Дифракционные in-situ эксперименты для исследования пъезо- и сегнетоэлектриков при приложении электрического поля

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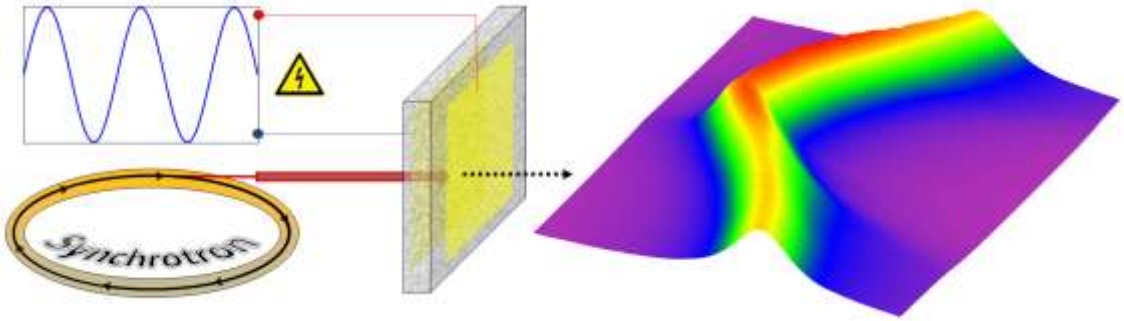


UNIVERSITÄT SIEGEN

FESTKÖRPERPHYSIK

Krombacher

Biggest brewery in Germany

dscapes

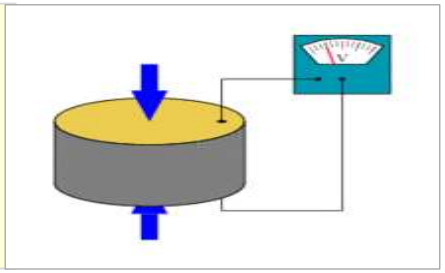
Peter Paul Rubens
(1577-1640) born in Sieg

2014: International year of crystallography

The content

1. Piezoelectricity

- *Physical crystallography*
- *Piezoelectric effect and symmetry*



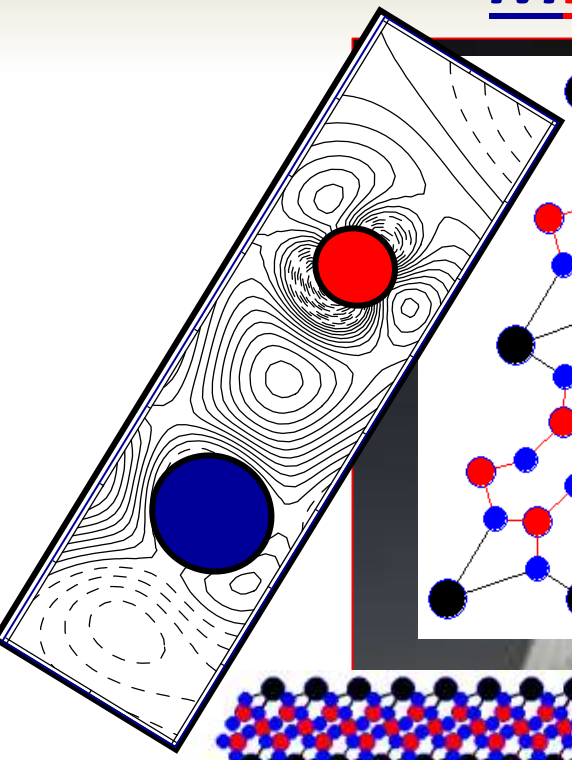
2. Ferroelectricity / Сегнетоэлектричество

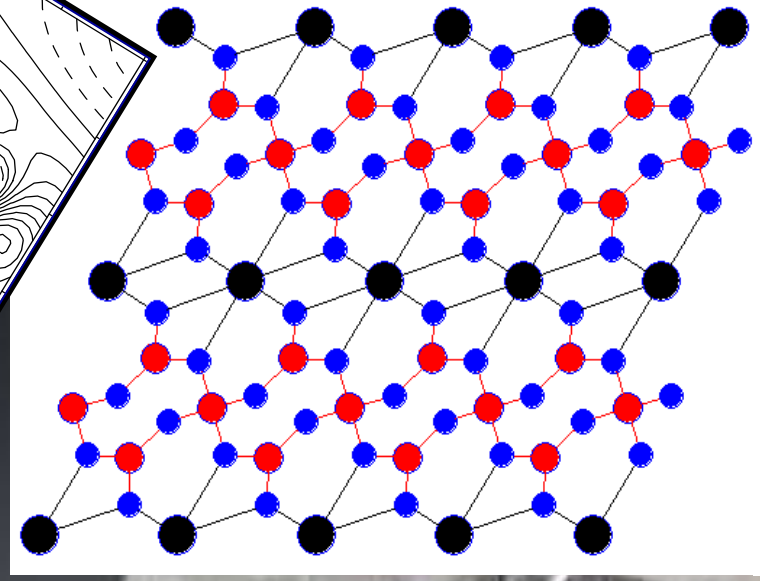
- *Formation of domain structure*
- *Piezoelectricity in ferroelectrics*

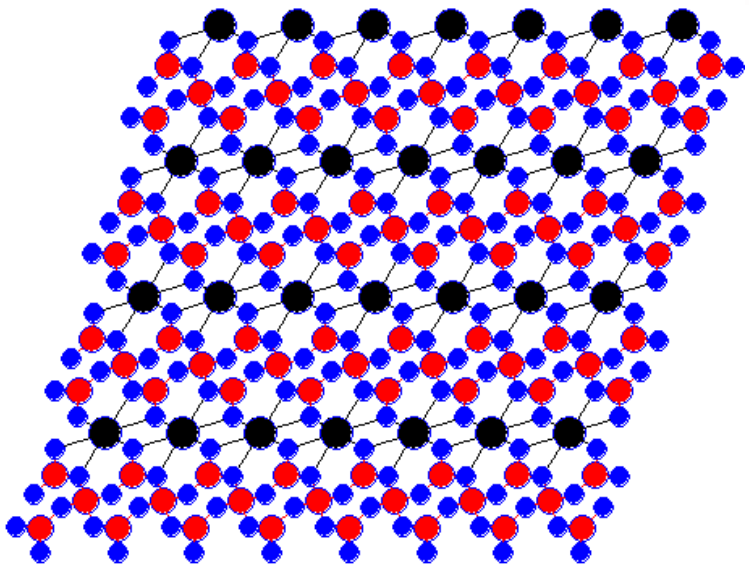
3. In-situ X-ray diffraction under electric field

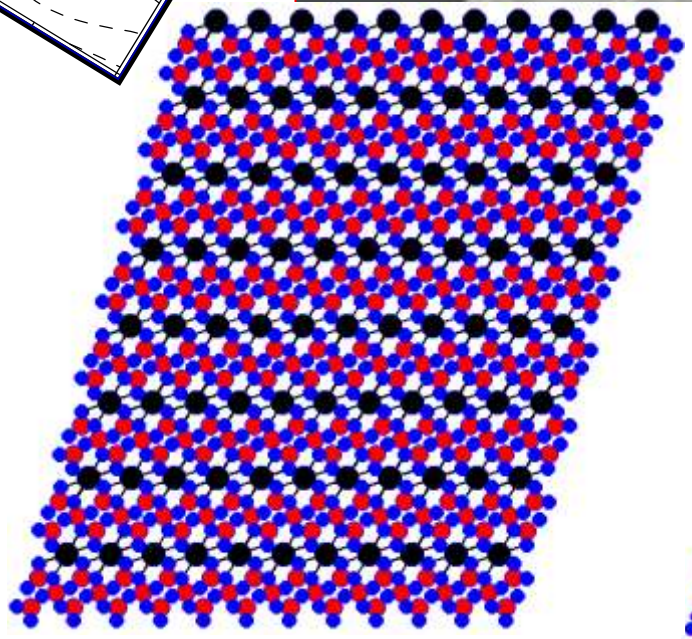
- *Methodology of in-situ diffraction experiment*
- *Application of electric field to a crystal*
- *Stroboscopic data collection*
- *Diffraction on single crystals, powders, multi-domain systems*
- *Investigation of piezoelectricity in uniaxial ferroelectrics*

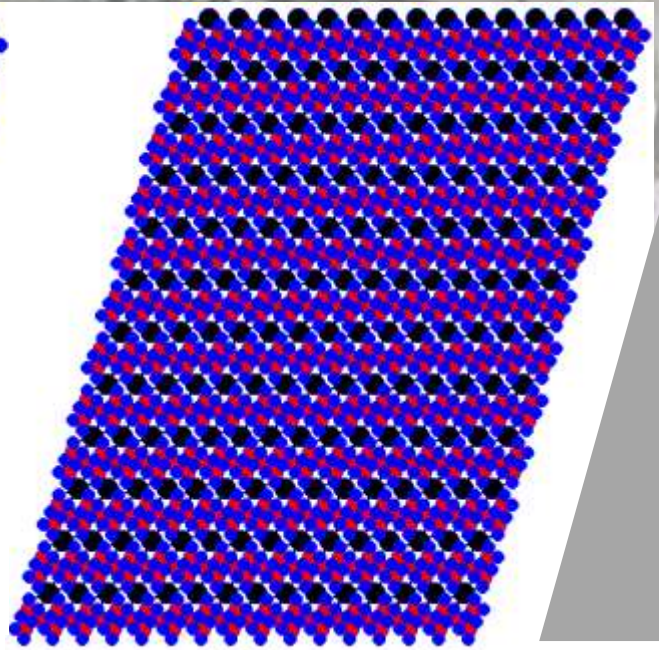
Microscopic → Macroscpic



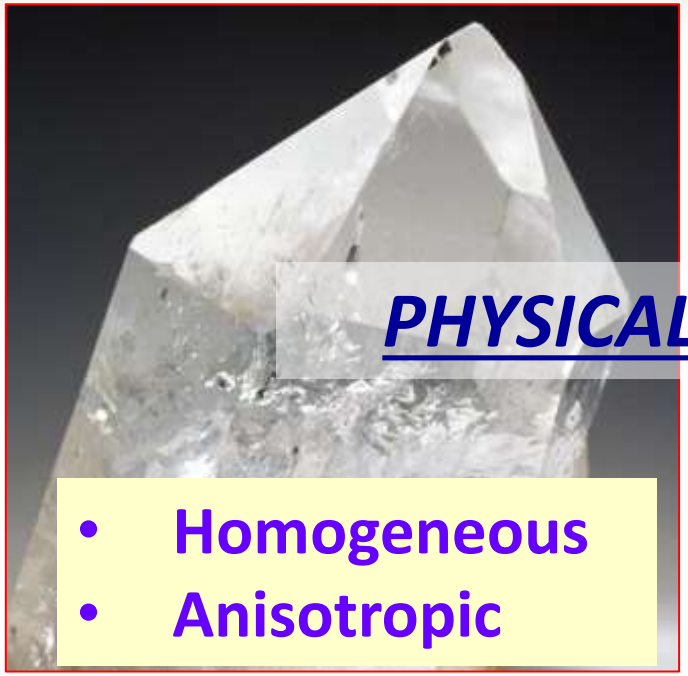






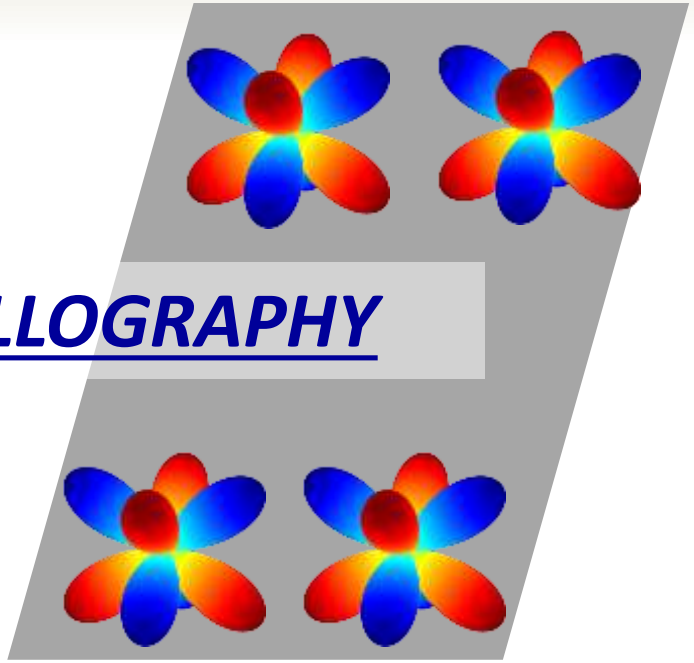


Macroscopic 'black box' concept of a crystal



PHYSICAL CRYSTALLOGRAPHY

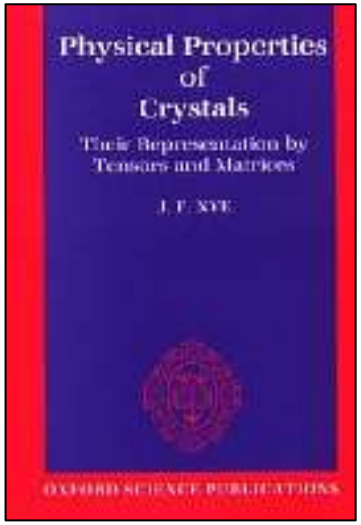
- Homogeneous
- Anisotropic



J.F. Nye

Physical properties of crystals and their representations by tensors and matrices

Oxford University Press, 1985.



Physical properties

Perturbation	*Response*	*Property*
Electric field	Dielectric polarization	Dielectricity
Mechanical stress	Deformation	Elasticity
Temperature change	Deformation	Thermal expansion
Magnetic field	Magnetization	Magnetism

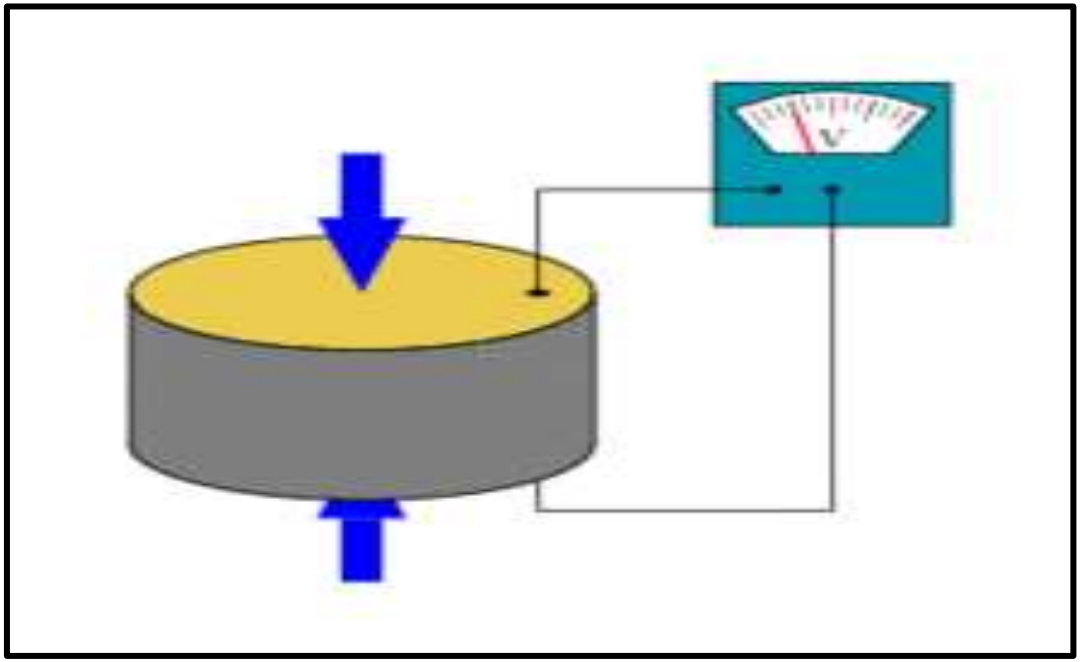
ARE 'CROSS-OVER' PHYSICAL PROPERTIES POSSIBLE?

Yes: electromechanical properties

STRESS

ELECTRIC FIELD

Elasticity



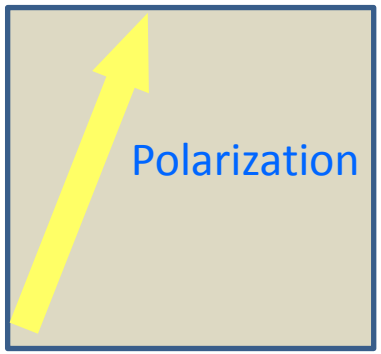
Dielectricity

Deformation

POLARIZATION

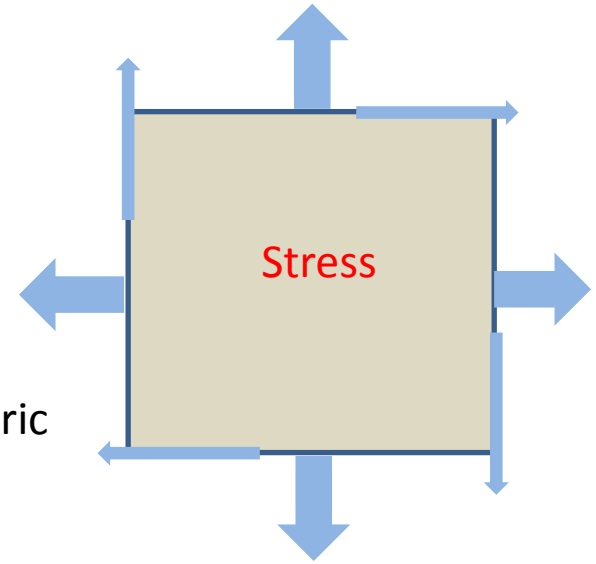
Tensor of piezoelectric coefficients

Direct piezoelectric effect

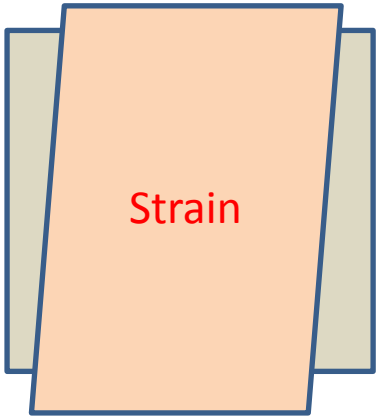


$$P_k = d_{kij}\sigma_{ij}$$

Third-rank tensor of direct piezoelectric effect

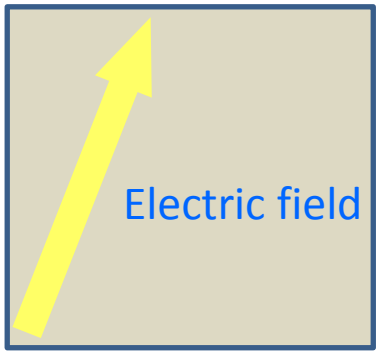


Converse piezoelectric effect

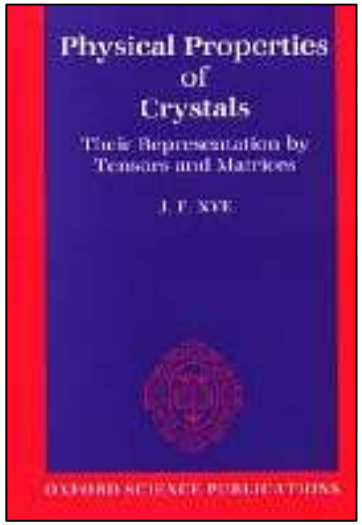


$$\epsilon_{ij} = d_{kij}E_k$$

Third-rank tensor of converse piezoelectric effect



Properties of piezoelectric effect



a) Direct and converse effects are described by the <u>same</u> tensor [pC / N]. Follows from THERMODYNAMICS

b) Intrinsic symmetry

$$d_{kij} = d_{kji}$$

Nothing to do with a crystal symmetry

Tensor notations, *ij*	*11*	*22*	*33*	*23*	*13*	*12*
Voigt notations, m	*1*	*2*	*3*	*4*	*5*	*6*

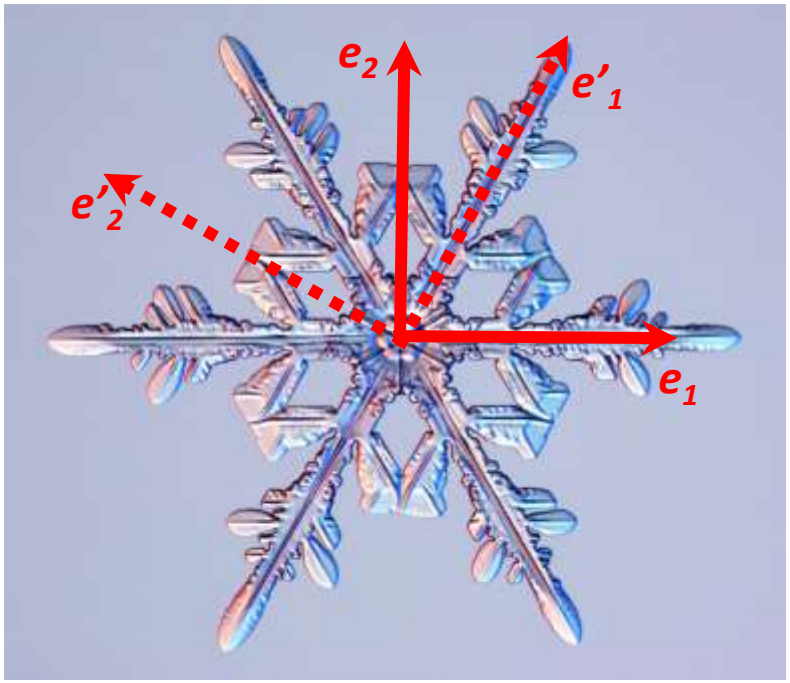
$$[d_{km}] = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix}$$

18 independent piezoelectric constants

Piezoelectric effect / crystal symmetry

Neumann's principle:

If a crystal is invariant with respect to a certain symmetry operations, any of its physical properties must also be invariant with respect to the same symmetry operations



Relative to $\{\boldsymbol{e}'_n\}$ $\boxed{d'_{ijk}} = \boxed{d_{ijk}}$ Relative to $\{\boldsymbol{e}_n\}$

The matrix of transformation between the coordinate systems, $[a_{ij}]$:

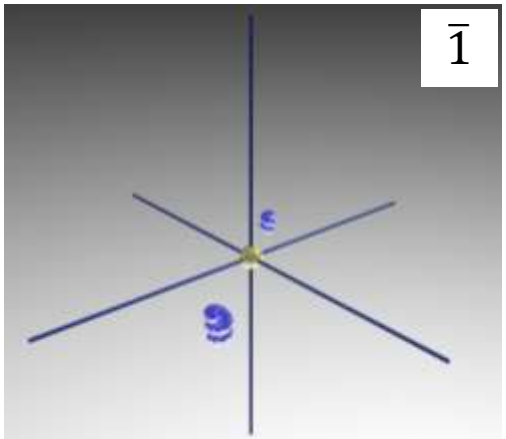
$$\boldsymbol{e}'_i = a_{ij}\boldsymbol{e}_j$$

Mathematical expression of Neumann's principle

$$d_{ijk} = a_{ii_1}a_{jj_1}a_{kk_1}d_{i_1j_1k_1}$$

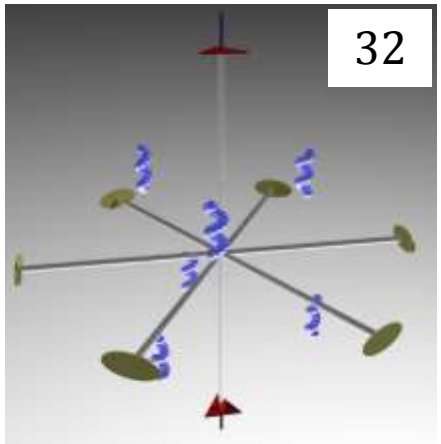
Piezoelectric effect / crystal symmetry

Centrosymmetric point group



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

α-quartz



$$\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

11 centrosymmetric (Laue) point groups

432

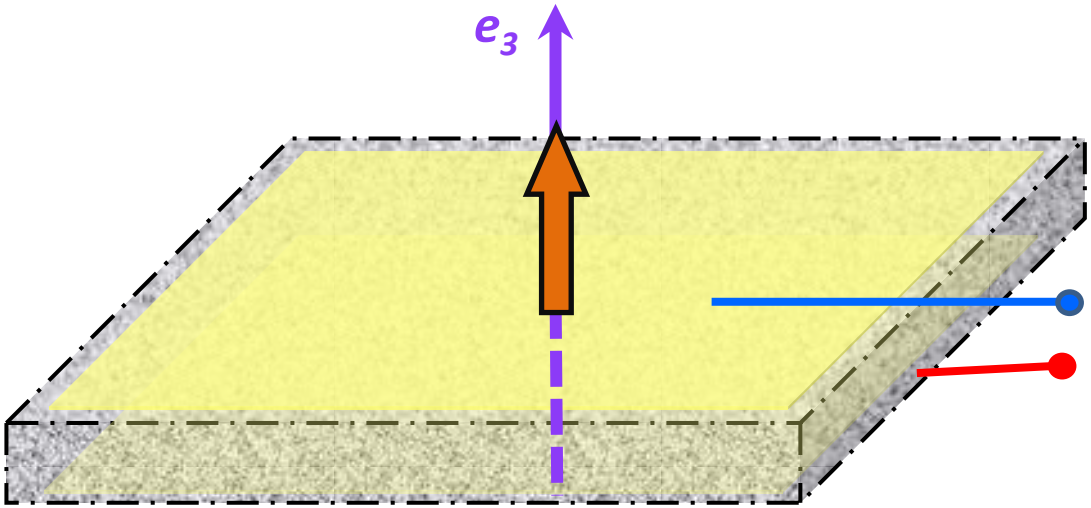
21 non-centrosymmetric point groups

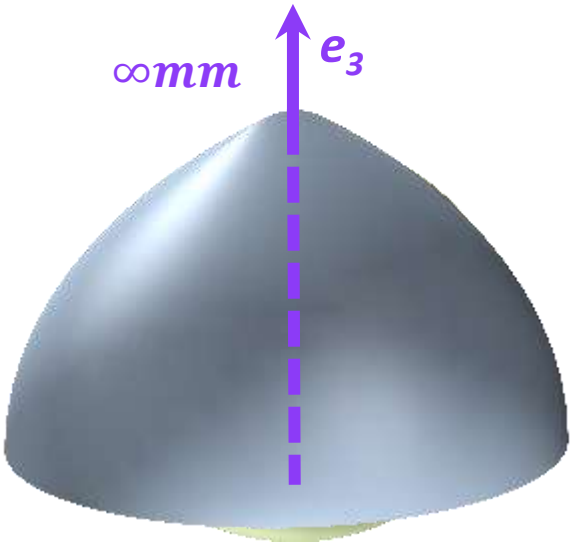
10 polar classes:
1, m, 2, mm2, 4, 4mm, 3, 3m, 6, 6mm

20 piezoelectric point groups

Piezoelectric ceramics (point group ∞mm)

…is a powder, which can be artificially made piezoelectric by poling. The most notorious example of ferroelectric ceramics is $PbZr_{1-x}Ti_xO_3$ (PZT)





Material remains poled (even after electric field is removed)

$$[d_{km}] = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ \boldsymbol{d_{31}} & \boldsymbol{d_{32}} & \boldsymbol{d_{33}} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{pmatrix}$$

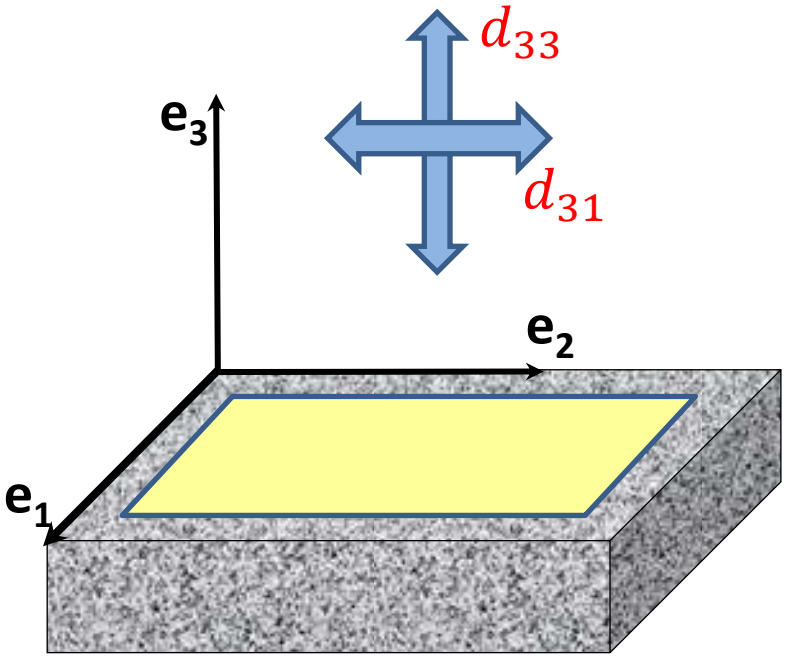
$$d_{31} = d_{32}$$

$$d_{24} = d_{15}$$

The meaning of d_{31} and d_{33}

$$[d_{km}] = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ \boldsymbol{d_{31}} & \boldsymbol{d_{31}} & \boldsymbol{d_{33}} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{pmatrix}$$

$$\epsilon_m = d_{km} E_k$$



Assume that electric field is applied along the polar axis

$$[\epsilon_{ij}] = \begin{pmatrix} d_{31}E & 0 & 0 \\ 0 & d_{31}E & 0 \\ 0 & 0 & d_{33}E \end{pmatrix}$$

Application of piezoelectric effect

- Pressure sensors
- Actuators
- Piezo motors
- Car fuel injectors
- Frequency generators

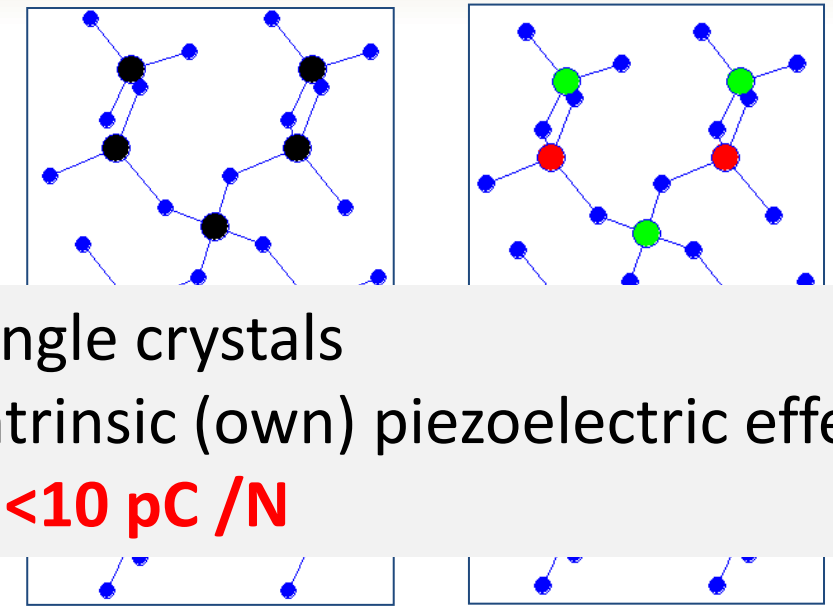
There is a permanent request to design new piezoelectrics for example environmentally friendly alternatives to the currently dominating PZT.

The global market of piezoelectric devices in 2014 is estimated as €9.7 billion with the annual growth rate of 13.2 %.

- *Luminous dance floors*

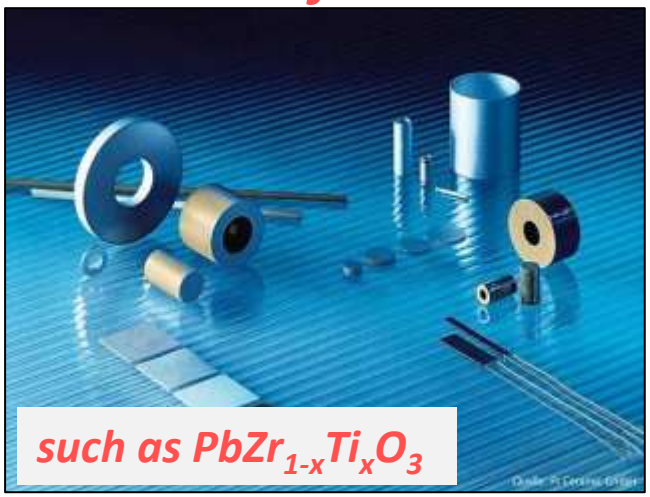
What stands behind a piezoelectricity

Natural



- Single crystals
- Intrinsic (own) piezoelectric effect
- **d <10 pC /N**

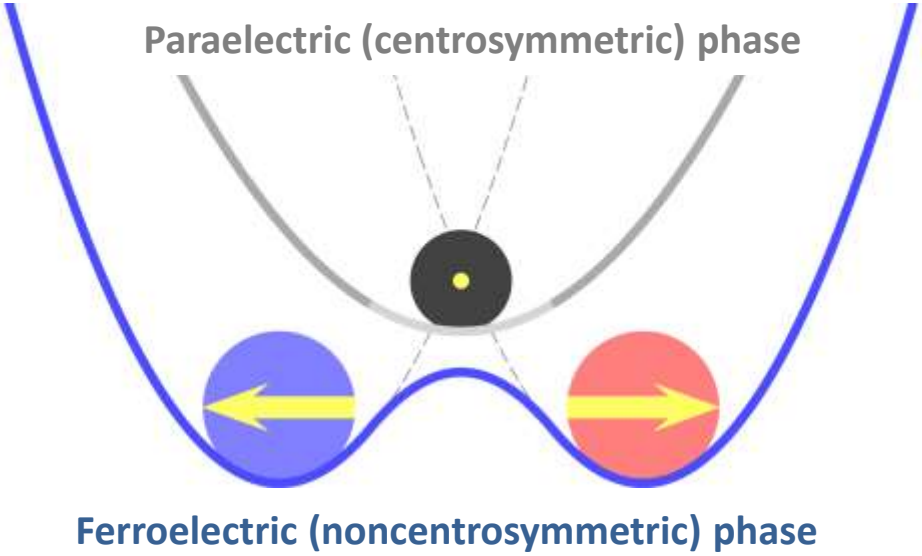
Artificial



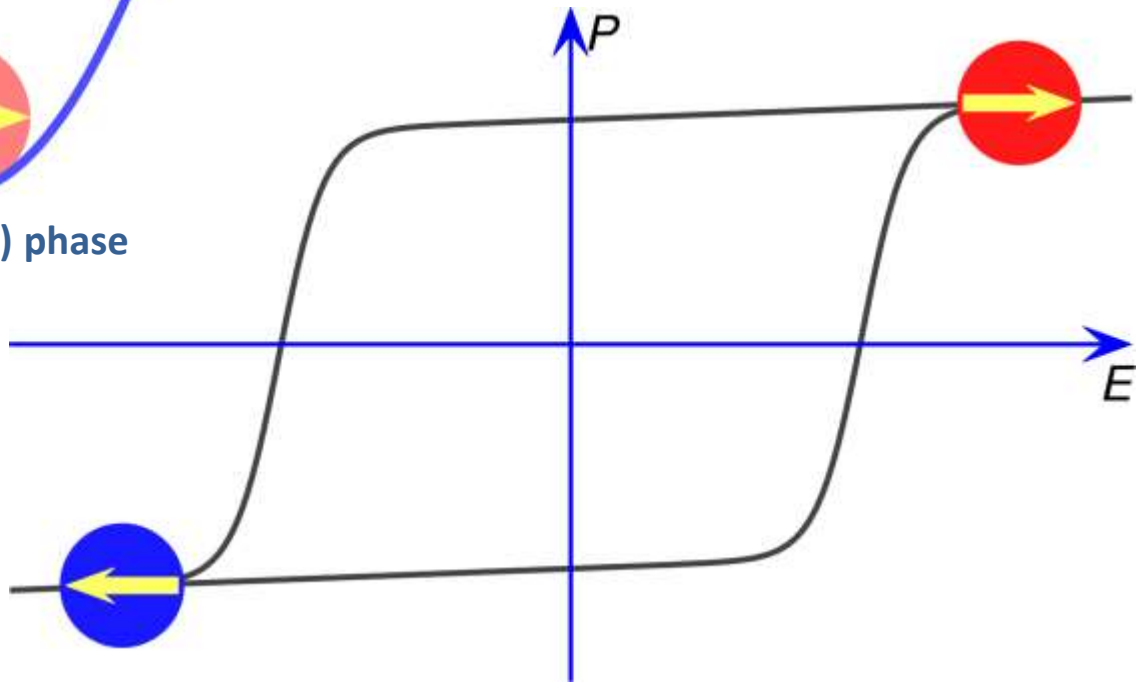
- Powders / ceramics
- **d ~ 100 – 2000 pC /N**
- Lower stability
- Toxic (lead based)
- <u>Ferroelectric</u>

Ferroelectrics

…the materials in which two (or more) spontaneous polarization states can be switched by an external electric field



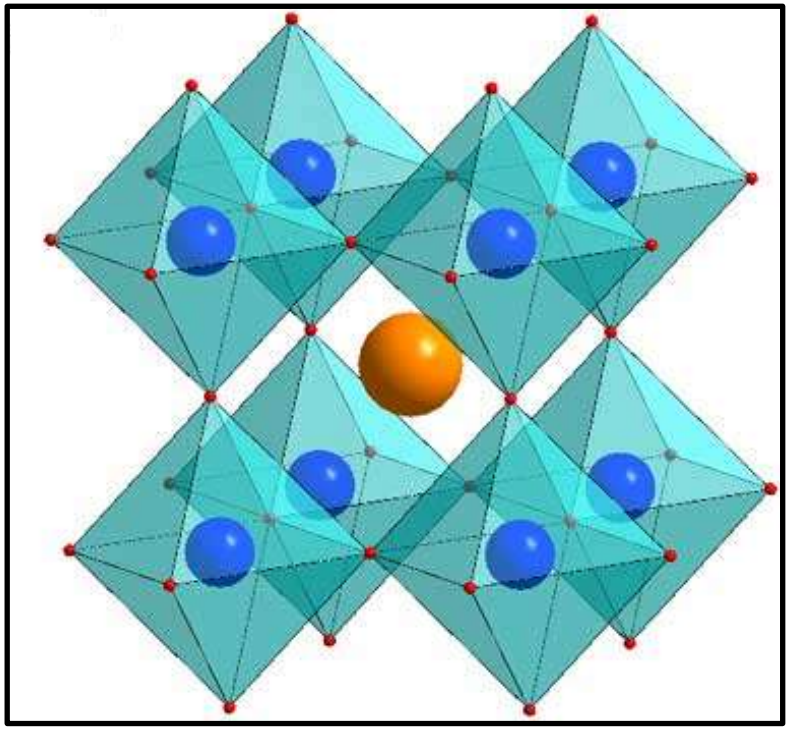
The switching between pure domain states in ferroelectrics is described by a hysteresis loop



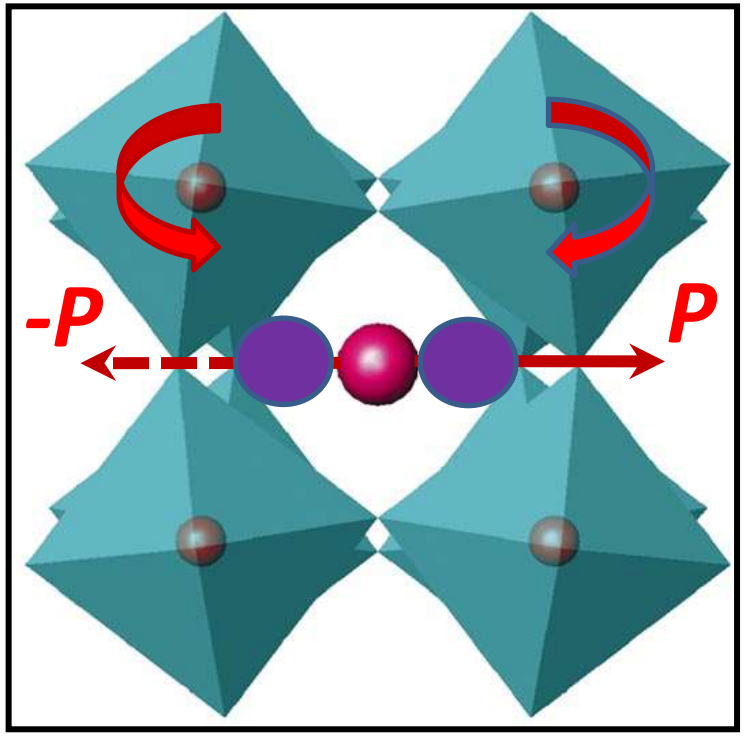
Ferroelectric perovskites

High-temperature | **Low temperature**

Ideal perovskite structure, cubic symmetry ($Pm\bar{3}m$).



Distorted perovskite structure, lower symmetry ($R3c$, $P4bm$,...):



The development of macroscopic polarization is combined with the development of strain

Development of a macroscopic strain

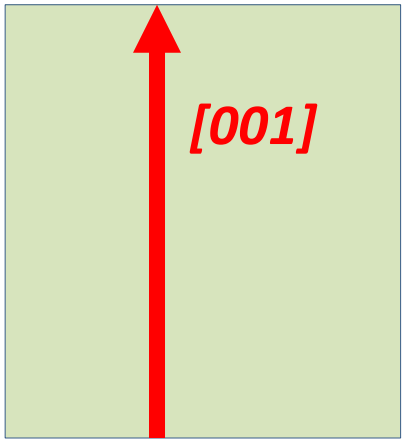
High-temperature

Cubic $(Pm\bar{3}m)$

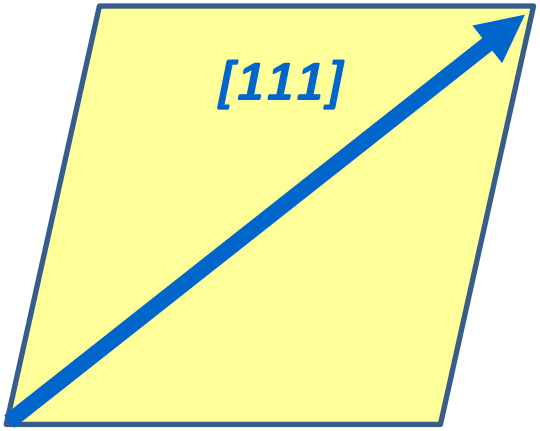
$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Low temperature

Tetragonal $(P4mm)$



$$\begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$$



$$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{12} \\ \epsilon_{12} & \epsilon_{11} & \epsilon_{12} \\ \epsilon_{12} & \epsilon_{12} & \epsilon_{11} \end{pmatrix}$$

Rhombohedral $(R3m)$

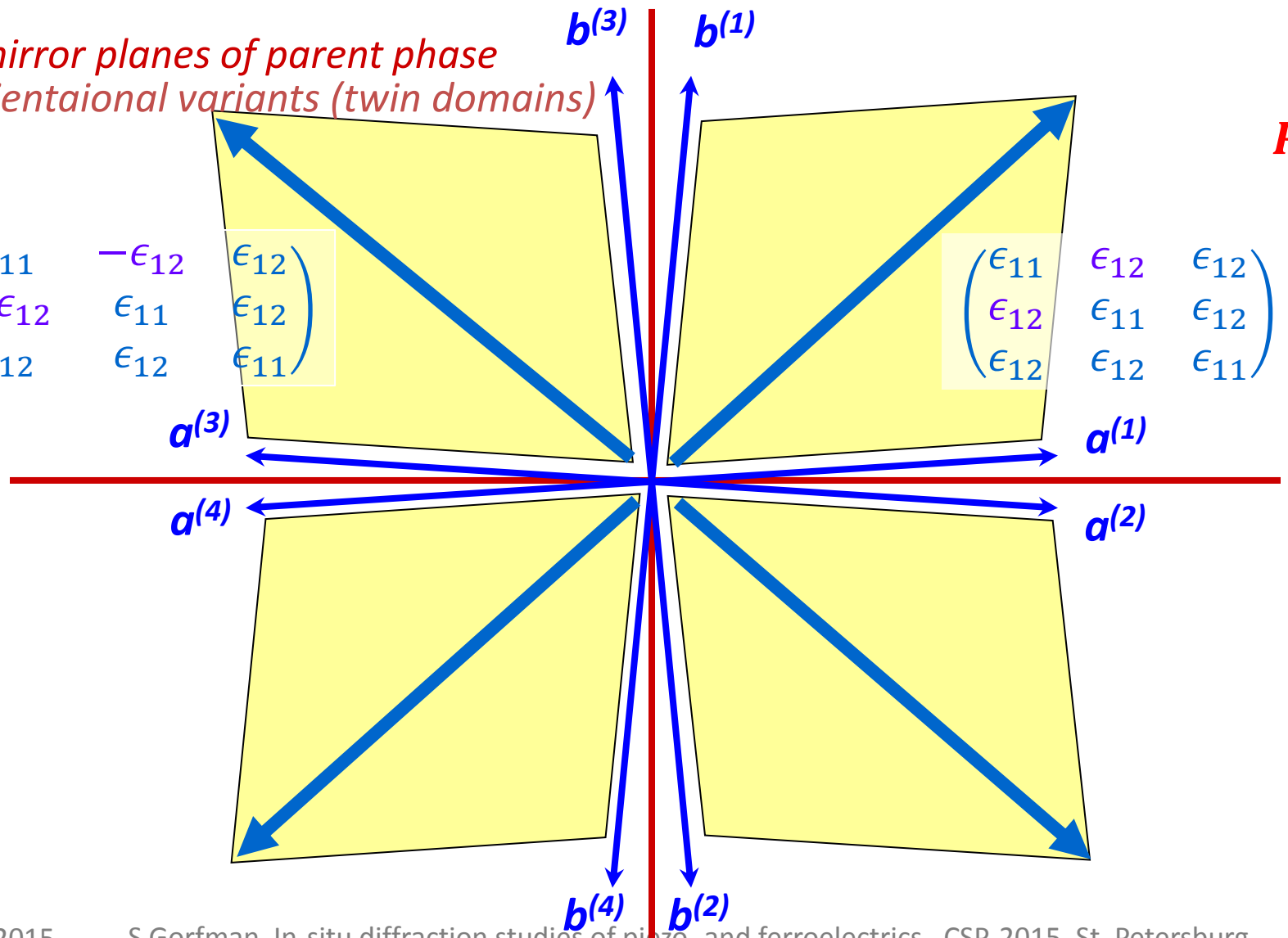
Formation of ferroelectric / ferroelastic domains (2D case)

mirror planes of parent phase

Orientaional variants (twin domains)

$$\begin{pmatrix} \epsilon_{11} & -\epsilon_{12} & \epsilon_{12} \\ -\epsilon_{12} & \epsilon_{11} & \epsilon_{12} \\ \epsilon_{12} & \epsilon_{12} & \epsilon_{11} \end{pmatrix}$$

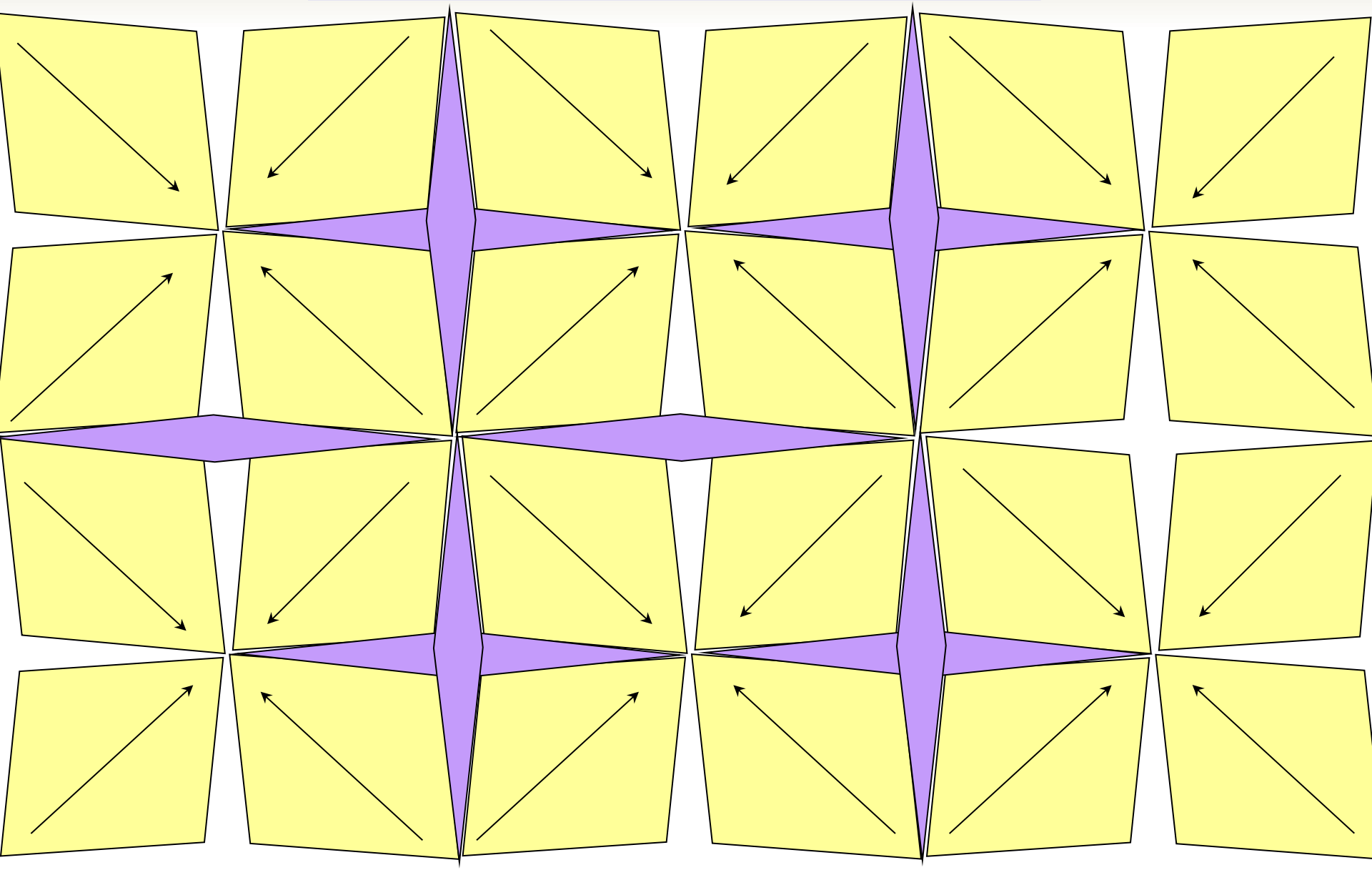
$$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{12} \\ \epsilon_{12} & \epsilon_{11} & \epsilon_{12} \\ \epsilon_{12} & \epsilon_{12} & \epsilon_{11} \end{pmatrix}$$



$Pm\bar{3}m$

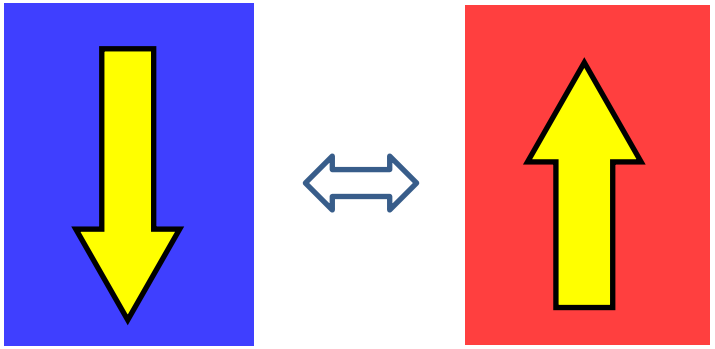
$R3m$

Example of domain pattern



Classification of ferroic domains

180˚ (inversion) domain patterns / uniaxial ferroelectrics

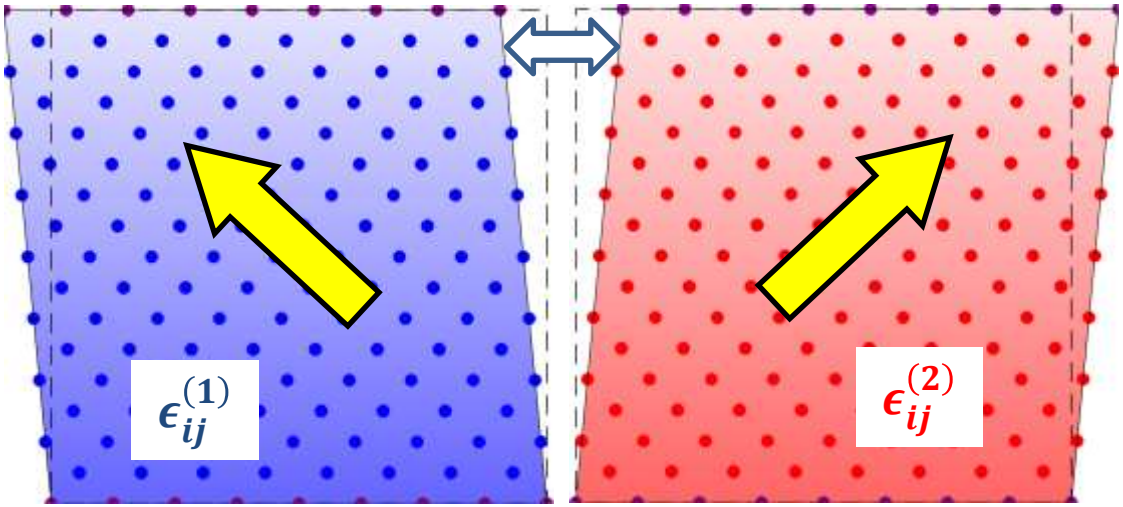


$\epsilon_{ij}^{(1)} = \epsilon_{ij}^{(2)}$

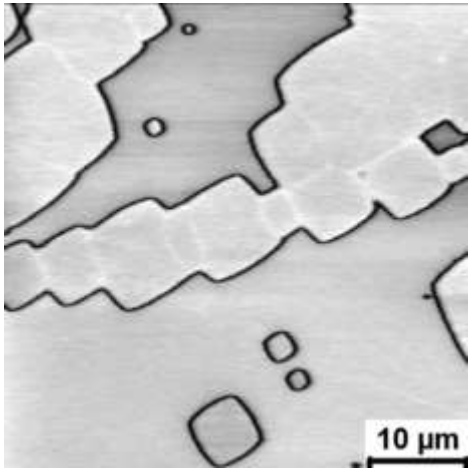
No strain relationship between domains. Domain switching does not affect the shape of the sample

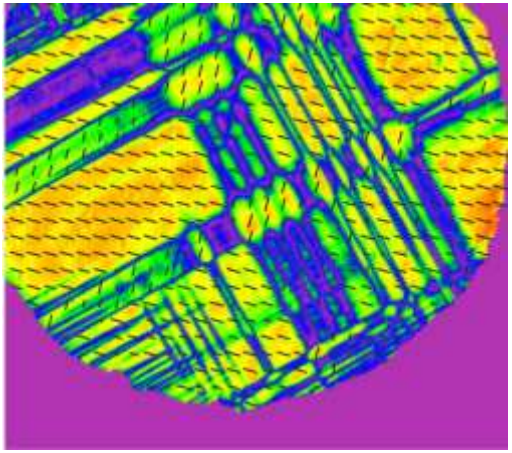
Non-180˚ (ferroelastic) domain

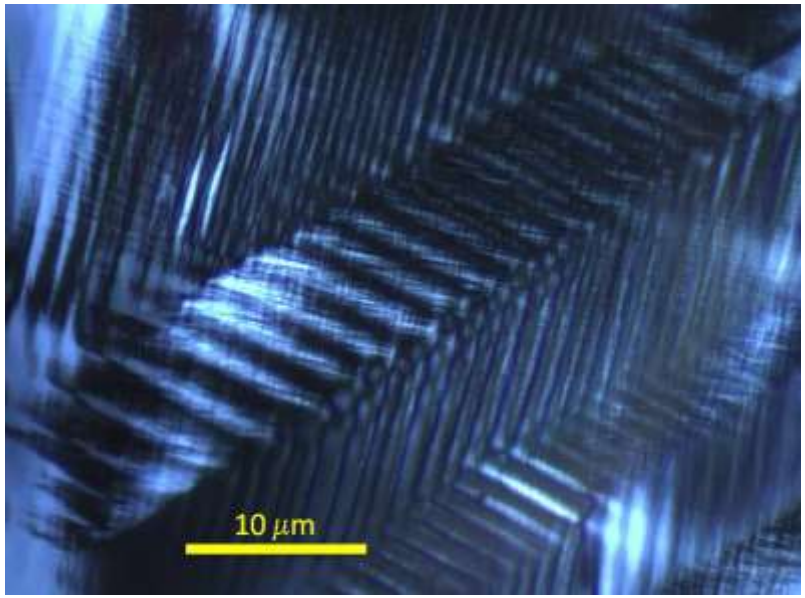
Domains are deformed relative to each other. Domain switching causes mechanical deformation

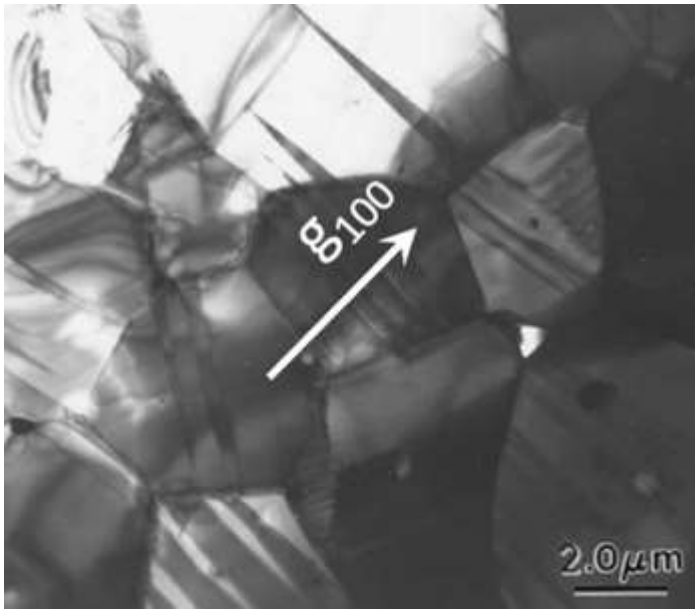


Examples of real domain structures in ferroelectrics





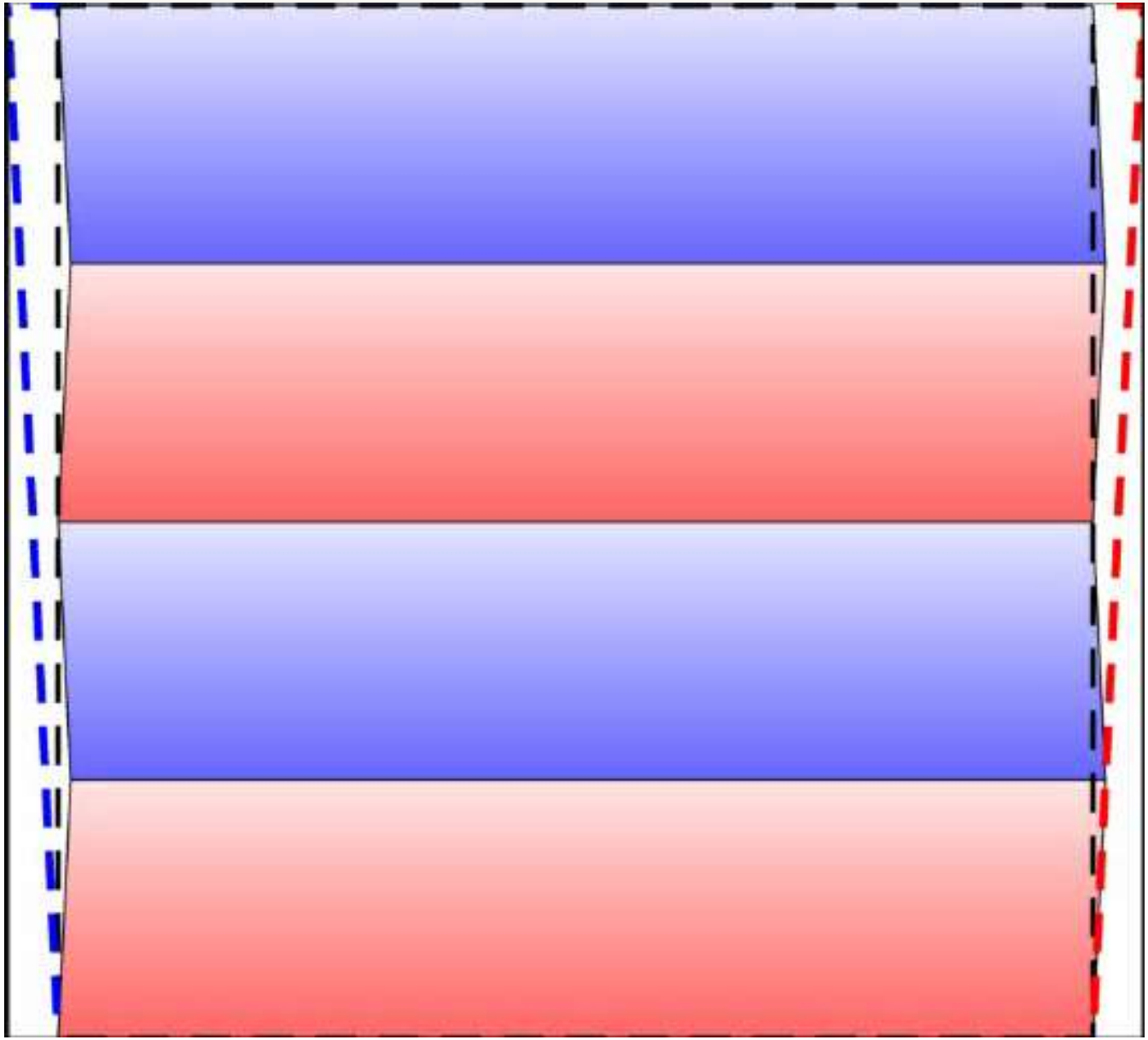




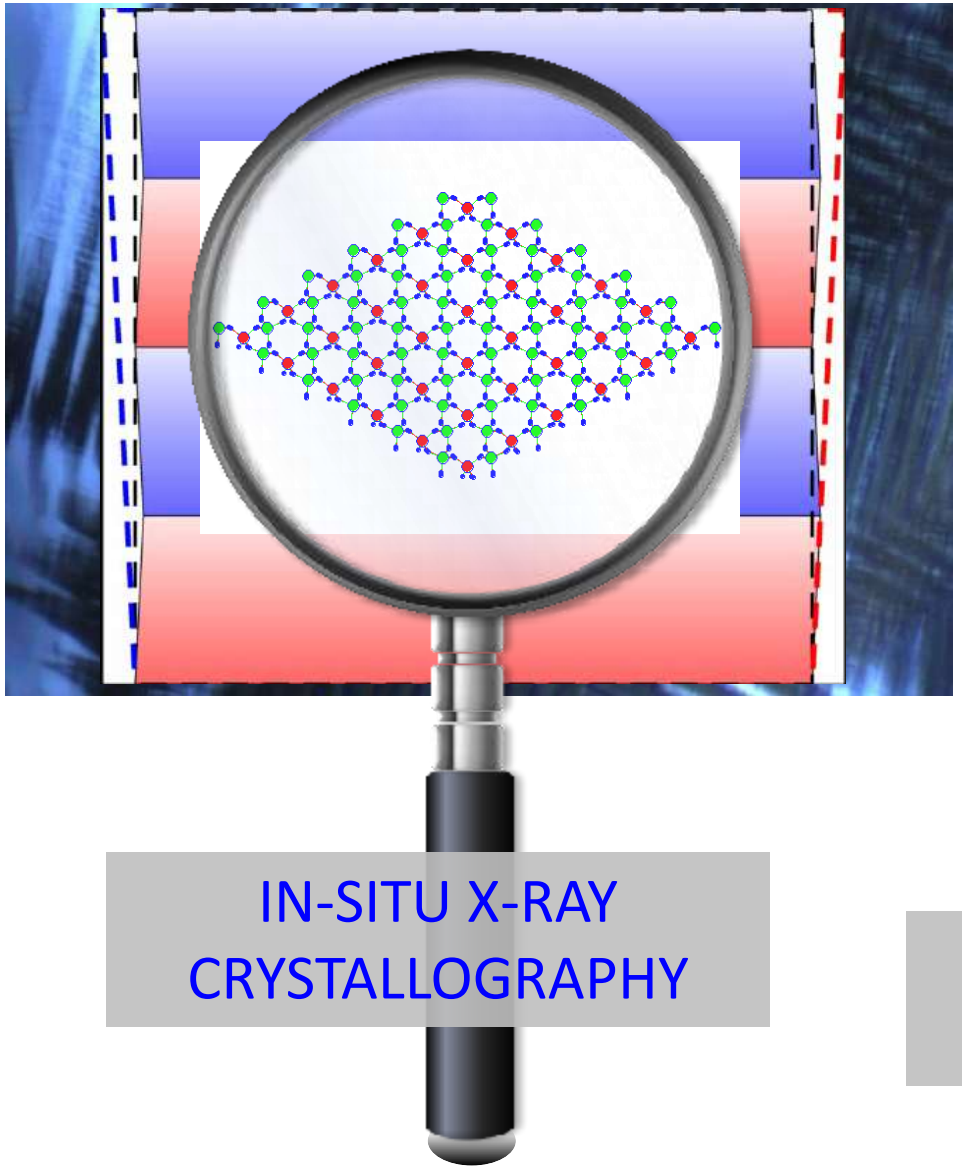
Wu et al. J Eur Ceram Soc, 35 (2015)
Shur et al. J Appl Phys 112, 064117 (2012)
*Shwartsman et al. Phys Rev B**77**, 054105, (2008)*

- ***Polarized light /birefringence microscopy***
- ***Confocal Raman scattering***
- ***Transmission electron microscopy***
- ***Piezoresponse force microscopy***

Deformation, mediated by a domain wall motion



What exactly drives piezoelectricity?

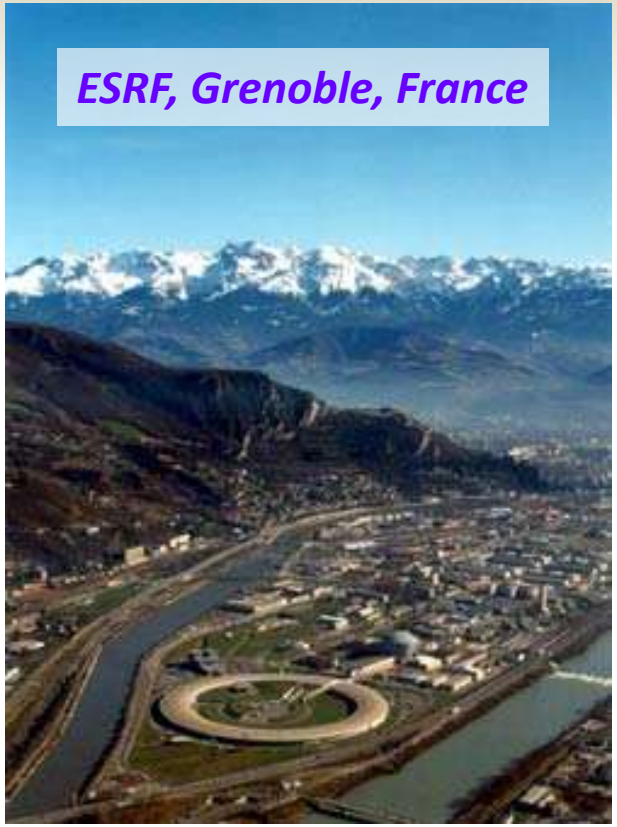


IN-SITU X-RAY CRYSTALLOGRAPHY

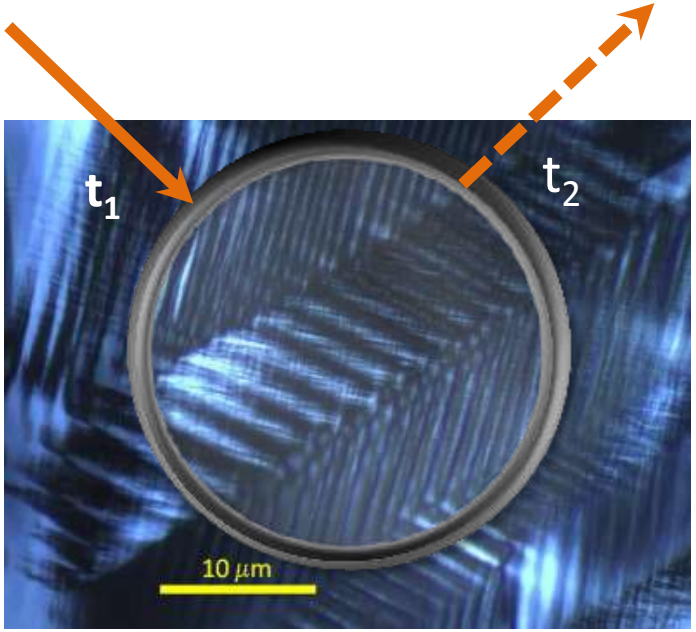
- Probing bulk of a material, macroscopic multi-domain volumes
- Domains resolving power
- Average domain sizes
- Macroscopic strain (lattice parameters)
- Atomic positions

IN-SITU (AS IT HAPPENS) UNDER ELECTRIC FIELD

Modern tools: synchrotrons



Probing the bulk / penetration depth

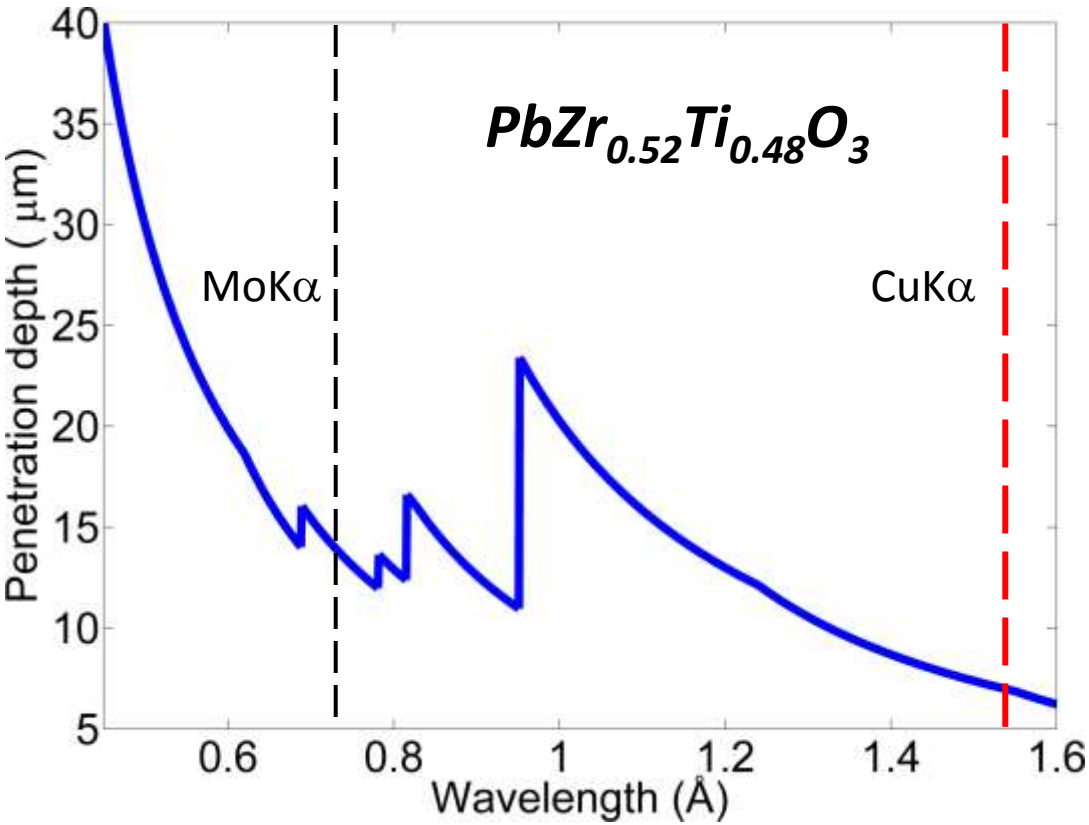


$$I = I_0 \cdot \exp(-\mu \cdot (t_1 + t_2))$$

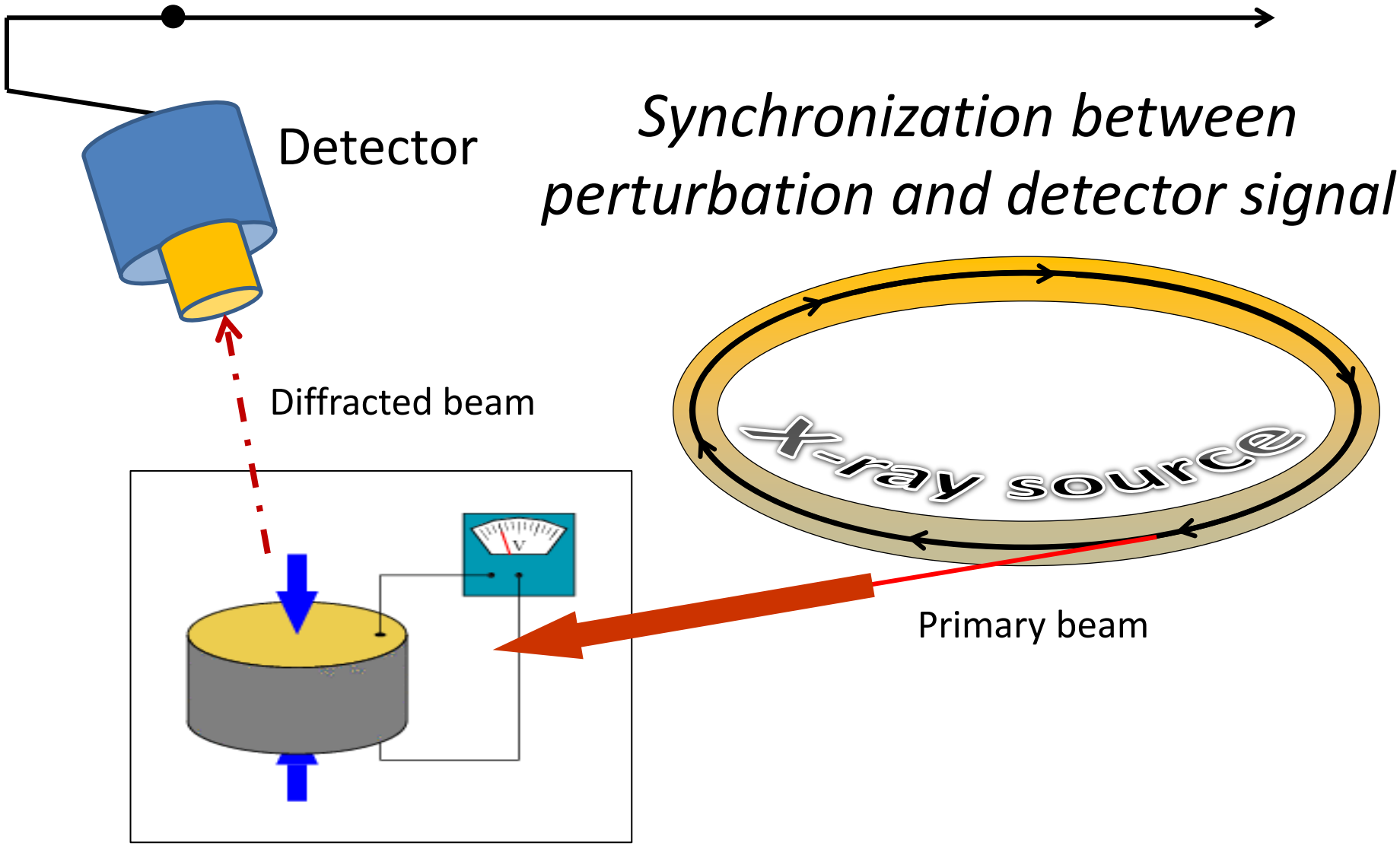
X-ray attenuation coefficient

Beam path through a sample

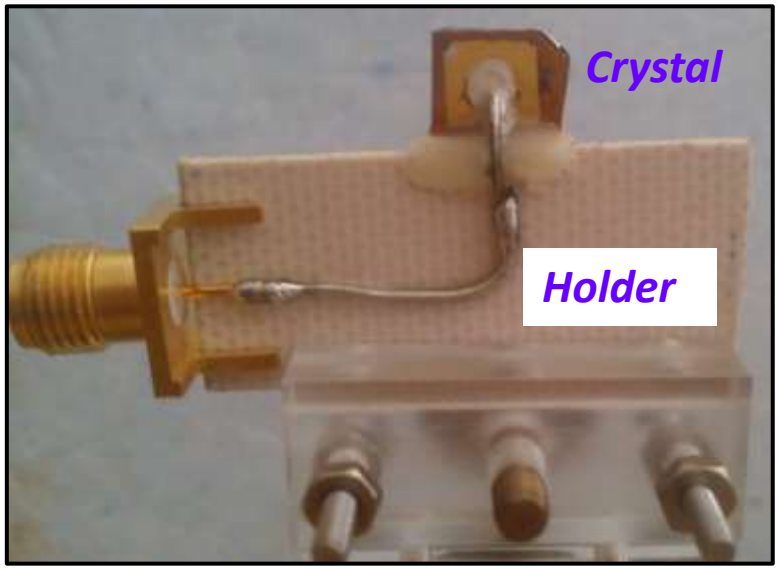
Synchrotron radiation –> bulk

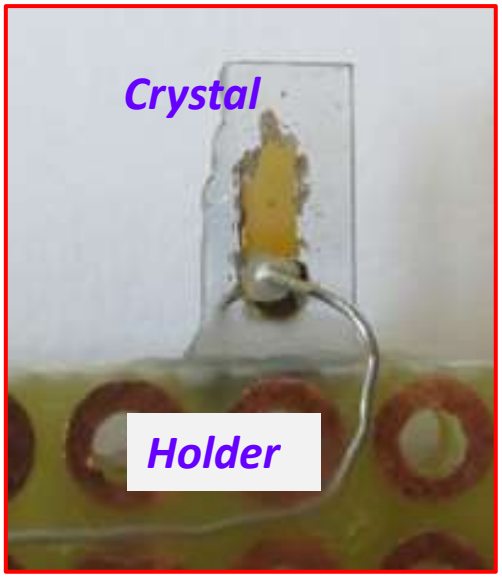


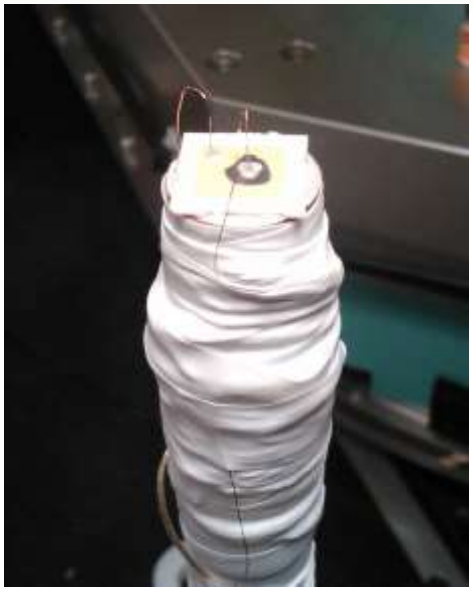
In situ X-ray diffraction

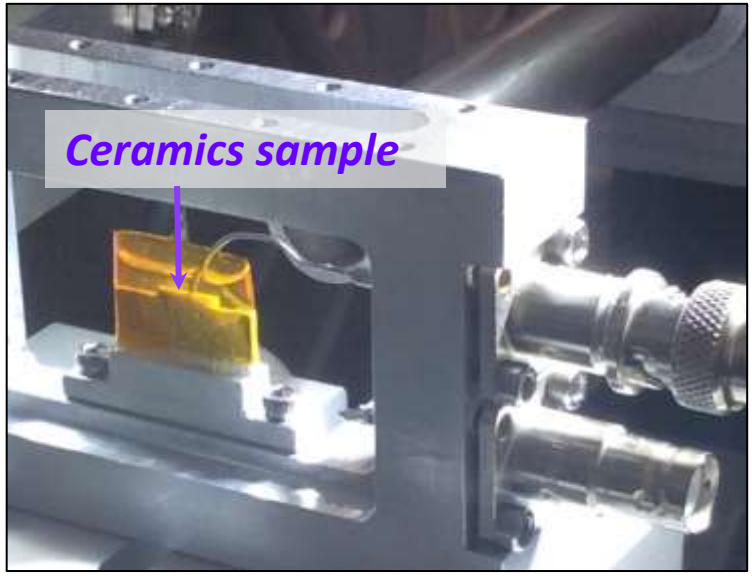


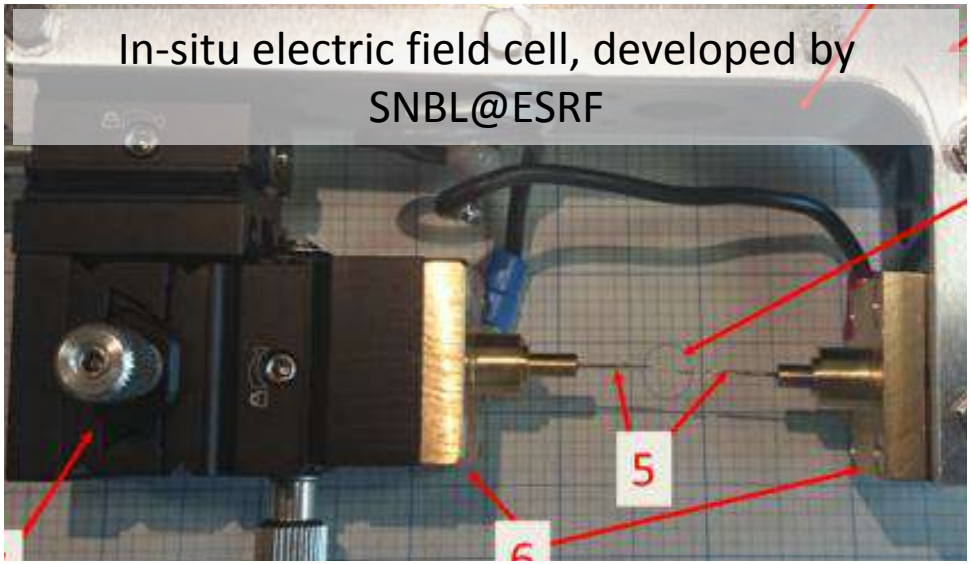
Application of electric field



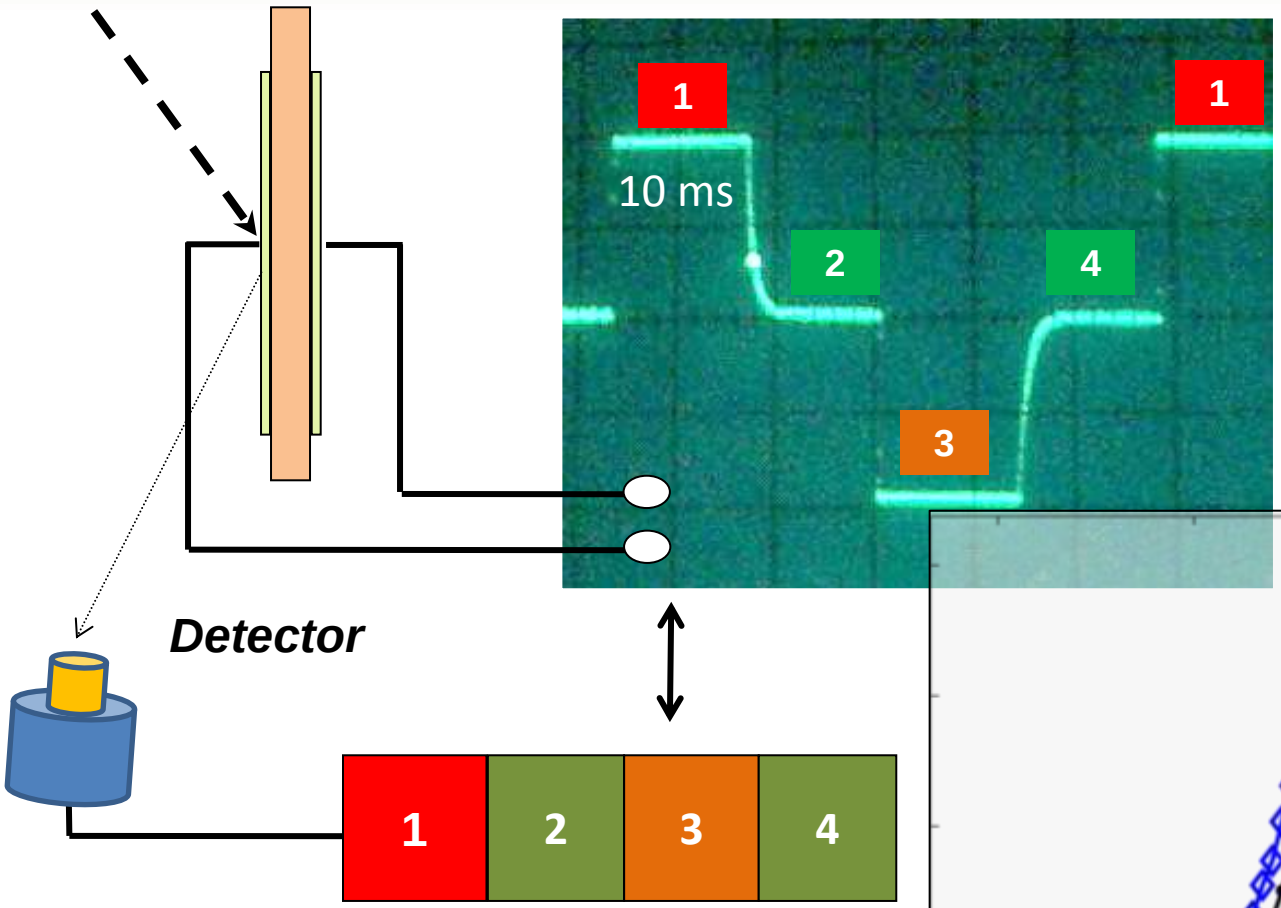






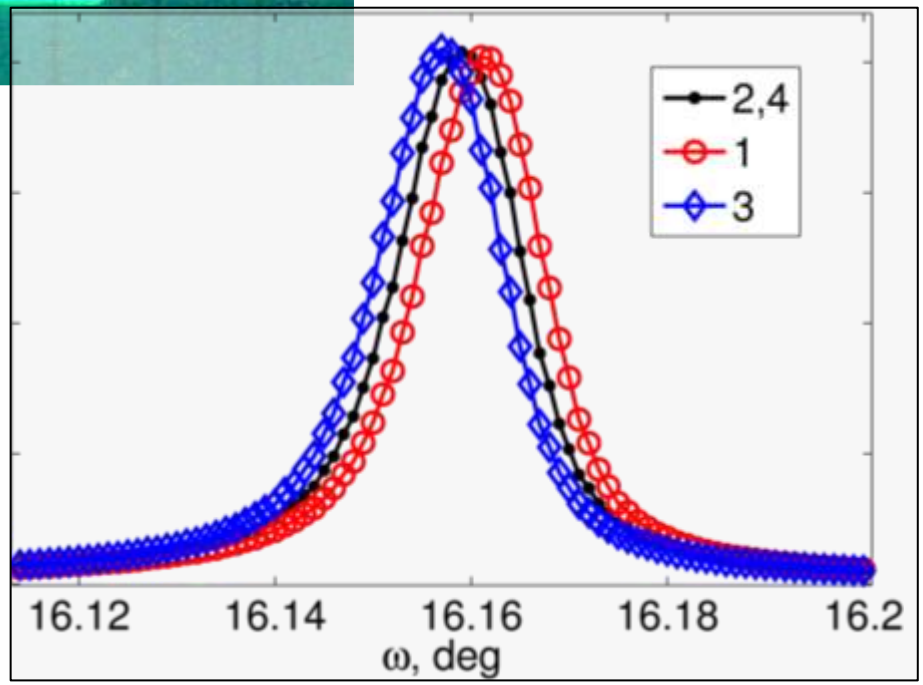


The principle of stroboscopic data collection



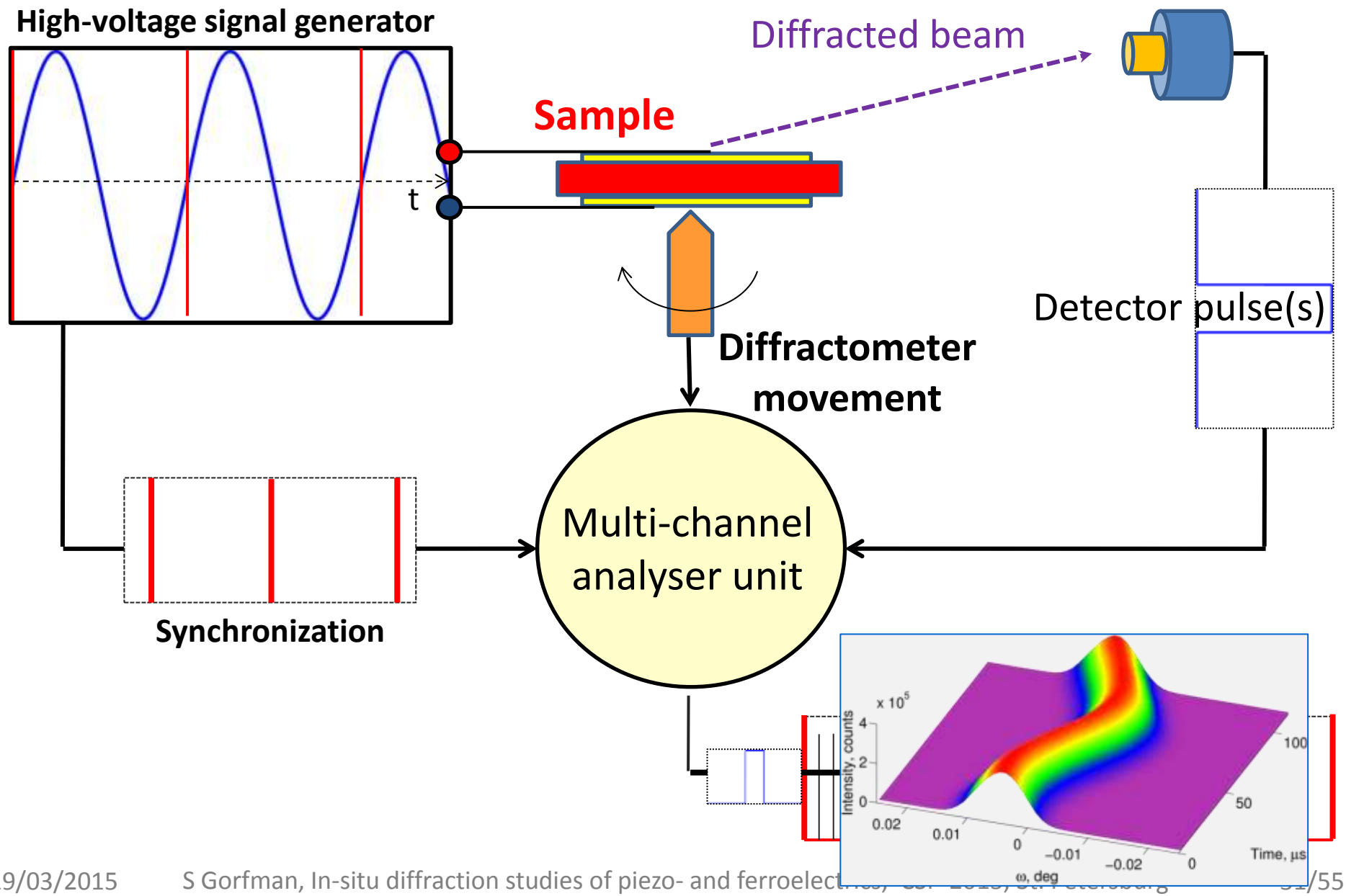
Electric field is applied periodically

Detector counts are time-stamped and redistributed between multiple channels



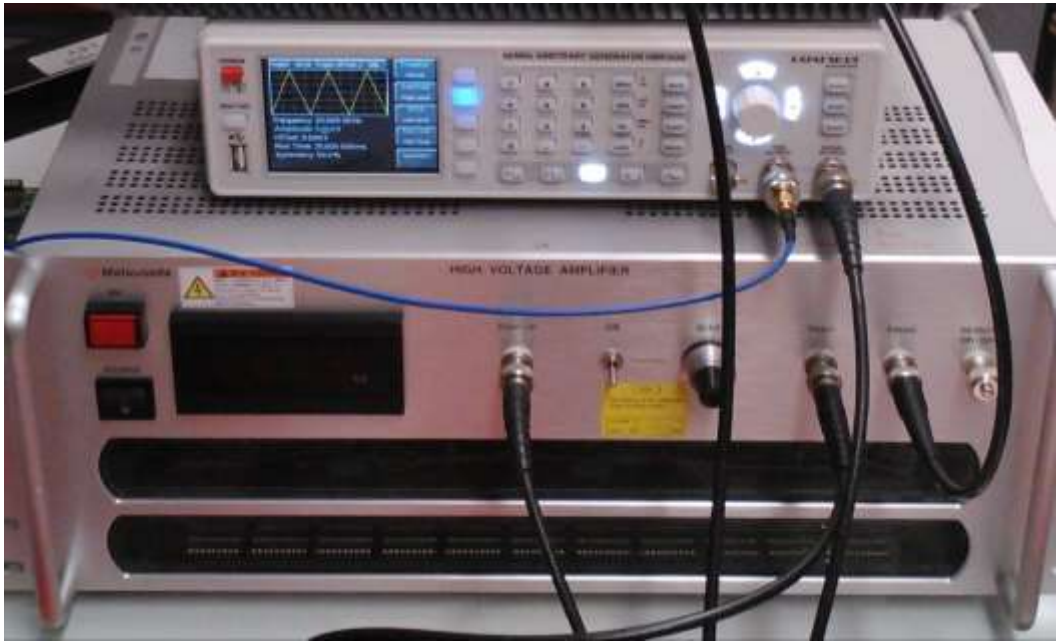
Systematics / Repetitive changes only

Modern realization of stroboscopic experiement



Experimental equipment

- Single crystal four circle diffractometer
- High-resolution powder diffraction

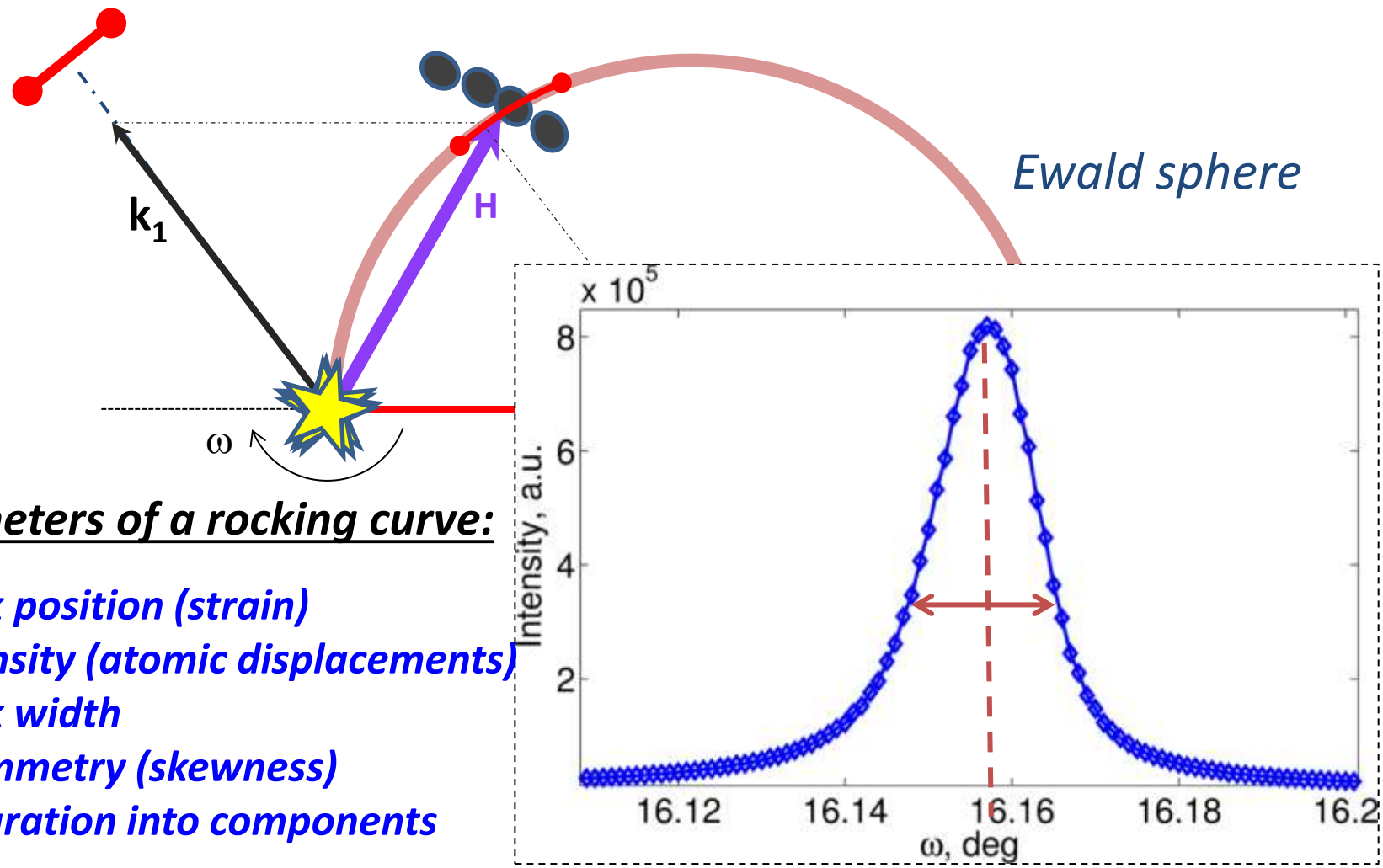


- ***Function generator***
- ***High-voltage amplifier***
- ***Multi-channel analyser***
- ***Voltage monitor***
- ***Current monitor***
- ***Point detector***

Single crystal X-ray diffraction: rocking curve

Point detector

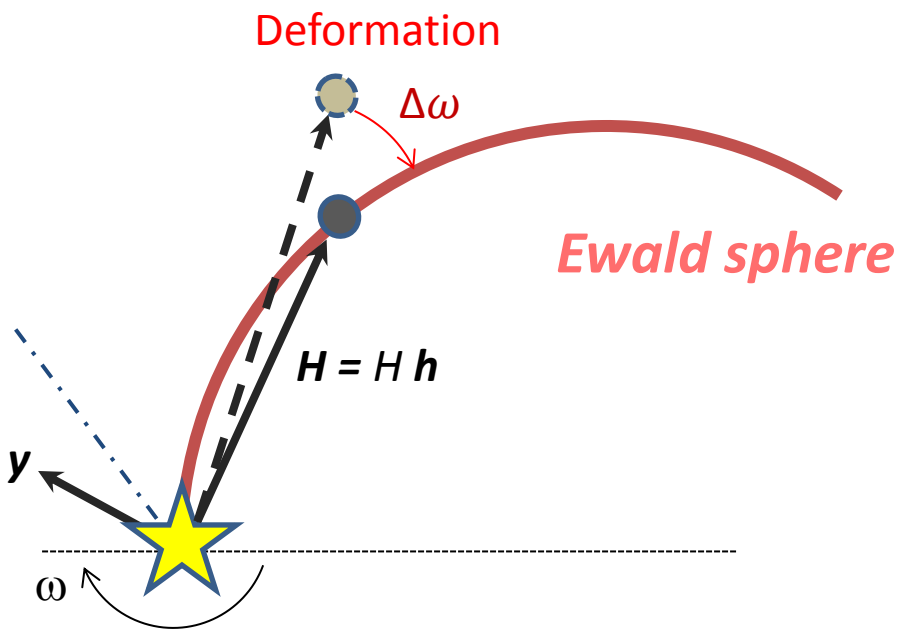
Reciprocal lattice vector

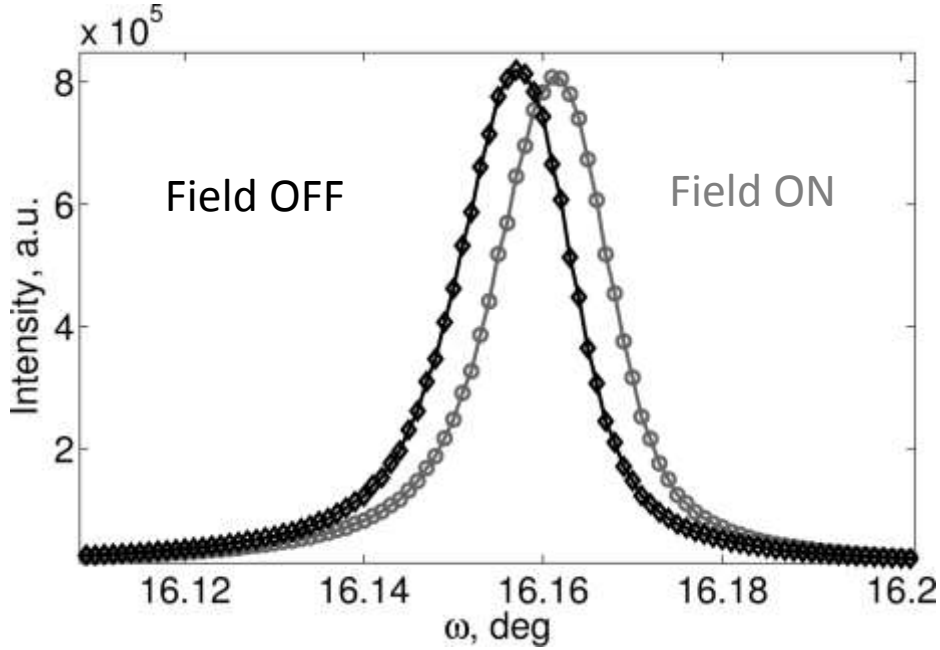


Parameters of a rocking curve:

- ***Peak position (strain)***
- ***Intensity (atomic displacements)***
- ***Peak width***
- ***Asymmetry (skewness)***
- ***Separation into components***

Determination of field induced strain





S. Gorfman, O. Schmidt, U. Pietsch, L. Bohaty and P. Becker. Z. Krist. 222 (2007), 396-401

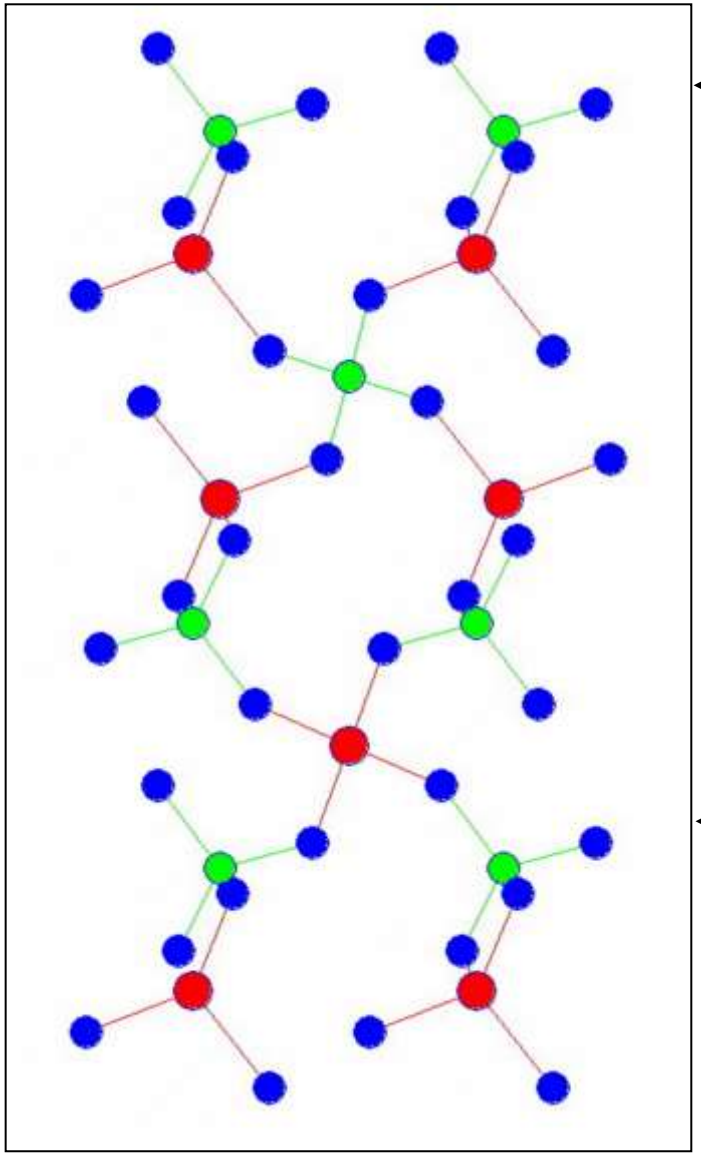
$$\Delta\omega = -tan\theta\,\epsilon_{ij}h_ih_j - \epsilon_{ij}h_iy_j + r_{ij}h_iy_j$$

Components of strain tensor

Components of rotation tensor

Field induced peaks shifts → Strain → Piezoelectric constants

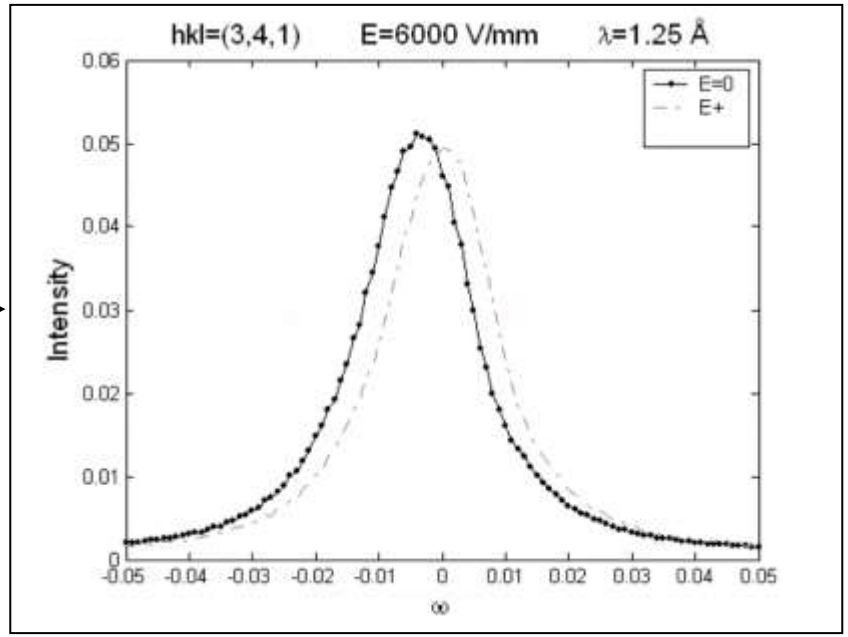
Accessing atomic displacements



$$F_E(H) = \sum_{\mu} f_\mu(\boldsymbol{H}) T_\mu(\boldsymbol{H}) \exp\{2\pi i \boldsymbol{H}(\boldsymbol{R}_\mu + \Delta \boldsymbol{R}_\mu)\}$$

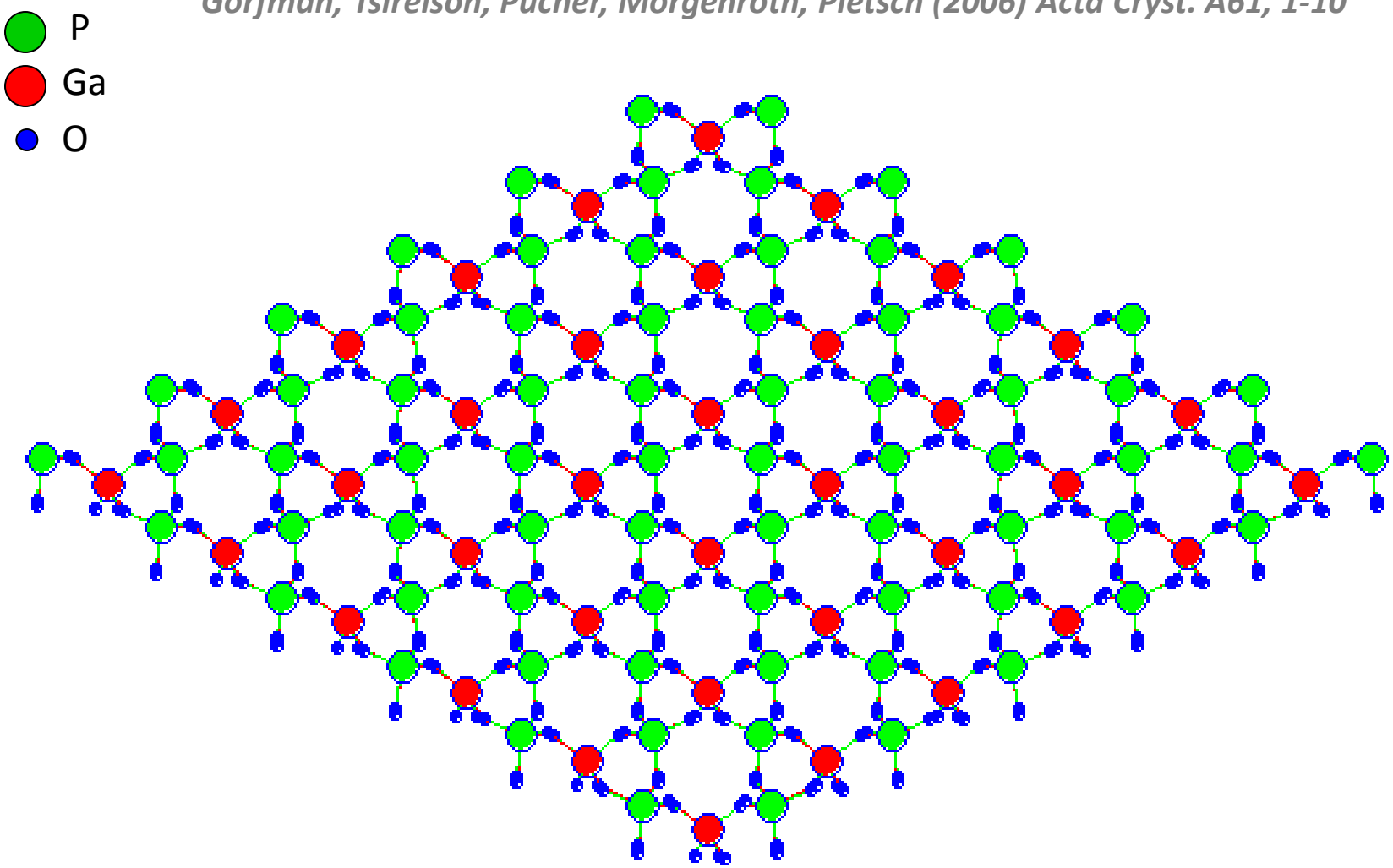
$$\frac{\Delta I}{I} = \frac{|F_E(\boldsymbol{H})|^2 - |F_0(\boldsymbol{H})|^2}{|F_0(\boldsymbol{H})|^2}$$

Intensity variation ↔ **Atomic displacements**



α-$GaPO_4$ ($P3_121$)

Gorfman, Tsirelson, Pucher, Morgenroth, Pietsch (2006) Acta Cryst. A61, 1-10



1000*Electric field (*E* = *4 kV/mm*) is applied in [110] direction

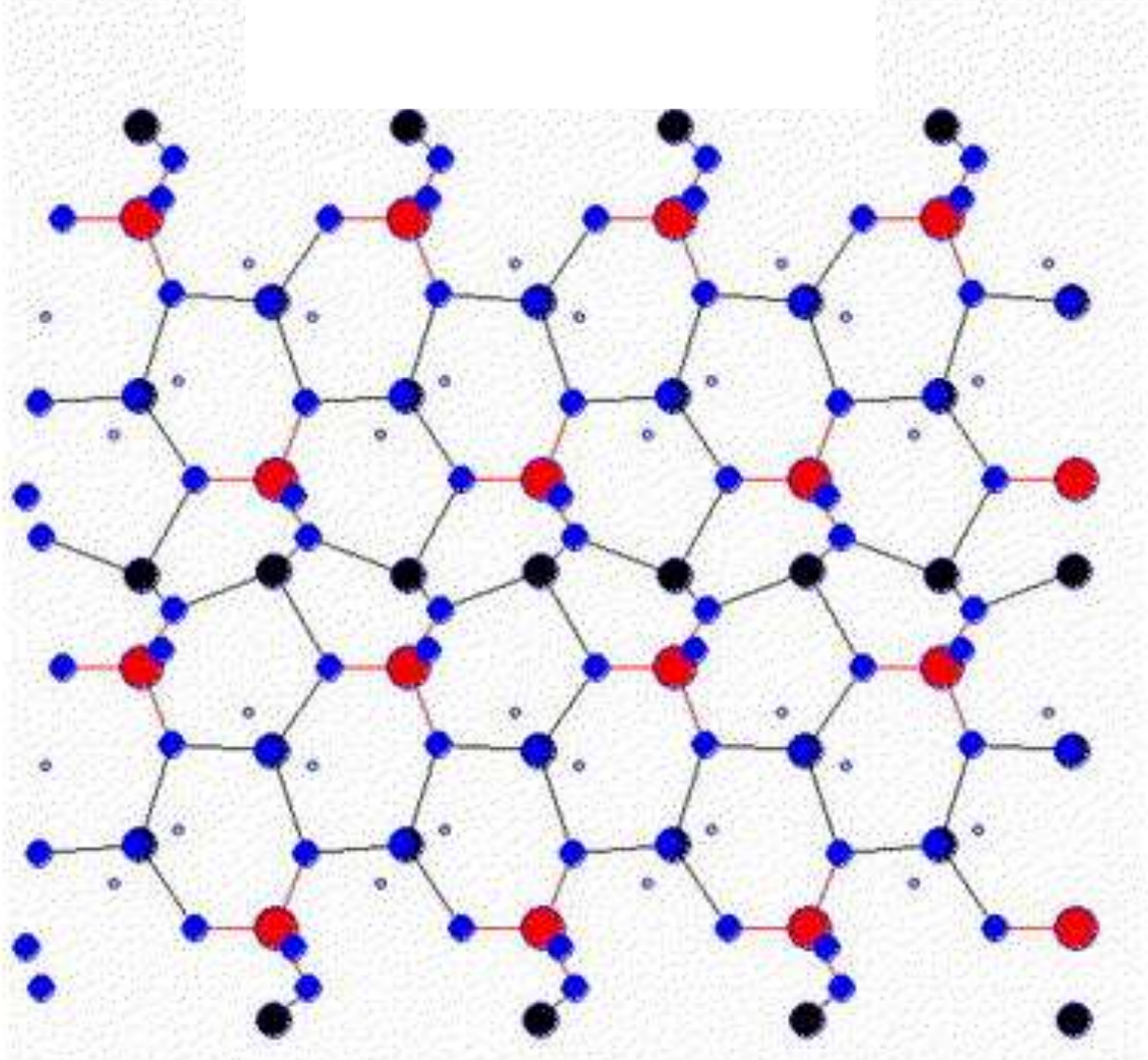
$Li_2SO_4 \cdot H_2O$ ($P2_1$)

Schmidt, Gorfman, Neumann, Engelen, Bohaty, Pietsch (2009) Acta Cryst A65, 267 - 275

S

O

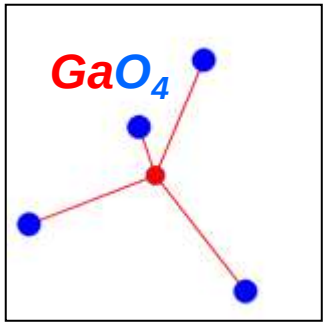
Li

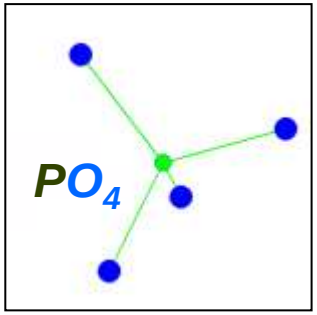


1000 * Electric field (E = 1 kV / mm) is applied along [010] direction

What do we learn from these results?

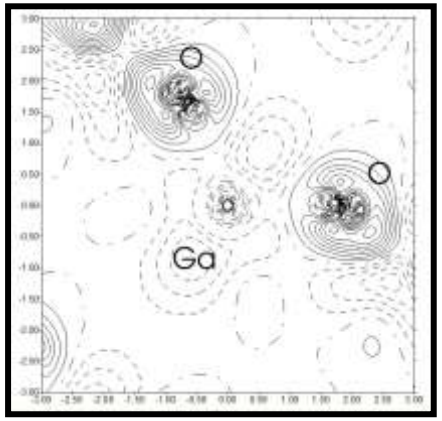
S. Gorfman, O. Schmidt, V. Tsirelson, M. Ziolkowski, U. Pietsch. ZAAC, 639(11), 1953 – 1962 (2013)





1. Characterizing individual structural units - *rotation* and deformation parts.

2. Evaluating individual bonds properties under external electric field.

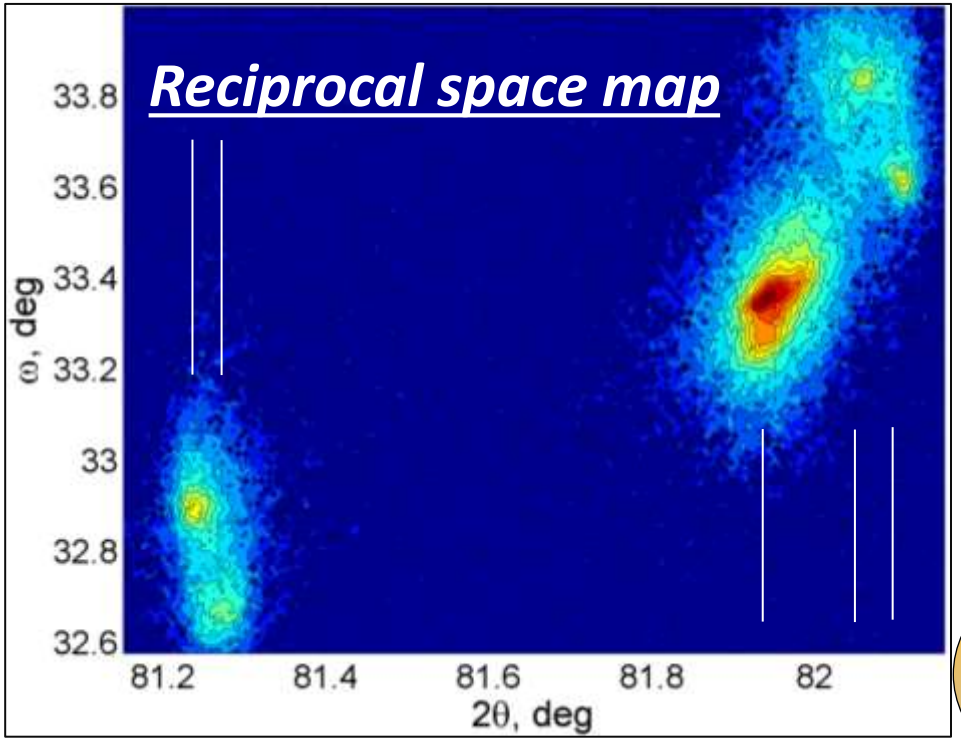


Δ(Ga-O) = $1.8\cdot10^{-5}$ Å / (kV/mm) Δ(P-O) = $4.1\cdot10^{-5}$ Å / (kV/mm)

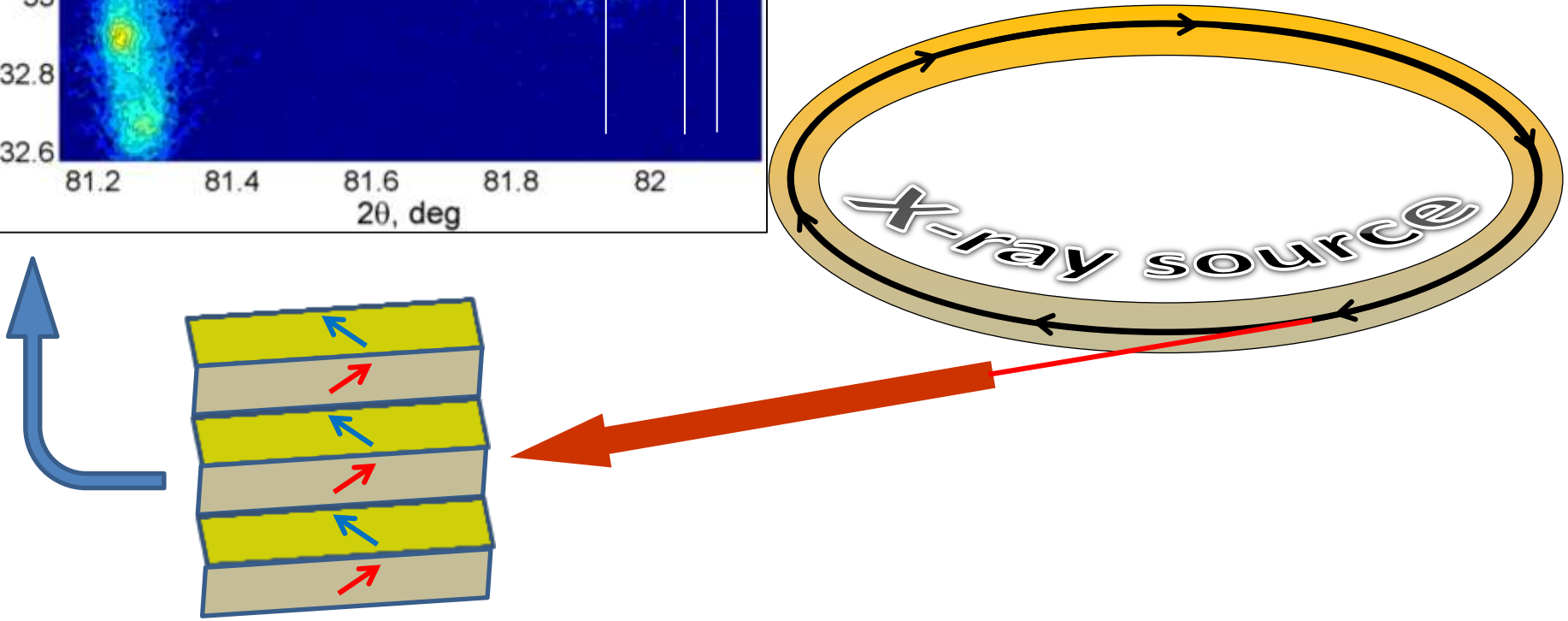
Δ(S-O) = $1.6\cdot10^{-5}$ Å / (kV/mm) Δ(Li-O) = $11.3\cdot10^{-5}$ Å / (kV/mm)

3. Comparing dynamics of bond distortion and piezoelectric deformation under external electric field. What happens first, what is the reason of what?

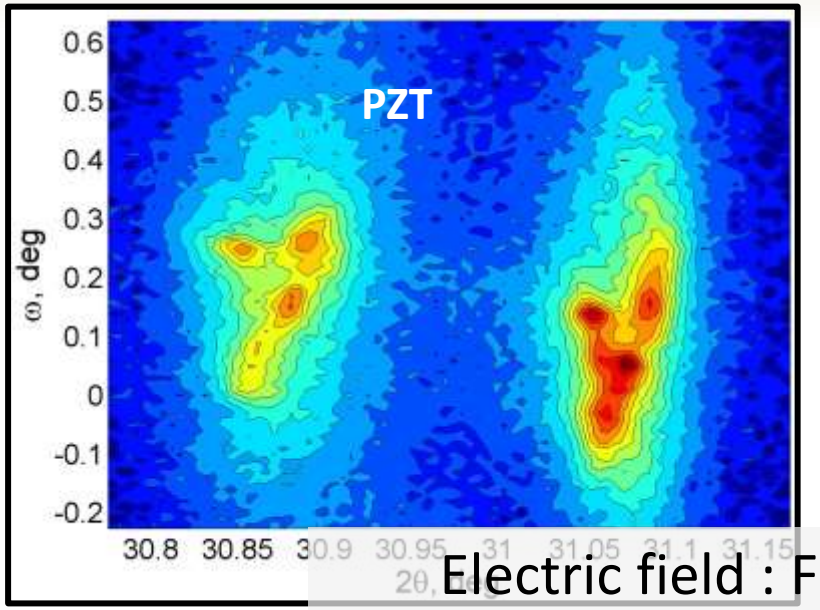
Diffraction from a multi-domain ferroelectrics

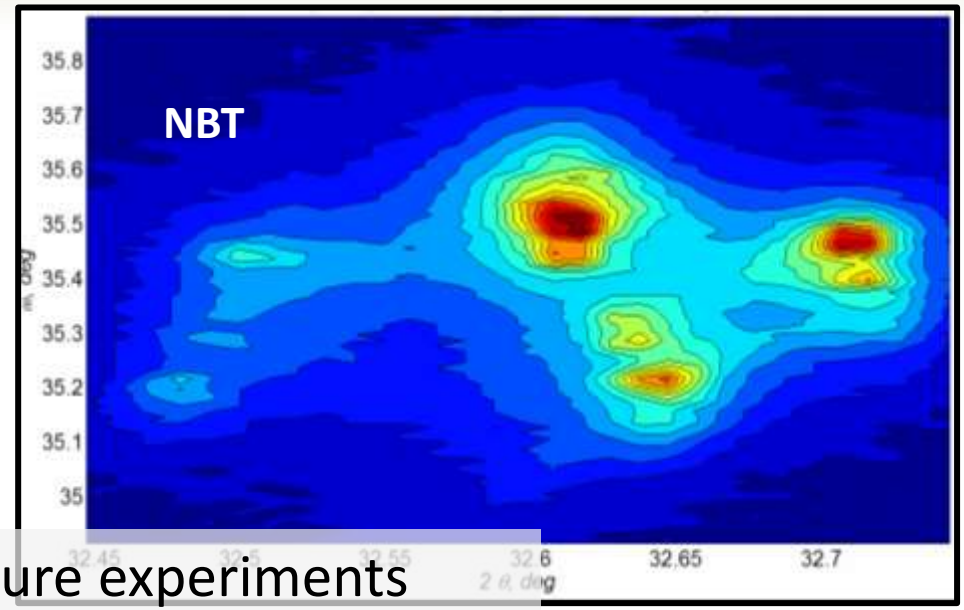


Bragg peak separation -> Identification of a single domain -> Separation

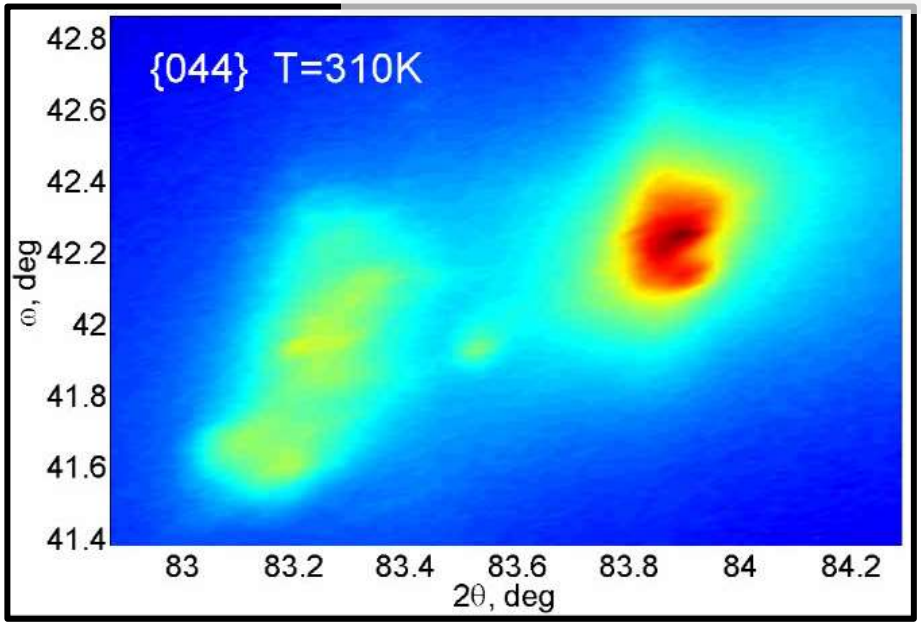


Reciprocal space maps of ferroelectric crystals





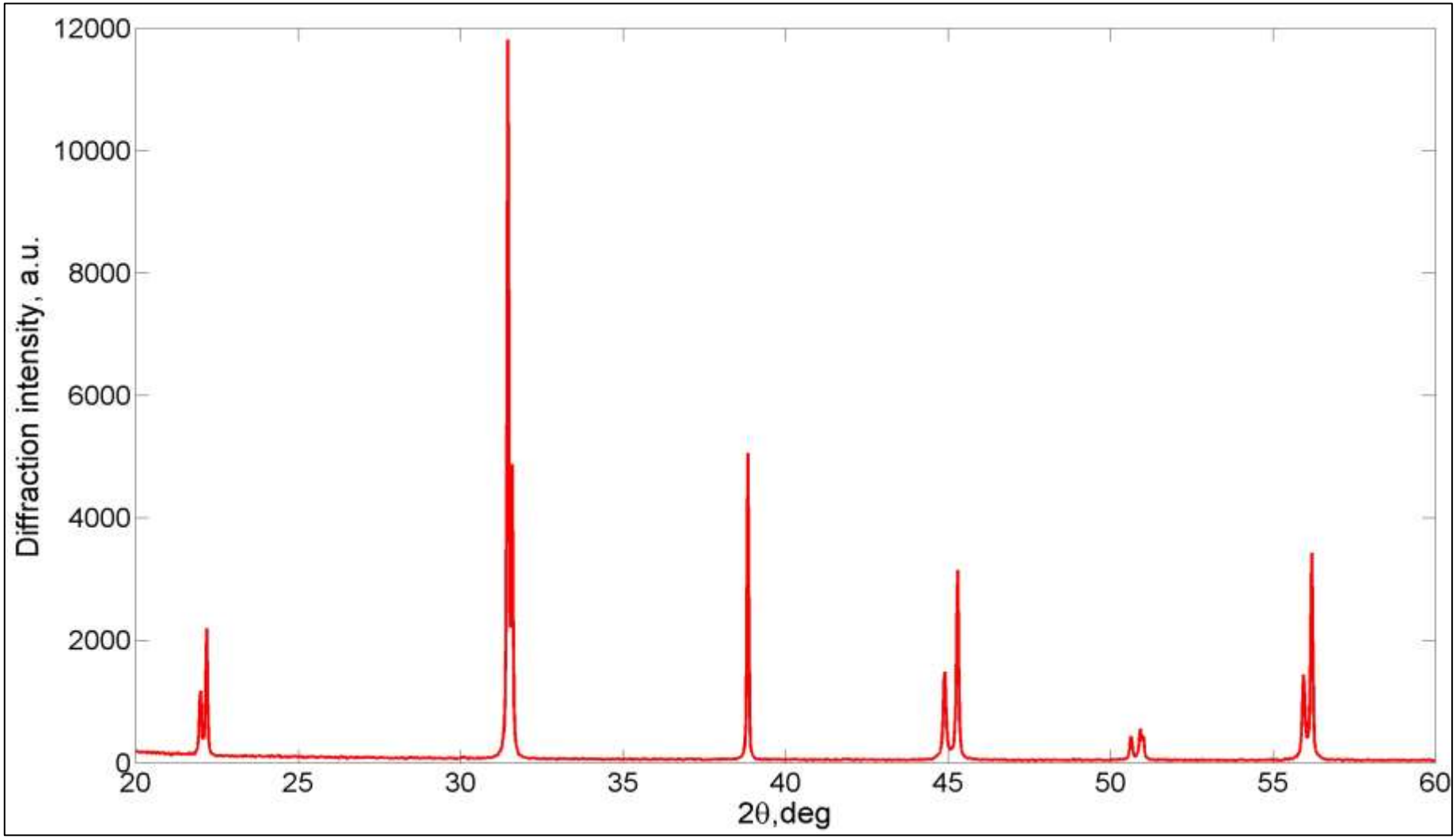
Electric field : Future experiments



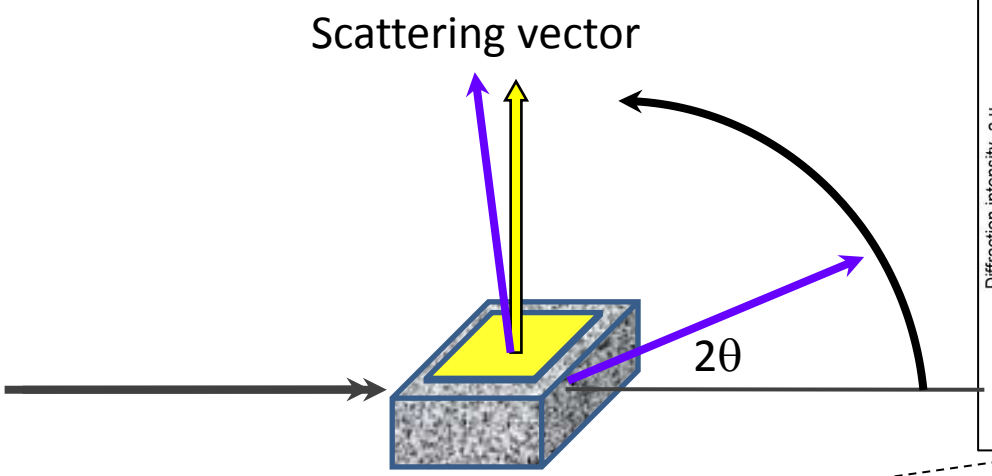
S. Gorfman, P.A. Thomas
J. Appl. Cryst 43, 1409 - 1414, (2010)

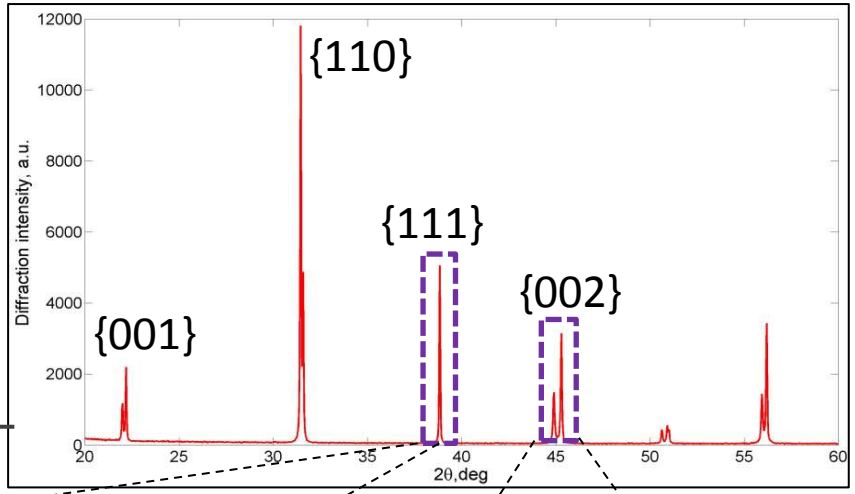
S. Gorfman, D.S. Keeble, A.M. Glazer, X. Long, Y. Xie, Z.-G. Ye, S. Collins, P.A. Thomas
Phys Rev B84, (020102R), (2011)

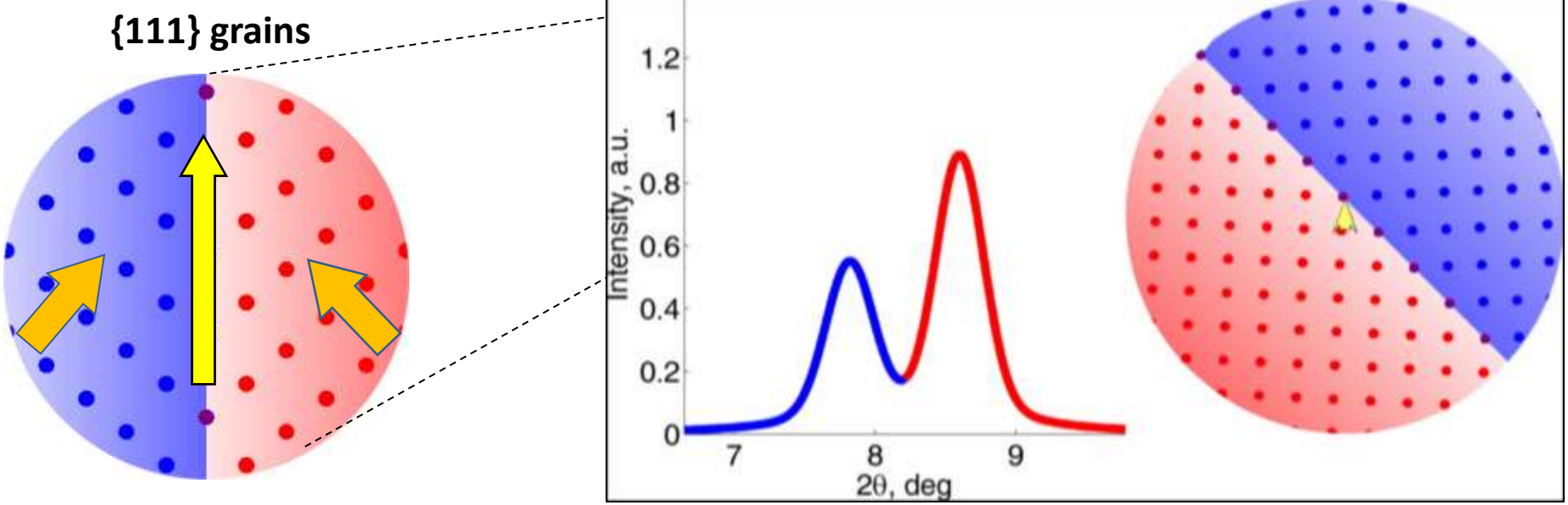
Powder diffraction on ferroelectrics



High-energy X-ray diffraction study of tetragonal ferroelectric ceramics



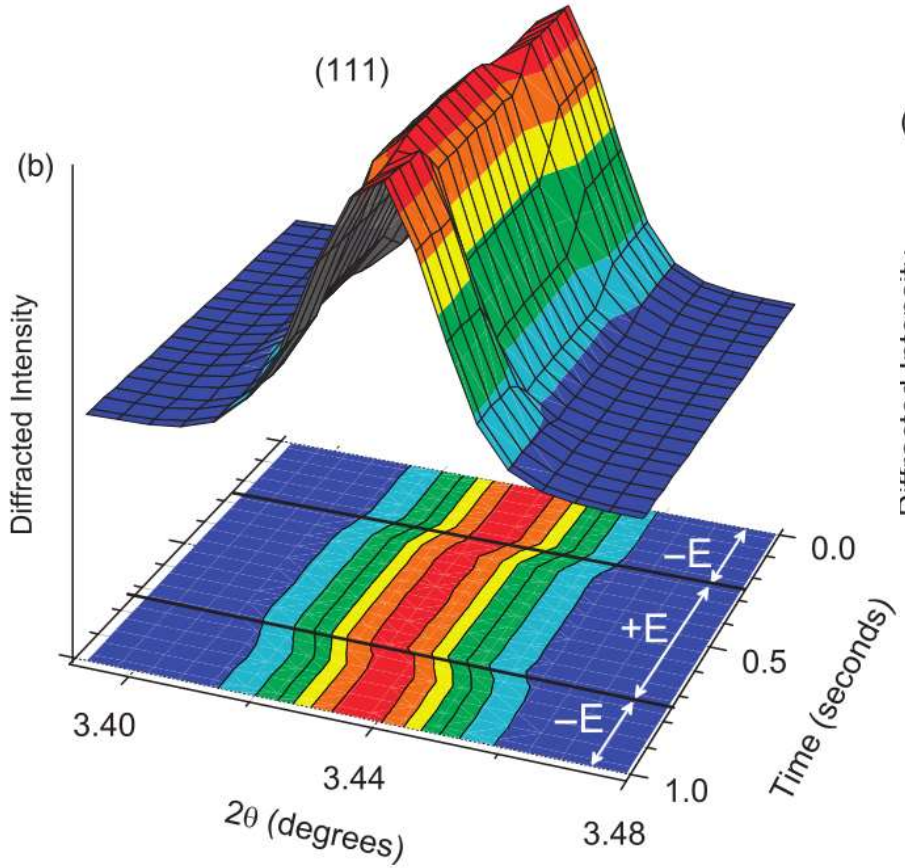




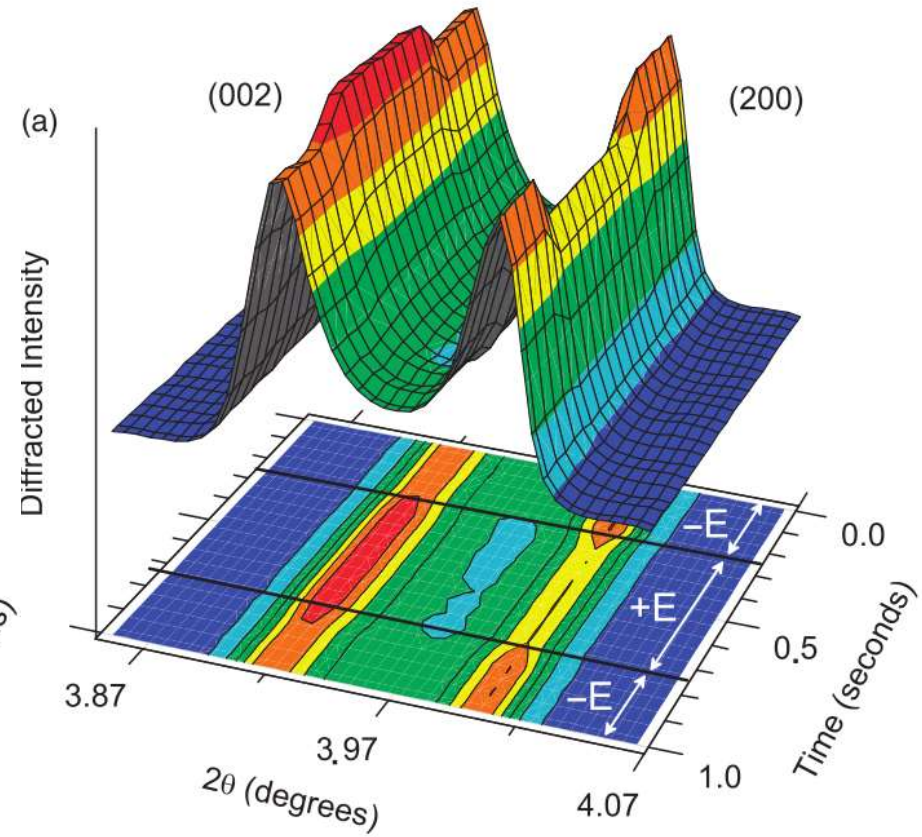
High-energy X-ray diffraction study of ferroelectric ceramics

A. Pramanick, D. Damjanovic, J. E. Daniels, J. C. Nino, and J. L. Jones, J Am Ceramic Soc, 94(2), 293-309 (2011)

Jones JL, Aksel E, Tutuncu G, Uscher TM, Chen J, Xing X, Studer AJ. Phys Rev B, 86, 024104 (2012)



Strain



Domain wall motion

Time-resolved X-ray diffraction study of $Sr_{0.5}Ba_{0.5}Nb_2O_6$

PRL **114,** 097601 (2015) PHYSICAL REVIEW LETTERS week ending 6 MARCH 2015

Time-Resolved X-Ray Diffraction Reveals the Hidden Mechanism of High Piezoelectric Activity in a Uniaxial Ferroelectric

Semën Gorfman,[1,*] Hyeokmin Choe,[1] Vladimir V. Shvartsman,[2] Michael Ziolkowski,[1] Marco Vogt,[1] Jörg Strempfer,[3] Tadeusz Łukasiewicz,[4] Ullrich Pietsch,[1] and Jan Dec[5]
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[2]*Institute for Materials Science, University of Duisburg-Essen, D-45141 Essen, Germany*
[3]*Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22603 Hamburg, Germany*
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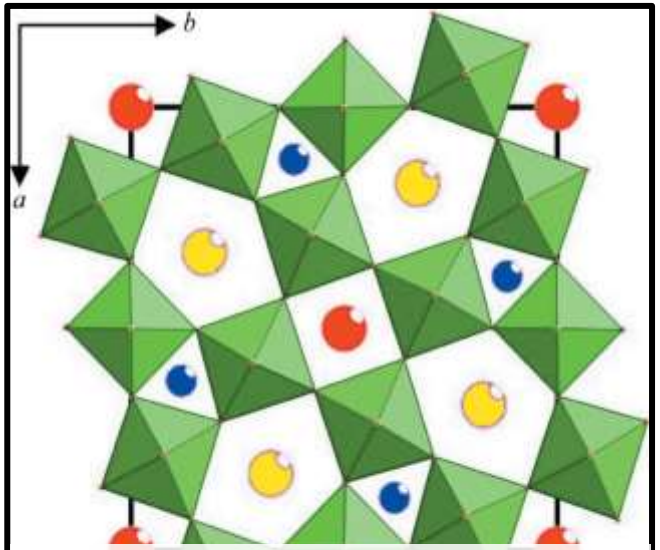
[5]*Institute of Materials Science, University of Silesia, 12 Bankowa Street, PL-40-007 Katowice, Poland*
(Received 8 October 2014; published 3 March 2015)

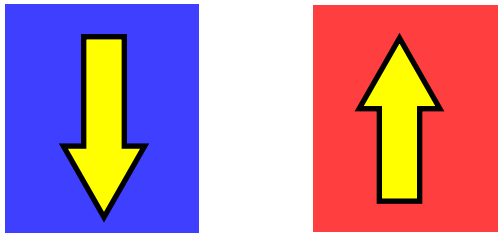


Podlozhenov *et al.* Acta Cryst B**62**, 960, (2006)

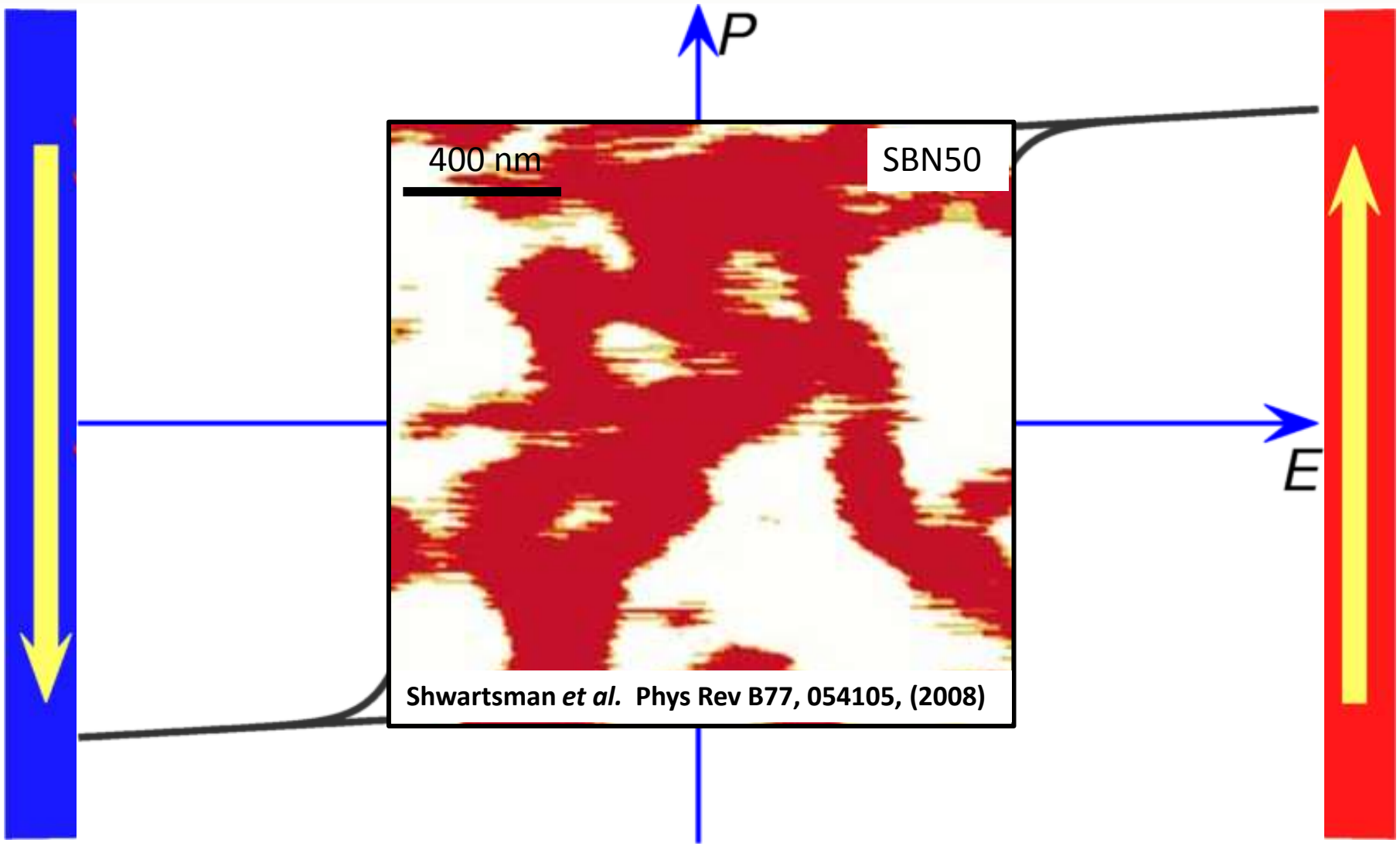
- ***Unfilled tungsten bronze structure***
- ***Uniaxial (tetragonal), P || c***

Paraelectric
4/mmm

Ferroelectric
4mm

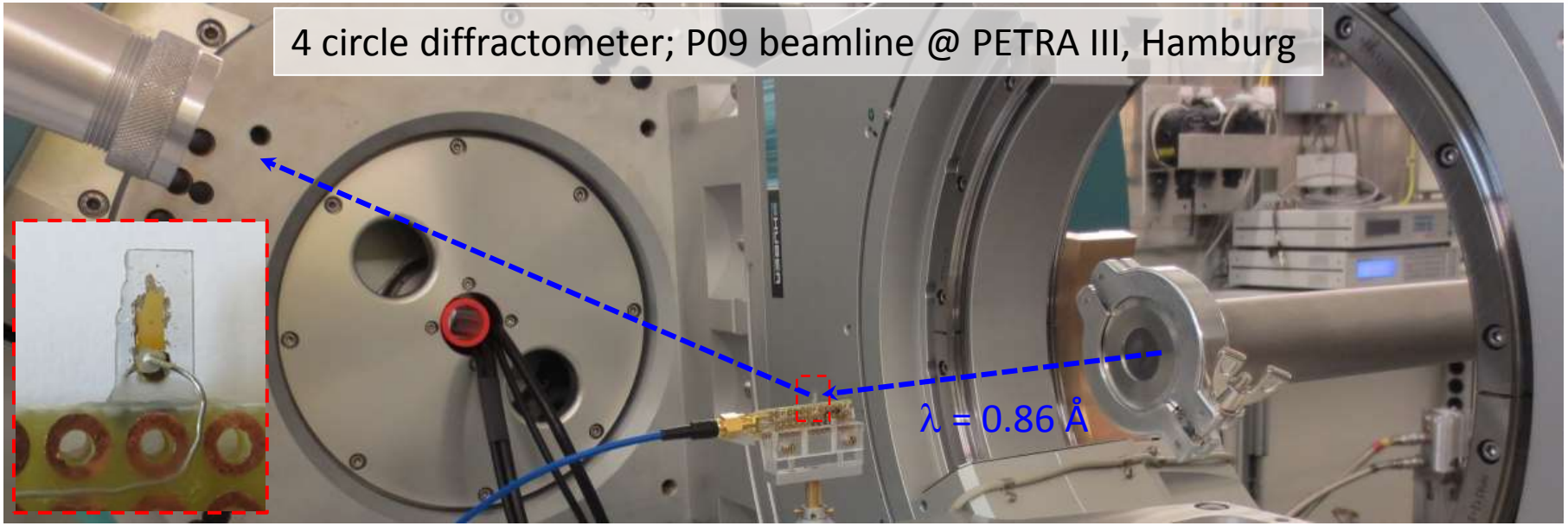


Across a virtual antiphase boundary



Time, electric field

X-ray diffraction experiment on SBN50

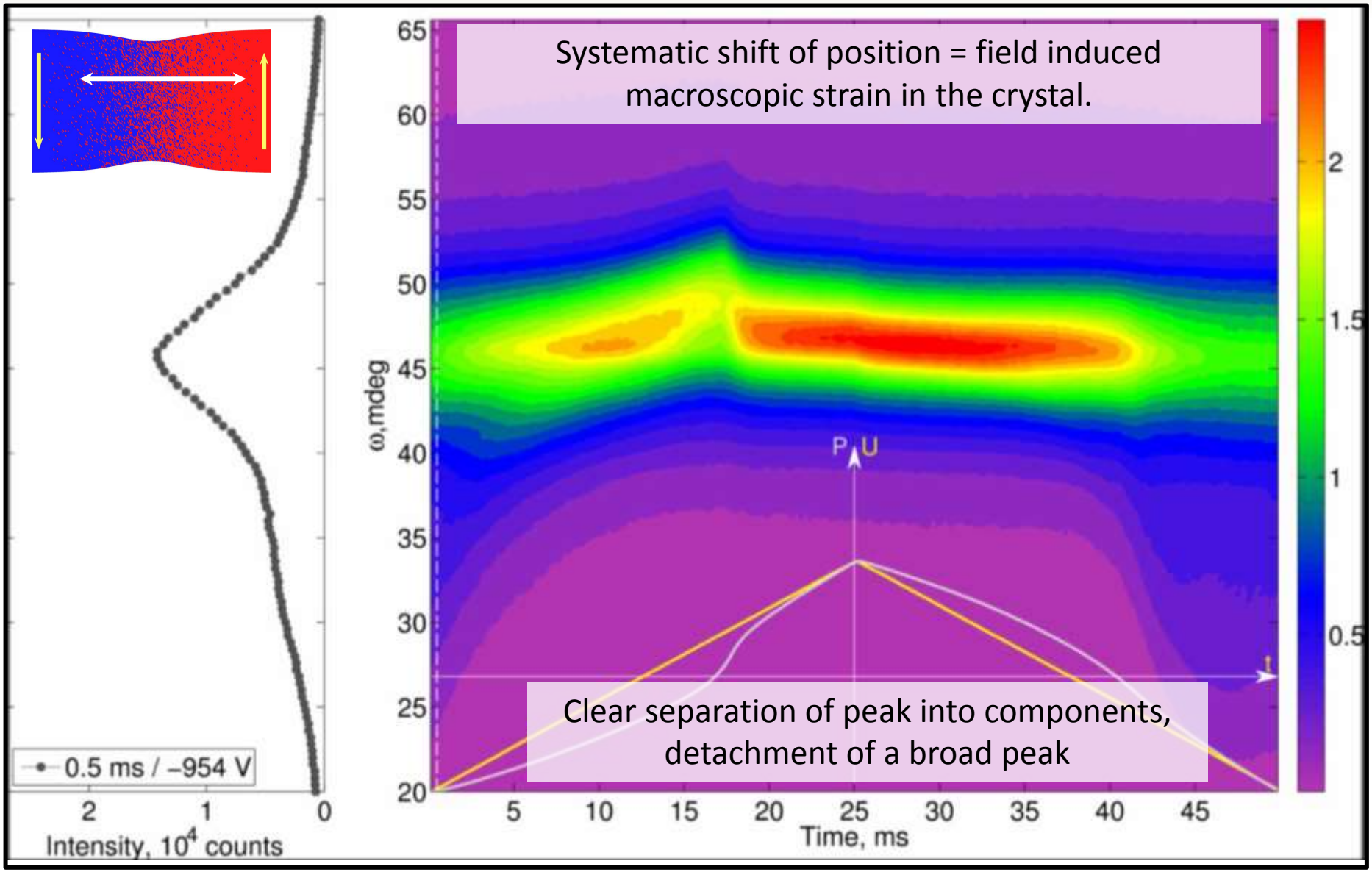


- *X-ray penetration depth:* ***10 - 20 μm***
- Electric field shape : ***triangular***
- Frequency: ***20 Hz***
- Simultaneous monitoring of dielectric (voltage current) and diffraction (rocking curve) response

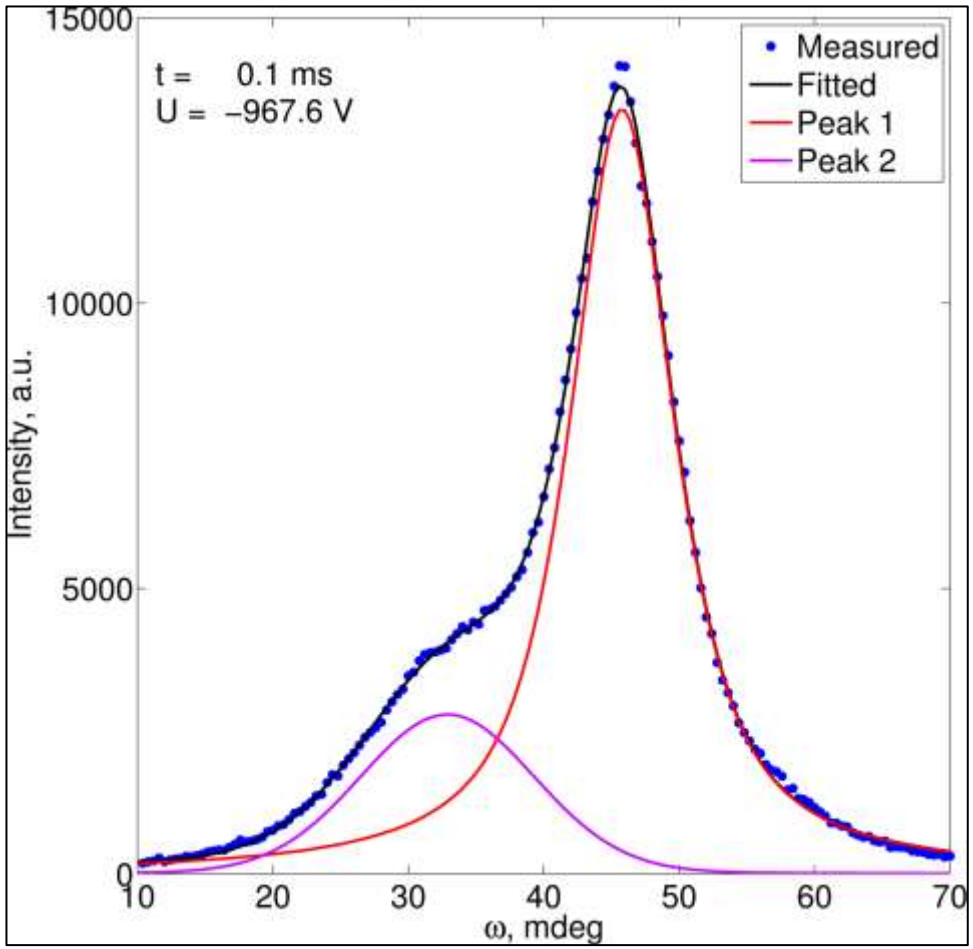
  1850 V / mm (above coercive field)

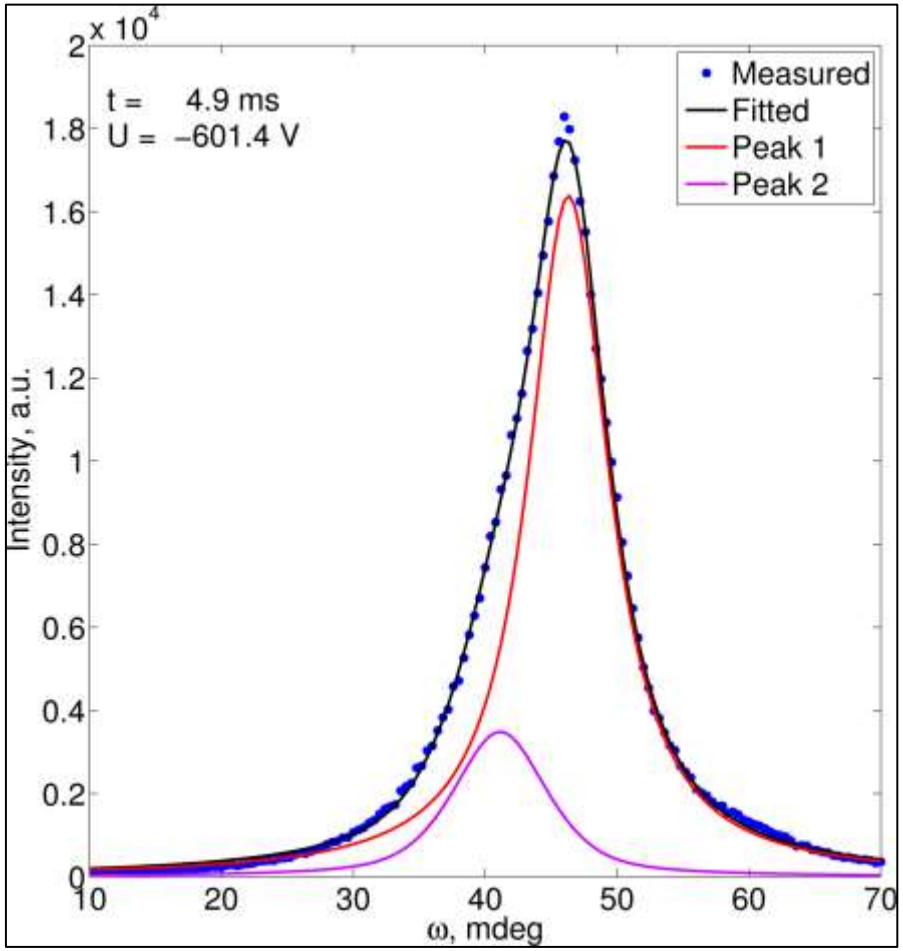
  300 V / mm (sub-coercive field)

Strong electric field, 0 0 7 peak



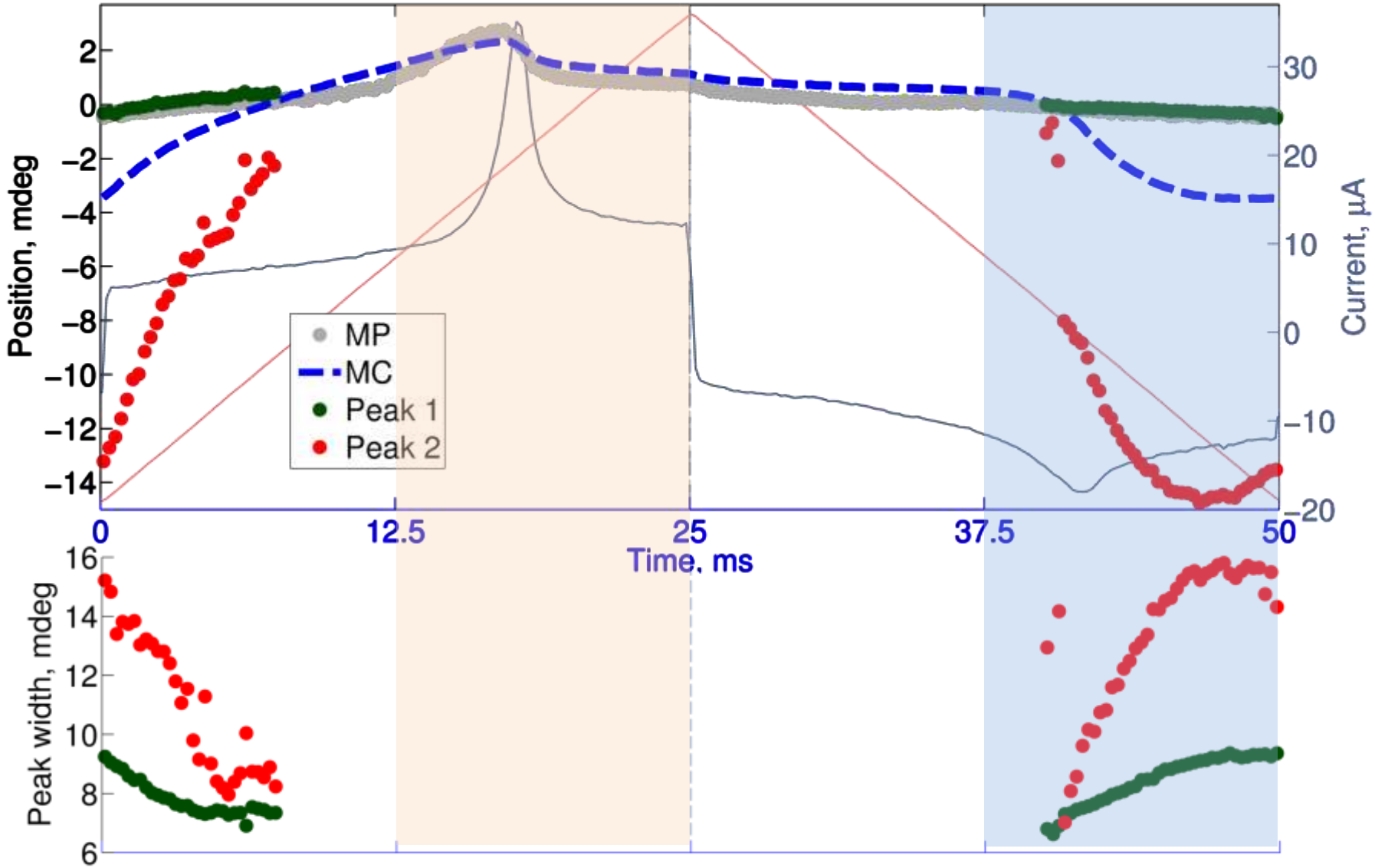
Separation of peak into two components





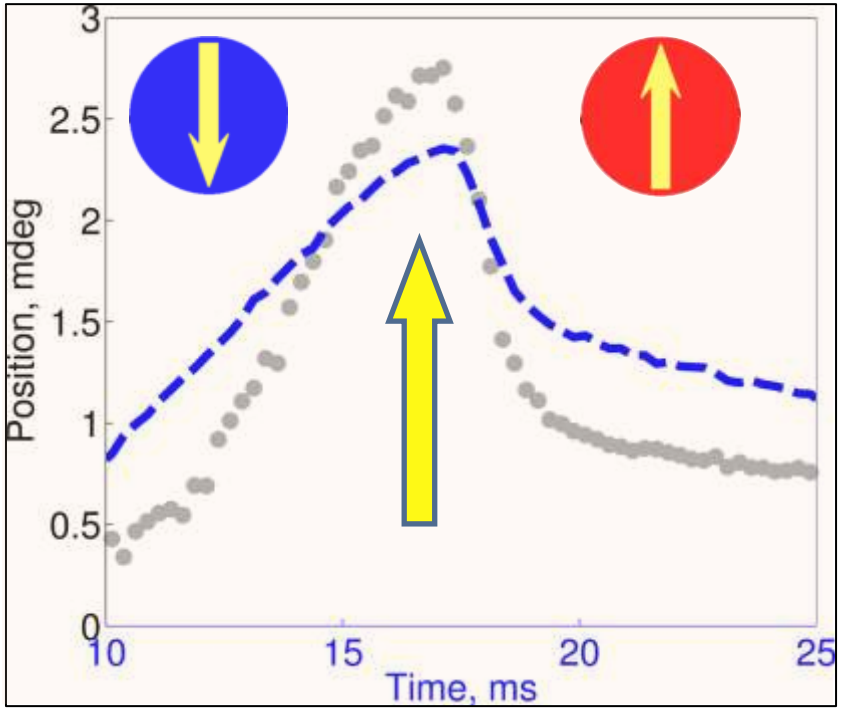
Direct separate analysis of domain dynamics is possible for some time ranges. Calculations of mass centres and peak width

Peak positions and peak width of 0 0 7

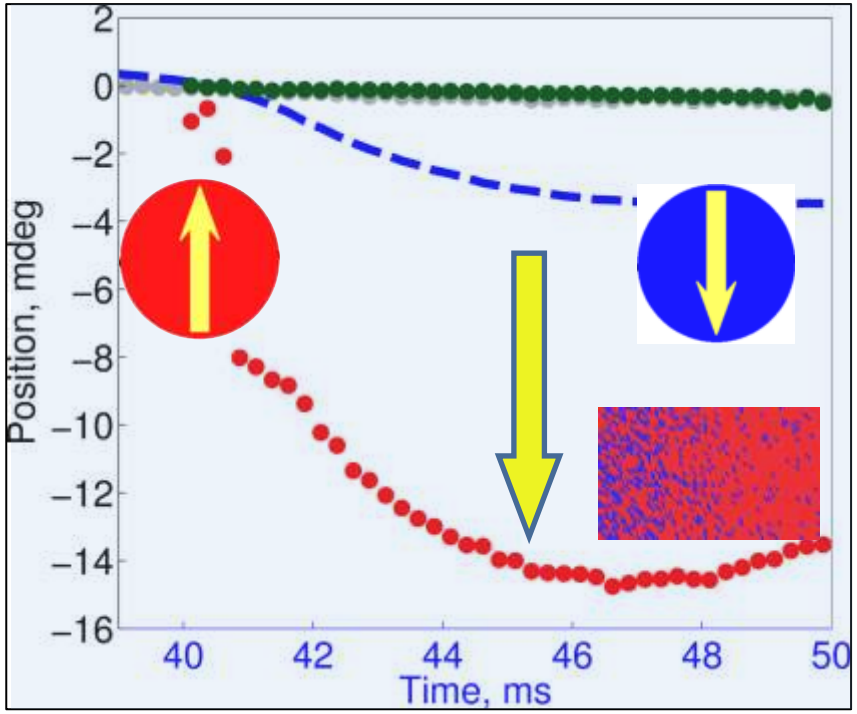


Two different routes of polarity switching

Time range 1



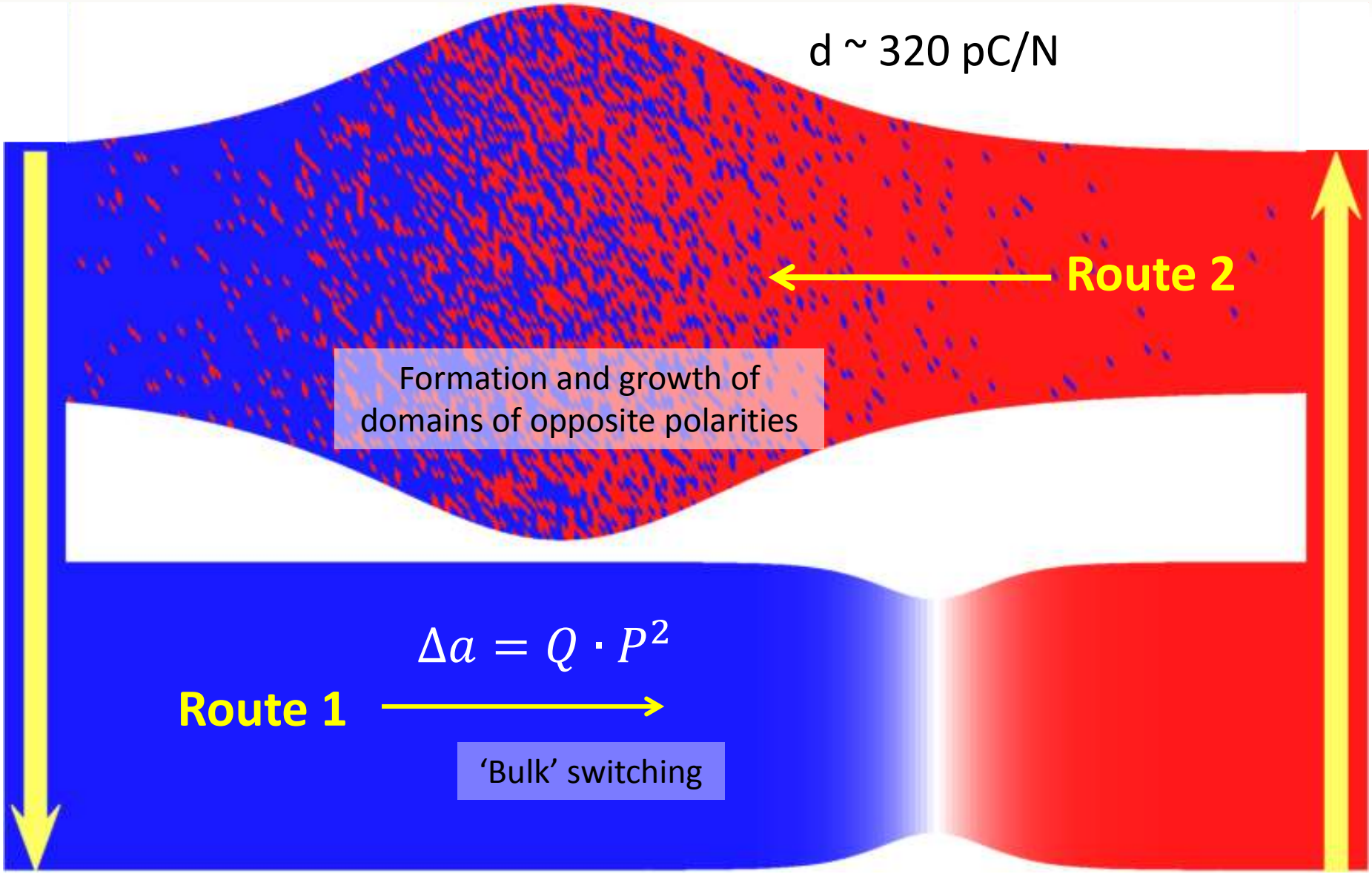
Time range 2



- Inversion of the effective piezoelectric constant

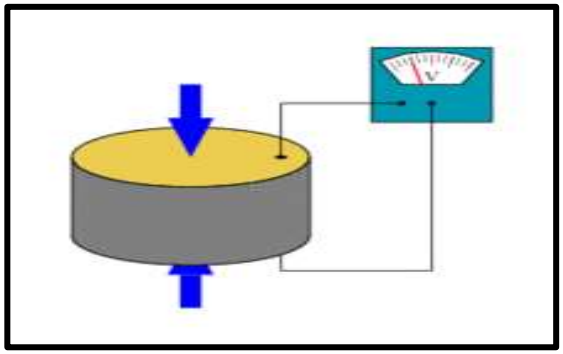
- Formation of small domains under electric field
- Large increase of the lattice constant

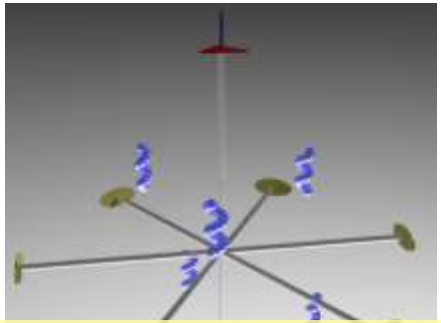
Two virtual antiphase boundaries



Conclusions, Part 1

Piezoelectric effect: mechanical response to electrical perturbation / electrical response to a mechanical perturbation.

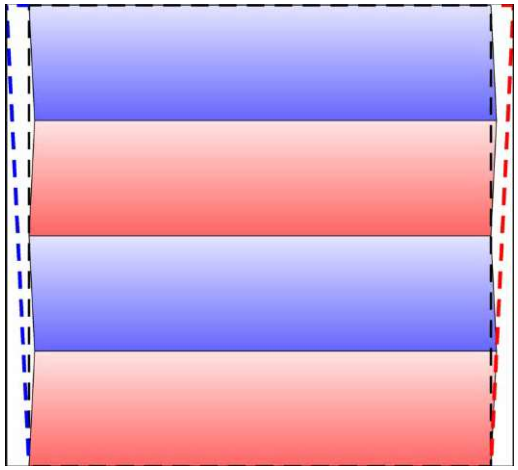




$$\begin{pmatrix} \eta & -\eta & 0 & \alpha & 0 & 0 \\ 0 & 0 & 0 & 0 & -\alpha & -2\eta \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Piezoelectric effect is described macroscopically by a third rank tensor. This description does not need any microscopic information.

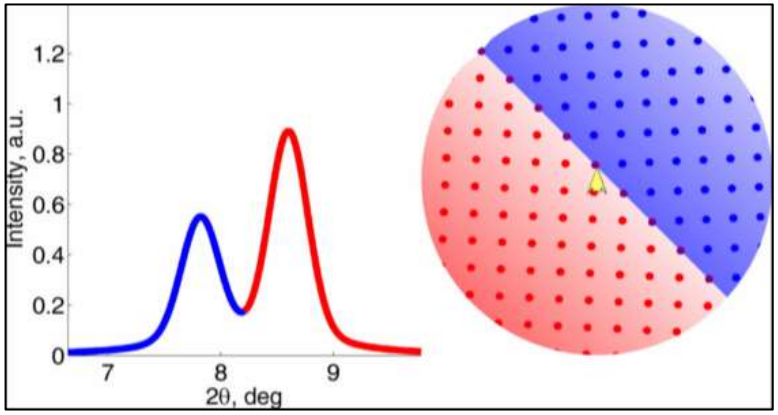
Piezoelectric effect is particularly strong in ferroelectrics. It may be connected to the existence of ferroelastic/ferroelectric domains

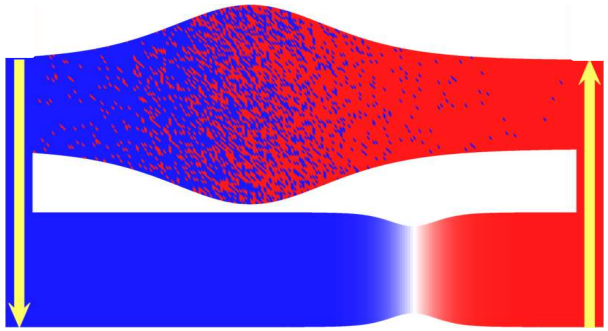


Conclusions, Part 2

Experimental method for studying mechanisms of piezoelectric effect: time-resolved stroboscopic X-ray diffraction. It involves analysis of structure factor and small angular shifts of the Bragg peak

X-ray diffraction provide the access to intrinsic and extrinsic piezoelectric effect





Uniaxial ferroelectrics: new mechanism of high electromechanical activity has been recently discovered

Acknowledgements

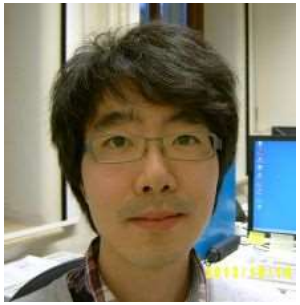
German Federal Ministry for Education and Research

05K13PSA. STROBO-DAQ, Time-resolved X-ray diffraction study of functional materials under external electric field.

Bundesministerium für Bildung und Forschung

Crystallography in Siegen:

- Prof Dr Ullrich Pietsch
- Hyeokmin Choe
- Behnam Khanbabaee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