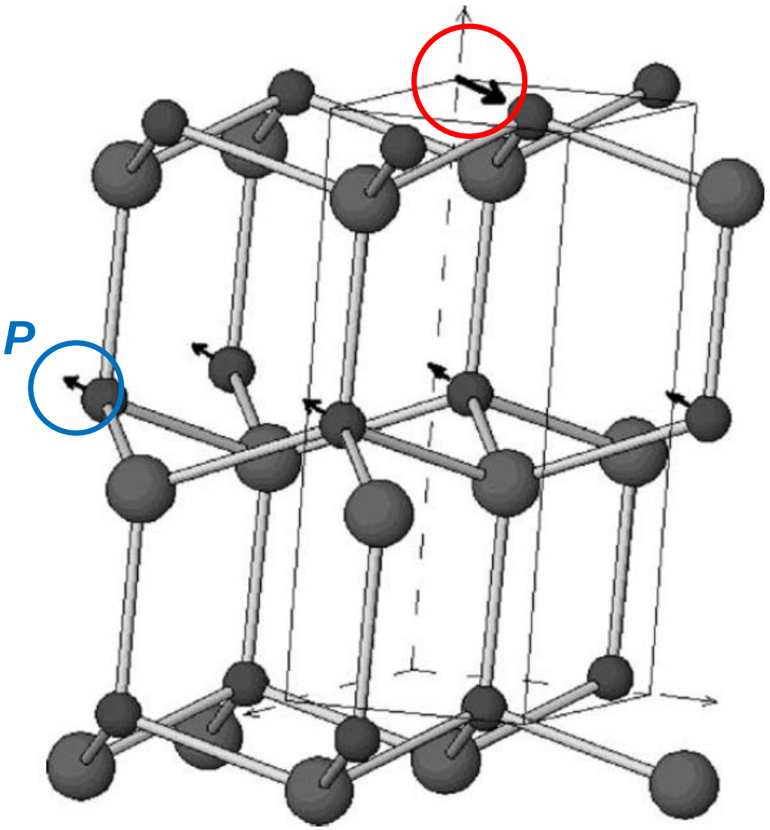
3. Shear in *ab*-plane (*next slide*)

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

Piezoresponse to shear in ZnO



Stress along *c* ("33")

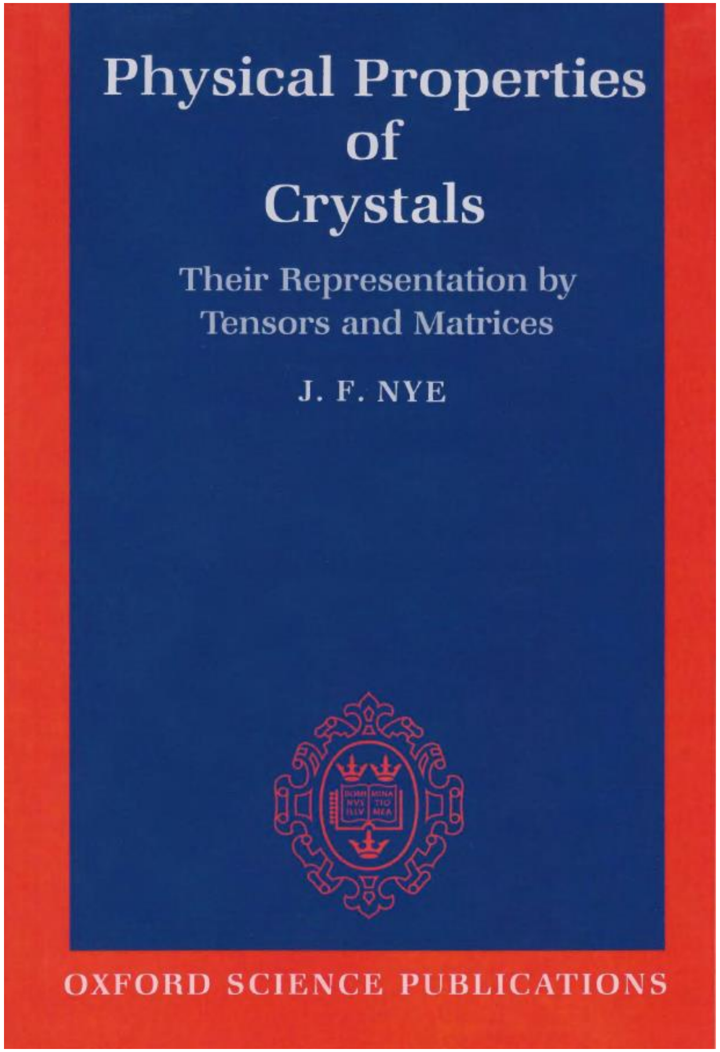


Shear in *ab* plane ("15")

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



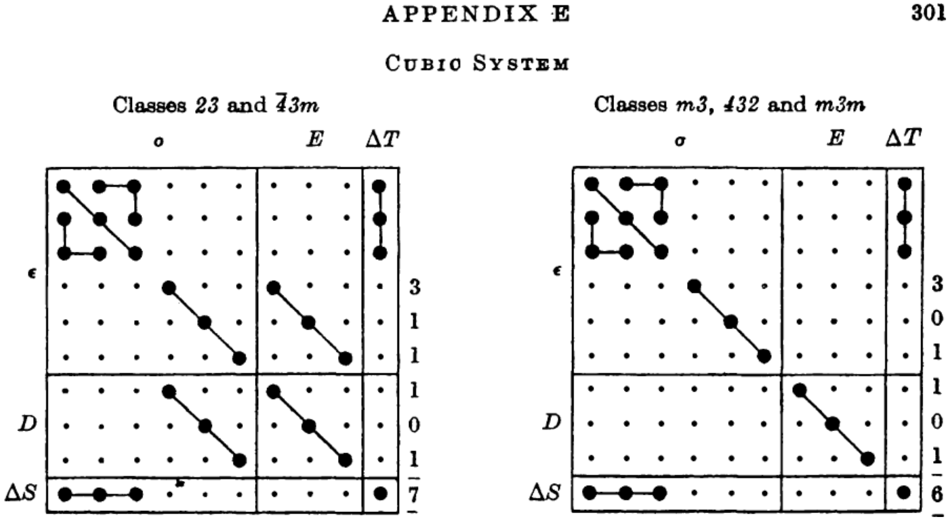
Physical Properties of Crystals

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)



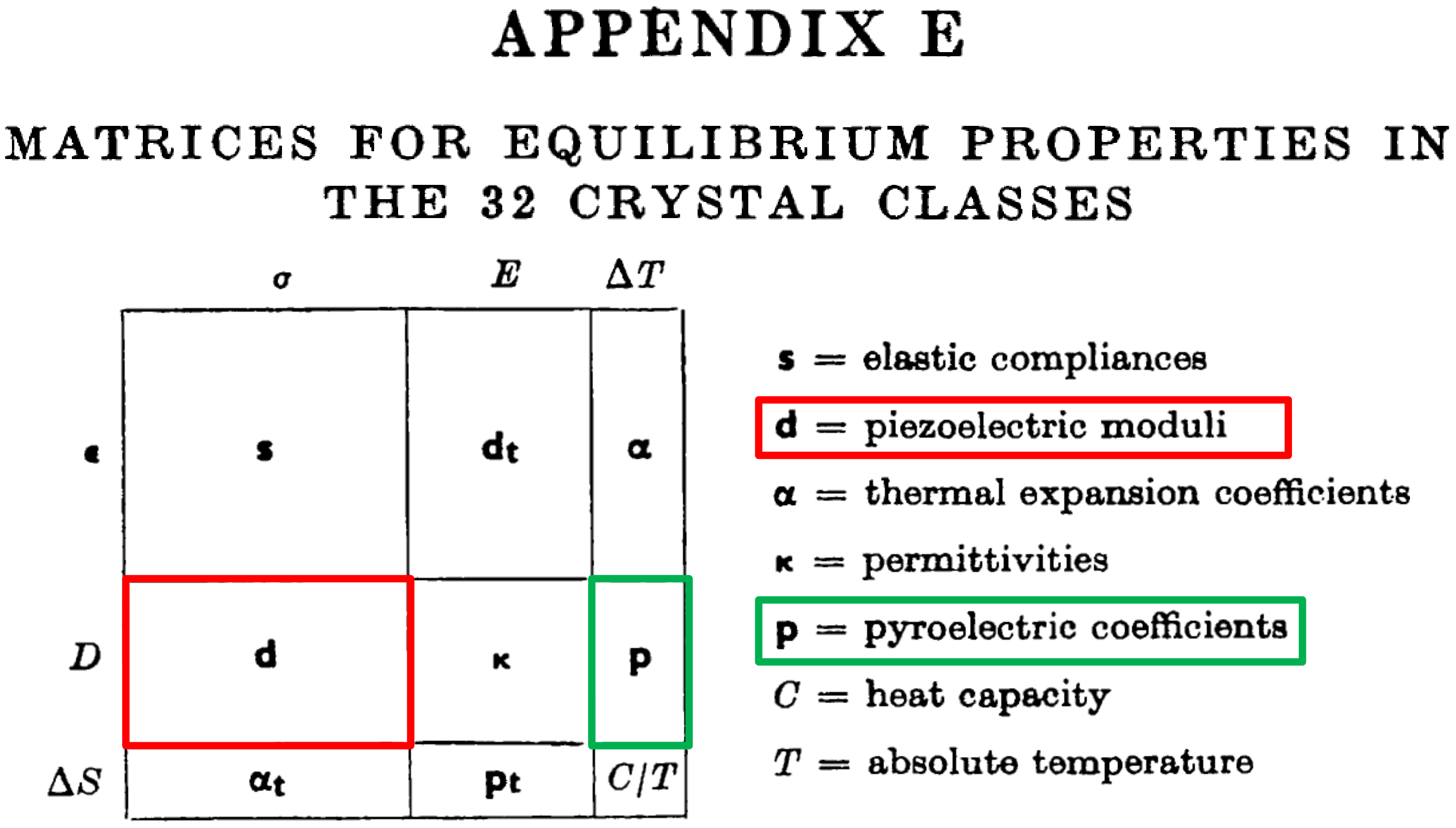
APPENDIX E 301

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

	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

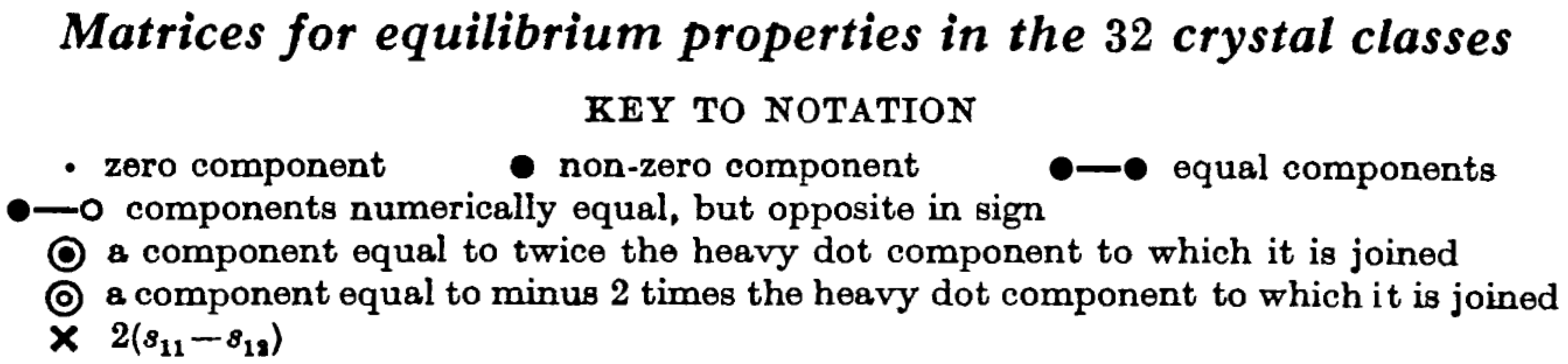
$\boldsymbol{\kappa}$ = permittivities

$\mathbf{p}$ = pyroelectric coefficients

C = heat capacity

T = absolute temperature

Physical property tensors (Nye)



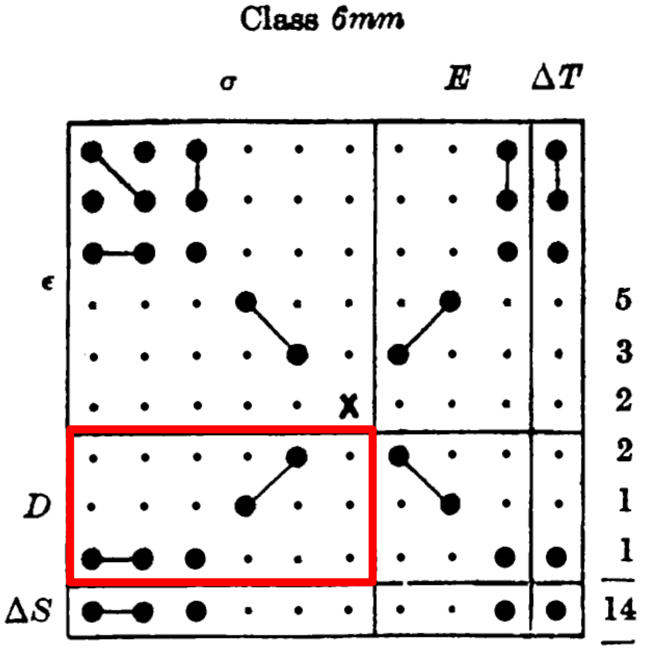
Matrices for equilibrium properties in the 32 crystal classes

KEY TO NOTATION

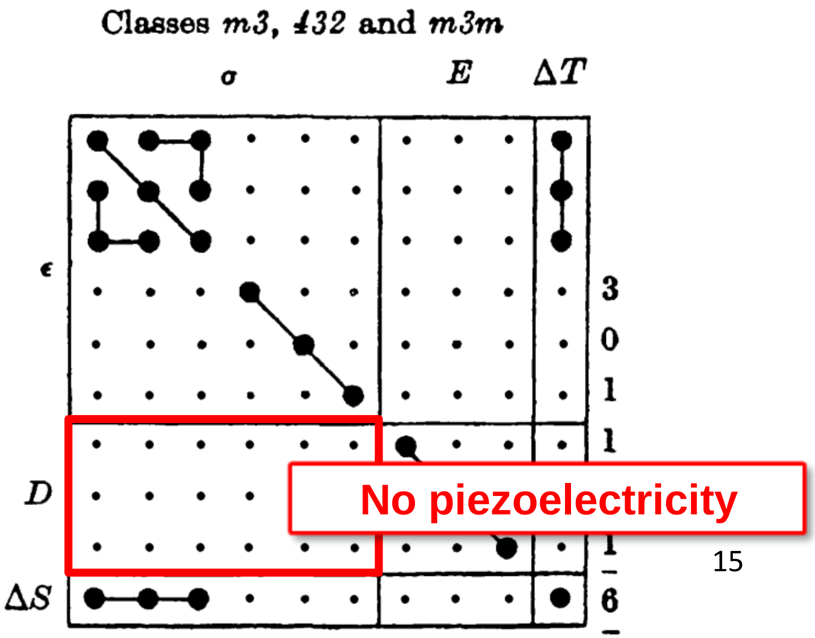
- • zero component
- ● non-zero component
- ●—● equal components
- ●—○ components numerically equal, but opposite in sign
- ◉ a component equal to twice the heavy dot component to which it is joined
- ◎ a component equal to minus 2 times the heavy dot component to which it is joined
- × $2(s_{11}-s_{12})$

For example, ZnO (*P*6$_3$*mc*)

For example, Cu$_2$O (*Pn*-3*m*)



Class 6*mm*



Classes *m*3, 432 and *m*3*m*

No piezoelectricity

ZnO piezoelectricity tensor

ZnO (space group $P6_3mc$)

Three independent non-zero components in the piezoelectric tensor

What do they actually mean:

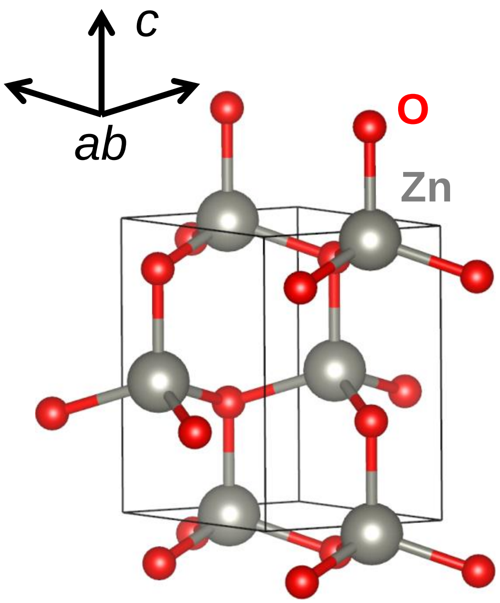
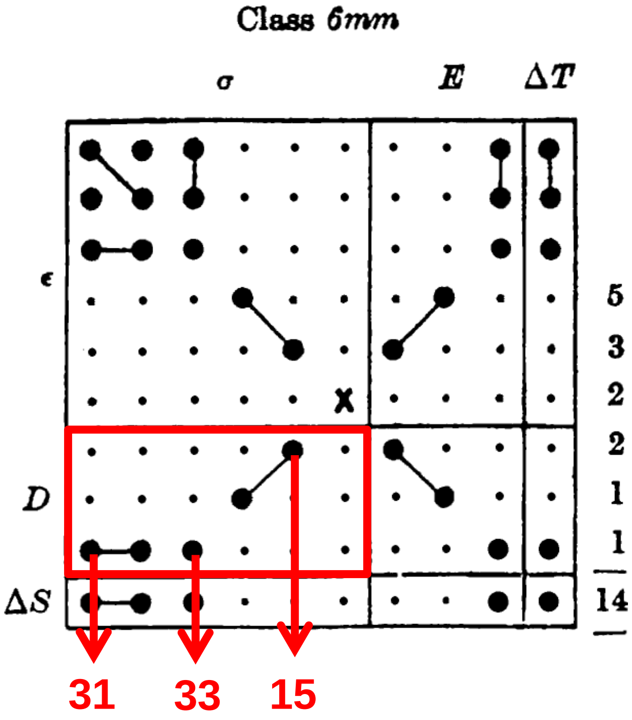
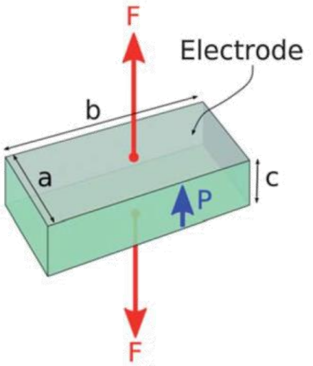
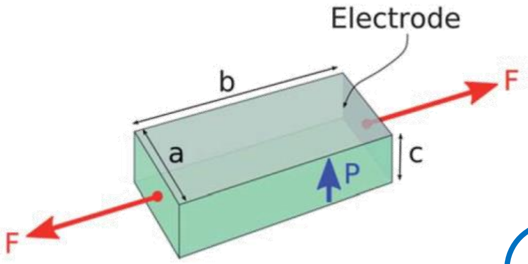


Figure: AJK

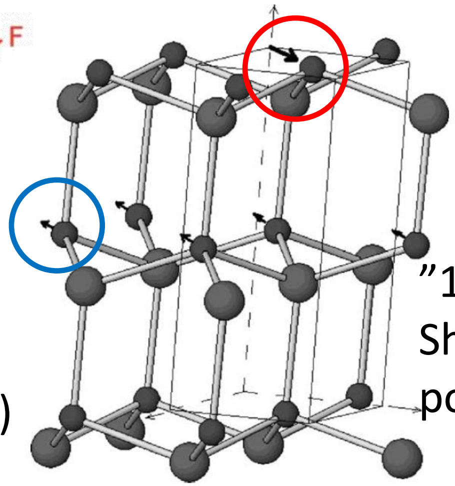




”33” component:
Stress along *c* (3),
polarization along *c* (3)



”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.

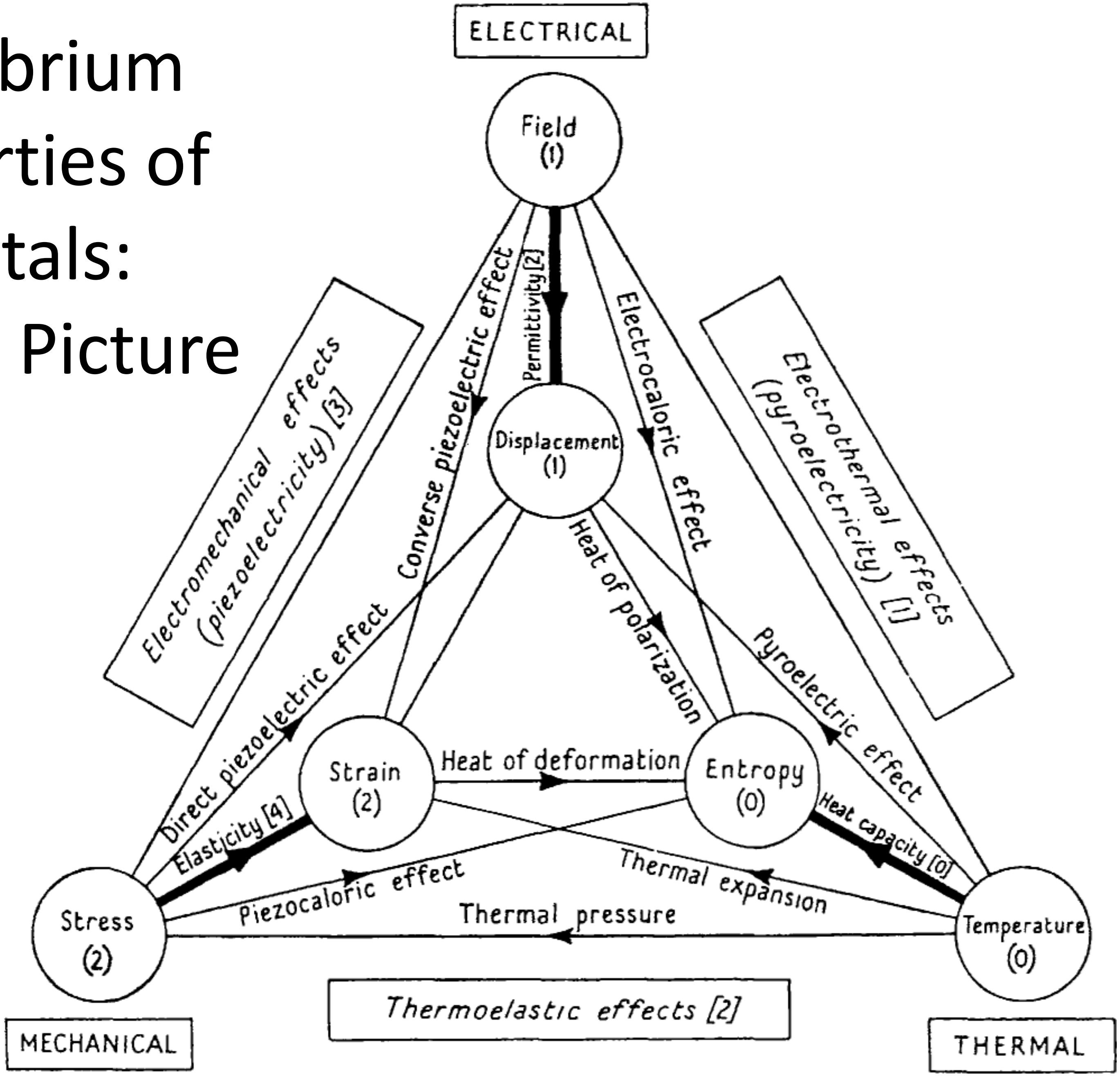
Piezoelectricity is an equilibrium property

- Equilibrium properties may be described by reference to ***thermodynamic equilibrium states*** and ***thermodynamically reversible 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 irreversible 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

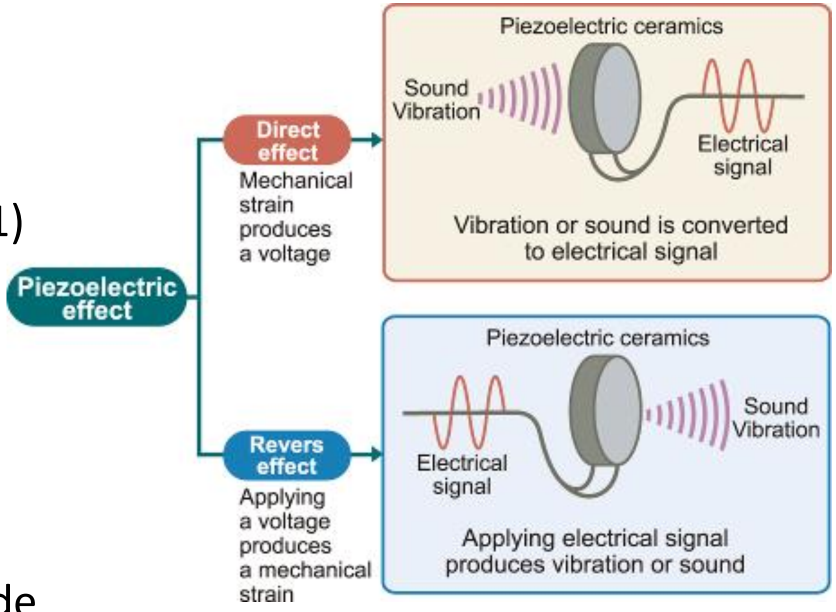


Figure: Honda

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

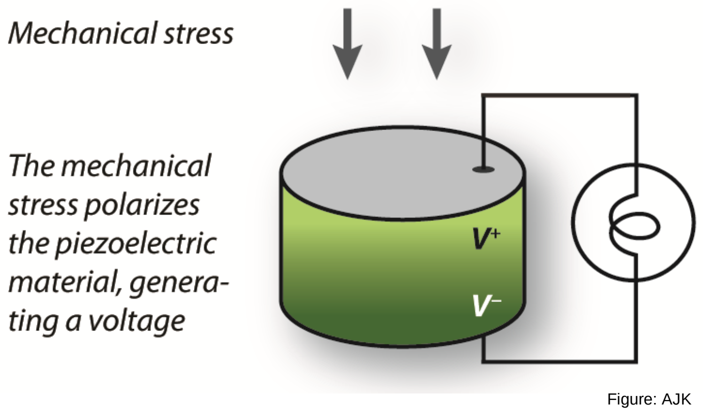


Figure: AJK

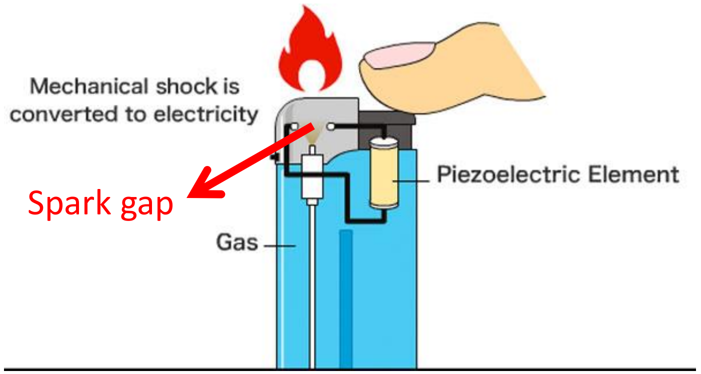
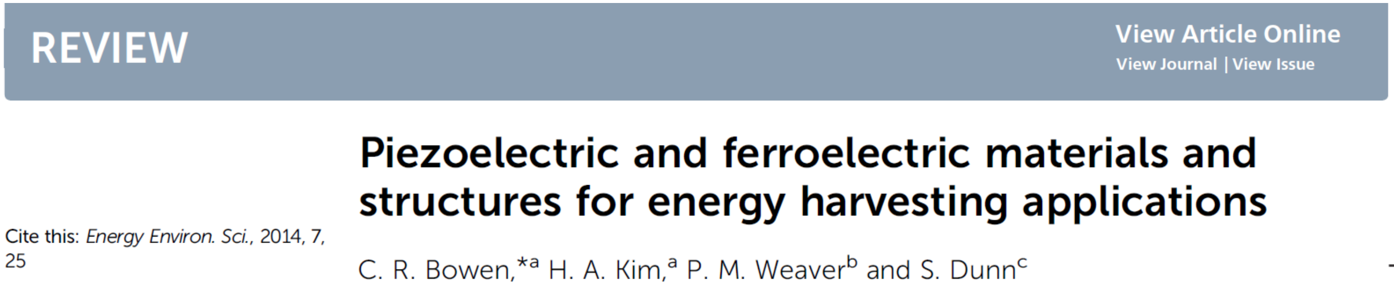


Figure: www

Piezoelectric lighter

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

Property data for piezoelectrics



REVIEW

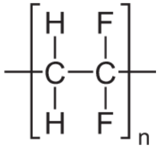
View Article Online
View Journal | View Issue

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

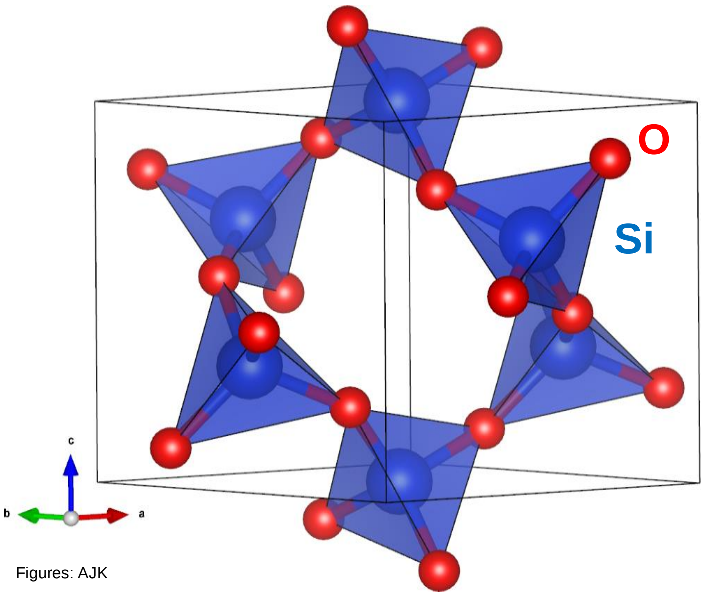


	GaN	ZnO	SiO_2	$BaTiO_3$	PZT-5H ("soft")	PMN-PT	$LiNbO_3$	PVDF
Structure	Wurzite	Wurzite	α-quartz	Perovsk.	Perovsk.	Perovsk.	$LiNbO_3$	Polymer
Piezoelectric	X	X	X	X	X	X	X	X
Pyroelectric	X	X	-	X	X	X	X	X
Ferroelectric	-	-	-	X	X	X	X	X
d_{33} (pC N^{-1})	3.7	12.4	-2.3 (d_{11})	149	593	2820	6	-33
d_{31} (pC 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

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

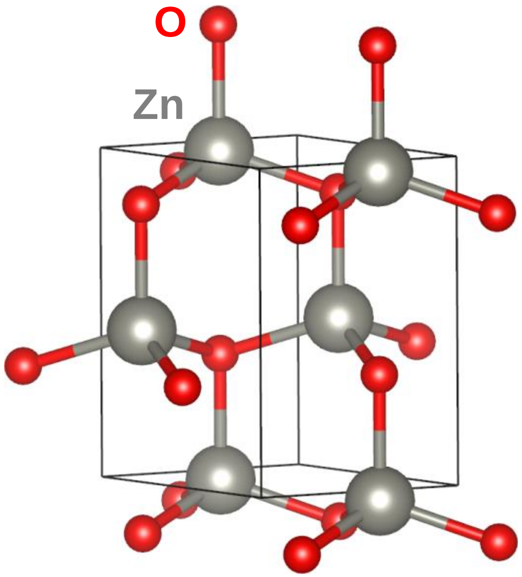
$(1\text{-}x)Pb[Mg_yNb_{1-y}]O_3 - xPbTiO_3$

Important crystal structures for piezoelectrics

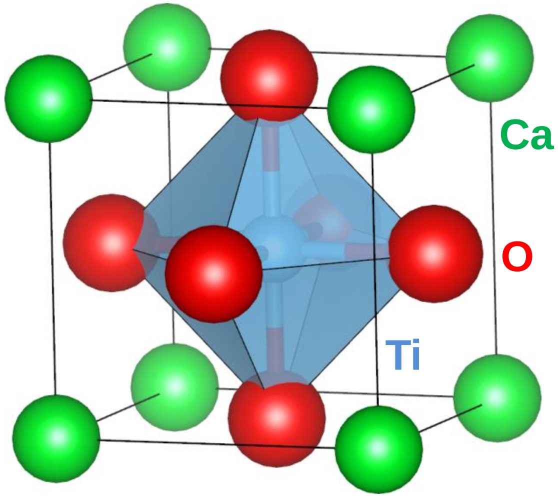


Figures: AJK

Quartz
α-SiO_2 ($P3_221$)



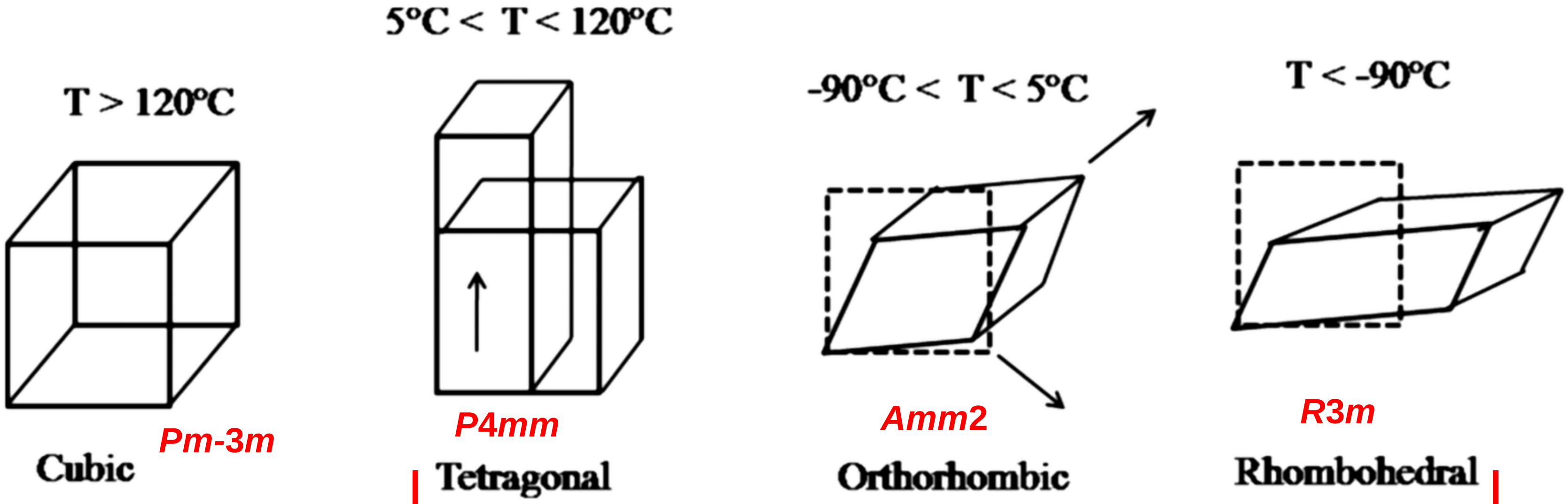
Wurtzite
ZnO ($P6_3mc$)



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

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

$BaTiO_3$ phases (perovskite structure)



Pm-3m

P4mm

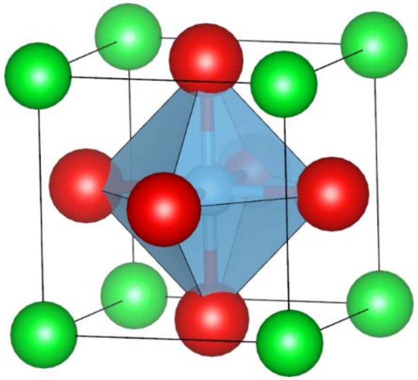
Amm2

R3m

Centrosymmetric, no piezoelectric effect

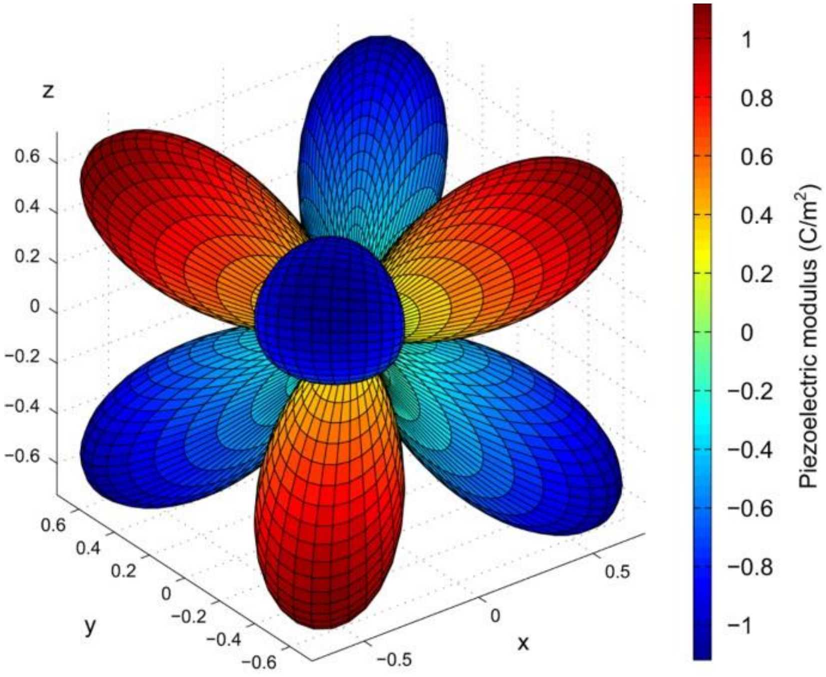
Non-centrosymmetric, piezoelectric effect

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



High-throughput screening for piezoelectric materials (1)

- Piezoelectricity has been determined experimentally or computationally only for a small fraction of all inorganic compounds which display compatible crystallographic symmetry
- Persson and coworkers used Density Functional Theory (DFT) to calculate the piezoelectric tensors for nearly 1000 inorganic compounds.[1]
  - The amount of available piezoelectricity data was increased by more than an order of magnitude.



Visualization of the piezoelectric tensor: directional dependence of the longitudinal piezoelectric constant in cubic LaOF.

---

[1] de Jong, M., Chen, W., Geerlings, H., Asta, M., Persson, K. A. A database to enable discovery and design of piezoelectric materials. Sci Data 2, 150053 (2015). https://doi.org/10.1038/sdata.2015.53

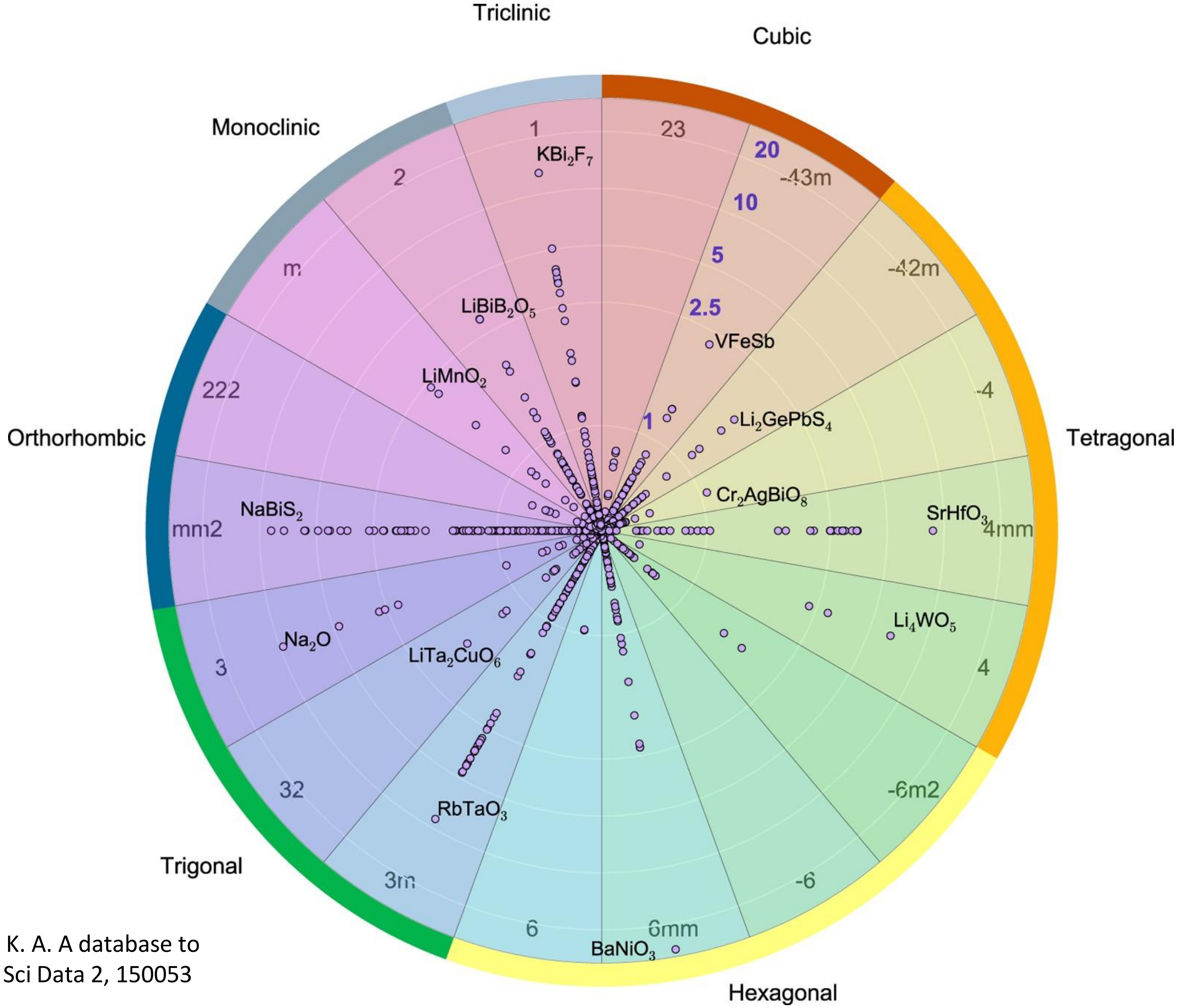
High-throughput screening for piezoelectric materials (2)

A graphical representation of the piezoelectric dataset, currently comprising of 941 materials.

A series of concentric circles indicate constant values of the maximum longitudinal piezoelectric modulus, $\|e_{ij}\|_{\max}$.

Concentric circles corresponding to moduli of 1, 2.5, 5, 10 and 20 C/m^2 are indicated explicitly in the figure.

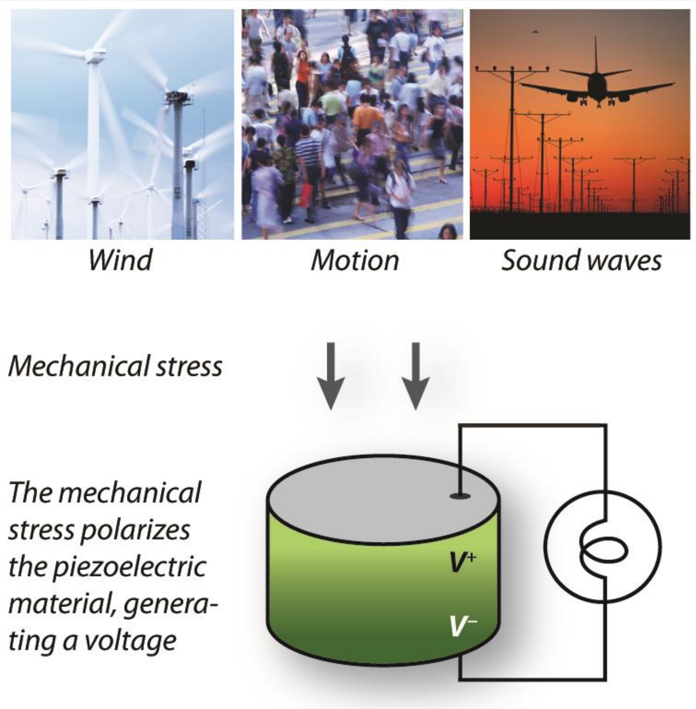
The compounds are broken up according to the crystal system and the different point group symmetry-classes

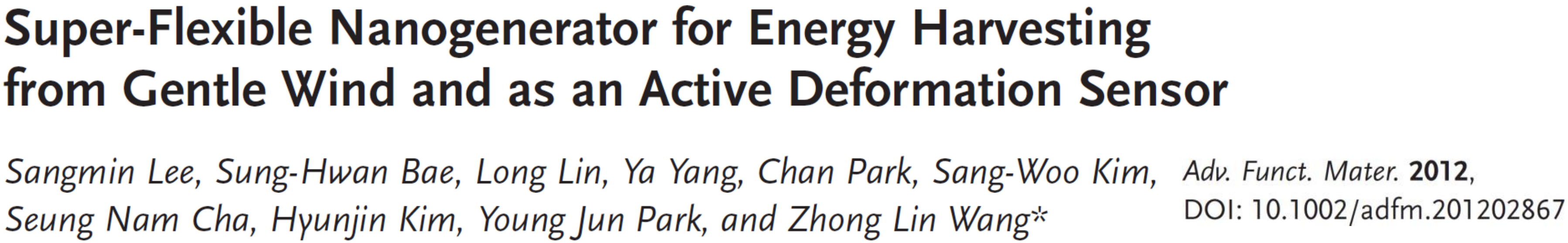


de Jong, M., Chen, W., Geerlings, H., Asta, M., Persson, K. A. A database to enable discovery and design of piezoelectric materials. Sci Data 2, 150053 (2015). https://doi.org/10.1038/sdata.2015.53

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

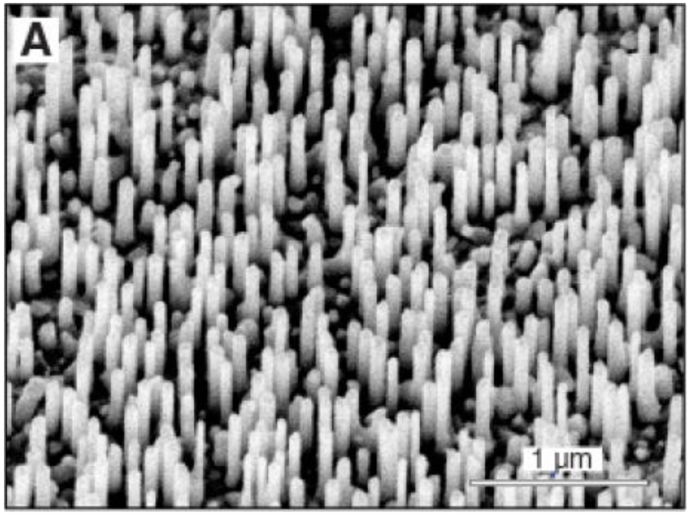
*Sangmin Lee, Sung-Hwan Bae, Long Lin, Ya Yang, Chan Park, Sang-Woo Kim, Seung Nam Cha, Hyunjin Kim, Young Jun Park, and Zhong Lin Wang**

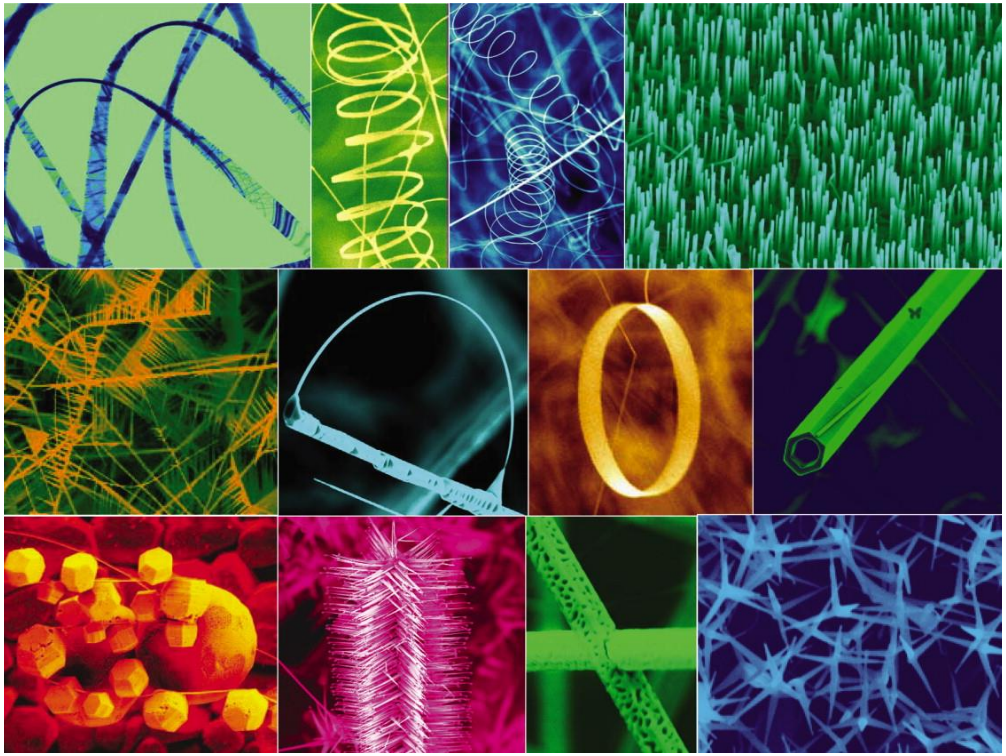
Adv. Funct. Mater. **2012**,
DOI: 10.1002/adfm.201202867

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).

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

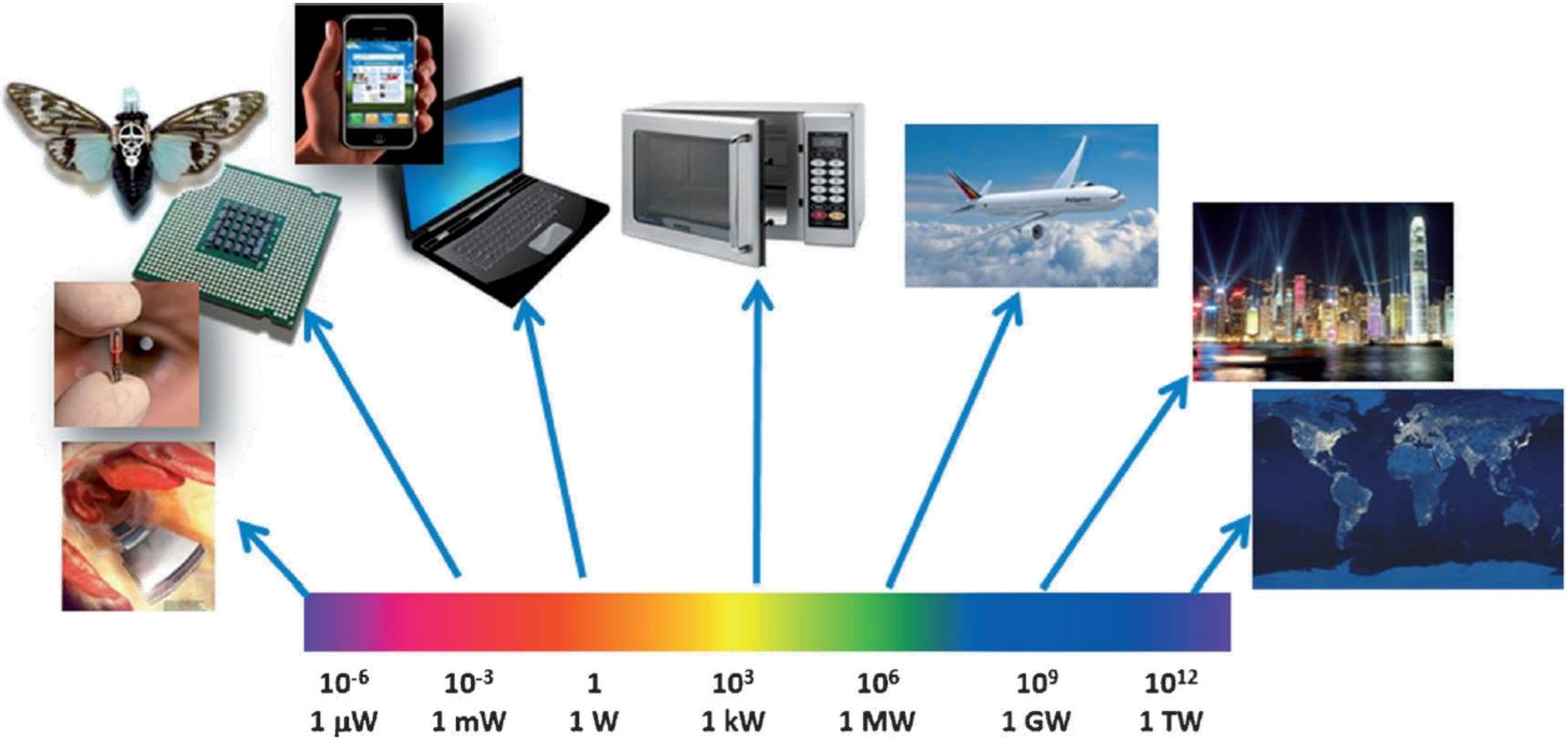


Figure 1. Power requirements for different applications: In the future there will be a great demand for mobile/implantable electronics with extremely low power consumption.

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