Ecole WURM de spectroscopie Raman

Characterization of functional oxides

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Outline

Introduction:

- Functional ferroic perovskites

Raman on ferroic perovskites:

- Soft mode / hard mode spectroscopy
- Domain structures and domain walls
- Polar and « oblique » modes
- Magnetism

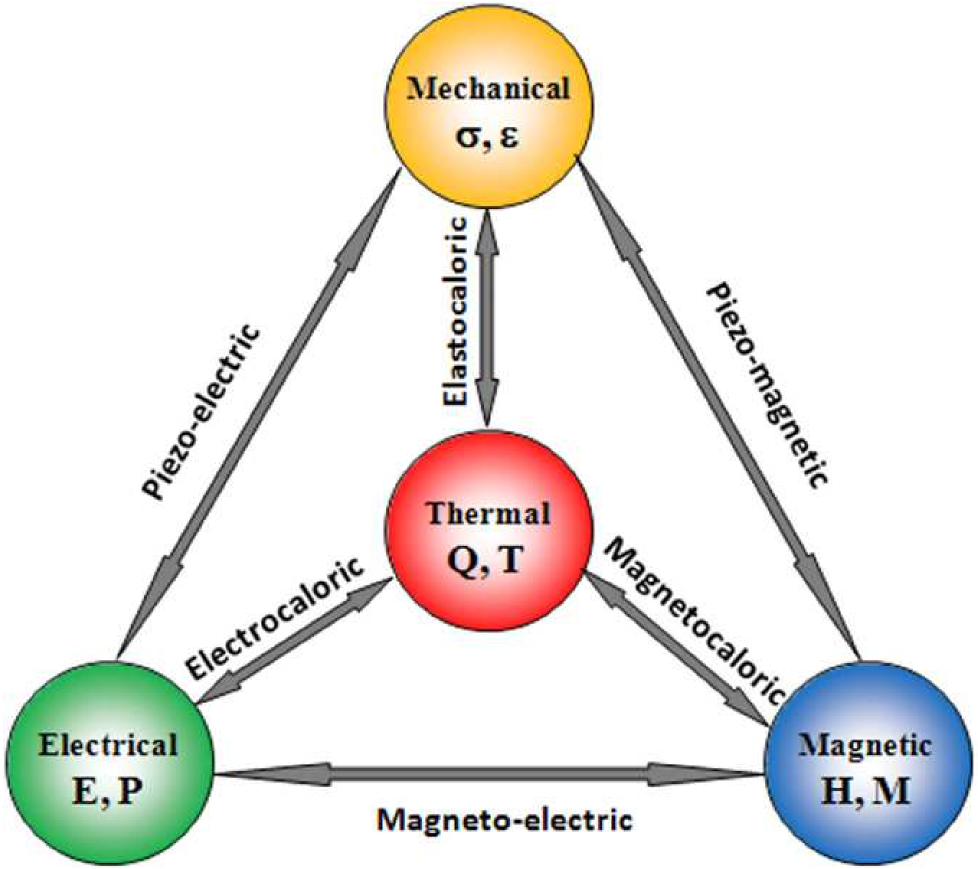
Beyond the bulk:

- Thin films
- Heterostructures
- Multilayers

Introduction

Multi-functional oxides

Stress σ – Strain ε



Electric field E – Polarisation P

Magnetic field H – Magnetisation M

Sketch from Vopson, J. Phys. D: Appl. Phys. 46 345304 (2013)

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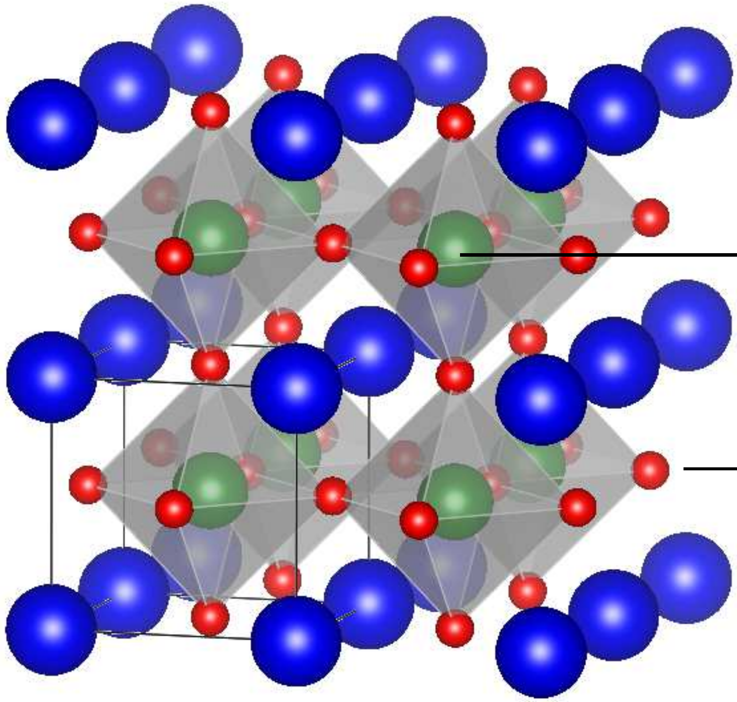
Introduction

The perovskite structure



A-site: Bi, Pb, rare earth, …

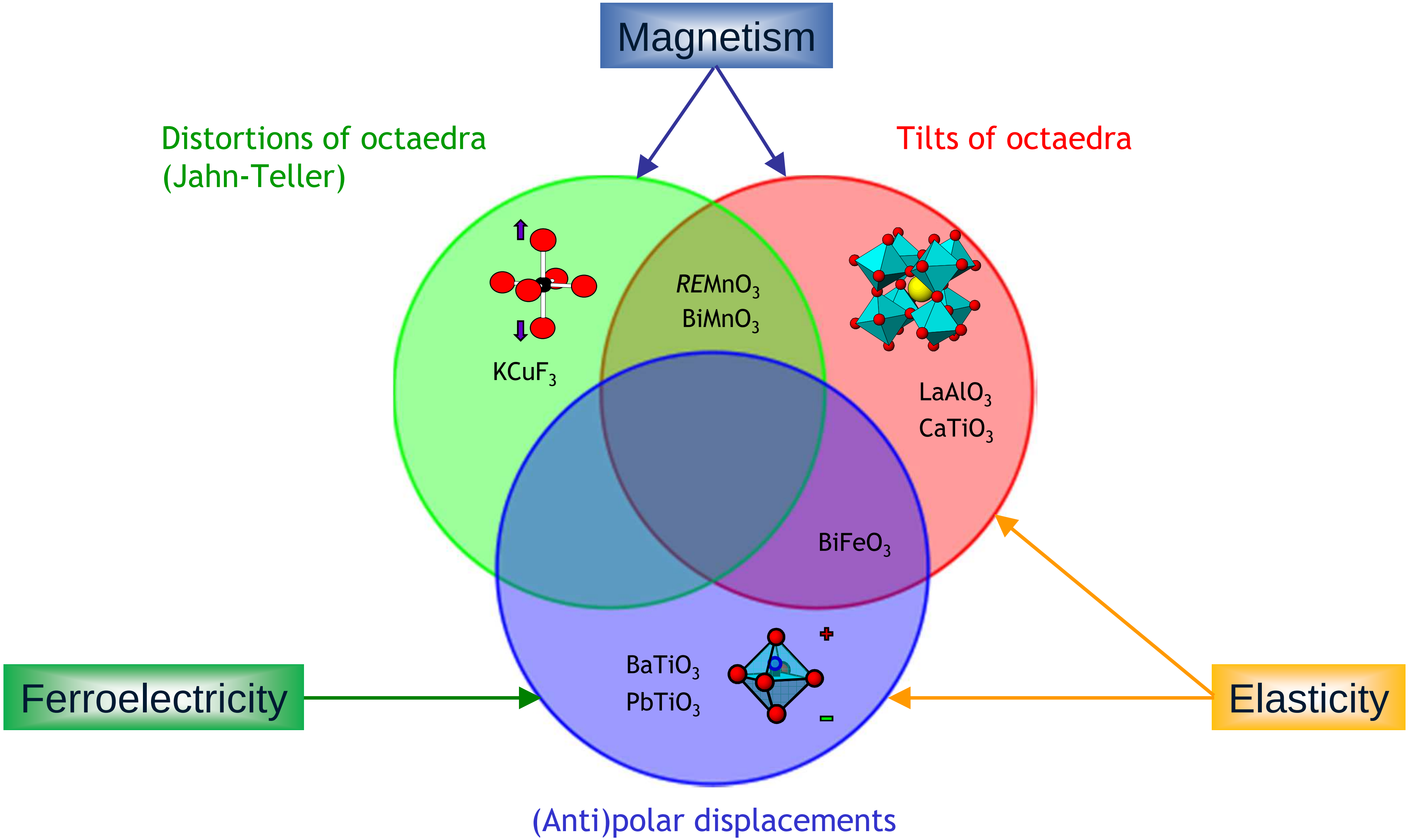
B-site: (transition) metal, …

O^{2-}, F^{-}, …

Ferroelectricity, magnetism, giant magnetoresistance, superconductivity, ionic conductors, photovoltaic…

Introduction

Distortions of the perovskite structure



Structural distortions and phase transitions pilot the physics!

Introduction

Uses of Raman spectroscopy

Structural phase transitions
Identification of structural distortions
Metal-insulator transitions
Domain structures and domain walls
Strain states
Order-disorder phenomena
Magnetism
etc.

Temperature
High-pressure
Electric field
Epitaxial strain
…

At the CRP Gabriel Lippmann:

- Micro-Raman
- 5 excitation wavelengths: 325, 442, 532, 633, 785 nm
- Coupled to the AFM

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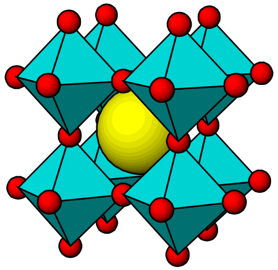
Raman on ferroic perovskites

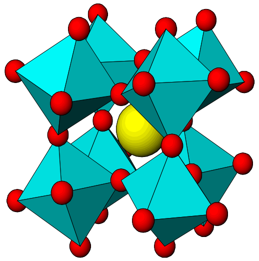
The cubic phase Pm-3m



Phonon modes = $3T_{1u} + T_{2u}$
i.e. no Raman spectrum in the cubic phase

Order-disorder transition
↓
Central peak

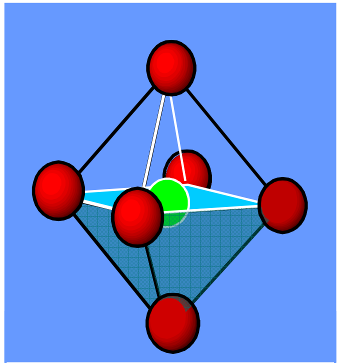
Soft-mode driven transition
↓
Soft phonon mode



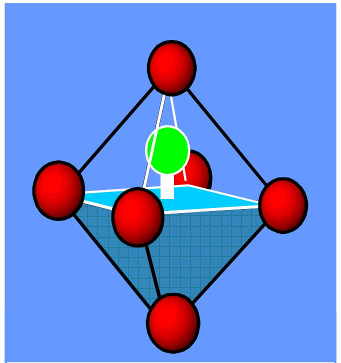
Symmetry lowering
Lift of the mode degeneracy
Emergence of Raman-active modes

Soft-mode in Raman spectroscopy

Soft-mode driven transition



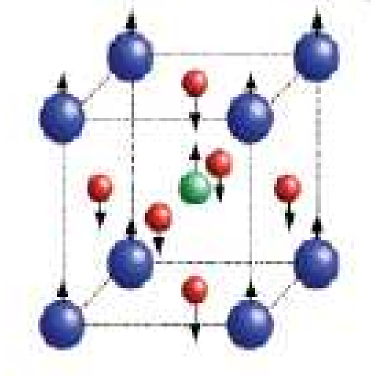
paraelectric
cubic

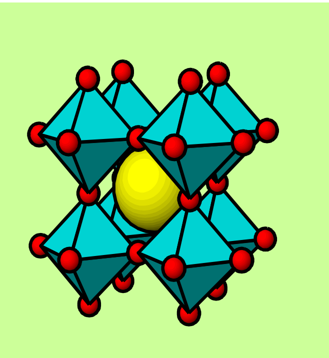


ferroelectric
non-cubic

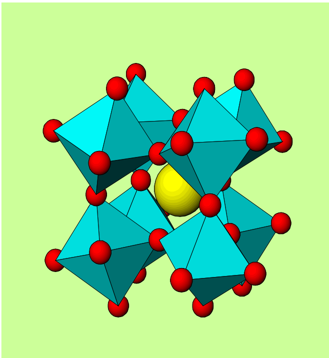
Following polar displacements

(➔ ferroelectricity)



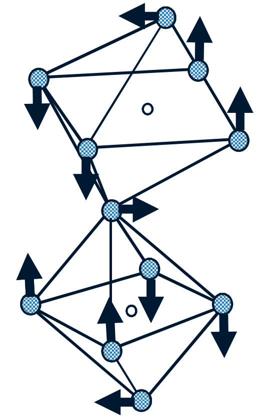


cubic



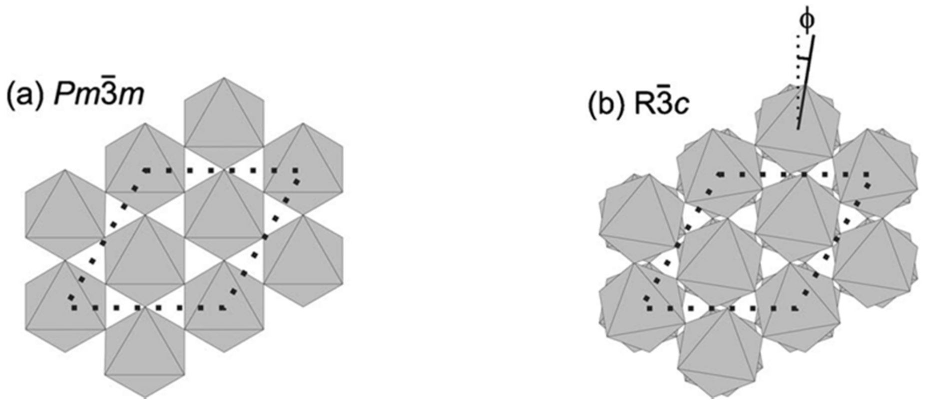
ferroelastic
non-cubic

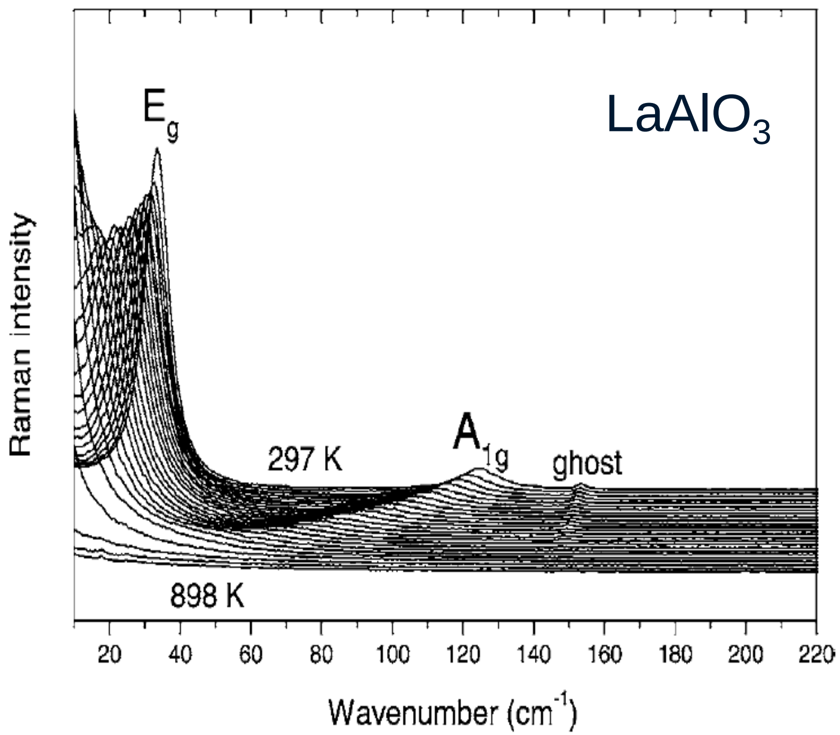
Following rotation angle of octahedra

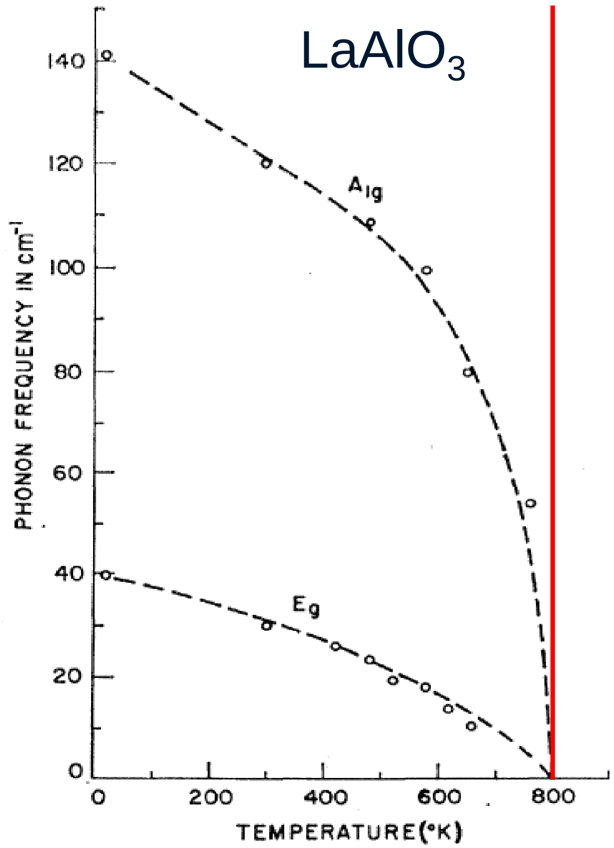


Soft mode in Raman spectroscopy

Phase transition in $LaAlO_3$ at high temperatures







P. A. Fleury et al., Phys. Rev. Lett. **21**, 16 (1968).

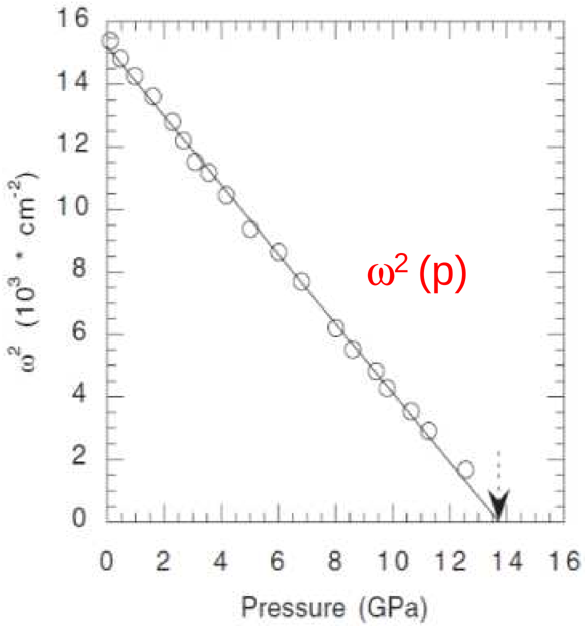
Soft-modes in Raman spectroscopy

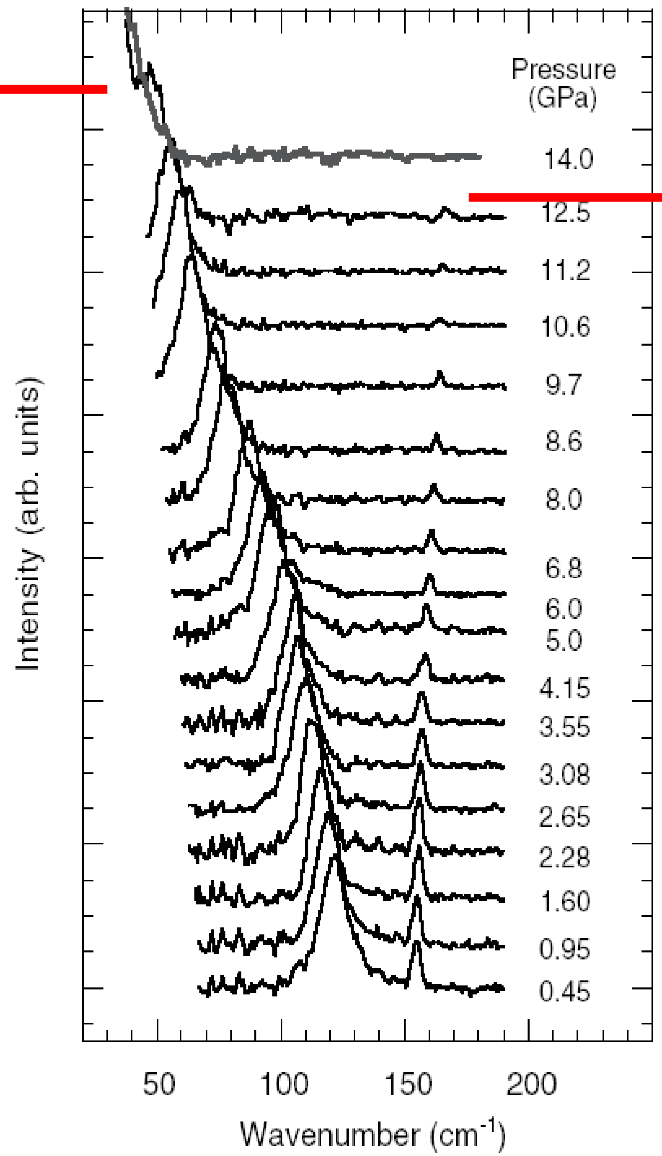
Phase transition in $LaAlO_3$ at high pressure

"Soft mode"

$\omega^2(p) = \omega_0^2\ (P_c - P)$

Rotation of octahedra





"Hard mode"

$$\frac{\delta\omega}{\omega} = -\gamma \frac{\delta V}{V}$$

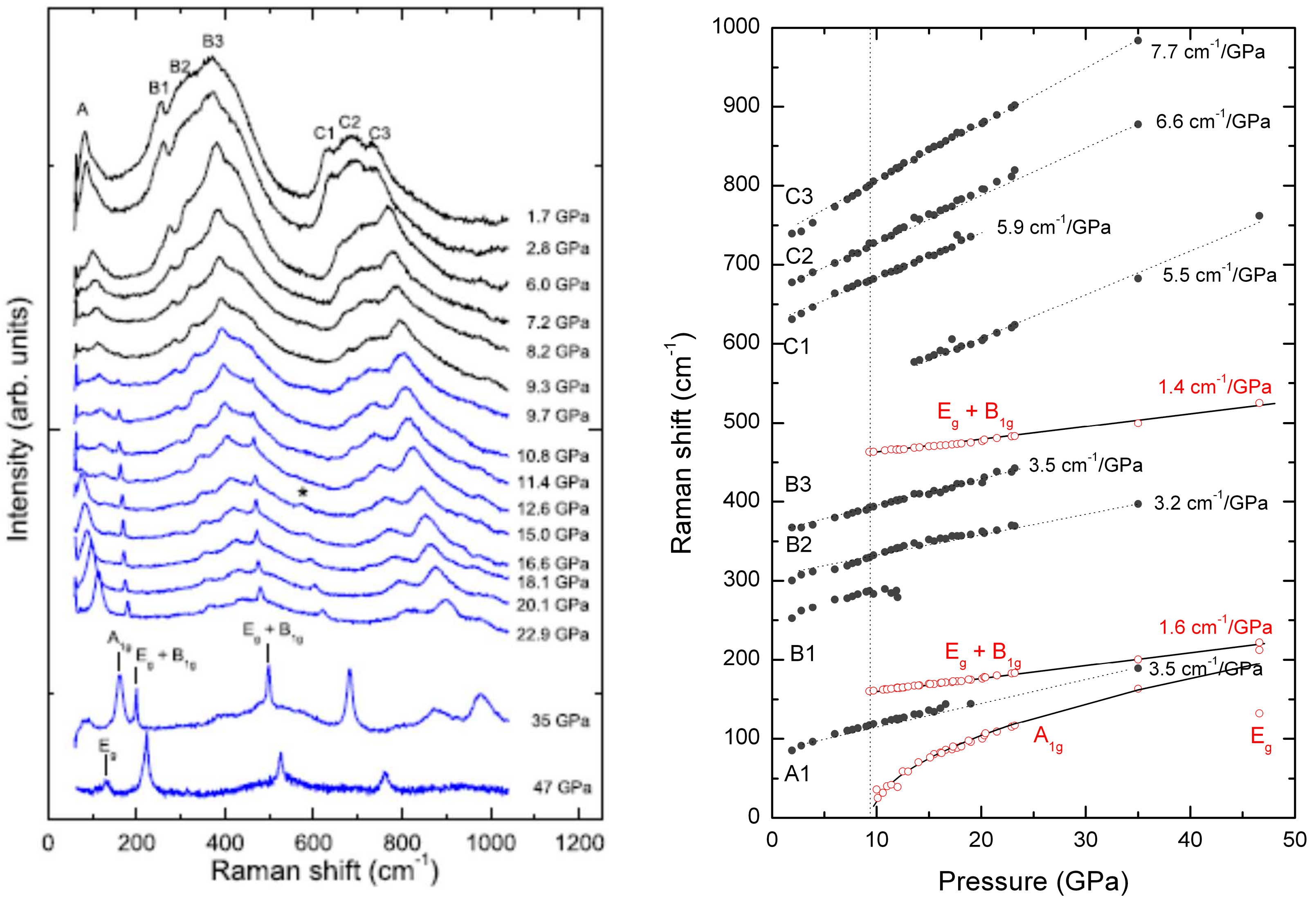
"Grüneisen" parameter

Intensity → 0
at the transition

P. Bouvier & J. Kreisel J. Phys.: Condens. Matter **14**, 3981 (2002)

Soft-modes in Raman spectroscopy

Phase transition in $SrTiO_3$ at high pressure

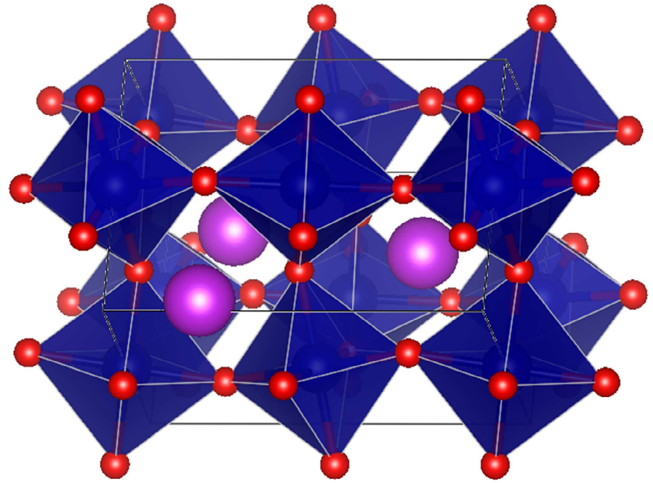


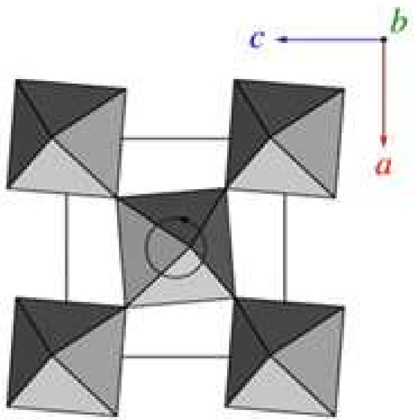
Guennou et al., Phys. Rev. B **81**, 054115 (2010)

Raman phonons and tilt angles

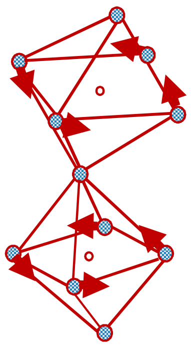
The orthorhombic Pnma structure

- Most common structure of perovskites
- Can be described by <u>two</u> octahedra rotations
- Two associated « quasi-soft » modes

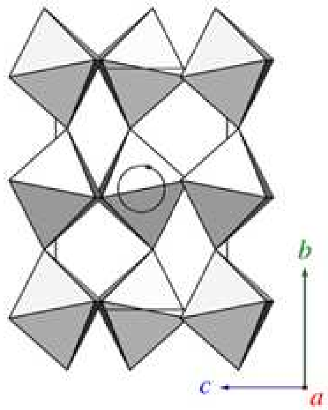




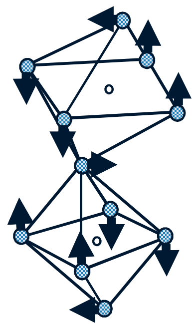
Raman mode $A_g(3)$
[010] rotation



+

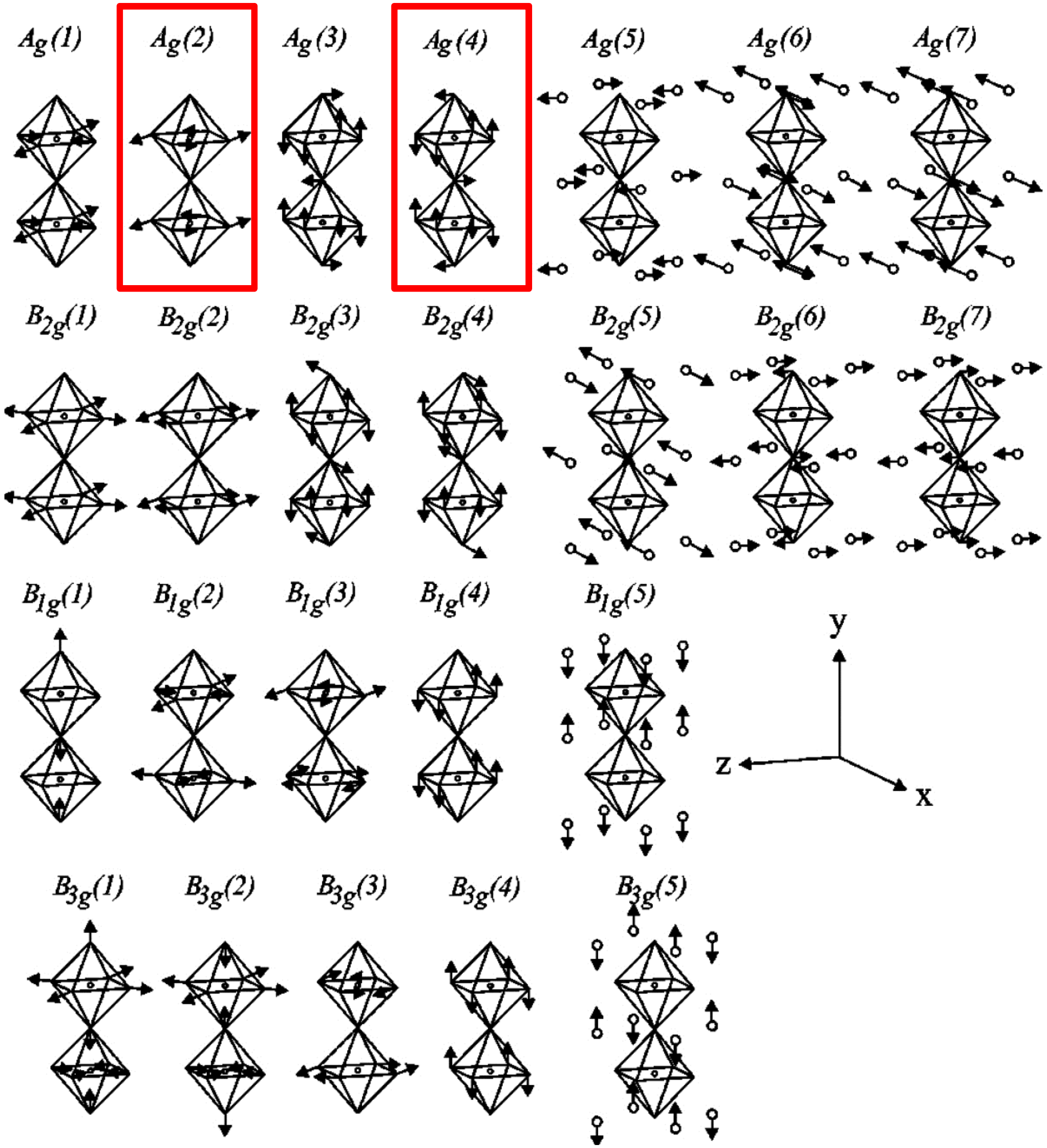


Raman mode $A_g(5)$
[101] rotation

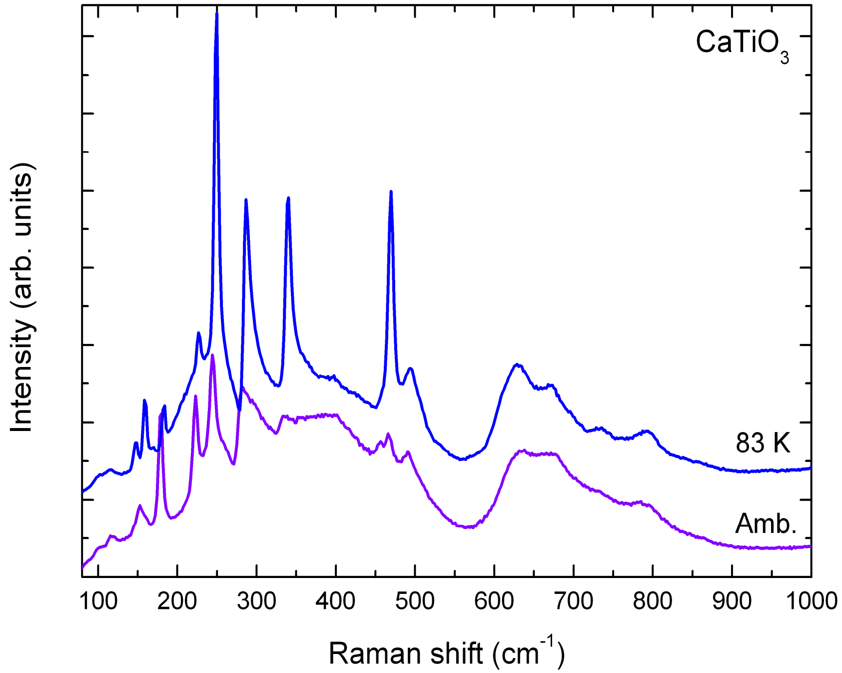


Raman phonons and tilt angles

Raman-active modes of the Pnma structure



Mode assignment?

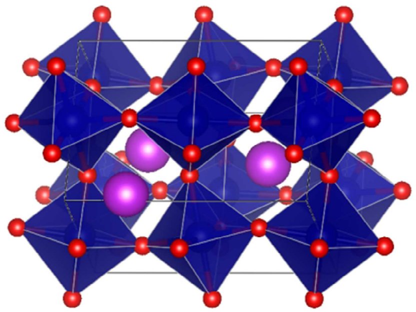


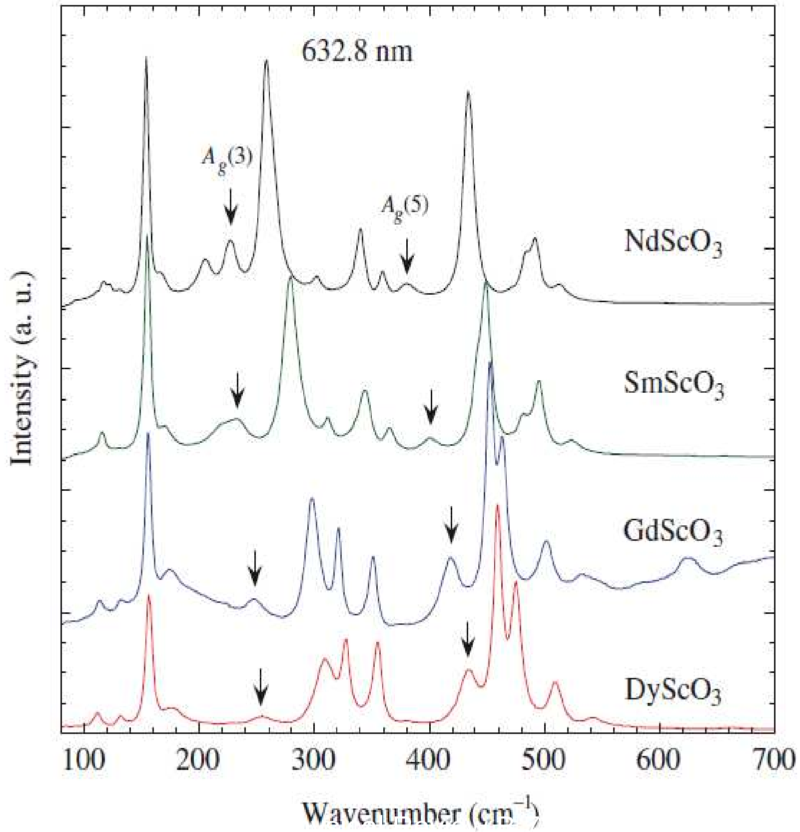
Need for calculations:

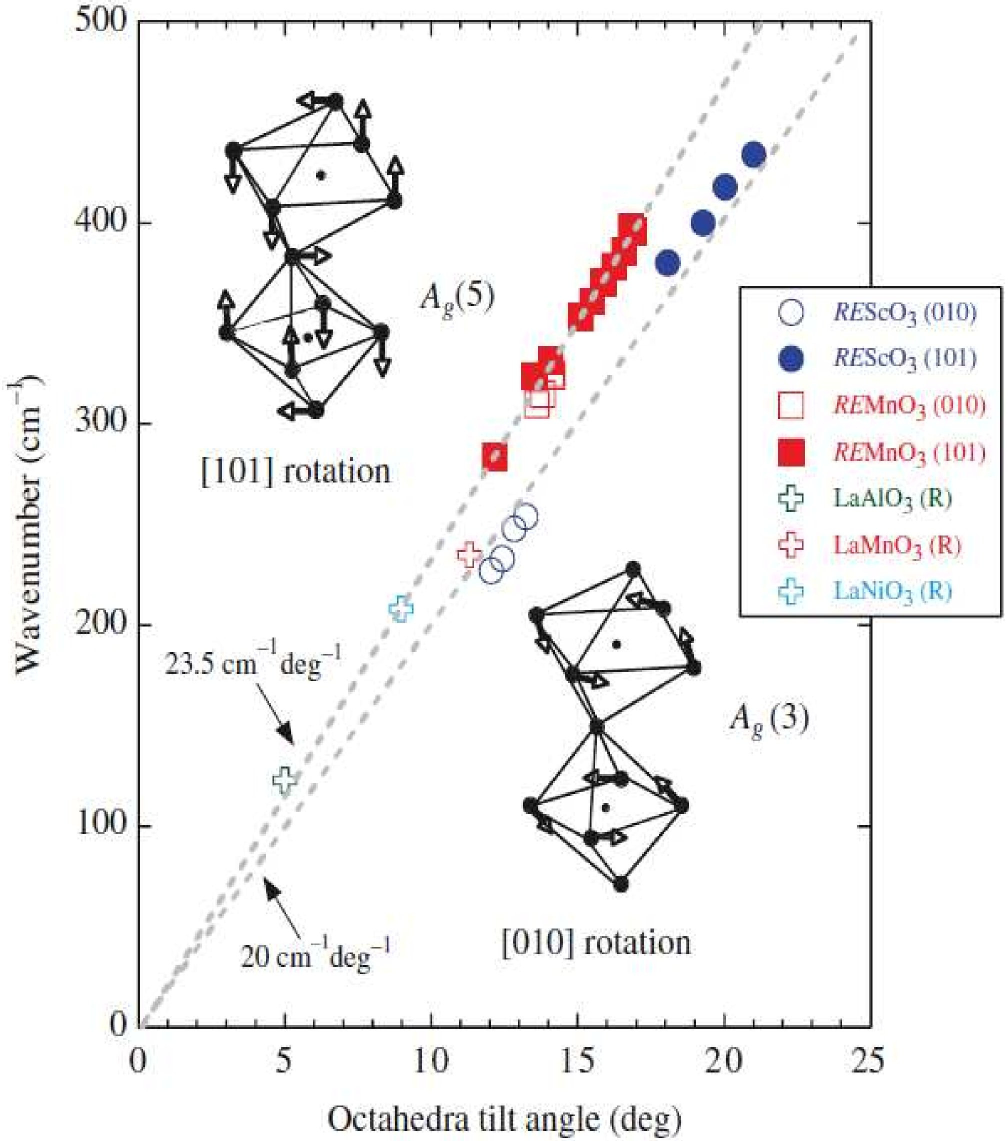
- DFT
- Shell models

Raman phonons and tilt angles

Tilt modes in rare-earth scandates $AScO_3$



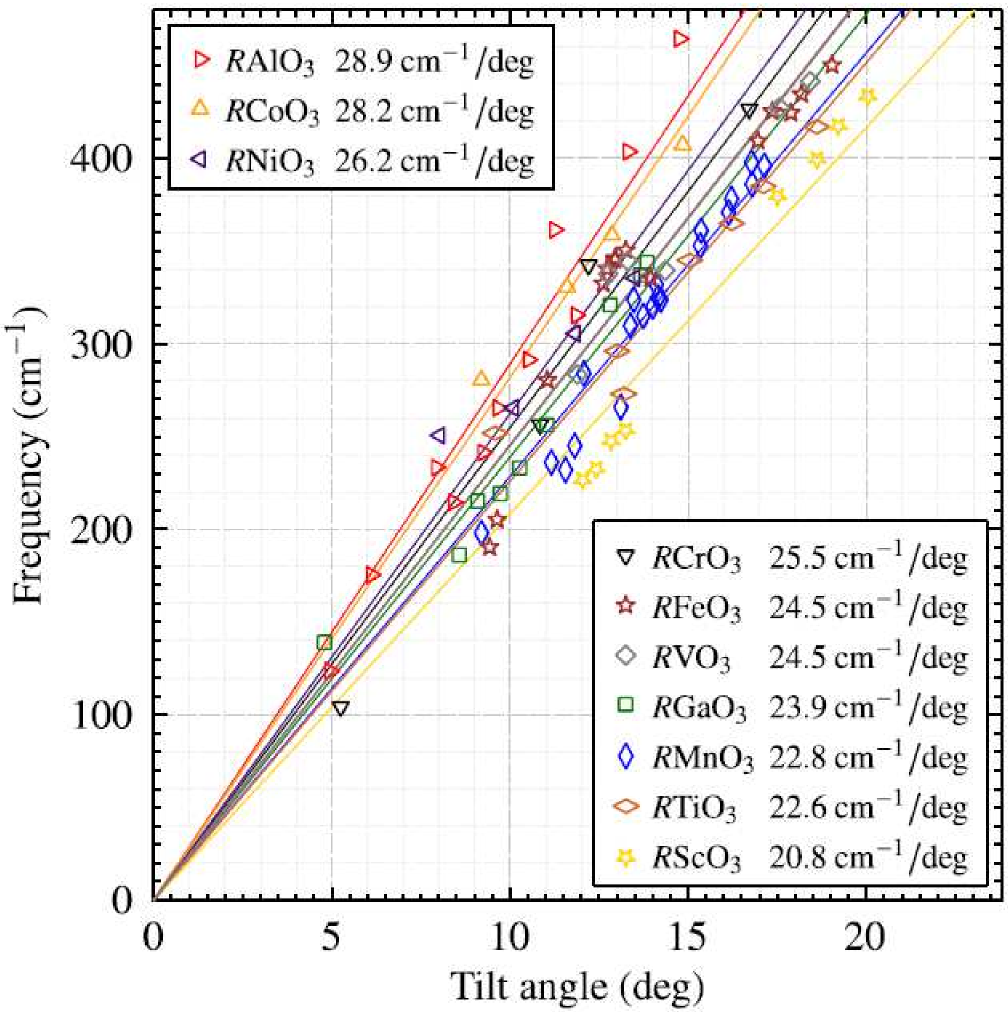




Chaix-Pluchery et al., Phase Transitions (2011)

Raman phonons and tilt angles

Tilt modes in rare-earth scandates $AScO_3$



The tilt mode gives you the tilt angle

…

If you can find it.

N. Todorov et al., J. Phys.: Condens. Matter **24**, 175404 (2012)

Ferroic domains and domain walls

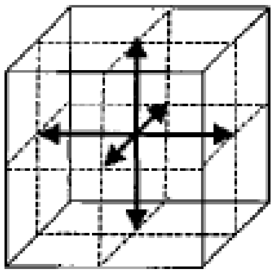
Archetypical ferroelectric $BaTiO_3$

$BaTiO_3$

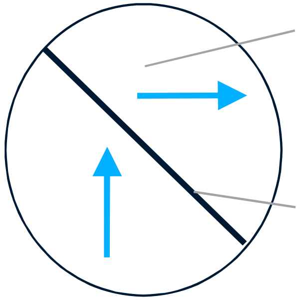
Cubic
Paraelectric P=0

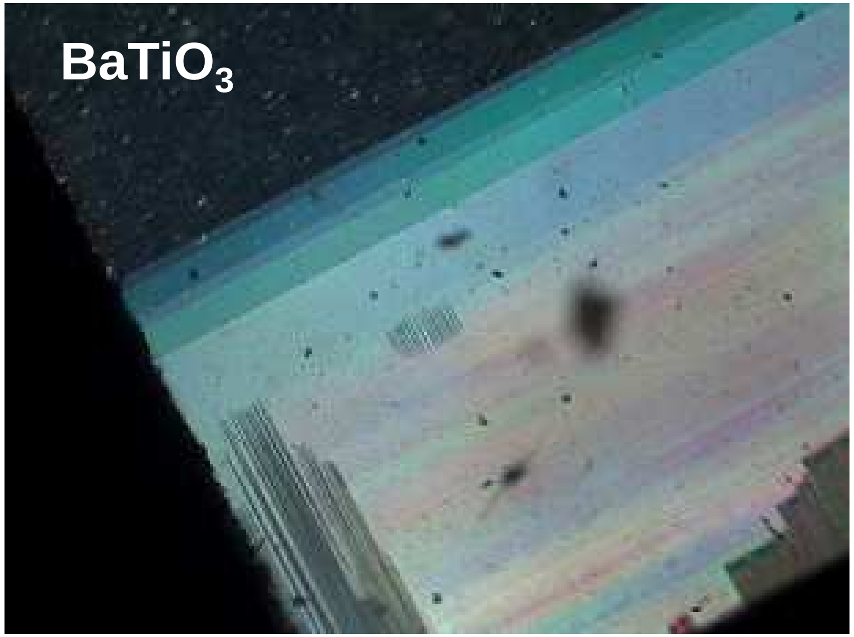
$T_c \approx 120°C$

Tetragonal
Ferroelectric $P \neq 0$
6 equivalent directions



Coexistence of several polarisation directions

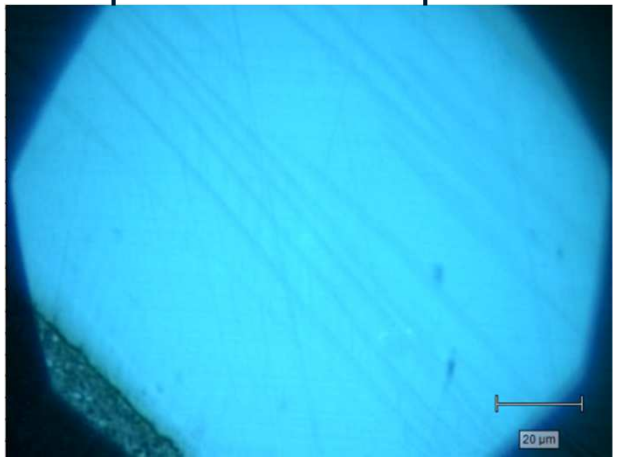




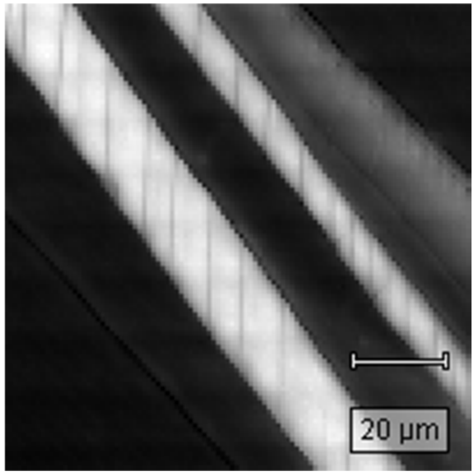
Domain structures and domain walls

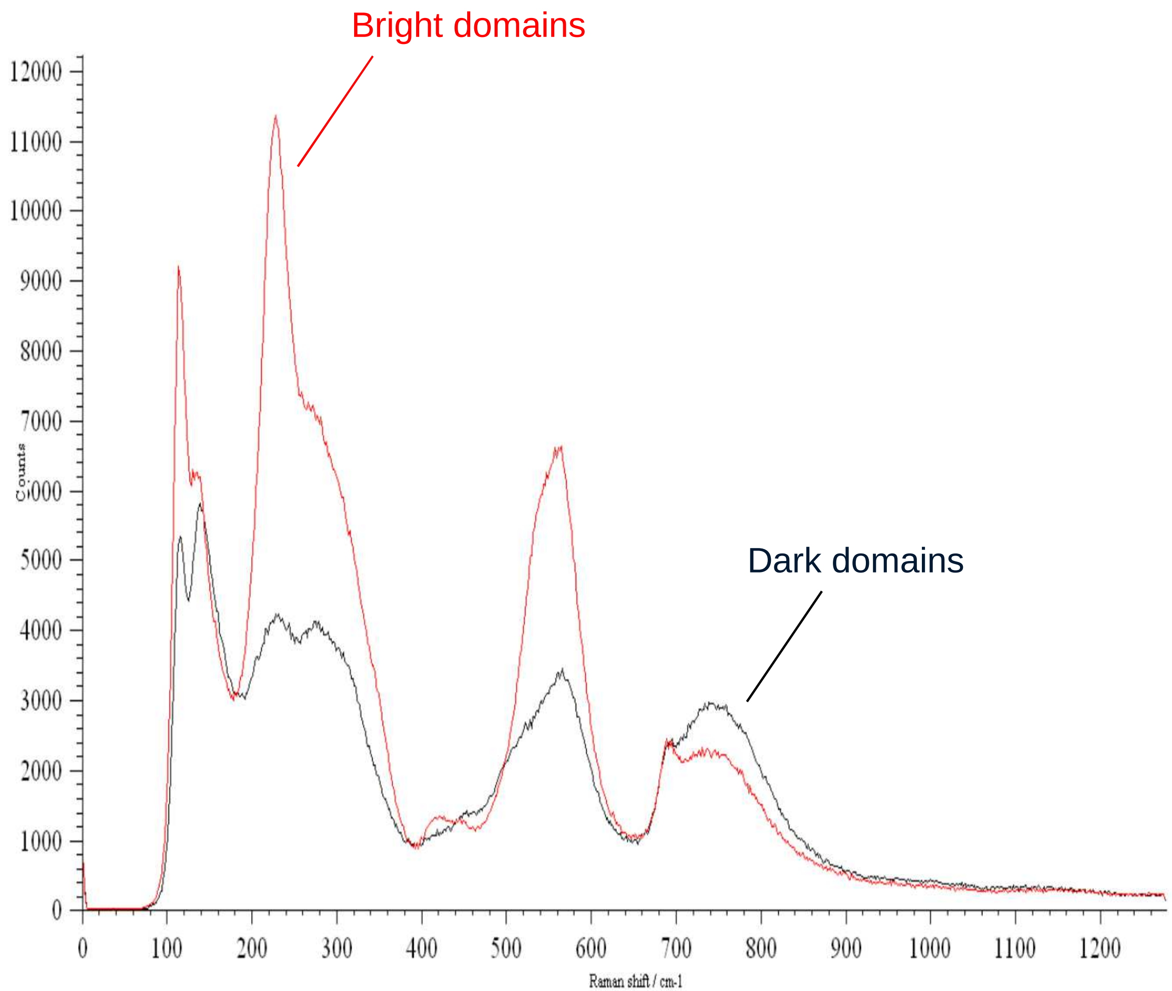
Mapping of ferroic domains in $Pb(Zr,Ti)O_3$ single crystal

Optical microscope



Raman mapping
200 cm^{-1} mode



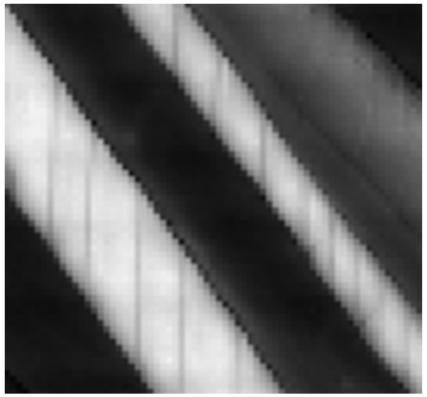


Domain structures and domain walls

Mapping of ferroic domains in $Pb(Zr,Ti)O_3$ single crystal

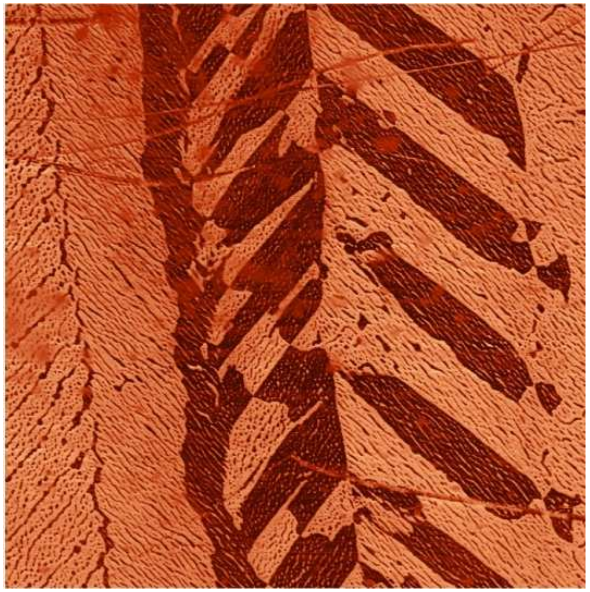
Optical

Raman

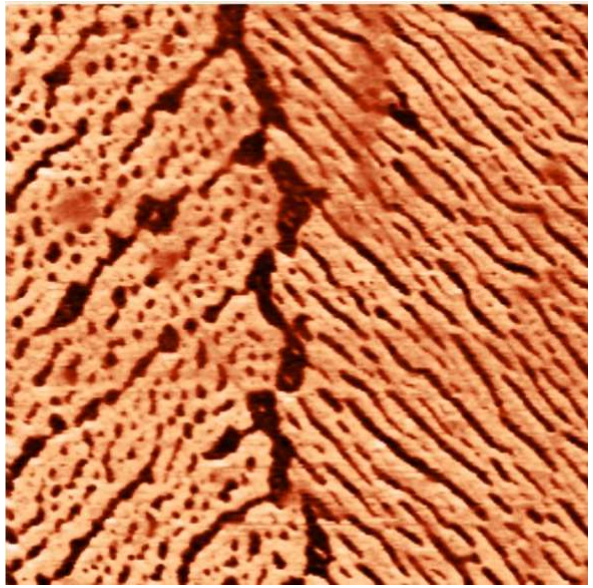


Piezoresponse force microscopy:

Phase image 40 x 40 µm²



Phase image 10 x 10 µm²

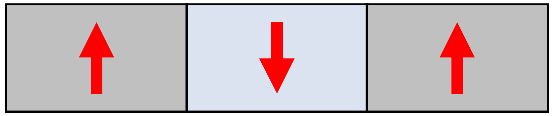


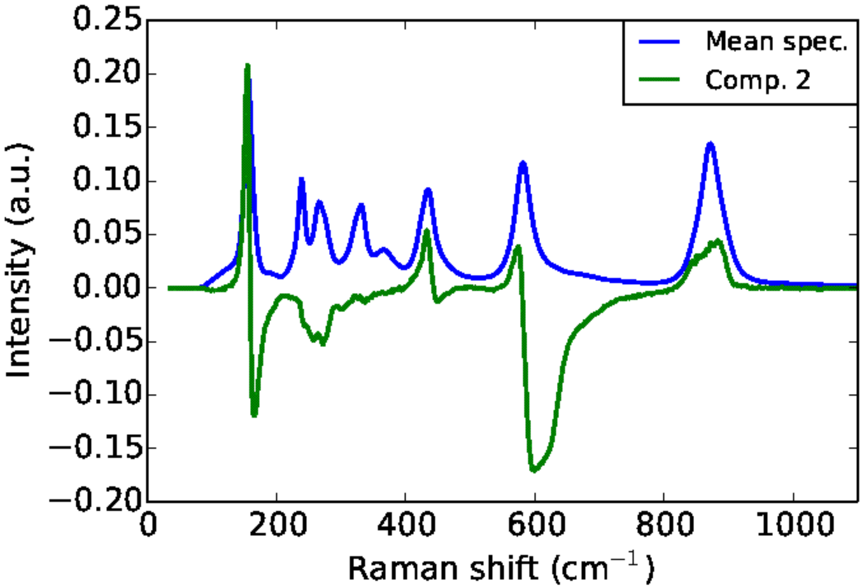
Raman (in-plane orientation) and PFM (out of plane polarization) needed for a full picture

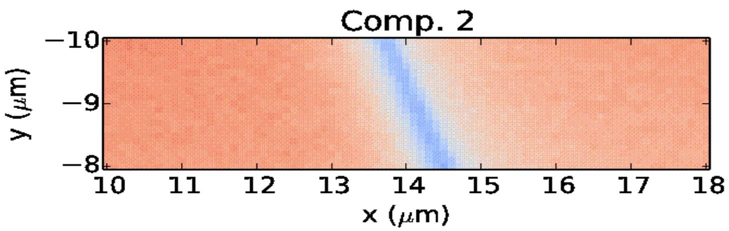
Domain structures and domain walls

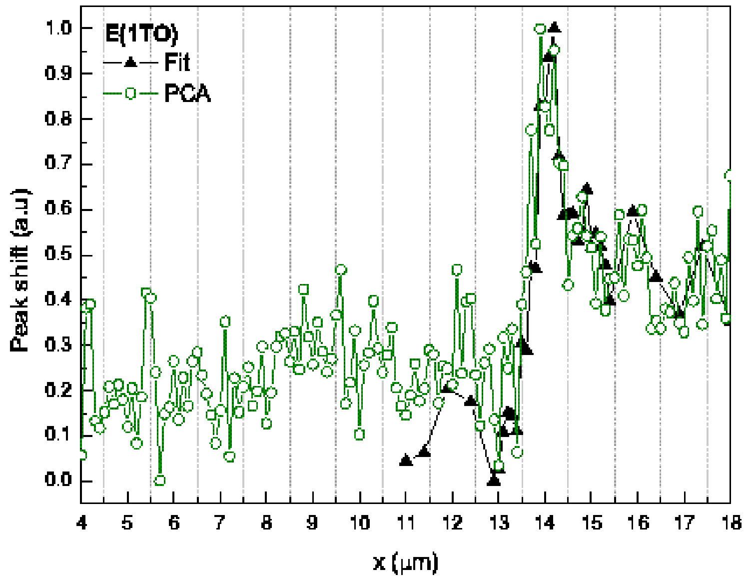
Mapping of domain walls in $LiNbO_3$ by principal component analysis

Perfect 180° domain structure:









- PCA used to detect and quickly map very small changes of the Raman spectrum.
- Information on strain and internal electric fields at the domain walls.

Polar and oblique modes

Raman scattering by polar modes

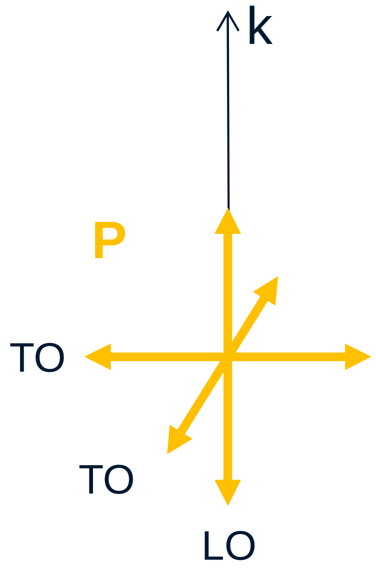
Exclusion rule:
In centrosymmetric crystals, Raman-active modes are not IR-active and vice versa.

By definition:
Ferroelectric crystals are non-centrosymmetric.

Scattering by polar modes has to be considered.

Polar and oblique modes

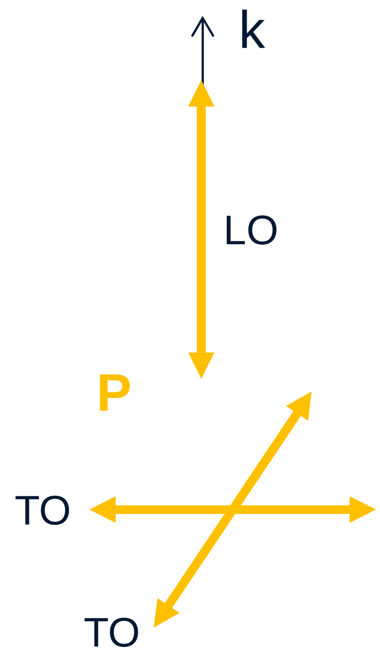
LO-TO splitting in a cubic crystal



Transverse TO modes:
No associated macroscopic electric field

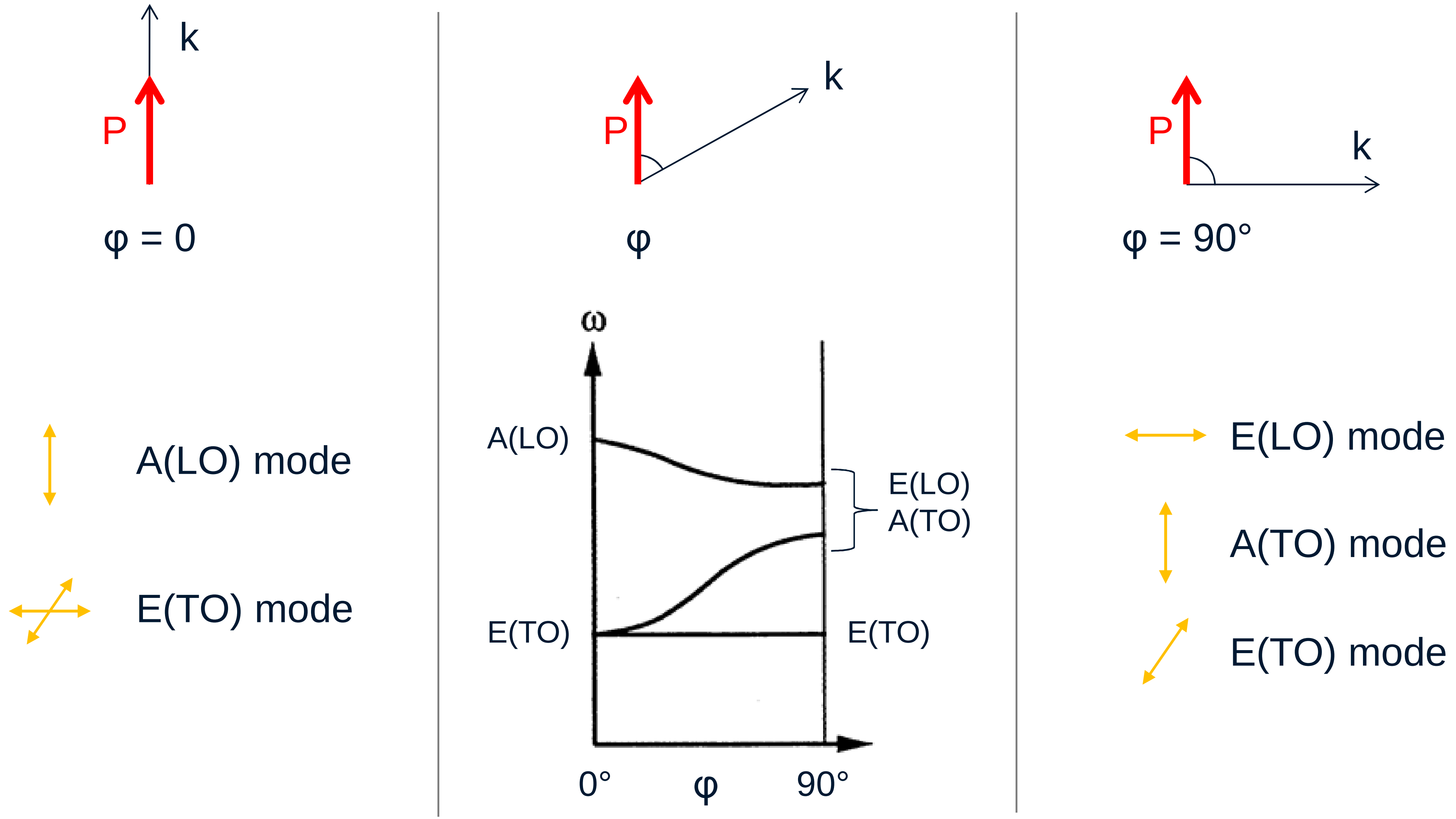
Longitudinal LO mode:
Associated electric field coupling to the polarization
Shift of the vibration frequency

LO-TO splitting



Polar and oblique modes

Oblique modes: scattering by polar modes in uniaxial crystals



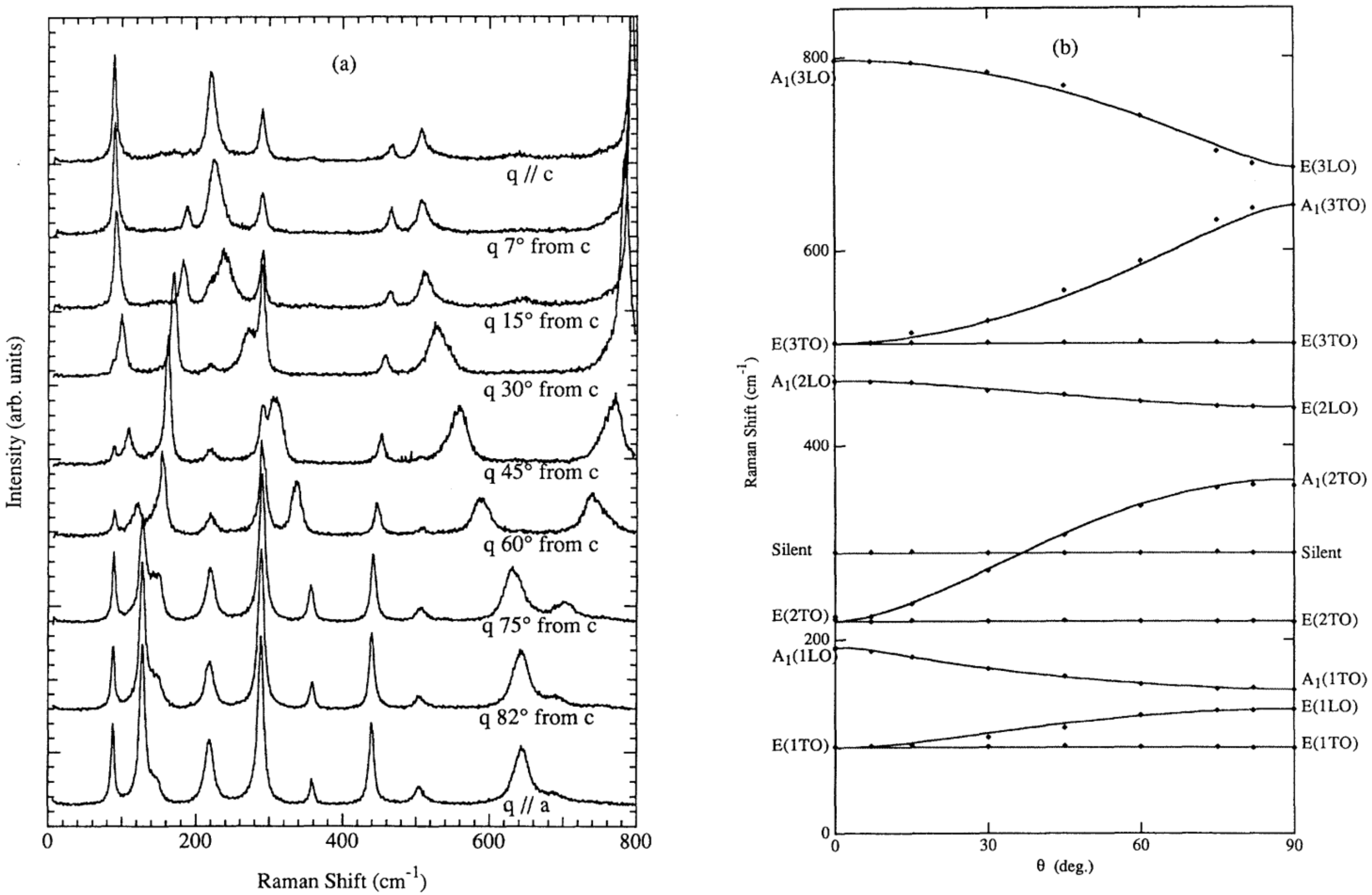
4 frequencies to be determined: A(TO), A(LO), E(TO), E(LO)

Polar and oblique modes

Oblique modes in $PbTiO_3$ in a platelet geometry

- Tetragonal P4mm structure, 4 atoms per unit cell

  $\Gamma = 3(A_1 + E) + (B_1 + E)$
- All modes are IR and Raman active



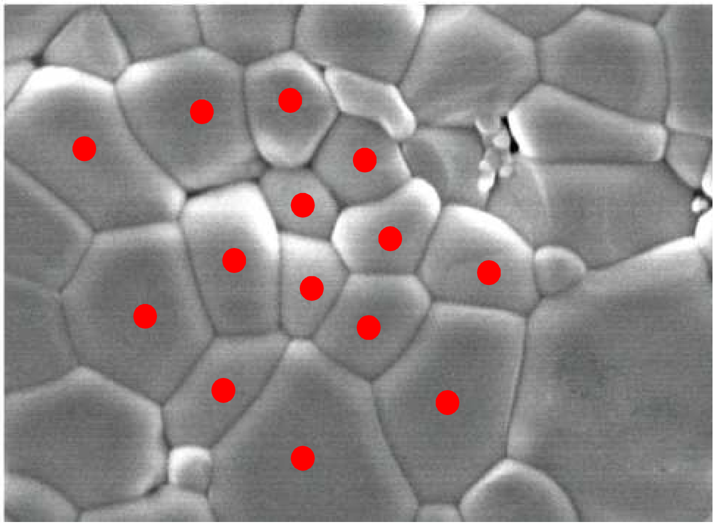
Foster *et al.*, Phys. Rev. B **48**, 10160 (1993)

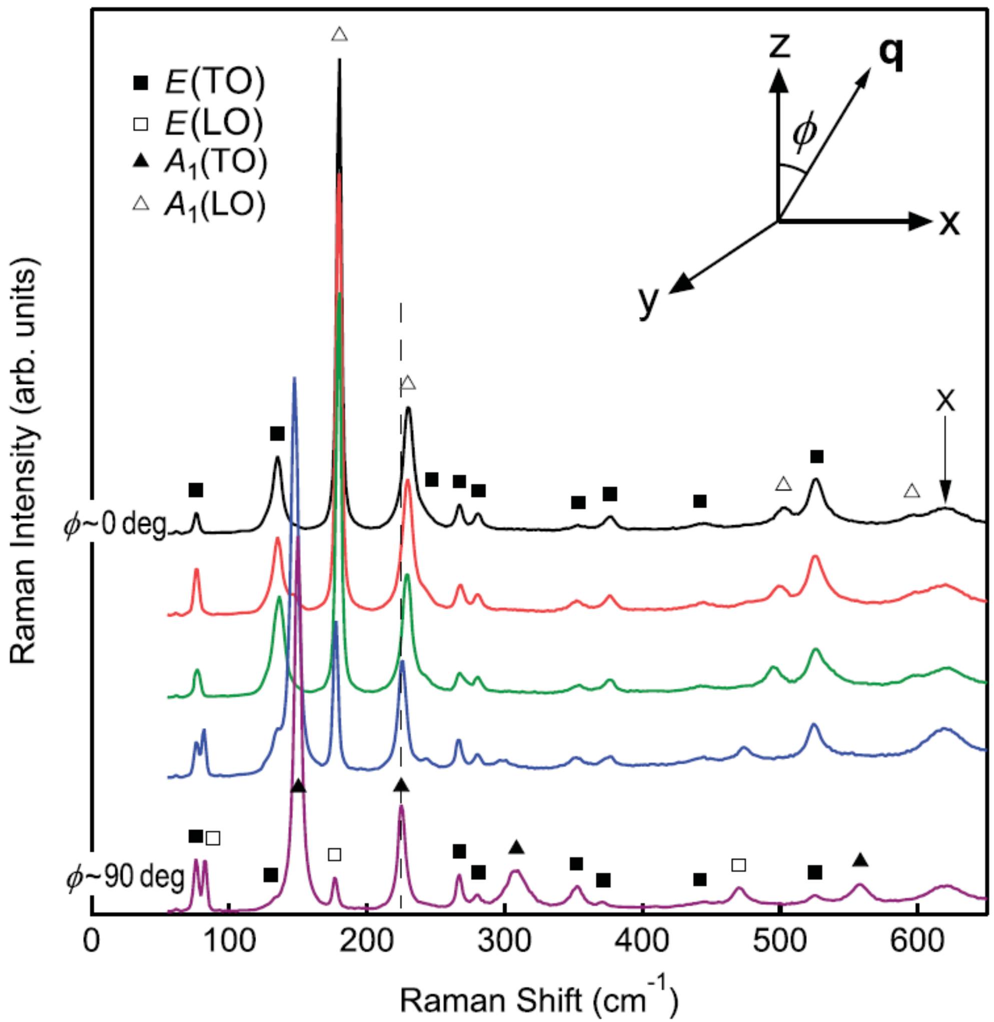
Polar and oblique modes

Oblique modes in $BiFeO_3$

- Rhombohedral *R3c* structure
- 10 atoms per unit cell,
- $\Gamma = 4(A_{1g} + E_g) + 5(A_{2g} + E_g)$
- All Raman active vibrations are polar.

Approach:
Multiple spectra on a coarse grain ceramic





Hlinka *et al.*, Phys. Rev. B **83**, 020101 (2011)

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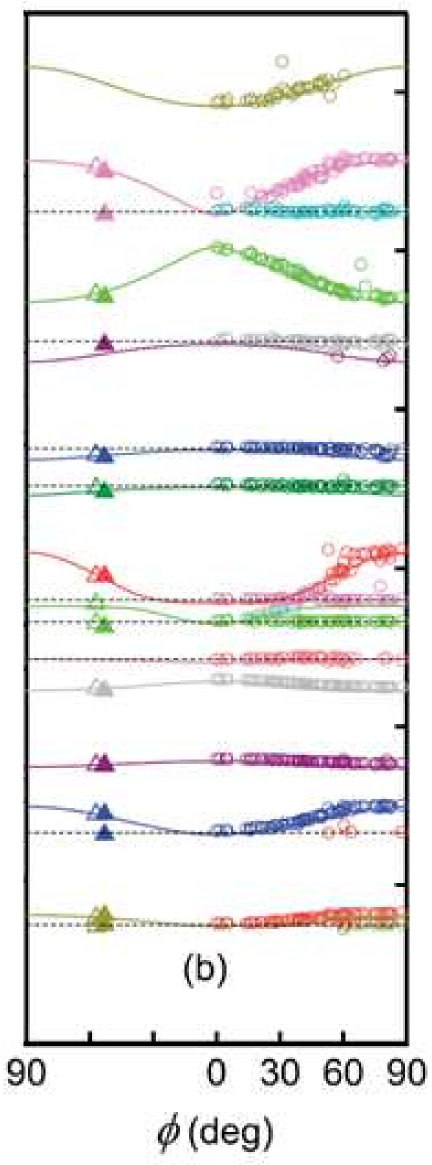
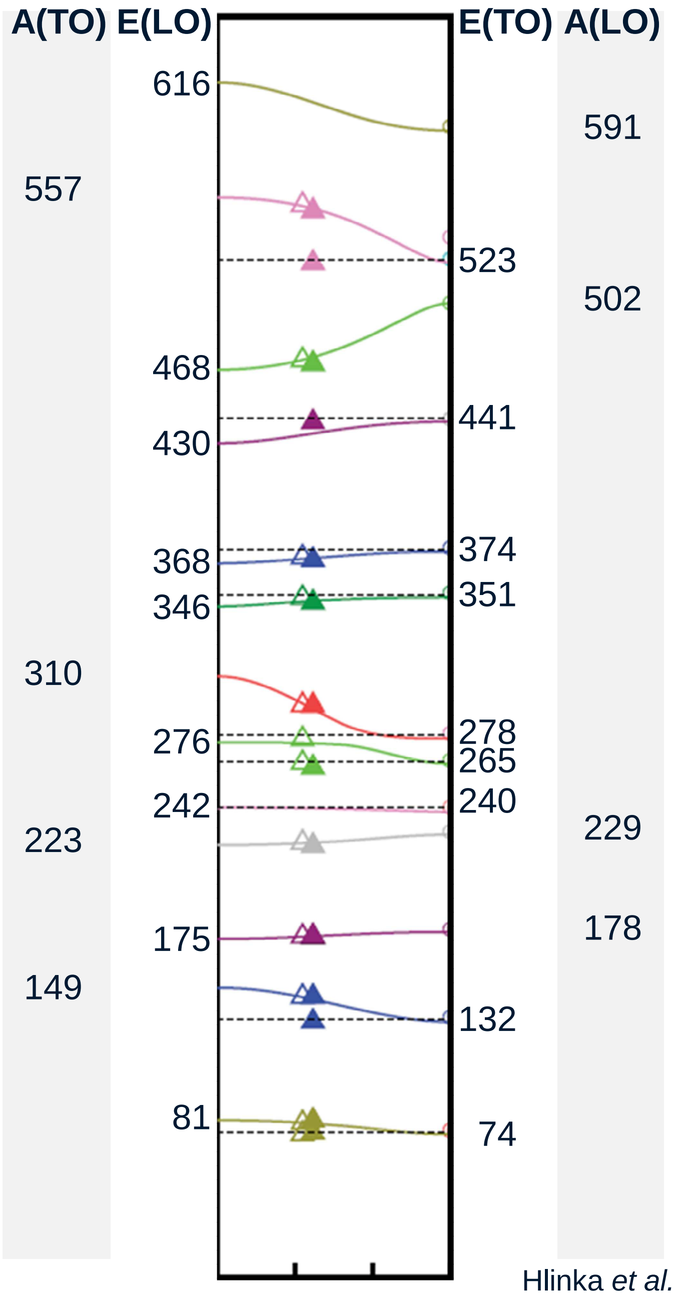
Polar and oblique modes

Oblique modes in $BiFeO_3$

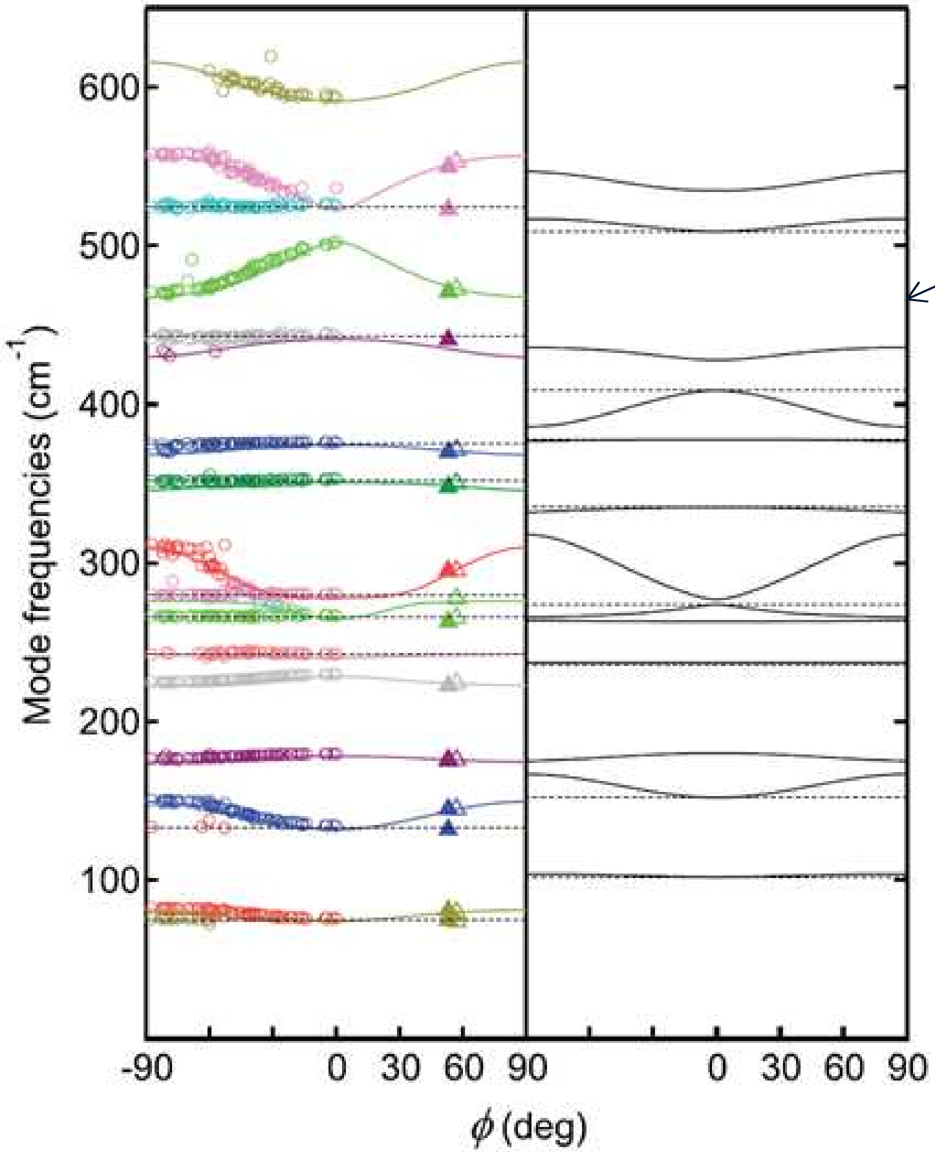




Hlinka *et al.*, Phys. Rev. B **83**, 020101 (2011)

Raman spectrum of $BiFeO_3$

Comparison with theoretical frequencies



Phonon frequencies by DFT

Qualitative agreement only

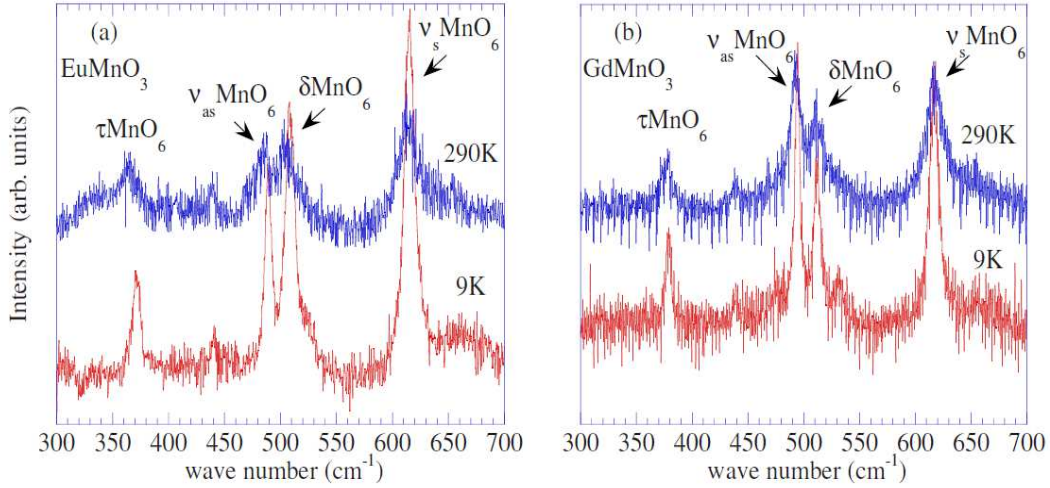
Hlinka *et al.*, Phys. Rev. B **83**, 020101 (2011)
Hermet *et al.*, Phys. Rev. B **75**, 220102 (2007)

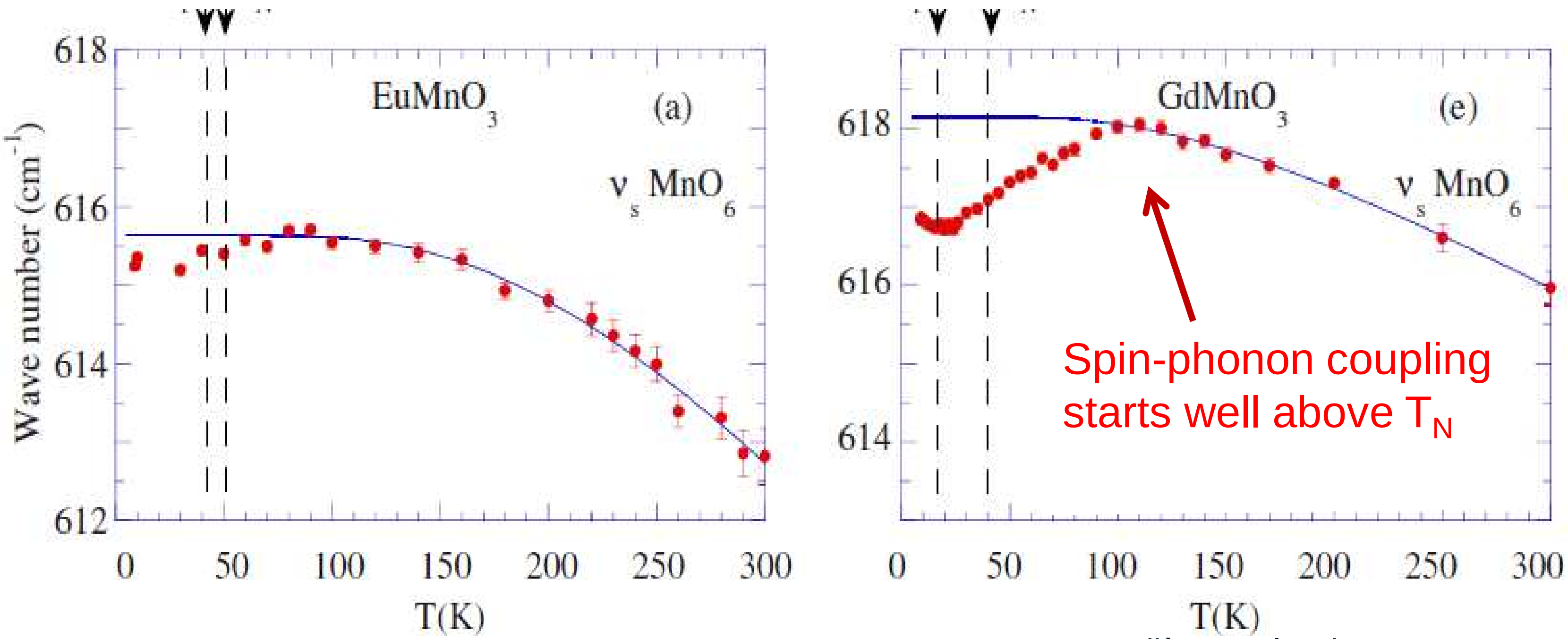
Magnetism

Spin-phonon coupling

Phonon frequencies are affected by the correlation of spins

$$\omega = \omega_0 + \lambda \langle S_i \cdot S_j \rangle$$





J. Laverdière et al., Phys. Rev. B **73**, 214301 (2006)

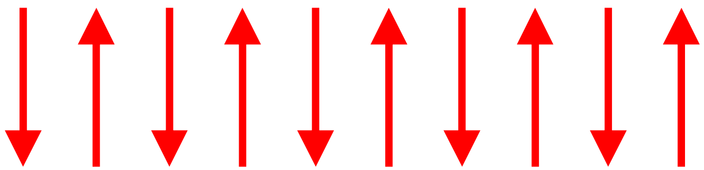
J. A. Moreira et al., *Phys. Rev. B* **79**, 054303 (2009), *Phys. Rev. B* **82**, 094418 (2010)

Magnetism

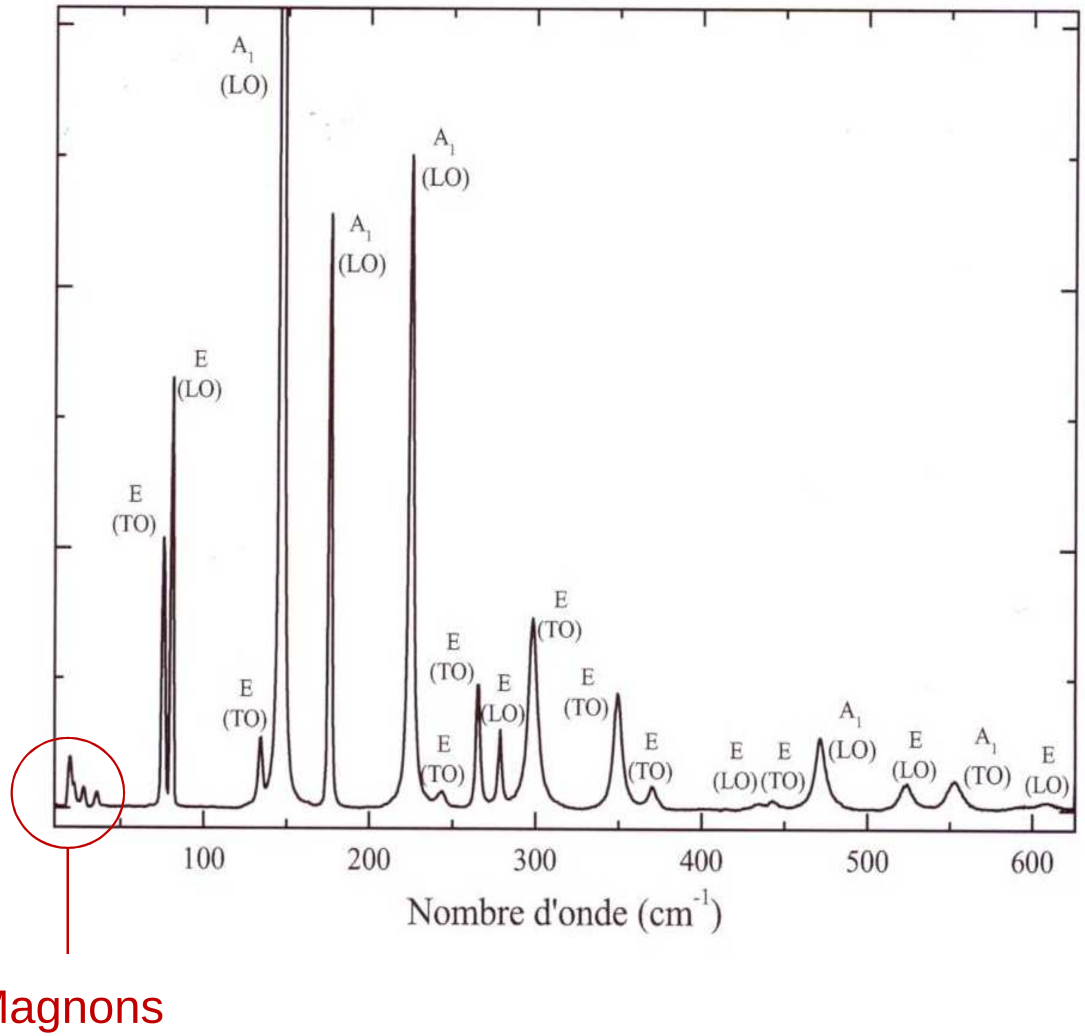
Raman scattering by magnons in $BiFeO_3$

Measures the exchange constant of the Heisenberg model

$$E = -\sum_{i,j} J\,\vec{S}_i \cdot \vec{S}_j$$



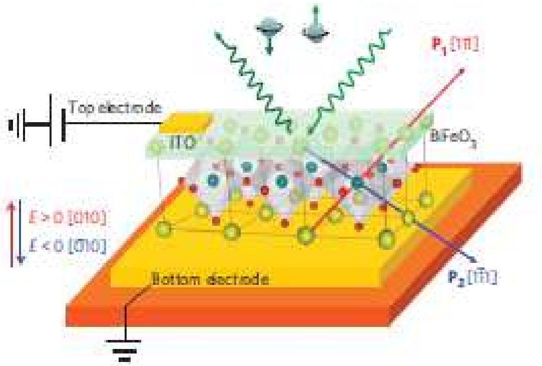
In $BiFeO_3$:
Antiferromagnetic with T_N = 640 K

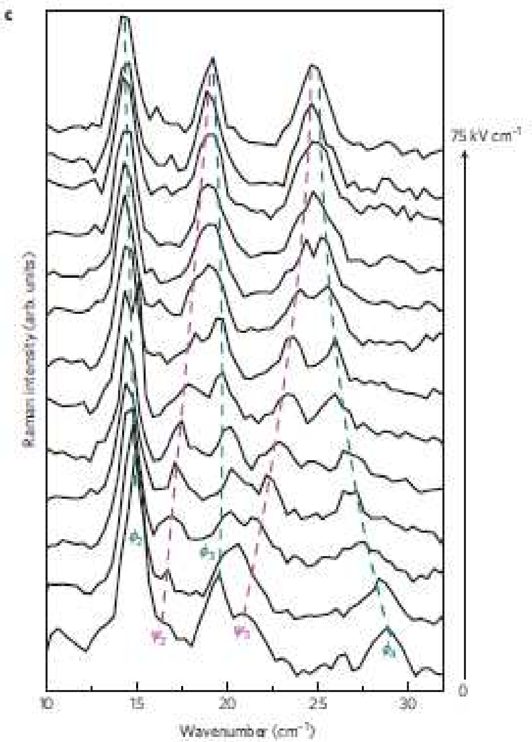


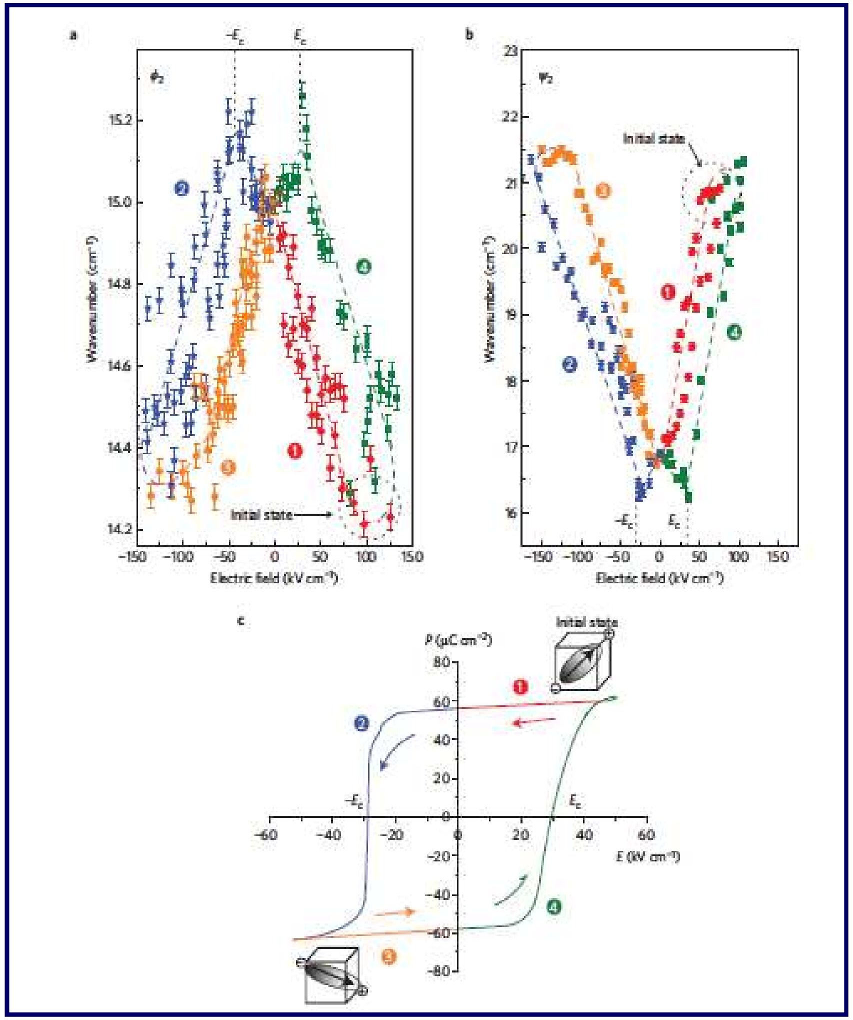
P. Rovillain, PhD Thesis.

Magnetism

E-field control of spin waves in $BiFeO_3$







P. Rovillain et al., Nature Mat. **9**, 975 (2010)

Outline

Introduction:

Functional ferroic perovskites

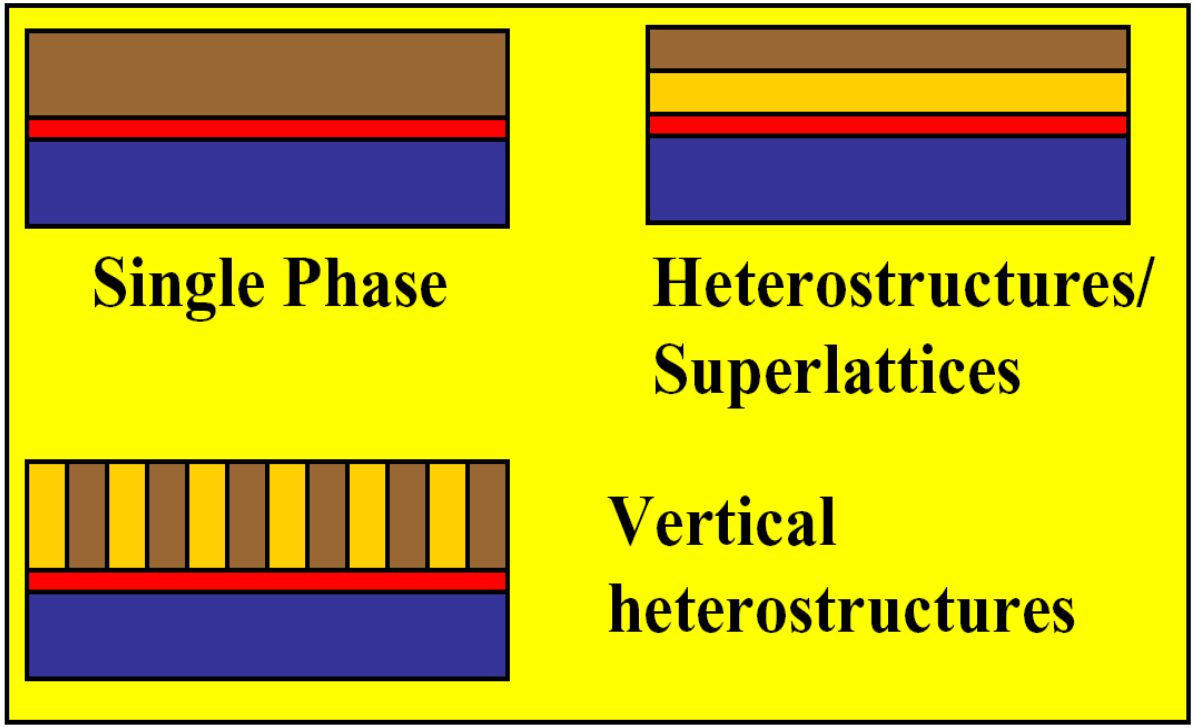
Raman on ferroic perovskites:

Soft mode / hard mode spectroscopy
Domain structures and domain walls
Polar and « oblique » modes
Magnetism

Beyond the bulk:

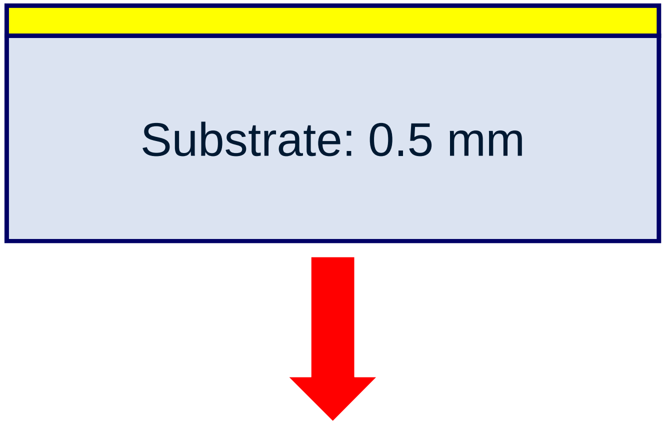
Thin films
Heterostructures
Multilayers

Heterostructures

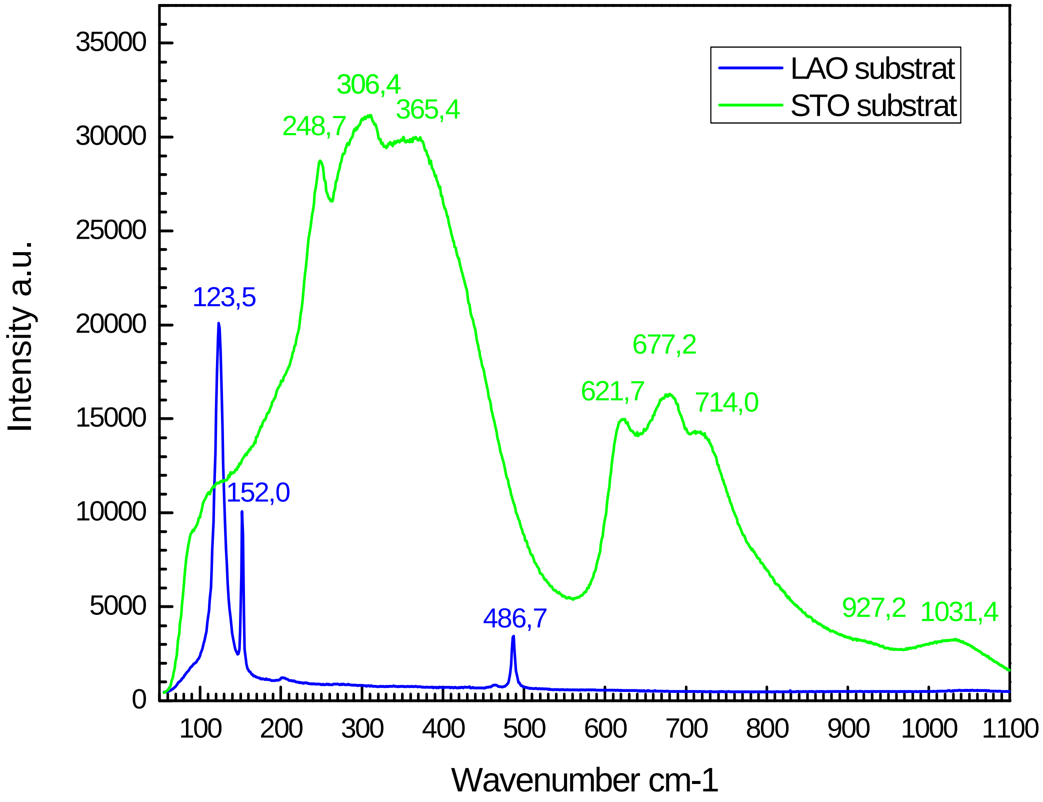


Thin films & their substrates

« Thin » film
0.4 nm < t < 100 nm and more



Very small scattering volume
Signal hidden by the substrate



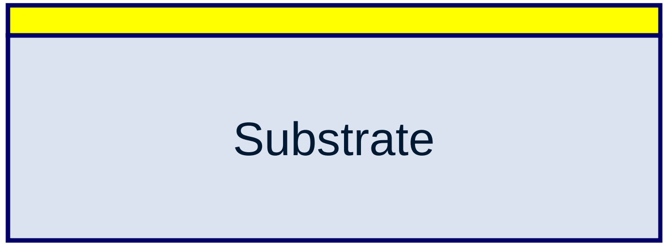
Is there a limiting thickness?... Depends…

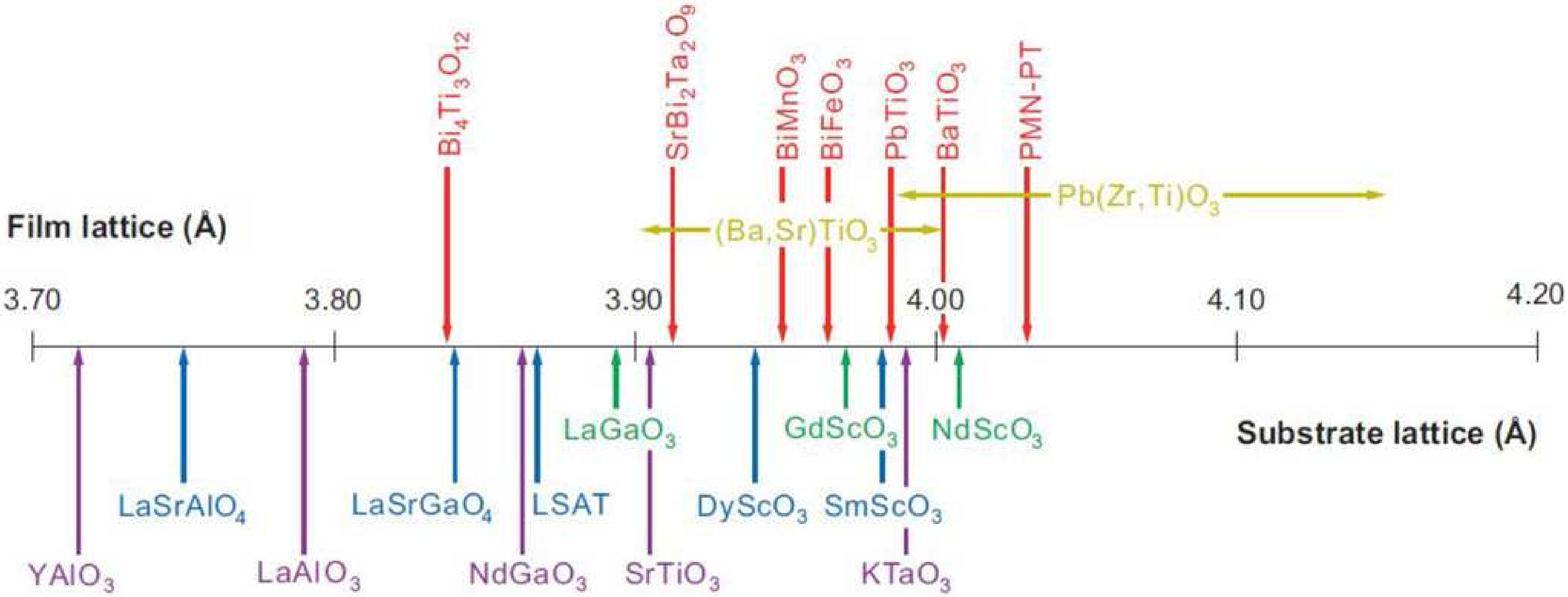
- ➔ Excitation wavelength
- ➔ Sample absorption
- ➔ Local enhancement

Thin films & their substrates

Phase transition induced by epitaxial strain: $LaNiO_3$

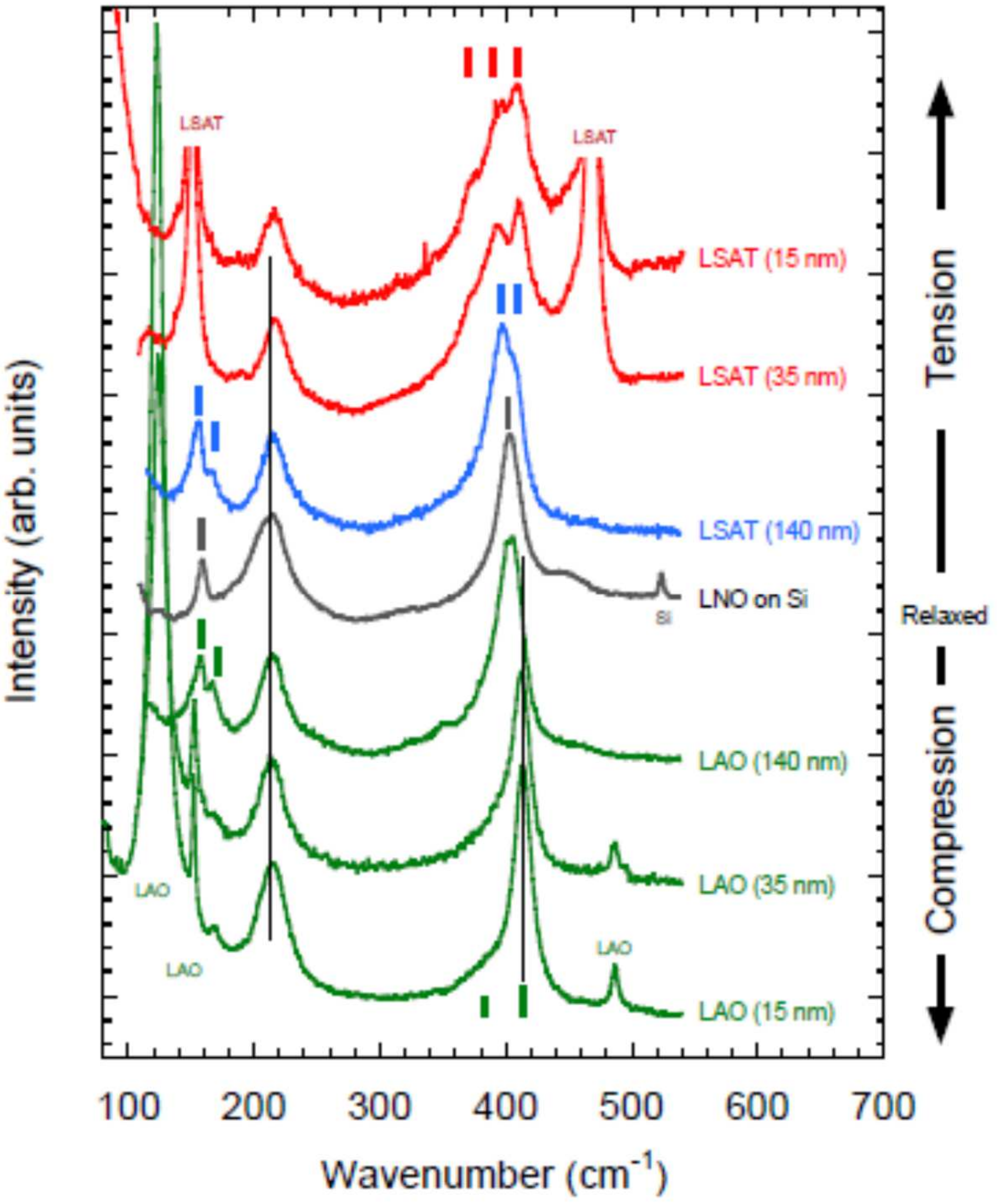
Phase transition
- Symmetry of the film / substrate
- Lattice parameters of the film / substrate
- Film thickness





Thin films & their substrates

Phase transition in $LaNiO_3$ by epitaxial strain



On cubic LSAT

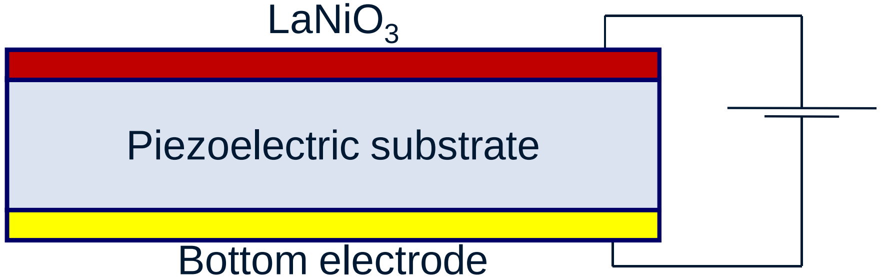
Bulk $LaNiO_3$: rhombohedral R-3c

On pseudo-cubic LAO

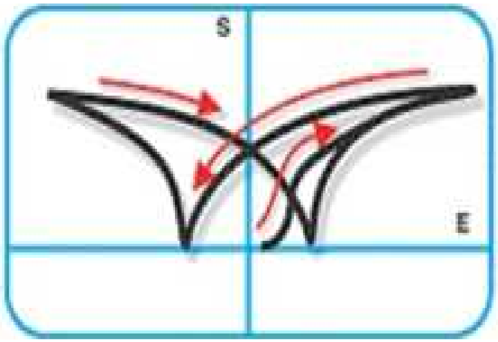
Centre de Recherche Public Gabriel Lippmann

Thin films & their substrates

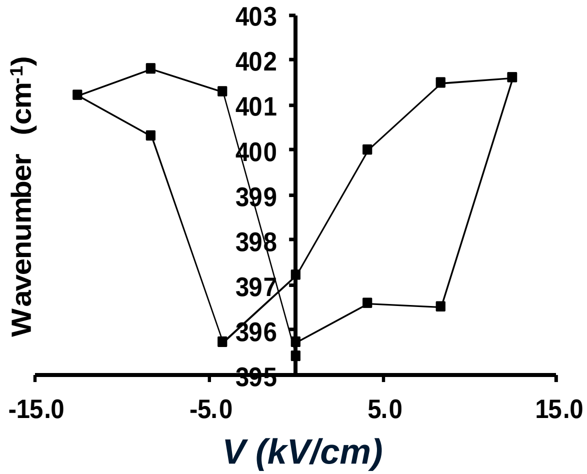
Strain in $LaNiO_3$ by a piezoelectric substrate



Strain as a fct. of E
(piezo substrate)

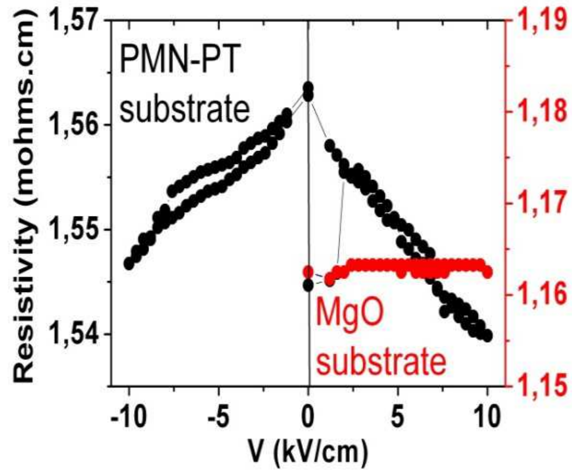


Raman phonon frequency as a fct. of E
($LaNiO_3$ thin film)



Transmission of strain to thin film !

Resistivity as a fct. of E
($LaNiO_3$ thin film)



➔ *2% change in resistivity*

Chaban et al., *Appl. Phys. Lett.* **97**, 031915 (2010)

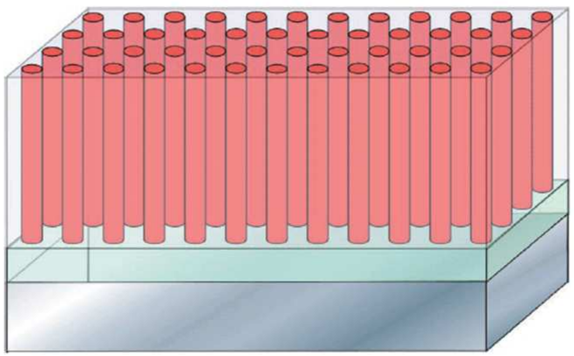
Centre de Recherche Public
Gabriel Lippmann

Multiferroic nanocomposites

$CoFe_2O_4$ – $BiFeO_3$ nanocomposite

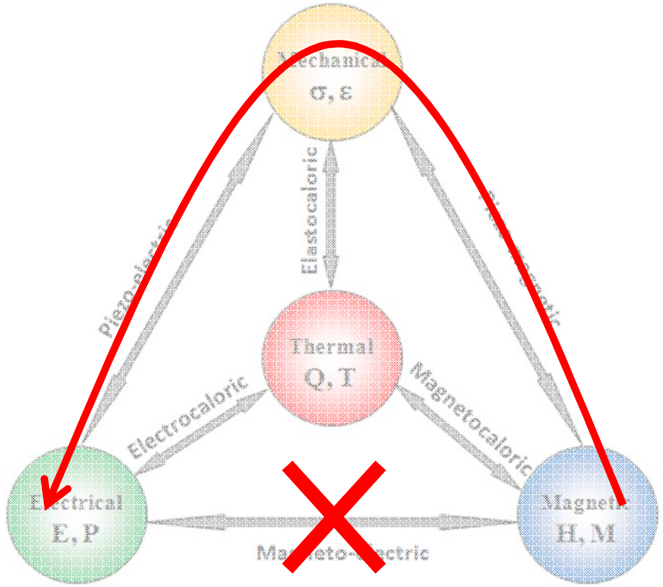
Ferromagnetic
$CoFe_2O_4$ matrix

Ferroelectric
$BiFeO_3$ pilars



$SrTiO_3$ substrate

« Extrinsic » magnetoelectric coupling



Strain-state and strain-coupling in multiferroic perovskite/spinel nano-composite ?

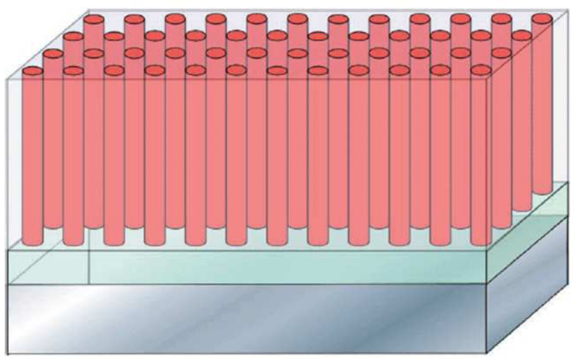
H. Zheng et al., Appl. Phys. Lett. **90**, 113113 (2007)

Multiferroic nanocomposites

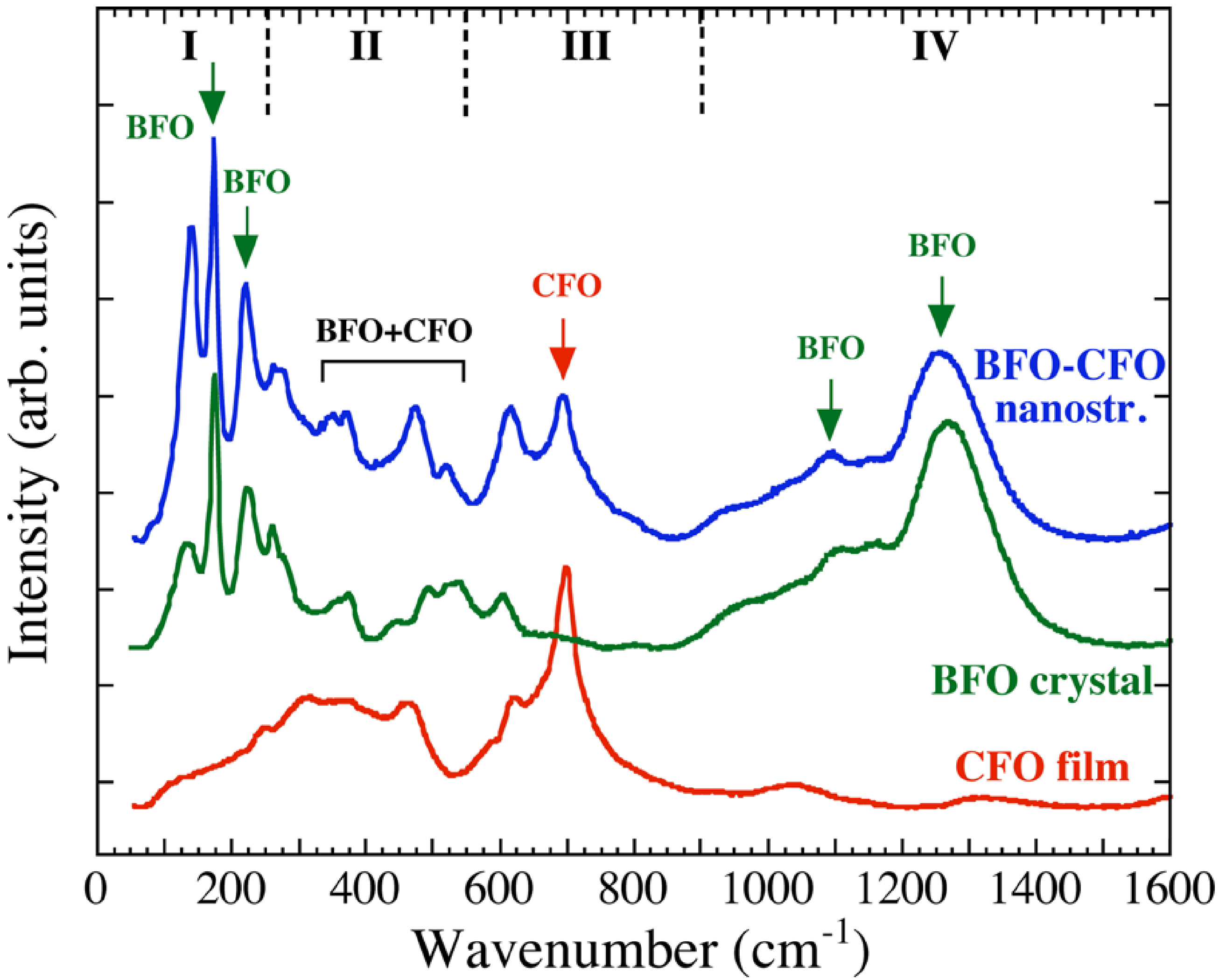
$CoFe_2O_4$ – $BiFeO_3$ nanocomposite

Ferromagnetic $CoFe_2O_4$ matrix

Ferroelectric $BiFeO_3$ pilars



$SrTiO_3$ substrate



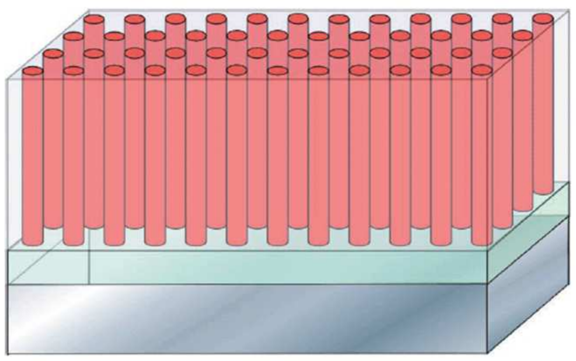
Chaix-Pluchery et al., Appl. Phys. Lett.. **99**, 072901 (2011)

Multiferroic nanocomposites

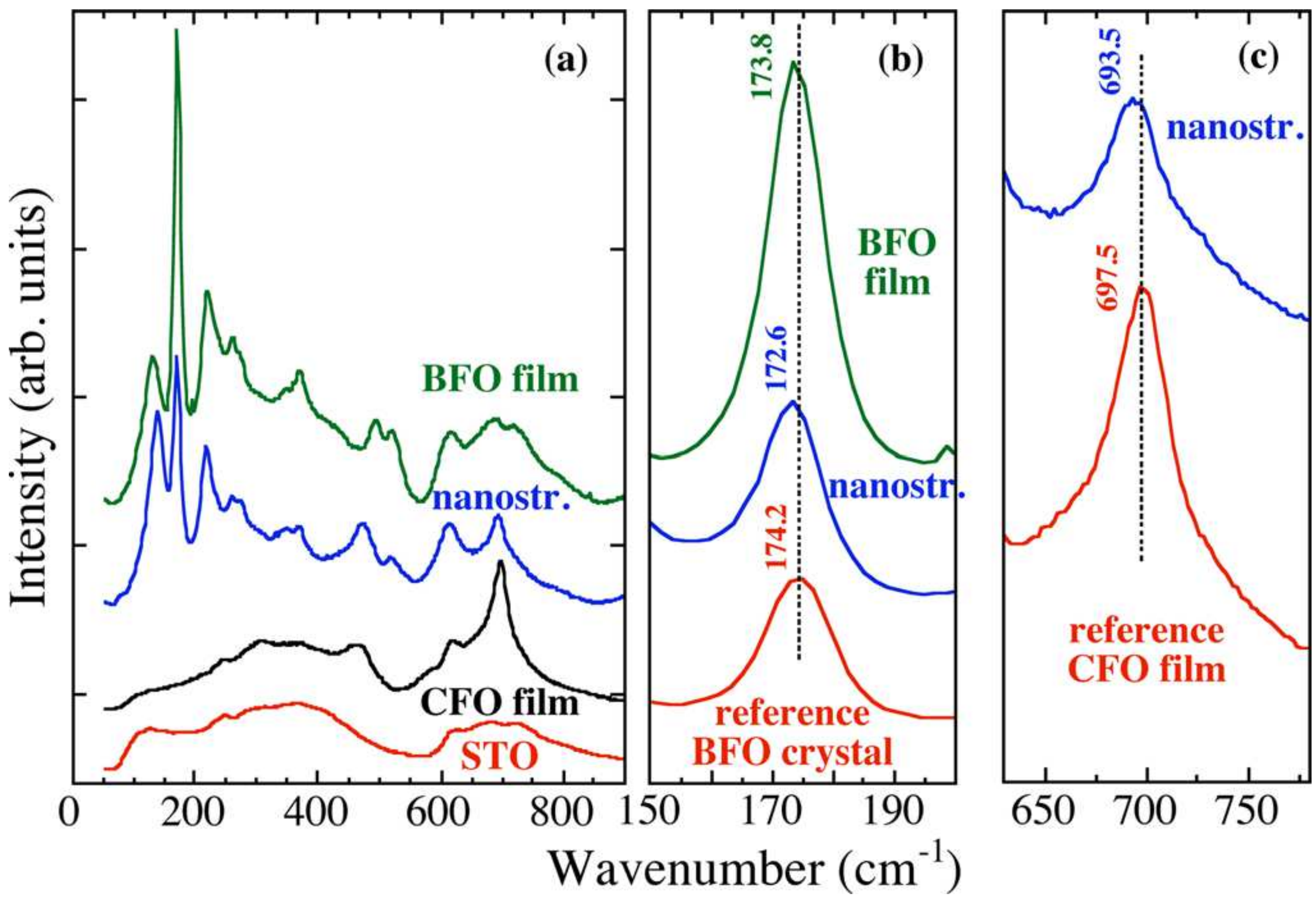
$CoFe_2O_4$ – $BiFeO_3$ nanocomposite

Ferromagnetic $CoFe_2O_4$ matrix

Ferroelectric $BiFeO_3$ pilars



$SrTiO_3$ substrate

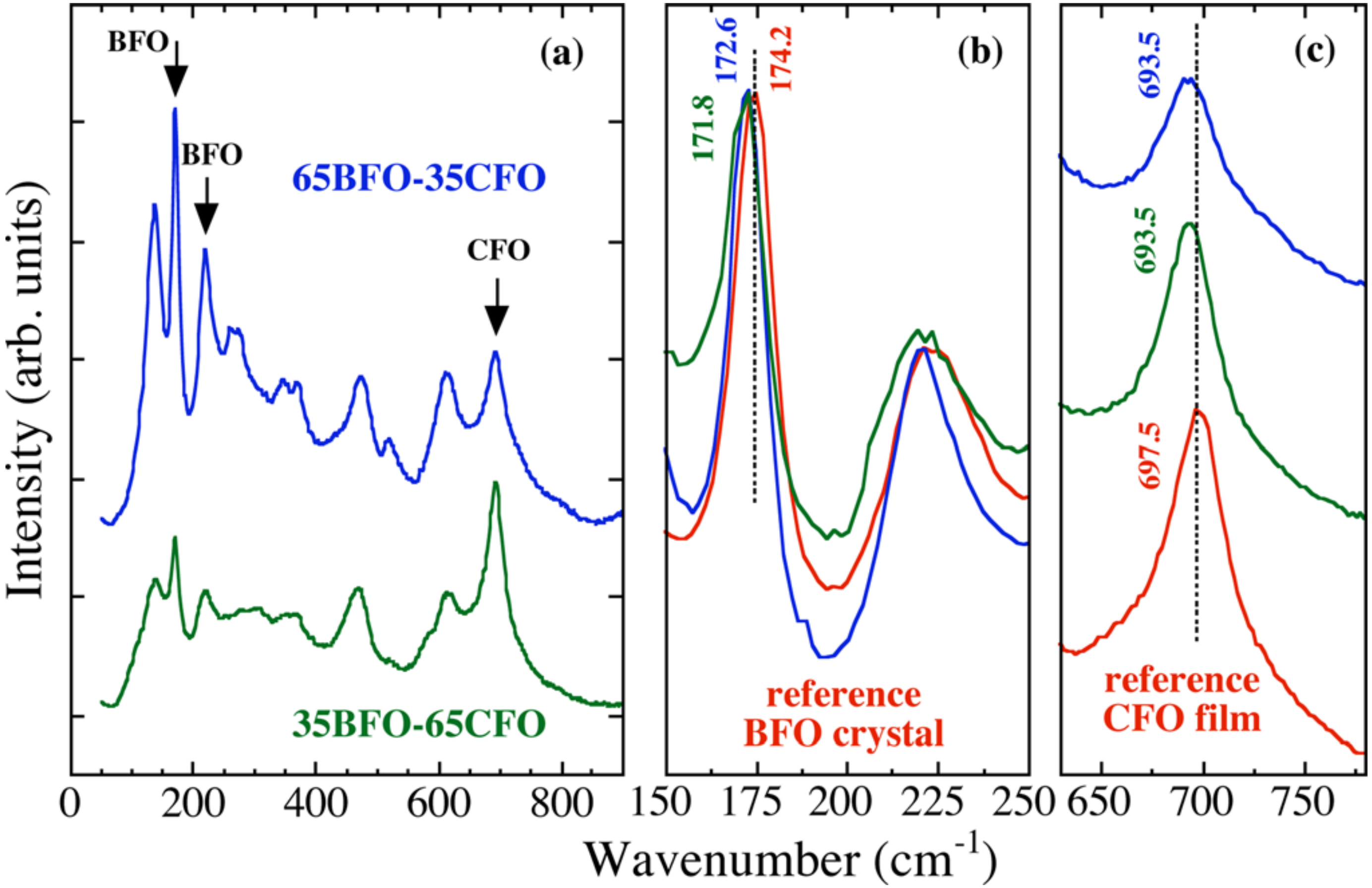


Multiferroic nanocomposites

$CoFe_2O_4$ – $BiFeO_3$ nanocomposite

Comparisons of two nanostructures with different pillar/matrix ratios & sizes

➔ Do they have the same strain state?



$CoFe_2O_4$ (CFO)

➔ equally strained

$BiFeO_3$ (BFO)

➔ Different strain state

➔ Thinner pillars more strained

Multilayer

Investigation of multilayer with multiple wavelengths

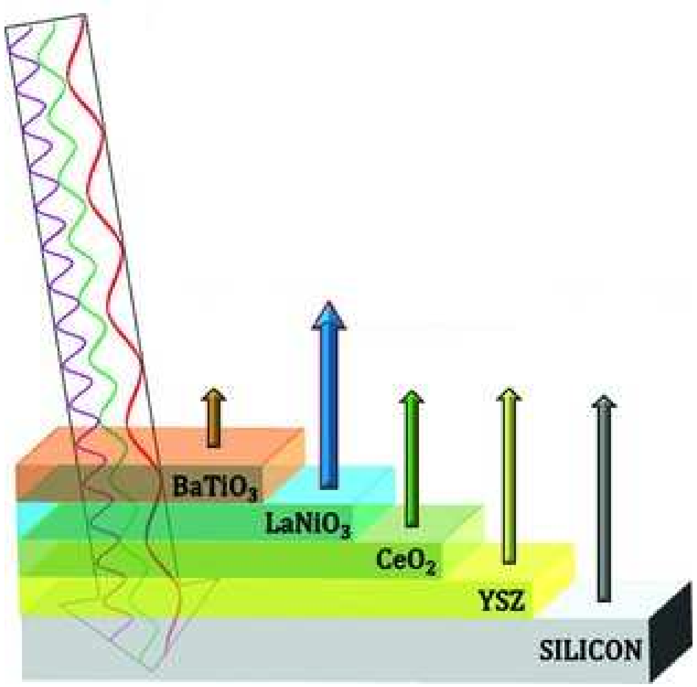
Importance of the wavelength comes from:

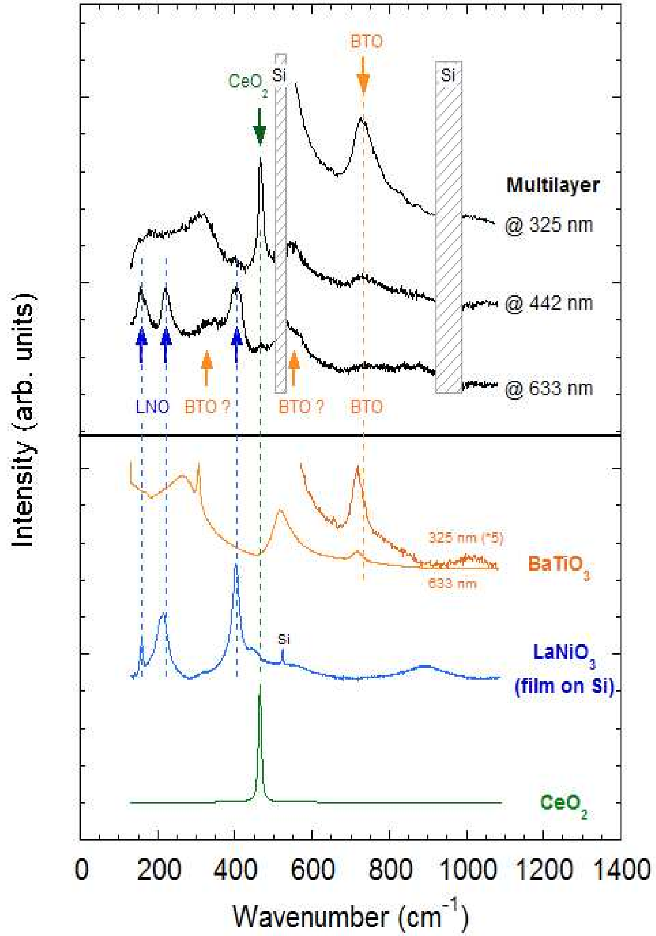
- different absorption at different wavelength
- interaction with other excitations (electronic…)

Such interactions can be

- desirable: signal enhancement by <u>resonant</u> Raman scattering
- a plague: unwanted fluorescence etc.

Thicknesses:
55 nm
35 nm
20 nm
40 nm





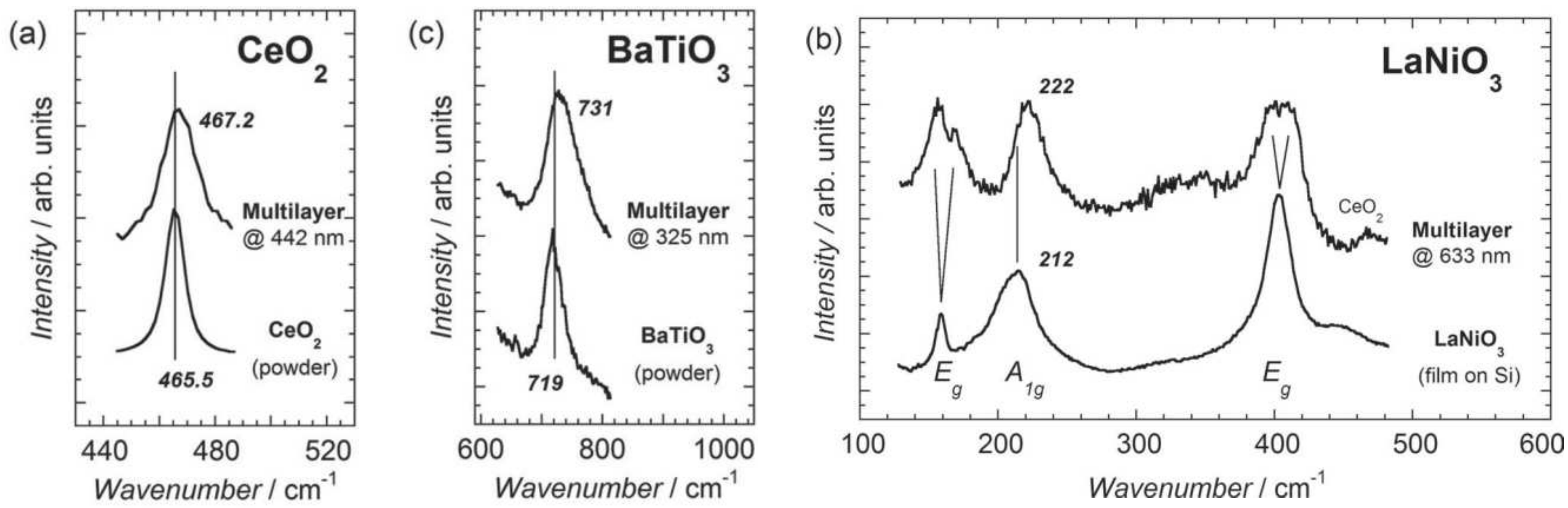
Raman spectra of the different layers revealed at different wavelengths.

J. Kreisel et al., Adv. Funct. Mater. ***22****, 5044 (2012)*

Multilayer

Investigation of multilayer with multiple wavelengths

Analysis of strain/stress states of individual layers or components.



- CeO_2: compressive strain state ~ 0.5 GPa
- $BaTiO_3$: compressive strain state ~ 2.5 GPa
- $LaNiO_3$: mode degeneracy lifted due to in plane stress.

J. Kreisel et al., Adv. Funct. Mater. ***22****, 5044 (2012)*