H2020-MSCA ITN
Grant n. 956099

Normandie Université

NanED

3D ED on Nanomaterials

Philippe BOULLAY - Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, Caen, France

CNRS - Caen (FR) : a brief introduction

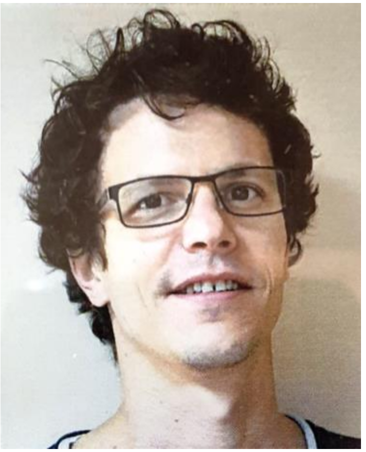
CRISMAT Laboratory

- **73 permanent staff** (18 CNRS Res., 34 Univ. and 21 ITA)
- **10 PhD graduated per year**
- Synthesis and characterization of inorganic materials in various forms (ceramics, thin films, single crystals, powder, nanoparticles, …) for various applications.

CNRS - Caen (FR) : a brief introduction

CRYSTALLOGRAPHY *and* TEM

O. PEREZ
single crystal



N. BARRIER
powder diffraction

D. CHATEIGNER
strain and texture

D. PELLOQUIN
TEM

P. Boullay
electron diffraction

- Rigaku Synergy-S dual microfocus + Dectris Eiger 1M + 28K to 1273K
- Rigaku SmartLab dual rotating anode + HyPix 3000 + 12 K to 1400 K + gas (Pmax 10 bars)
- JEOL ARM 200F cFEG 80-200 + CEOS Cc and Cs correctors + GATAN EELS spectrometer + …
- JEOL F200 cFEG 80-200

CNRS - Caen (FR) : a brief introduction

3D ED Experimental setup

JEOL F200 TEM / STEM cFEG 80-200 kV

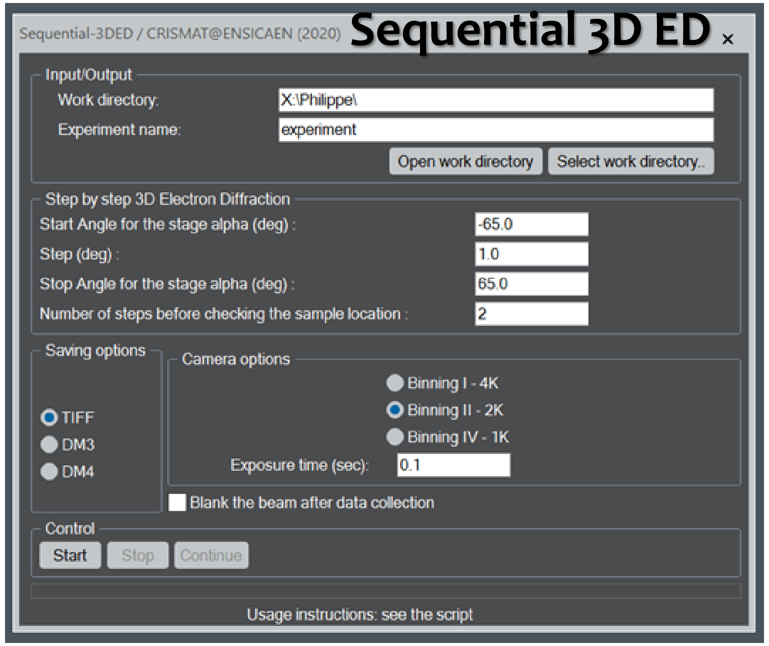
Silicon Drift Detector for EDS

HAADF / ABF detectors

Tilt range: +/- 30° (***tomo +/- 70°***)

NANOMEGAS Digistar + Astar

Cryo-Transfer Tomography Holder



GATAN RIO16 4096x4096 fiber-optic coupled CMOS

max. speed 160 fps (1kx1k); high dynamic range; in-situ mode

+ cRED

instaDMatic

ASI Cheetah M3 512x512 CMOS hybrid pixel direct electron detector

max. speed 1750 fps; high dynamic range; no noise

interface with Instamatic for data acquisition

CNRS - Caen (FR) : a brief introduction

MATERIALS *and* SYNTHESIS

A. DAVID
Oxide thin films

E. GUILMEAU
Thermoelectrics

V. PRALONG
Battery Materials

M. DEBOST
Nanoparticles

S. MINTOVA
@ LCS – Caen (FR)

- Pulsed Laser Deposition (PLD)
- Ceramics Processing (spark plasma sintering, microwave, …)

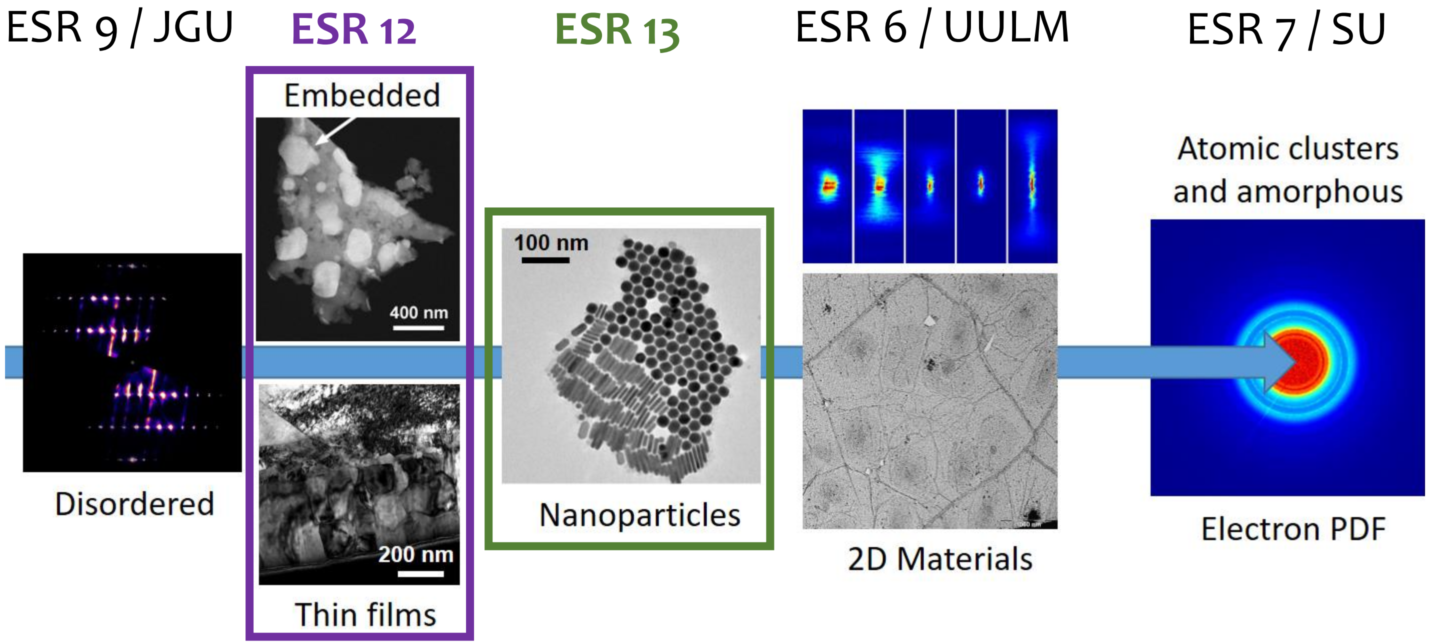
▶ESR 12

- Chemistry and Electrochemistry
- Chemistry in aquous solutions

▶ESR 13

Work Package 4 – Crystallography beyond nanocrystals

Road Map to Nano



start October 2021 (M8)

3D ED

minimum crystal size ?

minimum beam size ?

Are small crystals same as larger ones ?

Electron Crystallography of nanoparticles

Between particles and atoms: exploring the size limit of crystals

Erica CORDERO | MSc in Nanoscience and Molecular Nanotechnology – Universidad Autonoma de Madrid

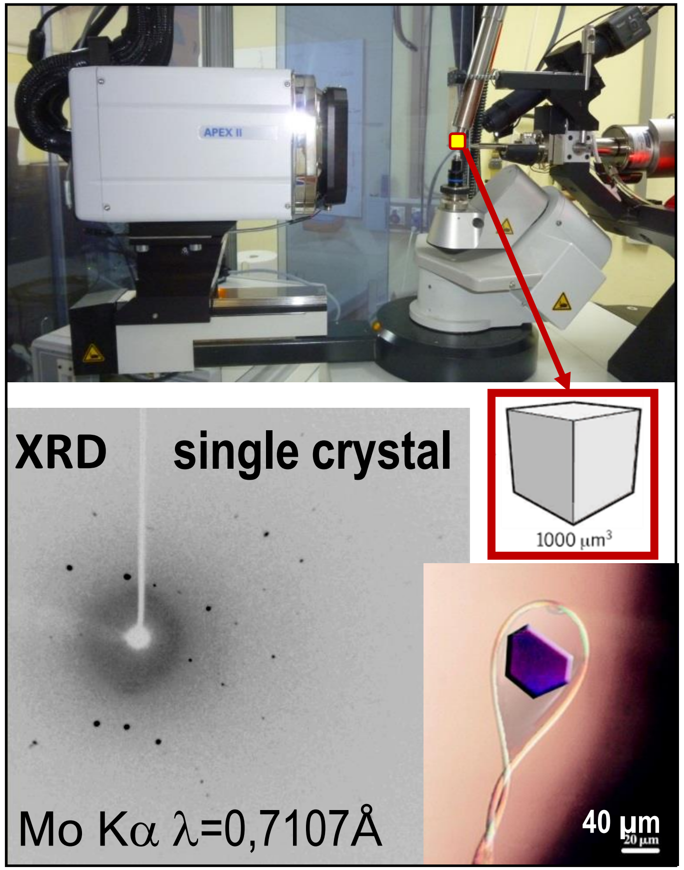
Electron Crystallography of nanodomains in functional materials

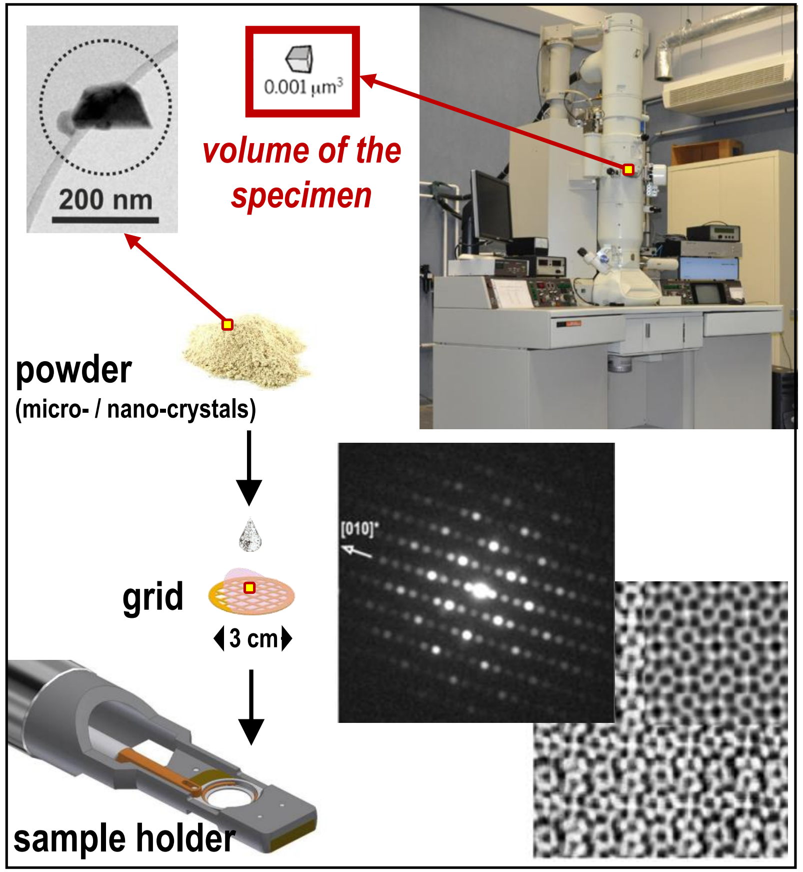
Combining EM techniques to analyze the needle in the haystack

Sara PASSUTI | MSc in Materials and Nanotechnology – Universita di Pisa

Solving the structure of an unknown inorganic material by 3D ED is usually not a problem

SC-XRD ◄ tens of micrometer ► **3D ED**





Accurate structure refinement may be an issue

▼

WP3

ESR 13 / ESR 12

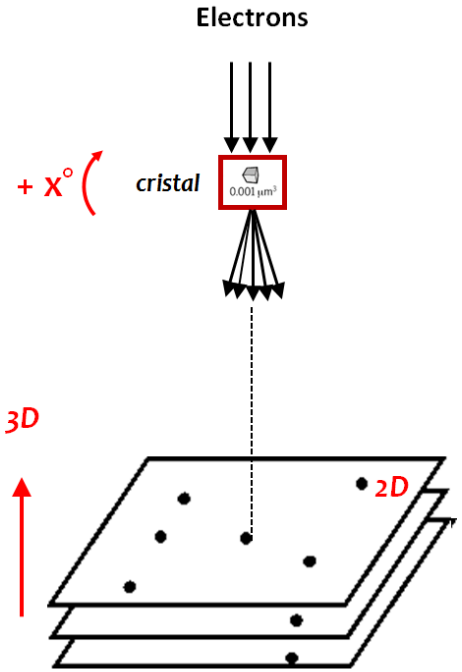
Are small crystals same as larger ones ?

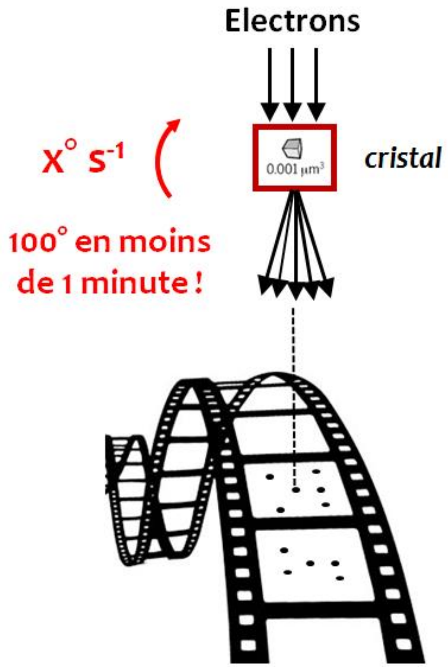
Nanomaterials ?

Electron **Nano**crystallography ? ► What are Nanomaterials?

Nanomaterials can be defined as materials possessing, at minimum, **one external dimension measuring 1 to 100 nm.**

European Commission states that the particle size of at least half of the particles in the number size distribution must measure 100nm or below.



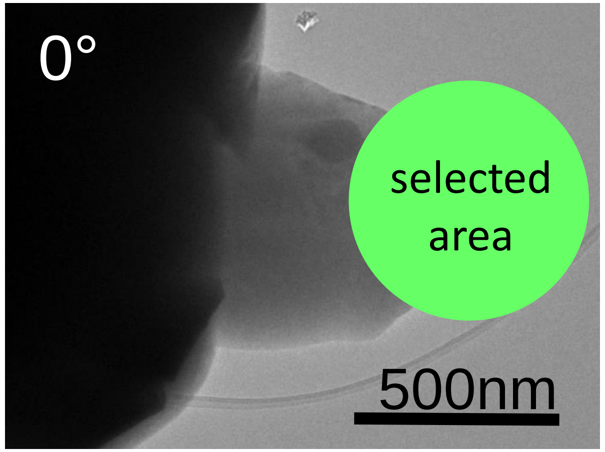


3D ED experiments are not supposed to be always done on Nanomaterials ?

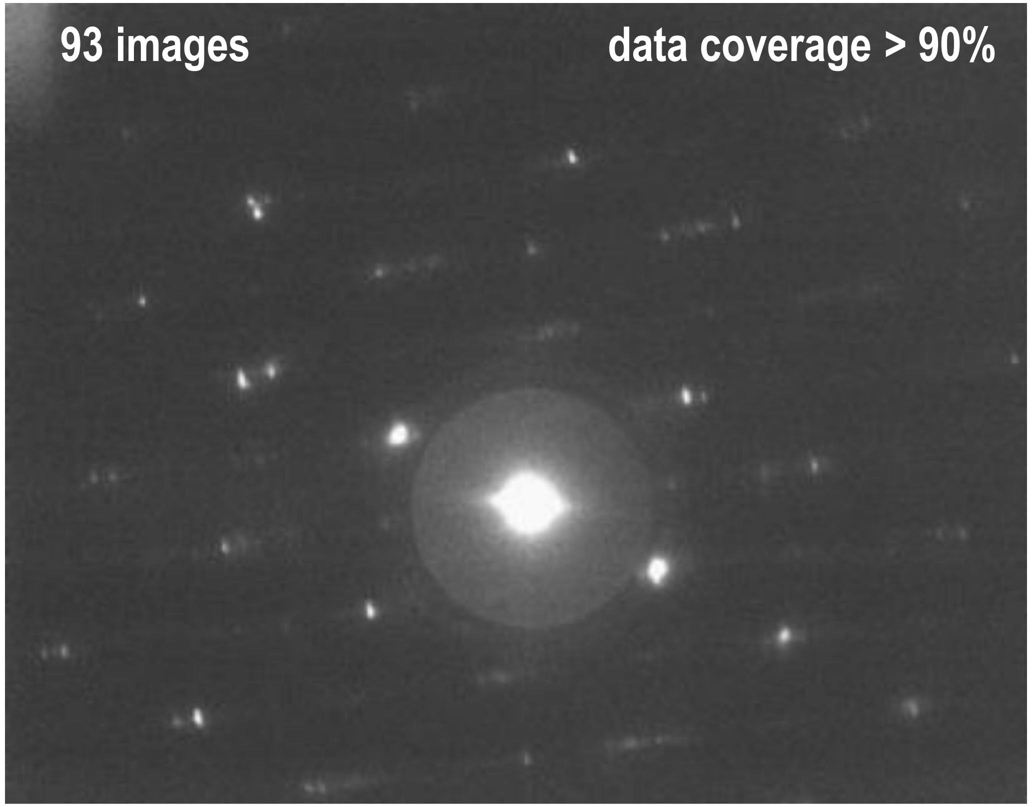
3D ED ► step-by-step or ►continuous rotation

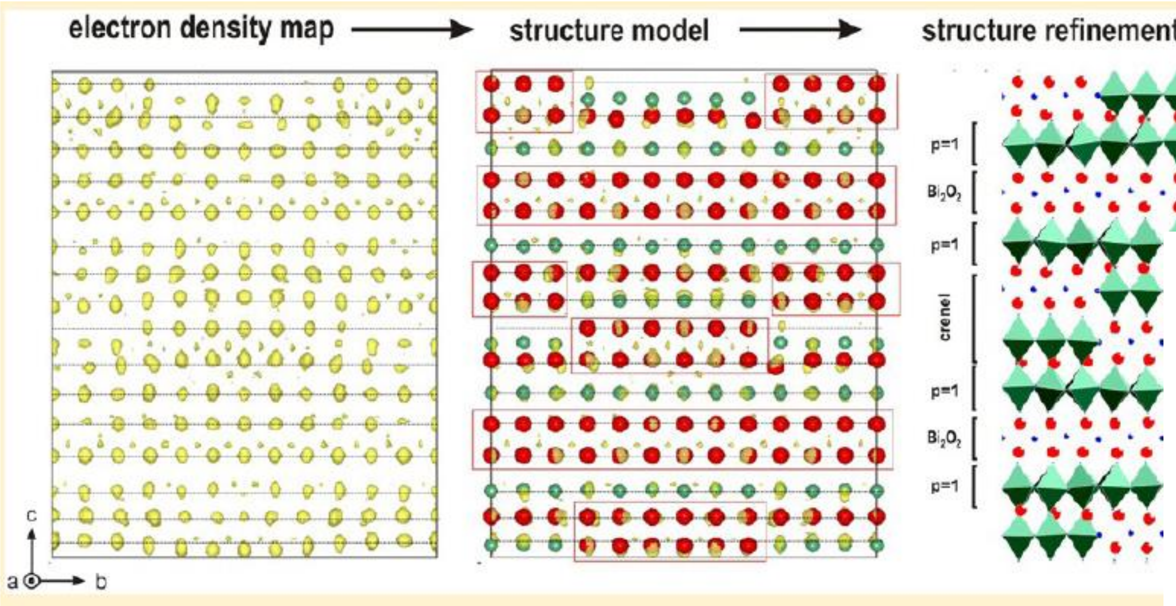
$Bi_5Nb_3O_{15}$

no good single crystals for SC-XRD



3D ED ▼ single crystal diffraction ▼ structure solution





Incommensurately Modulated Compounds

Inorganic Chemistry
Article
pubs.acs.org/IC

Precession Electron Diffraction Tomography for Solving Complex Modulated Structures: the Case of $Bi_5Nb_3O_{15}$

Philippe Boullay,*[†] Lukas Palatinus,[‡] and Nicolas Barrier[†]

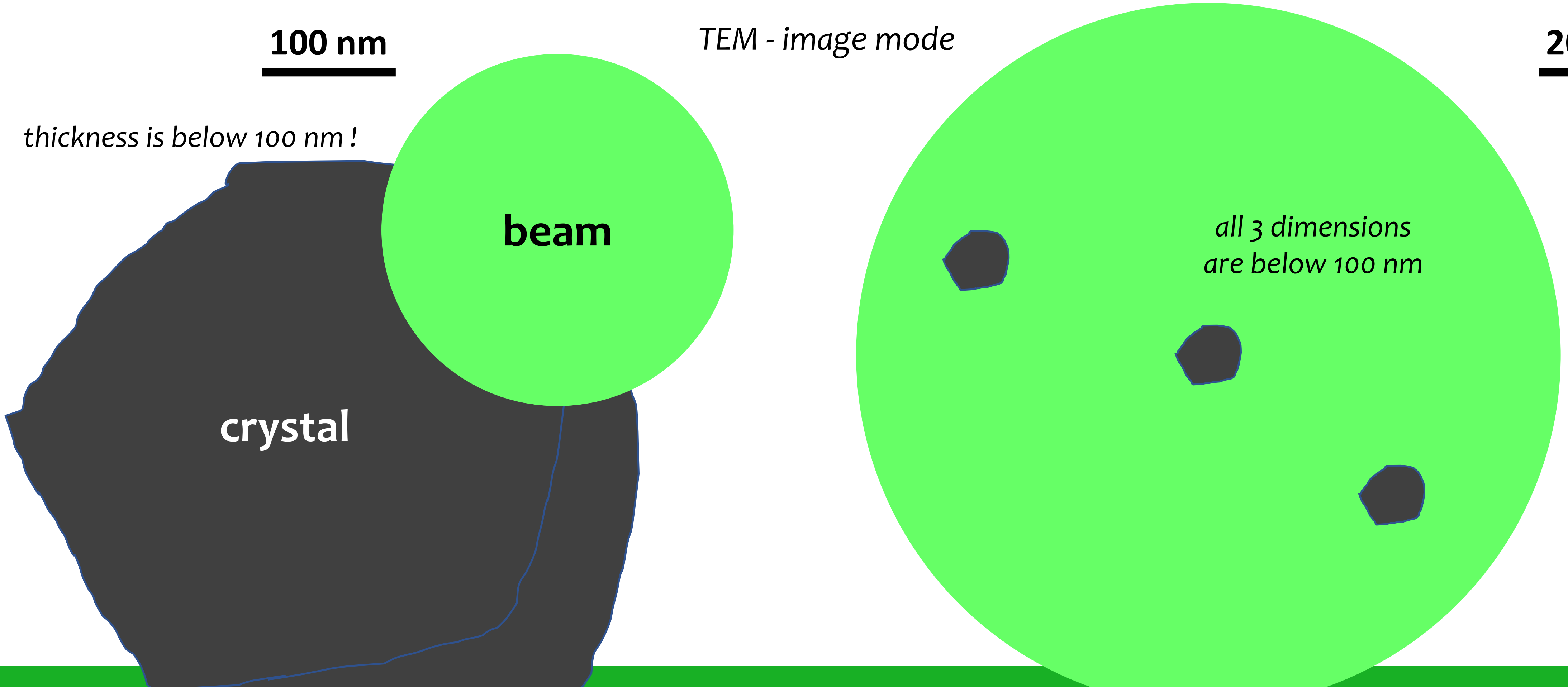
[†]Laboratoire CRISMAT, UMR CNRS 6508, ENSICAEN, 6 Bd Maréchal Juin, F-14050 Caen Cedex 4, France
[‡]Institute of Physics of the AS CR, v.v.i. Na Slovance 2, 182 21 Prague, Czechia

dx.doi.org/10.1021/ic400529s | *Inorg. Chem.* 2013, 52, 6127−6135

Does size matters ?

Data acquisition

You will experience that in 3D ED data acquisition when the goniometer rotates the crystal tends to move !

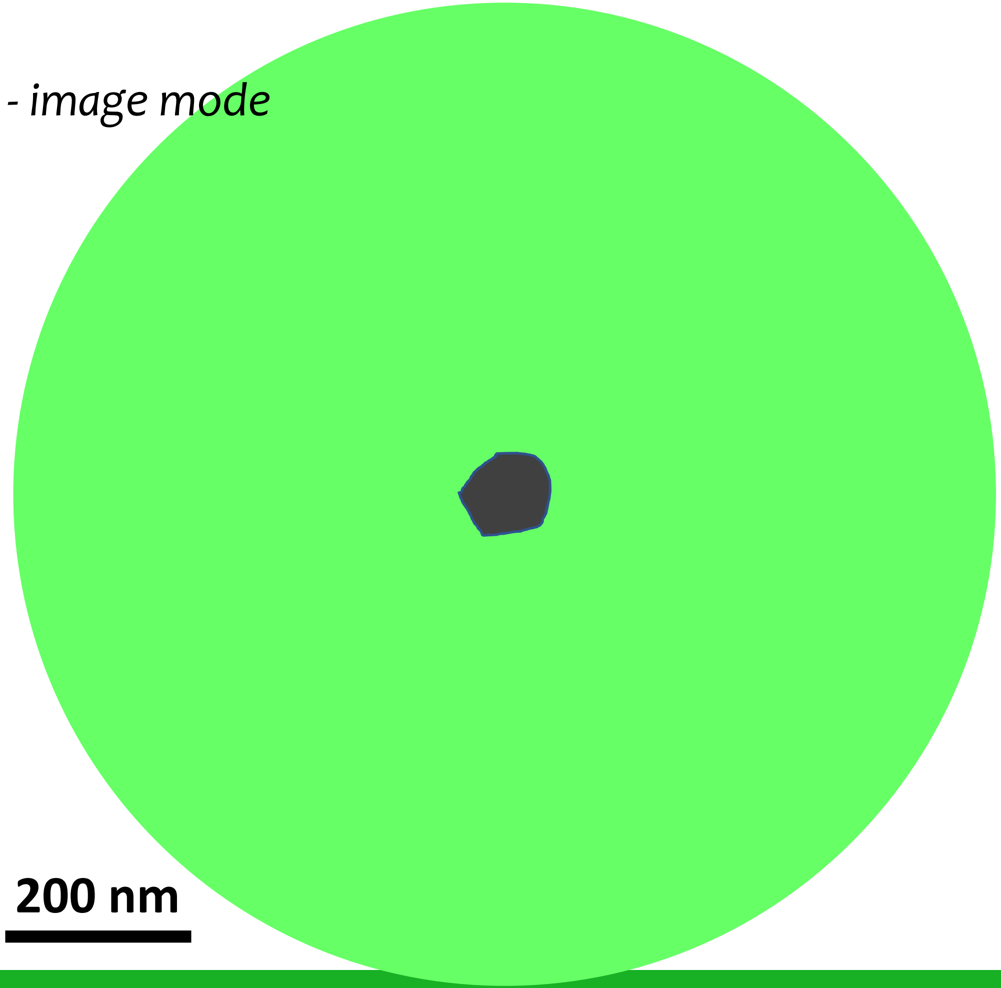


Does size matters ?

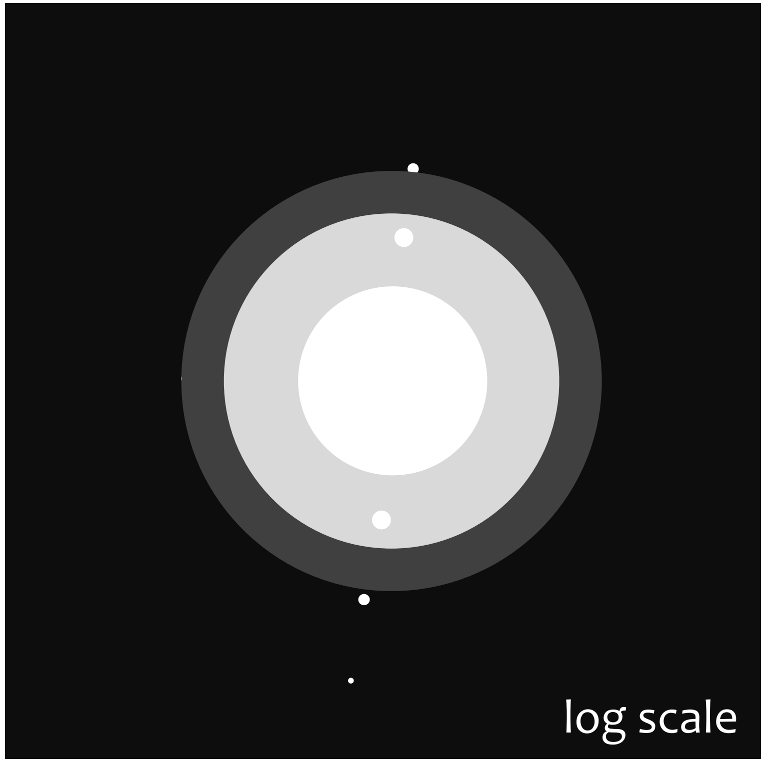
Data acquisition

You will experience that in 3D ED data acquisition when the goniometer rotates the crystal tends to move !

TEM - image mode

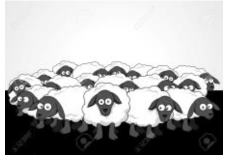


diffraction mode – parallel beam



supervisor reaction
depending on camera
and electron dose

The herd behaviour !



Data acquisition

You will experience that in 3D ED data acquisition when the goniometer rotates the crystal tends to move ► *solved but …*

You will experience that nanoparticles have a herd behaviour !

Pair Distribution Function Analysis

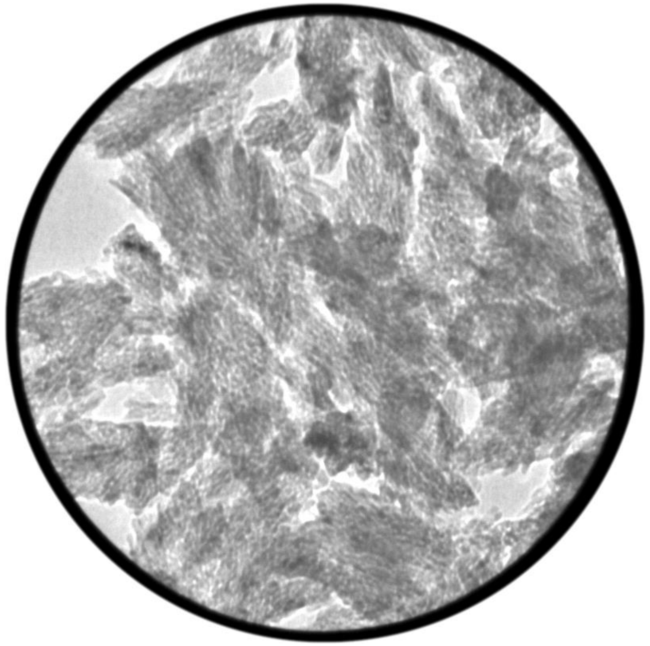
▲

ESR 13 + ESR 7

▼

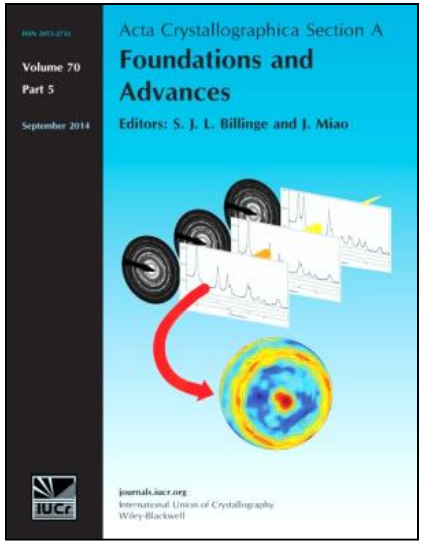
Rietveld Analysis

Selected area



0.5µm diameter

Diffraction patterns = Ring patterns > powder-like patterns



P. Boullay et al., Acta Cryst. A 70 (2014) 448-456

Fast Microstructure and Phase Analyses of Nanopowders using Combined Analysis of TEM scattering patterns

The more nanoparticles you have the better it is / no need to tilt !

Deals with the herd behaviour for 3D ED!

Data acquisition

You will experience that in 3D ED data acquisition when the goniometer rotates the crystal tends to move !

You will experience that nanoparticles have a herd behaviour !

1- find a way to isolate the nanoparticules  … TEM sample preparation.

2- reduce the size of the beam ► minimal reachable parallel beam size will depend on the microscope.

► use STEM (**ESR 9 / JGU**) or TEM (**ESR 13 / CNRS**) ?

3- track the isolated nanoparticle while tilting ! 

Deals with the herd behaviour for 3D ED!

Data acquisition

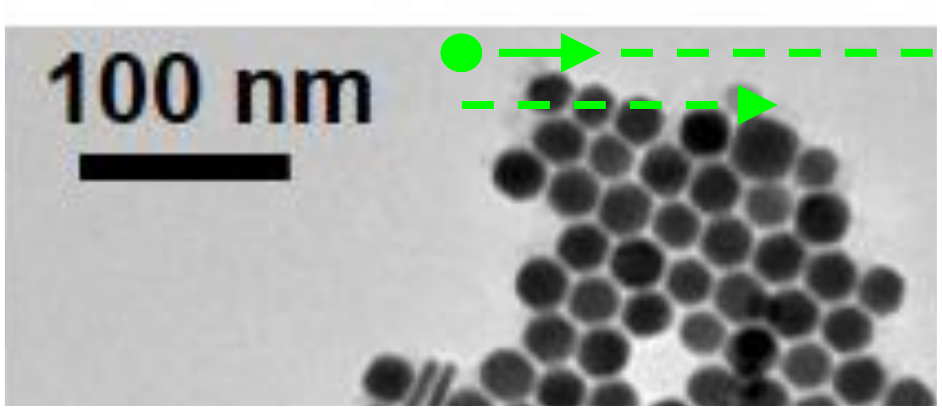
You will experience that in 3D ED data acquisition when the goniometer rotates the crystal tends to move !

You will experience that nanoparticles have a herd behaviour !

Alternative 1 :

skip the tracking

possible with STEM and with TEM (*)



1- scan a tiny parallel beam on nanoparticles and collect ED.

2- use tools develop for serial ED to analyse the data.

3- rotate the sample to collect more data.

Alternative 2 :

YOU must think of other alternatives and defines protocols for data acquisition!

(*) *you will find interesting literature from Paul Midgley's group or from my French colleagues E. Rauch and M. Véron !*

ESR 13 : Electron Crystallography on Nanoparticles

GOALS

link with WP1 / JGU

- **Determine the minimal beam and crystal size at which it is possible to collect 3D ED data suitable for structure solutions and refinements.**

nanoparticles >|< *atomic clusters* >|< *amorphous*

1-2 nm (?)

⇨ synthesize nanoparticles (NP) with controlled size and shape (oxydes : Mn_3O_4, TiO_2, …)

⇨ develop an experimental protocol for 3D ED data collection with parallel nanobeams

⇨ control NP dispersion and use efficient on-going tracking of a sample or an alternative approach

- **Compare the structure obtained from Rietveld refinement on powder x-ray data with dynamical refined structure from 3D ED data.** **link with WP3**

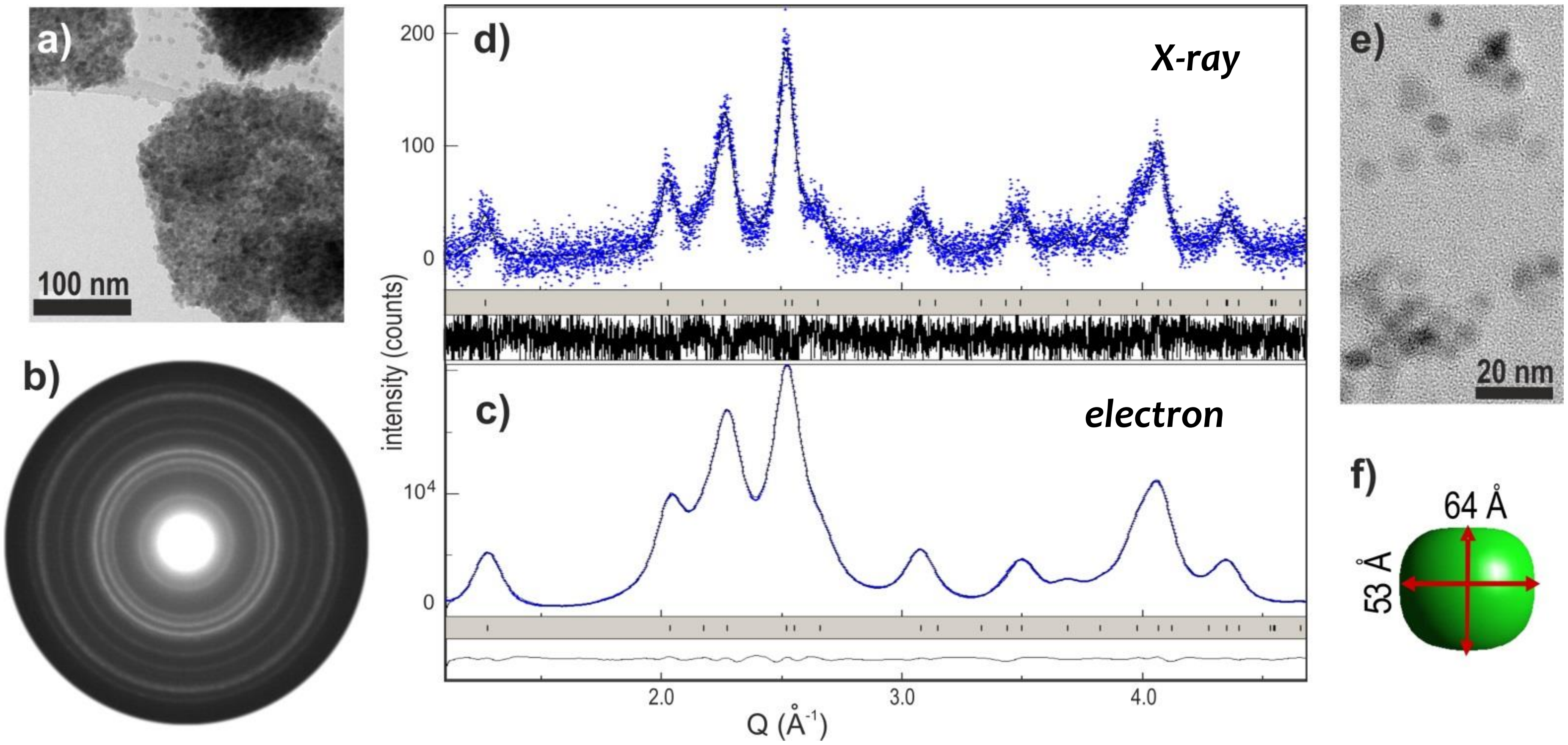
ESR 13 : Electron Crystallography on Nanoparticles

GOALS

link with ESR 7 / SU

- **From electron powder diffraction (ring patterns) of nanoparticles aggregates to 2D ePDF.**
  - ► Apply and test protocols define by ESR 7 @ SU

Mn_3O_4



ESR 13 : Electron Crystallography on Nanoparticles

GOALS

- **Application of the protocols for the structure determination of nanoparticles of fundamental and industrial interest (thermoelectrics, zeolites, energy materials, …)**

⇨ materials of fundamental and industrial interests will be found locally @ Caen or **link here** *academic or PO ?*

⇨ **will be good:** solve compounds with unknown structure in the form of nanoparticles

Electron Crystallography of nanoparticles

Between particles and atoms: exploring the size limit of crystals

Erica CORDERO | MSc in Nanoscience and Molecular Nanotechnology – Universidad Autonoma de Madrid

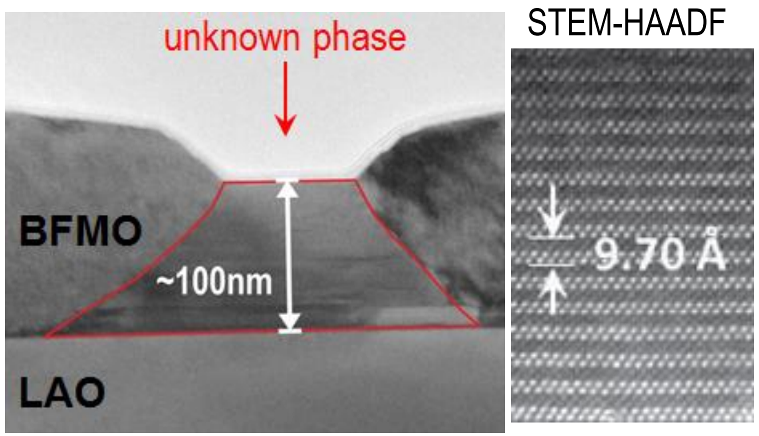
Planned secondments: *UA: J. Hadermann (in situ 3D ED and imaging, M24-25)*

ULM: U. Kaiser (TEM imaging on 2D materials, M26)

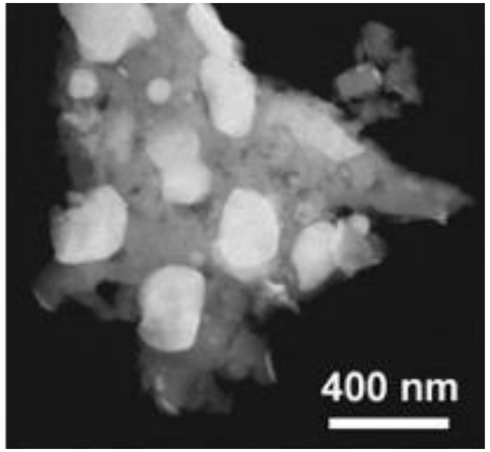
EST: J. Plaisier (synchrotron powder x-ray diffraction, M29-30)

CDX: S. Séguier (marketing and commercial skills in an R&D lab, M31-32)

Nanomaterials ?



What if the nanomaterials are embedded in a matrix or grown on a substrate ?

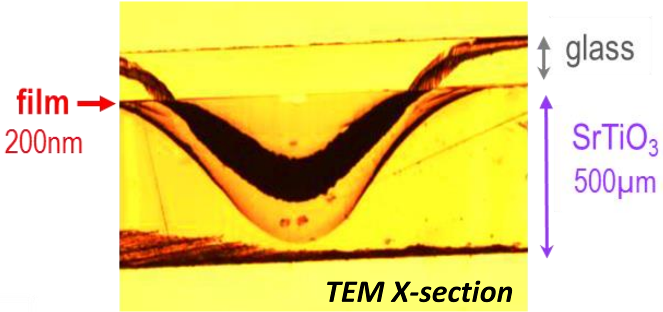


Nanomaterials ?

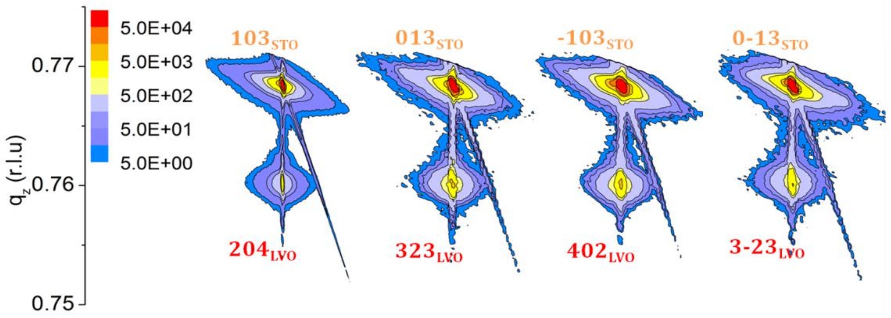
XRD limitations in the case of thin films

Sample geometry:

- small diffracting volume.
- large contribution from the substrate.
- Epitaxy.



H. Rotella et al., "Structural analysis of strained $LaVO_3$ thin films", J. Phys.: Condens. Matter. 27 (2015) 175001



substrate: $SrTiO_3$ (STO) *perovskite*

film: $LaVO_3$ (LVO) *tilted perovskite*

What can we get from laboratory XRD ?

- lattice parameters.
- epitaxial relationships.
- If the structure is known:

  quantify some structural features like octahedral tiltings in perovskite oxides.
- If the structure is unknown ?

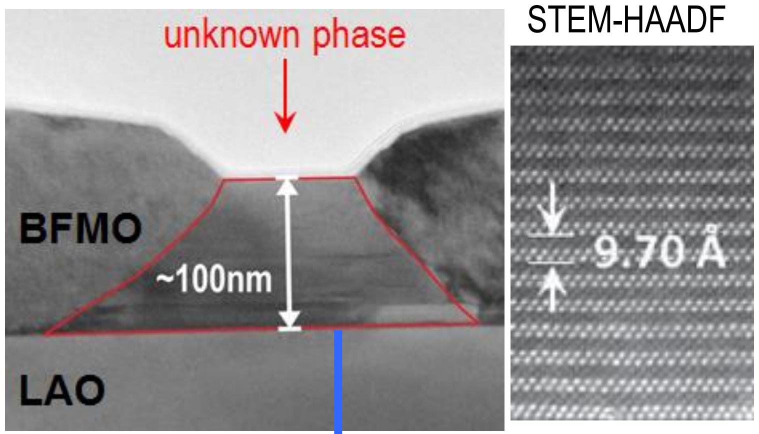
Experimental setup: reflection configuration

- blind area / long acquisition time / few reflections.

laboratory XRD: few tens of reflections for several days of data collection.

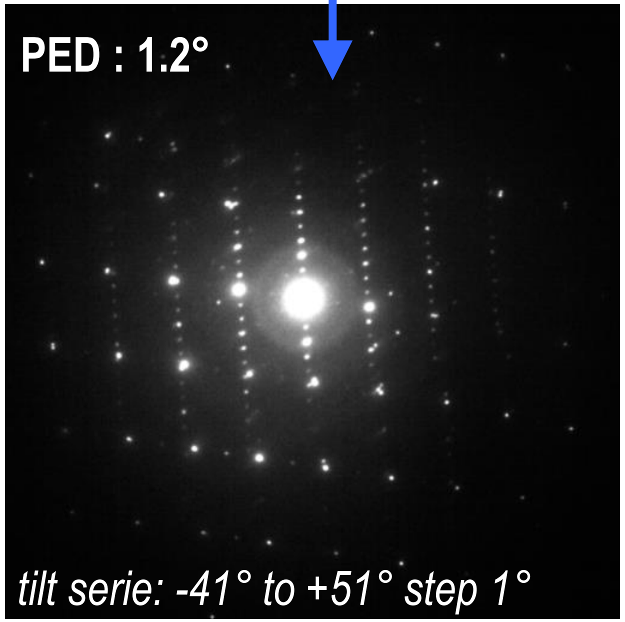
Find an alternative to XRD for structure solution

Nanomaterials ?

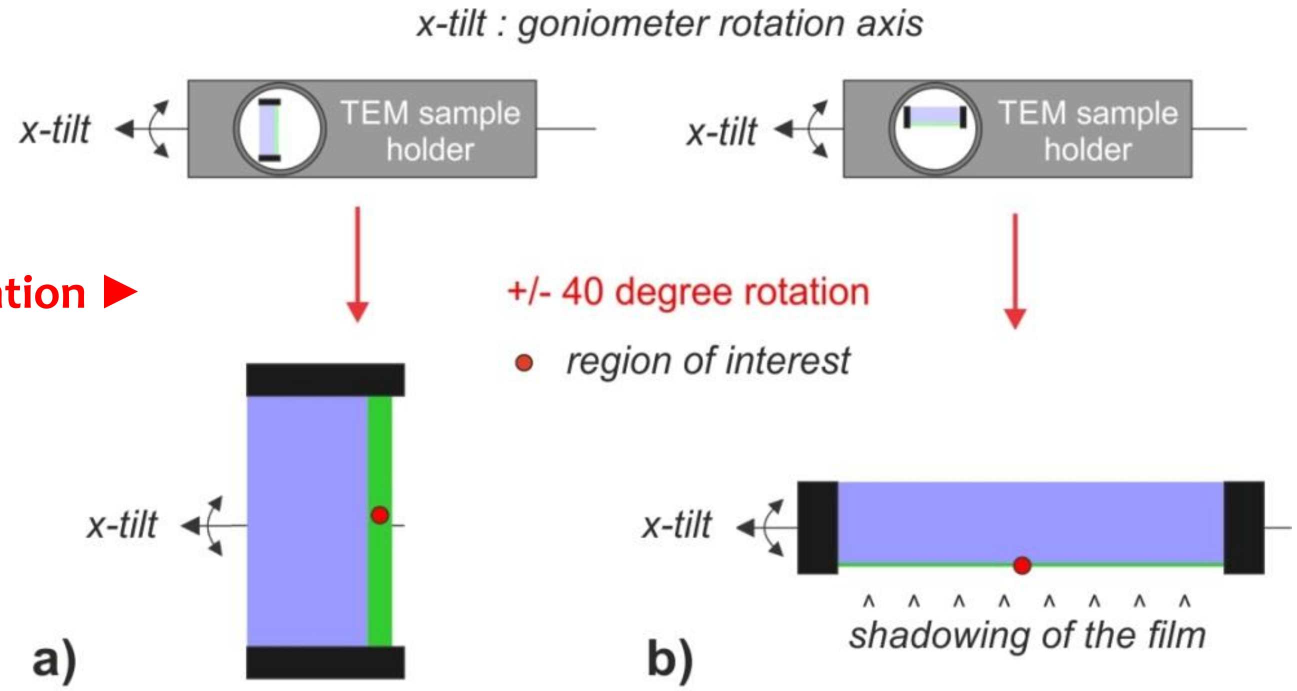


What if the nanomaterials are embedded in a matrix or grown on a substrate ?

from G. Steciuk et al., J. Appl. Cryst. (2019) 626

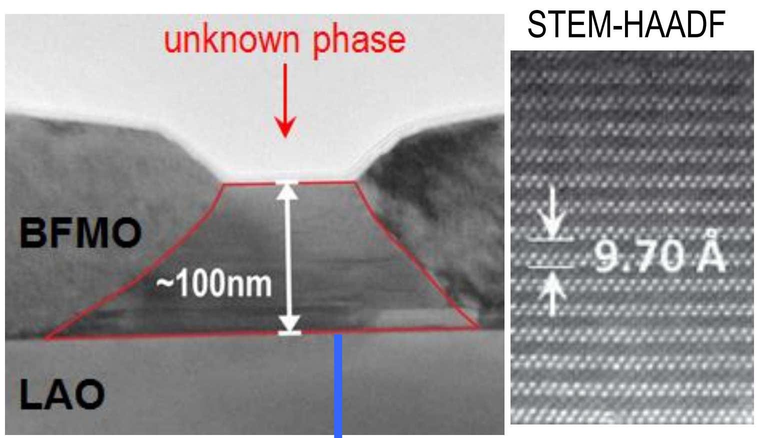


geometry limitation ►

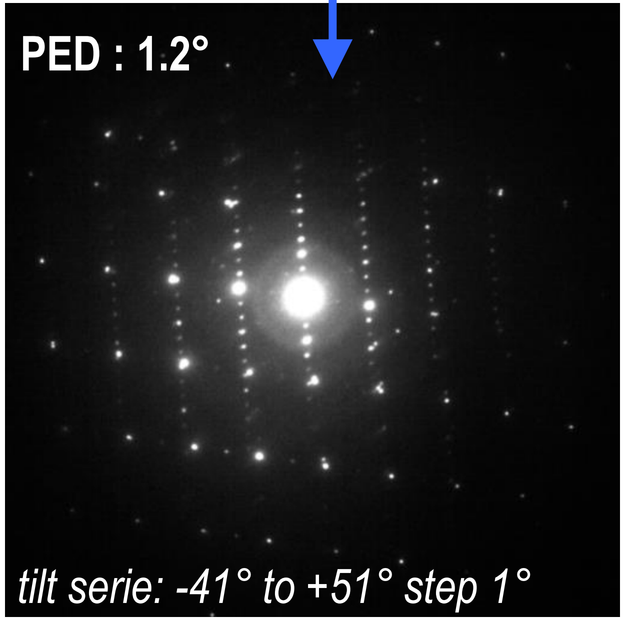


Nanomaterials ?

Solving the structure of an unknown thin film by 3D ED is usually not a problem



What if the nanomaterials are embedded in a matrix or grown on a substrate ?



Two-Dimensional Layered Oxide Structures Tailored by Self-Assembled Layer Stacking via Interfacial Strain,

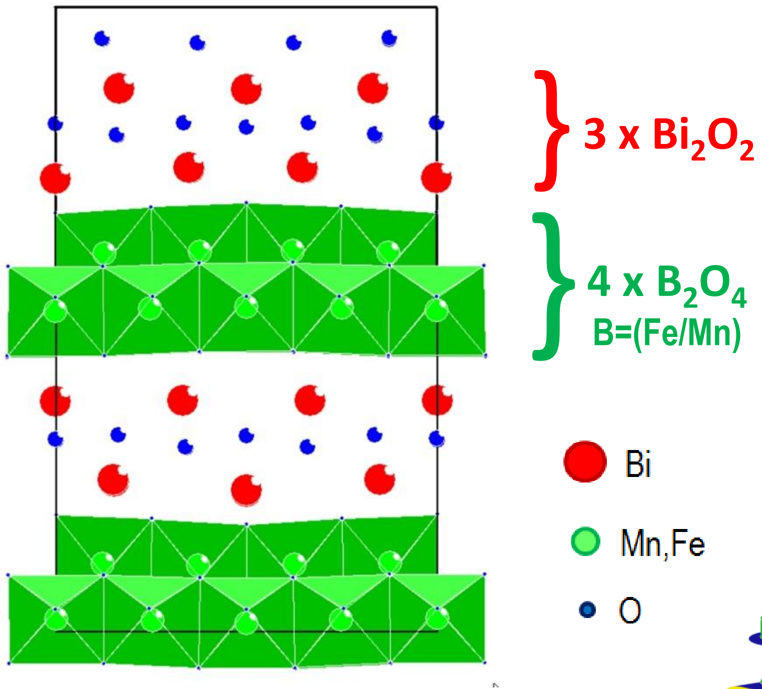
W. Zhang et al., ACS Appl. Mater. Interfaces 8 (2016) 16845

Intensity integration

Data analysis
(unit cell & symmetry)

Data reduction

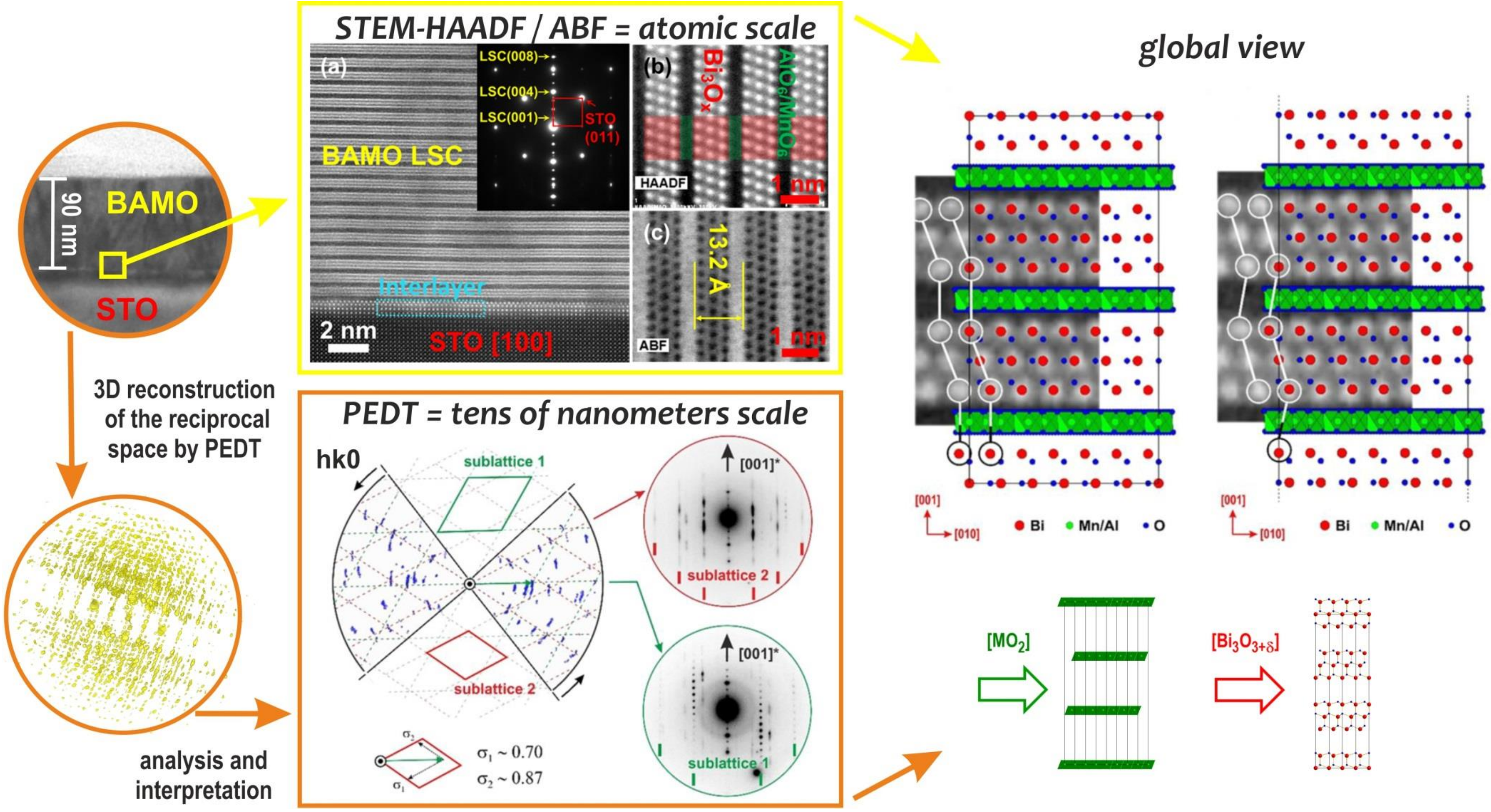
Structure solution



Amm2 (SG n°38) a=3.96Å, b=11.78Å and c=19.37Å

Nanomaterials ?

Are small crystals same as larger ones ?



Novel Layered Supercell Structure from Bi_2AlMnO_6 for Multifunctionalities,

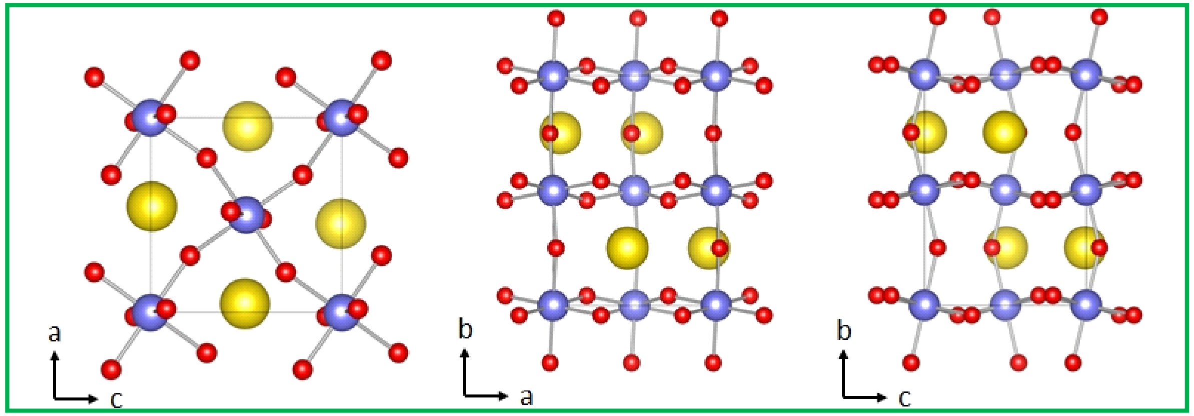
L. Li et al., Nano Lett. 17 (2017) 6575-6582 to answer this question we need accurate structure refinement

▼

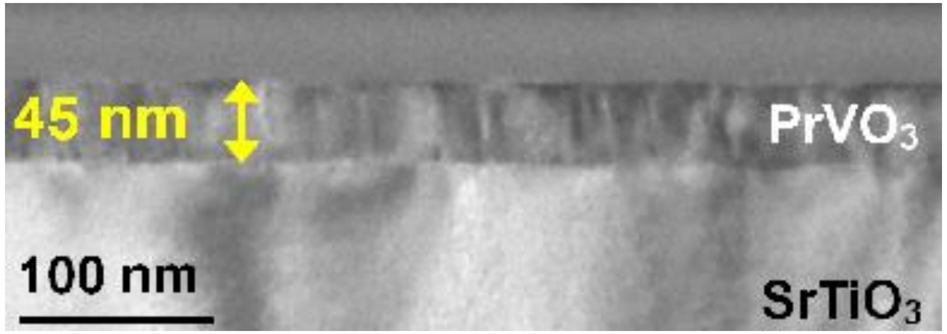
PEDT + dynamical refinements

$PrVO_3$ (PVO) thin films

PVO bulk ▶



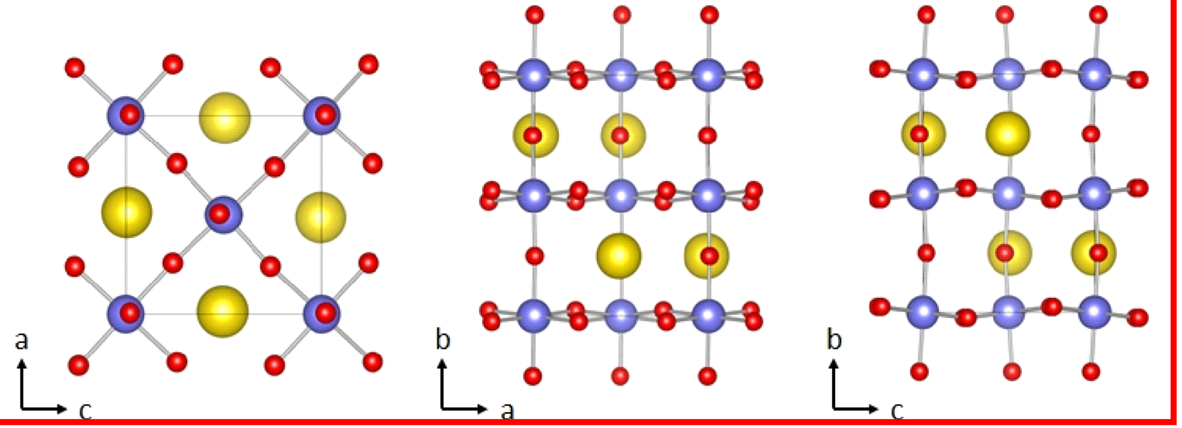
PVO film ▼



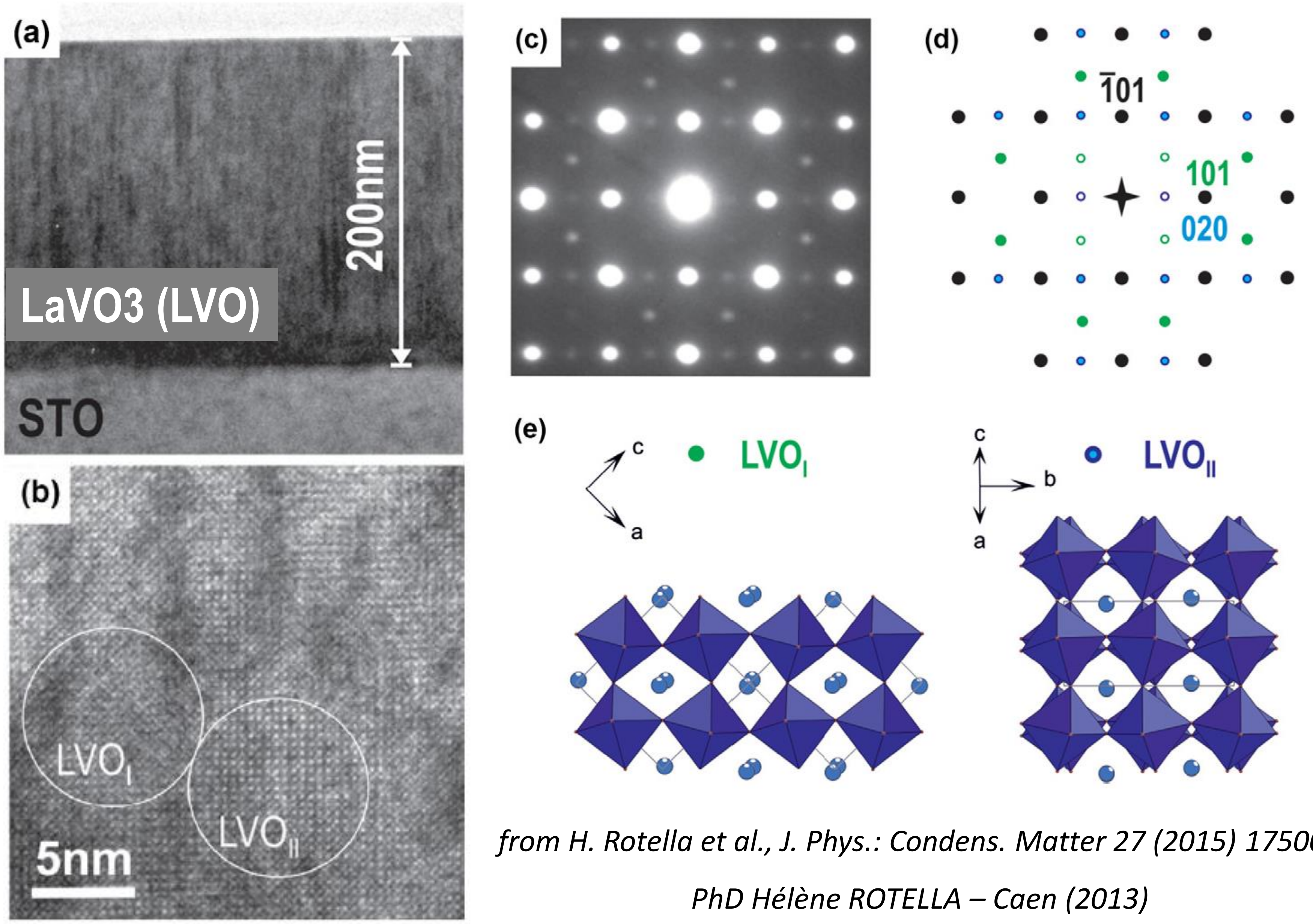
What is the problem ?

… OK : what are the problems ?

quantify octahedra tiltings in perovskite materials deposited in thin films ?



Electron diffraction for accurate structure refinement of thin films ?



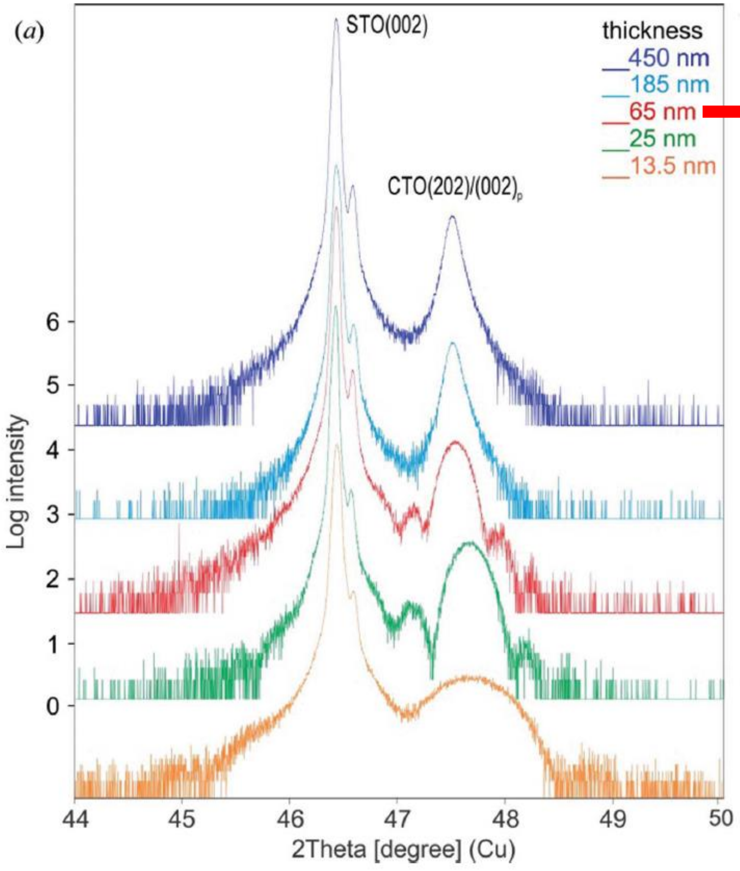
from H. Rotella et al., J. Phys.: Condens. Matter 27 (2015) 175001

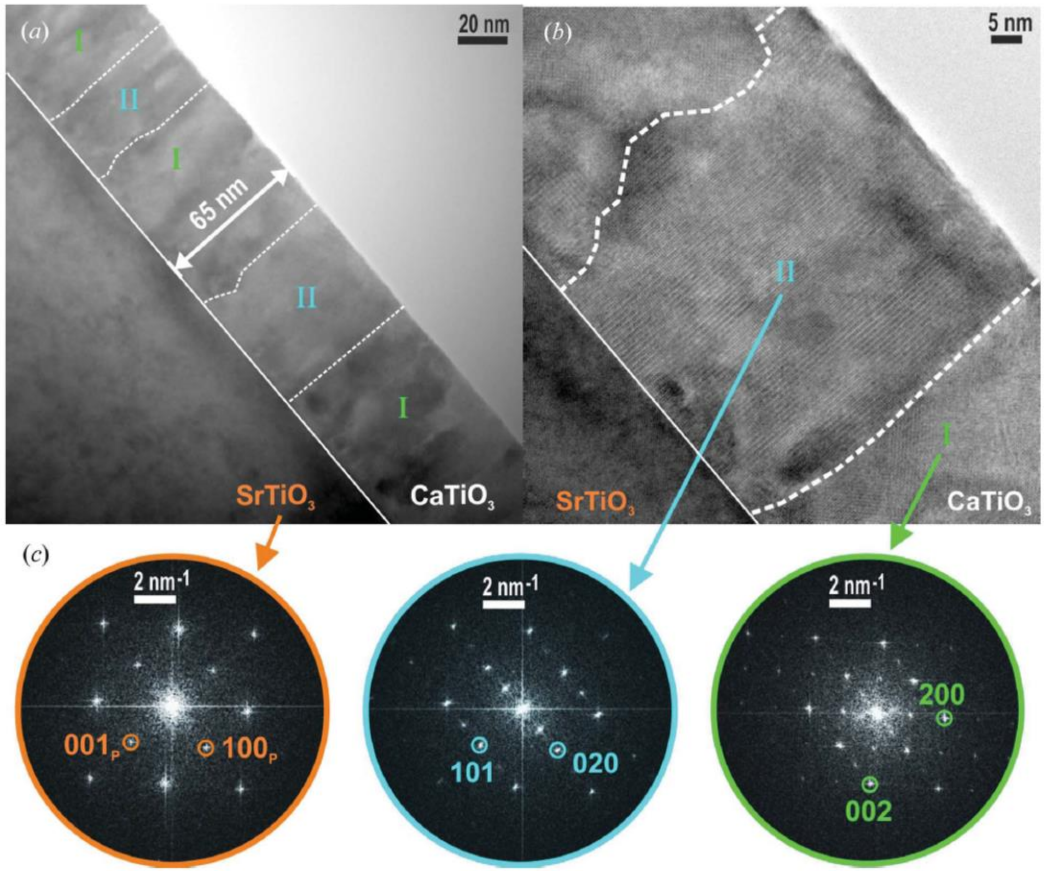
PhD Hélène ROTELLA – Caen (2013)

Electron diffraction for accurate structure refinement of thin films ?

For thin films: 3D ED data collected from twinned crystals + substrate contribution

Test case ► $CaTiO_3$ (CTO) films on STO



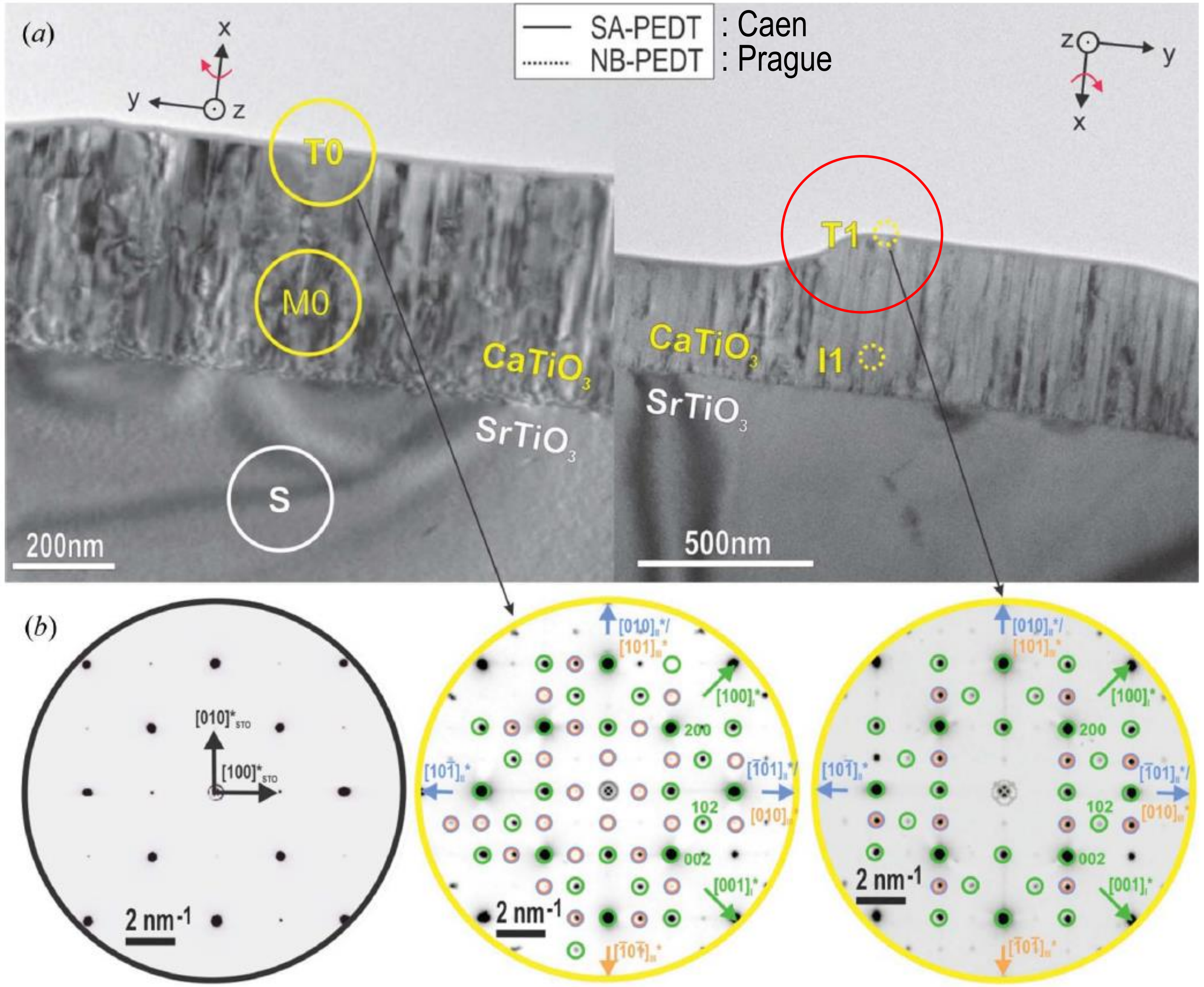


from G. Steciuk et al., J. Appl. Cryst. 52 (2019) 626

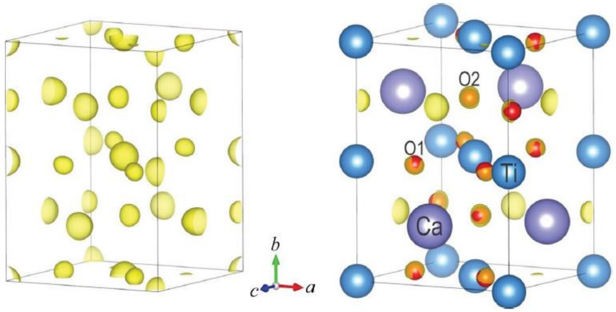
PhD Gwladys STECIUK – Caen (2016)

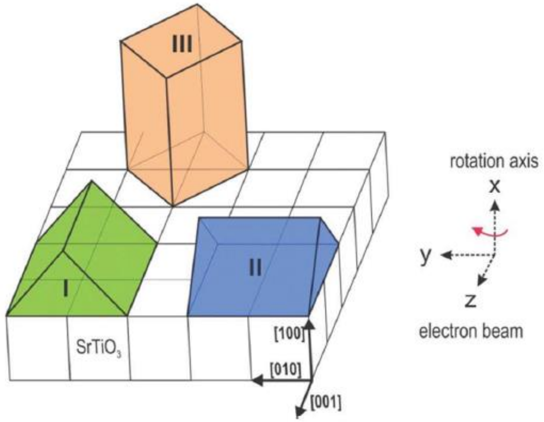
Electron diffraction for accurate structure refinement of thin films ?

► **CTO on STO : 450 nm thick film**



► **structure solution ✓**





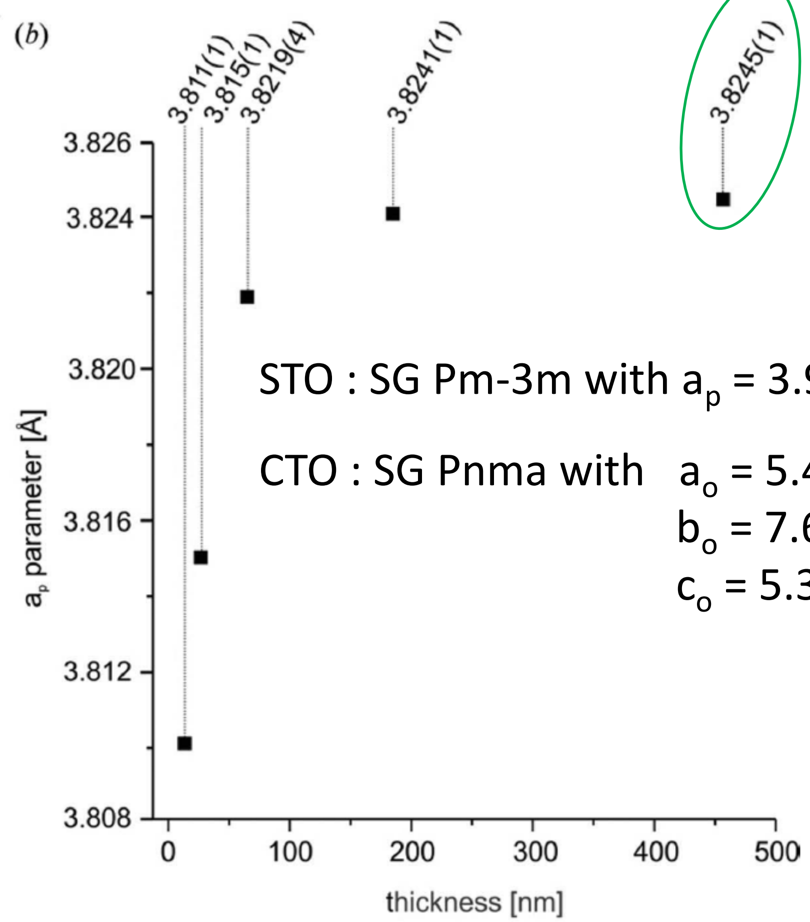
from G. Steciuk et al., J. Appl. Cryst. 52 (2019) 626

PhD Gwladys STECIUK – Caen (2016)

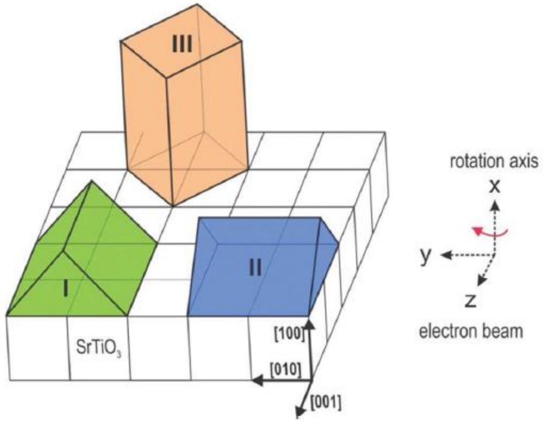
Electron diffraction for accurate structure refinement of thin films ?

► **CTO on STO : tensile strain** ► *octahedral tilting smaller than in CTO bulk*

► **CTO far from substrate** ► *strain relaxation = CTO bulk*

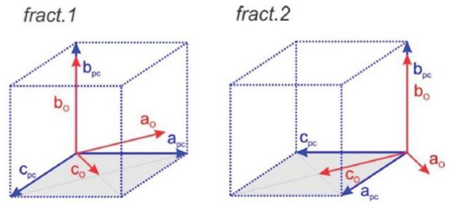


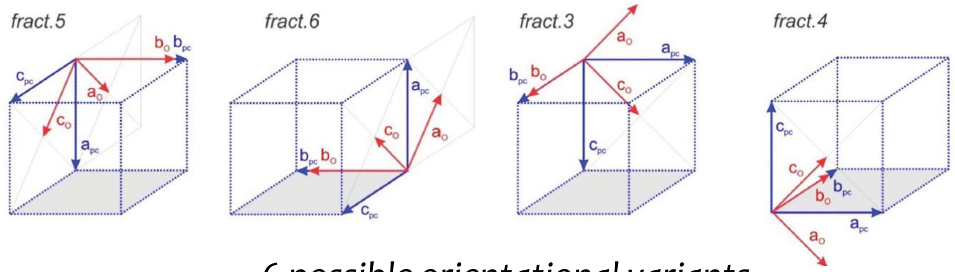
d_{010} / 2 = 3.8286
d_{101} / 2 = 3.8227



STO : SG Pm-3m with a_p = 3.905 Å

CTO : SG Pnma with a_o = 5.4458(3) Å *strain = -1.4%*
b_o = 7.6453(4) Å *strain = -2.1%*
c_o = 5.3829(3) Å *strain = -2.5%*





6 possible orientational variants

Electron diffraction for accurate structure refinement of thin films ?

► **CTO on STO : tensile strain** ► *octahedral tilting smaller than in CTO bulk*

► **CTO far from substrate** ► *strain relaxation = CTO bulk*

Data	SC-PEDT	T1	T1	T1
Structural distortions				
$\Delta d(\mathrm{Ca})_{\mathrm{XRD}}$ (Å)	0.0034 (19)	0.081 (5)	0.016 (3)	0.007 (2)
$\Delta d(\mathrm{O1})_{\mathrm{XRD}}$ (Å)	0.011 (3)	0.064 (10)	0.018 (4)	0.009 (4)
$\Delta d(\mathrm{O2})_{\mathrm{XRD}}$ (Å)	0.013 (5)	0.030 (12)	0.029 (6)	0.004 (5)
$\langle \Delta d \rangle_{\mathrm{XRD}}$ (Å)	0.009 (3)	0.058 (12)	0.021 (5)	0.007 (4)
$\langle \Delta d \rangle_{\mathrm{STO}}$ (Å)	0.329 (4)	0.360 (12)	0.328 (6)	0.335 (4)
Ti—O1—Ti (°)	156.3 (2)	153.9 (5)	155.8 (2)	155.5 (2)
Ti—O2—Ti (°)	157.4 (3)	158.2 (7)	156.8 (4)	156.4 (3)
Twin fractions				
fract. 1	1	0.56 (2)		0.585 (12)
fract. 2	–	0.34 (2)		0.350 (8)
fract. 3	–	0.01 (1)		0.020 (4)
fract. 4	–	0.01 (1)		0.007 (4)
fract. 5	–	0.00 (1)		0.017 (5)
fract. 6	–	0.07 (1)		0.021 (5)
Refinement results				
Nref.(obs/all)	1577/2526	625/1401	1458/2107	1560/4180
Nparam. all	108	13	121	126
Nparam. struct.	11	11	11	11
R(obs) (%)	13.01	23.27	15.58	13.12
wR(obs) (%)	15.48	29.33	18.10	15.04
Thickness (Å)	402 (4)		150 (3)	142 (2)

NB-PEDT

CTO powder = PEDT accuracy

CTO film : kin. with twinning

CTO film : dyn. no twinning

CTO film : dyn. with twinning

Electron diffraction for accurate structure refinement of thin films ?

▶ **CTO on STO : tensile strain** ▶ *octahedral tilting smaller than in CTO bulk*

▶ **what happens when going closer to the substrate ?**

Data	SC-PEDT	I1	I1	I1
Structural distortions				
$\Delta d(\mathrm{Ca})_{\mathrm{XRD}}$ (Å)	0.0034 (19)	0.099 (5)	0.032 (3)	0.008 (2)
$\Delta d(\mathrm{O1})_{\mathrm{XRD}}$ (Å)	0.011 (3)	0.055 (10)	0.023 (4)	0.009 (4)
$\Delta d(\mathrm{O2})_{\mathrm{XRD}}$ (Å)	0.013 (5)	0.040 (13)	0.038 (6)	0.025 (6)
$\langle\Delta d\rangle_{\mathrm{XRD}}$ (Å)	0.009 (3)	0.065 (12)	0.031 (5)	0.014 (4)
$\langle\Delta d\rangle_{\mathrm{STO}}$ (Å)	0.329 (4)	0.383 (12)	0.318 (6)	0.335 (4)
Ti—O1—Ti (°)	156.3 (2)	154.6 (5)	156.8 (2)	156.0 (2)
Ti—O2—Ti (°)	157.4 (3)	154.3 (7)	156.5 (4)	155.2 (3)
Twin fractions				
fract. 1	1	0.45 (3)		0.508 (12)
fract. 2	–	0.31 (2)		0.273 (8)
fract. 3	–	0.12 (1)		0.113 (4)
fract. 4	–	0.08 (1)		0.067 (4)
fract. 5	–	0.02 (1)		0.010 (4)
fract. 6	–	0.00 (1)		0.030 (5)
Refinement results				
Nref.(obs/all)	1577/2526	1024/1397	1773/2070	2493/4128
Nparam. all	108	13	121	126
Nparam. struct.	11	11	11	11
R(obs) (%)	13.01	26.70	15.79	13.71
wR(obs) (%)	15.48	33.17	19.69	16.94
Thickness (Å)	402 (4)		362 (5)	360 (3)

NB-PEDT

Are small crystals same as larger ones ?

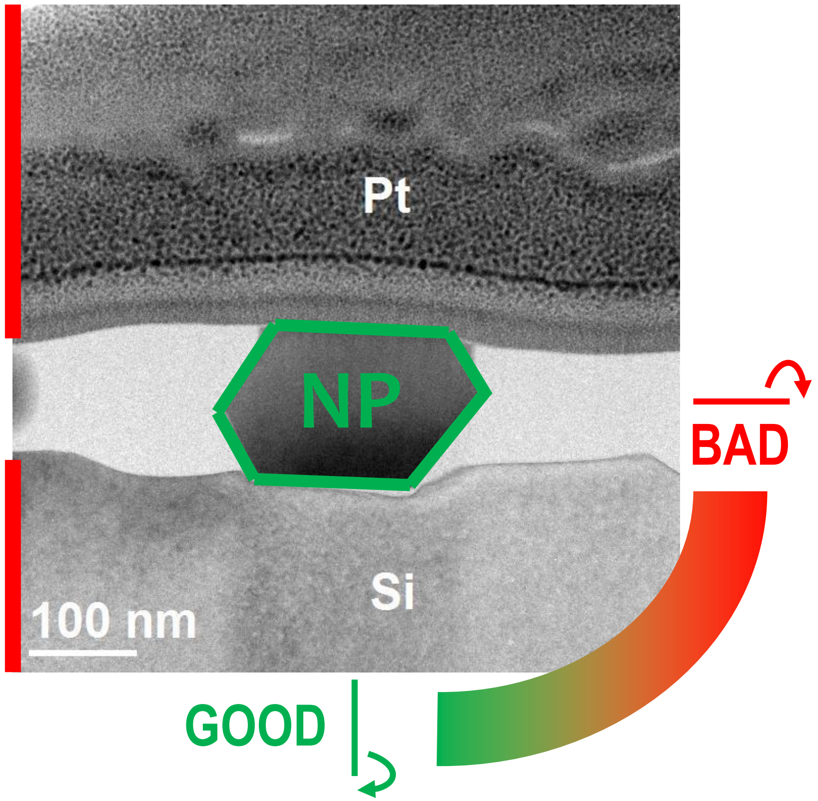
Work with small nanobeams to analyze smaller domains (for embedded) and/or get finer details in the evolution of the structure with respect to bulk (for thin films)

ESR 12 : Nanodomains in functional materials

GOALS | **link with ESR 13 @ Caen** | **link with WP1** | **ESR9 @ JGU**

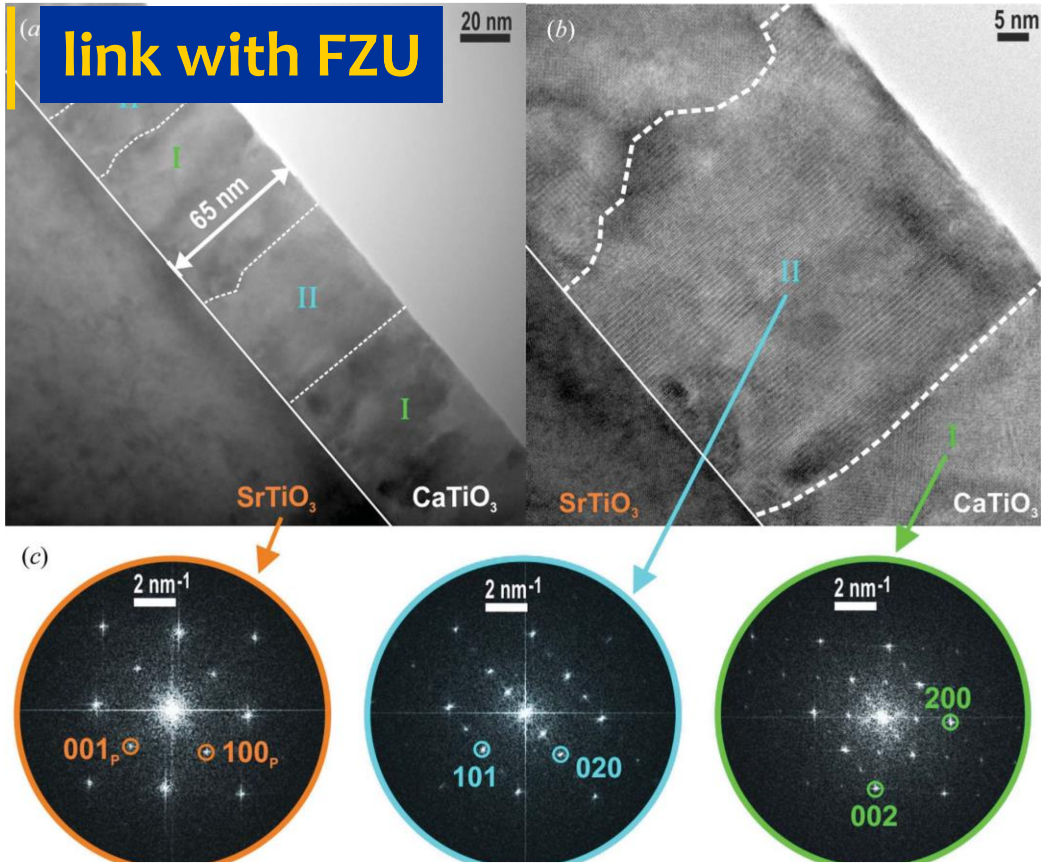
- *Determine the minimal beam and **domain** size at which it is possible to collect 3D ED data suitable for structure solutions and refinements.*

From C. Leroux, PhD @CRISMAT (D. Pelloquin)



From G. Steciuck et al., J. Appl. Cryst. (2019) 52, 626–636

link with FZU



ESR 12 : Nanodomains in functional materials

GOALS

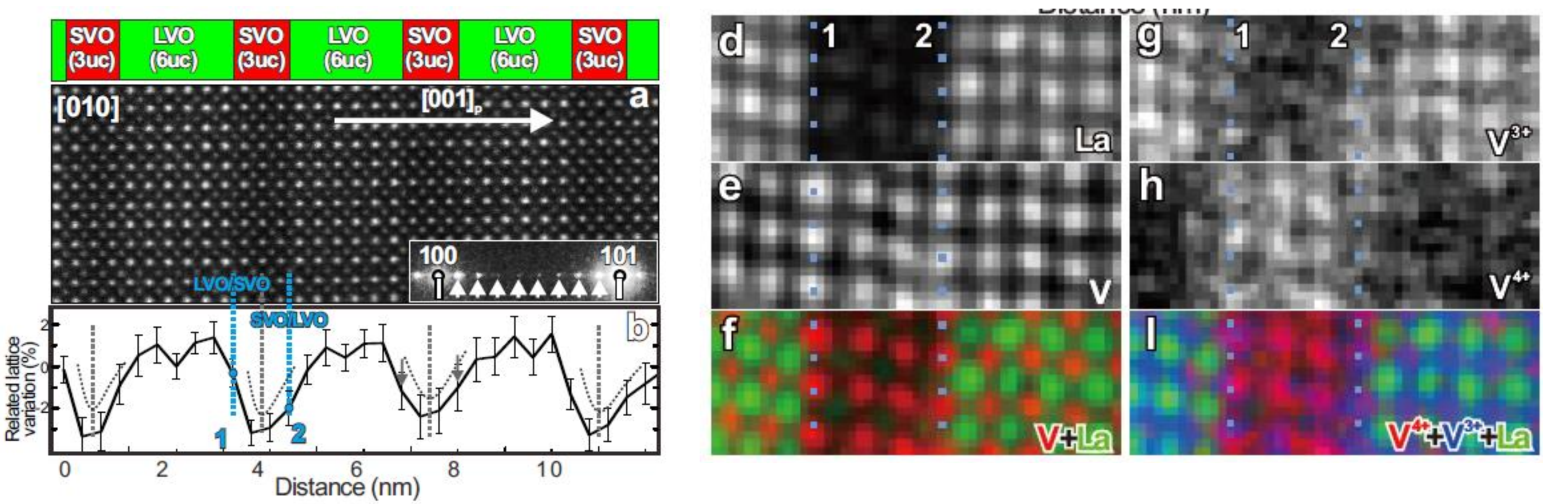
⇨ Preparation of ceramics with submicronic grains using micro-wave and SPS sintering.

⇨ **Preparation of thin films and heterostuctures of transition metals oxides using pulsed laser deposition.** *On going project with Joke (UA).*

@ CNRS

- Compare structure obtained from 3D ED with atomic-scale structures obtained from electron microscopy images (HRTEM and/or STEM-HAADF).

link with UA



From former collaboration with EMAT @ Antwerp

What can we do with 3D ED ?

ESR 12 : Nanodomains in functional materials

GOALS

- **Development of a dedicated protocol for sample preparation**

⇨ to investigate submicronic grains in dense ceramics.

⇨ based on FIB technology to optimize 3D ED data collection on thin films.

link with TSC or other ?

- **Application of the protocols to functional materials**

links here

Electron Crystallography of nanodomains in functional materials

Combining EM techniques to analyze the needle in the haystack

Sara PASSUTI | MSc in Materials and Nanotechnology – Universita di Pisa

Planned secondments:

FZU: L. Palatinus (dynamical refinement, M24-25)

JGU: U. Kolb (3D ED on defective materials, M26-28)

TSC: D. van der Wal (FIB sample preparation, M32)

3D ED on Nanomaterials

Philippe BOULLAY - Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, Caen, France

Questions