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Fundamentals of Piezoelectric and Ferroelectric Materials

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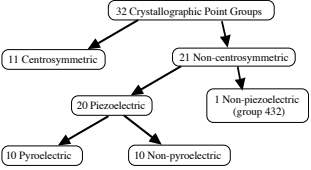


Outline

- Basic Definitions
- Constitutive Equations
- Crystal Chemistry of Important Piezoelectric Systems
 - Wurtzite Structured Compounds
 - Perovskites
 - Tungsten bronzes
 - Bismuth layer structures
 - LiNbO_3
- Domain Structures
- Low and High Field Piezoelectric Responses
- Summary

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Hierarchy of Symmetry



```

graph TD
    A[32 Crystallographic Point Groups] --> B[11 Centrosymmetric]
    A --> C[21 Non-centrosymmetric]
    C --> D[20 Piezoelectric]
    C --> E[1 Non-piezoelectric (group 432)]
    D --> F[10 Pyroelectric]
    D --> G[10 Non-pyroelectric]
  
```

Piezoelectric: Coupling between electrical and mechanical energies in a material, i.e. an applied stress leads to a change in polarization

Pyroelectric: A material with a temperature-dependent polarization
This requires a material with a unique polar axis

Ferroelectrics are a sub-group of the pyroelectric classes in which the spontaneous polarization can be reoriented between "equilibrium" states by an applied electric field
⇒ ALL FERROELECTRICS ARE BOTH PYROELECTRIC AND PIEZOELECTRIC!

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Symmetry Elements

Translation

Mirror

m

4

The slide illustrates two types of symmetry elements. The top row shows three identical portraits of a man with glasses, shifted horizontally to the right, labeled 'Translation'. The bottom row shows two identical portraits of the same man, one on the left and one on the right, separated by a vertical red line labeled 'm', labeled 'Mirror'.

Mirror/Reflection Symmetry

vertical mirror plane

horizontal mirror plane

symbol m

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The slide illustrates mirror symmetry. On the left, two hands are shown as mirror images across a vertical line labeled 'vertical mirror plane'. On the right, a character's face is shown as a mirror image across a horizontal line labeled 'horizontal mirror plane'. The symbol 'm' is written in orange below the vertical line.

Rotational Symmetry

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The slide illustrates rotational symmetry. It shows three portraits of a man with glasses. One is upright at the bottom, and two are rotated 120 degrees clockwise and counter-clockwise from the upright position, arranged around a central red triangle.

Rotational Symmetry

180° rotation

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Inversion

8

Combination Symmetry Elements

apply two symmetry operations to the same object at once

e.g. Roto-inversion axis: rotation + inversion:

$\bar{2}$ $\bar{3}$ $\bar{4}$ $\bar{6}$ $\bar{\quad}$ $\bar{\quad}$ $\bar{\quad}$ = inversion

$\bar{2}$ = m

mirror is horizontal
if rotation is about
vertical axis

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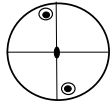
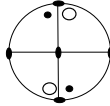
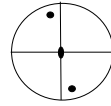
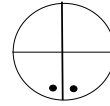
Polar Crystals

- In order to have a net polarization in the absence of an applied electric field, the crystal must be **polar**, i.e., it needs to have a vector direction unrelated by symmetry to any other direction
- Built-in, spontaneous polarization is typically temperature dependent, yielding **pyroelectricity**

$$\Delta P_i = \pi_i \Delta T$$

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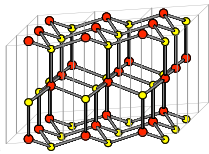
Stereographic Projections

<p>2/m</p> 	<p>222</p> 	<p>2</p> 	<p>m</p> 
<p>Every dipole cancelled by equal and opposite Non-polar No piezoelectricity or pyroelectricity</p>	<p>No net P_s Not Pyroelectric P can be generated under stress, therefore this point group is potentially piezoelectric</p>	<p>Net dipole is possible Pyroelectric and piezoelectric net $P_s \parallel 2$</p>	<p>Net dipole is possible Pyroelectric and piezoelectric net P_s in mirror plane</p>

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ZnO

Pyroelectrics



Pyroelectricity due to:
Primary: Thermal displacement of O relative to Zn
Secondary: Thermal expansion and piezoelectricity
 $\pi_3 = -9.4 \mu\text{C/m}^2 \text{ K}$

ZnO is polar, but not ferroelectric

$$\text{Polarization} = \frac{-(16z - 6)q}{\sqrt{3}a^2}$$

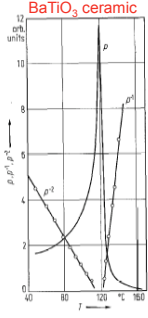
First approximation to calculation π_3 :
 Zn - O tetrahedra is distorted. O positioned at $(1/3, 2/3, z)$, Zn at $(1/3, 2/3, 0)$
 q = effective charge of ions
 a = lattice parameter

z moves by $\sim 0.264 \times 10^{-4} \text{ \AA/K}$

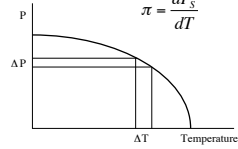
More quantitative calculations require determining the electronic redistribution as a f $\bar{1}$

Pyroelectricity in Ferroelectrics

BaTiO₃ ceramic



Landolt-Bornstein Tables



$\pi = \frac{dP_s}{dT}$

Polarization change during a second order ferroelectric transition

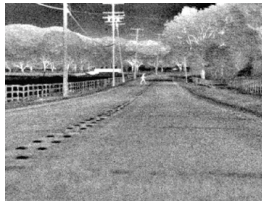
- Pyroelectric current appears as ferroelectric is heated
- Can develop large pyroelectric coefficients near phase transition temperatures
- Typically, full polarization change is not used due to depoling

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Pyroelectric Detectors

Uses

- Intruder alarms
- Thermal imaging
- Gas detection
- Heat source detection for air conditioning



Advantages to film-based devices

- Low heat capacity (enabling high frequency imaging)
- Integration with on-chip electronics possible
- Uncooled detection is possible

Thermal image courtesy of A. Amin and H. Beratan, TI

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The Constitutive Equations

- In a 1D model of piezoelectric material, the *electrical polarization* caused by strain consequent upon an applied stress can be expressed as

$$P = eS$$

S = strain (dimensionless)
 e = piezoelectric stress constant (C/m²)
- For a conventional dielectric

$$D = \epsilon E$$

ϵ = permittivity (F/m = CV⁻¹ m⁻¹)
 D = electric displacement (C/m²)
 E = electric field (V/m¹)

Piezoelectricity

The figure illustrates piezoelectricity through several diagrams. At the top left, a hysteresis loop plots polarization P_k against electric field E , showing a 'VIRGIN CURVE' and a remanent polarization P_r . To its right, a graph shows the piezoelectric coefficient S_3 versus electric field E . Below these are two piezoelectric crystal blocks: one with $V=0$ and $V=V$ applied, and another with $V=0$ and $V=V$ applied. At the bottom left, the 'Direct Effect' is shown as a piezoelectric crystal under stress X generating a charge Q , with the equation $P_i = d_{ijk} T_{jk}$. At the bottom right, the 'Converse Effect' is shown as a piezoelectric crystal under an electric field E generating a strain S , with the equation $S_{jk} = d_{ijk} E_i$. The source is cited as Randall et al., in *Piezoelectric Single Crystals* (2004).

- For a piezoelectric material

$$D = \epsilon^s E + P \quad \epsilon^s = \text{permittivity at constant strain}$$

$$= \epsilon^s E + eS$$
- It can also be shown (for a piezoelectric material) that

$$T = c^E S - eE \quad c^E = \text{elastic stiffness at constant } E$$
- Together, the expressions for D and T unambiguously relate the electrical and mechanical properties and are known as *constitutive relations*
 - The constitutive relations can also be expressed by three other pairs of equations, and in three dimensions

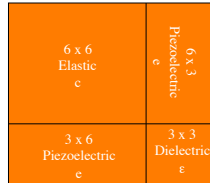
Reduced Notation

- Material properties such as stiffness, $c \equiv c_{ijkl}$ express relationships between second rank tensors such as stress, $T \equiv T_{ij}$, and strain, $S \equiv S_{kl}$, in 3D
- Generally this requires four subscript indices, i, j, k and l
- A reduced ("engineering") notation is often used

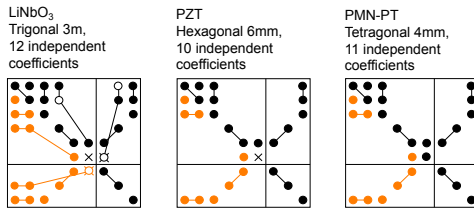
$ij, kl:$	11	22	33	23 = 32	31 = 13	12 = 21
	↓	↓	↓	↓	↓	↓
$i, J:$	1	2	3	4	5	6
- The indices $i, J = 1, 2$ and 3 represent primary directions (i.e. compression coefficients) and the indices $i, J = 4, 5$ and 6 represent rotation around these (i.e. shear coefficients)

The Piezoelectric Matrix

- Piezoelectric materials are anisotropic and thus require their parameters defined in three dimensions
- This is often done using the piezoelectric (or elasto-electric) matrix
- The general matrix (relating to the triclinic I crystal structure) has 45 independent coefficients



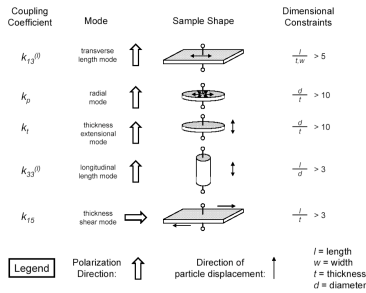
- Symetric crystal structures allow the matrix to be simplified too



● Defined by symmetry
 — Numerical equality
 ⊗ Twice negative of linked value
○ Negative of linked value $\times (c_{11} - c_{12}) / 2$

From D.A. Berlincourt, D.R. Curran and H. Jaffe "Piezoelectric and Piezomagnetic Materials" in W.P. Mason (ed.) *Physical Acoustics IA* 169 – 270 (1964)

Electromechanical Coupling Coefficients



Structural Origin of Piezoelectricity: ZnO

All Zn tetrahedra are in the same orientation

NOT

Compressive stress || c

- ZnO bond length is less compressible than O - Zn - O bond angle
- Zn moves closer to 3 basal O, that side becomes (+)

Compressive stress c

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Piezoelectricity in Quartz

Piezoelectric effect develops due to rigid rotation of tetrahedra

Piezoelectric Ceramics

- Commercially most important piezoelectric ceramics are based on $PbZr_{1-x}Ti_xO_3$ (PZT) solid solution
- Multi-axial ferroelectrics enhance poling efficiency
- Morphotropic phase boundaries used to enhance response

Temperature (°C)

Composition (mol%) $PbZrO_3$ $PbTiO_3$

25°C

Rhombo. Tetra.

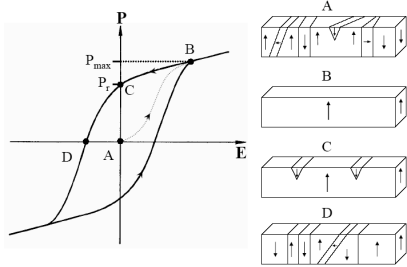
PIEZOELECTRIC CHARGE COEFFICIENT d_{31} ($10^{-12} C/m^2$)

Mole Fraction $PbTiO_3$ in PZT

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Definition of a Ferroelectric

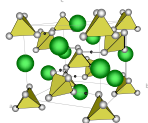
In the limit of a properly oriented single crystal, a ferroelectric phase is one in which the spontaneous polarization can be reoriented between possible equilibrium directions (determined by the crystallography of the system) by a realizable electric field.



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Order-Disorder Ferroelectrics

KDP KH_2PO_4 $T_c = 123\text{K}$
 KD₂PO₄ $T_c = 220\text{K}$



Potassium dihydrogen phosphate

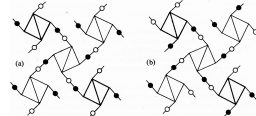
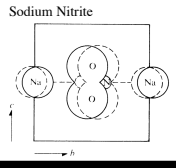
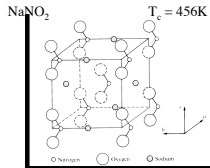


Fig. 20a and b: Ordering of hydrogen ions on the O-H-O bonds in (a) ferroelectric KH_2PO_4 and (b) antiferroelectric $\text{NH}_4\text{H}_2\text{PO}_4$. Full and empty proton sites are represented by solid and open circles, respectively.

TGS $(\text{NH}_2\text{CH}_2\text{COOH})_3 \text{H}_2\text{SO}_4$ $T_c = 322\text{K}$ Triglycine Sulphate



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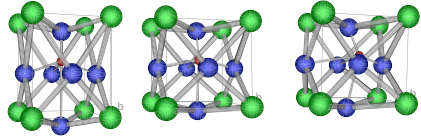
Phase Transition Sequence in BaTiO₃

BaTiO₃ Phase Transition Sequence

All displacements have been multiplied by 5

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Phase Transitions in BaTiO₃



Tetragonal
Orthorhombic
Rhombohedral

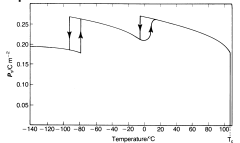
P_s develops along (referenced to the cubic prototype cell):

Tetragonal	<100>	6 equivalent directions
Orthorhombic	<110>	12 equivalent directions
Rhombohedral	<111>	8 equivalent directions

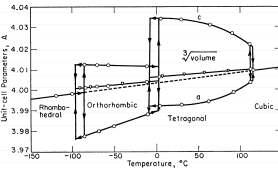
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Ferroelectric Phase Transitions (Ex. BaTiO₃)

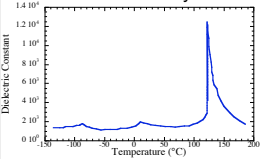
Spontaneous Polarization



Symmetry/Structure Changes



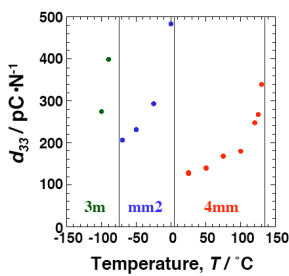
Dielectric Permittivity



$\epsilon_r = k = \text{relative dielectric permittivity}$

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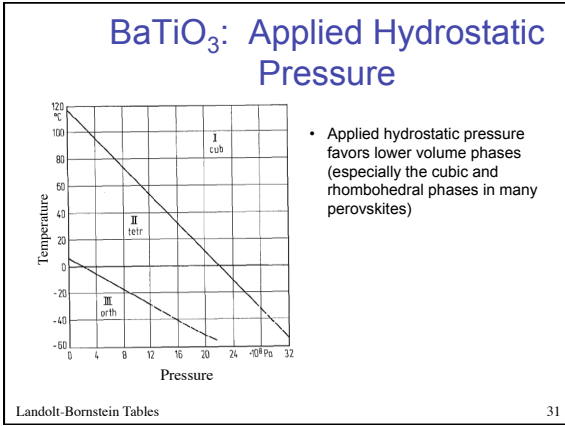
Temperature Dependence of Piezoelectric Response: BaTiO₃

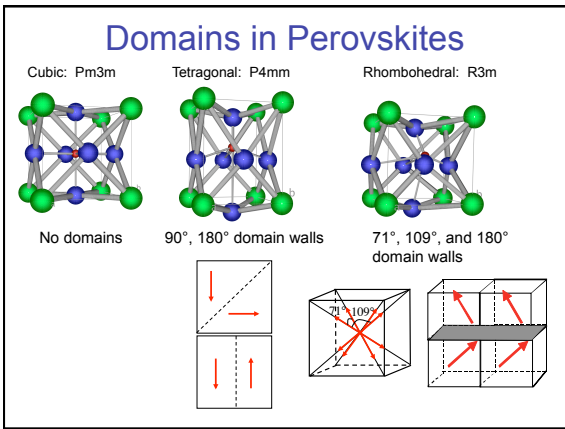


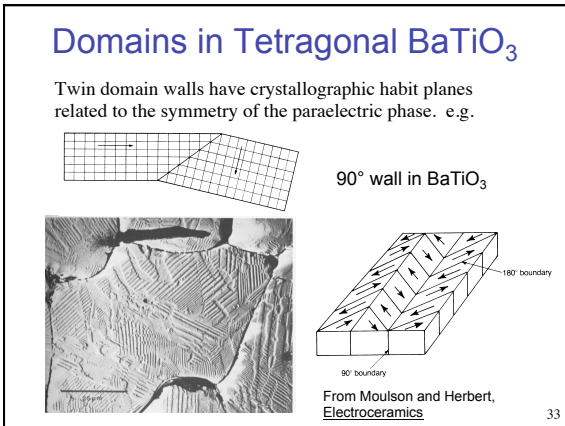
- Piezoelectric coefficients increase as transition temperature is approached (at least until samples depole)
- Large piezoelectric coefficients are available over a narrow temperature range near polymorphic phase transformations

Wada and Tsurumi, in Piezoelectric Single Crystals and Their Application

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Tilt Transitions in Perovskites

Untilted perovskite

Tilted

A site coordination

- Many perovskites show tilt transitions, some of which are non-polar. Ex. SrTiO_3 , NaNbO_3 , CaTiO_3
- Perovskite structure collapses around small A-site ions
- This often leads to antiparallel rotation motions, and no ferroelectricity (though a ferroelectric phase can often be induced by an applied electric field)

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Bi-Layer Structure Ferroelectrics

$\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$, $n = 1, 2, 3, 4, 5$

Bi_2O_3 layers interleaved with perovskite-like $\text{M}_{n-1}\text{R}_n\text{O}_{3n+1}$ layers

SBT

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$

$\text{Bi}_2\text{Ti}_2\text{O}_{12}$

P_s develops 2 components: $\sim 50 \mu\text{C}/\text{cm}^2$ along a, $\sim 4 \mu\text{C}/\text{cm}^2$ along c (\perp to layers)

$\text{SrBi}_2\text{Ta}_2\text{O}_9$

P_s develops parallel to layers (\perp c)

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LiNbO₃

LiNbO₃

- LiNbO₃ has $T_c \sim 1170^\circ\text{C}$
- Polarization develops along c axis (180° domain walls only)
- An important material for electrooptics, and high frequency or high temperatures transducers

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Small Signal Dielectric Properties

(i) Phase Transition Behavior

(a) BaTiO₃ is first order: $\epsilon' = \frac{C}{T-\theta} - 1.8 \times 10^5 \text{ } ^\circ\text{C}$

(b) LiTaO₃ is second order: $\epsilon' = \frac{C}{T-T_C} - 1.6 \times 10^5 \text{ } ^\circ\text{C}$

(c) In order-disorder ferroelectrics, e.g. TGS, KDP; $C \sim 10^3 \text{ } ^\circ\text{C}$

(d) Often the dielectric a.c. measurements are adiabatic in the presence of a polarization. Only in the centrosymmetric phase are the dielectric constants under isothermal and adiabatic conditions equivalent.

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(ii) Piezoelectric and Elastic Clamping

If material is not free to deform, its polarizability changes relative to free state

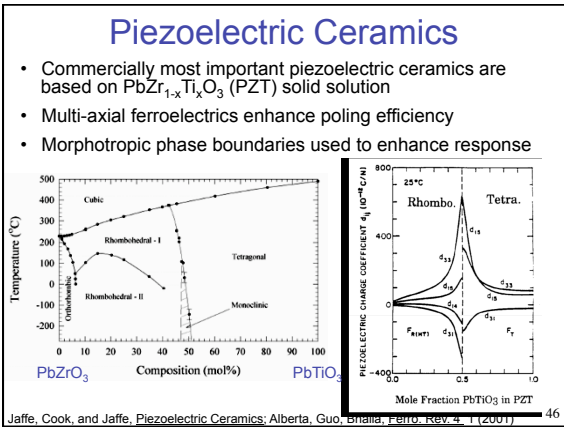
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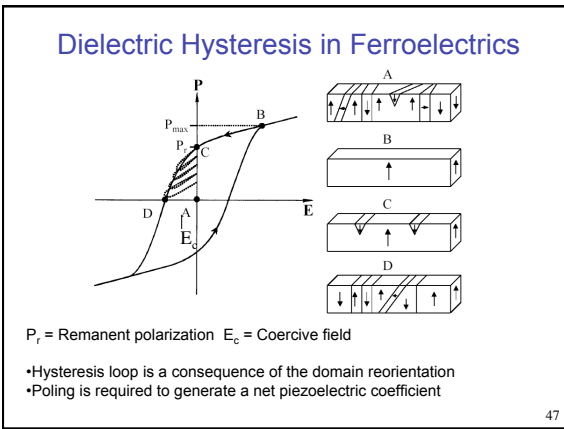


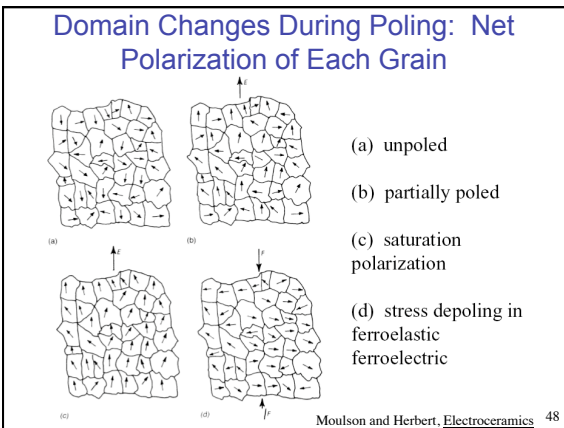
X-ray Measurements of Grain-grain Coupling

Pramanick, *J. Am. Ceram. Soc.* 94 (2011)









Hard and Soft PZT Ceramics

Property	Undoped PZT 52/48	Hard PZT - 4	Soft PZT - 5
T_c	386°C	328°C	365°C
ϵ_r (1 kHz)	730	1300	1700
$\tan \delta$ (1 kHz)	0.004	0.004	0.02
d_{33} (pC/N)	220	289	374
d_{31} (pC/N)	-93	-123	-171
d_{15} (pC/N)	494	496	584
k_p	0.52	0.58	0.60
k_{33}	0.67	0.70	0.70
k_{31}	0.31	0.33	0.34
k_{15}	0.69	0.71	0.68

Piezoelectrically *soft materials* have lower T_c , e.g. PZT-5H, $T_c = 200^\circ\text{C}$, are easy to pole and depole, and typically have larger electromechanical coefficients

Piezoelectrically *hard materials* have higher T_c , e.g. PZT-4 or PZT-8 $T_c = 350^\circ\text{C}$, are difficult to pole and depole, and typically have smaller electromechanical coefficients

From Jaffe, Cook, and Jaffe, Piezoelectric Ceramics

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Aliovalent Dopants

Doping can be compensated IONICALLY or ELECTRONICALLY

Ionic Compensation:

Donor Doping: $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ doped with La^{3+}

$$[\text{La}_{\text{Pb}}] = 2[\text{V}_{\text{Pb}}^{\bullet\bullet}]$$

Acceptor Doping: $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ doped with Fe^{3+}

$$2[\text{V}_{\text{O}}^{\bullet\bullet}] = [\text{Fe}_{\text{Ti}}]$$

Electronic Compensation

Donor Doping: BaTiO_3 doped with La^{3+}

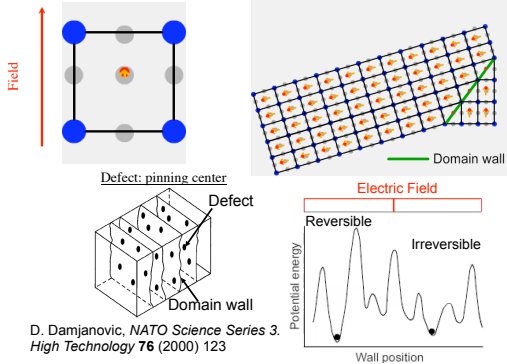
$$[\text{La}_{\text{Ba}}] = n \quad \text{a free electron!}$$

- Reorientation of defect dipoles distinguishes soft and hard PZT
- $\text{V}_{\text{O}}^{\bullet\bullet}$ are often mobile at room temperature under field. These strongly affect reliability

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Pinning Creates Hysteretic Responses

Intrinsic – deformation of lattice Extrinsic – domain wall or phase boundary motion



D. Damjanovic, NATO Science Series 3, High Technology 76 (2000) 123

Intrinsic and Extrinsic Contributions

- Intrinsic contribution: response from single domain**
- Extrinsic Contribution: response from domain wall motion and defects**
- Domain wall motion contributes to about 50% of the dielectric and piezoelectric response in PZT ceramics**

Q. M. Zhang et al., J. Appl. Phys., 75, 454(1994)
D. Damjanovic et al., Proc. IEEE Ultrasonics Symposium, pp 251

Intrinsic Contribution

180° domain wall motion

non-180° domain wall motion

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Domain Wall Contributions to Properties (Extrinsic)

<p>Intrinsic</p> <ul style="list-style-type: none"> Response associated with appropriate averaging of single domain single crystal properties Can be predicted from thermodynamic theory 	<p>Extrinsic</p> <ul style="list-style-type: none"> Response associated with motion of domain walls or defects Donor dopants in PZT (e.g. La³⁺, Nb⁵⁺, Sb⁵⁺) enhance extrinsic contributions => soft piezoelectric materials Acceptor dopants in PZT (e.g. Fe³⁺) reduce domain mobility, => hard piezoelectric materials Extrinsic properties are thermally activated. As temperature => 0K, observed properties are due to intrinsic contribution Phenomenology: ~50% of room temperature piezoelectric response is extrinsic (Haun, Ph. D. thesis, Penn State) Hydrostatic measurements: Domain wall motion contributes ~60% of room temperature d₃₃ (Zhang et al., JAP 75 454; Zhang et al., J. Mat. Sci. 18, 968) Phase measurements: at MPB, ~19% of d₃₃ due to irreversible wall motion, ~30% at PZT 63/47 (Damjanovich et al., ISAF Proc. 1996)
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Rayleigh law

$$\epsilon' = \epsilon'_{init} + \alpha_{\epsilon}' E_{ac} \quad d'_{33} = d'_{33,init} + \alpha_d' E_{ac}$$

ϵ'_{init} is the relative dielectric constant and $d'_{33,init}$ the piezoelectric constant at zero field due to intrinsic lattice and reversible contributions.

$\alpha_{\epsilon}' E_{ac}$ is due to the irreversible displacement of the domain walls or phase boundaries under ac field drive.

Validity limits

Only at sub-switching conditions, where the density and the structure of the domain walls and phase boundaries remain unchanged with field cycling.

Sub-switching fields
1/3-1/2 of E_C

Neel L., *Cahier de Physique*, 1942, 12, 1
Damjanovic, D., Taylor, D.N., *Ferroelectrics*, 1999, 221, 137
Damjanovic, D., *Phys. Rev. B*, 1997, 55, R649

Factors Affecting Domain Wall Mobility in Ferroelectrics

Grain boundaries produce grain size dependence

Defect dipoles producing pinching $V_{Ba}^{2+}-V_o^{2-}$

Oxygen vacancy itself is not effective in pinning domain walls

High $[V_o^{2-}]$

Defect dipole in the shell produced the sublinear response. Mn_{Ti}^{3+} and $Mn_{Ti}^{2+}-V_o^{2-}$

Dielectric / electrode interface produces thickness dependence

Amplitude and Frequency Dependence

Data for PZT ceramics

Piezoelectric coefficients are complex numbers that depend on the excitation field, frequency, and time

Damjanovic et al., Sens. Act. A53 353 (1996) 56

Hysteresis and Amplitude Dependence

Rayleigh approach

$$d_{33}(\sigma_o) = d_{lin} + \alpha \sigma_o$$

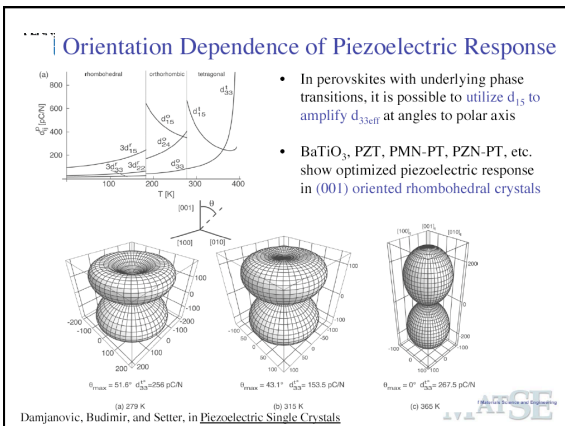
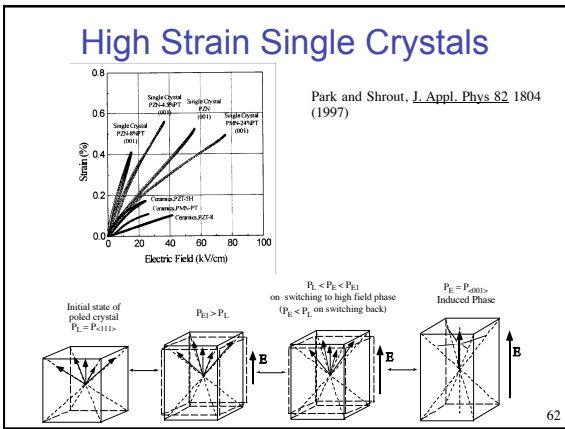
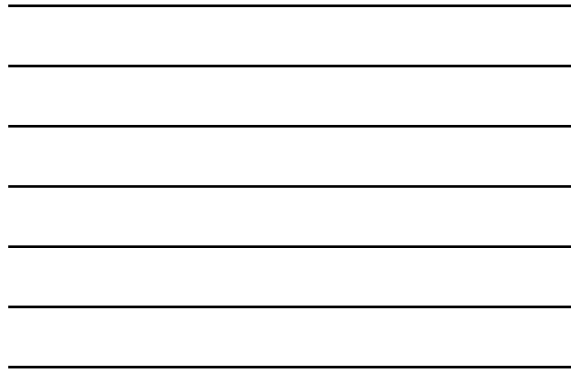
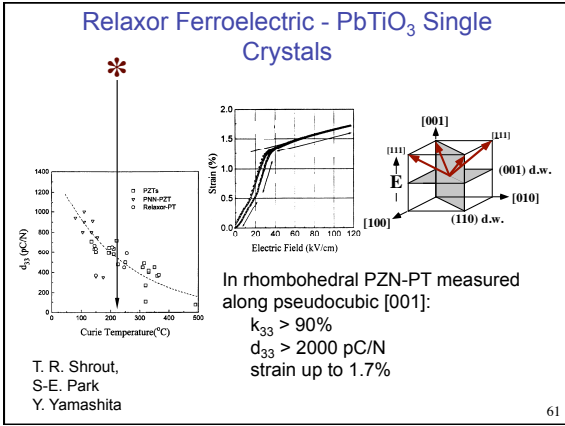
$$Q = (d_{lin} + \alpha \sigma_o) \sigma \pm \frac{\alpha}{2} (\sigma_o^2 - \sigma^2)$$

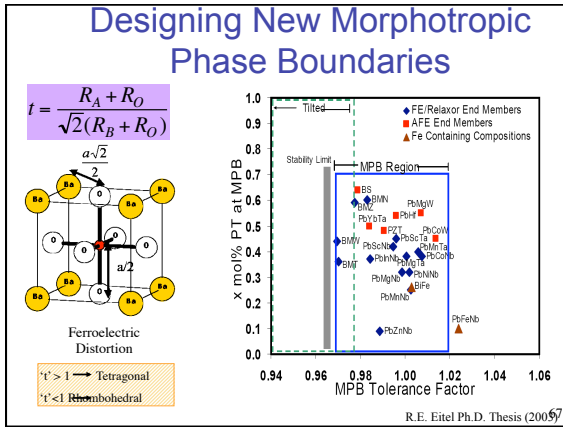
• Describes motion of domain walls in random local fields

• α quantifies irreversibility of wall motion

• Appropriate for small excitation fields

DeMartin and Damjanovic, J. Phys. C: Cond. Matter 9 (1997) 4943-4953.
D. Damjanovic, J. Appl. Phys. 82 1788 (1997)





Summary

- Symmetry hierarchy in polar materials
- Important piezoelectric materials and their structures
- Intrinsic and extrinsic contributions to the piezoelectric coefficient
