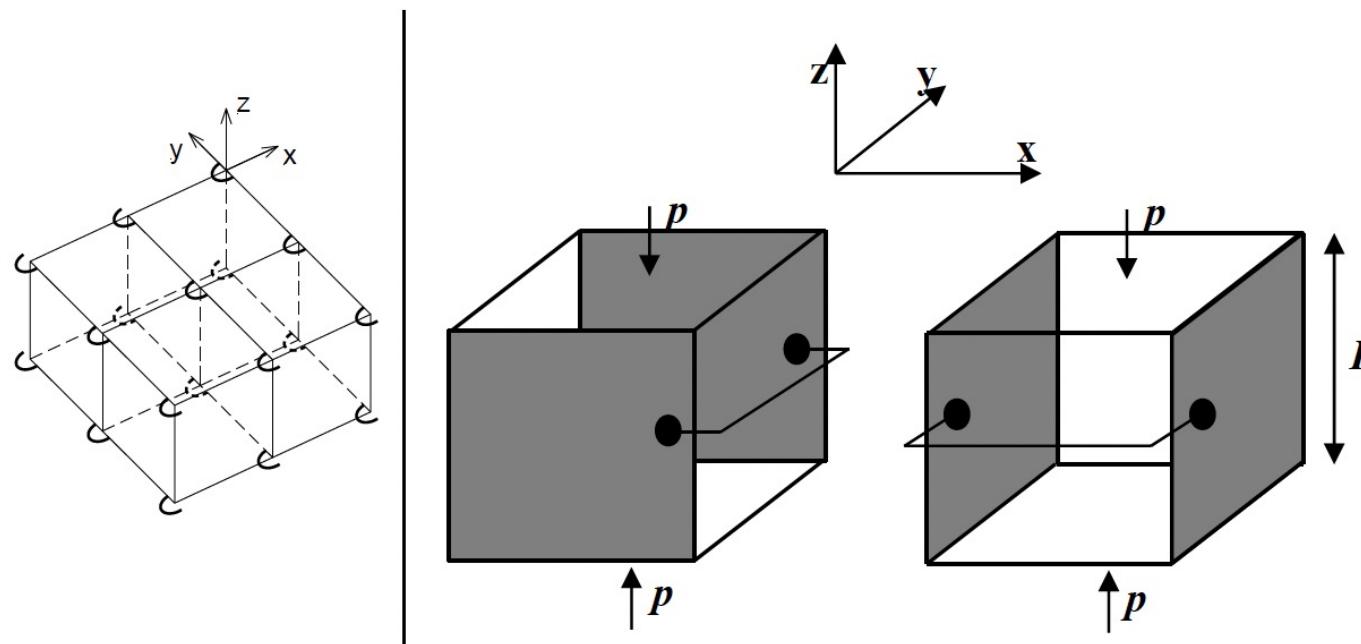


Exercise 7.2 Comments

7.2 A hypothetical material is made of molecules having the horseshoe shape placed in the sites of a cubic lattice, laying in the plane XY as shown in Fig.1 (a). To measure Young modulus, two samples are made from this material (Fig.1(b)). The experimental technique is following: the pressure p is applied on (001) faces, and the change in distance between these faces ΔL is measured in order to obtain Young modulus, the other 4 faces are kept mechanically free.

The electrode configuration is following: in sample **I**, the faces parallel to (010) are electroded and electrically connected; in sample **II**, the (100) faces are electroded and connected.

Show that the measured Young moduli will be different. In which sample the Young modulus is larger?



These two cases are different: polar axis!

Exercise 7.2 Comments

$$\begin{aligned}\sigma_1 &= \sigma_2 = \sigma_4 = \sigma_5 = \sigma_6 = 0, \\ \sigma_3 &= -p.\end{aligned}$$

The linear contraction along x_3 direction is $\frac{\Delta L}{L} = -\varepsilon_{33}$, and Young modulus can be found as:

$$Y = \frac{p}{\Delta L/L} = \frac{\sigma_3}{\varepsilon_3}.$$

Constitutive equations are:

$$\begin{aligned}D_i &= \varepsilon_0 K_{ij} E_j + d_{ij} \sigma_j, \\ \varepsilon_i &= d_{ji} E_j + s_{ij} \sigma_j.\end{aligned}$$

When, among the stress components, only $\sigma_3 \neq 0$, the equation for ε_3 is rewritten as

$$\varepsilon_3 = d_{j3} E_j + s_{3j} \sigma_j = d_{13} E_1 + d_{23} E_2 + d_{33} E_3 + s_{33} \sigma_3$$

Exercise 7.2 Comments

The piezoelectric tensor for $mm2$ symmetry, for the reference frame where the 2-fold axis is parallel to [001] direction, has the following form (see Symmetry Tables):

$$d = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}.$$

This tensor is not for the reference frame of the problem!

To make the 2-fold axis be directed along [100], one should make e.g. following transformation of the reference frame:

$$x_1 \rightarrow -x_3, \quad x_2 \rightarrow x_2, \quad x_3 \rightarrow x_1 \quad (\text{rotation by } 90^\circ \text{ with respect to [010]})$$

Then, the piezoelectric tensor transforms into:

$$d = \begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{26} \\ 0 & 0 & 0 & 0 & d_{35} & 0 \end{pmatrix}.$$

With these symmetry restrictions, $d_{23} = d_{33} = 0$, and the constitutive equation for ε_3 is rewritten as follows:

$$\varepsilon_3 = d_{13}E_1 + s_{33}\sigma_3$$

In order to obtain relationship $Y = \sigma_3/\varepsilon_3$, one has to know the value of the electric field E_1 .

Exercise 7.2 Comments

I. In sample I, where the (100) surfaces are not electroded and not connected, the induction D_1 must be zero since the surfaces cannot exchange their charges. The electric displacement D_1 is given by the equation:

$$D_1 = \varepsilon_0 K_{11} E_1 + \varepsilon_0 K_{12} E_2 + \varepsilon_0 K_{13} E_3 + d_{1n} \sigma_n$$

$d_{1n} \sigma_n = d_{13} \sigma_3$ since, among stress components, only $\sigma_3 \neq 0$. In the coordinate system of the problem, the symmetry restrictions of *mm2* group impose $K_{12} = K_{13} = 0$. Therefore,

$$D_1 = \varepsilon_0 K_{11} E_1 + d_{13} \sigma_3 = 0 \Rightarrow E_1 = -\frac{d_{13}}{\varepsilon_0 K_{11}} \sigma_3,$$

$$\varepsilon_3 = d_{13} E_1 + s_{33} \sigma_3 = \left(s_{33} - \frac{d_{13}^2}{\varepsilon_0 K_{11}} \right) \sigma_3,$$

$$Y = \frac{1}{s_{33} - \frac{d_{13}^2}{\varepsilon_0 K_{11}}}.$$

II. In sample II, the (100) surfaces are electroded and connected, so $E_1 = 0$.

$$\varepsilon_3 = s_{33} \sigma_3 \Rightarrow Y = \frac{1}{s_{33}}.$$

Since $\frac{d_{13}^2}{\varepsilon_0 K_{11}} > 0$, one can conclude that in sample I the measured Young modulus is larger.

Lecture 8 (week 8: 7-8 April 2025)

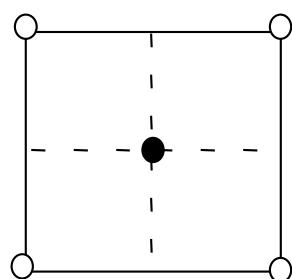
Structural phase transitions, ferroelectricity

- Structural phase transitions: ferroelectricity
- Ginzburg Landau theory – phenomenological description of ferroelectricity
- Ferroelectric domains
- ***Reminder - written test in class: 15 April***

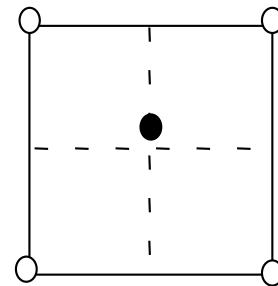
Example of structural phase transition



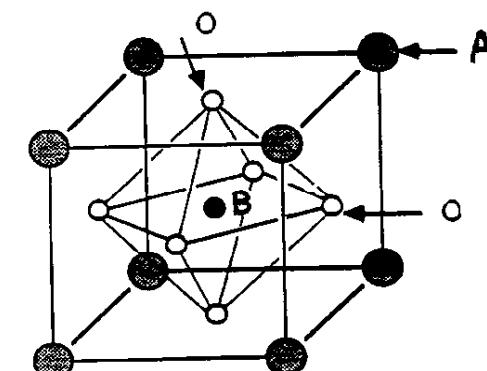
$T_c = 720 \text{ K}$



$T > T_c$



$T < T_c$



$A = \text{Pb}$
 $B = \text{Ti}$

$m\bar{3}m$

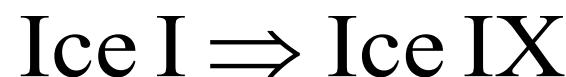
$4mm$

T_c - Transition temperature

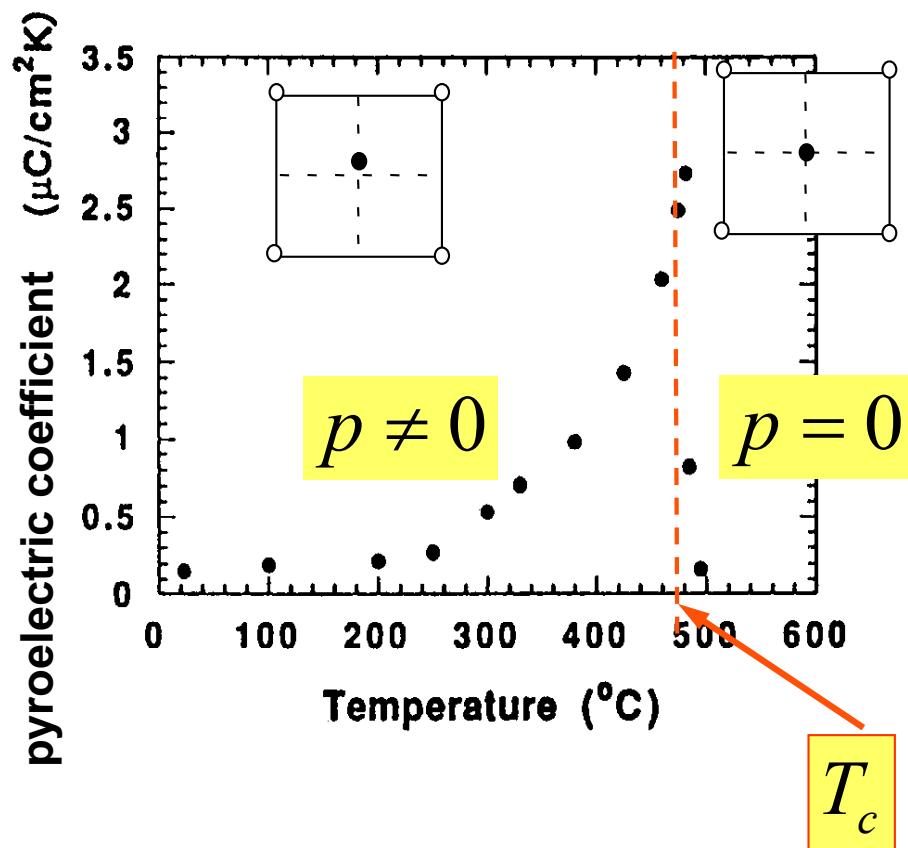
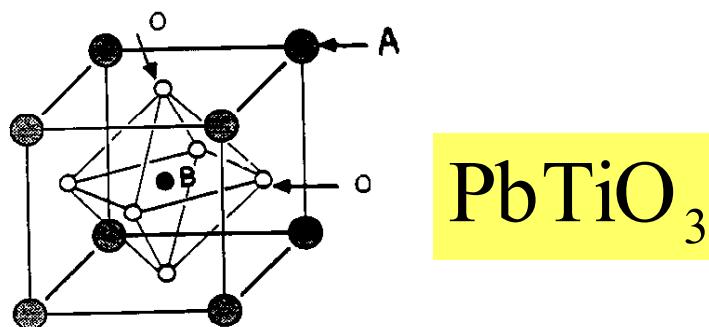
Ferroelectric phase transition

 1 (C ₁)			 1-bar (C ₁)			
 2 (C ₂)				 m (C _s)		 2/m (C _{2h})
				 mm2 (C _{2v})	 222 (D ₂)	 mmm (D _{2h})
 3 (C ₃)			 3-bar (S ₆)	 3m (C _{3v})	 3 (D ₃)	 3-bar (D _{3d})
 4 (C ₄)	 4-bar (S ₄)	 42m (D _{2d})	 4/m (C _{4h})	 4mm (C _{4v})	 422 (D ₄)	 4/mmm (D _{4h})
 6 (C ₆)	 6-bar (C _{3h})	 62m (D _{3h})	 6/m (C _{6h})	 6mm (C _{6v})	 622 (D ₆)	 6/mmm (D _{6h})
 23 (T)			 m3-bar (T _h)	 43m (T _d)	 432 (O)	 m3-bar (O _h)

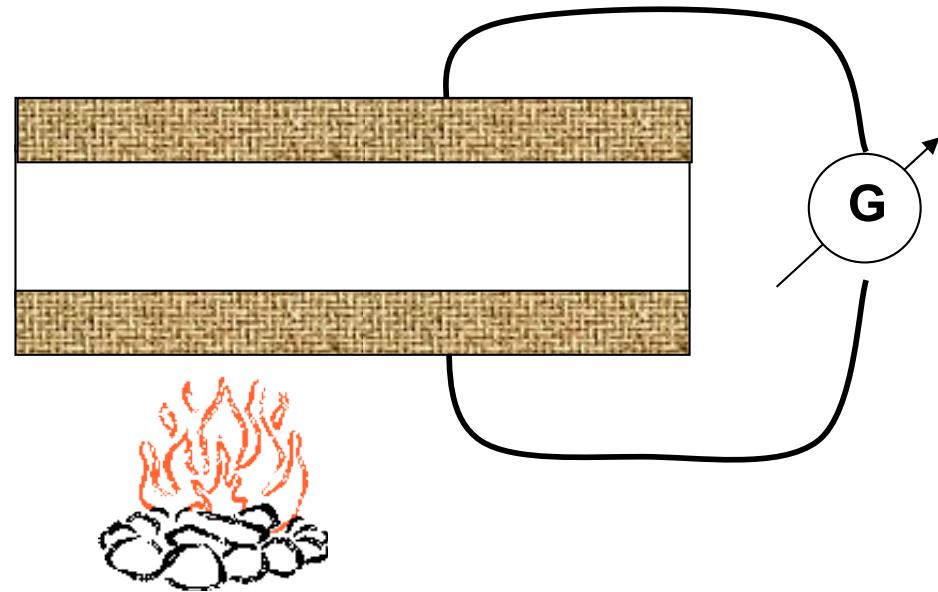
Structural transition from non-polar to a polar symmetry is called ferroelectric phase transition



Test for ferroelectric transition



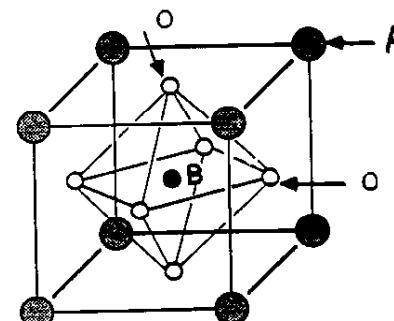
Appearance of pyroelectricity
at $T < T_c$



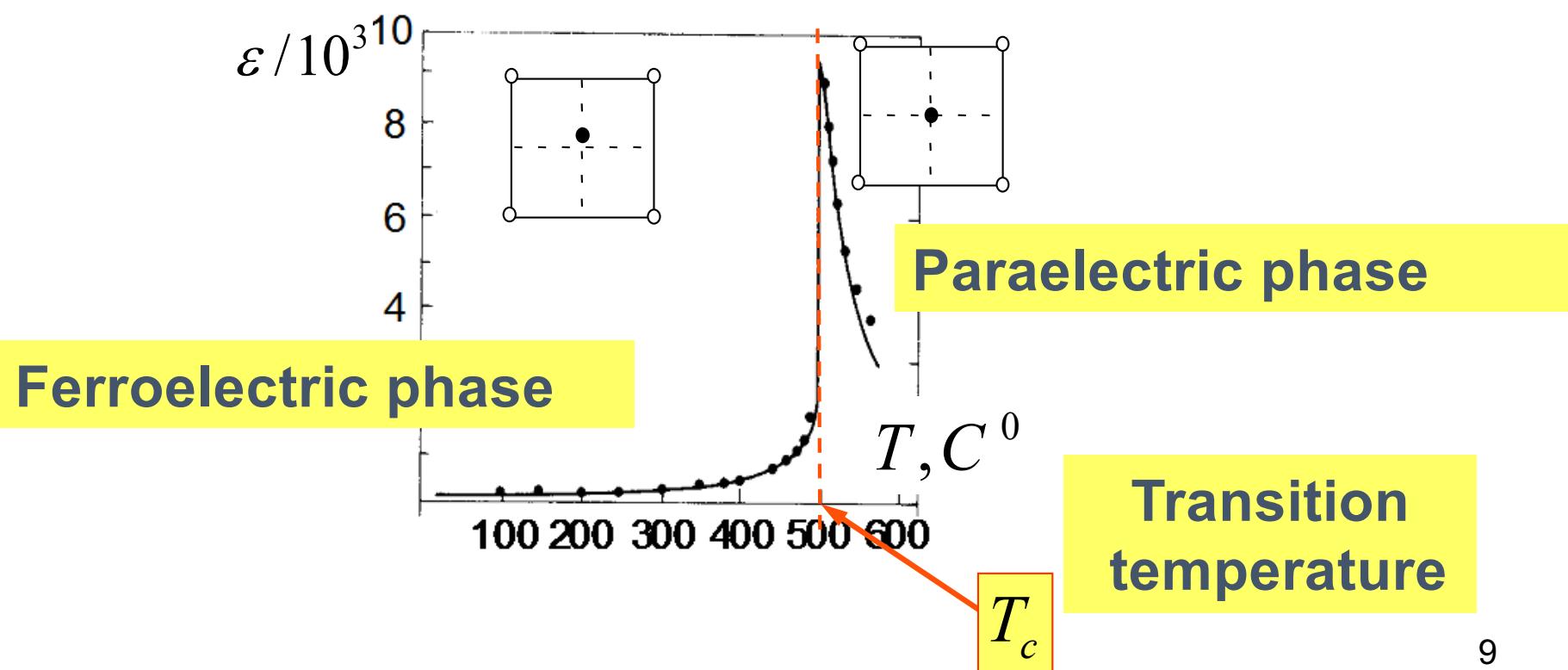
pyroelectric coefficient

$$p = \frac{\partial P}{\partial T}$$

Ferroelectric and paraelectric phases



Soft lattice at T_c

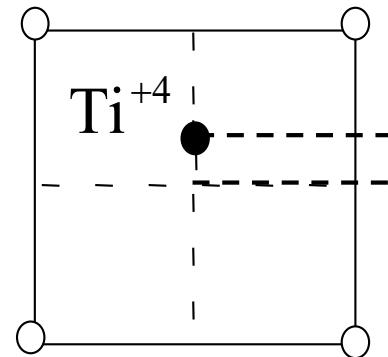
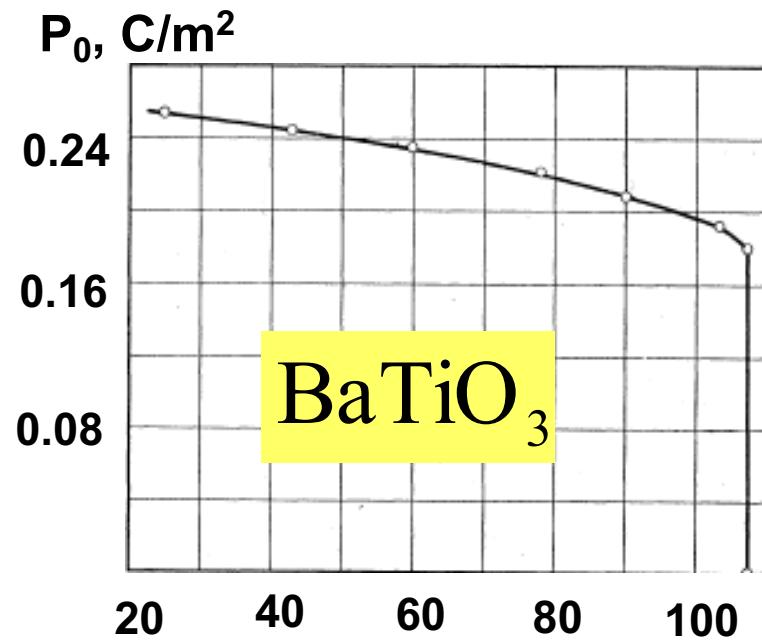
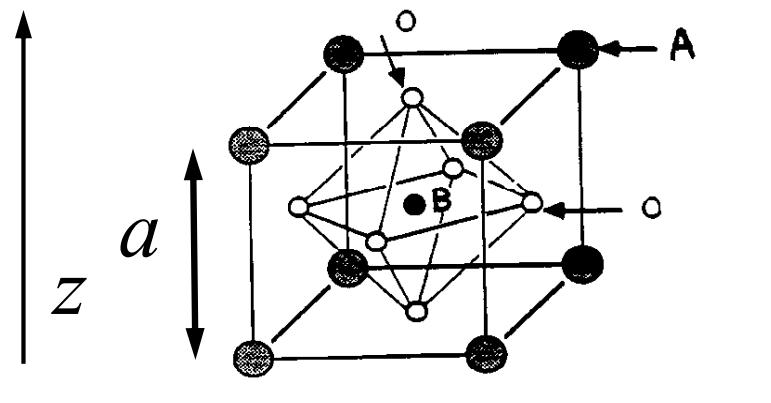


Ferroelectrics = materials exhibiting ferroelectric transitions

Key features of ferroelectrics

- 1. Spontaneous polarization (P_0)**
- 2. Ferroelectric domains**
- 3. Reorientation of P_0 with electric field**
- 4. Ferroelectric hysteresis**
- 5. Dielectric anomaly at transition temperature**
- 6. Anomalies at transition temperature of many other parameters (e.g, of pyroelectric coefficient)**

Spontaneous polarization



$$P_z \equiv P = \frac{Ze\eta}{a^3}$$

$$Z \simeq 4$$

$$T > T_c \quad T < T_c$$

$$\eta = 0 \quad \eta = \eta_0 \neq 0$$

$$P_{\text{at } E=0} = 0 \quad P_{\text{at } E=0} = P_0 \neq 0$$

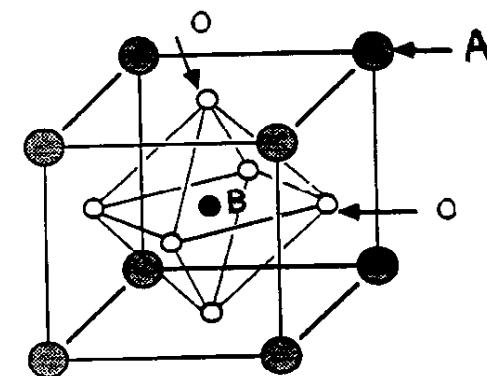
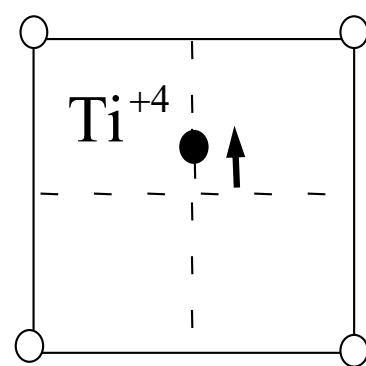
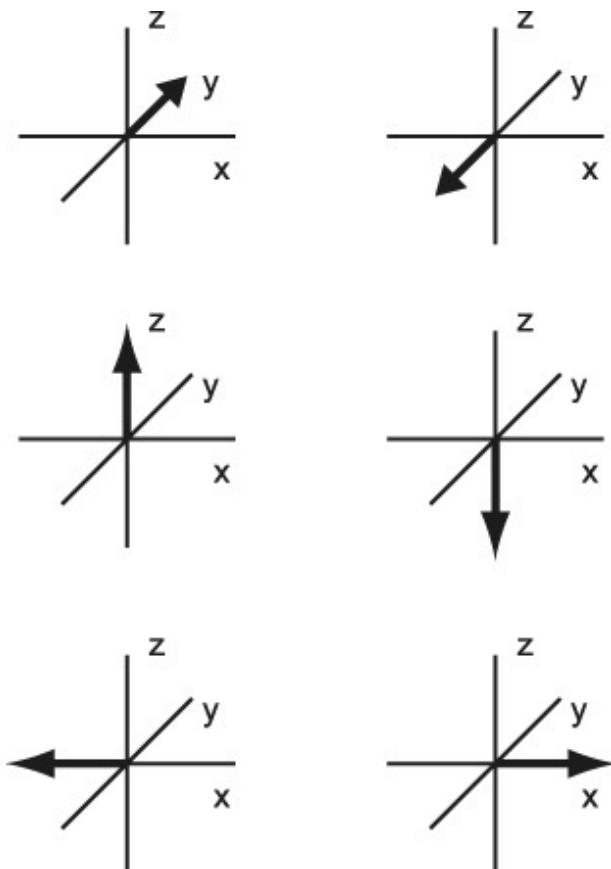
spontaneous polarization

$$P_0 = \frac{Ze\eta_0}{a^3}$$

Domain states

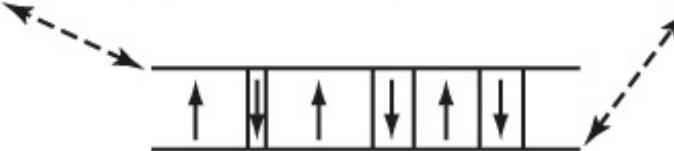
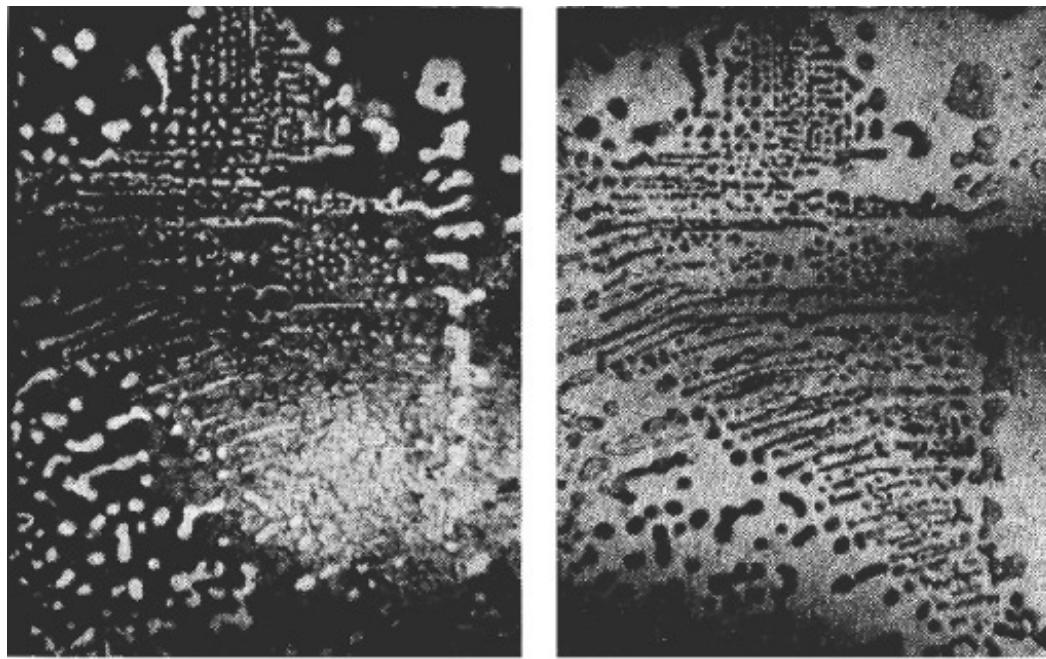
$m\bar{3}m$ → $4mm$

6 possible orientations of spontaneous polarization



6 domain states

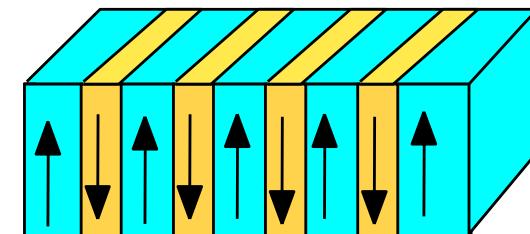
Domain - area of the sample occupied by one domain state



2-domain-state domain pattern

$m\bar{3}m$ \rightarrow $4mm$

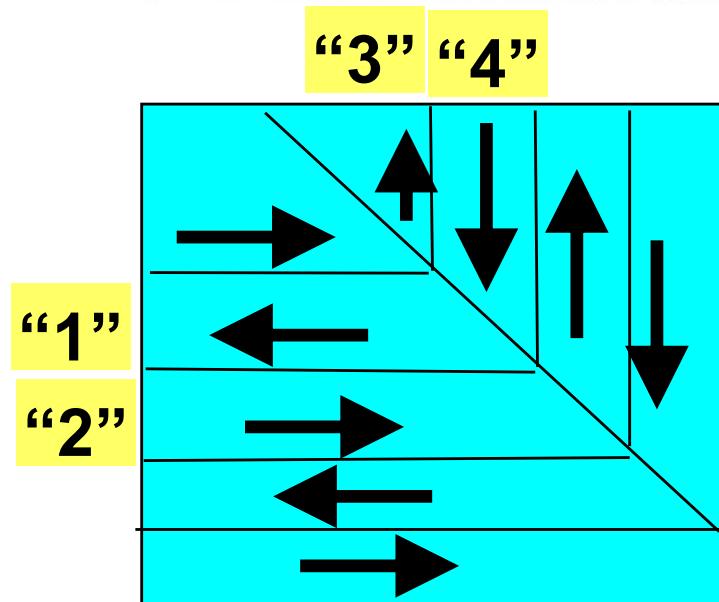
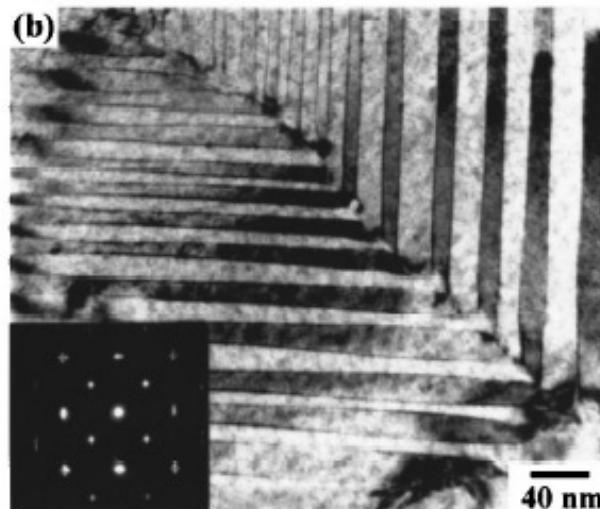
Schematic



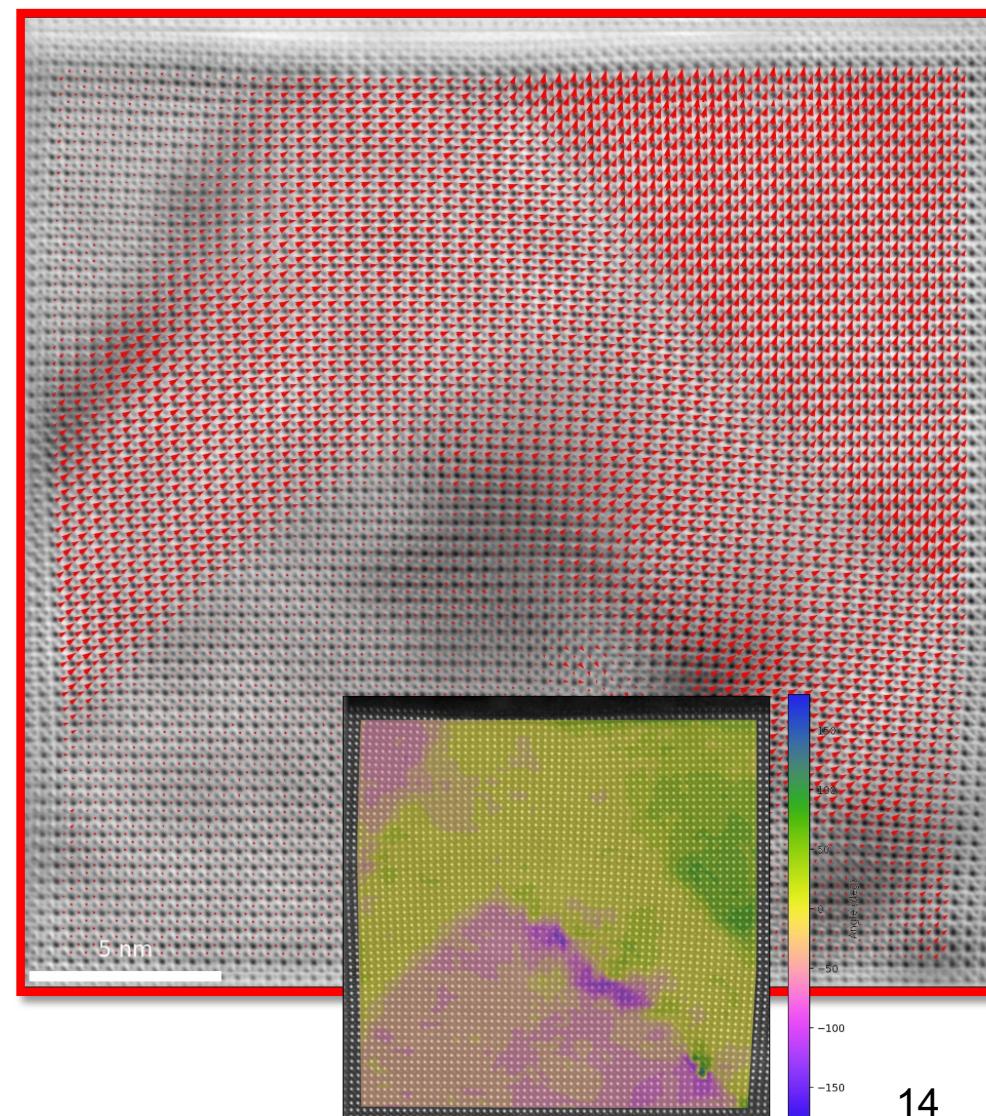
Domain - region occupied by one polarization state

$$m\bar{3}m \rightarrow 4mm$$

PbTiO_3 film



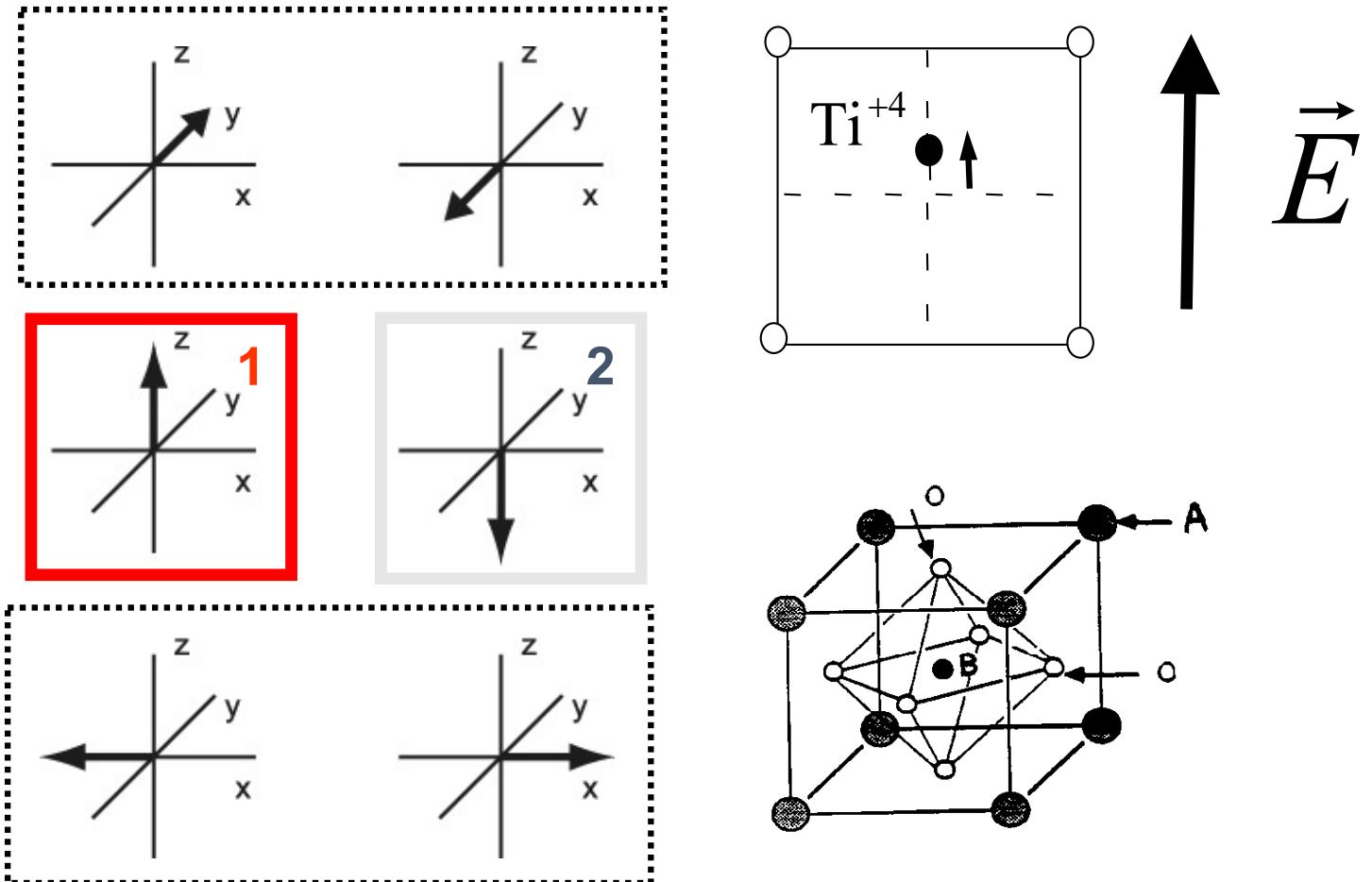
High resolution STEM



Reorientation of spontaneous polarization by electric field

1- lowest energy

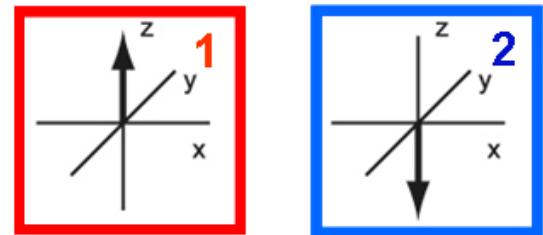
2- highest energy



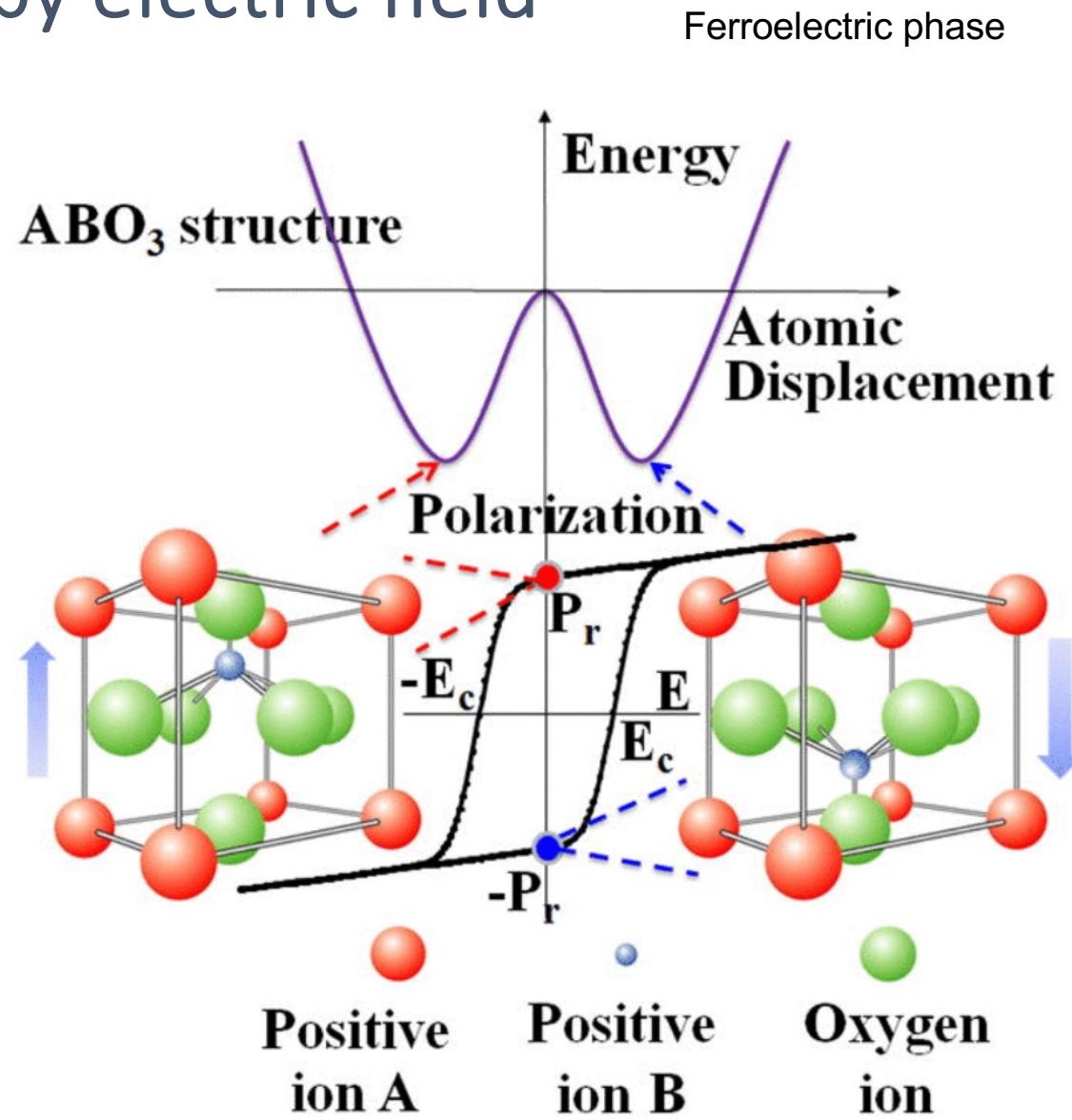
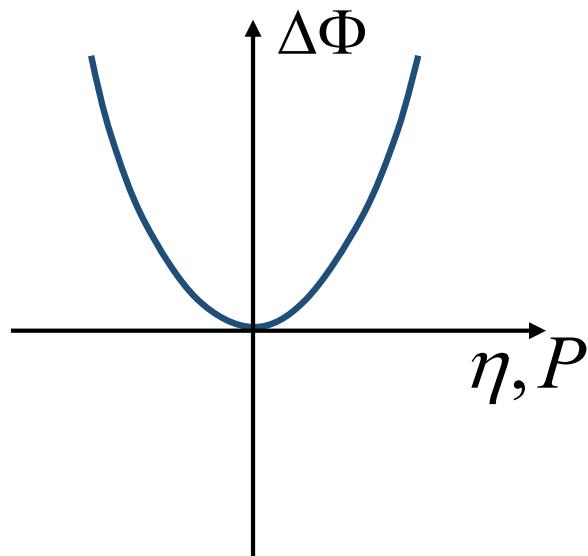
By application of electric field ferroelectric can be brought to one specified domain state!

Ferroelectric will remember this state when the electric field is switched off!

Reorientation of spontaneous polarization by electric field

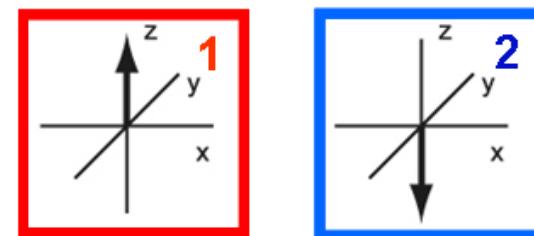


Paraelectric phase

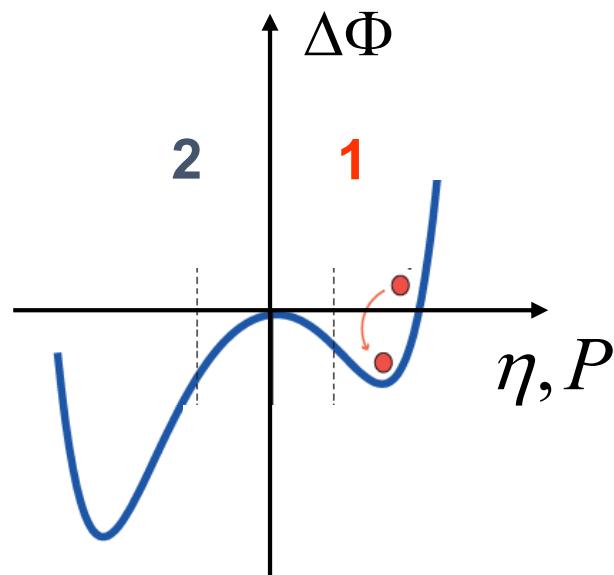


$\Delta\Phi$ - energy (free energy) as function of Ti displacement (polarization)

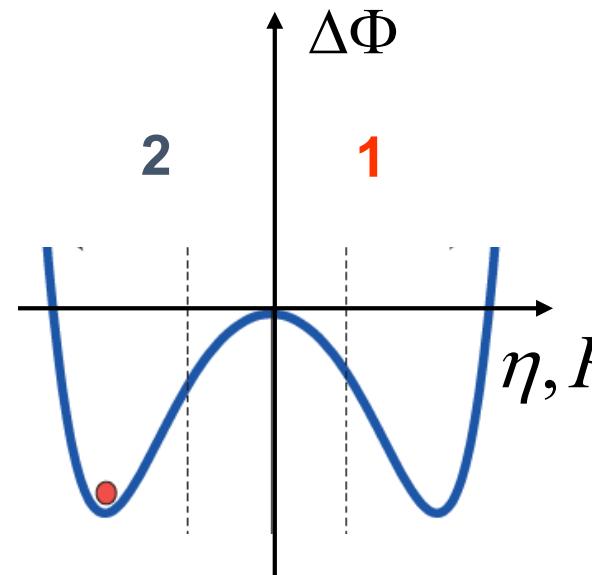
Reorientation of spontaneous polarization by electric field



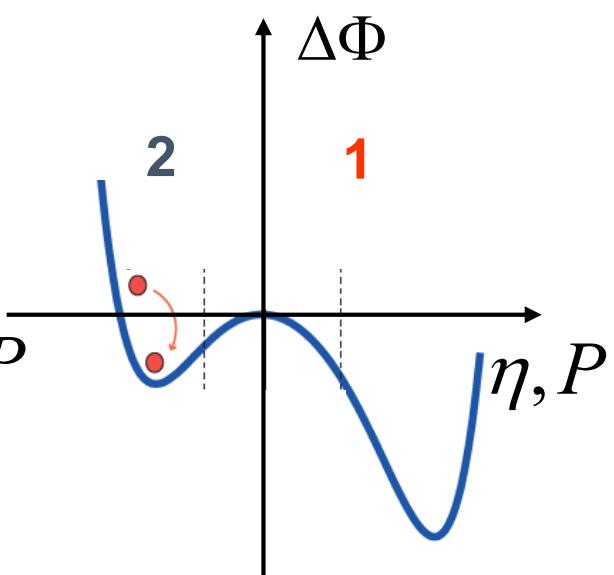
$E > 0$



$E = 0$



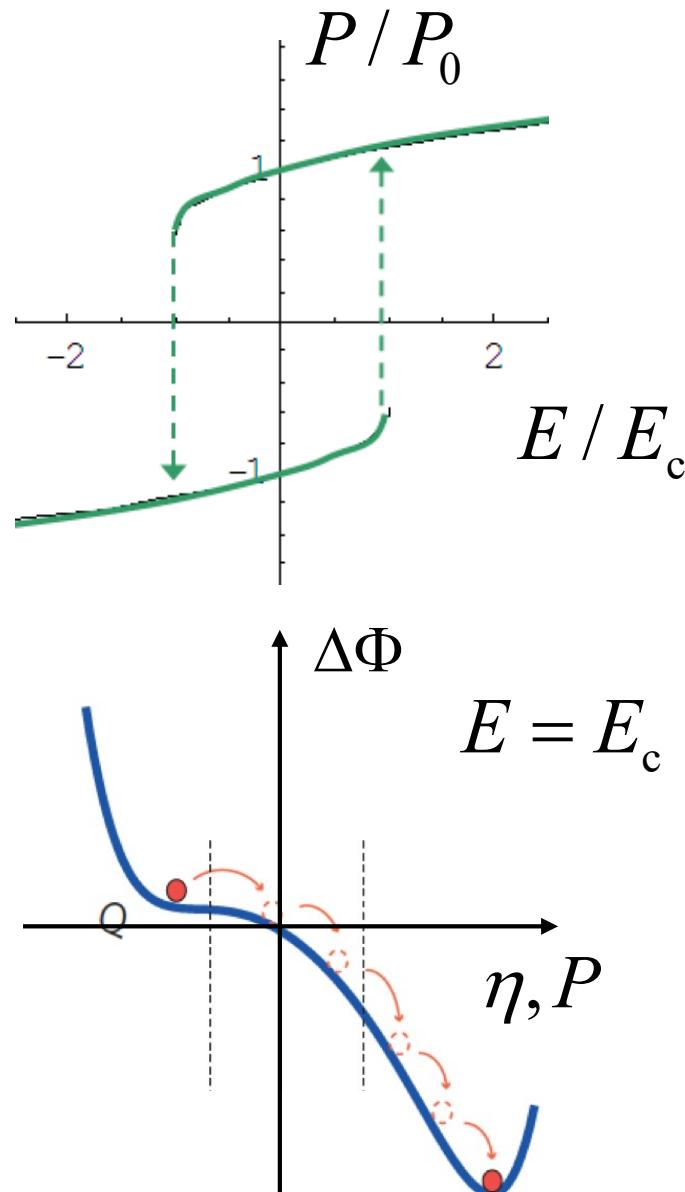
$E < 0$



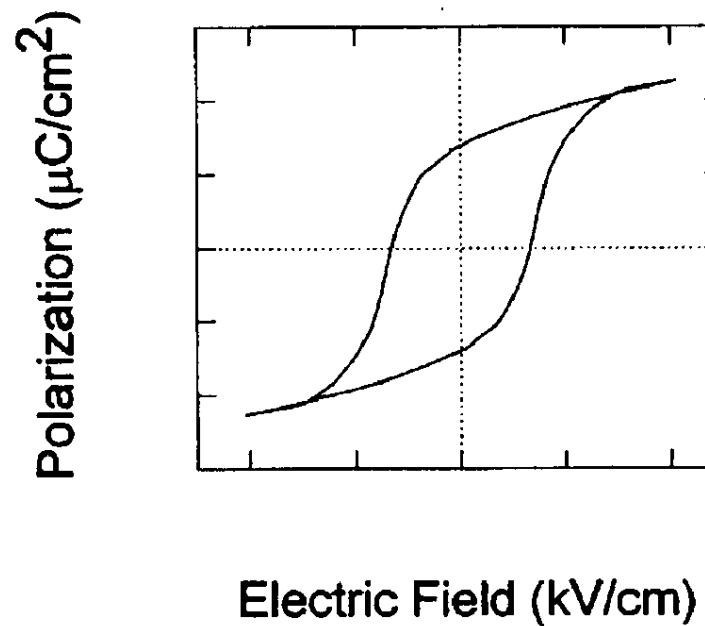
$\Delta\Phi$ - energy (free energy) as function of Ti displacement (polarization)

Ferroelectric hysteresis

Ideal hysteresis



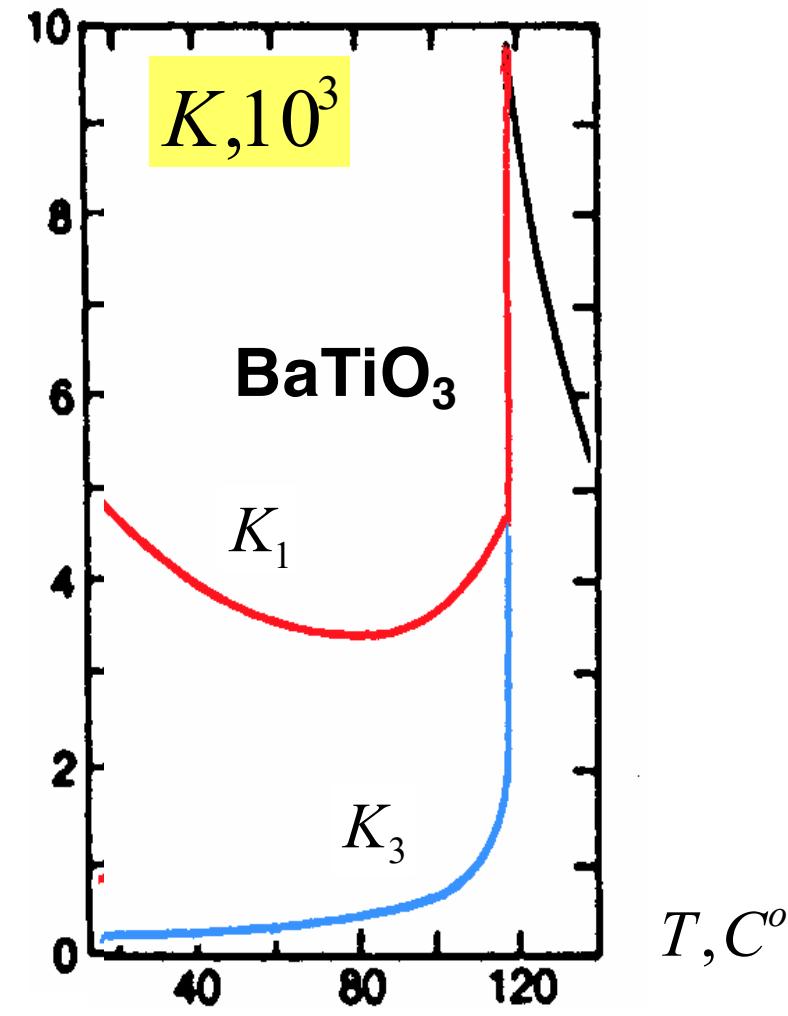
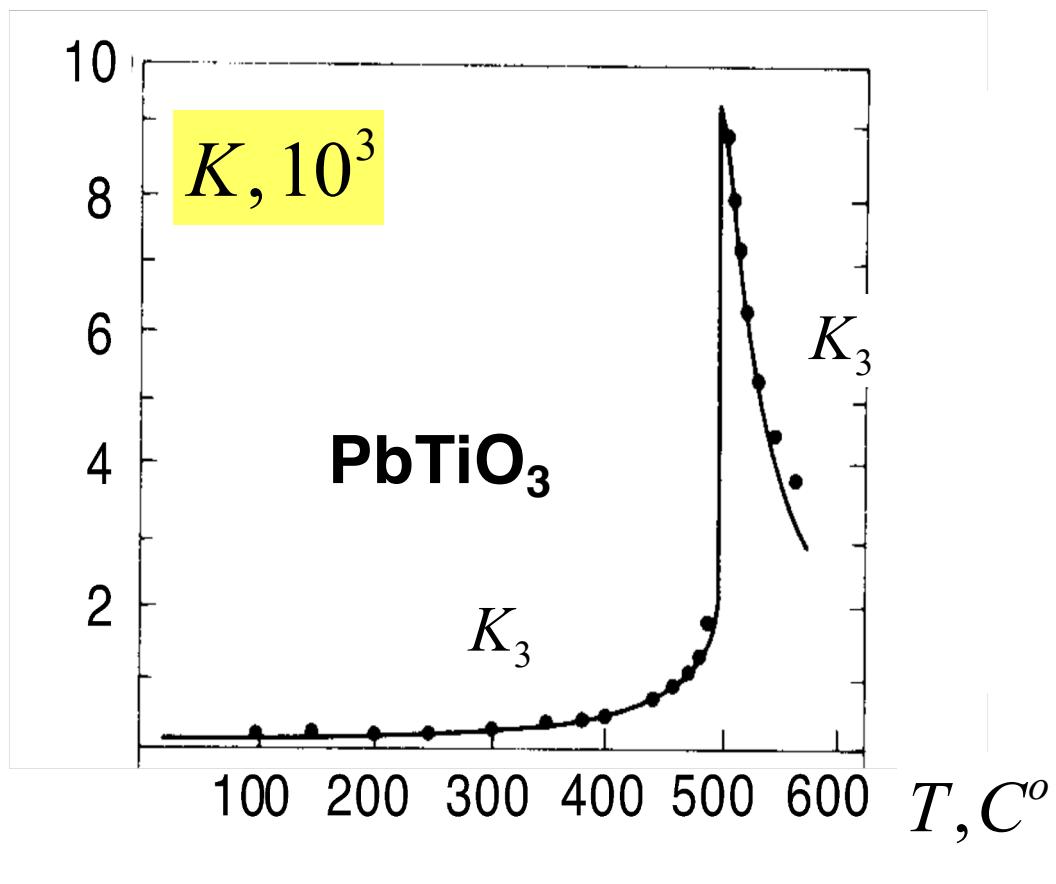
Real hysteresis



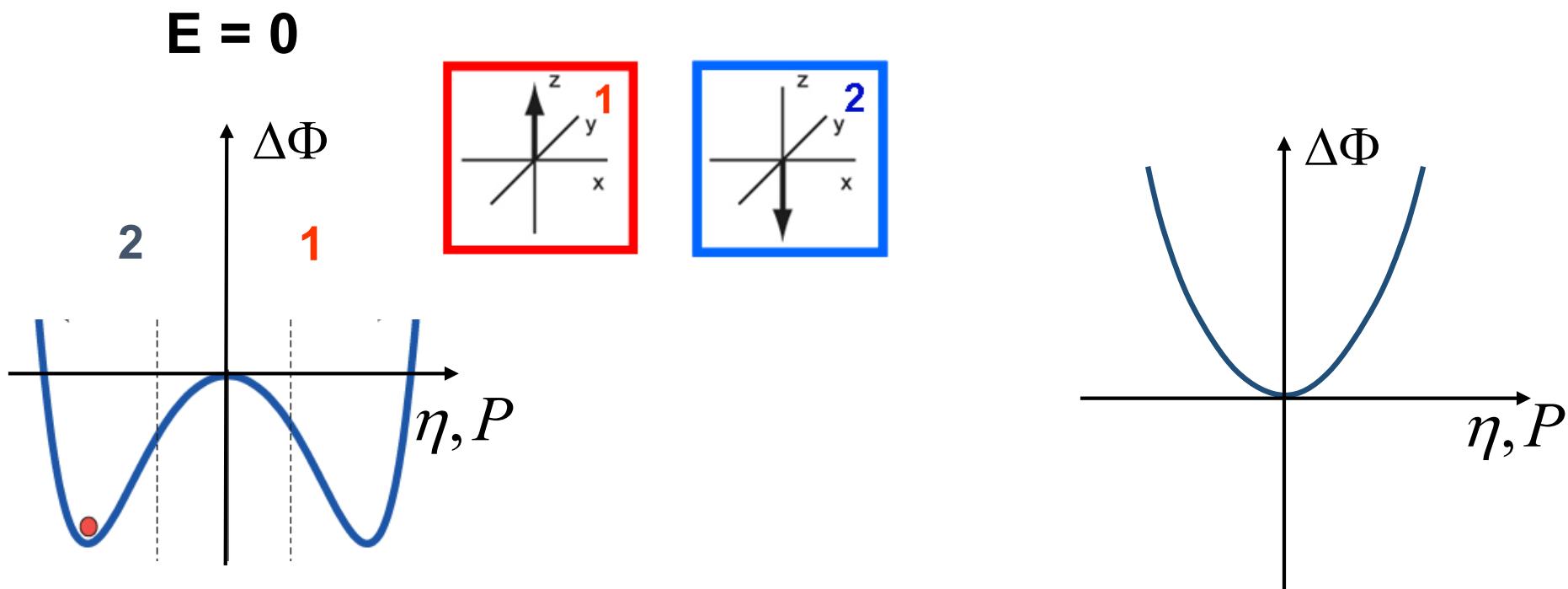
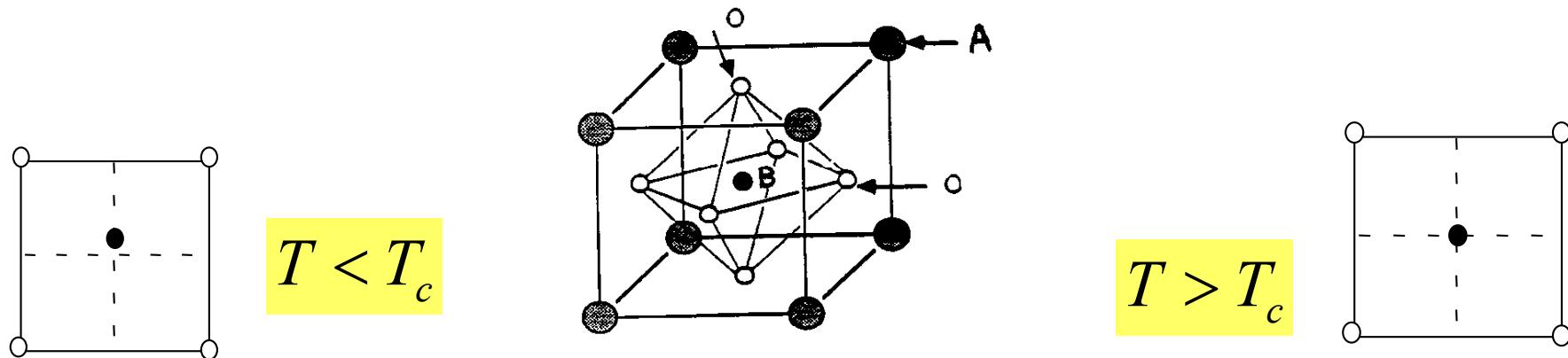
E_c **Coercive field**

$$P(E = E_c) = 0$$

Dielectric anomaly at ferroelectric phase transition



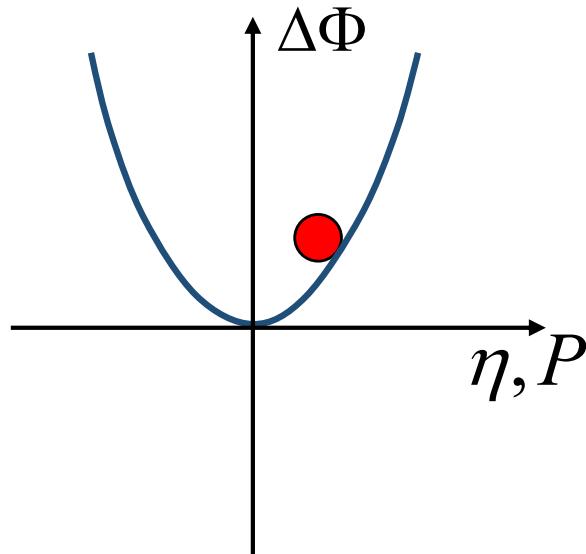
Dielectric anomaly at ferroelectric phase transition



$\Delta\Phi$ - energy (free energy) as function of Ti displacement (polarization)

Dielectric response

$\Delta\Phi$ - energy (free energy) as function of Ti displacement (polarization)



Equation of equilibrium at applied field E

$$eZE = G\eta$$

Coulomb force

restoring force

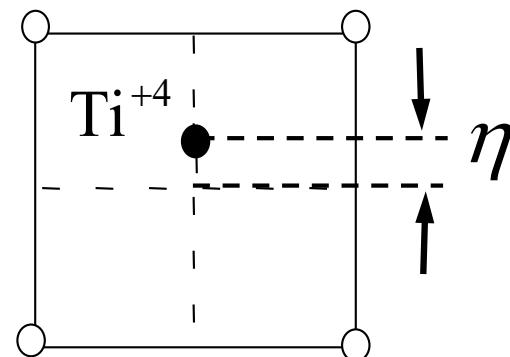
$$\Delta\Phi = \frac{G}{2}\eta^2$$

$$P_z \equiv P = \frac{Ze\eta}{a^3}$$

$$\eta = \frac{eZE}{G}$$

$$P = \frac{Z^2 e^2}{a^3 G} E$$

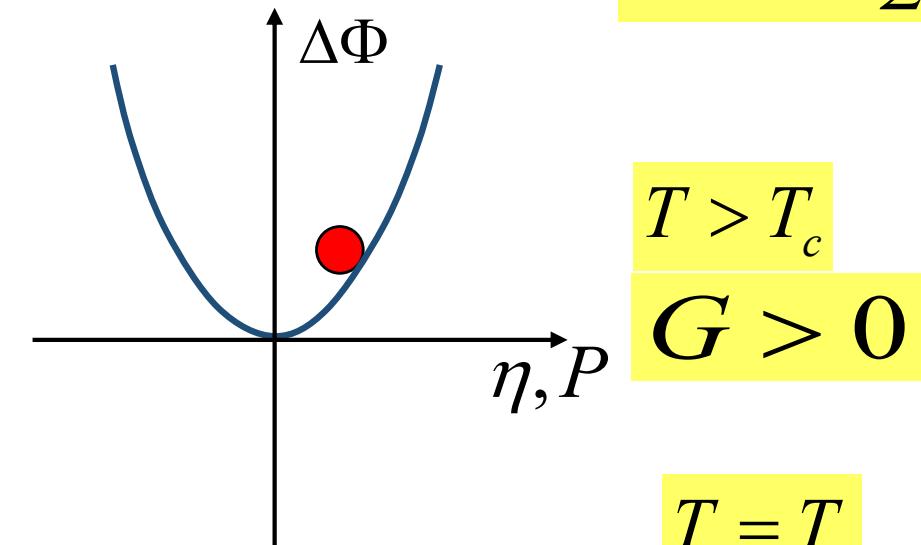
$$P = \frac{Ze\eta}{a^3}$$



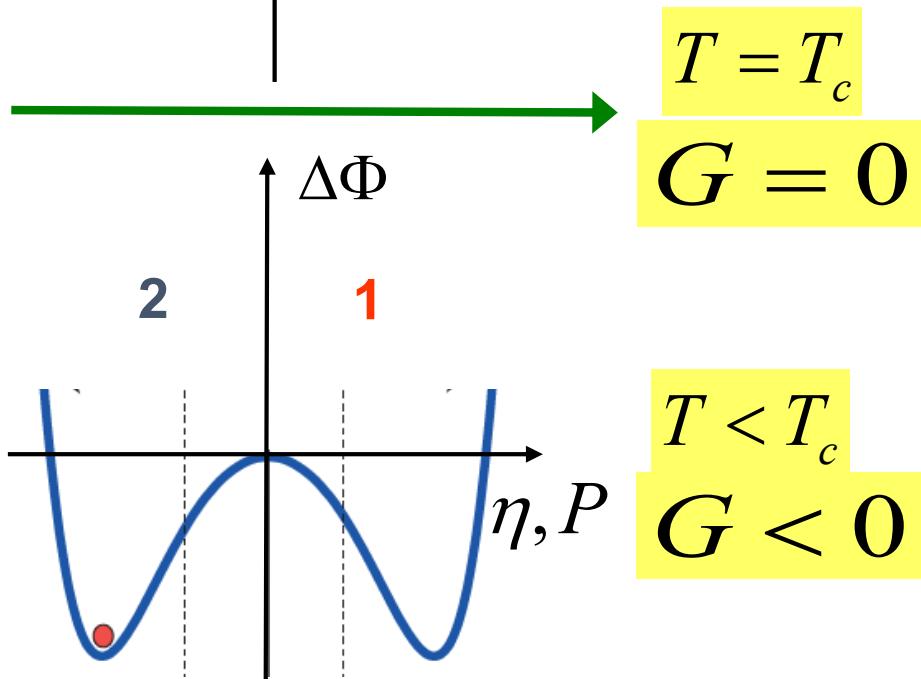
$$\chi = \frac{\partial P}{\partial E} = \frac{Z^2 e^2}{a^3 G}$$

Anomaly of dielectric response

$$\Delta\Phi = \frac{G}{2} \eta^2$$



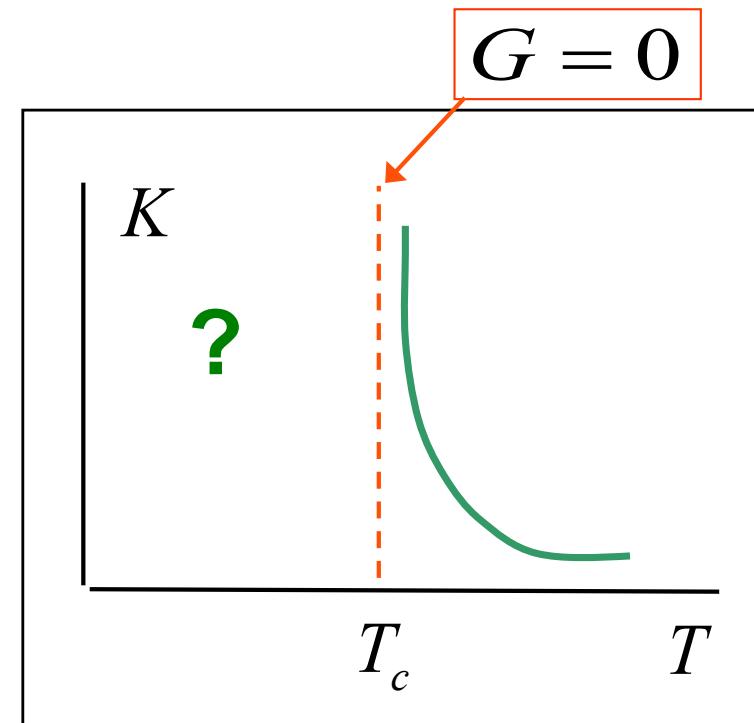
$$\begin{aligned} T &> T_c \\ G &> 0 \end{aligned}$$



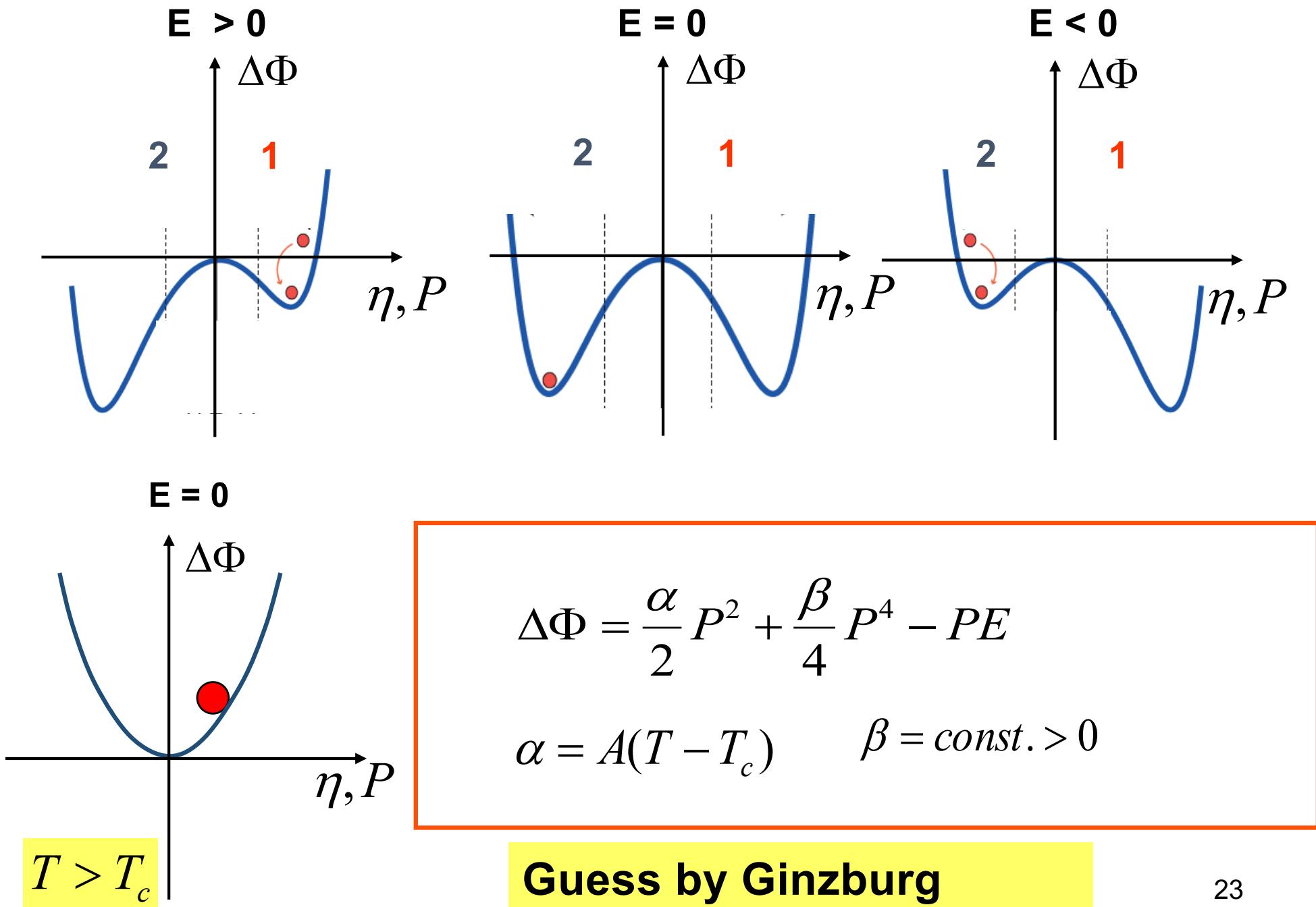
$$\begin{aligned} T &= T_c \\ G &= 0 \end{aligned}$$

$$\begin{aligned} T &< T_c \\ G &< 0 \end{aligned}$$

$$K = 1 + \frac{\chi}{\epsilon_0} = 1 + \frac{Z^2 e^2}{\epsilon_0 a^3 G}$$



Ginzburg-Landau theory



Ginzburg-Landau theory

$$\Delta\Phi = \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 - PE$$

$$\alpha = A(T - T_c) \quad \beta = \text{const.} > 0$$

$$\frac{\partial\Delta\Phi}{\partial P} = 0$$

$$\frac{\partial^2\Delta\Phi}{\partial P^2} > 0$$

Ginzburg-Landau equation of state of ferroelectric

$$E = \alpha P + \beta P^3$$

State of ferroelectric (no electric field)

$$E = \alpha P + \beta P^3$$

$$E = 0$$



$$\alpha P + \beta P^3 = 0$$

$$P = 0 \quad P^2 = -\alpha / \beta$$

$$T > T_c$$

$$\alpha > 0$$



$$P = 0$$

$$T < T_c$$

$$\alpha < 0$$

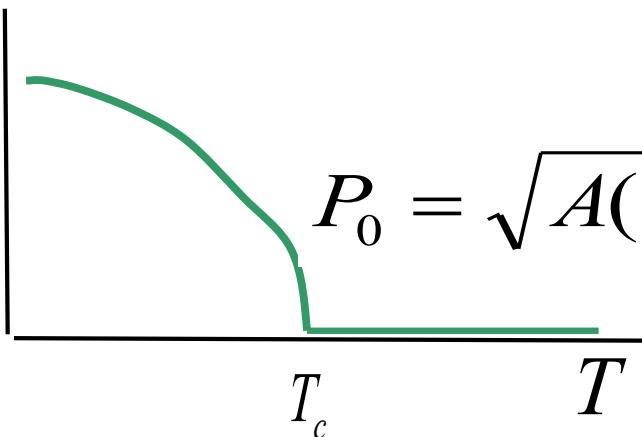


$$P = P_0 \equiv \sqrt{-\alpha / \beta}$$

unstable

$$\cancel{P = 0}$$

$$P$$



$$\alpha = A(T - T_c)$$

$$P_0 = \sqrt{A(T_c - T) / \beta}$$

Spontaneous polarization

Dielectric response

Differential permittivity

$$K = \frac{1}{\epsilon_0} \frac{\partial D}{\partial E} \bigg|_{E=0} = 1 + \frac{1}{\epsilon_0} \frac{\partial P}{\partial E} \bigg|_{E=0}$$

Permittivity

$$K_{av} = \frac{1}{\epsilon_0} \frac{D}{E} \bigg|_{E=0} = 1 + \frac{1}{\epsilon_0} \frac{P}{E} \bigg|_{E=0}$$

In “normal” dielectrics where

$$P \propto E \quad K_{av} = K$$

In ferroelectrics where

$$\alpha P + \beta P^3 = E \quad K_{av} \neq K$$

Differential permittivity under the field

$$K(E_0) = \frac{1}{\epsilon_0} \frac{\partial D}{\partial E} \bigg|_{E=E_0} = 1 + \frac{1}{\epsilon_0} \frac{\partial P}{\partial E} \bigg|_{E=E_0}$$

Dielectric response

Usually it is the differential permittivity that is measured.

Speaking about “differential permittivity” one usually omits “differential”.

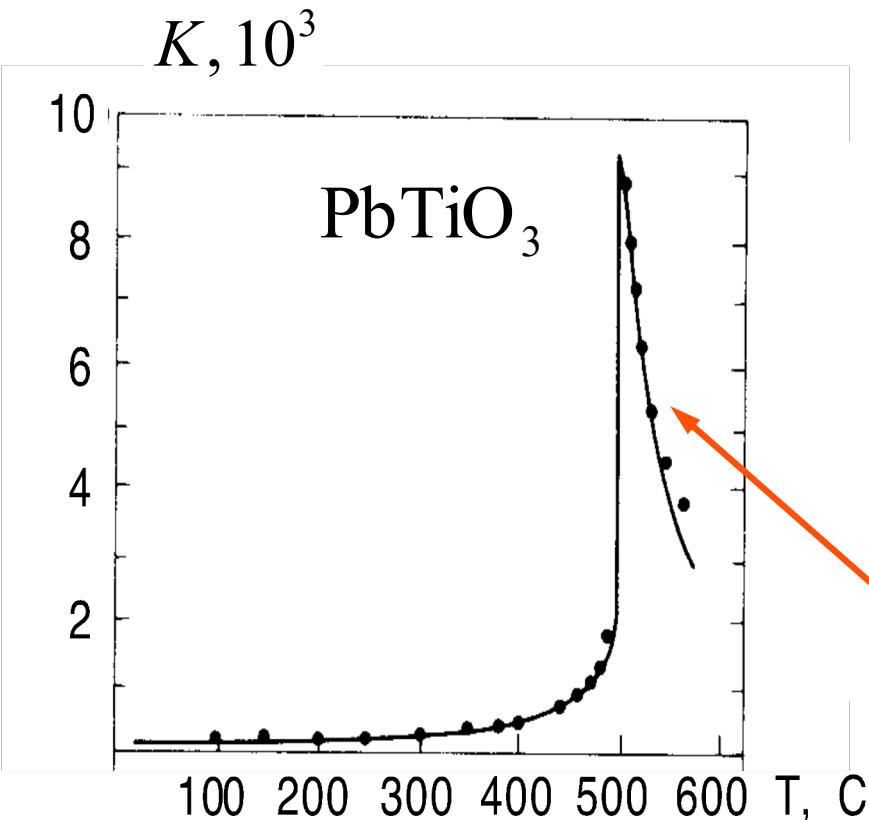
Hereafter in this course “differential” will be omitted.

“permittivity”=“differential permittivity” is defined as

$$K(E_0) = \frac{1}{\epsilon_0} \frac{\partial D}{\partial E} \bigg|_{E=E_0} = 1 + \frac{1}{\epsilon_0} \frac{\partial P}{\partial E} \bigg|_{E=E_0}$$

$K = K(E_0 = 0)$ unless specified otherwise

Dielectric response in paraelectric phase



correct trend

$$K = 1 + \frac{1}{\epsilon_0} \frac{\partial P}{\partial E} \Big|_{E=0}$$

$$\alpha P + \beta P^3 = E$$

$$\frac{\partial P}{\partial E} = \frac{1}{\alpha + 3\beta P^2} \quad \alpha = A(T - T_c)$$

$$T > T_c$$

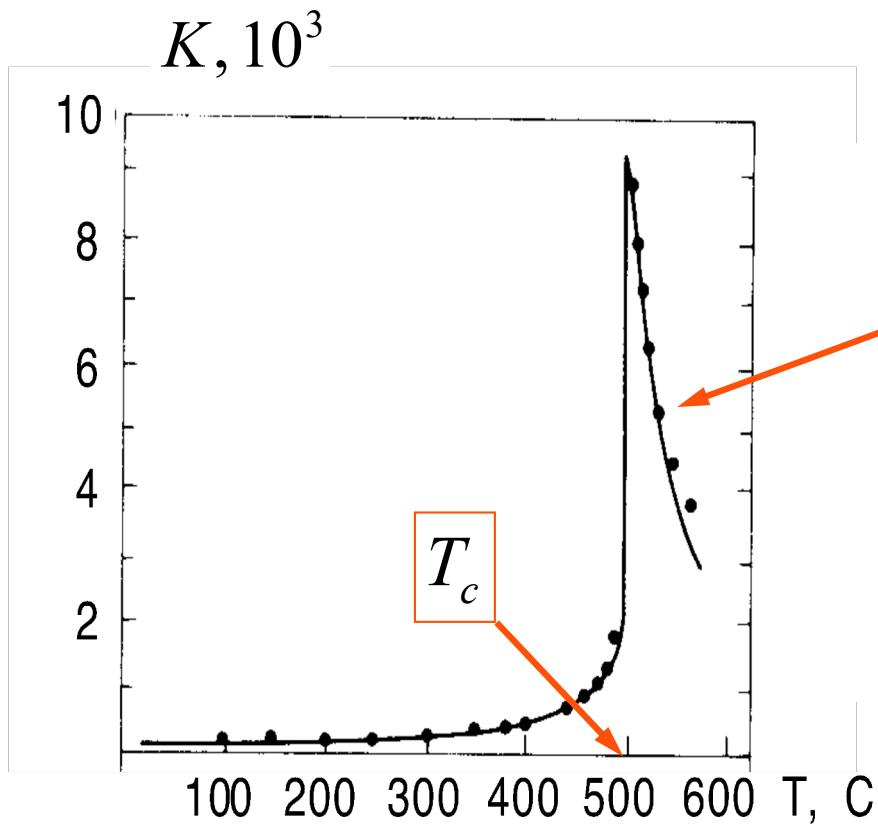
$$E = 0$$

$$P = 0$$

$$K = 1 + \frac{1}{\epsilon_0} \frac{1}{A(T - T_c)}$$

Curie-Weiss law

$$T > T_c$$



$$K = 1 + \frac{1}{\epsilon_0 A} \frac{1}{T - T_c}$$

Curie-Weiss constant

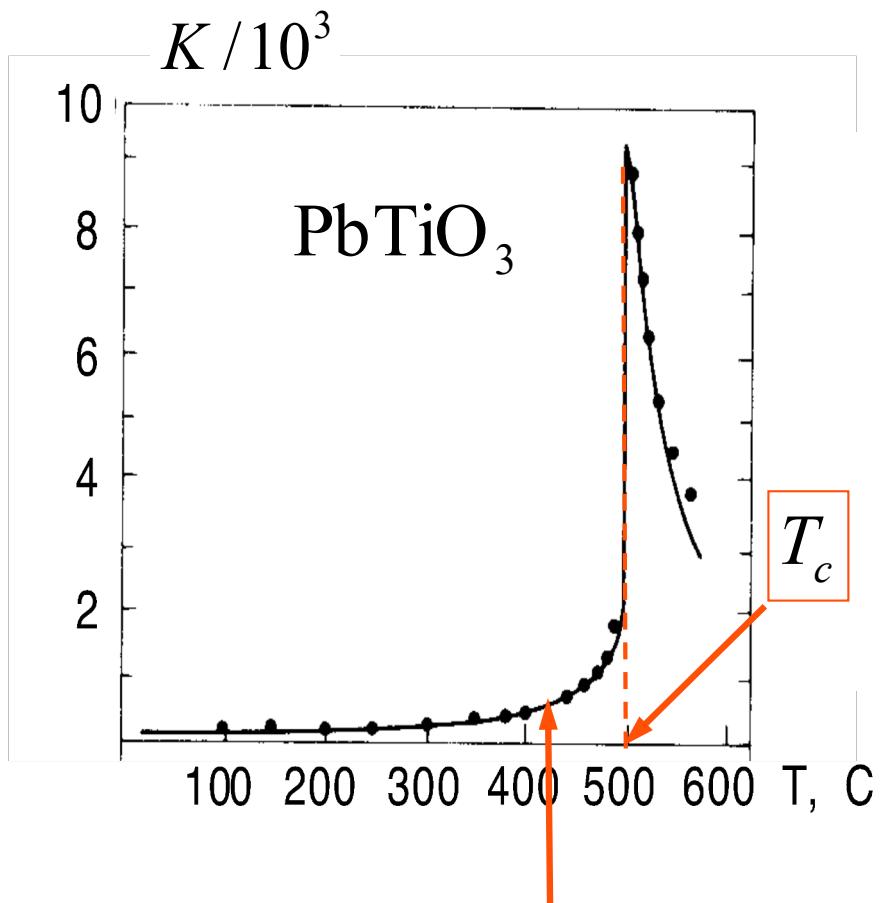
$$K \approx \frac{C_{\text{CW}}}{T - T_c}$$

PbTiO_3

$$C_{\text{CW}} = 1.7 \times 10^5 \text{ K}$$

$$C_{\text{CW}} = \frac{1}{\epsilon_0 A}$$

Dielectric response in ferroelectric phase



$$K = 1 + \frac{1}{\epsilon_0} \frac{1}{2A(T_c - T)}$$

$$K = 1 + \frac{1}{\epsilon_0} \frac{\partial P}{\partial E} \bigg|_{E=0} \quad T < T_c$$

$$\frac{\partial P}{\partial E} = \frac{1}{\alpha + 3\beta P^2}$$

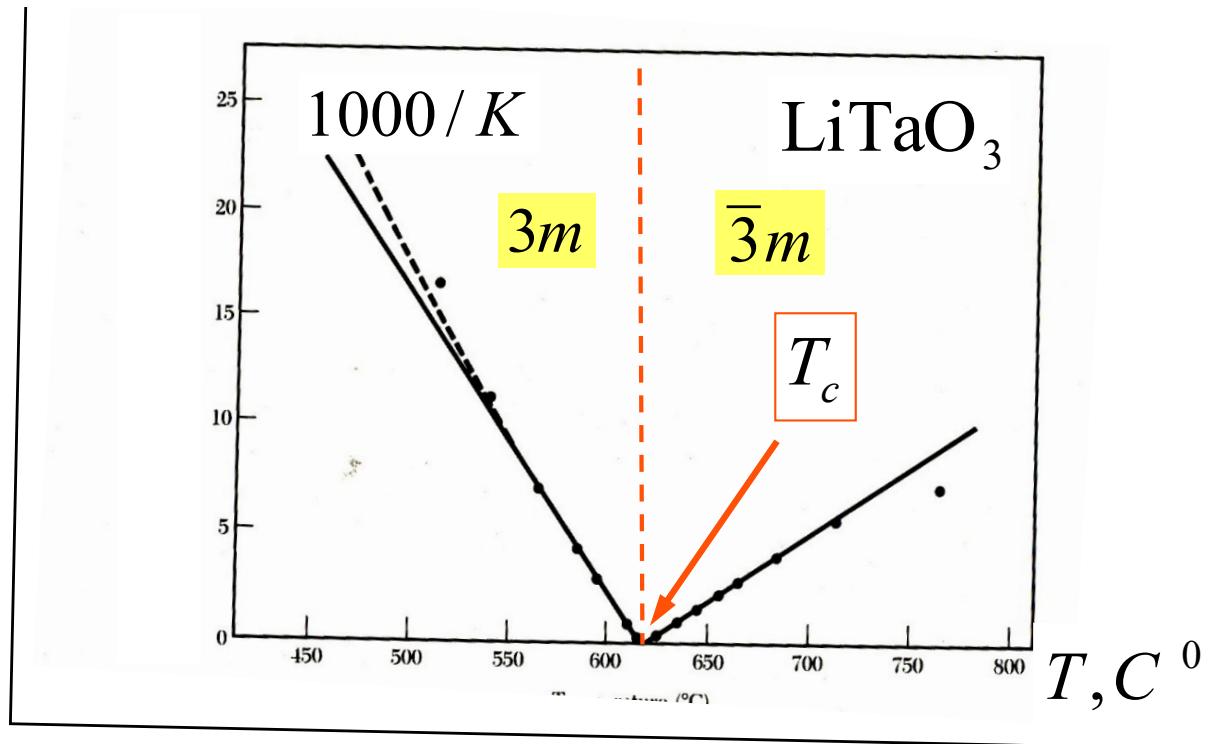
$$T < T_c \quad E = 0$$

$$P = P_0 = \sqrt{-\alpha / \beta}$$

correct trend

Dielectric response: “2” by Ginzburg

Inverse dielectric constant



$$T < T_c$$

$$K = 1 + \frac{1}{\epsilon_0} \frac{1}{2A(T_c - T)}$$

$$T > T_c$$

$$K = 1 + \frac{1}{\epsilon_0} \frac{1}{A(T - T_c)}$$

$$K^{-1} \approx 2\epsilon_0 A(T_c - T) \quad K^{-1} \approx \epsilon_0 A(T - T_c)$$

“2” by Ginzburg

Anomaly of pyroelectric response

$$p_i = \left. \frac{\partial P_i}{\partial T} \right|_{E=0}$$

$$P_i = \begin{pmatrix} 0 & 0 & 0 \end{pmatrix}$$

$$T > T_c$$

$$P_i = \begin{pmatrix} 0 & 0 & P_0 \end{pmatrix}$$

$$T < T_c$$

$$T > T_c$$

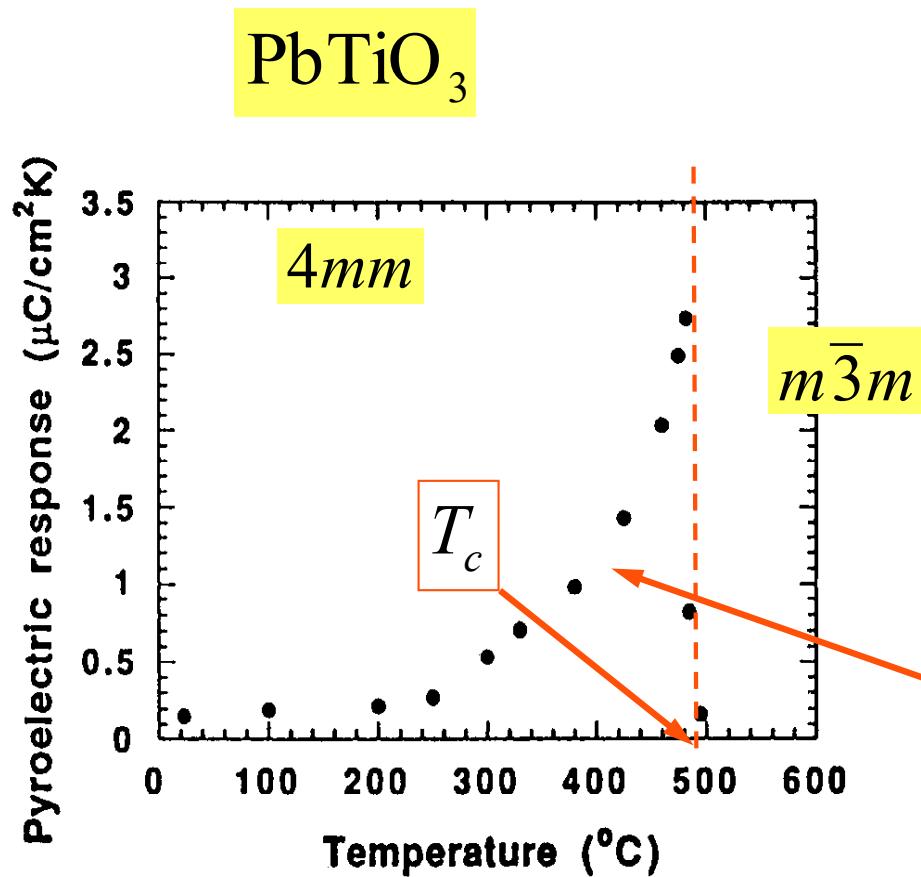
$$p_i = \begin{pmatrix} 0 & 0 & 0 \end{pmatrix}$$

$$T < T_c$$

$$p_i = \begin{pmatrix} 0 & 0 & \partial P_0 / \partial T \end{pmatrix}$$

$$p_3 = \frac{\partial P_o}{\partial T} = \frac{\partial}{\partial T} \sqrt{A(T_c - T) / \beta} = -\frac{A / \beta}{2} \frac{1}{\sqrt{A(T_c - T) / \beta}}$$

Checking – pyroelectric response

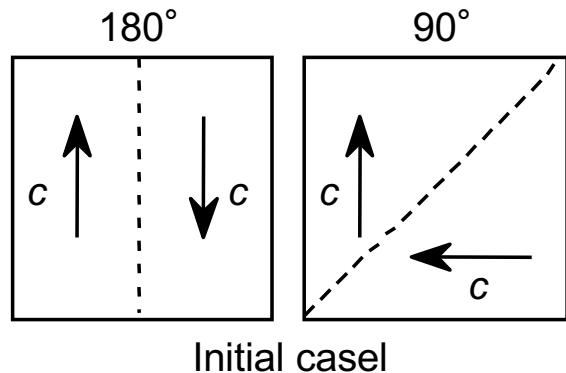


$$p_3 = -\frac{A/\beta}{2} \frac{1}{\sqrt{A(T_c - T)/\beta}}$$

correct trend

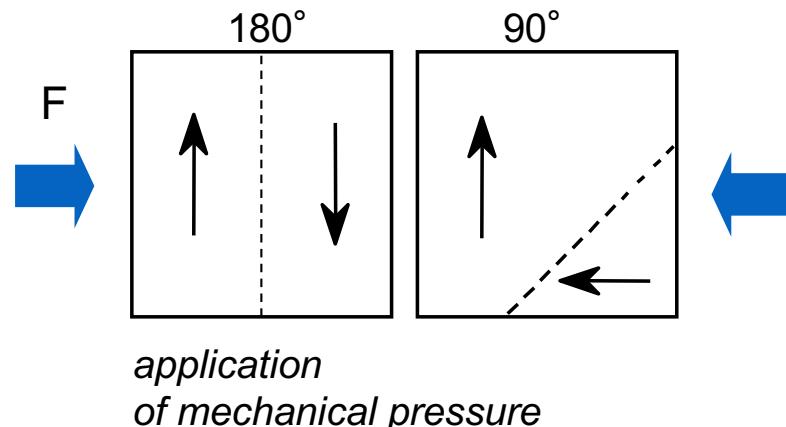
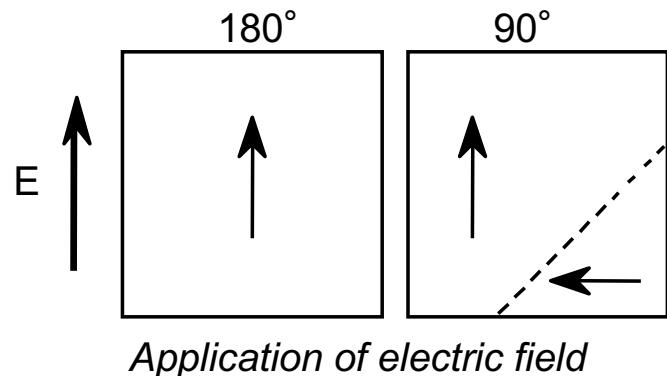
Ferroelectric domains

The regions of the material in which dipoles have the same orientation and direction are called ferroelectric domains



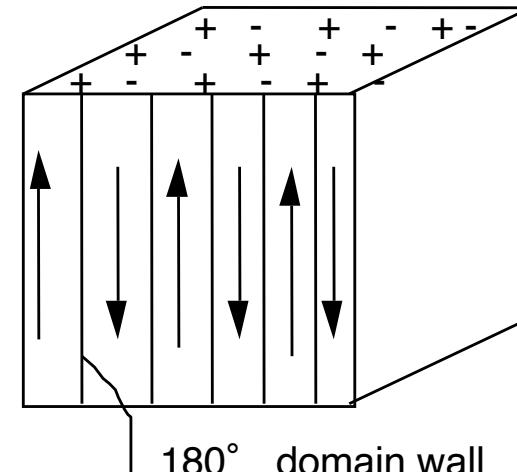
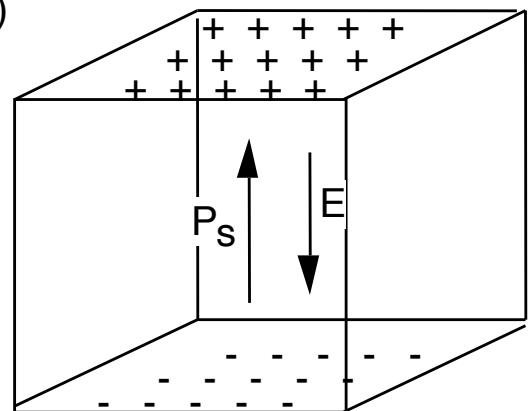
Tetragonal structure :
 180° and 90° domains

The domains can be inverted by electric field (180° and non 180°) or by a mechanical pressure (non- 180°)



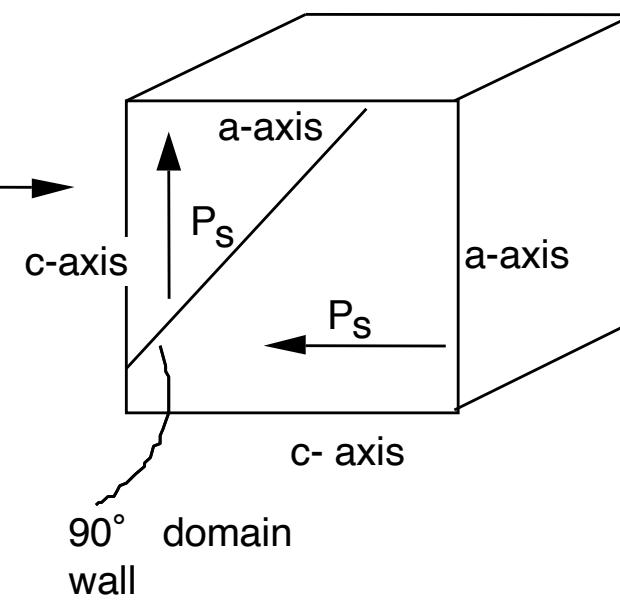
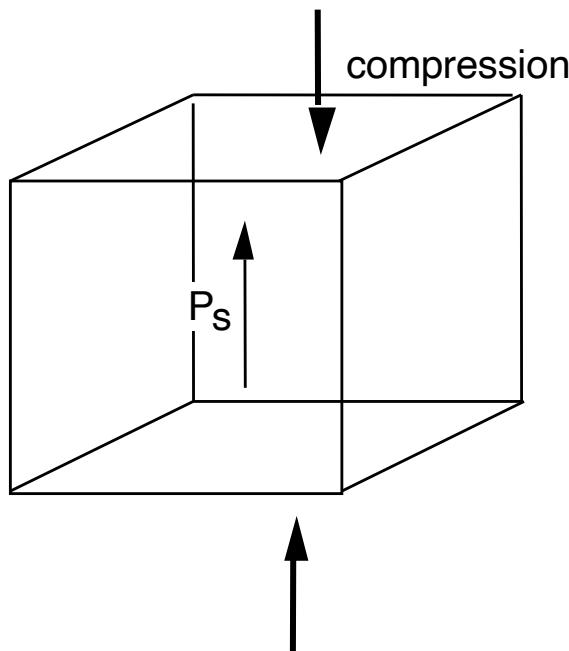
Ferroelectric domains

(a)



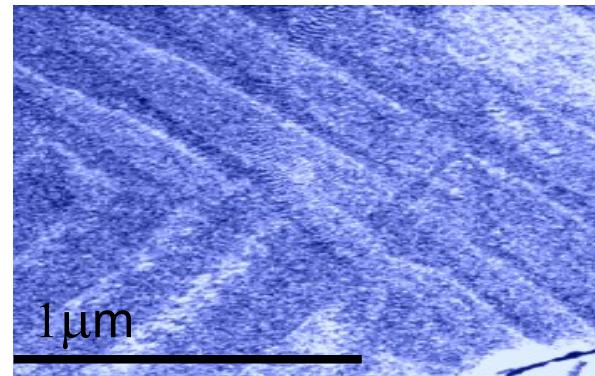
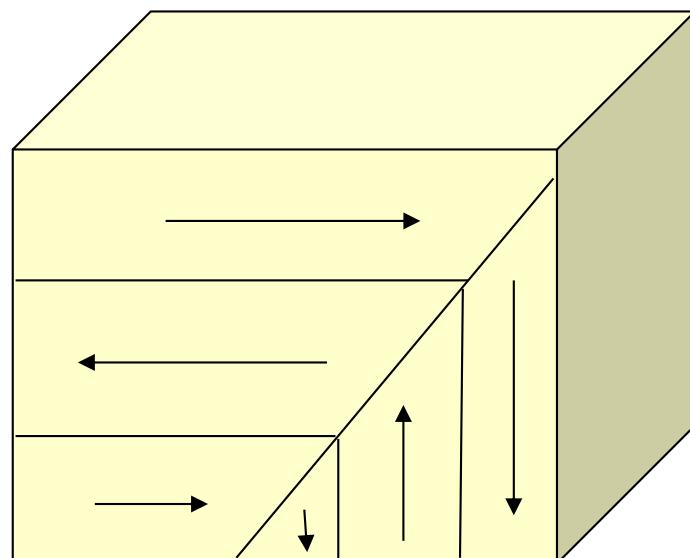
180° domain wall

(b)



Ferroelectric domains (cont.)

- In general, several types of domain walls (e.g., 180° et 90°) are present simultaneously

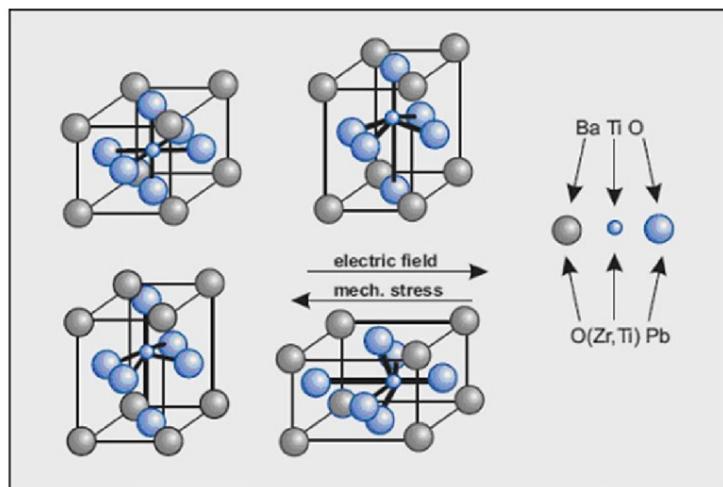


Micrograph (SEM) of a grain in a ferroelectric ceramic.

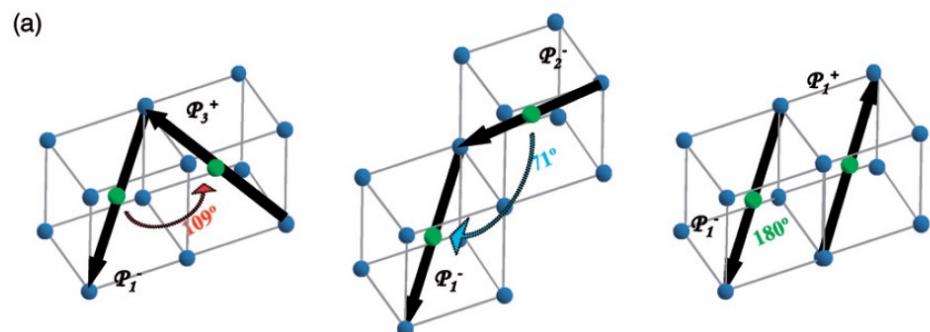
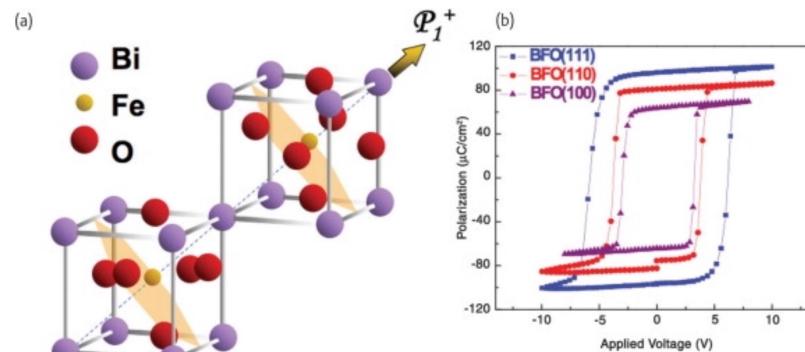
How to view/control ferroelectric domains at the nanometer scale

- Example of perovskite thin films (studied e.g. for information storage)

Example 1: tetragonal PZT ($\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$)



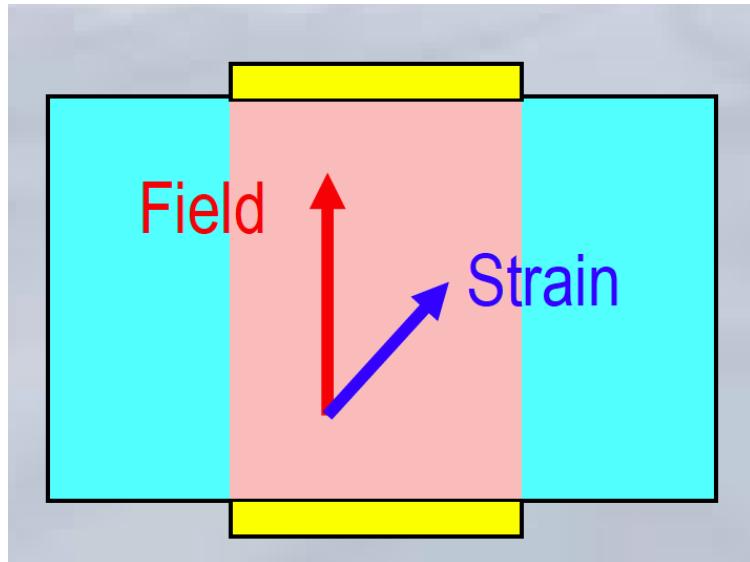
Example 2: rhombohedral BFO (BiFeO_3)



Probing nanoelectromechanics, mapping domains

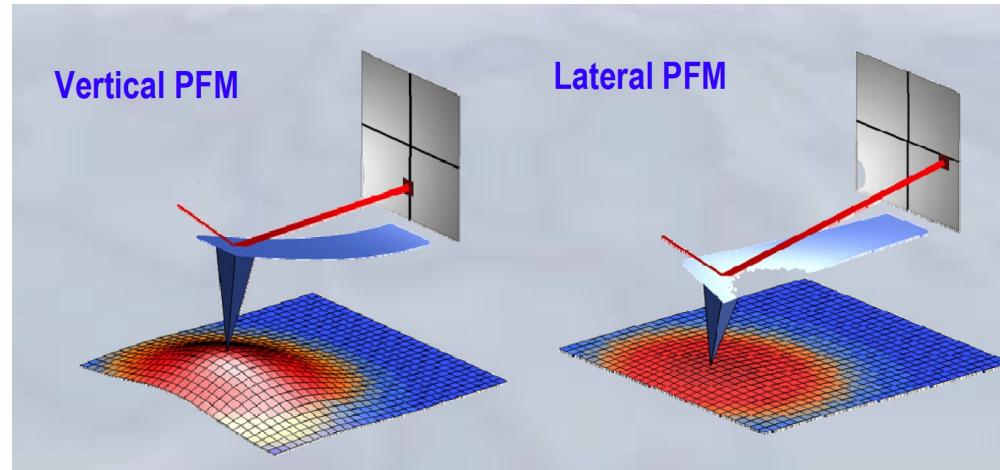
Piezoelectric response force microscopy (PFM)

In macroscopic systems, we measure response to the uniform external field (e.g. by interferometry)



Interpretation:

In general case the strain x is linked to the polarization P through the equation $x=QP^2$



Piezoresponse Force Microscopy:
**electromechanics can be
probed locally**

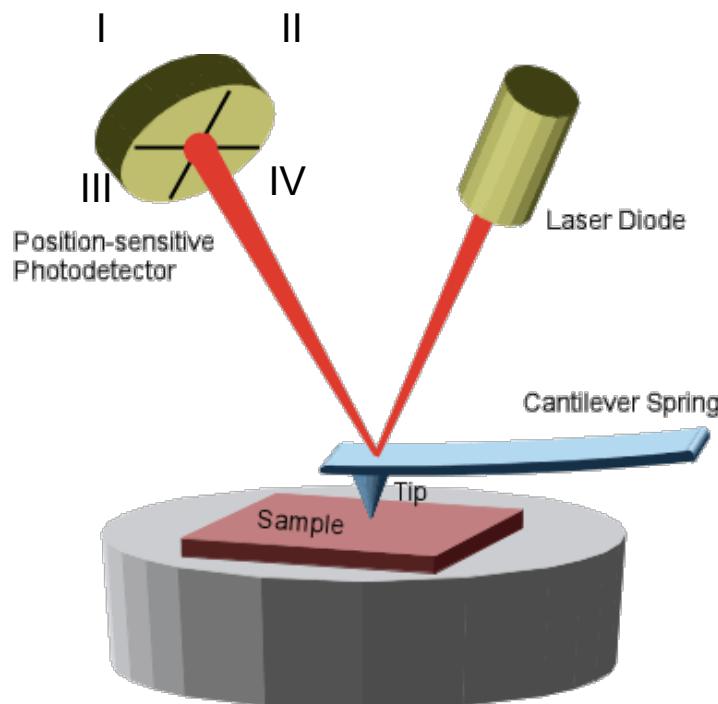
Application of AC + DC bias to the tip

$$V_{\text{tip}} = V_{\text{dc}} + V_{\text{a}} \cos(\omega t)$$

$$d = d_0 + A(\omega, V_{\text{dc}}) V_{\text{a}} \cos(\omega t + \varphi)$$

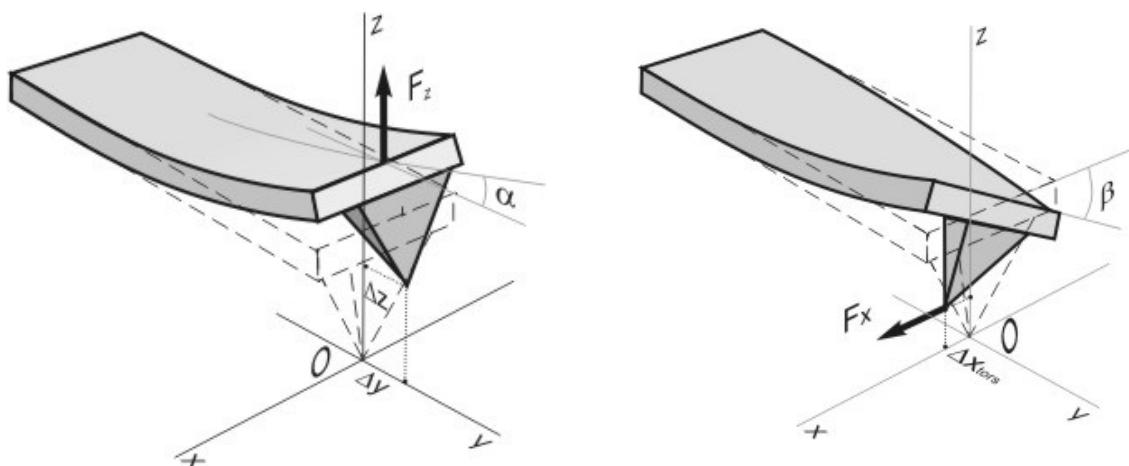
Modern AFM concept: deflection detected with laser

4-quadrant photodiode



Deflection:
 $(I + II) - (III + IV)$

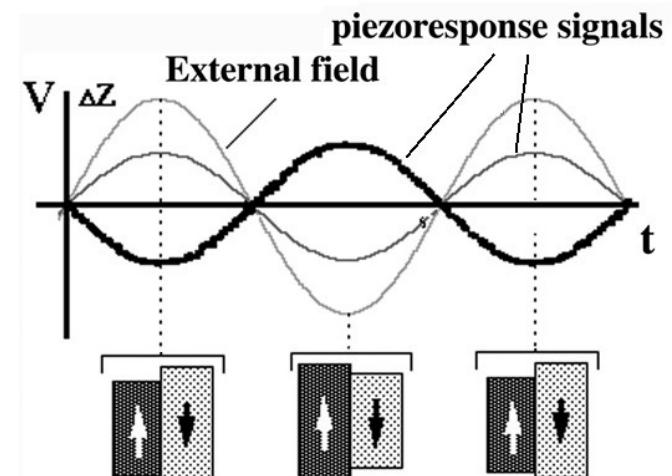
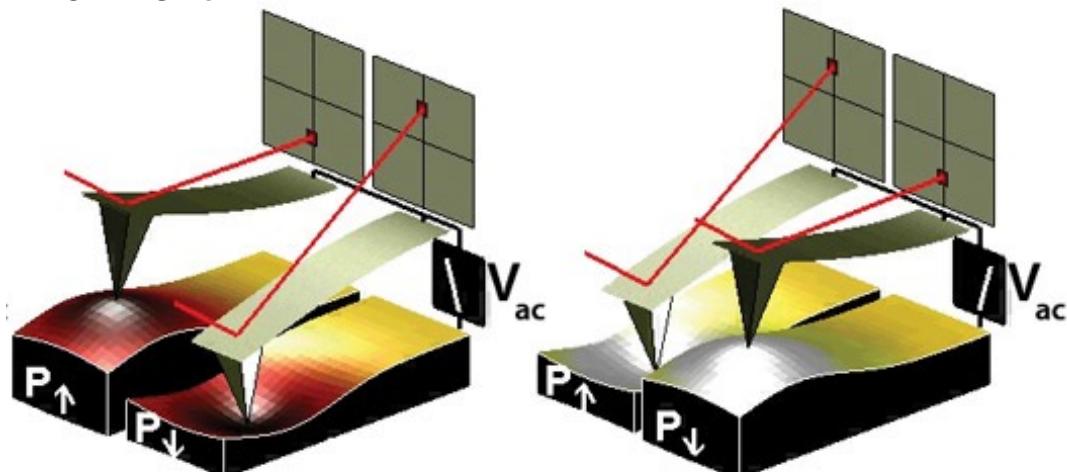
Torsion:
 $(I + III) - (II + IV)$



- In modern AFM the deflection is monitored by laser reflected from the back surface of the cantilever. The reflected intensity is measured by 4-quadrant photodiode
- The movement of cantilever is amplified by placing photodiode far (cm range) from the cantilever
- Vertical (deflection) and lateral (torsion) movement of the cantilever can be measured separately (vertical and lateral force microscopy)

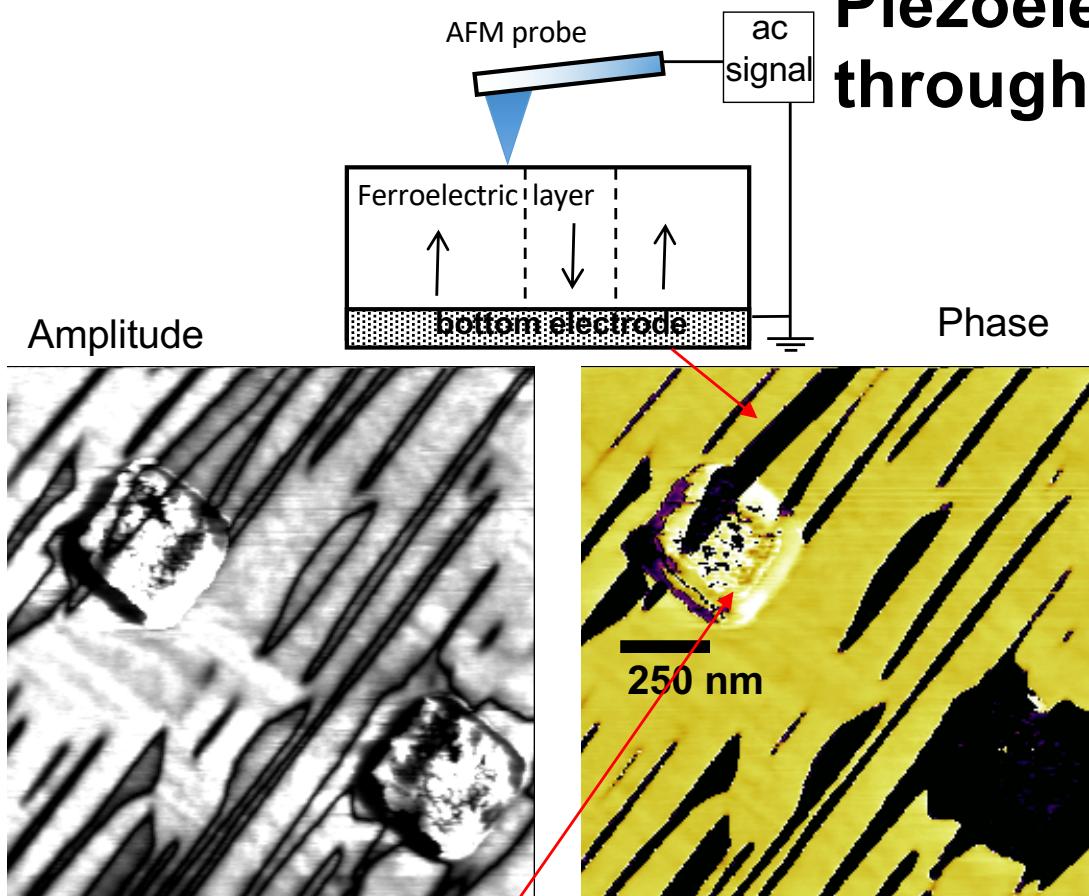
Piezoelectric response force microscopy (PFM)

- The most efficient way to probe local piezoelectric response is to drive the conductive tip with a small ac voltage $V_{ac} = V_0 \sin(\omega t)$
The mechanical displacement at the same frequency (both amplitude and phase) is detected – **lock-in**
- in many materials typical piezoelectric response is of order of magnitude of $d_{33}=10$ pm/V. The driving ac voltage for thin films and nanostructures is typically kept below 1V in order to avoid polarization switching, high conduction and other undesired effect. Hence the expected response amplitude may be below 10 pm ($<0.1\text{\AA}$)
- **lock-in technique** permits filtering out such a small response even if the high-noise environment



- If the material consists of polarization domains (regions where the polarization points in different directions), which is typically observed in ferroelectrics the map of phase of local piezoelectric response corresponds to the map of ferroelectric domains

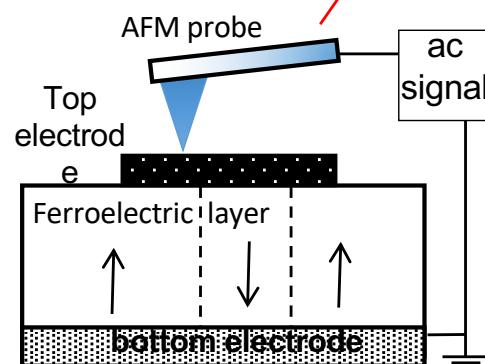
Piezoelectric response mapping, through-electrode imaging



This example shows amplitude and phase of local piezoresponse measured on a thin (50 nm) film of ferroelectric bismuth ferrite (BiFeO_3).

In the phase image the domains with the spontaneous polarization pointing up are represented by bright color while the domains with polarization pointing down are black.

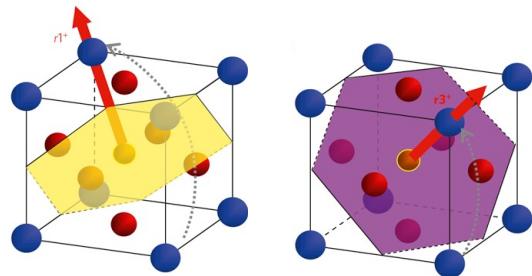
In the amplitude image the boundaries of domains are black (zero amplitude)



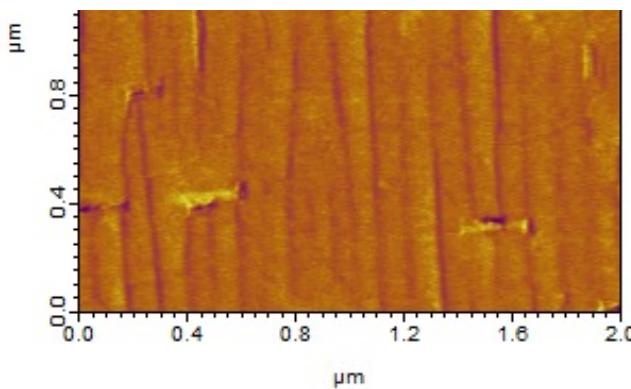
Rectangular Au electrodes are deposited on the film surface for electrical measurements. Remarkably the domains can be sensed through the thick (50 nm) gold layer. Lower image shows a sketch of the electrical configuration used for probing piezoelectric response through the electrode

Another rectangular electrode have been poled and then mechanically removed by the probe. The area underneath is fully poled (big black spot)

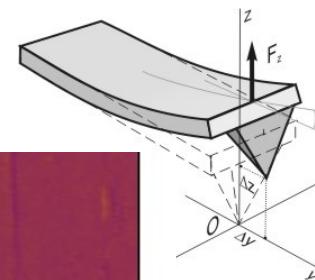
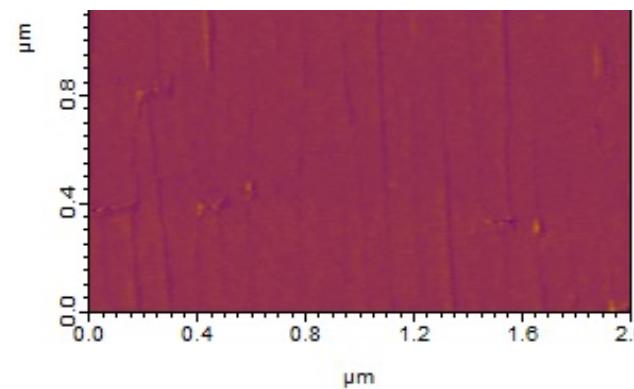
Lateral PFM



amplitude



Vertical PFM phase

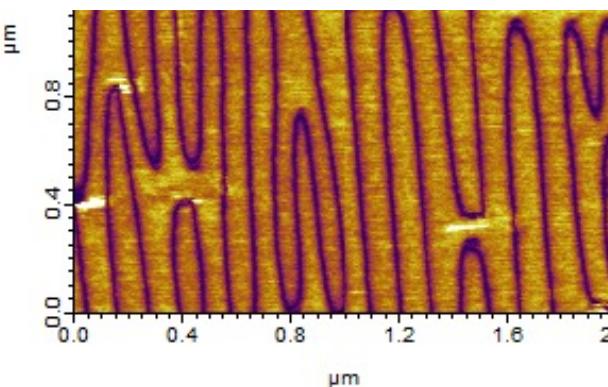


-Substrate:
DSO/SRO(5nm)

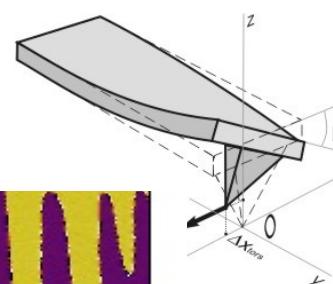
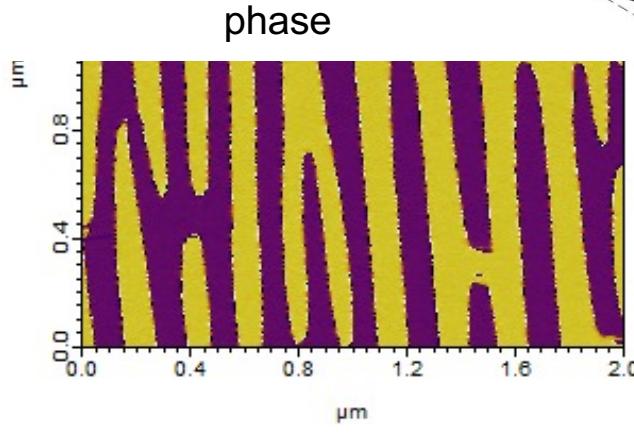
-Thickness 60 nm

-Very smooth
BFeO₃ ferroelectric
film
(regular monolayer
terraces)

amplitude



Lateral PFM



-Arrays of regular domains with 71° DWs
(vertical polarization component unchanged)

PFM: ultimate limit of sensitivity: fractions of pm

Genuinely Ferroelectric Sub-1-Volt-Switchable Nanodomains in $\text{Hf}_x\text{Zr}_{(1-x)}\text{O}_2$ Ultrathin Capacitors

Igor Stolichnov,^{*,†} Matteo Cavalieri,[†] Enrico Colla,[‡] Tony Schenk,[§] Terence Mittmann,[§] Thomas Mikolajick,^{||} Uwe Schroeder,[§] and Adrian M. Ionescu[†]

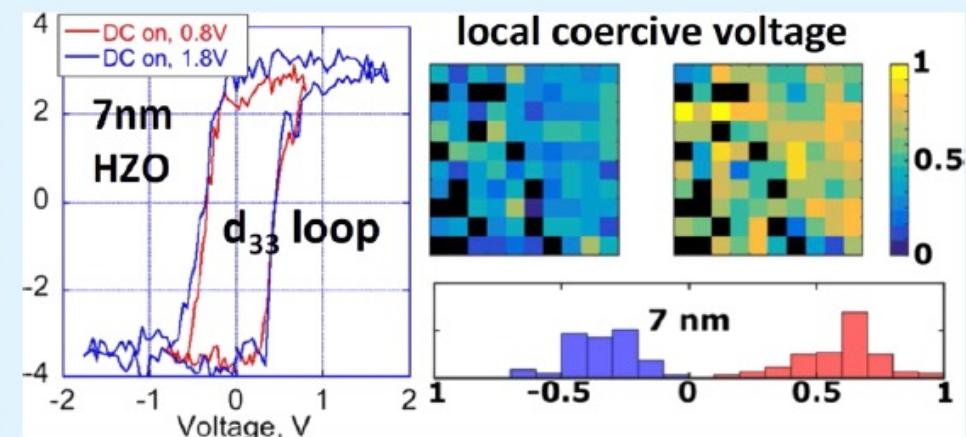
[†]Nanoelectronic Devices Laboratory and [‡]Materials Department, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne 1015, Switzerland

[§]Namlab gGmbH, Noethnitzer Strasse 64, 01187 Dresden, Germany

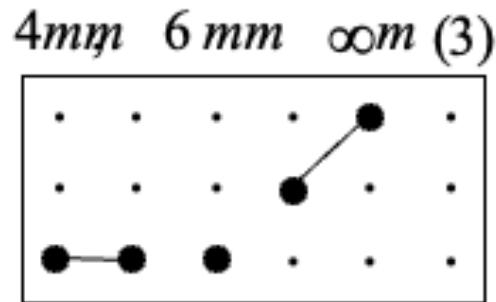
^{||}Chair of Nanoelectronic Materials, TU Dresden, 01062 Dresden, Germany

Supporting Information

ABSTRACT: The new class of fully silicon-compatible hafnia-based ferroelectrics with high switchable polarization and good endurance and thickness scalability shows a strong promise for new generations of logic and memory devices. Among other factors, their competitiveness depends on the power efficiency that requires reliable low-voltage operation. Here, we show genuine ferroelectric switching in $\text{Hf}_x\text{Zr}_{(1-x)}\text{O}_2$ (HZO) layers in the application-relevant capacitor geometry, for driving signals as low as 800 mV and coercive voltage below 500 mV. Enhanced piezoresponse force microscopy with sub-picometer sensitivity allowed for probing individual polarization domains under the top electrode and performing a detailed analysis of hysteretic switching. The authentic local piezoelectric loops and domain wall movement under bias attest to the true ferroelectric nature of the detected nanodomains.



Is it possible to detect shear modes of piezoelectric response? - yes!



Typical values for piezo moduli for PZT

Piezoelectric coefficients	Values
d_{31} (m/V)	-210×10^{-12}
d_{33} (m/V)	472×10^{-12}
d_{15} (m/V)	758×10^{-12}

Shear piezocoefficient:

How to find deformation ε_{13}

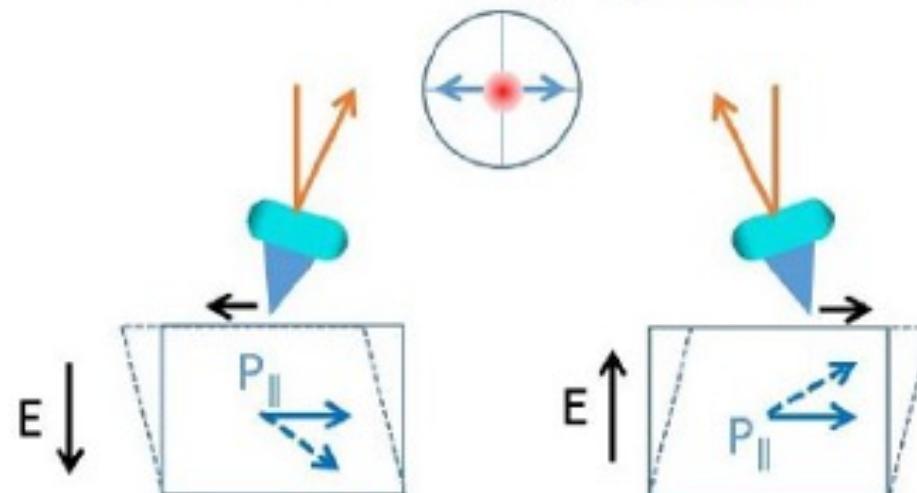
$\varepsilon_n = d_{in} E_i - \text{inv. piezoeffect}$

$$\varepsilon_5 = \varepsilon_{13}$$

$$d_{15} = d_{113}$$

$$\varepsilon_{13} = d_{113} E_1 \quad (E - \text{electric field})$$

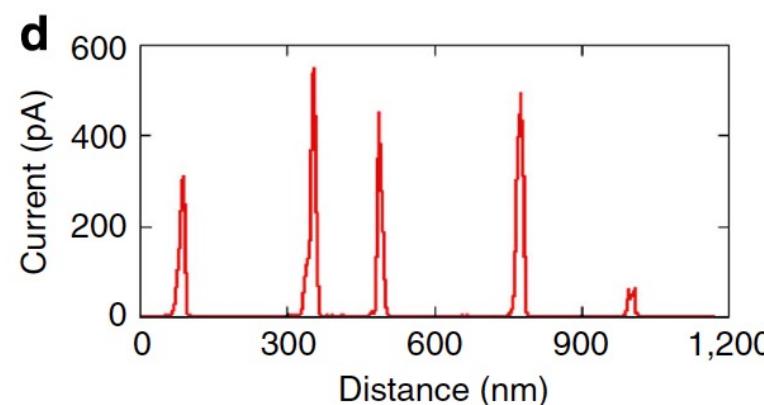
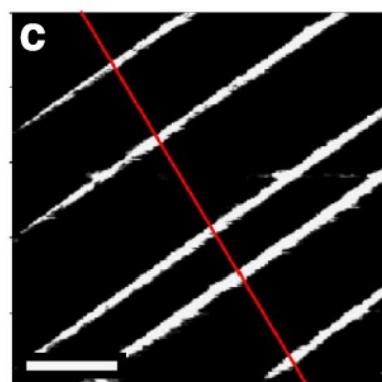
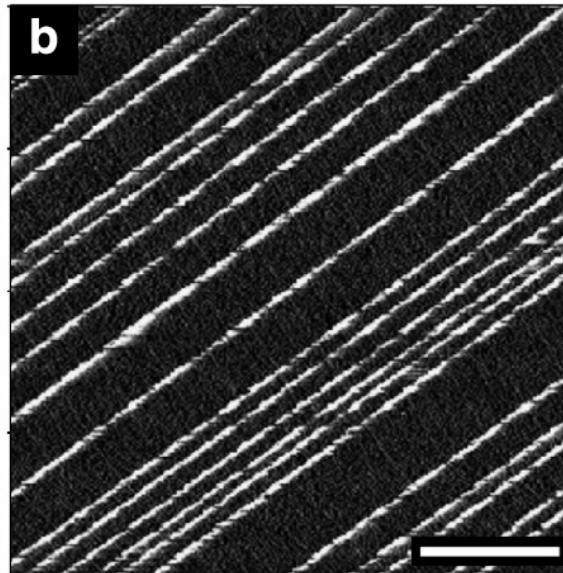
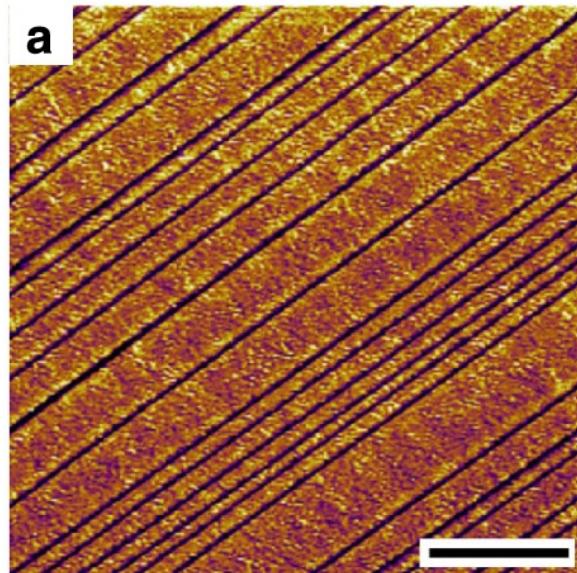
Lateral PFM: torsional mode
azimuthal angle $\varphi = 90^\circ$



Functional properties of domain walls in PZT: combination of PFM and Conductive AFM (c-AFM)

PZT film with 1D array of ferroelectric domains (90° domains)

Combination of PFM and c-AFM: narrow 90° domains provide conductive channels



- a) PFM amplitude, 4x4 μm scan
- b) c-AFM, constant $V=4\text{V}$, same area
- c) Zoom in: 1x1 μm c-AFM
- d) Current profile, cross-section

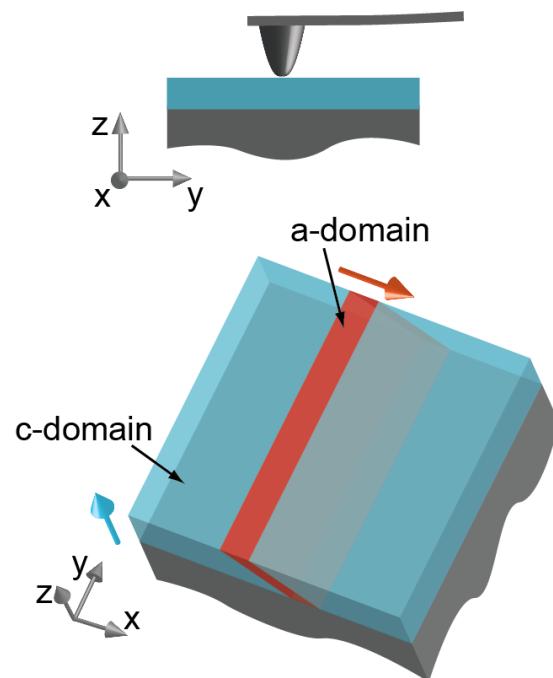
• Domain walls can be conductive!!

• Potential for use in domain-wall electronics

Conductive AFM, example: PZT with 90° ferroelastic domains: conductive domain boundaries

90° domains of polarization are formed in thin (50nm) epitaxial PZT films in order to reduce the mechanical energy (reduce lattice mismatch). They can be seen in topography (sub-nm vertical resolution).

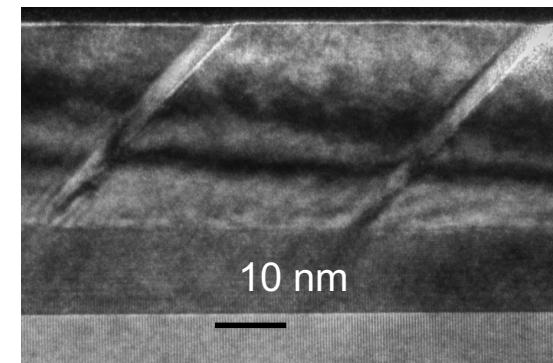
Theoretical analysis suggests that the domain boundaries can show metallic conduction (conductive channels in dielectric media, which can be reconfigured!)



Simulation

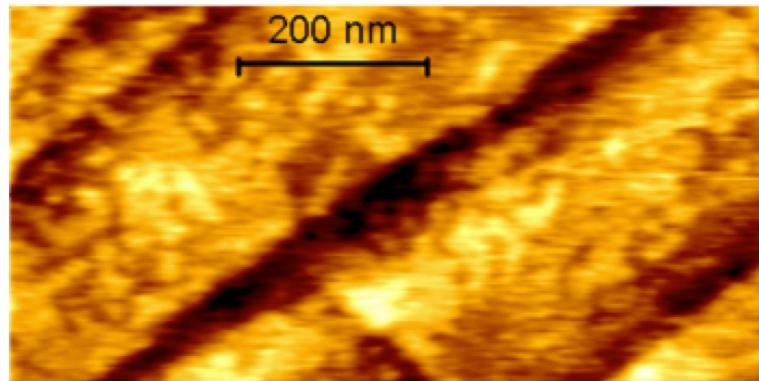


TEM image

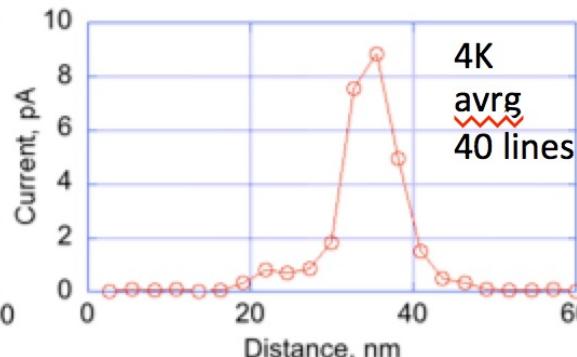
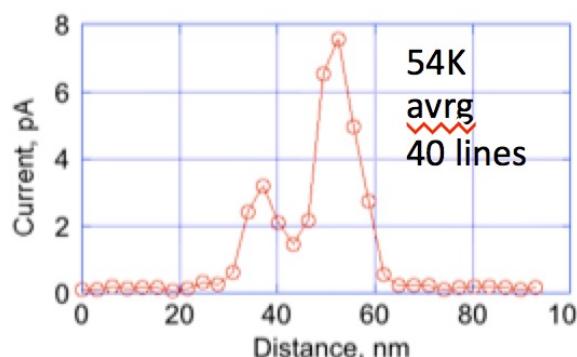
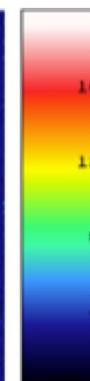
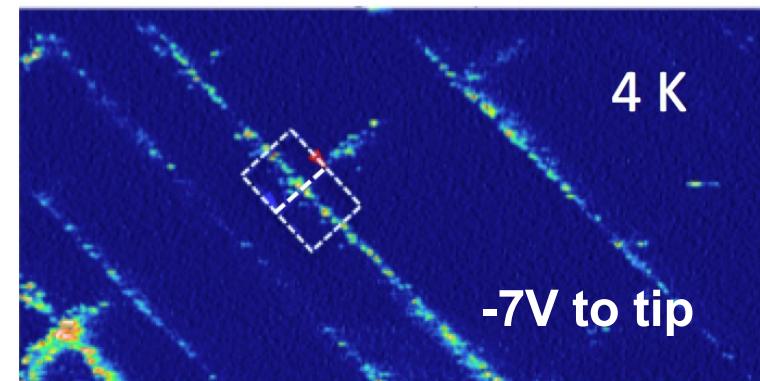
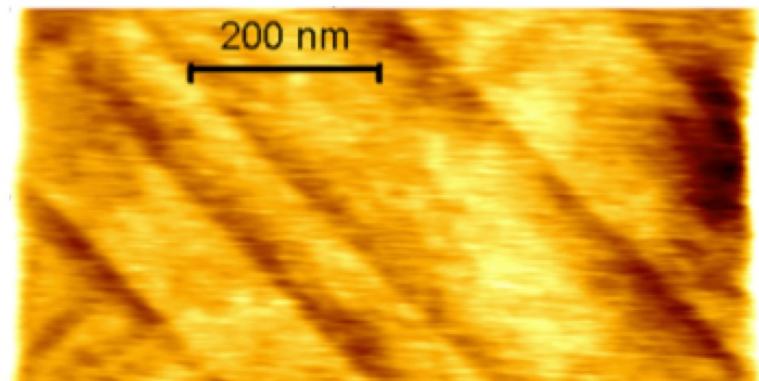
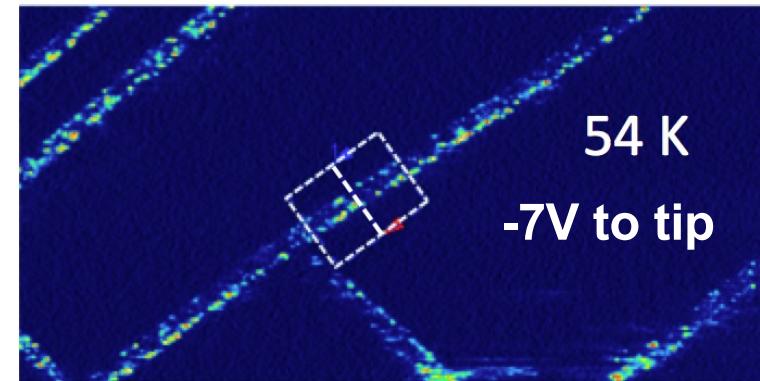


Conductive AFM, example: PZT with 90° domains: conductive domain boundaries

topography



Conductive AFM



4K vs 54K:
(same probe)

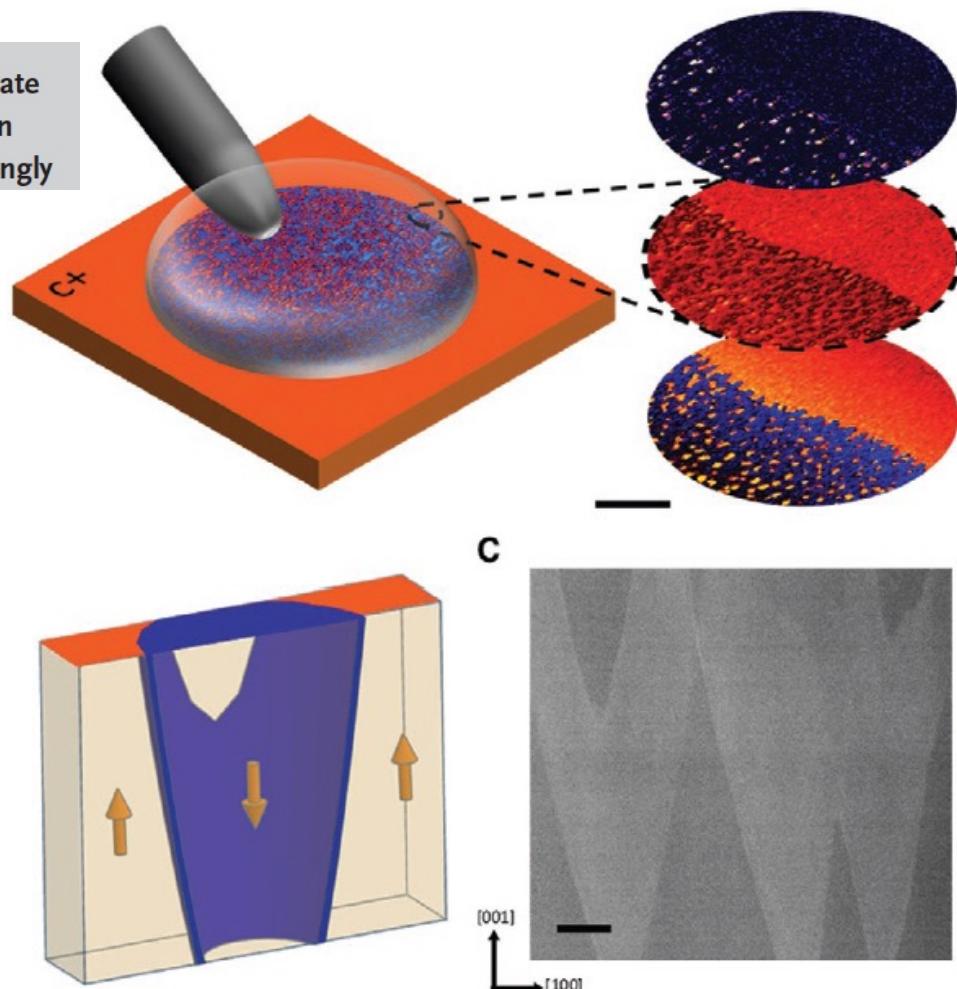
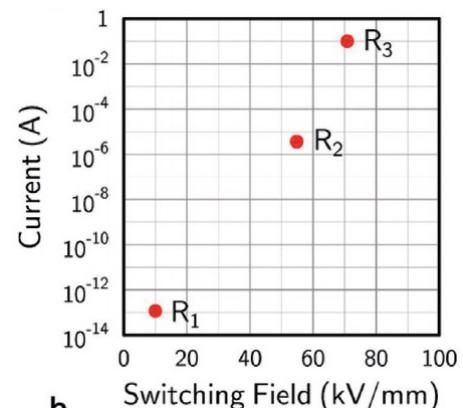
Current values
are close!

Ferroelectric Domain Wall Memristor

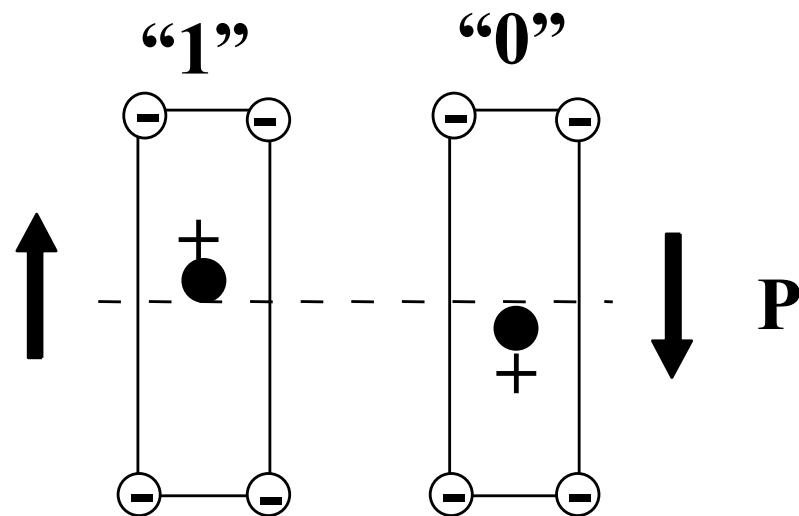
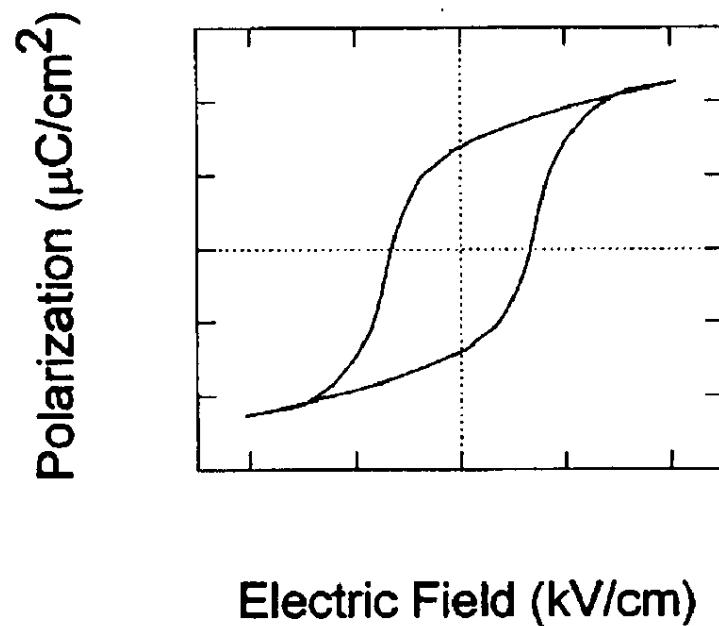
James P. V. McConville, Haidong Lu, Bo Wang, Yueze Tan, Charlotte Cochard, Michele Conroy, Kalani Moore, Alan Harvey, Ursel Bangert, Long-Qing Chen, Alexei Gruverman, and J. Marty Gregg*

A domain wall-enabled memristor is created, in thin film lithium niobate capacitors, which shows up to twelve orders of magnitude variation in resistance. Such dramatic changes are caused by the injection of strongly

- LiNbO_3 – uniaxial ferroelectric (trigonal)
- Slightly inclined domain walls – partially charged
- Domain wall conductivity
- Memristive behavior: variation of conductivity by 12 orders – control of multiple domains below the electrode



Information storage in a ferroelectric



Ferroelectric Random Access Memory - FeRAM

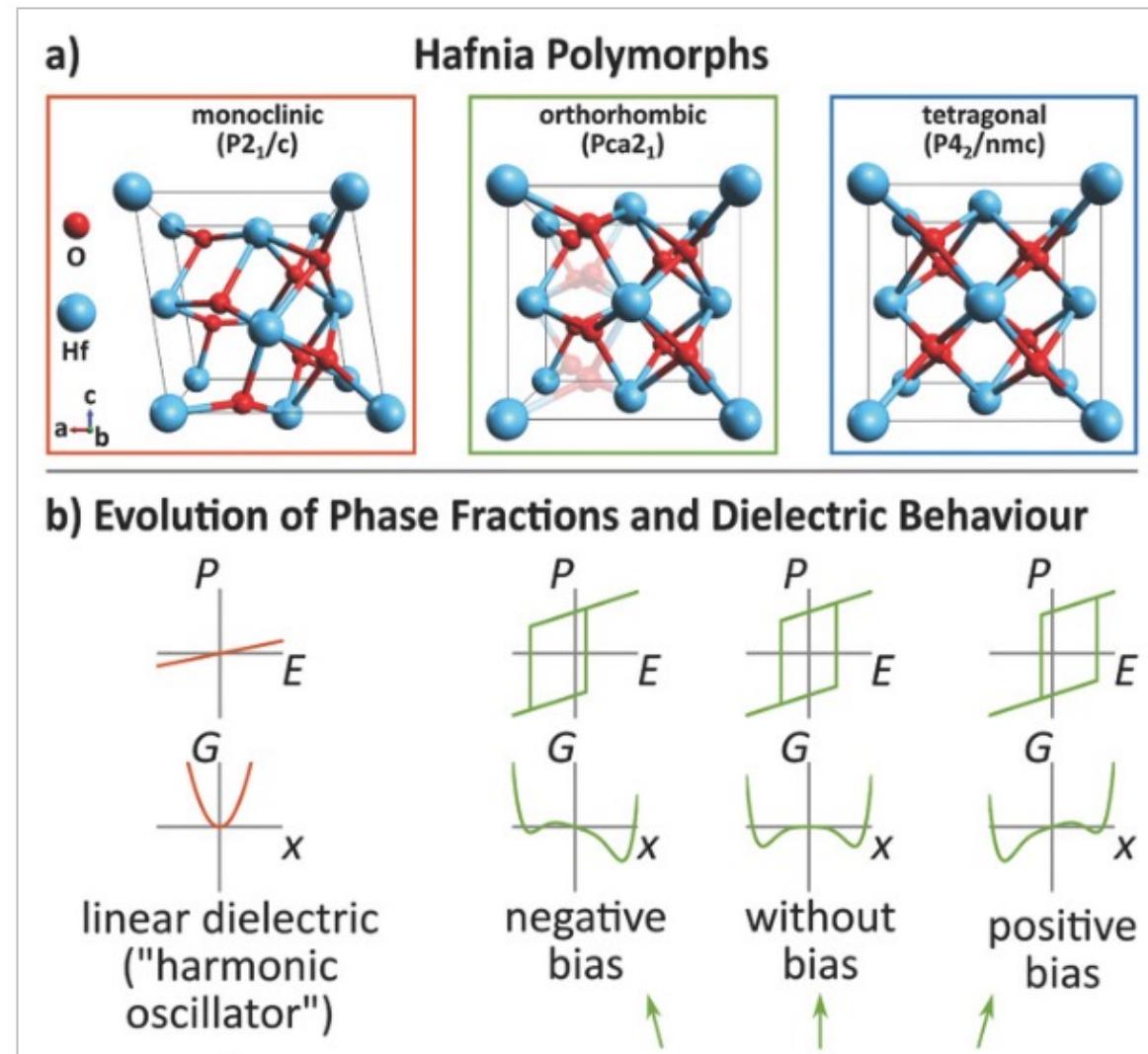
Si-doped HfO₂: a new CMOS-compatible ferroelectric

Si Doped Hafnium Oxide—A “Fragile” Ferroelectric System

Claudia Richter, Tony Schenk, Min Hyuk Park, Franziska A. Tscharntke, Everett D. Grimley, James M. LeBeau, Chuanzhen Zhou, Chris M. Fancher, Jacob L. Jones, Thomas Mikolajick, Uwe Schroeder 

First published: 22 August 2017 | <https://doi.org/10.1002/aelm.201700131> | Citations: 94

- Recently ferroelectricity had been discovered in HfO₂, that has been known and adopted by industry as a Si-compatible high-k dielectric material
- Its CMOS-compatibility, high remanent polarization of $20\mu\text{C}/\text{cm}^2$ and excellent scalability make it a strong candidate for ferroelectric memories



Essential

1. Phase transitions may occur between different states of a solid material. These are ***structural phase transitions***.
2. At a ***ferroelectric phase transition***, the material's symmetry changes from non-polar to polar (usually on cooling) .
3. **Ferroelectric** is a material exhibiting a ferroelectric phase transition.
4. The ***ferroelectric phase*** of a ferroelectric is characterized by:
 - 2 or more ***domain states*** of the material.
 - P-E ***hysteresis, polarization domains***
 - ***dielectric response anomaly near T_c***

Essential

1. Ginzburg-Landau theory describes ferroelectric phase transition (only second-order phase transition was discussed, some ferroelectrics are first-order, but also can be analyzed)

