International Hybrid Training school

Characterization techniques for epitaxial materials

Characterization of functional oxides thin films and heterostructures using Raman spectroscopy

J Agostinho Moreira

Departamento de Física e Astronomia
Faculdade de Ciências da Universidade do Porto
jamoreir@fc.up.pt

OPERA COST ACTION CA20116

OUTLINE

Chapter 1. Basis

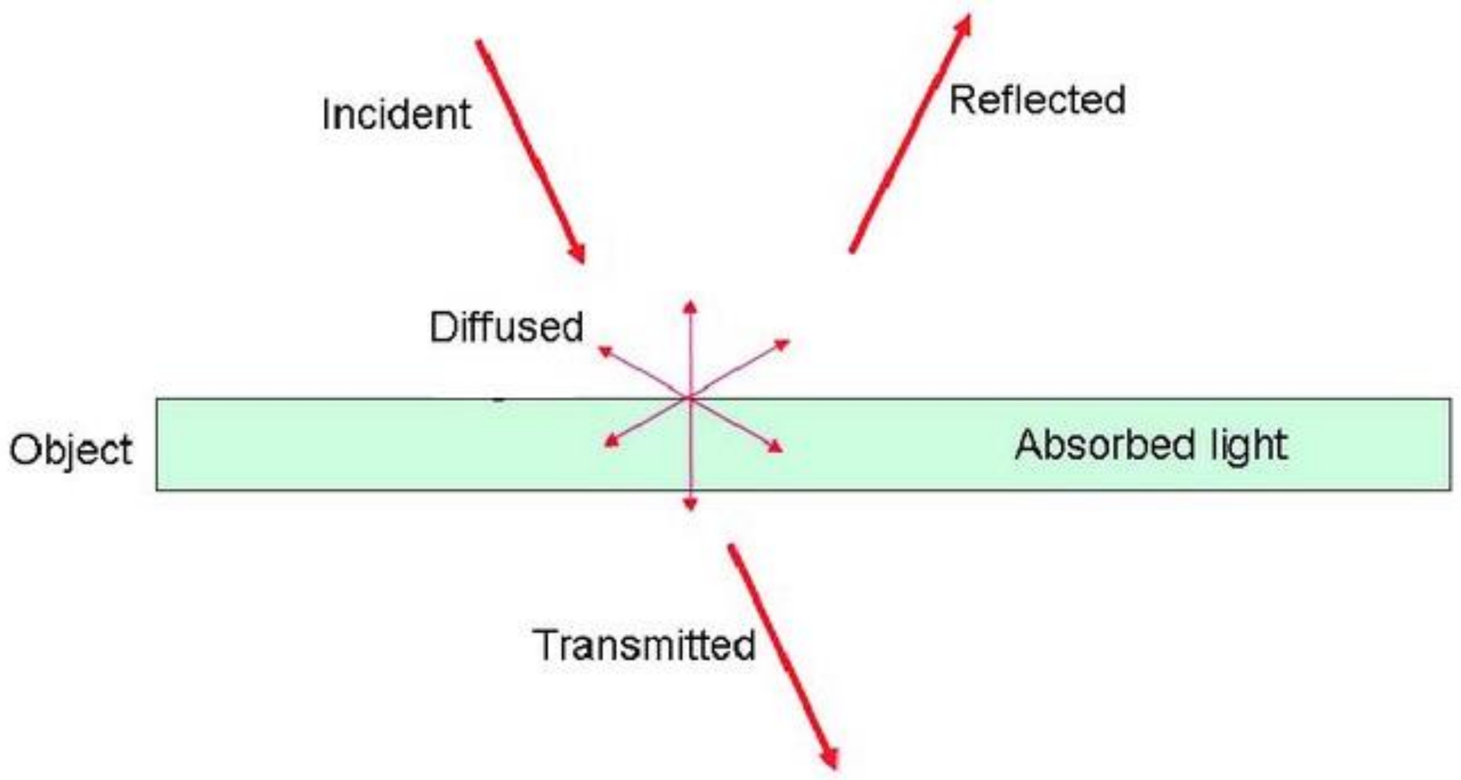
- Raman scattering - main concepts
- Instrumentation for Raman spectroscopy and imaging
- Raman spectrometer and its capabilities existing at LaPMET – IFIMUP

Chapter 2. Raman scattering as a tool for material characterization

- Uses of Raman scattering spectroscopy
- Few examples
  - ➢ Mapping and imaging: ferroic domains and internal stress
  - ➢ Multi-wavelength and penetration depth
  - ➢ Metal-to-insulating transitions and epitaxy

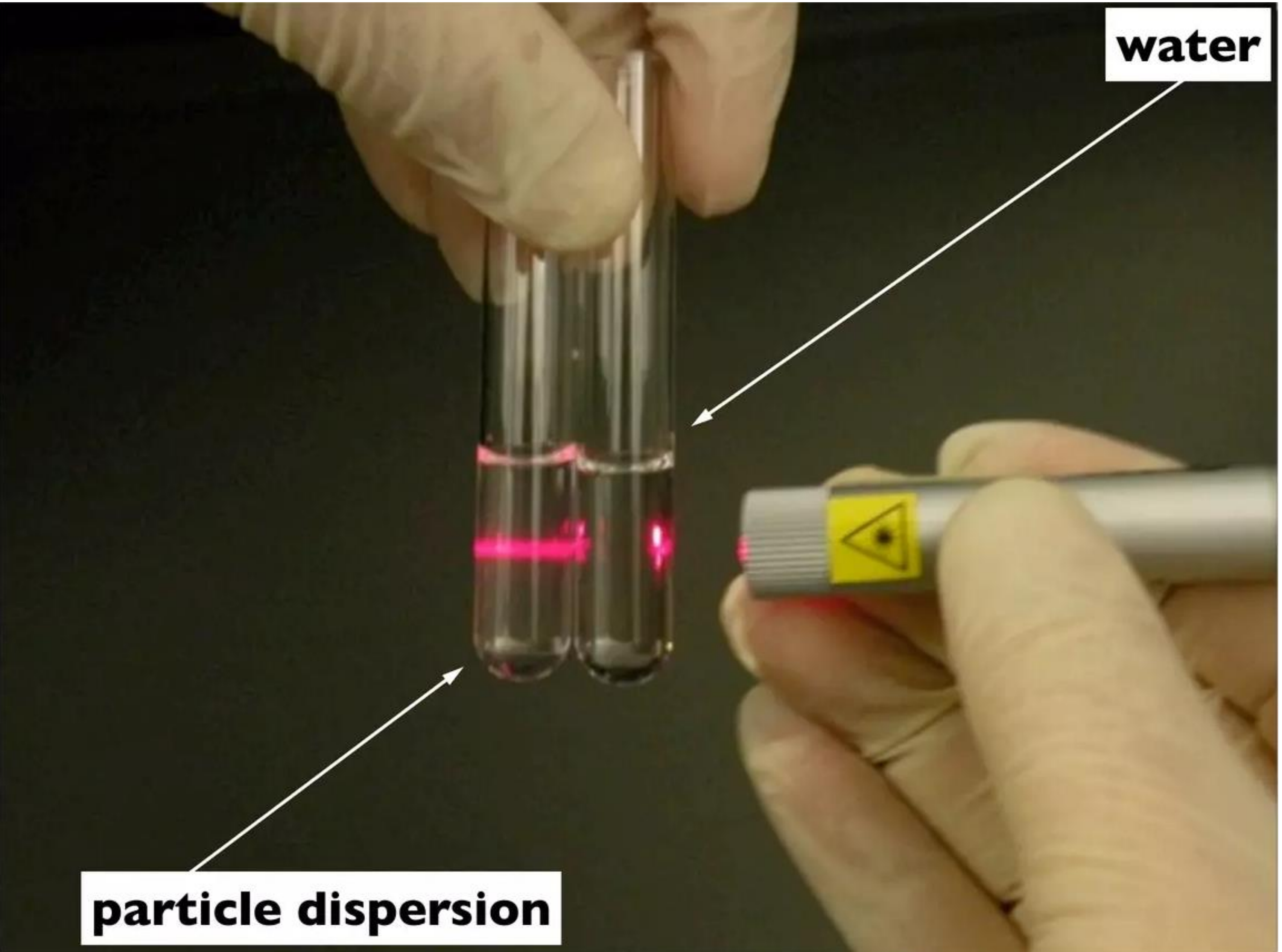
BASIS - Raman scattering - main concepts

Light-Matter interactions



Probing matter properties: structure, excitations, chemistry, dynamics, …

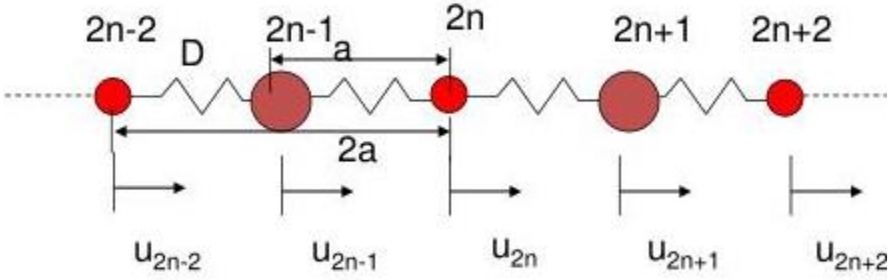
BASIS - Raman scattering - main concepts

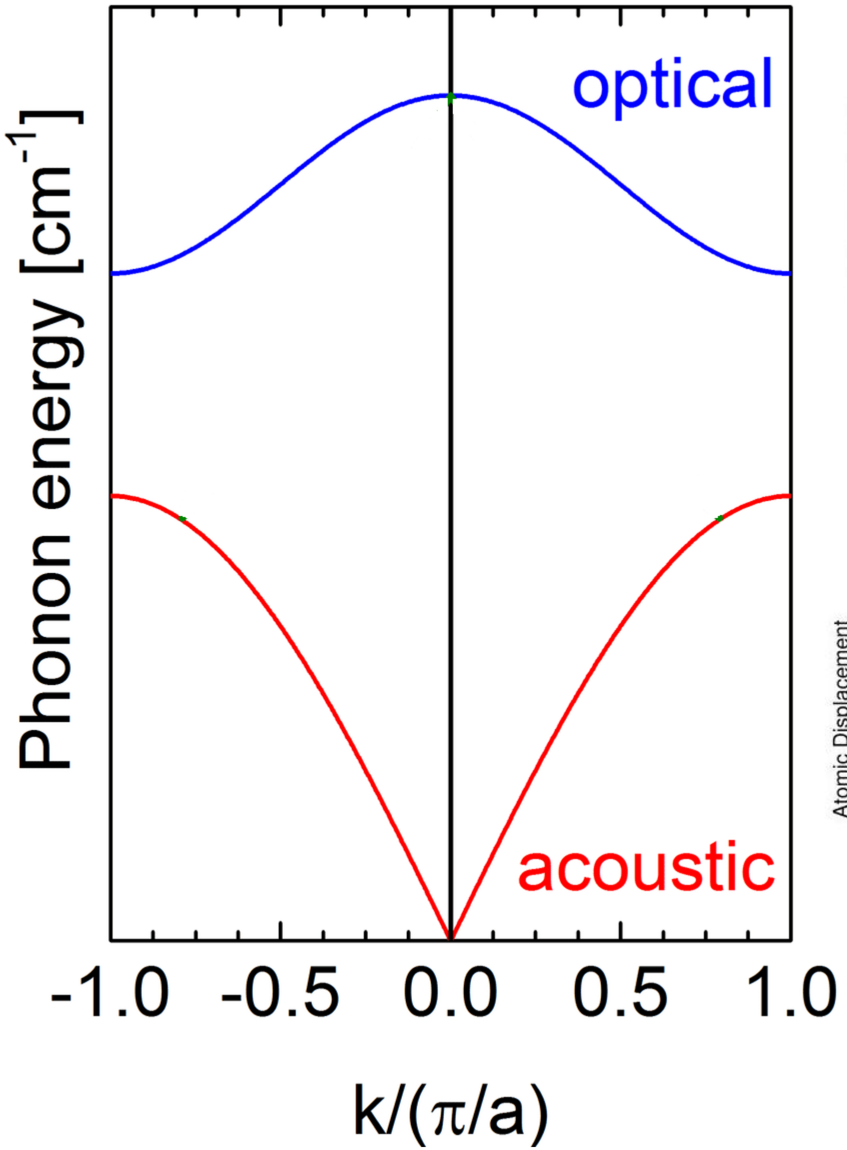


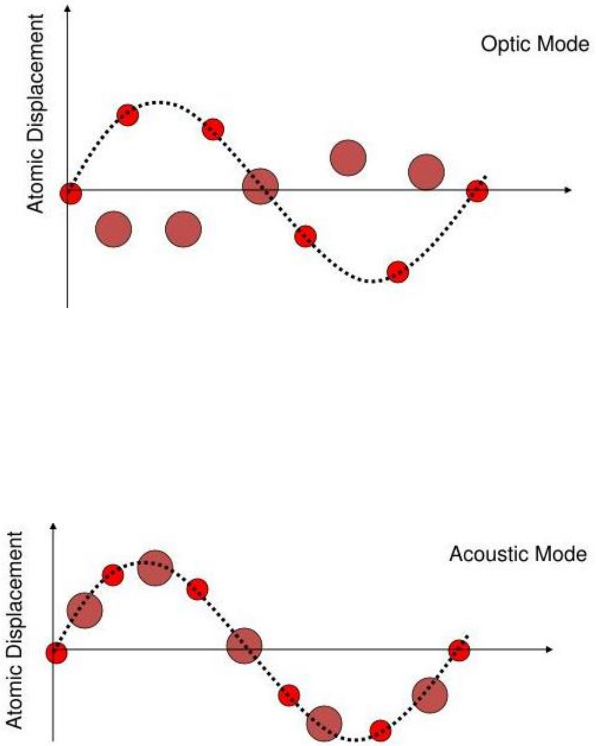
Light scattering by matter

- Particle suspensions
- Deffects
- Atomic vibrations

BASIS - Raman scattering - main concepts



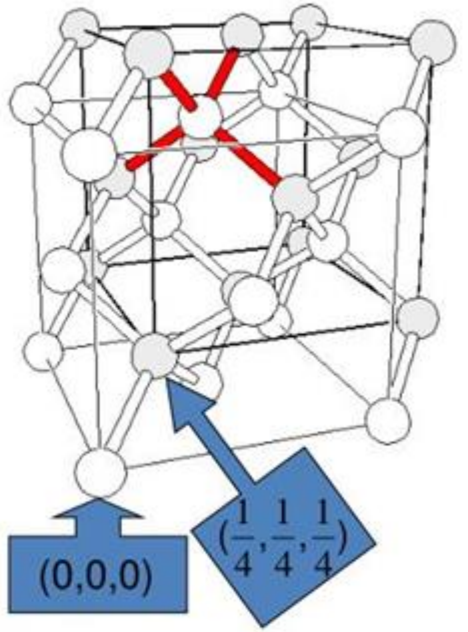


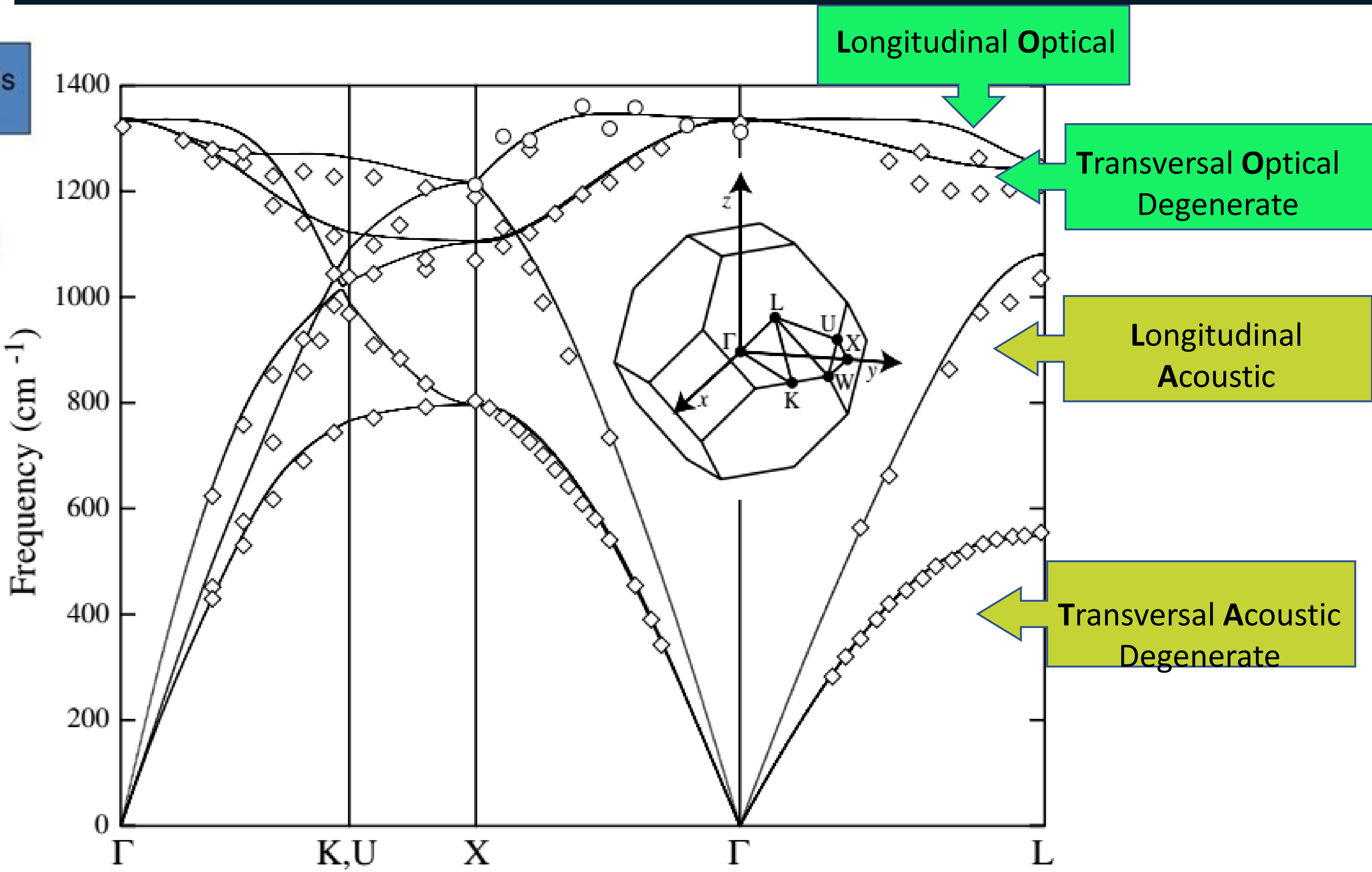


BASIS - Raman scattering - main concepts

diamond lattice: fcc lattice with basis

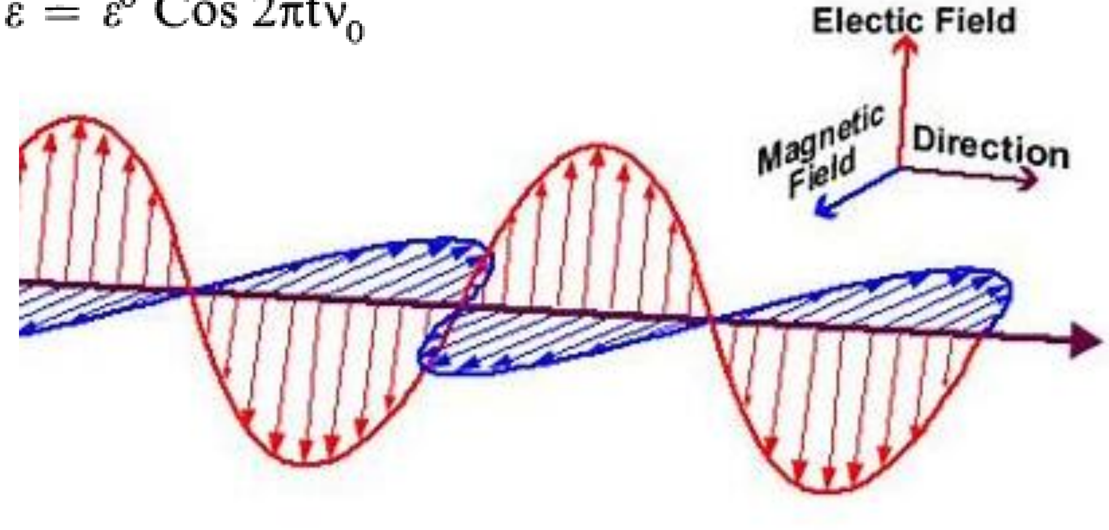
- n=2
- 2x3=6 branches expected



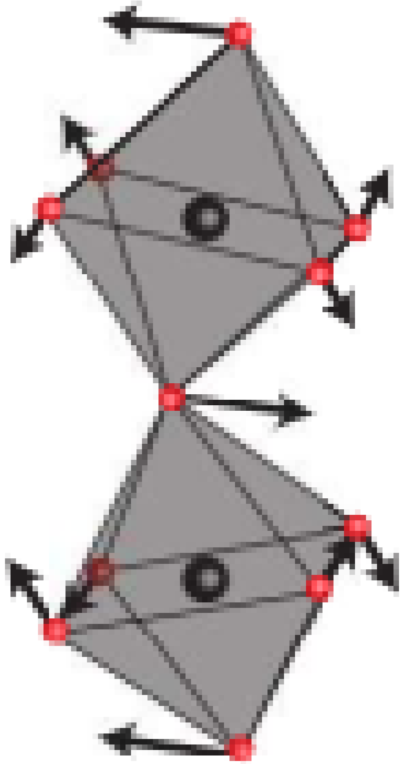


Spontaneous Raman effect – a classical approach

$$\varepsilon = \varepsilon^0 \, \mathrm{Cos}\, 2\pi t \nu_0$$



$$q_v = q_0 \, \mathrm{Cos}\, 2\pi \nu_v t$$

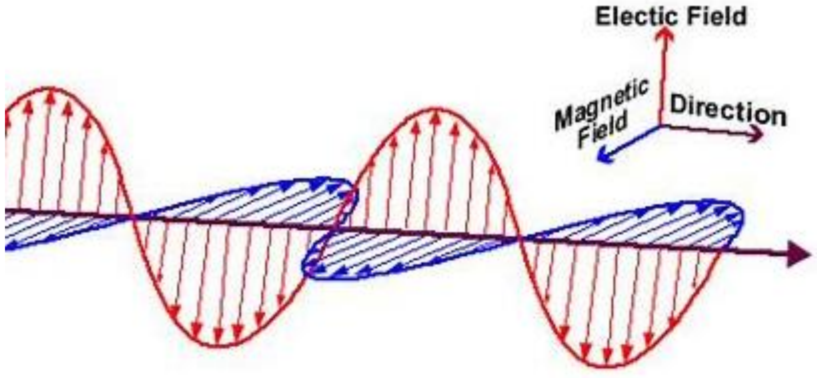


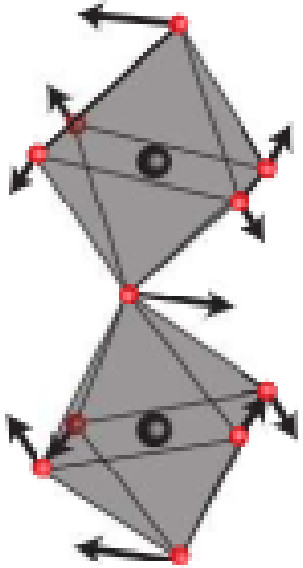
$$\mu_i = \alpha\varepsilon = \alpha\varepsilon^0 \, \mathrm{Cos}\, 2\pi \nu_0 t$$

BASIS - Raman scattering - main concepts

$$\varepsilon = \varepsilon^0 \text{ Cos } 2\pi t \nu_0$$

$$q_v = q_0 \text{ Cos } 2\pi \nu_v t$$





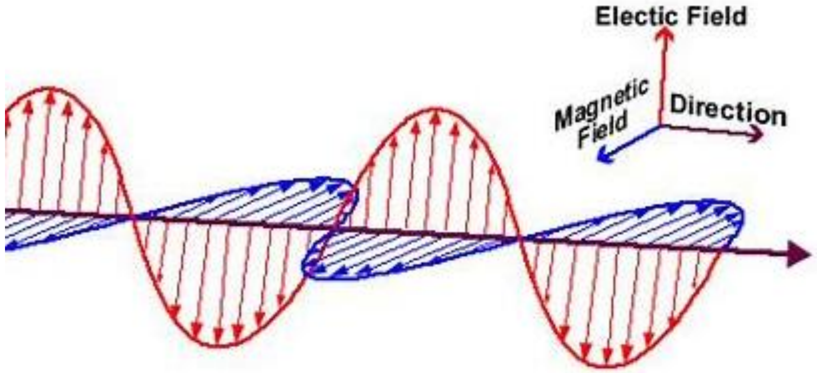
$$\alpha = \alpha^0 + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 q_0 \text{ Cos } 2\pi \nu_v t$$

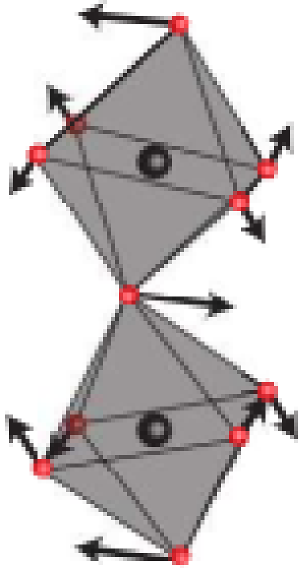
$$\alpha = \alpha^0 + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 q_v$$

BASIS - Raman scattering - main concepts

$$\varepsilon = \varepsilon^0 \, \mathrm{Cos}\, 2\pi t \nu_0$$

$$q_v = q_0 \, \mathrm{Cos}\, 2\pi \nu_v t$$





$$\alpha = \alpha^0 + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 q_v$$

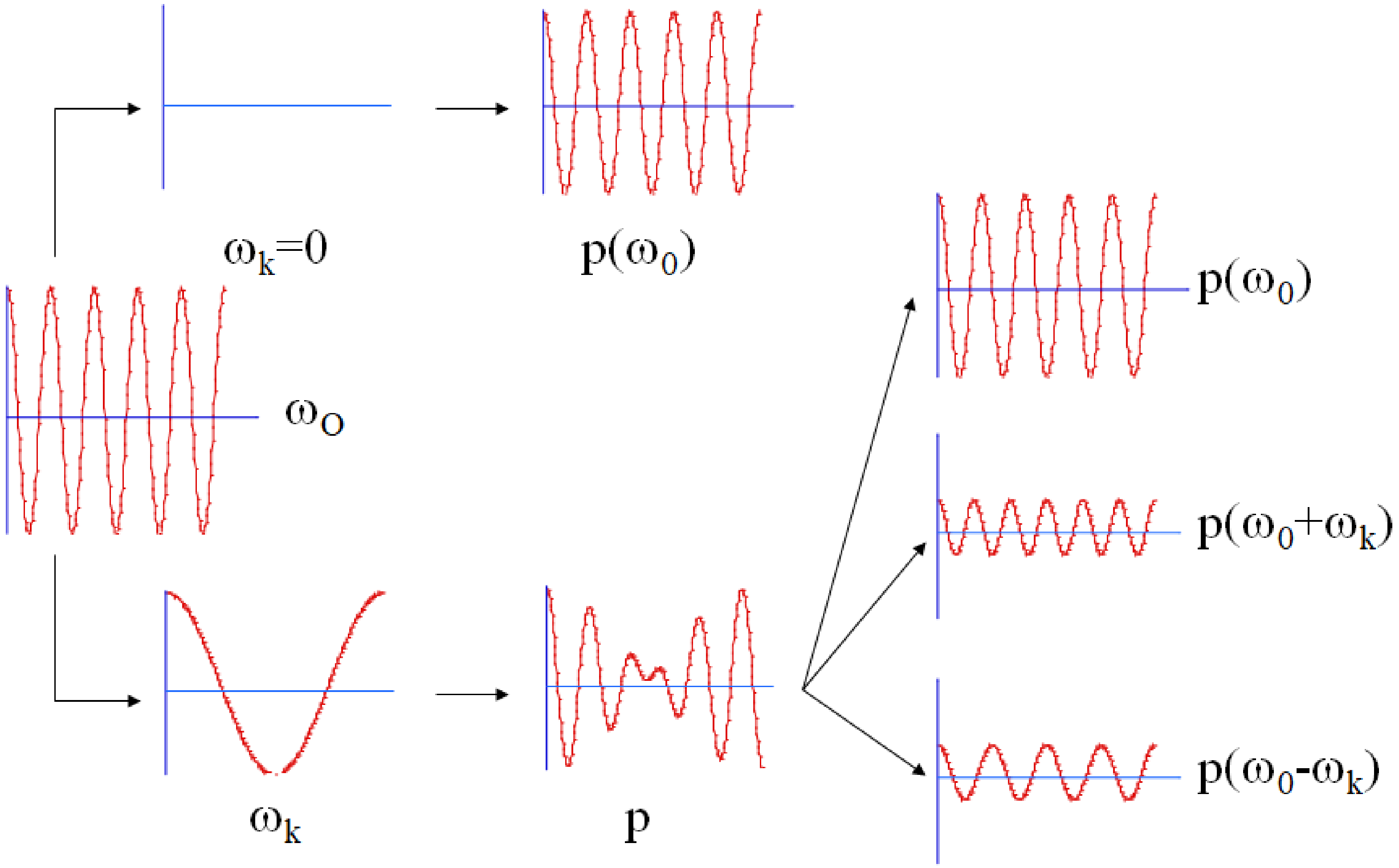
$$\alpha = \alpha^0 + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 q_0 \, \mathrm{Cos}\, 2\pi \nu_v t$$

$$\mu_i = \alpha \varepsilon = \alpha \varepsilon^0 \, \mathrm{Cos}\, 2\pi \nu_0 t$$

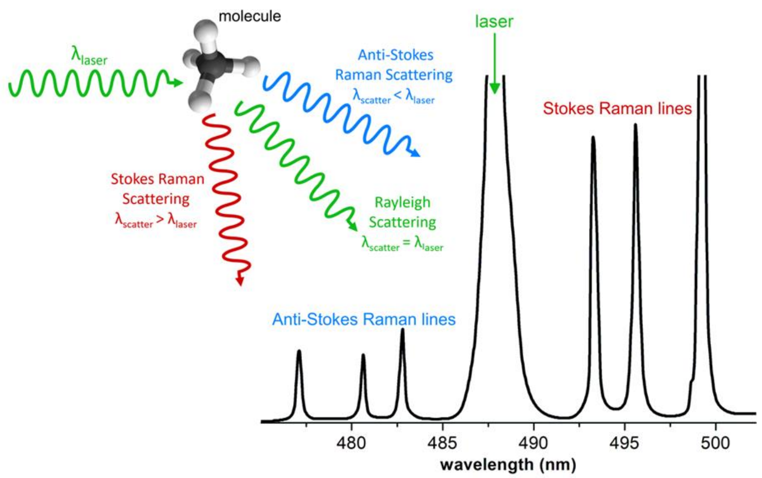
$$\mu_i = \alpha^0 \varepsilon^0 \, \mathrm{Cos}\, 2\pi \nu_0 t + \left(\frac{\partial \alpha}{\partial q_v}\right)_0 \varepsilon^0 q_0 \, \mathrm{Cos}\, 2\pi \nu_v t \, \mathrm{Cos}\, 2\pi \nu_0 t$$

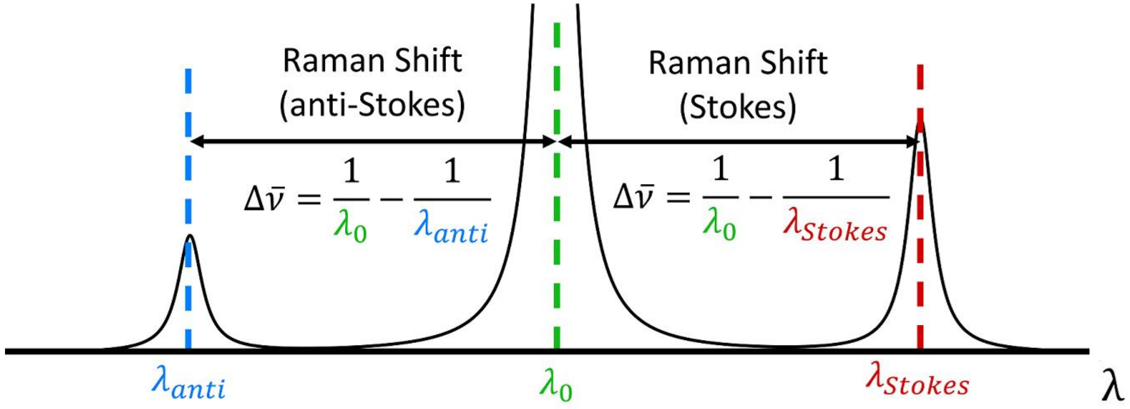
BASIS - Raman scattering - main concepts

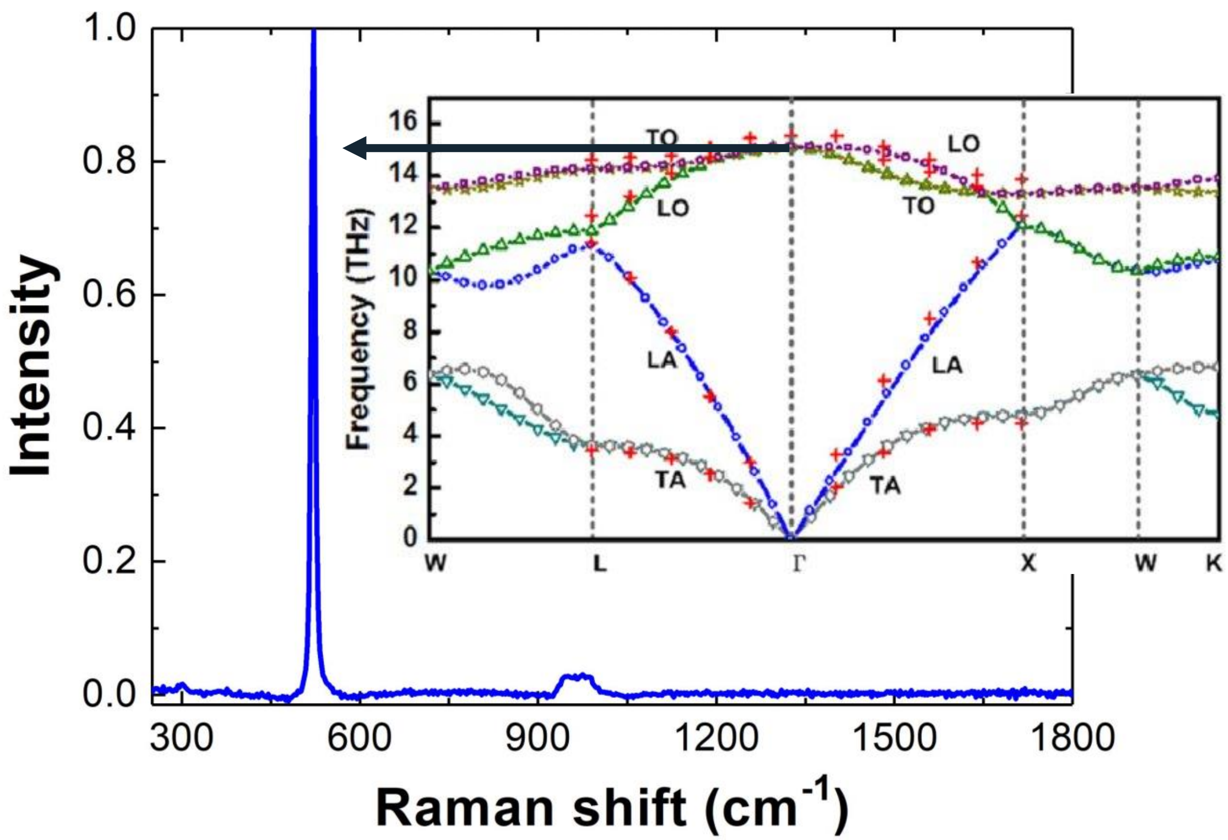
$$\mu_i = \alpha^0 F^0 \cos 2\pi\nu_0 t + \left(\frac{\partial\alpha}{\partial q_v}\right)_0 \frac{\varepsilon^0 q_0}{2} \times [\cos 2\pi(\nu_0 + \nu_v)t + \cos 2\pi(\nu_0 - \nu_v)t]$$



BASIS - Raman scattering - main concepts



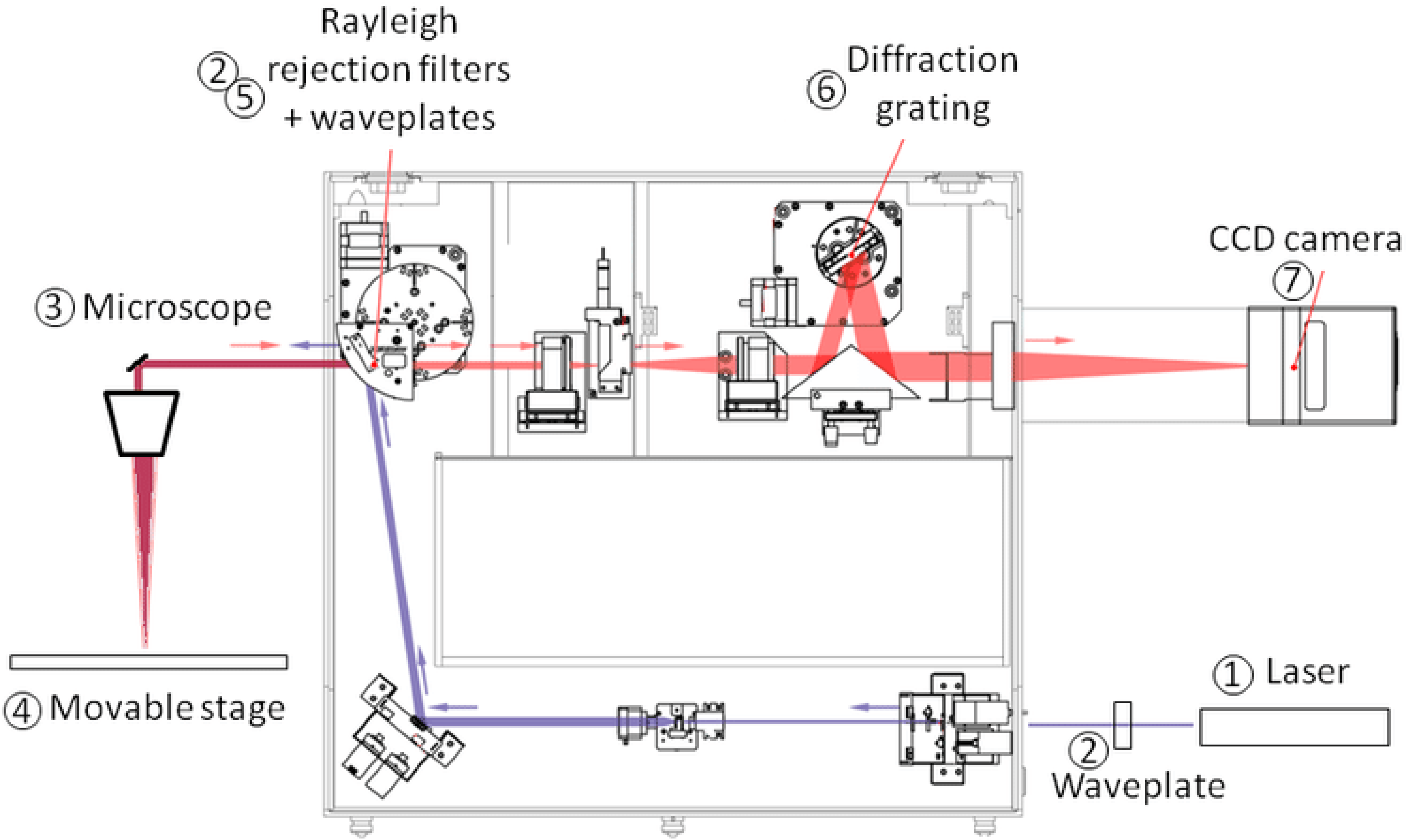




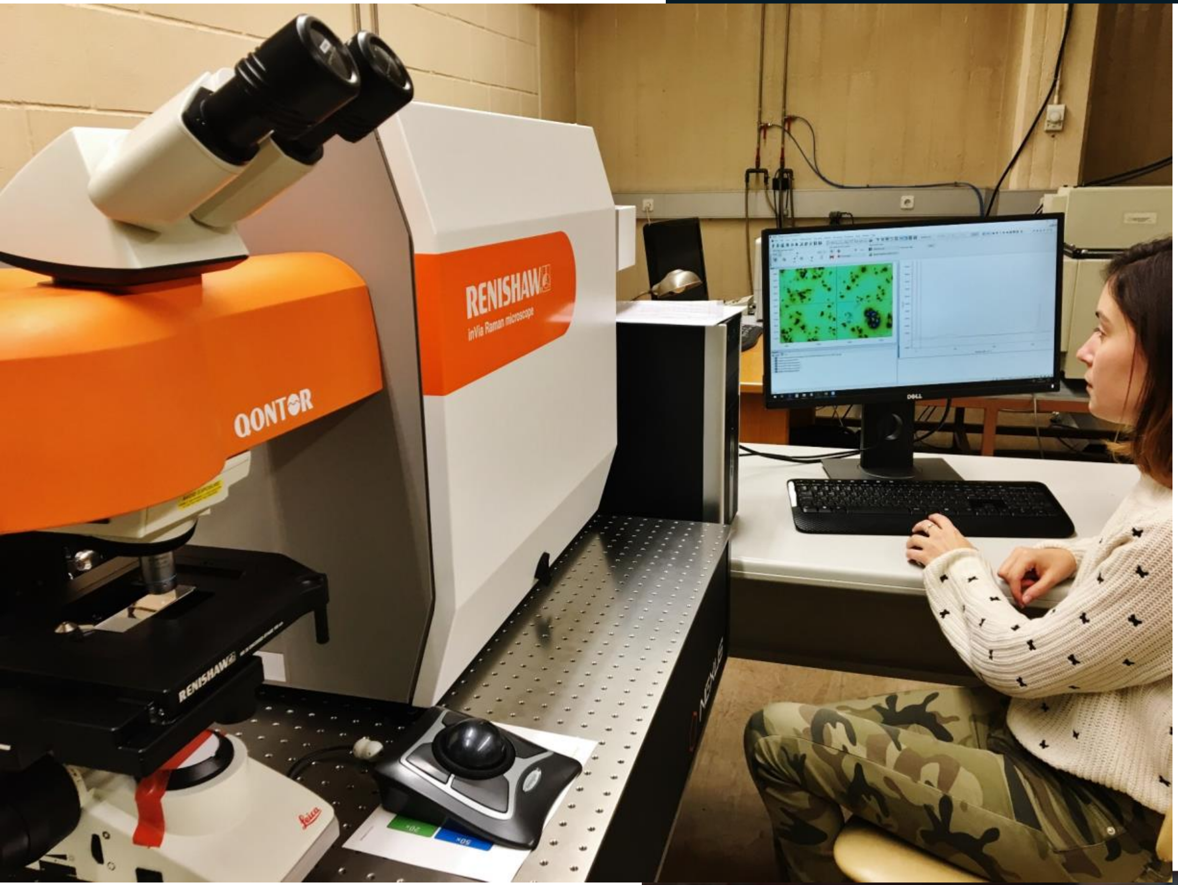
1THz = 33.356 cm^{-1} = 4.136 meV

BASIS - Basic instrumentation

inVia™ Qontor® Raman spectrometer



BASIS – Raman@LaPMET



Micro-Raman spectrometer;

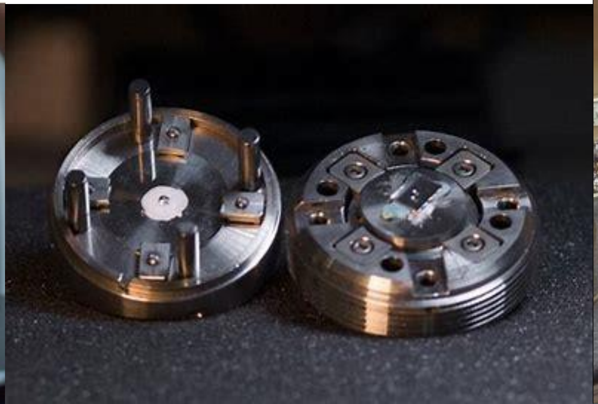
3 laser lines for excitation: 785 nm, 633 nm, and 532 nm

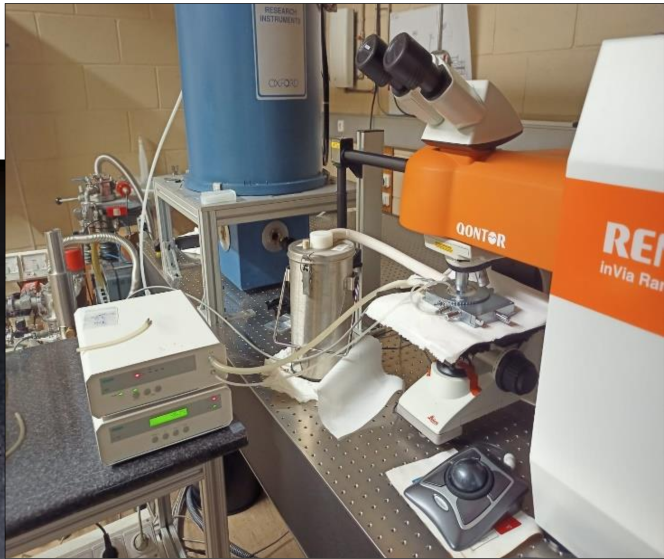
Linkam Stages: 80 to 1500 K

Diamond Anvil Cell: up to 100 GPa and 300 to 1000 K;

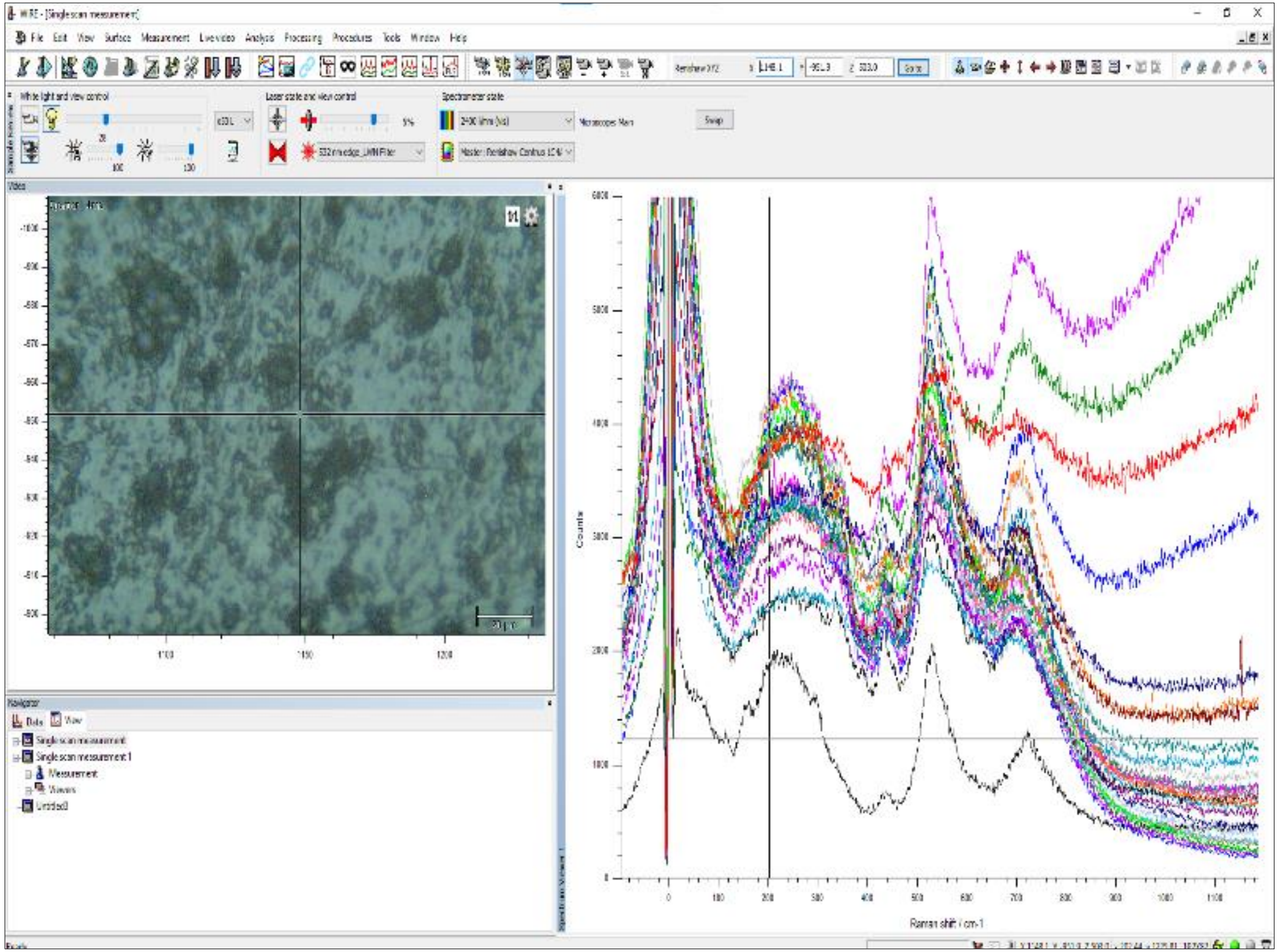
Closed-cycle He cryostat: 10 to 300 K;

Continuous-flow He cryostat with superconducting coil: 4 to 300 K and up to 7 T



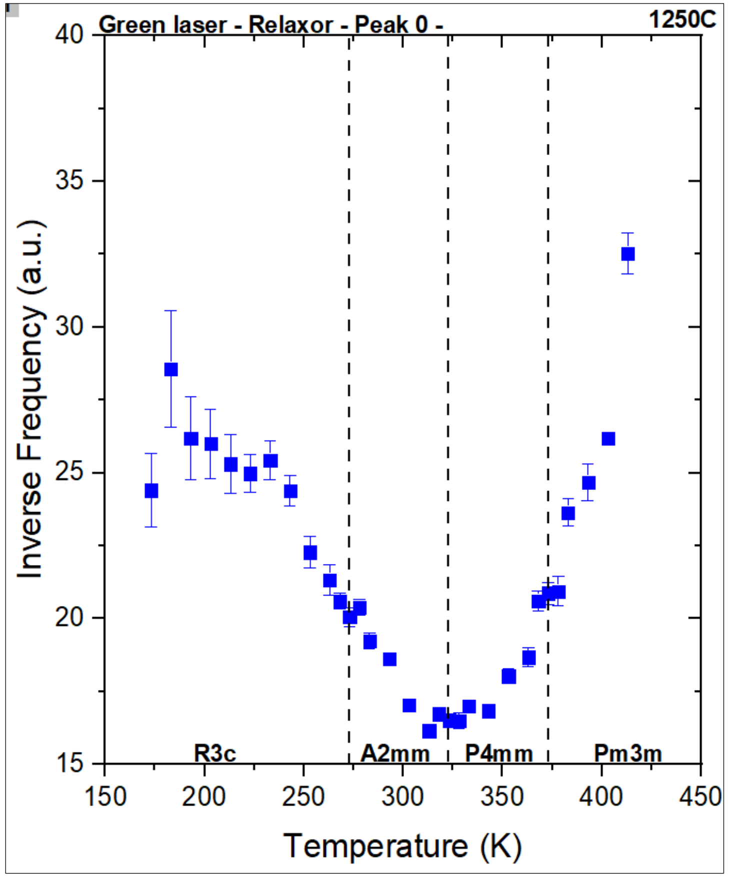


BASIS – Raman@LaPMET

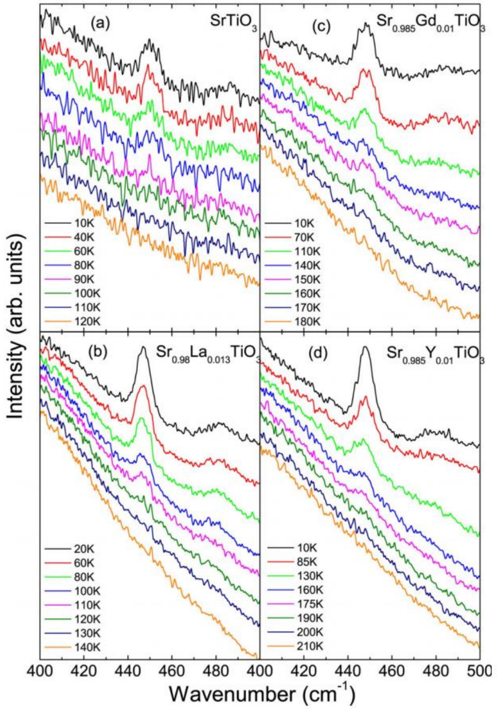


$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$

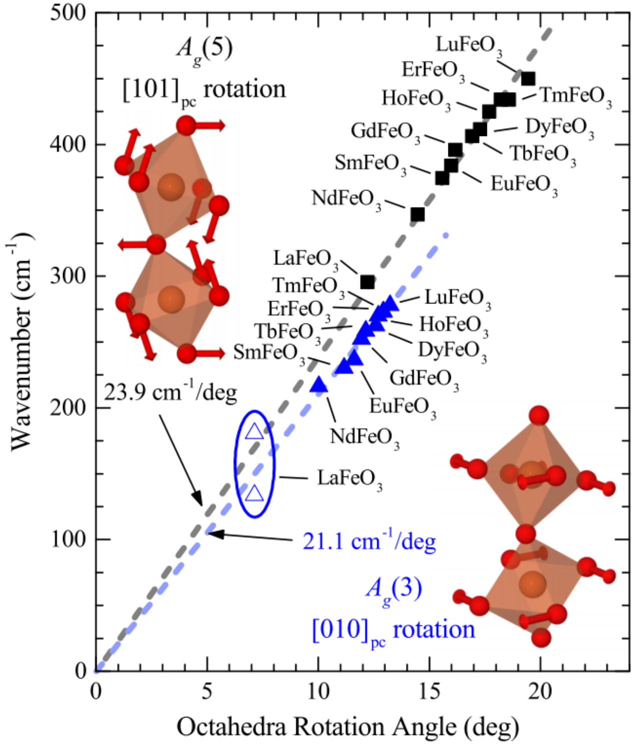
Dynamical central peak



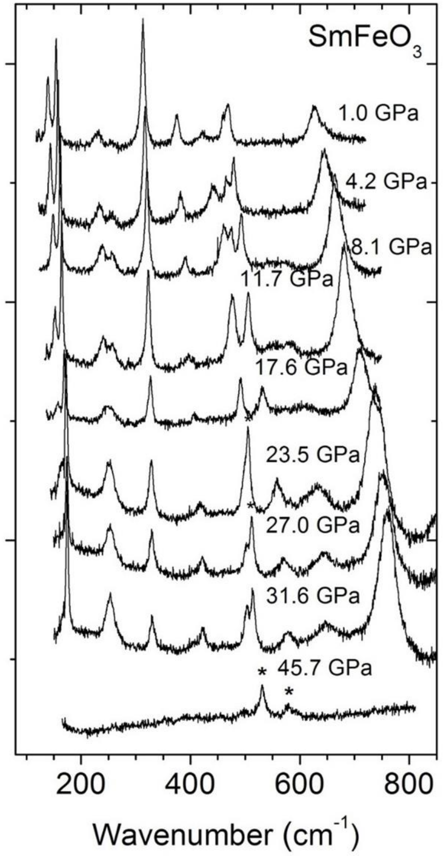
BASIS – Raman@LaPMET



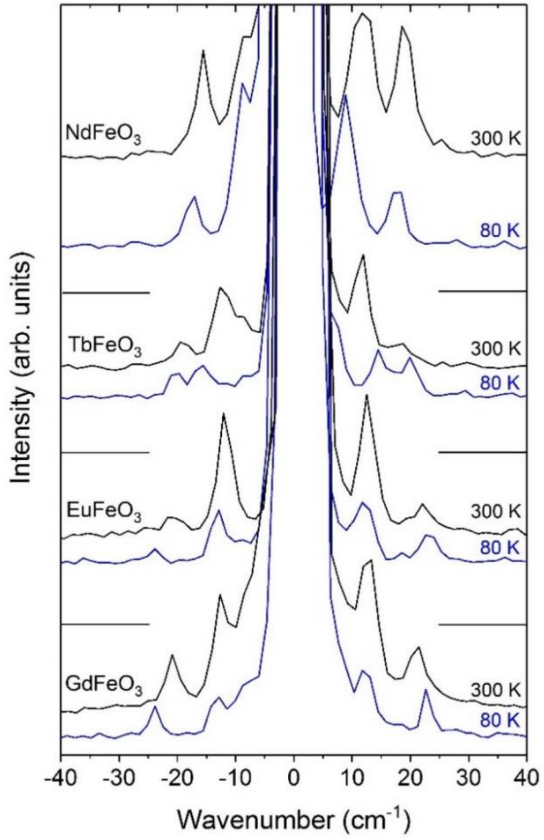
APPLIED PHYSICS LETTERS 98, 052903 2011



PHYSICAL REVIEW B 94, 214103 (2016)



PHYSICAL REVIEW B 99, 064109 (2019)



Scientifc Reports | (2022) 12:9697

OUTLINE

Chapter 1. Basis

- Raman scattering - main concepts
- Instrumentation for Raman spectroscopy and Raman imaging
- Raman spectrometer and its capabilities existing at LaPMET – IFIMUP

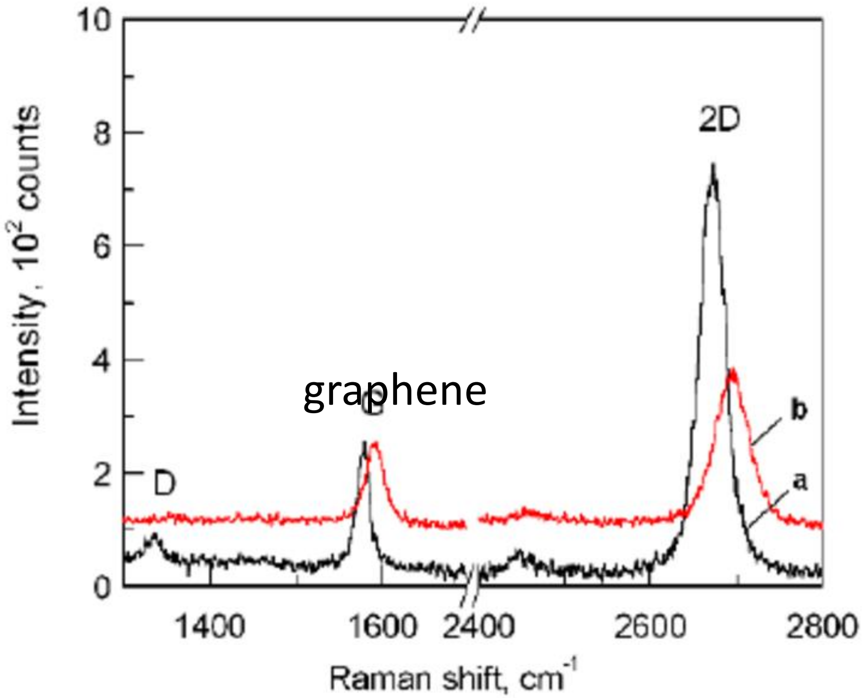
Chapter 2. Raman scattering as a tool for material characterization

- Uses of Raman scattering spectroscopy
- Few examples
  - ➢ Displacive phase transitions
  - ➢ Mapping and imaging: ferroic domains and internal stress
  - ➢ Multi-wavelength and penetration depth
  - ➢ Metal-to-insulating transitions and epitaxy

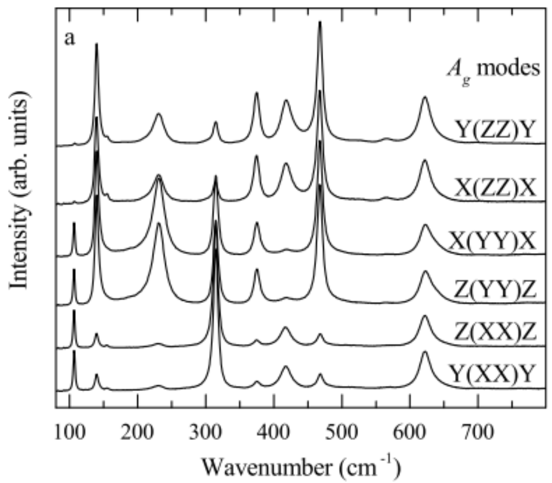
Uses of Raman scattering spectroscopy

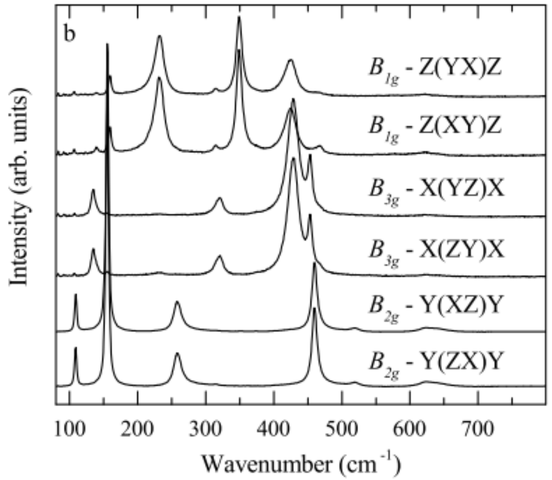
- ✓ **Structural phase transtions, induced by temperature, electric/magnetic fields, high-pressure, epitaxial strain**
- ✓ **Structural distortions**
- ✓ **Domain structures**
- ✓ **Strain states**
- ✓ **Order-disorder and displacive mechanisms**
- ✓ **Coupling between diferent elementar excitations with optical phonons**
- ✓ **Second order effects**

Uses of Raman scattering spectroscopy



What does Raman spectroscopy measure?





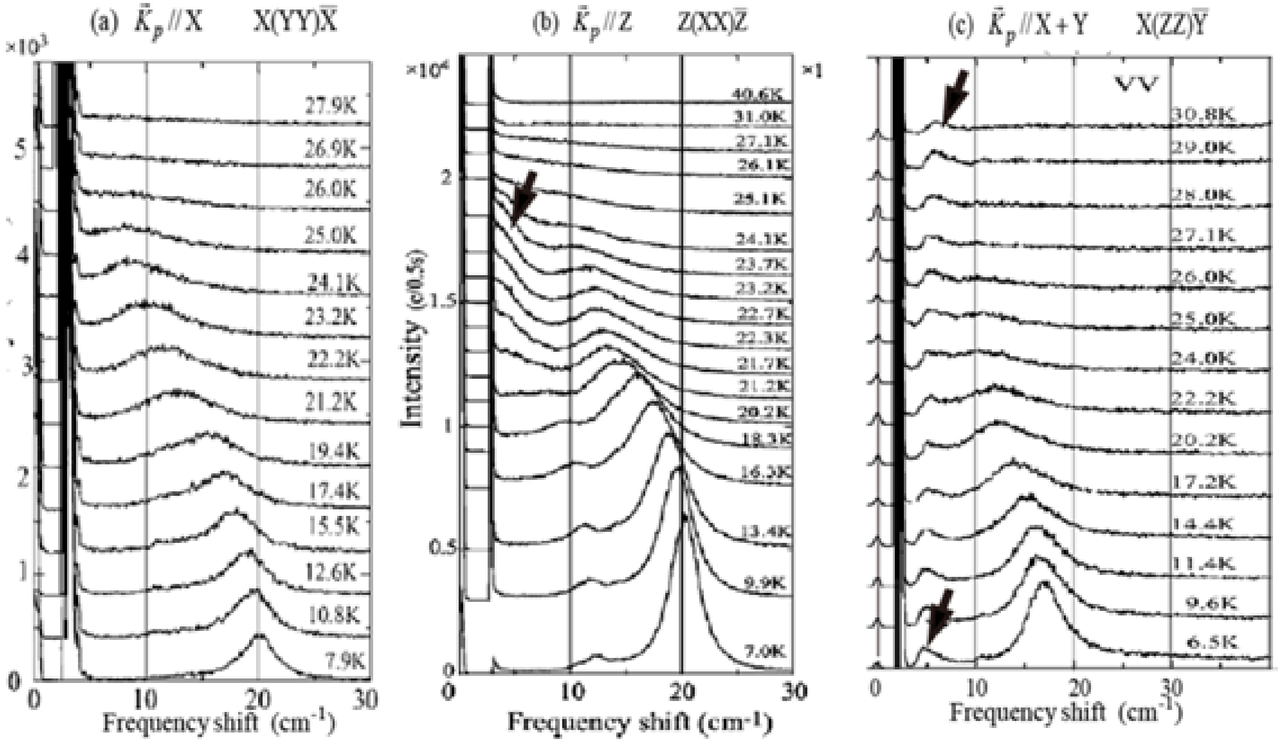
The normal mode frequencies and lifetimes

Polarization/symmetry properties/selection rules

Phys. Rev. B **94**, 214103 (2016)

Displacive phase transtions

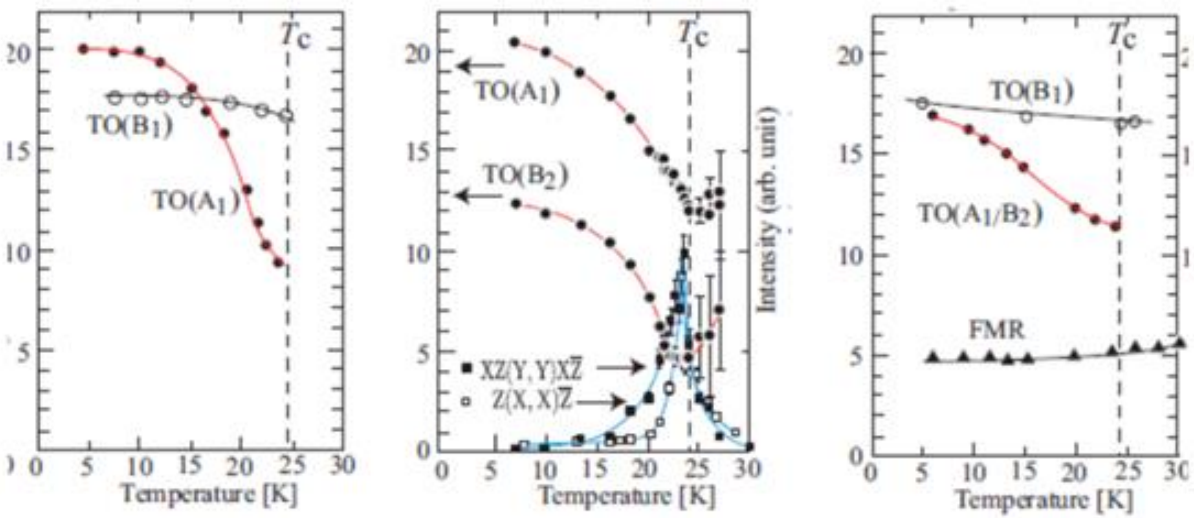
$SrTi^{18}O_3$



Soft mode spectroscopy

$$\omega^2_{TO}(q=0) = a\left|T - T_c\right|$$

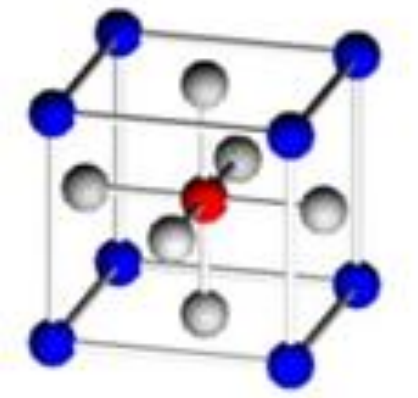
W.Cochran, Phil.Mag. Suppl. 10 401 (1961)



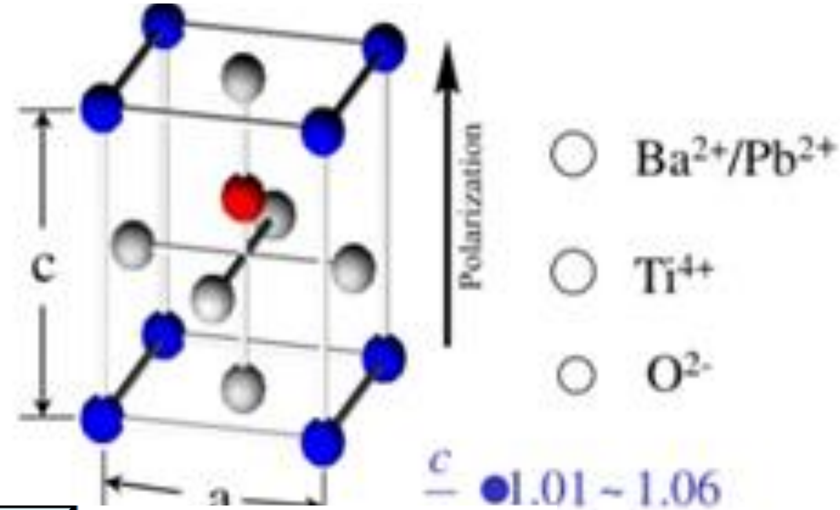
Mapping domain walls in ferroics

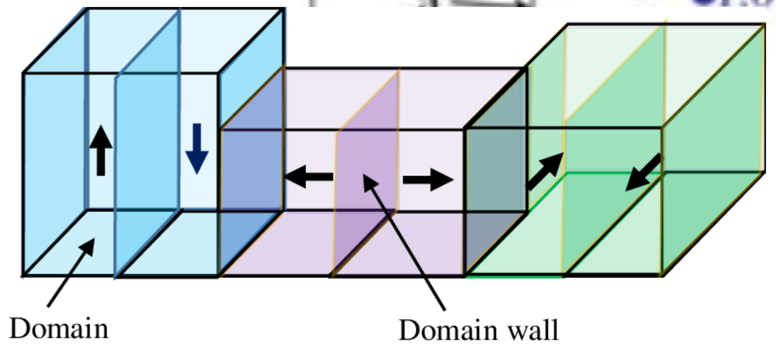
$BaTiO_3$ – a ferroelectric prototype

Cubic
Paraelectric P=0



Tetragonal
Ferroelectric P≠0
6 equivalent directions

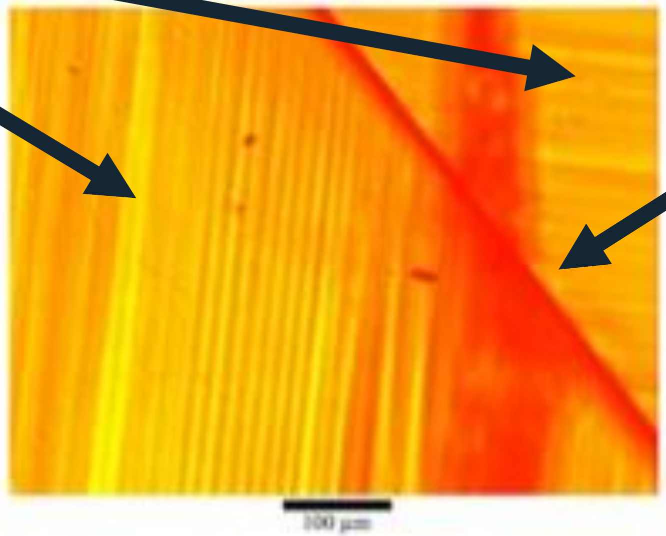




Mapping domain walls in ferroics

Domains

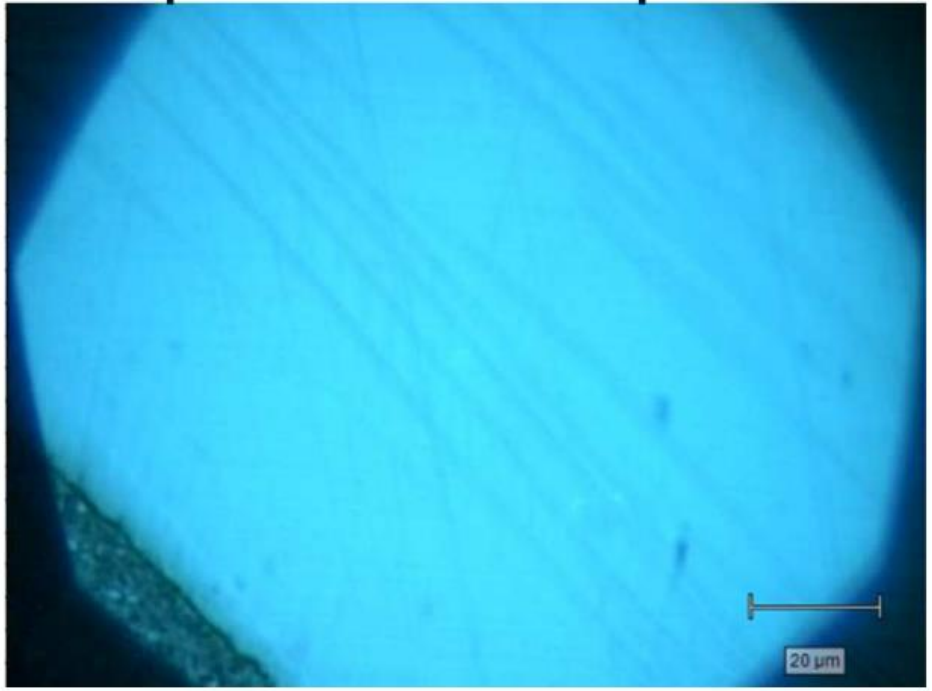
Domain wall

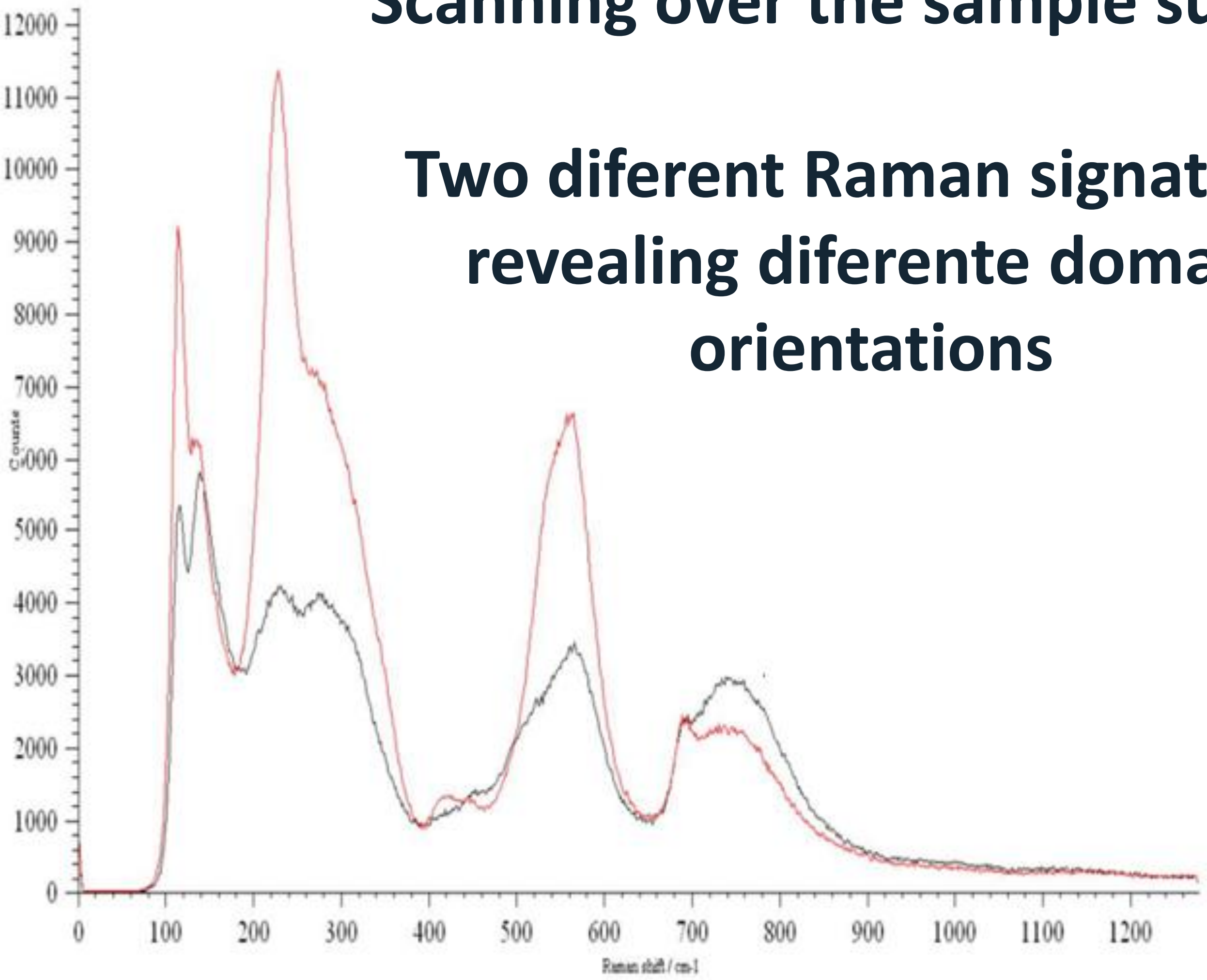


Mapping domain walls in ferroics

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

Optical microscope





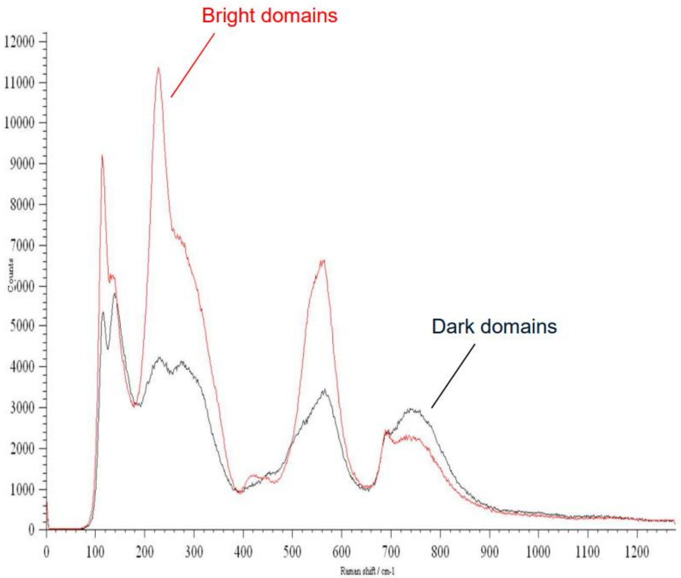
Scanning over the sample surface

Two diferent Raman signatures revealing diferente domain orientations

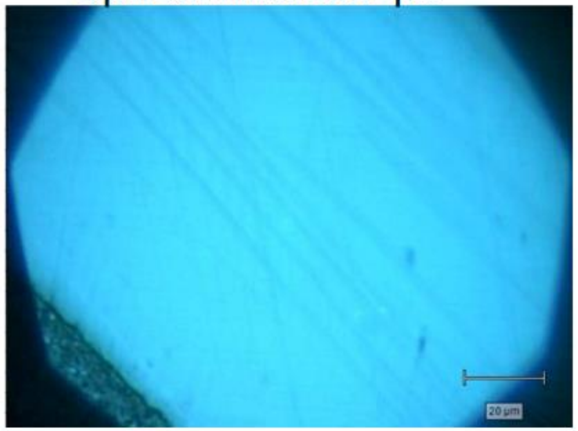
Data from Mael Guennou. LIST, Luxembourg

Mapping domain walls in ferroics

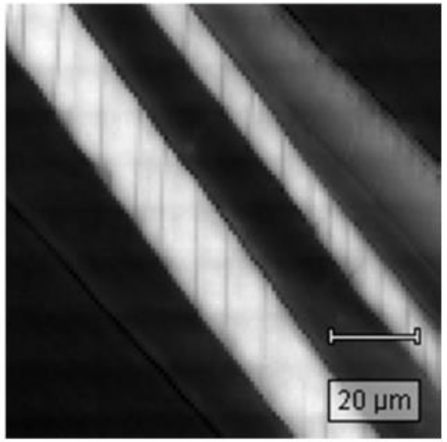
Mapping of ferroic domains in $Pb(Zr,Ti)O_3$ single crystal



Optical microscope



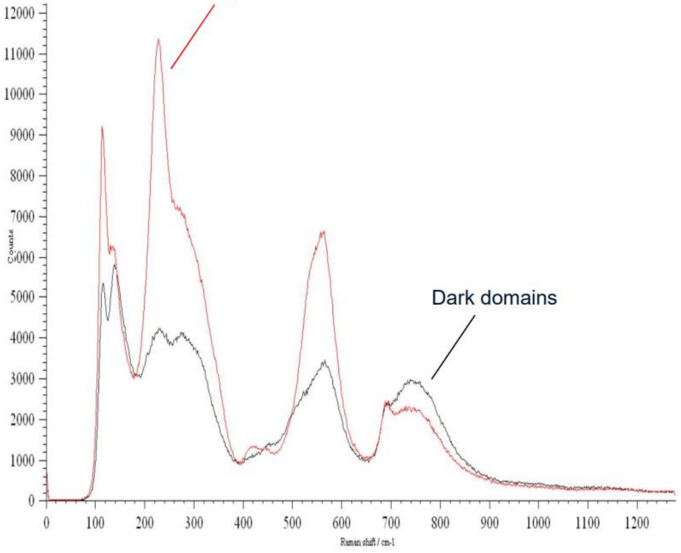
Raman mapping
200 cm^{-1} mode



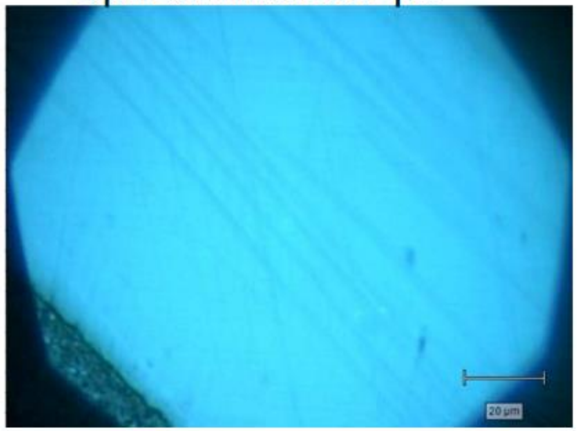
Data from Mael Guennou. LIST, Luxembourg

Mapping domain walls in ferroics

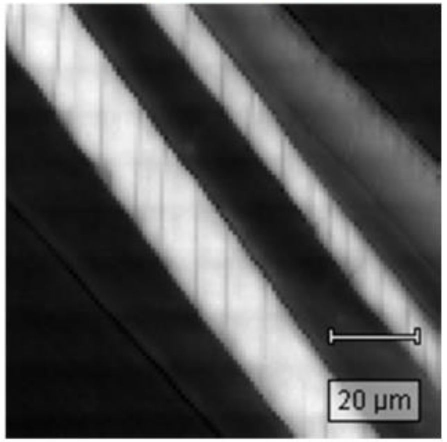
Mapping of ferroic domains in $Pb(Zr,Ti)O_3$ single crystal



Optical microscope

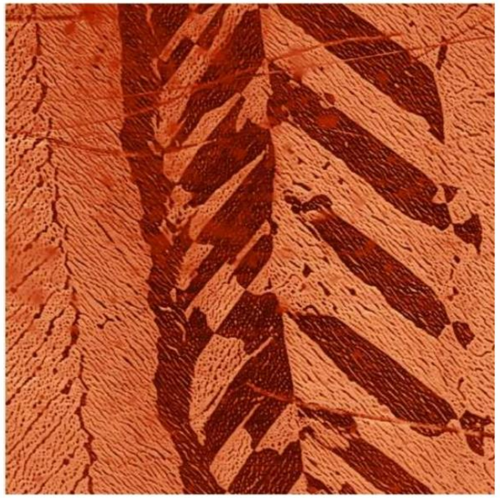


Raman mapping
200 cm^{-1} mode

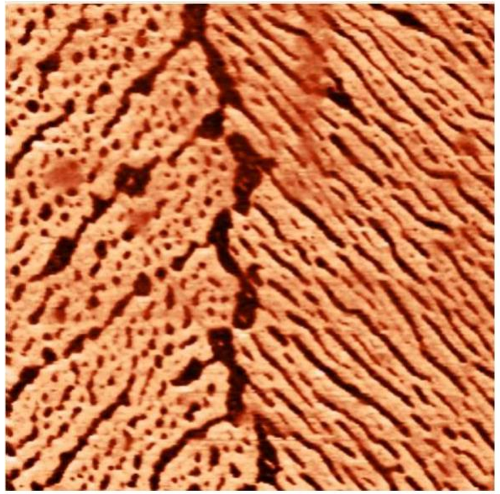


Piezoresponse force microscopy:

Phase image 40 x 40 µm²



Phase image 10 x 10 µm²

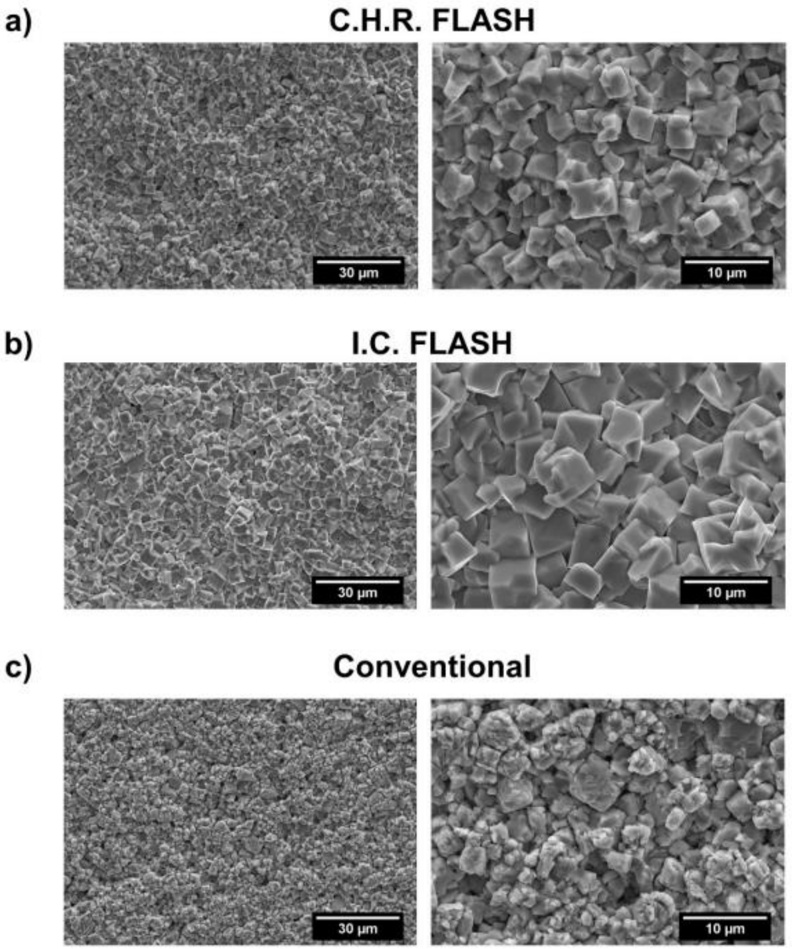


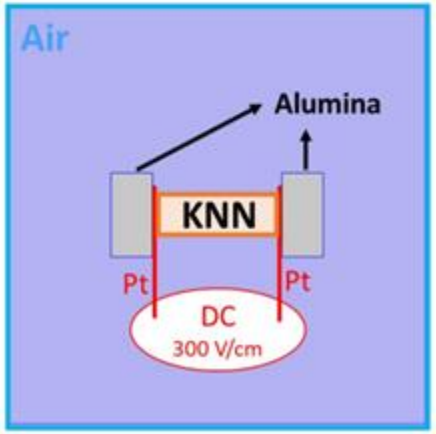
Raman (in-plane orientation) and PFM (out of plane polarization) needed for a full picture

Data from Mael Guennou. LIST, Luxembourg

Mapping internal stress

$K_{0.5}Na_{0.5}NbO_3$ (KNN)
a lead-free ferroelectric with interesting functional properties





Field-Assisted Sintering Techniques (FAST), more specifically, Electric Current-Assisted Sintering (ECAS) processes

Figure S2 – Scanning electron microscopy (SEM) micrographs of a) C.H.R. FLASH, b) I.C. FLASH and c) conventionally sintered KNN ceramics, acquired with a 15 keV accelerating voltage at different magnifications, 1000 and 3000 times, left and right, respectively, *from [6] R. Serrazina, A. M. O. R. Senos, L. Pereira, J. S. Dean, I. M. Reaney, and P. M. Vilarinho, "The Role of Particle Contact in Densification of FLASH Sintered Potassium Sodium Niobate," Eur. J. Inorg. Chem., vol. 2020, no. 39, pp. 3720–3728, 2020.*

J. Mater. Chem. C, 2022,**10**, 10916-10925

Mapping internal stress

$K_{0.5}Na_{0.5}NbO_3$ (KNN)
a lead-free ferroelectric with interesting functional properties

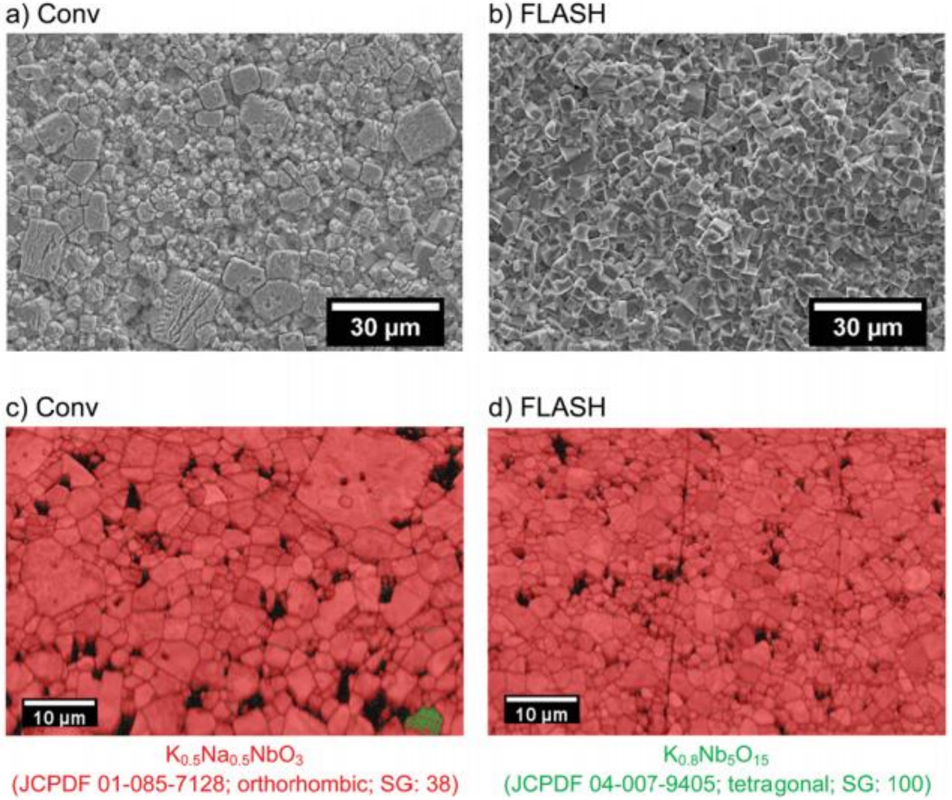
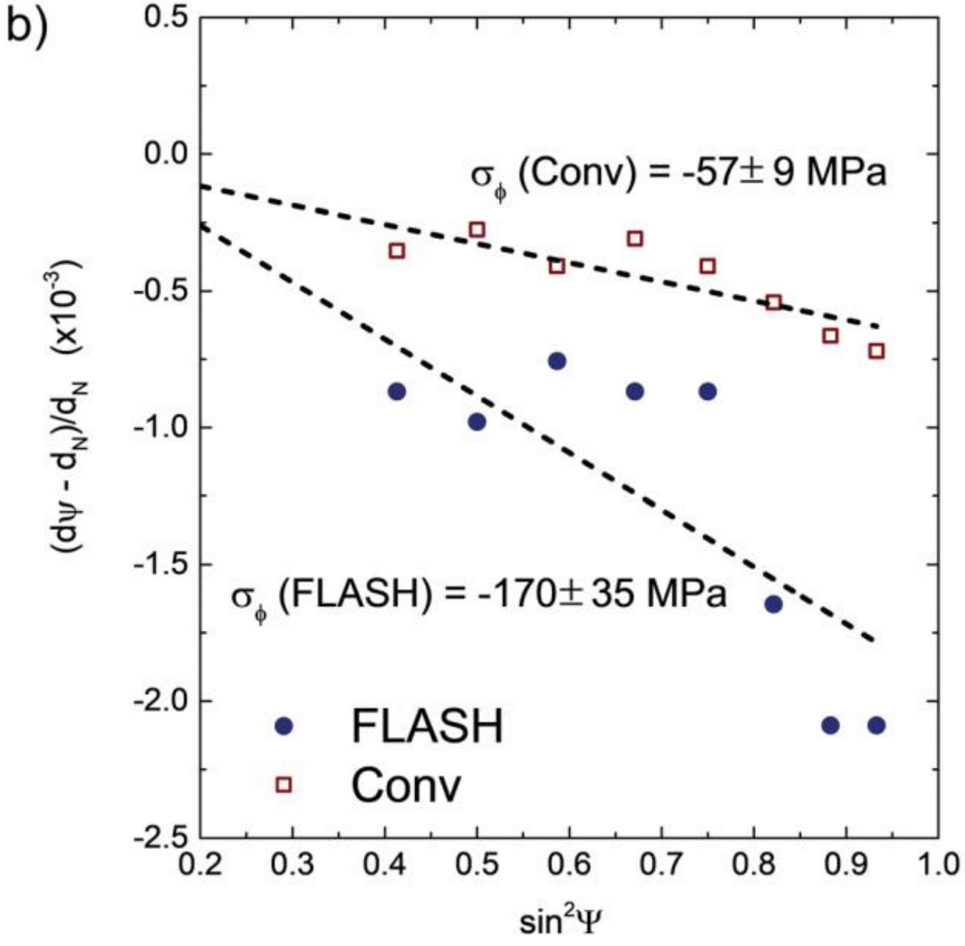
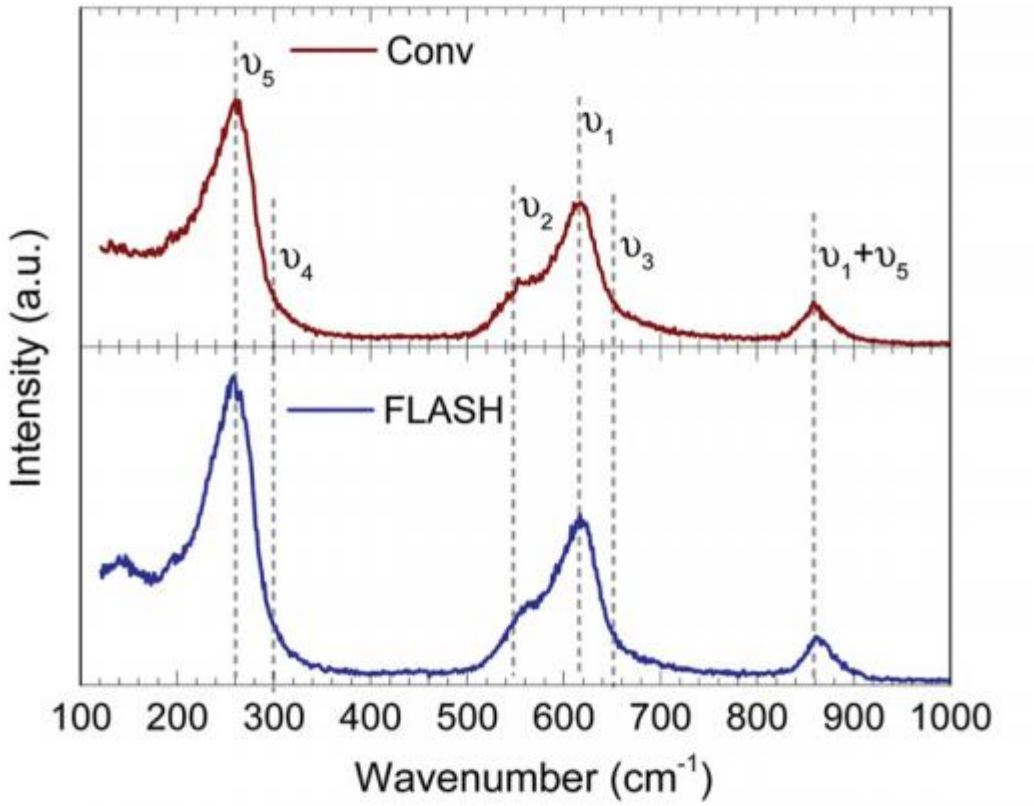


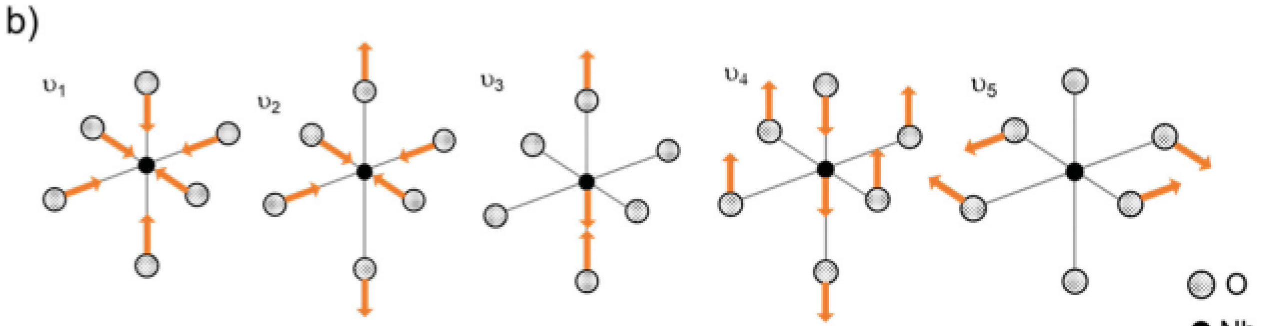
Fig. 1 SEM micrographs of (a) FLASH and (b) conventionally sintered KNN ceramics. EBSD phase maps are shown in (c) and (d), respectively. FLASH KNN presents a uniform grain size while conventionally sintered KNN exhibits some abnormal grain growth, together with more $K_{0.8}Nb_5O_{15}$ secondary phase.



J. Mater. Chem. C, 2022,**10**, 10916-10925

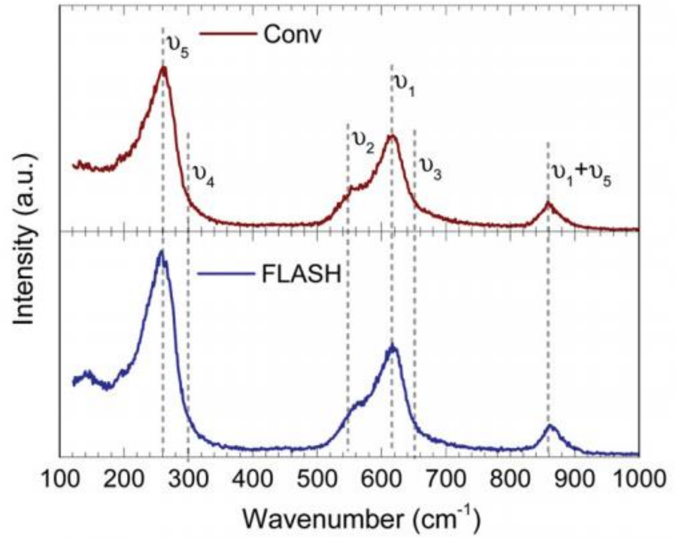
Mapping internal stress

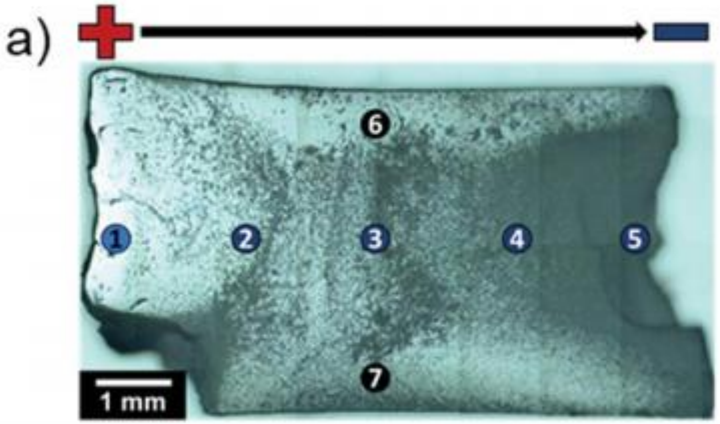


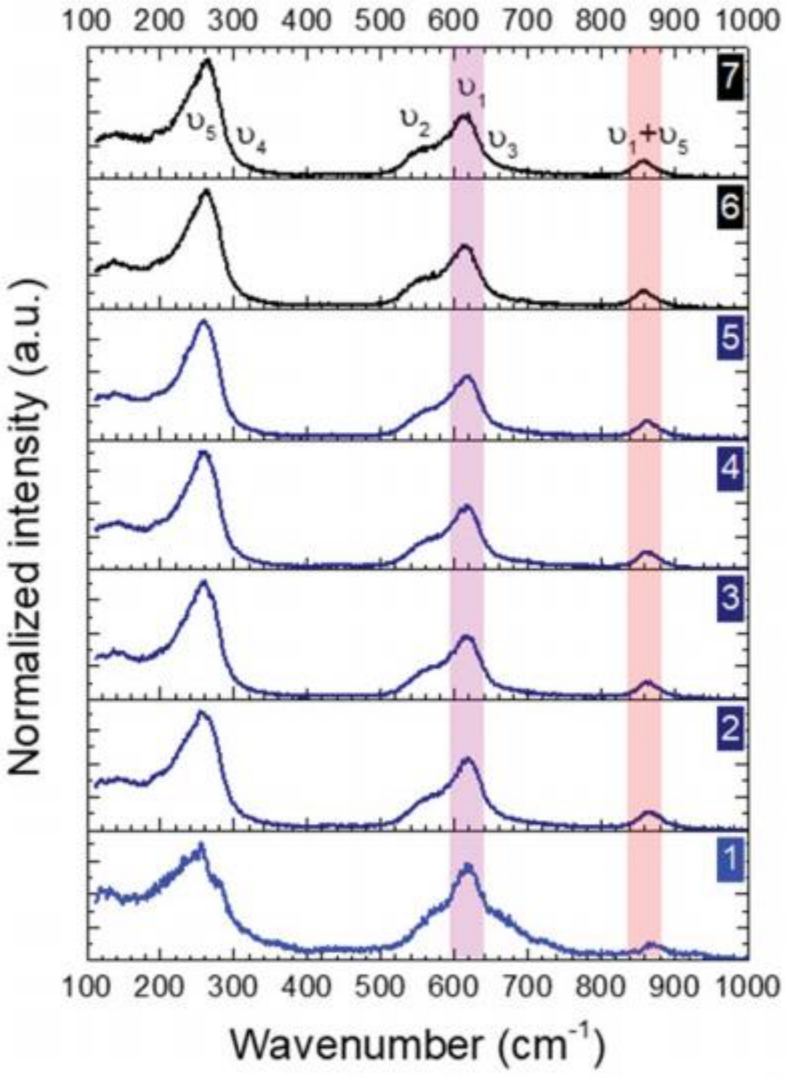


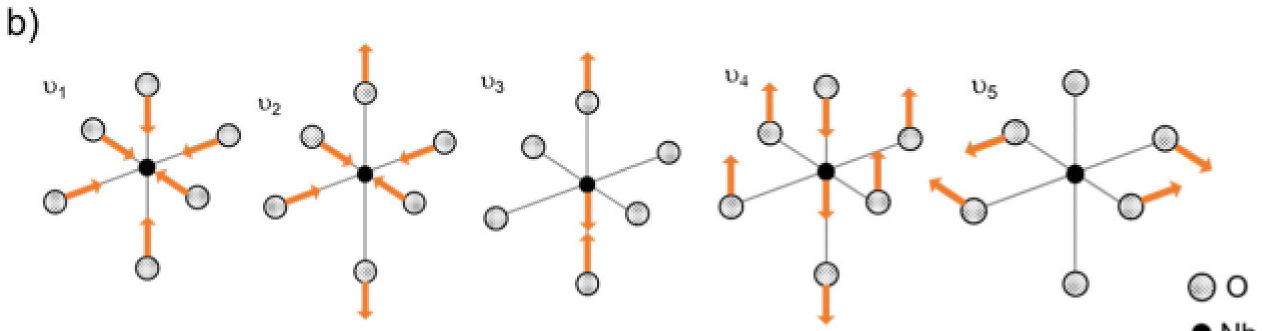
J. Mater. Chem. C, 2022,**10**, 10916-10925

Mapping internal stress



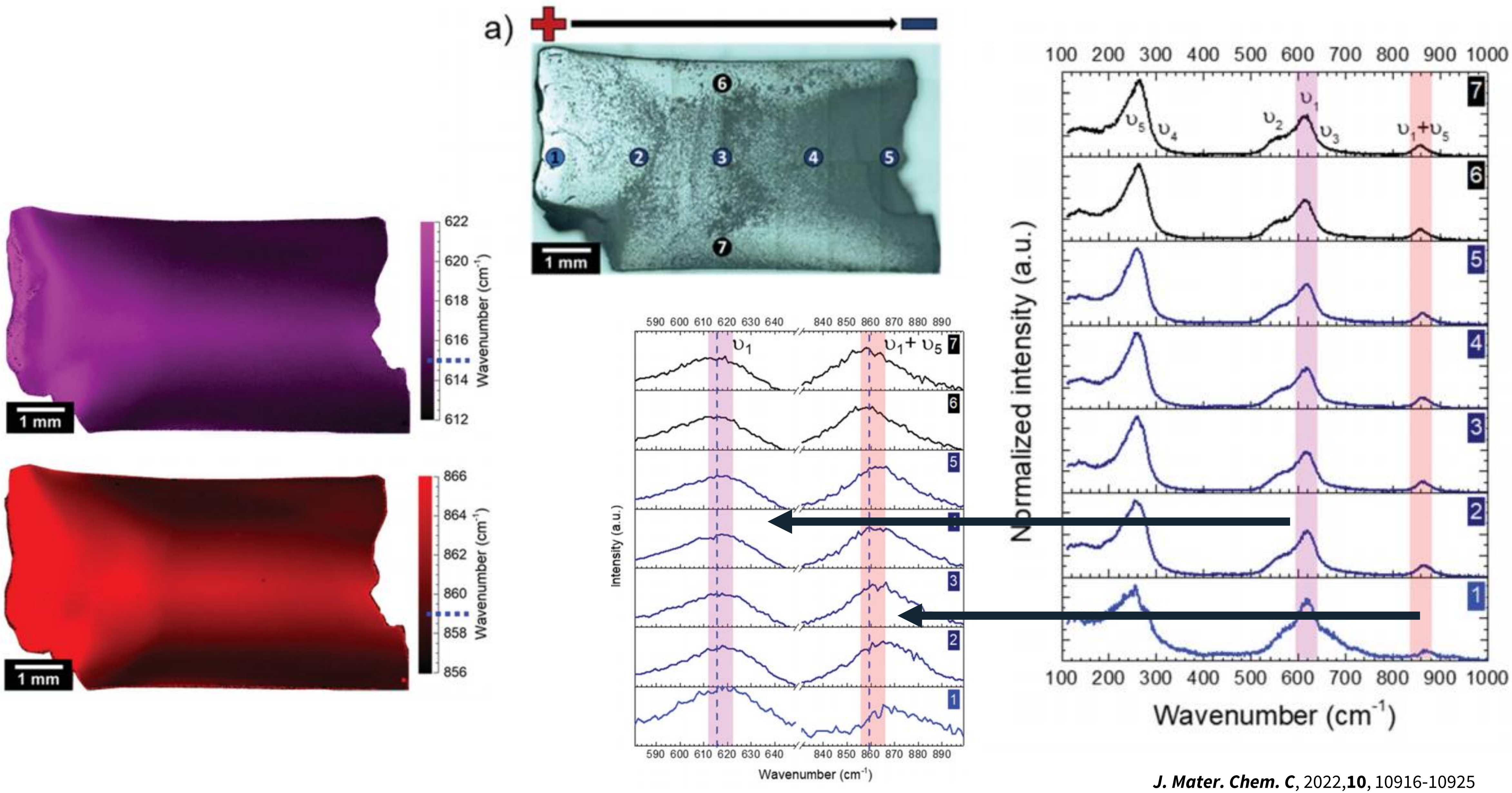






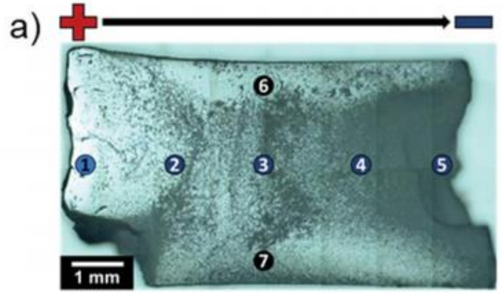
J. Mater. Chem. C, 2022,**10**, 10916-10925

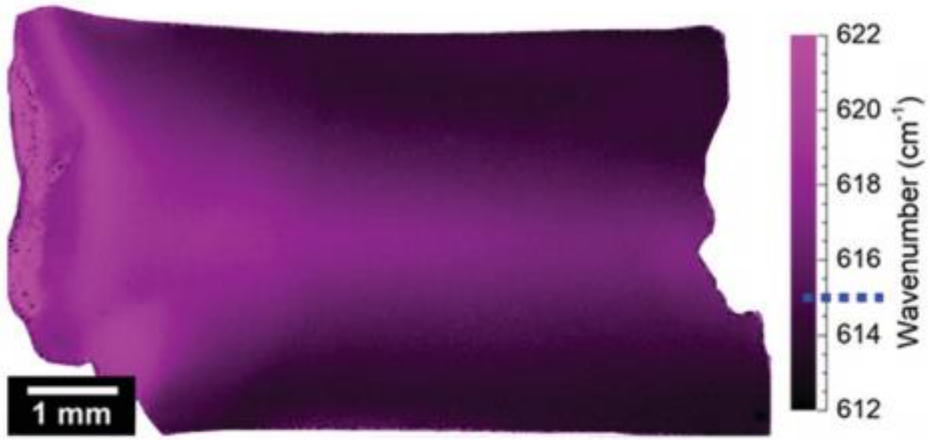
Mapping internal stress

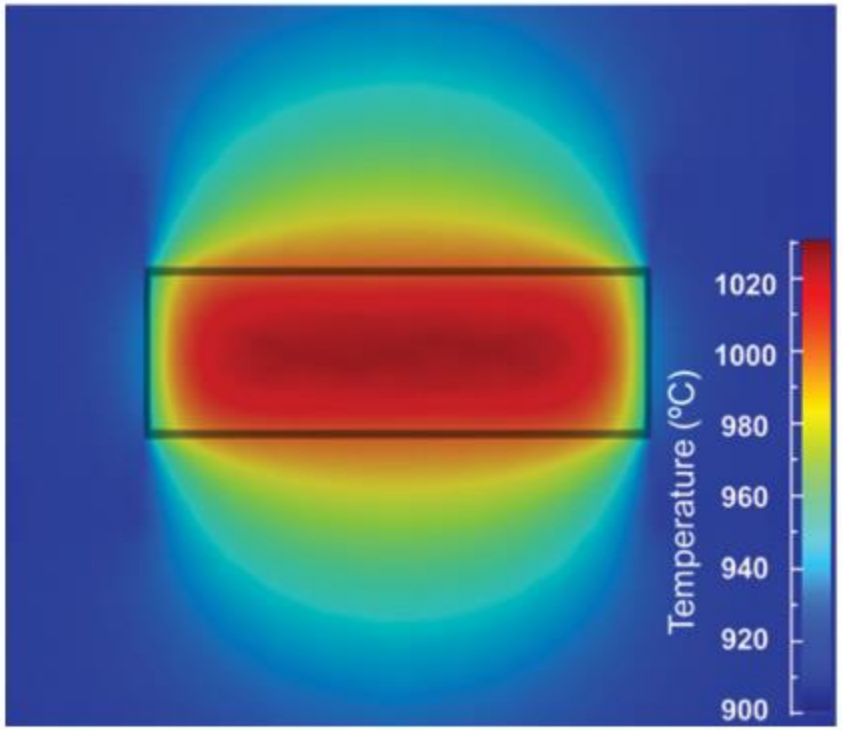


J. Mater. Chem. C, 2022,**10**, 10916-10925

Mapping internal stress

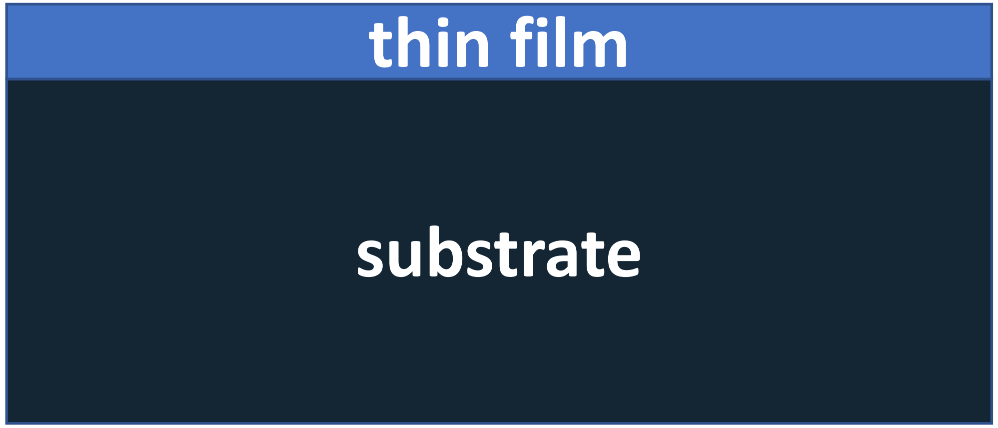






J. Mater. Chem. C, 2022,**10**, 10916-10925

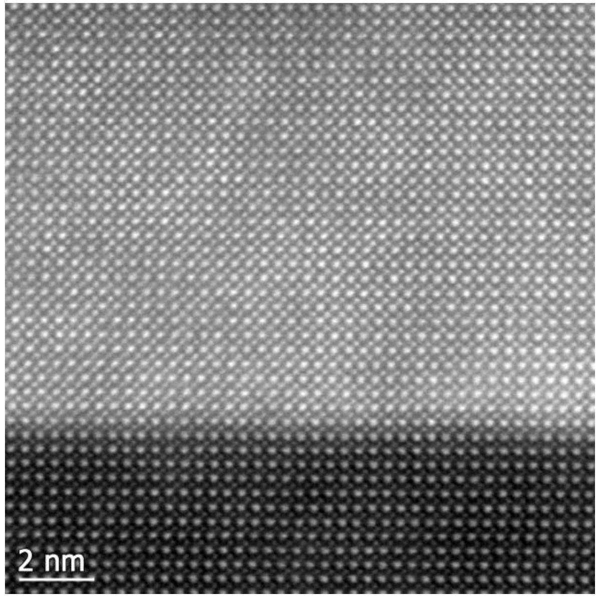
Thin films measurements

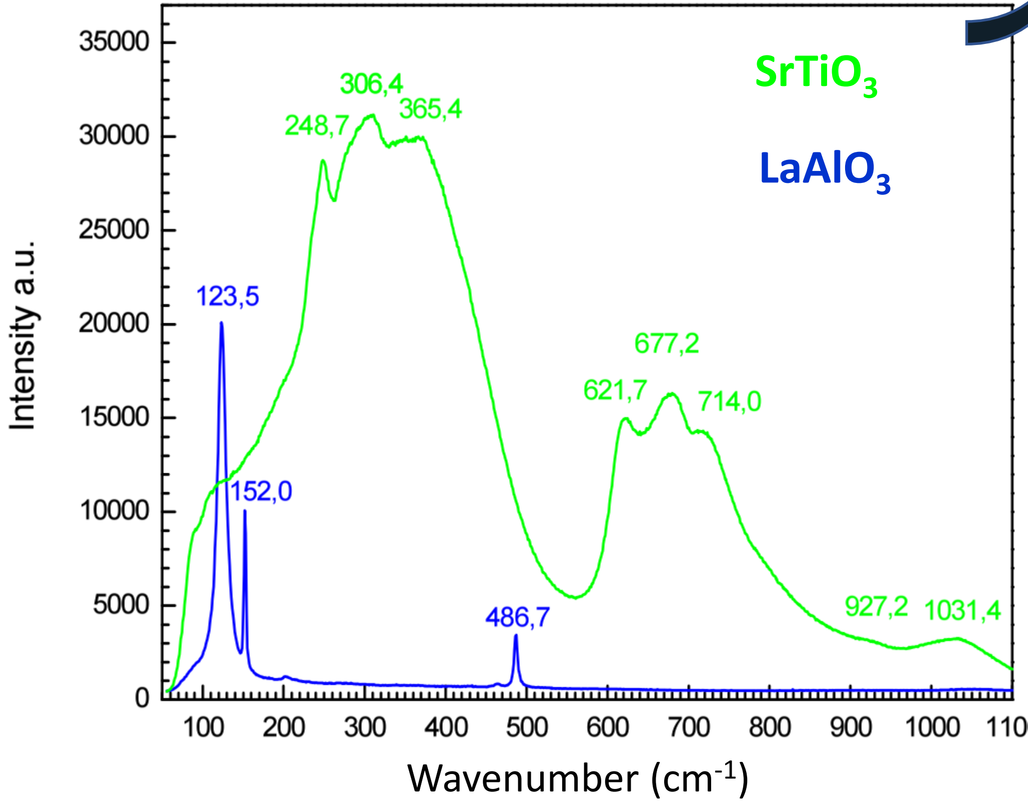


few atomic layes up to 100 nm

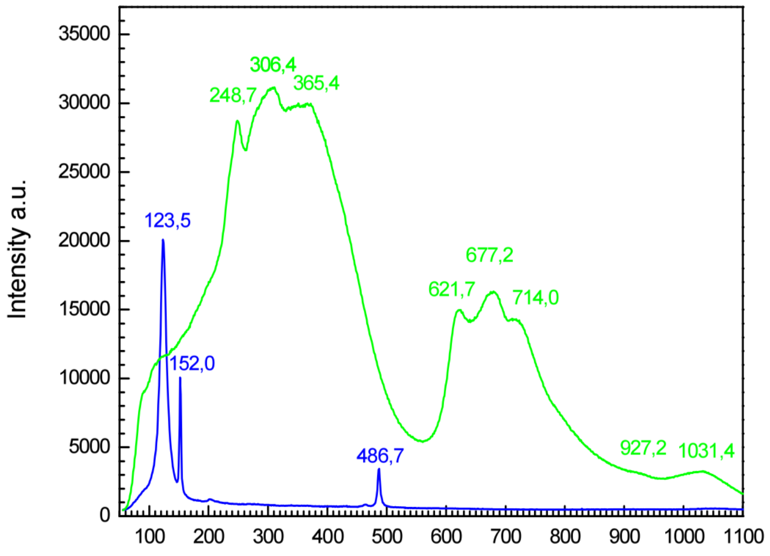
Film: Small scattering volume

Substrate Raman signal



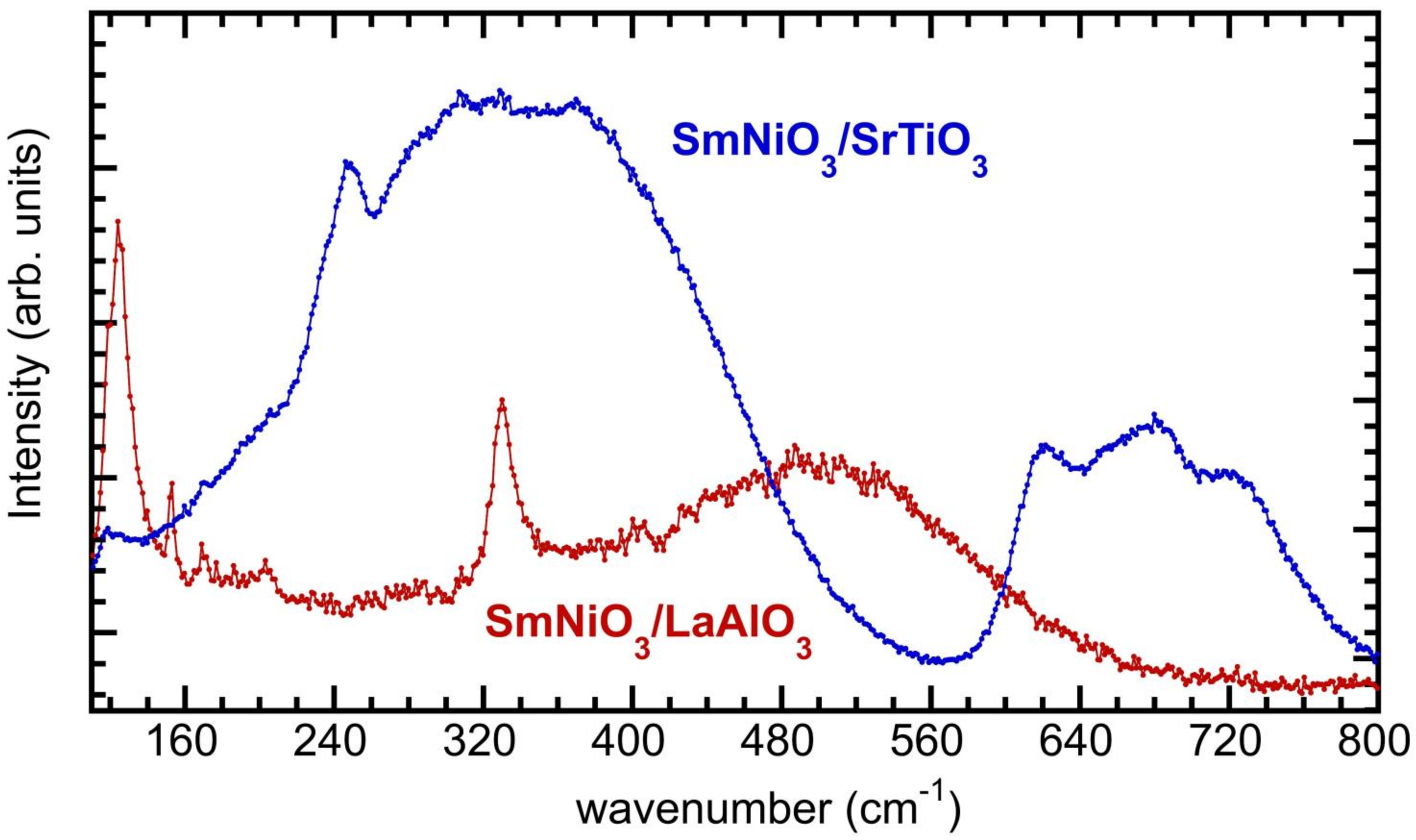


Thin films measurements



Sometimes…

… substrate signal superinposes over the film signal



Thin films measurements

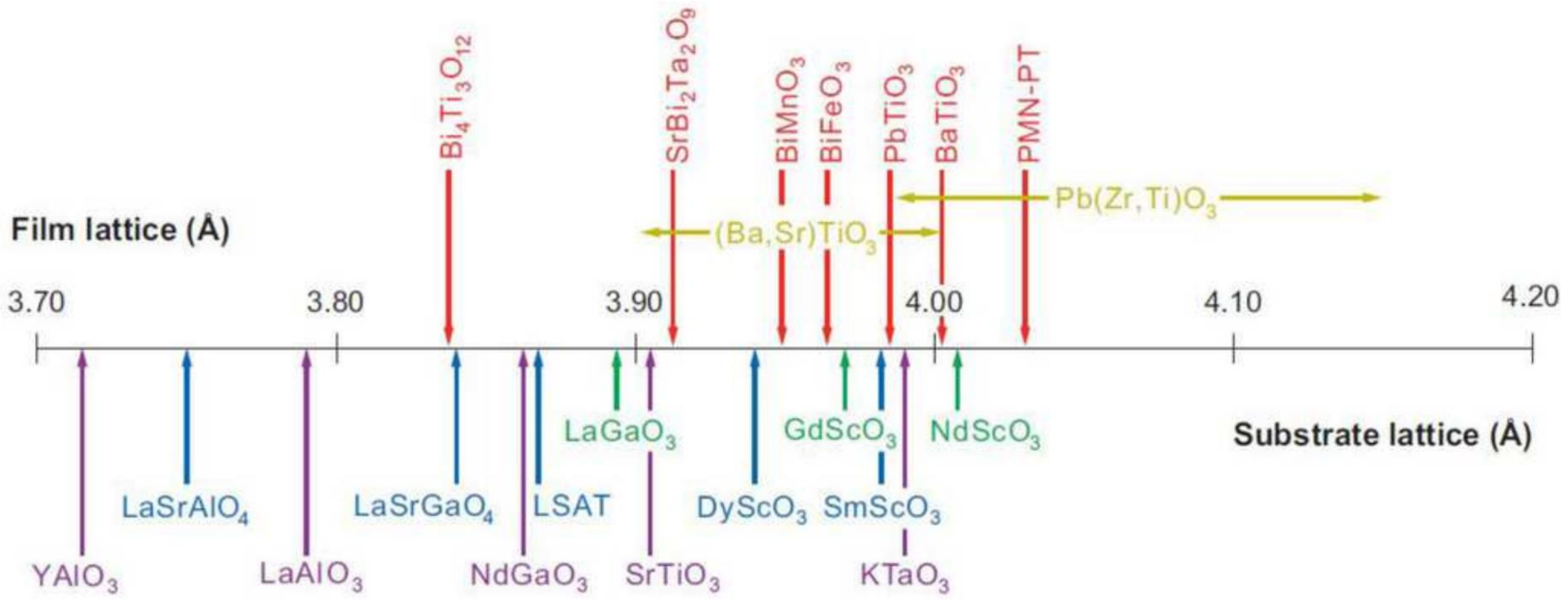
Limiting thickness? Yes!

- **Excitation wavelength – penetration depth**
- **Sample absorption and scattering cross section**
- **Local enhancement**

Thin films measurements

Stress-induced phase transitions: the $LaNiO_3$ case

Substrates to play with



Thin films measurements

Stress-induced phase transitions: the $LaNiO_3$ case

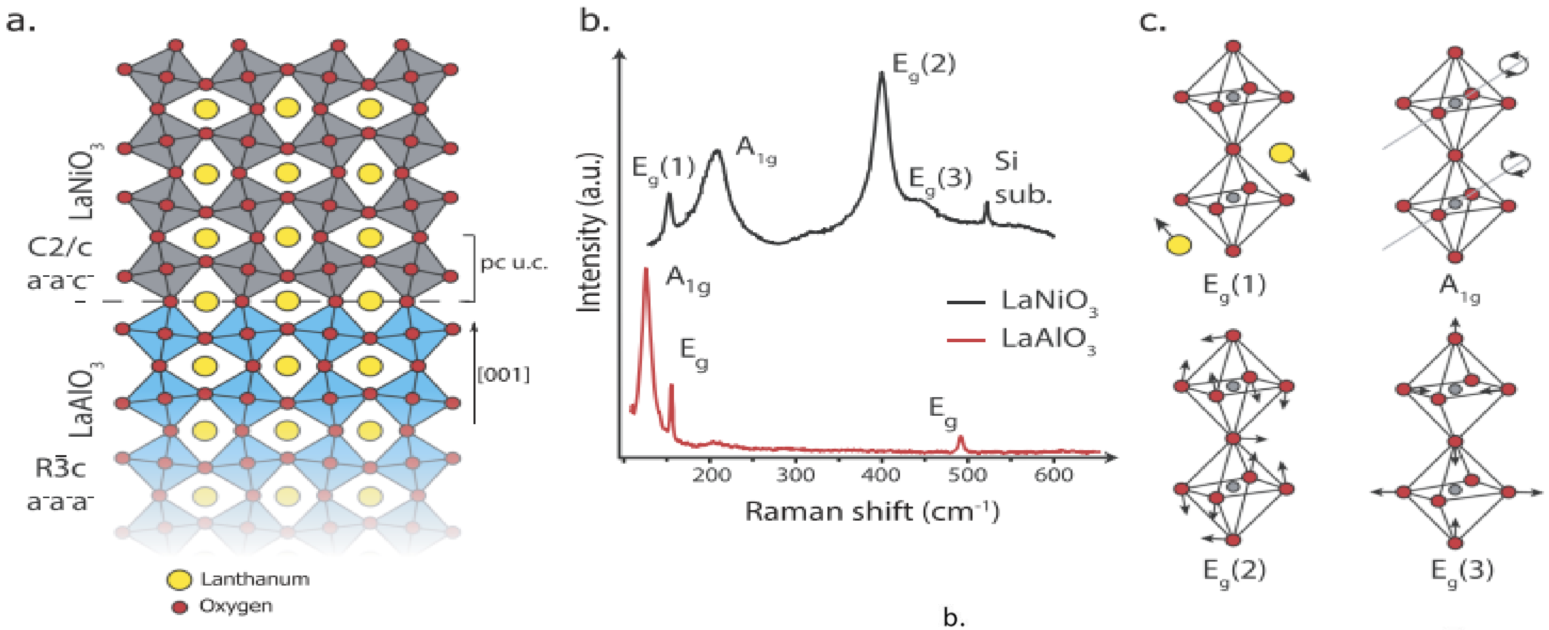
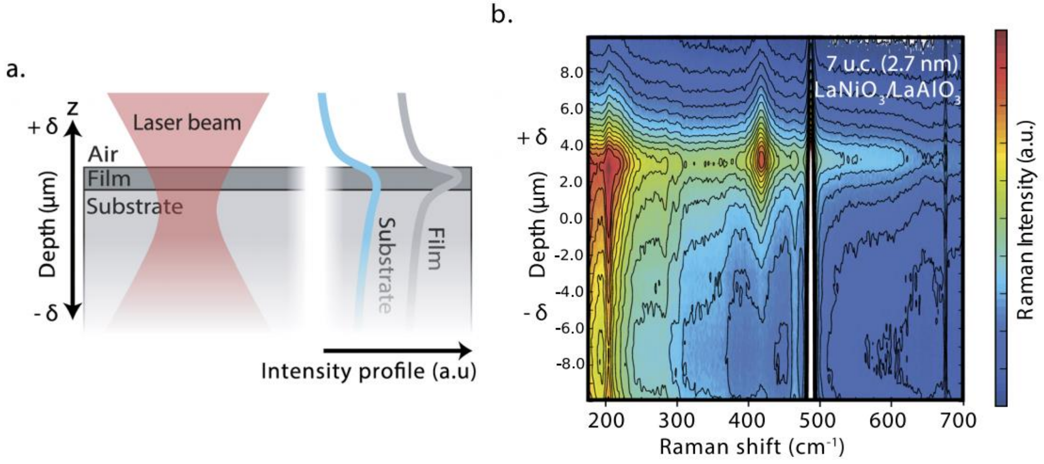


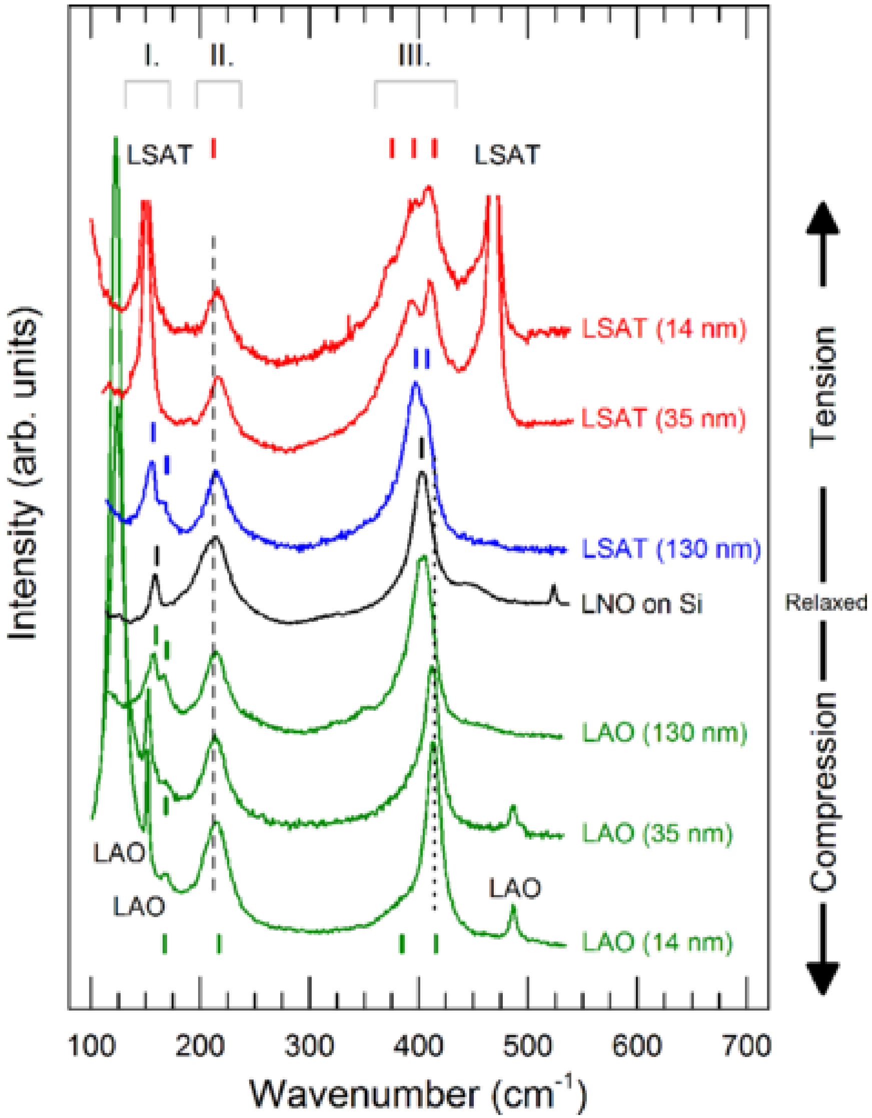
FIG. 1. (a) Sketch of the $LaNiO_3$ layers on [001]-oriented $LaAlO_3$ with the pseudocubic unit cell (pc u.c.) indicated. (b) Raman spectra of a thick polycrystalline $LaNiO_3$ film and a $LaAlO_3$ substrate. (c) Atomic displacement patterns of the $LaNiO_3$ Raman modes shown in (b), where the single A_{1g} soft mode is described as a composite octahedral rotation around the $[111]_{pc}$ vector.



A. Schober et al. APL Mater. 8, 061102 (2020)

Thin films measurements

Multiple strain-induced phase transtions in the $LaNiO_3$ thin film



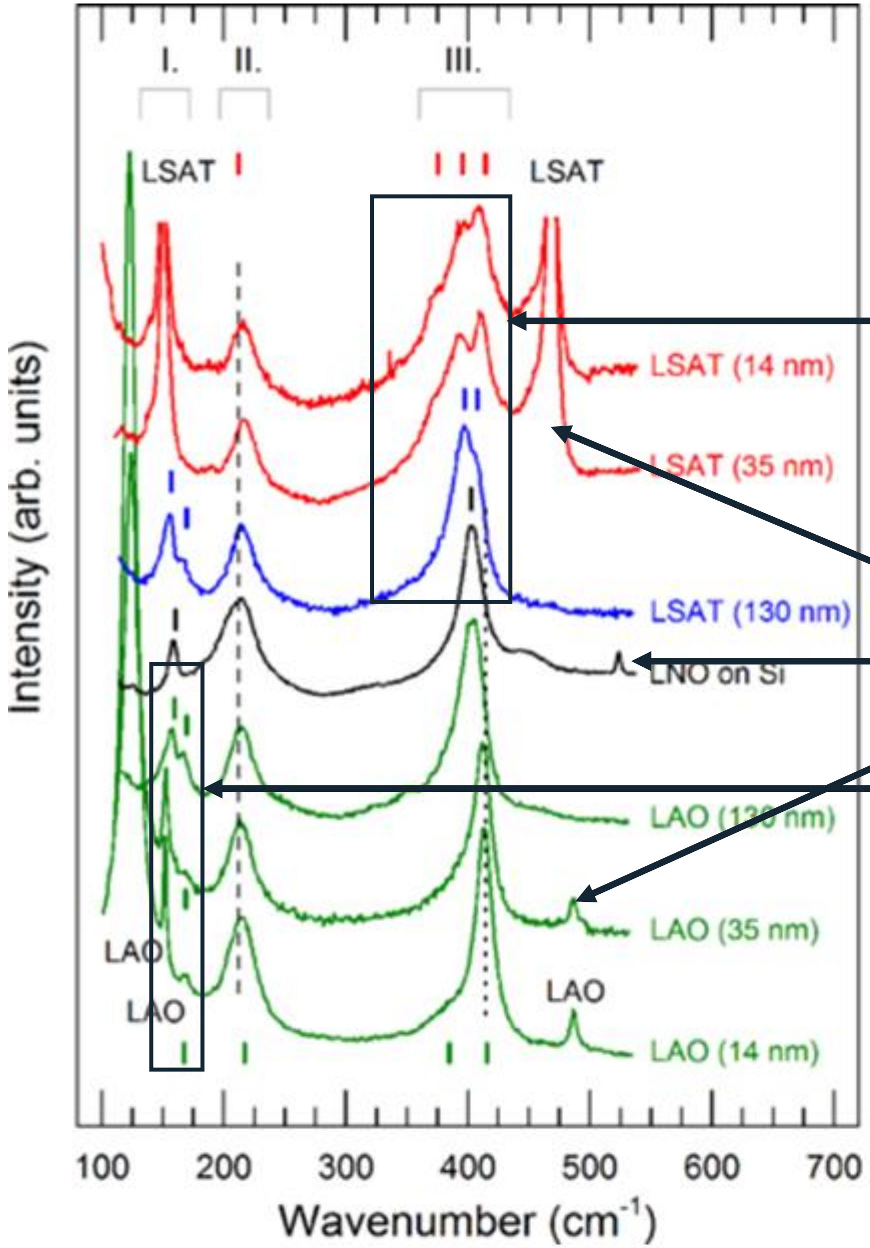
On cubic LSAT $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$

Bulk $LaNiO_3$: rhombohedral R-3c

On pseudo-cubic LAO $LaAlO_3$

M. C. Weber **et al. Phys. Rev. B 94, 014118 (2016)**

Thin films measurements



Raman spectra are well defined (even for the very thin 14 nm film)

Band splitting - **a strain-induced phase transition to a lower symmetry than rhombohedral structure**

Substrate signature

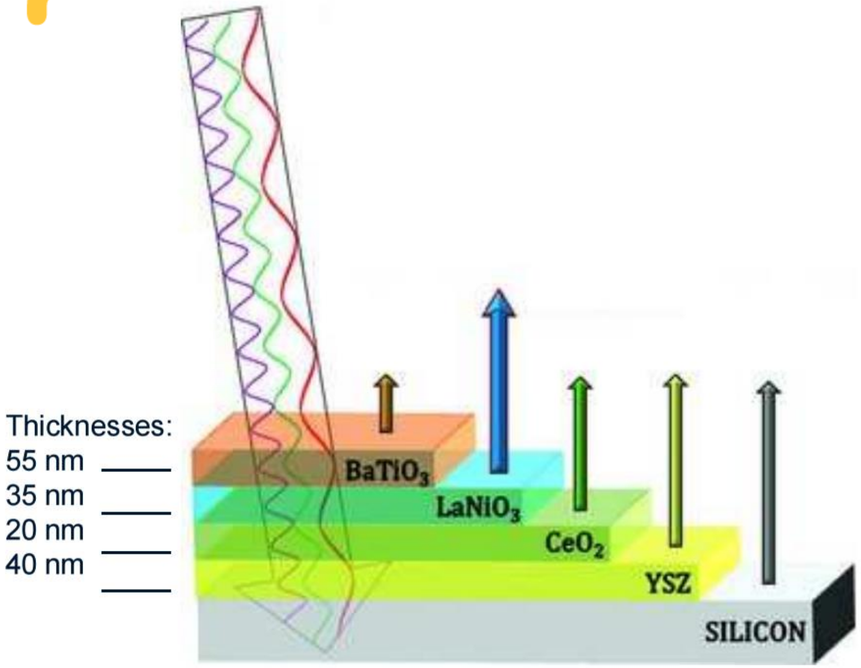
Band splitting - **splitting of the Eg mode (region I), a weak but distinct shoulder at 390 cm^{-1} (region III), while the band around 214 cm^{-1} (region II) remains a singlet. Again, symmetry lowering is observed.**

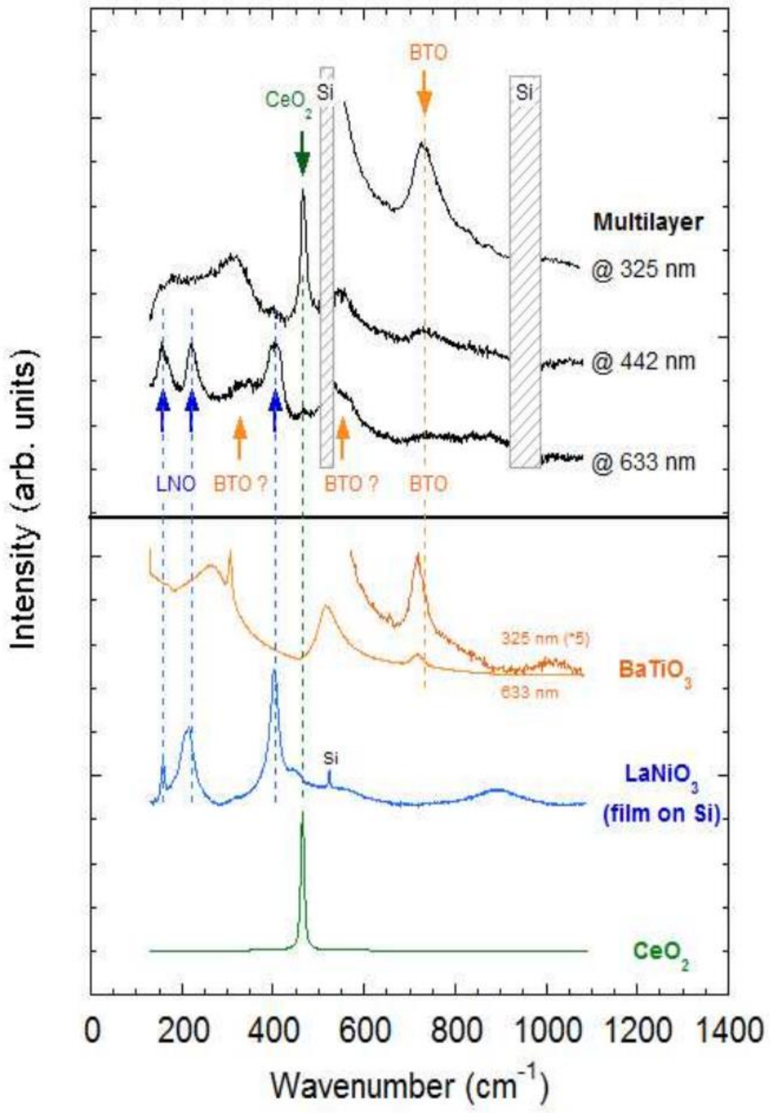
M. C. Weber **et al. Phys. Rev. B 94, 014118 (2016)**

Multiwavelength measurements

Why multiwavelength measurements?

- Multilayer systems
- Different absorption at different wavelengths
- Interactions with other excitations, like electronic transitions:
  - ➢ resonant Raman scattering – signal enhancement 👍
  - ➢ fluorescence 👎

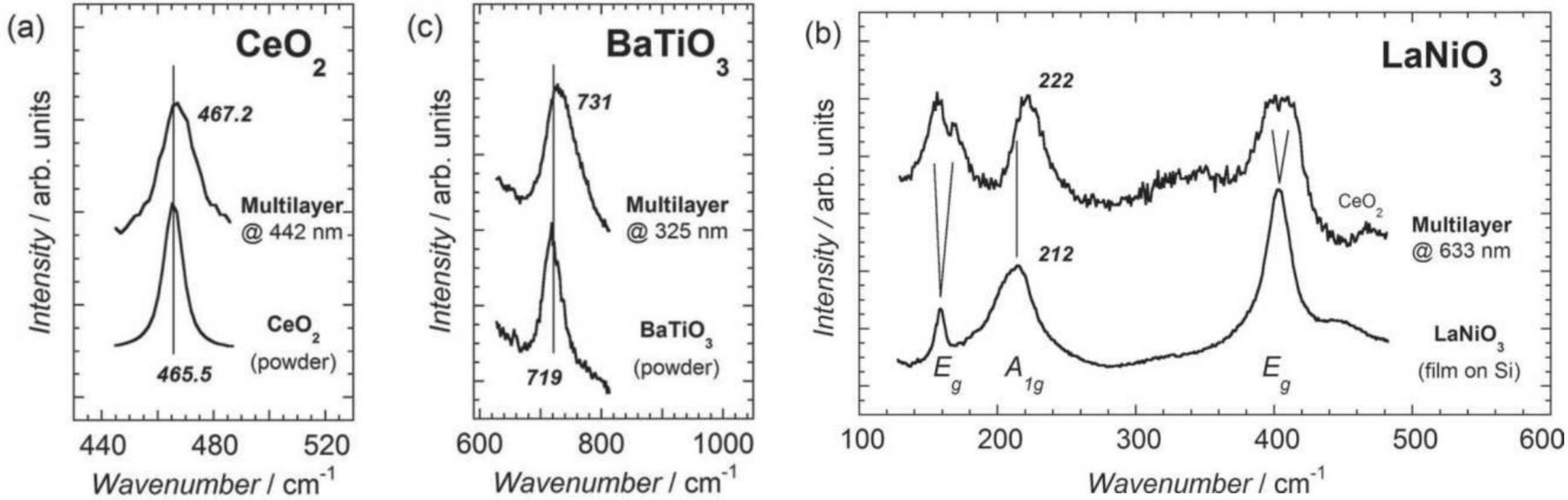




J. Kreisel et al., Adv. Funct. Mater. **22**, 5044 (2012)

Multiwavelength measurements

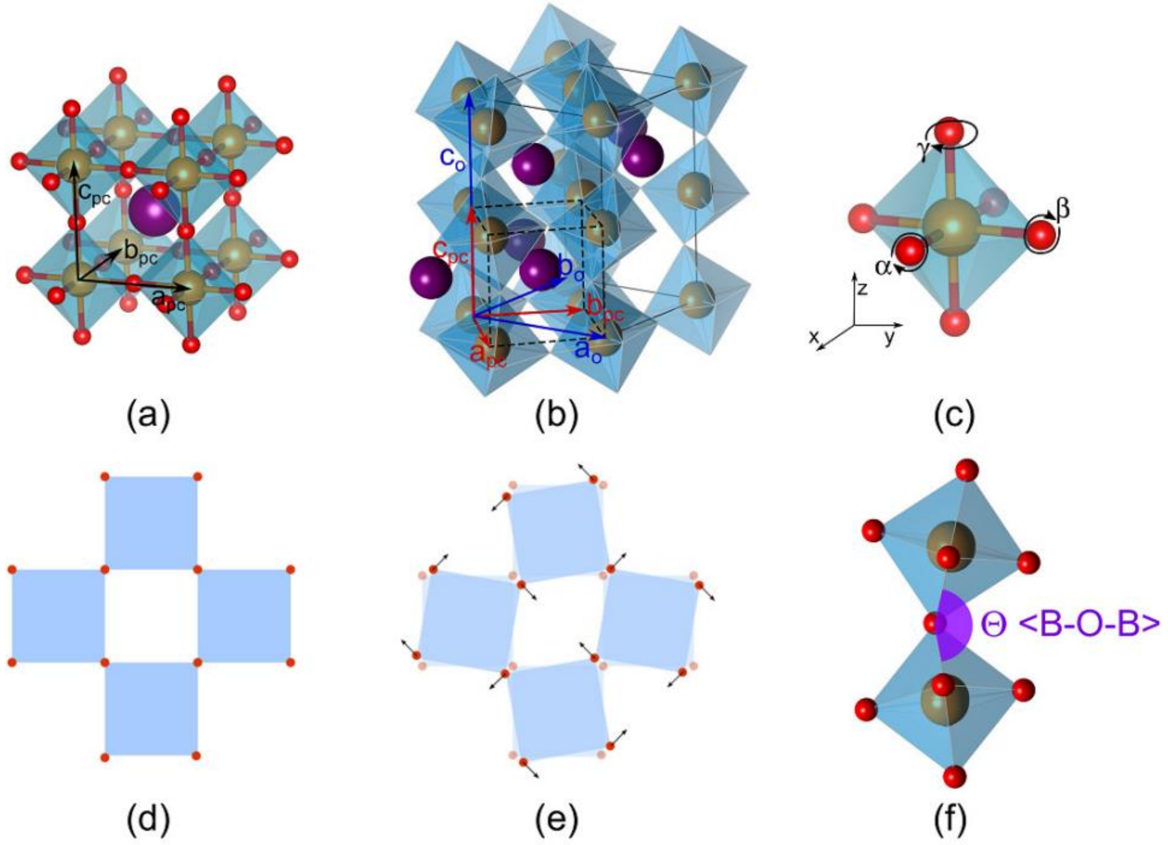
Analysis of the stress/strain states of each layer

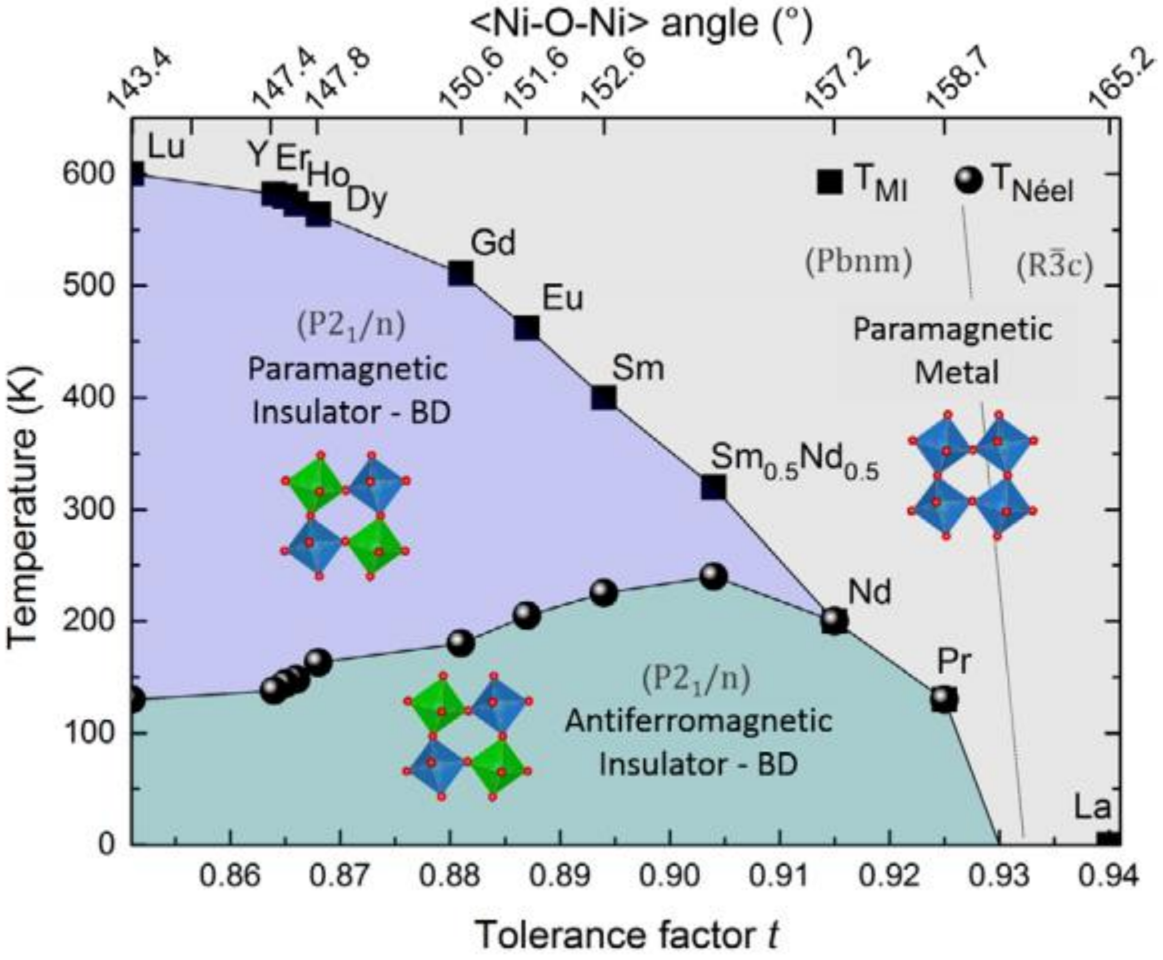


- CeO_2: compressive strain state ~ 0.5 GPa
- $BaTiO_3$: compressive strain state ~ 2.5 GPa
- $LaNiO_3$: mode degeneracy lifted due to in plane stress.

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

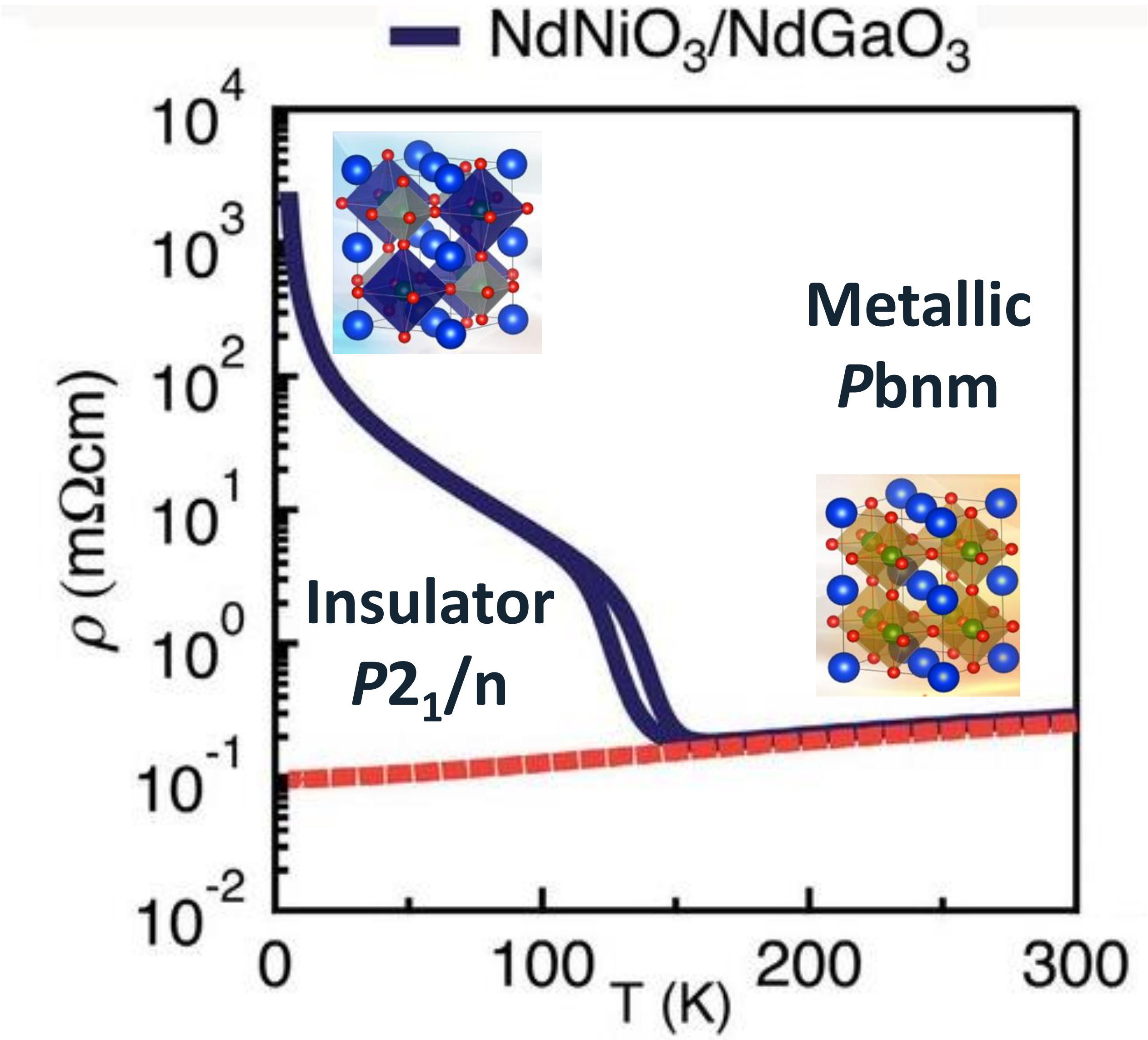
Other studies – the MIT in $NdNiO_3$





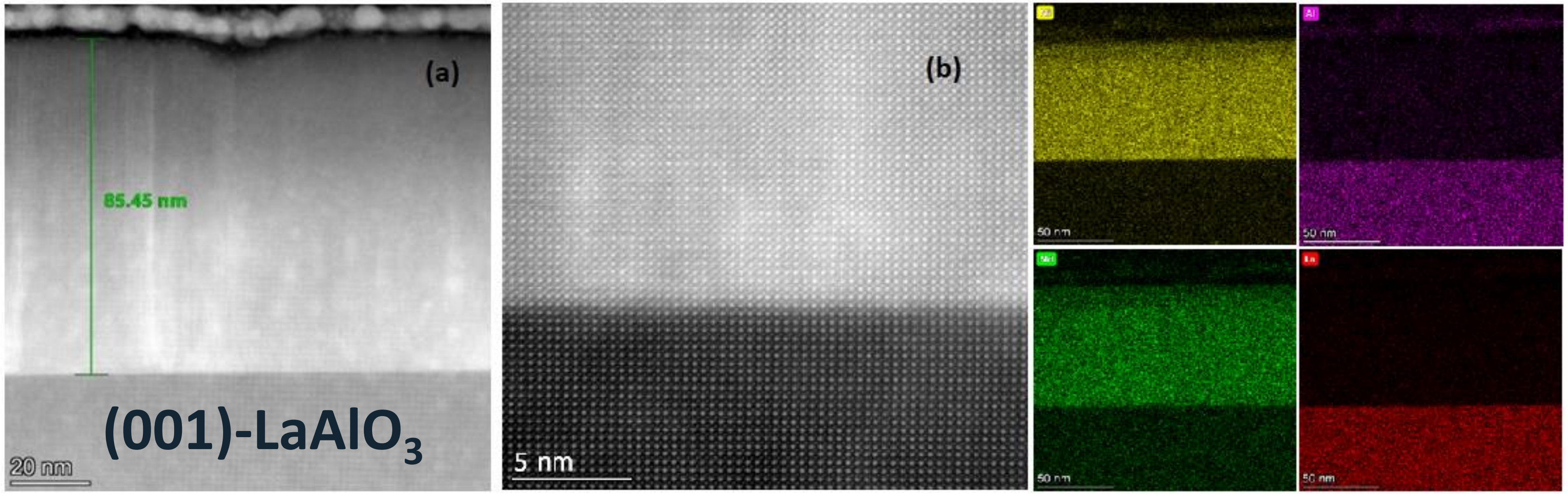
S Catalano et al 2018 Rep. Prog. Phys. 81 046501

Other studies – the MIT in $NdNiO_3$

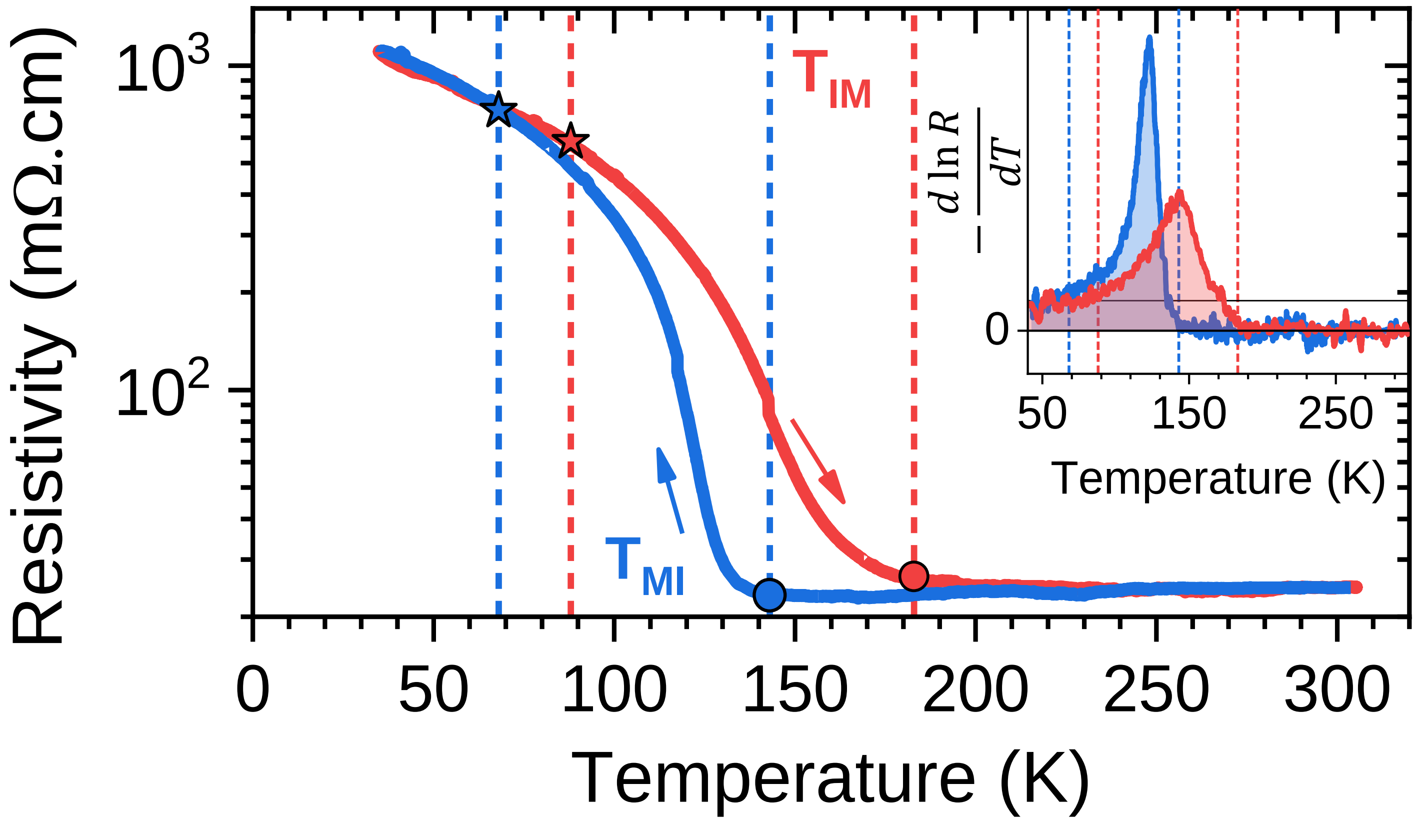


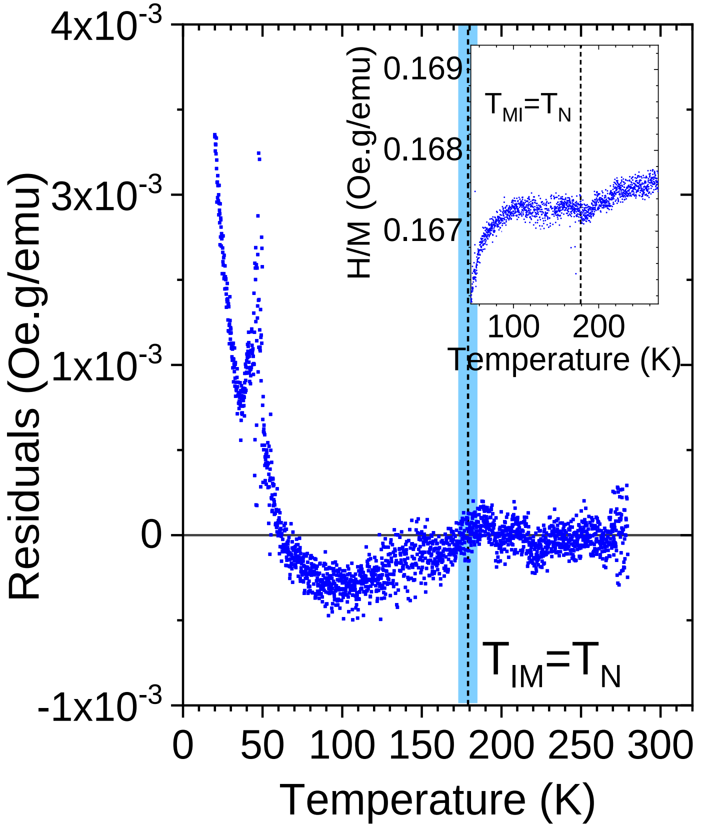
Other studies – the MIT in $NdNiO_3$

85 nm film

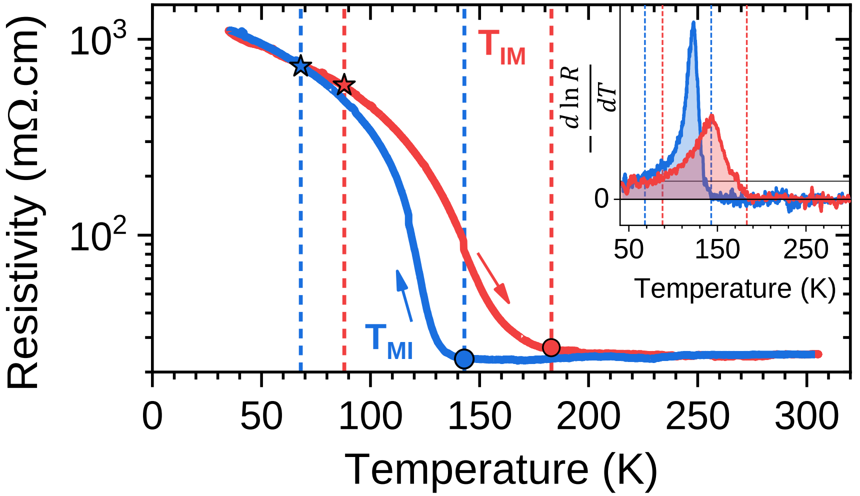


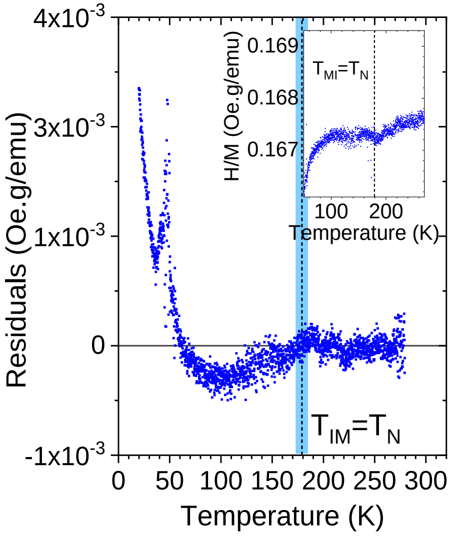
Other studies – the MIT in $NdNiO_3$

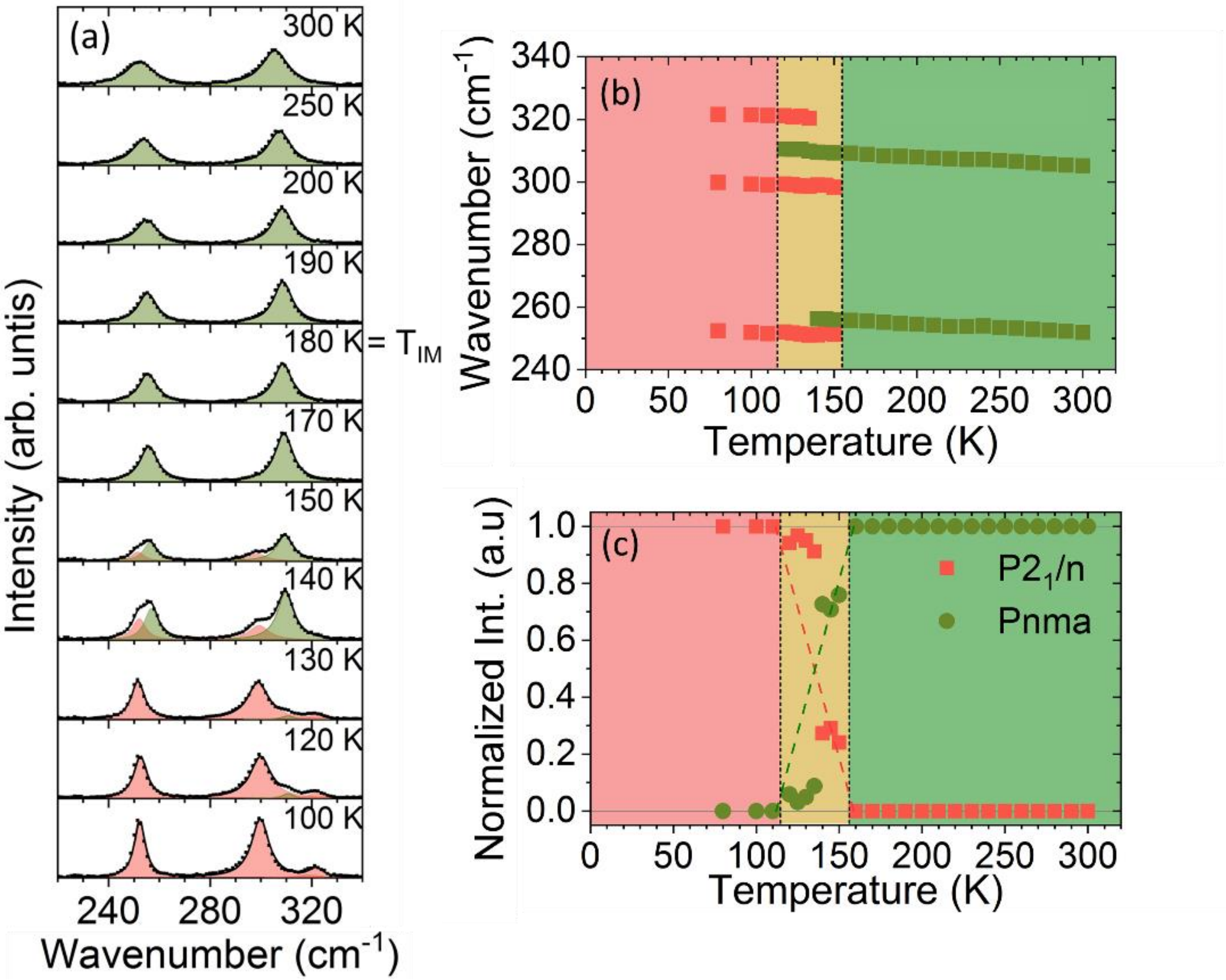




Other studies – the MIT in $NdNiO_3$







Other studies – the MIT in $NdNiO_3$