INSTITUT JEAN LAMOUR

www.ijl.univ-lorraine.fr

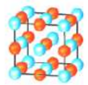
CNRS — UNIVERSITÉ DE LORRAINE

Ozone-MBE for the ultimate growth/design of layered oxide systems

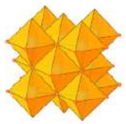
Karine Dumesnil

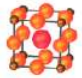
https://spin.ijl.cnrs.fr/

Rich playground of oxides

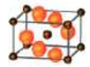


EuO

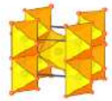


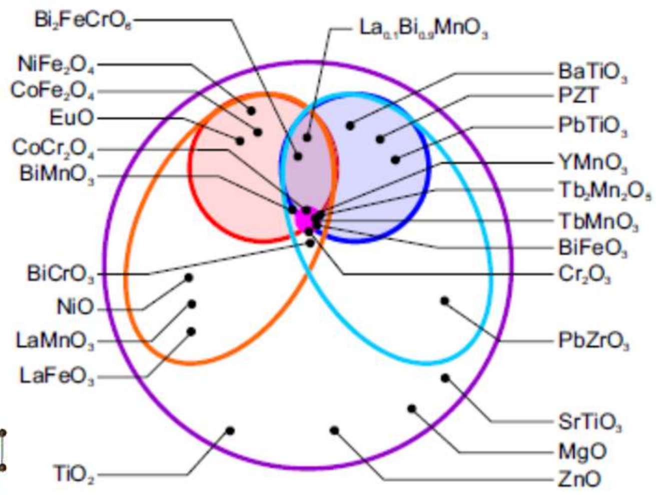


$SrTiO_3$



CrO_2





Magnetic — $(La,Ca,Sr)MnO_3$, NiO

Ferromagnetic — EuO

Piezoelectric — $LiTaO_3$

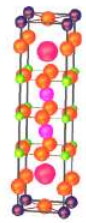
Paraelectric — $PbZrO_3$, $SrTiO_3$

Ferroelectric — $BaTiO_3$, $PbTiO_3$, $LiNbO_3$

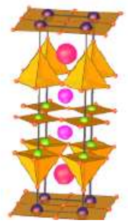
Multiferroic — $BiMnO_3$, $La_xBi_{1-x}MnO_3$...

Magnetoelectric — $BiFeO_3$, $REMnO_3$, Cr_2O_3

High T_c superconductor — $(La,Sr)_2CuO_4$, $YBa_2Cu_3O_7$, $NdBa_2Cu_3O_7$, $SmBa_2Cu_3O_7$

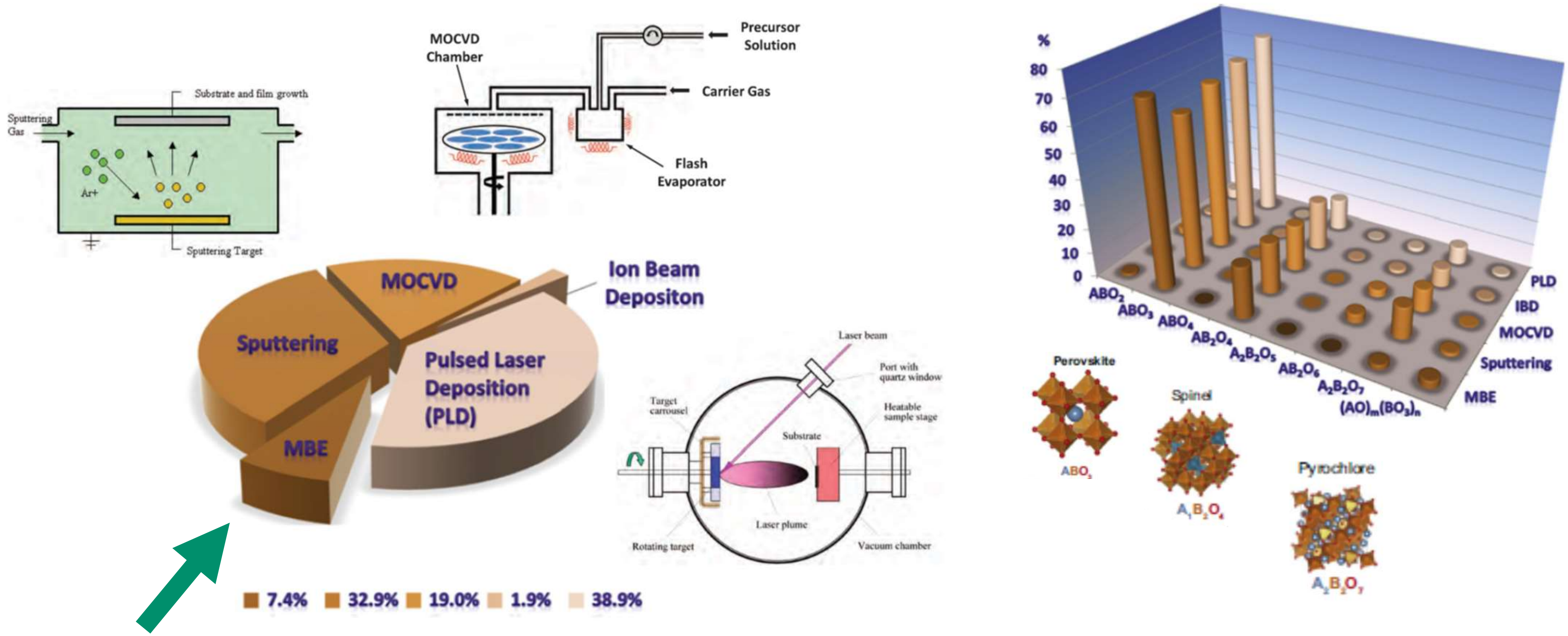


$HgBa_2Ca_2Cu_3O_{8+x}$



\+ strains
low dimension
interfaces

Growth of oxide thin films



R. Engel-Herbert
Molecular Bean Epitaxy: from research to mass production, Elsevier (2013)

Outline

- The choice of MBE
- Specificities related to oxide-MBE
    - Oxidizing gas
    - Stœchiometry / RHEED
- Examples of ALL-MBE grown oxide systems
- The ozone-MBE system @IJL
- Towards multiferroicity in RE Vanadates superlattices

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The choice of MBE

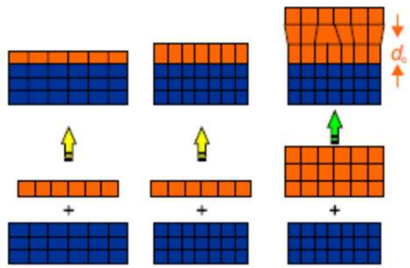
Well defined atomic/molecular beams (evaporation/sublimation)
Interaction with a cristalline surface to build an epitaxial film

Base pressure in 10^{-11} Torr range

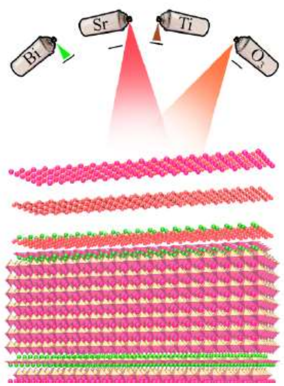
Mean free path ≈ characteristic distances

$$\lambda = \frac{k_B T}{\sqrt{2}\pi P D^2}$$

➡ Clean environment
No highly energetic species (thermal energy)
In-situ control of atomic arrangement (RHEED)



Growth of metastable phases/orders (strain, interface energy)



Ultimate control of the stacking (low rates, shutters)
Atomic Layer by Layer (ALL) deposition, digital doping

Specificities related to oxide growth

Oxidizing gas

- Specific pumping

  Compatibility with materials (cells, sample holders, filament…) ~~Mo~~ ~~PBN~~

  Stability of sources (distance, differential pumping, collimator, reductor…)

Thermodynamic of oxide growth

- Low mobility high deposition temperature to achieve crystal quality

- Low vapour pressure (except Bi, Pb)

  no adsorption controlled growth

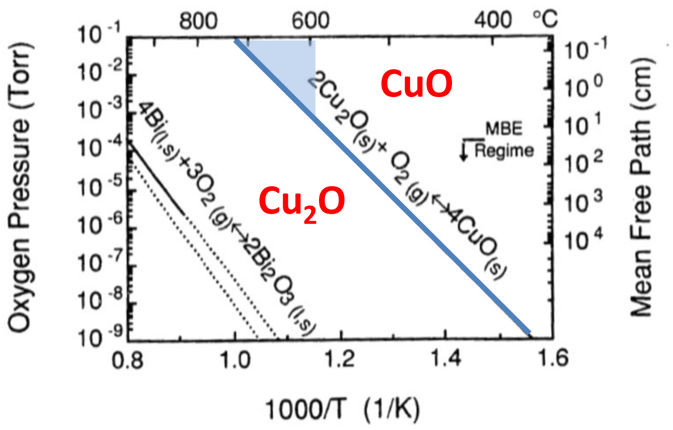
  more strict conditions (stoechioemetry, stability)

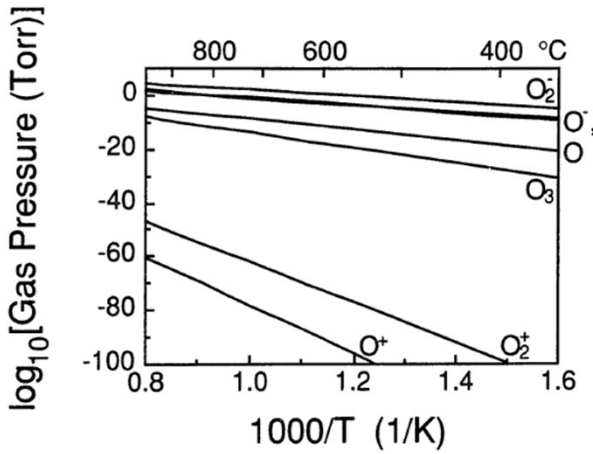
Choice of the oxidizing gas

Efficient oxidation
High pressure
Low temperature

Large mean free path/mobility
Low pressure
High temperature

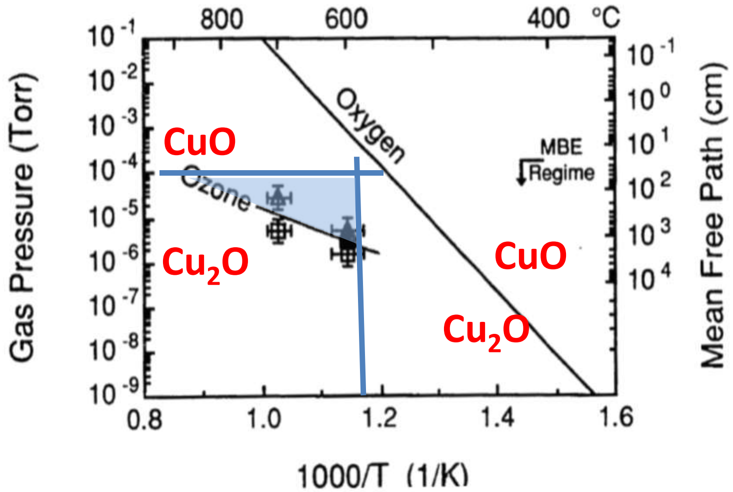
O_2





O species

O_2/O_3



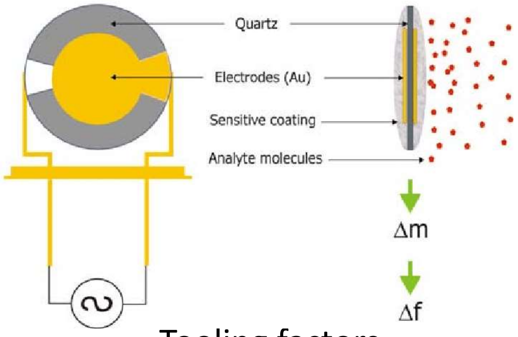
λ few 10's of cm
Deposition T > 600°C

Ozone

D.G. Schlom, PhD (1990)

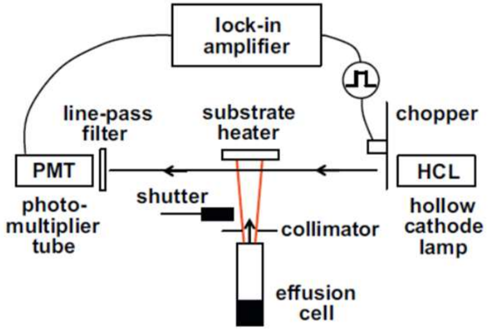
Deposition rates/ stoechiometry

Quartz Microbalance



Tooling factors
Pre-calibration

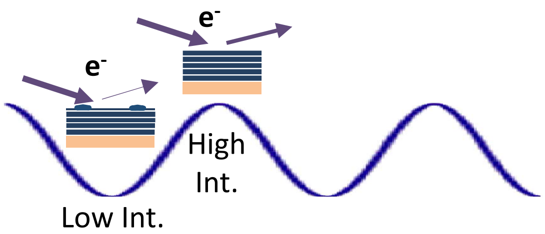
Atomic Absorption



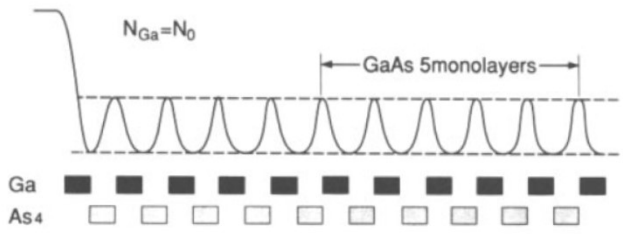
Accuracy better than 1%
Calibration via QCM
Feedback during deposition

RHEED oscillations

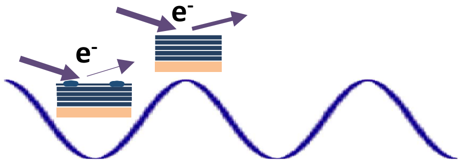
co-deposition

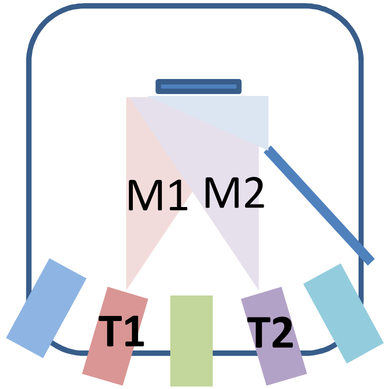


Shuttered/ALL deposition



RHEED oscillations - codeposition



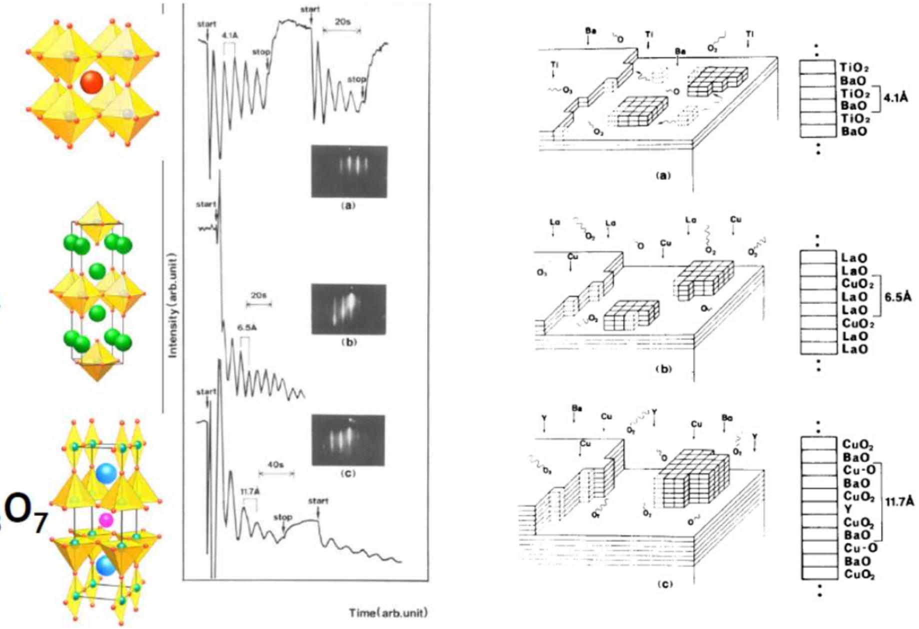


Adjust metal fluxes **(T1/T2)**
Relative calibration

$BaTiO_3$

La_2CuO_4

$YBa_2Cu_3O_7$

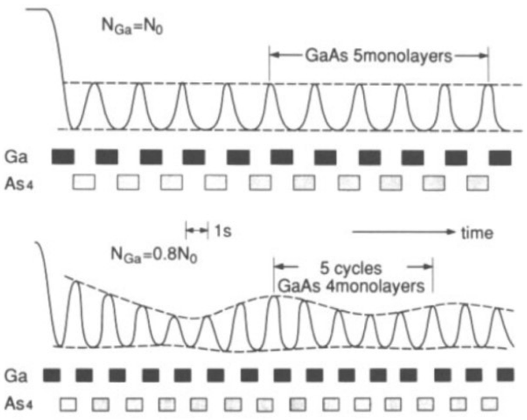


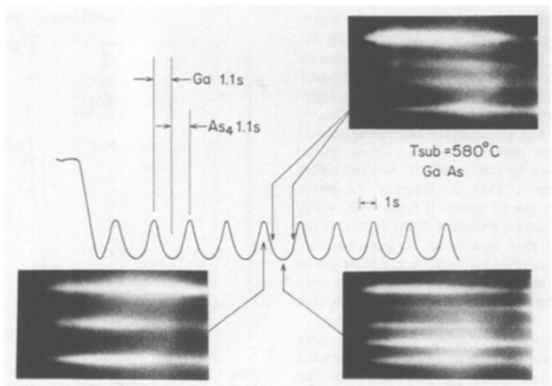
Minimum unit to satisfy: chemical composition
electric neutrality

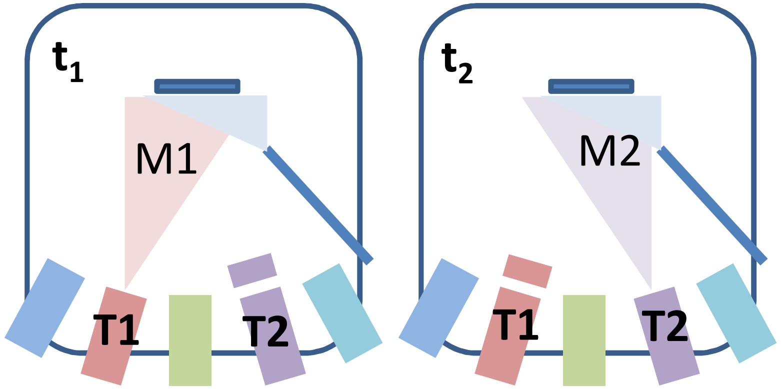
T. Terashima et al., Phys. Rev. Lett. (1990)

RHEED oscillations – shuttered deposition

MEE for GaAs







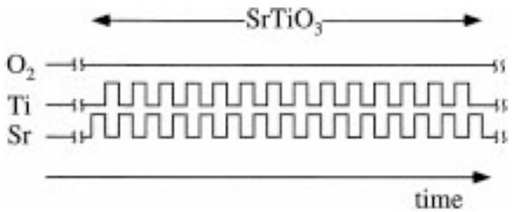
Adjust metal fluxes **(T1 and T2)**
Adjust atomic doses **(t_1 and t_2)**
Absolute calibration

Determination of doses
Increased interface quality
Reduced growth temperature

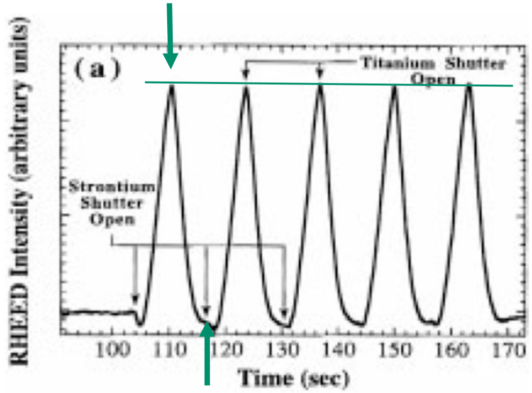
Y. Horikoshi et al., Jap. J. of Appl. Phys. (1988)
Y. Horikoshi et al., Semicond. Sci. Technol. 8, 1032 (1993)

RHEED oscillations – shuttered deposition / ALL for $SrTiO_3$

Flux ratio Sr:Ti

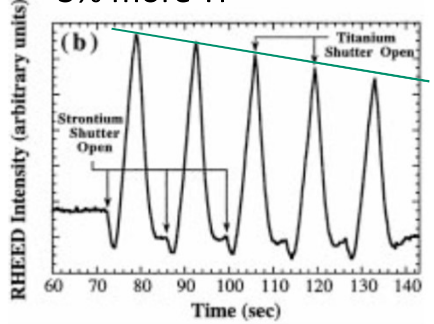


SrO

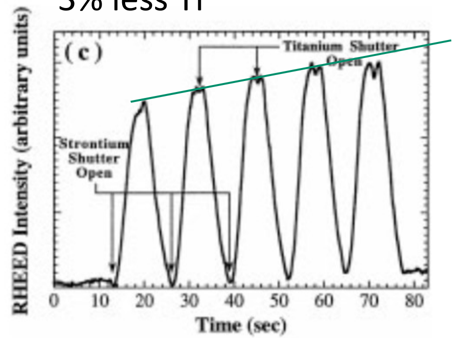


TiO_2

3% more Ti

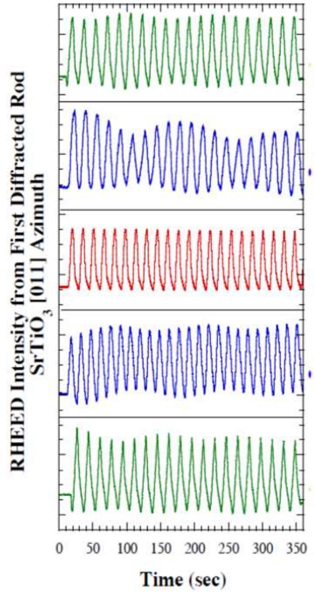


3% less Ti



Incomplete ML doses

Sr:Ti = 1



1.15 ML

1.10 ML

1 ML

0.9 ML

0.85 ML

J.H. Haeni et al., Journal of Electroceramics (2000)

J. Feng et al., AIP Advances (2012)

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  Oxidizing gas

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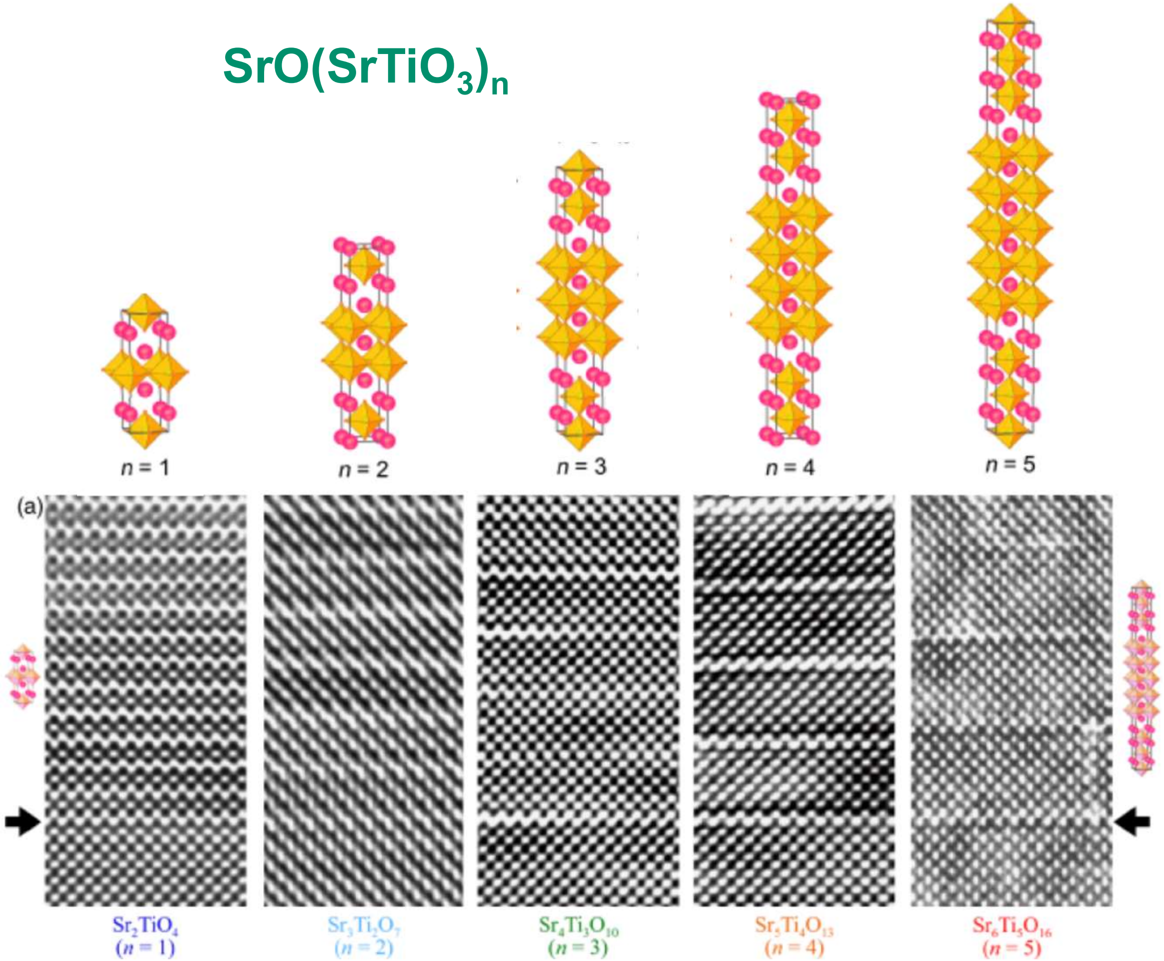
- **Examples of ALL-MBE grown oxide systems**

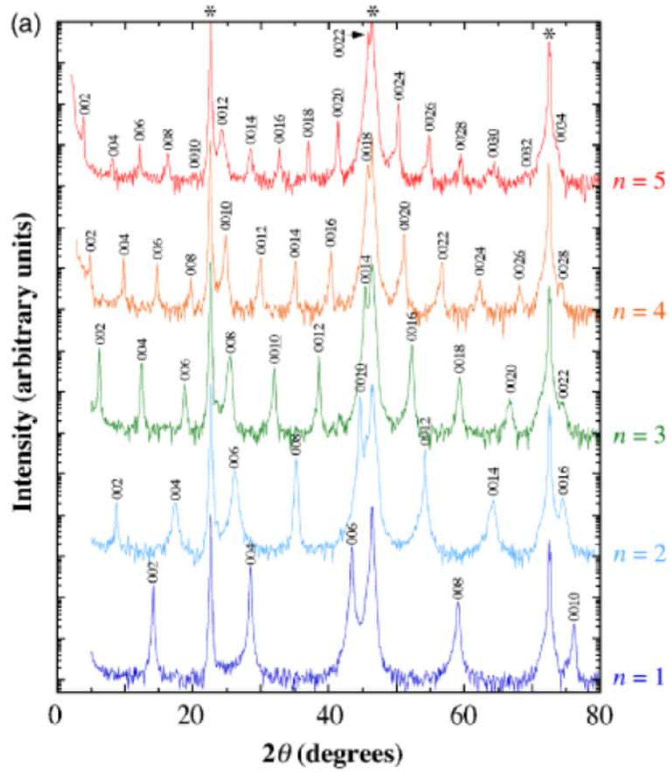
- The ozone-MBE system @IJL

- Our work on RE vanadates films and superlattices

Stabilisation of the Ruddlesden-Popper serie – $Sr_{n+1}Ti_nO_{3n+1}$

$SrO(SrTiO_3)_n$

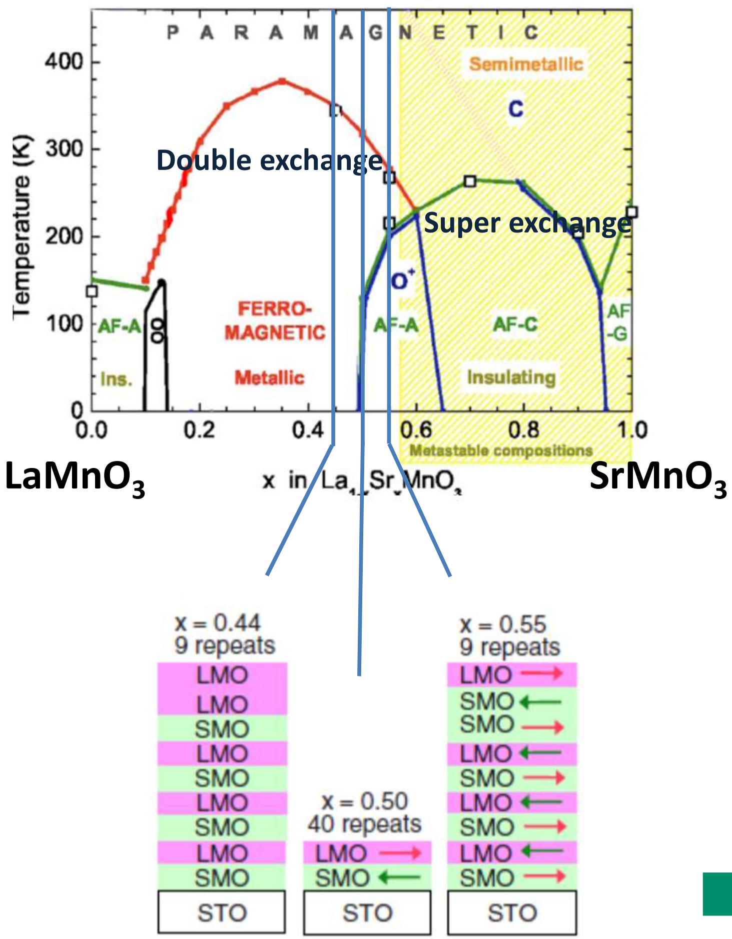




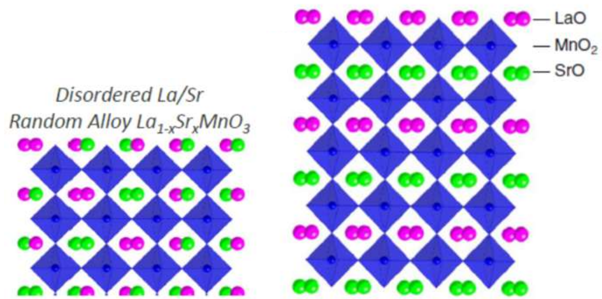
➡ Synthesis up to n=5, incl. metastable phases

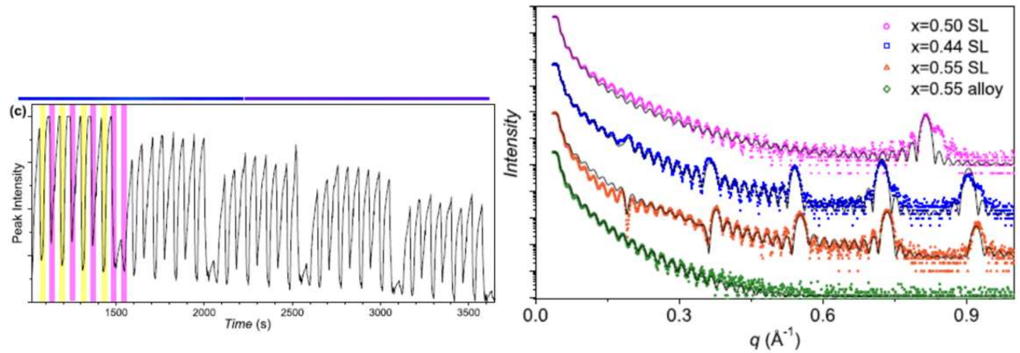
J. H Haeni et al. Appl. Phys. Lett. (2001)

FM → AFM in manganites - $La_{1-x}Sr_xMnO_3$



disordered / ordered

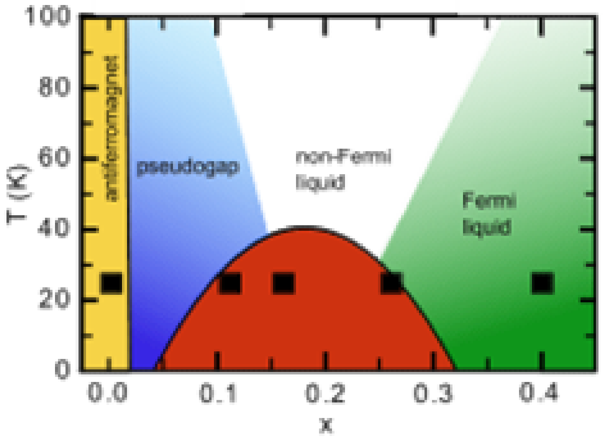


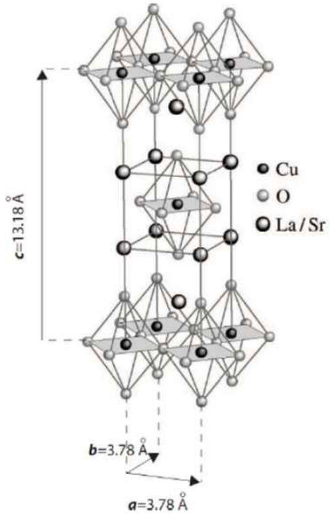


Stabilisation of the AFM metallic phase (x=0.55)
Effect of strains : suppression of the FM phase
Effect of La/Sr order on transport properties

T.S Santos et al., Phys. Rev. B (2009)

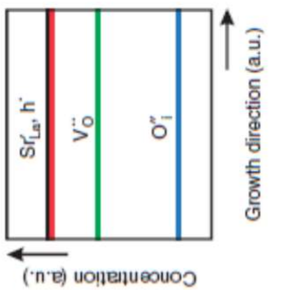
Interface superconductivity by 2D doping – $La_{2-x}Sr_xCuO_4$



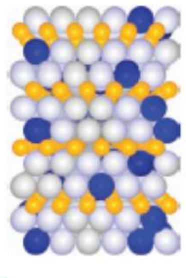


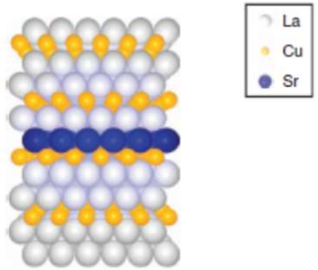
La_2CuO_4 → $La_{2-x}Sr_xCuO_4$
doping

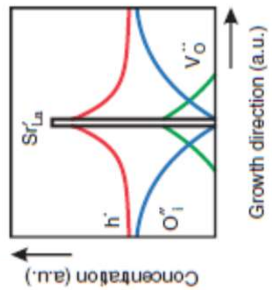
homogeneous / *heterogeneous*



holes vacancies interstitial

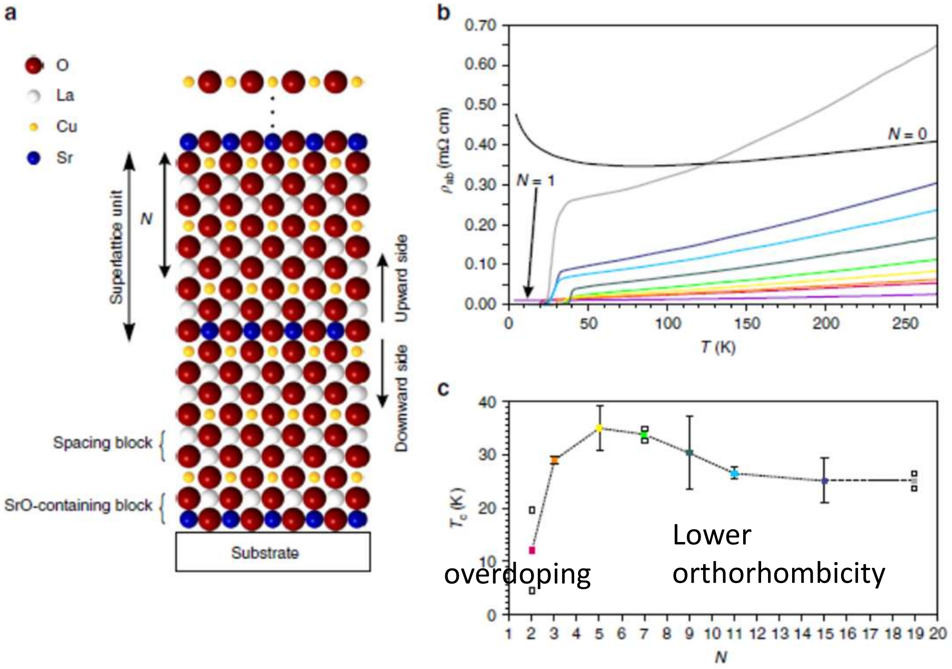


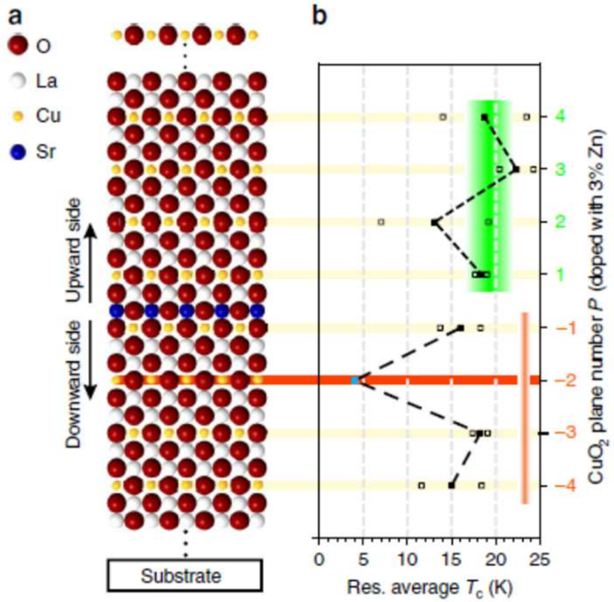




2D layer of confined charges
Sharp accumulation of mobile defects

Interface superconductivity – $La_{2-x}Sr_xCuO_4$





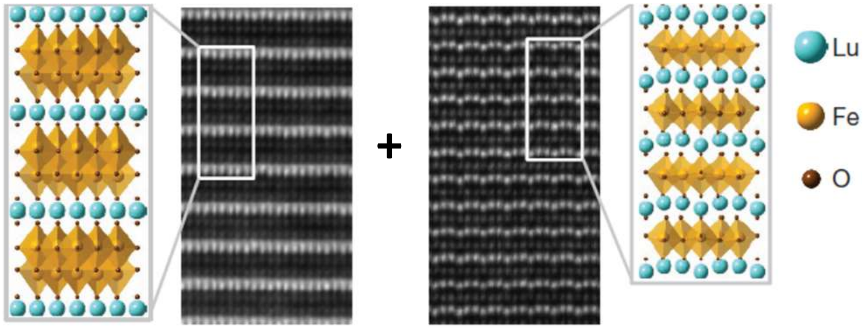
Confined superconductivity (2D), in the proximity of each SrO layer
Tuning of number, position, relative distance … of active layers

Layer-dependent superconductivity
Determination of CuO_2 active planes (Zn doping tomography)

G. Logvenov, Science 326, 699 (2009)
F. Baiutti et al., Nature Communications (2015)

Multiferroicity by design

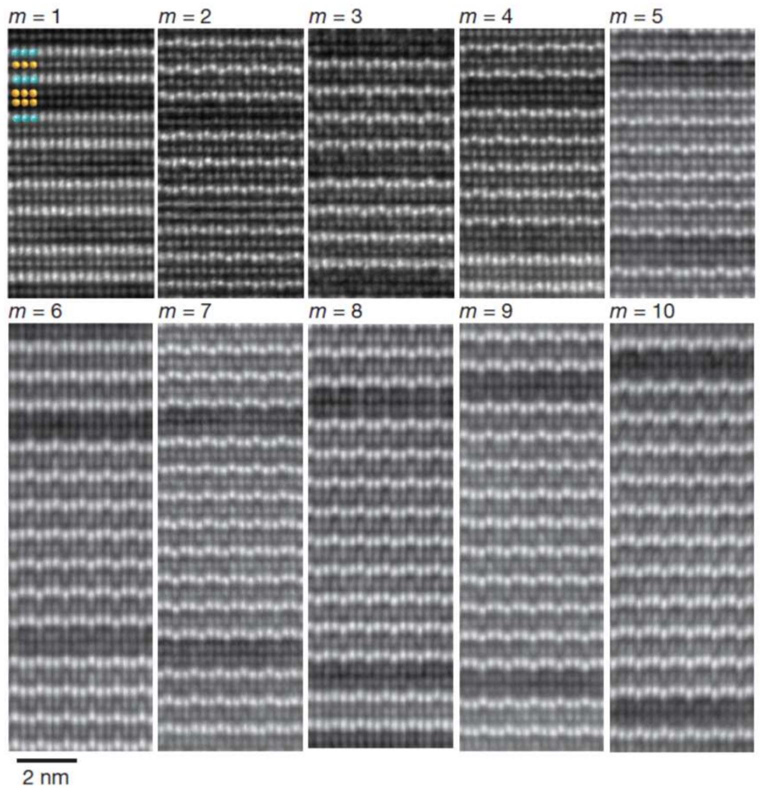
$LuFe_2O_4$ + **$LuFeO_3$**

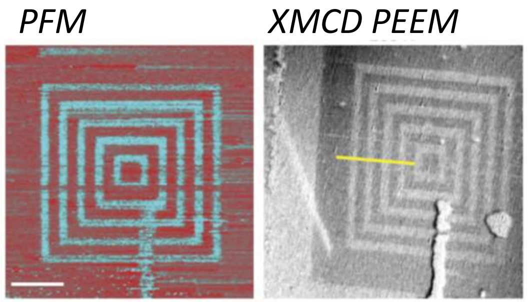


Ferrimagnetic
T<240K

Ferroelectric
AFM T<147K

$(LuFe_2O_4)_1/(LuFeO_3)_m$





➡ Magnetic order up to 281K (1/9)
Ferroelectric up to > 700K
+ magnetoelectric coupling @200K

J.A. Mundy et al., Nature (2016)

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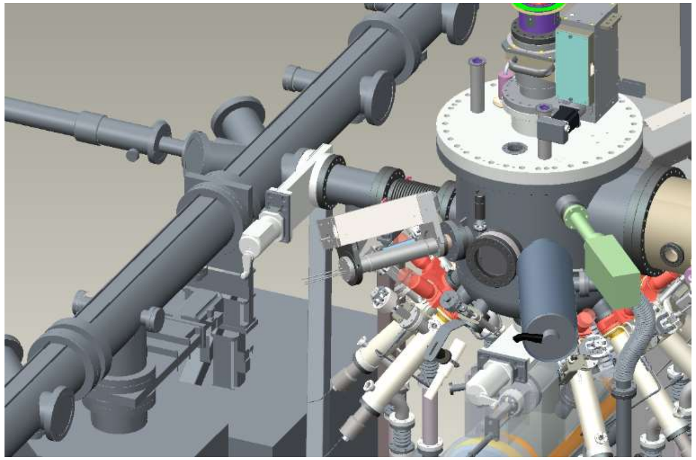
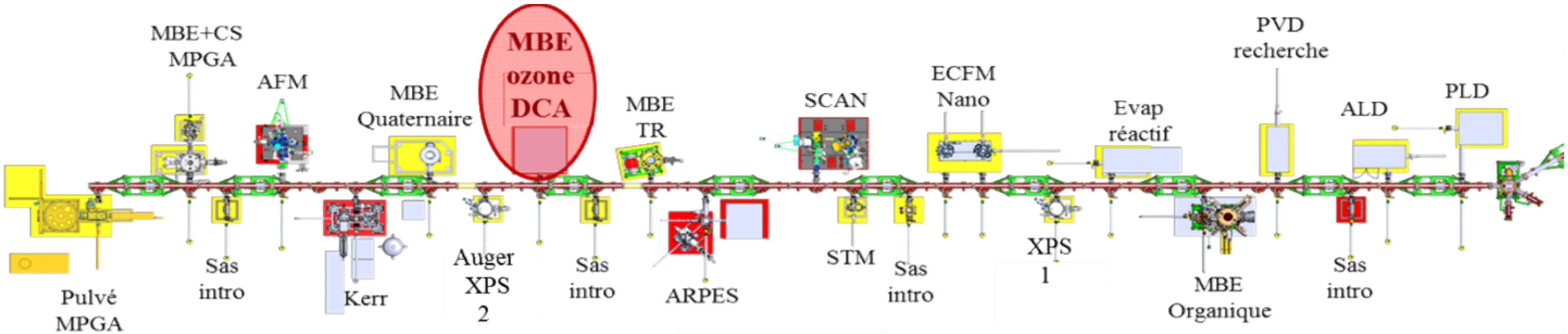
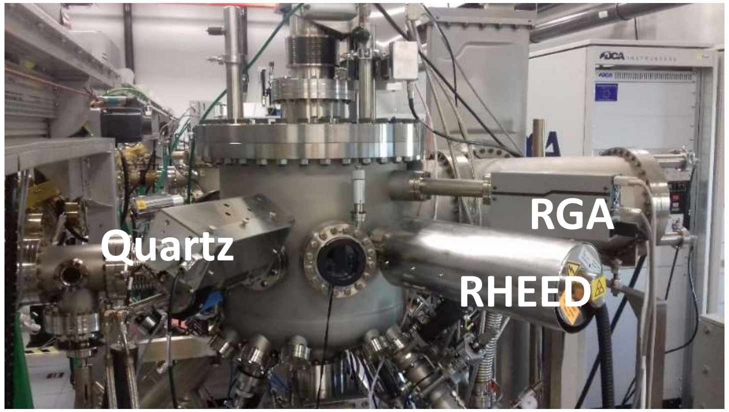
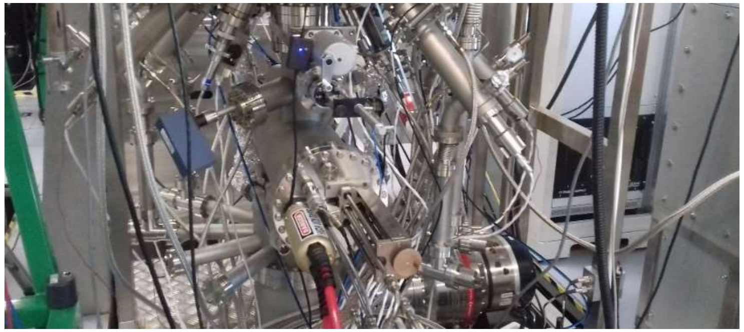
Ozone-MBE instrument @ IJL



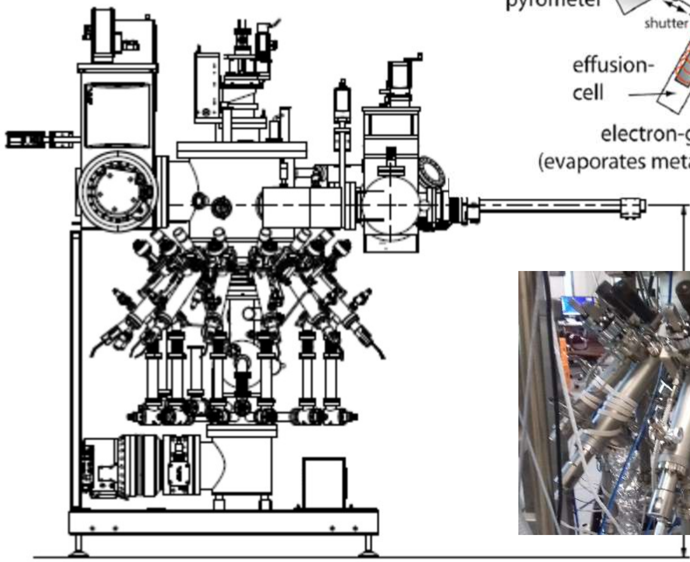


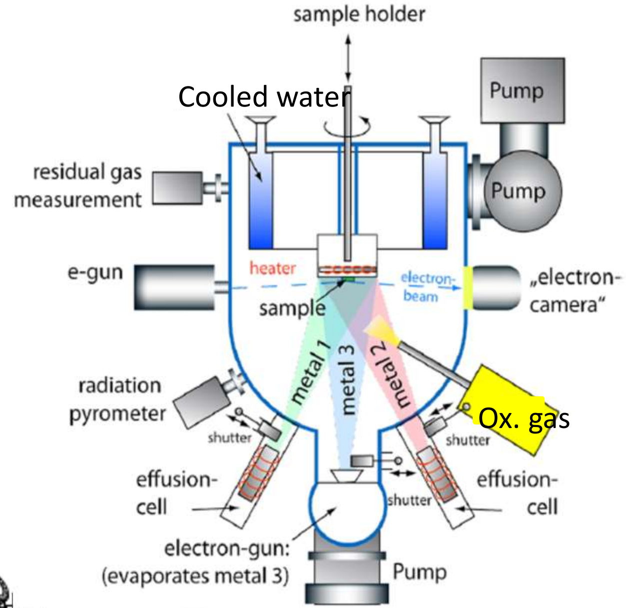
Ozone-MBE instrument @ IJL





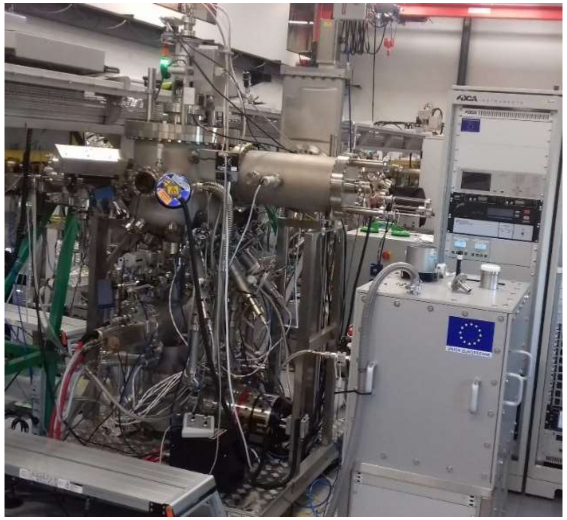
Four pockets e-gun

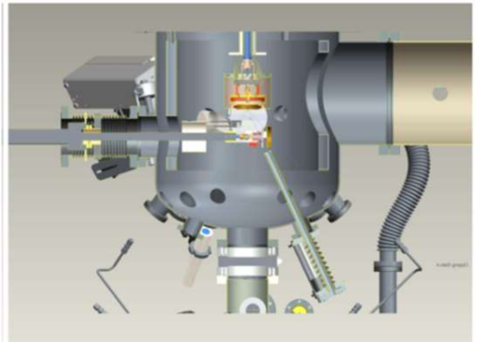


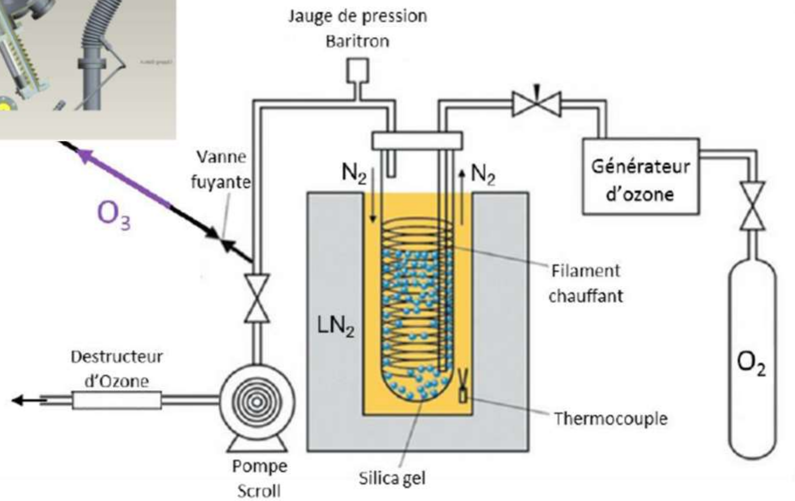


8 effusion cells (SF, DF, HT…)
Isolation valves
Collimators
Differential pumping

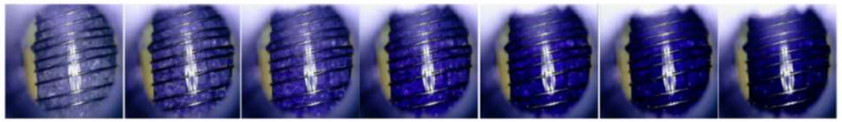
Ozone Delivery system







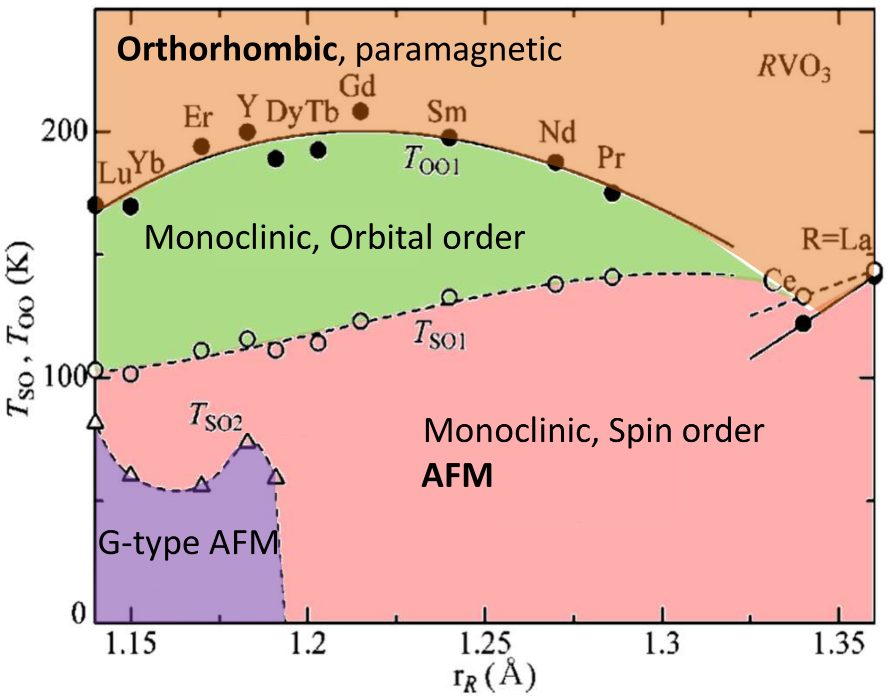
- Ozone generation from O_2
- Distillation (LN_2)
- Storage in silica gel
- Injection into the growth chamber
- Regulation by pressure/valve control

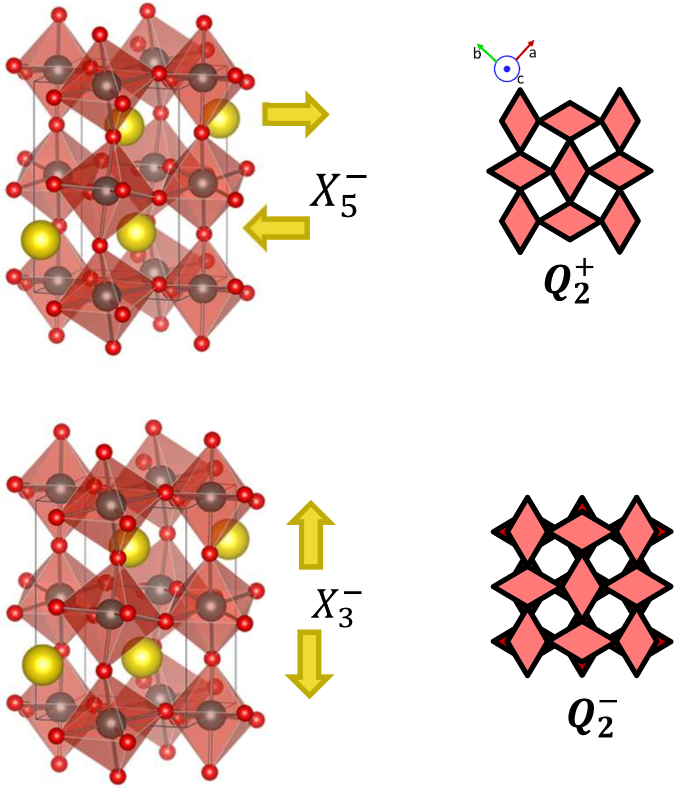


- O_3/O_2 at the sample ?

D.G. Schlom, PhD (1990)

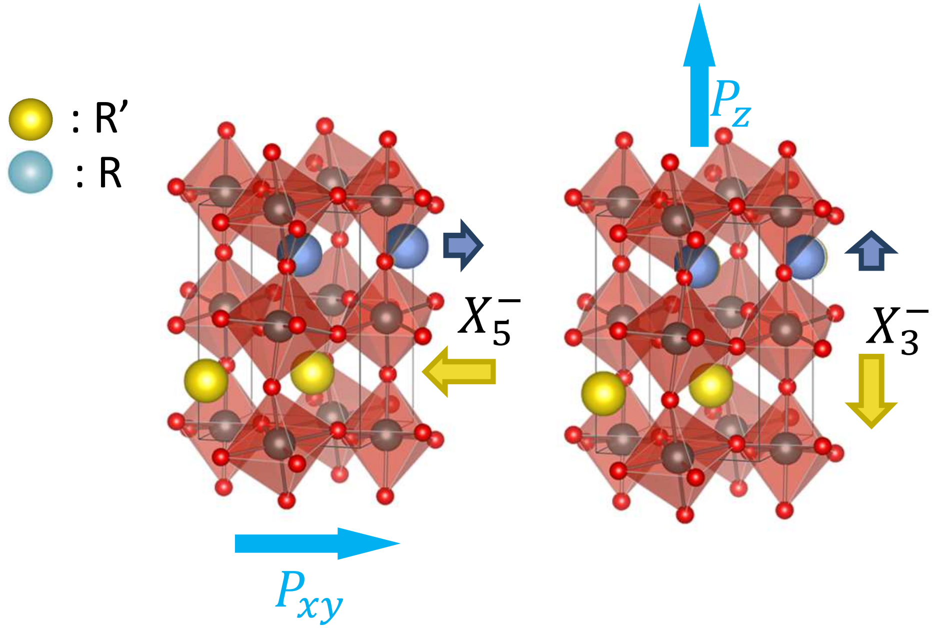
Rare Earth Vanadates





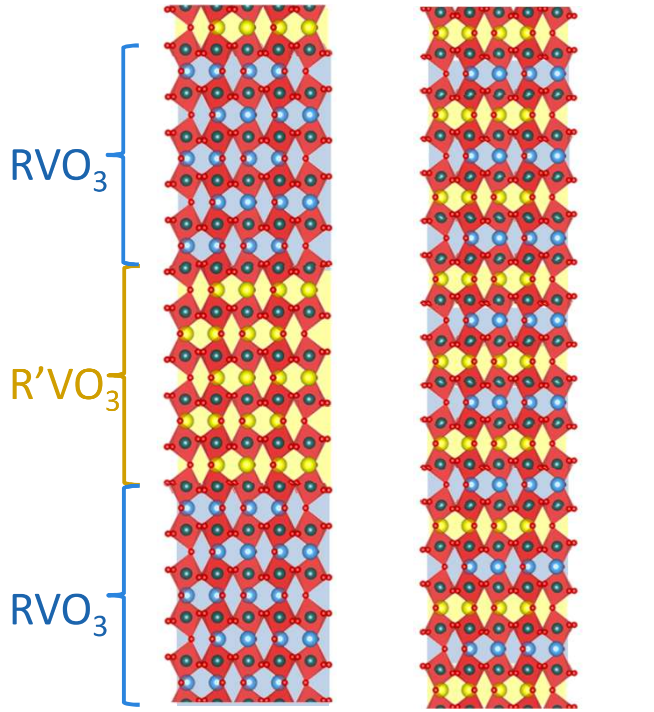
Oxygen octahedra rotation
Cations displacements
Jahn-Teller distortion

Multiferroicity by design in $REVO_3$ superlattices



$$\mathcal{F}_{R/R'} \propto \phi_{xy}^- \phi_z^+ P_{xy} + \phi_{xy}^- P_{xy} Q_2^+ + Q_2^+ Q_2^- P_z + \phi_z^+ P_z \phi_z^-$$

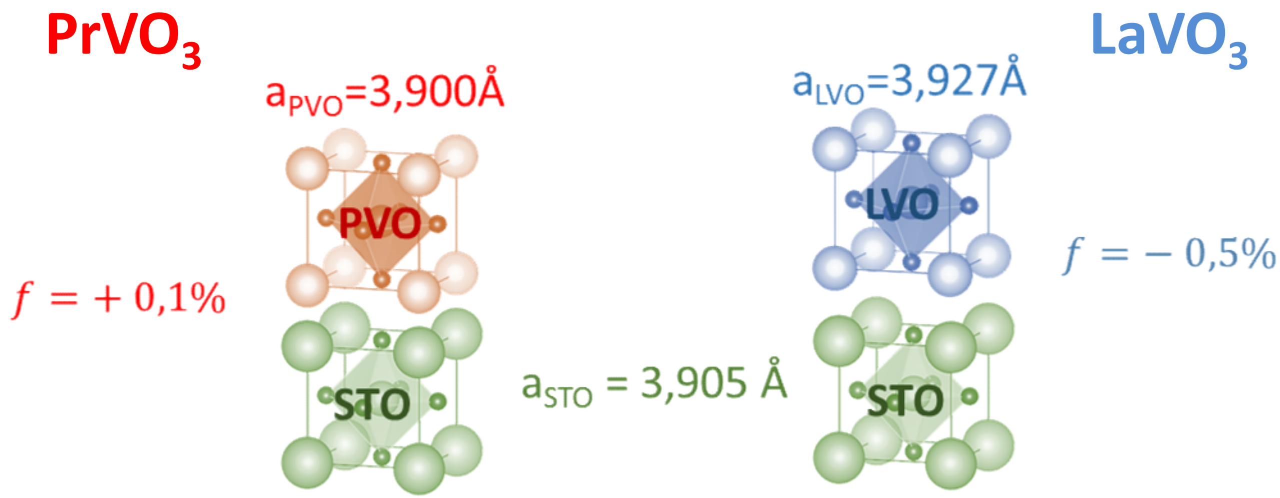
- Hybrid improper ferroelectricity
  Magnetoelectric coupling

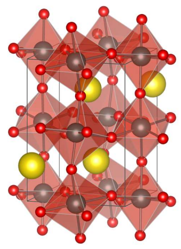


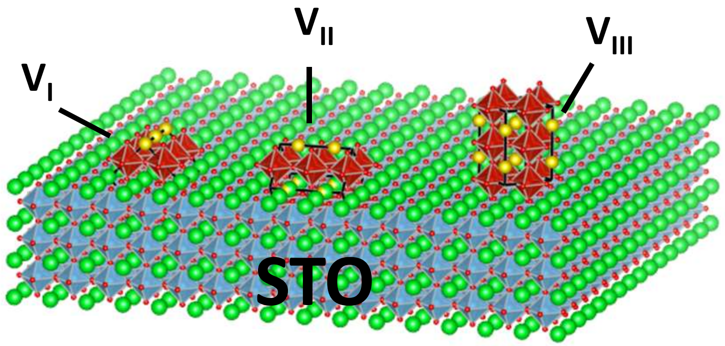
$(RVO_3)_1/(R'VO_3)_1$

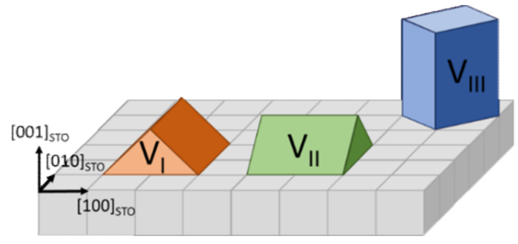
J. Varigon et al., Scientific Reports (2015)

Epitaxial growth of $REVO_3$ films and superlattices







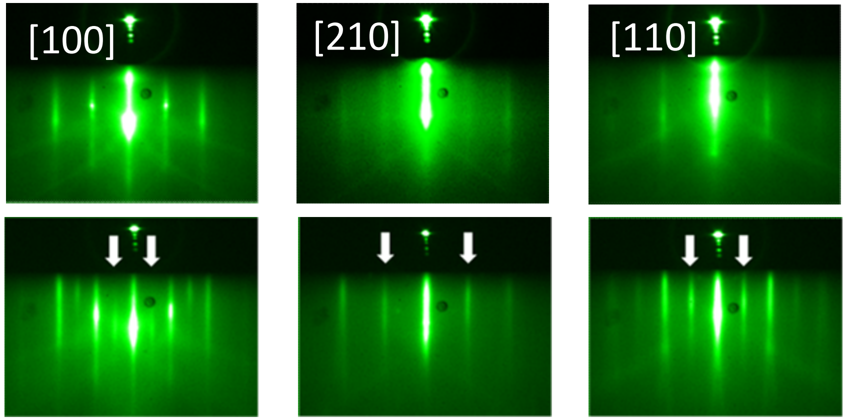


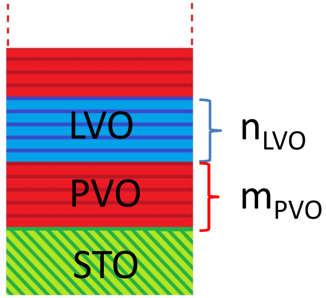
Epitaxial growth [$LaVO_3$/$PrVO_3$] superlattices

[$(LVO)_7$/$(PVO)_5$]$_{18}$

STO-TiO_2

SL

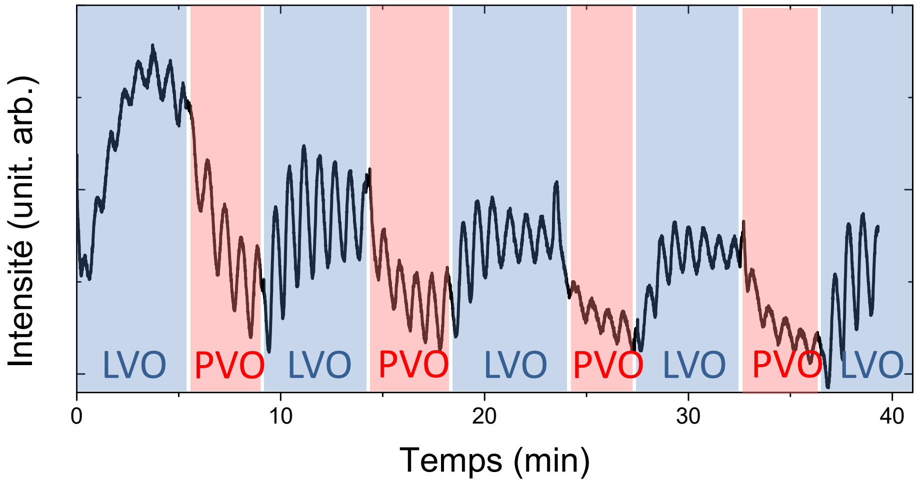


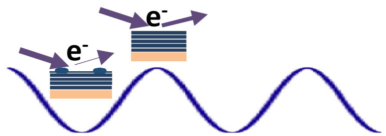


Equal La, Pr and V fluxes ≈ 1.5 10^{13} at/cm^2/s

$T_{Substrat}$= 850°C

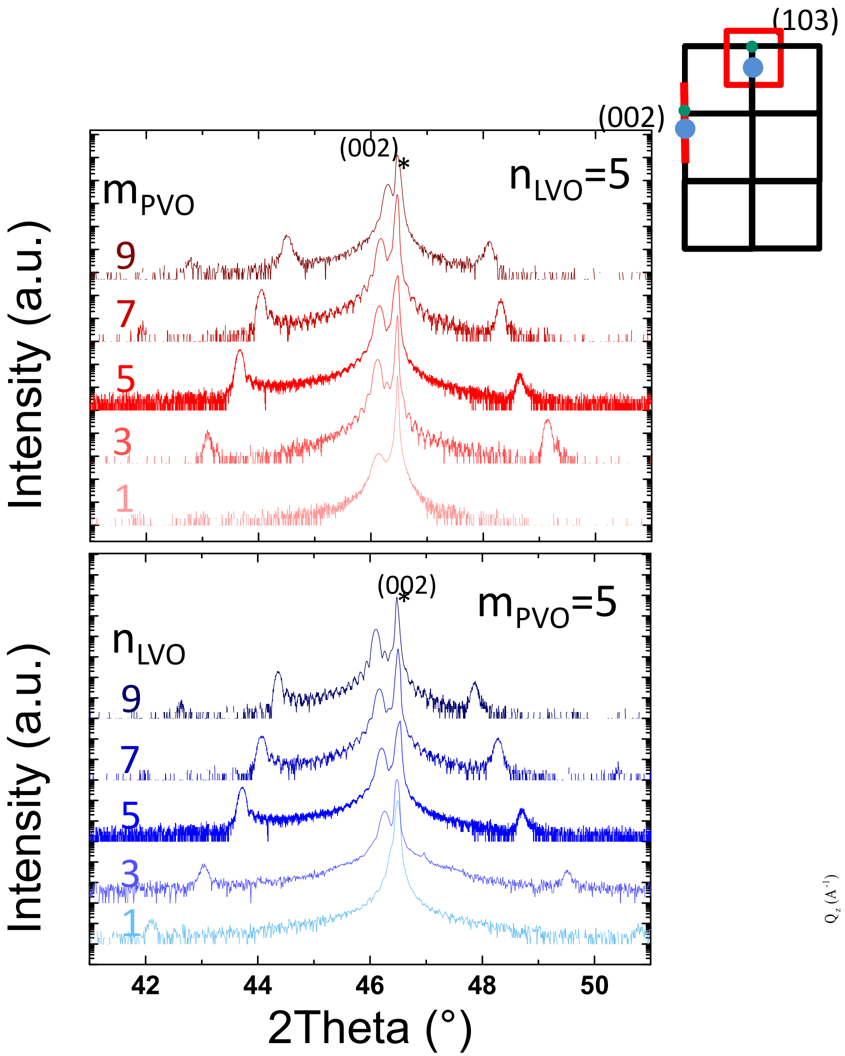
$P_{O_3} = 7.10^{-7}\ mbar$

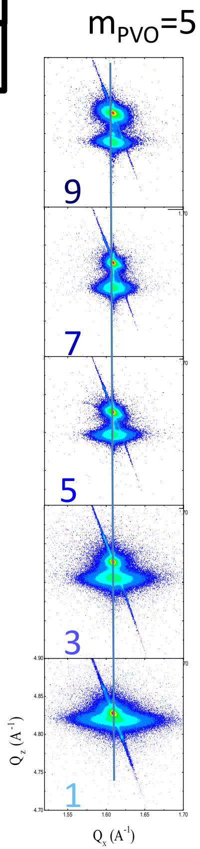


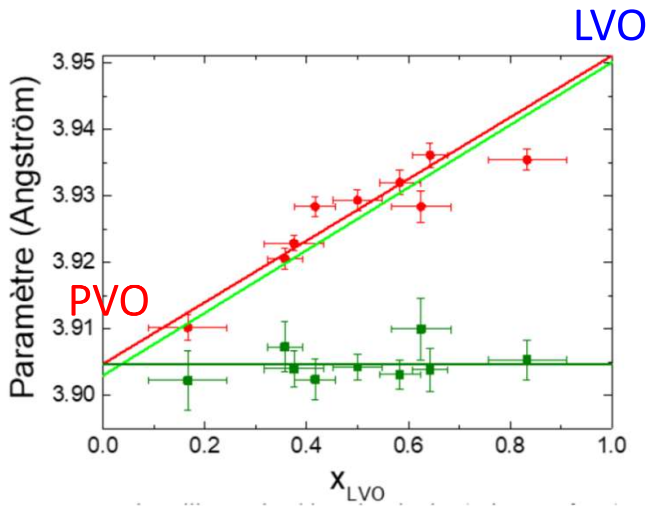


- Epitaxy with possible variants
- Growth by pseudo cubic unit cell RVO_3
- Oxide growth rate v_{ox} = $Flux_{tot}/\rho$
- 2D growth on STO, DSO and LSAT

Structural analysis - XRD



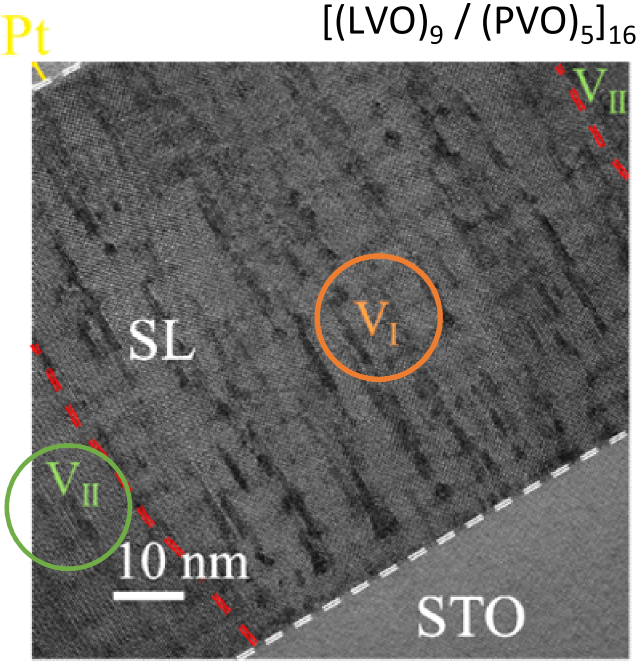




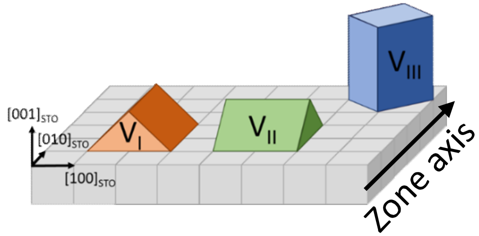
No parasite phases
Epitaxy
Excellent control of the periodic stacking

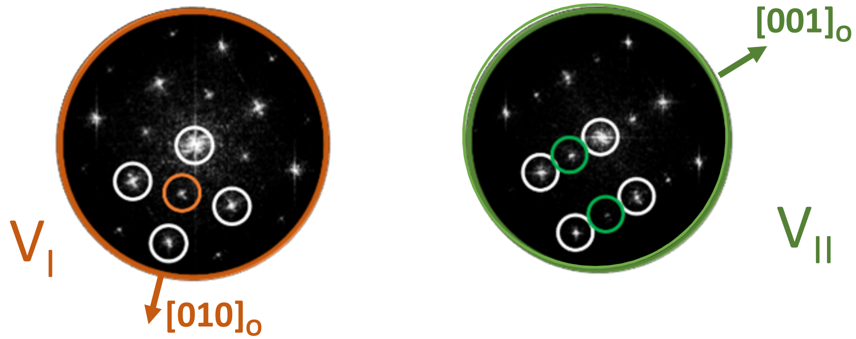
Growth variants – HRTEM/DRX

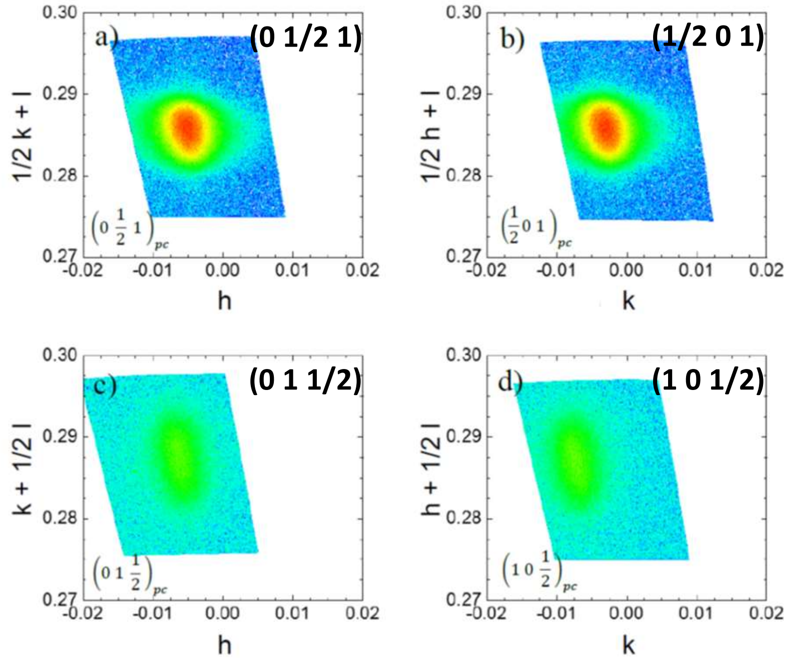
$[(LVO)_9 / (PVO)_5]_{16}$



[010] STO Zone axis



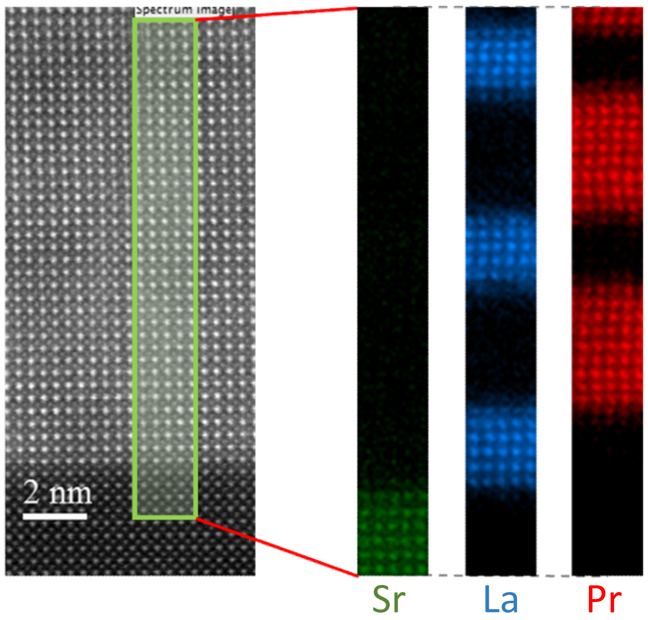


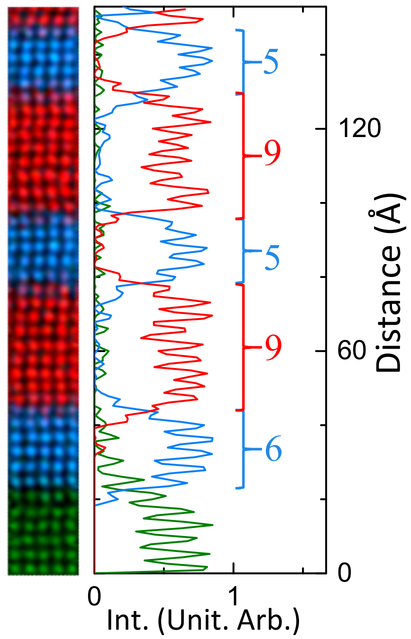


$[(LVO)_1/(PVO)_1]_{110}$

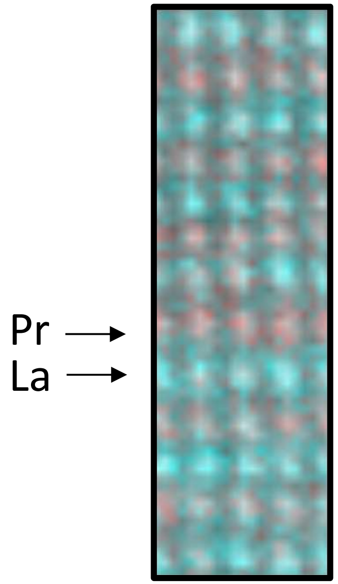
Chemical analysis - EELS

$[(LVO)_5/(PVO)_9]_{16}$





$[(LaVO_3)_1/(PrVO_3)_1]_{110}$

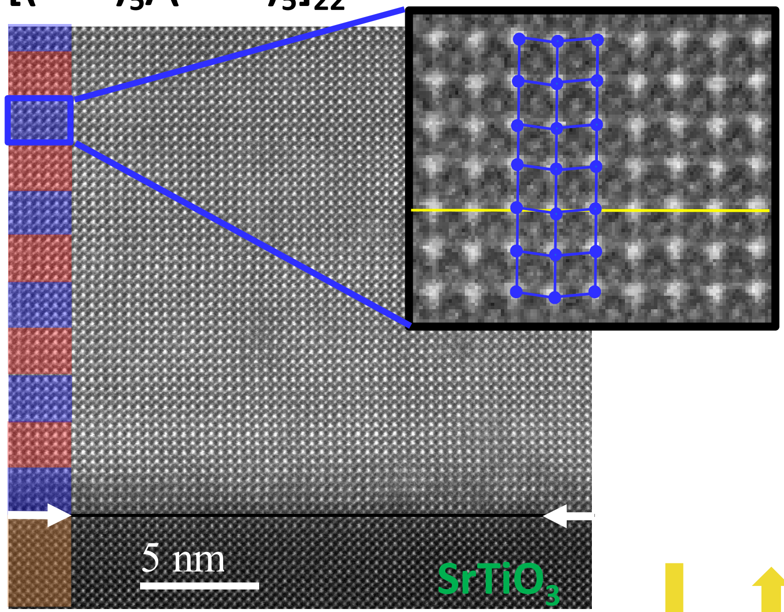


Abrupt interfaces (1 uc max)

Collab. Matthieu BUGNET (MATEIS)

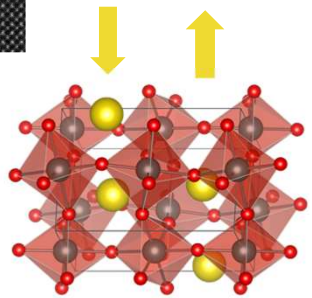
Cations displacements

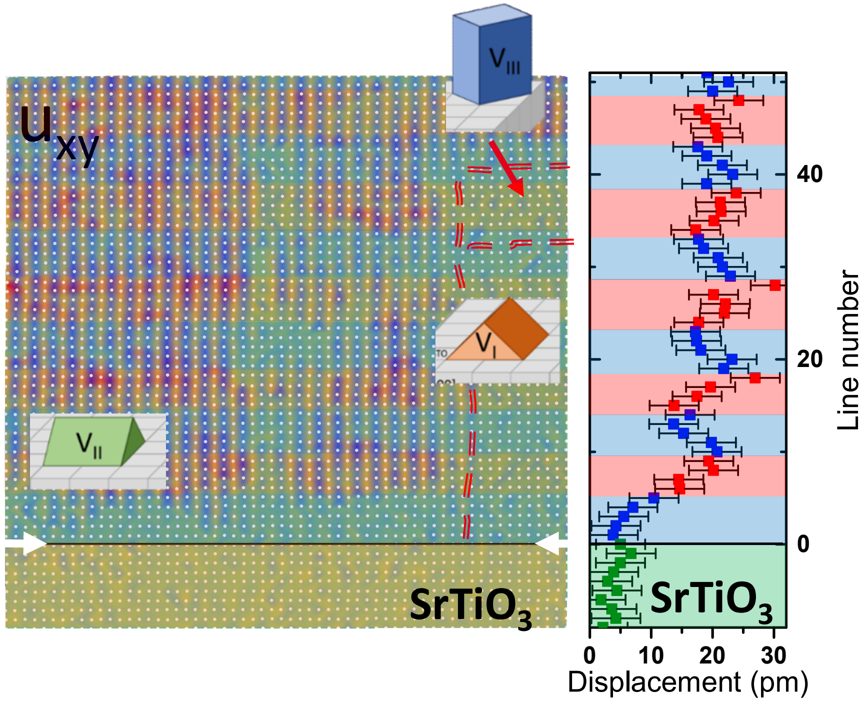
$[(LVO)_5/(PVO)_5]_{22}$

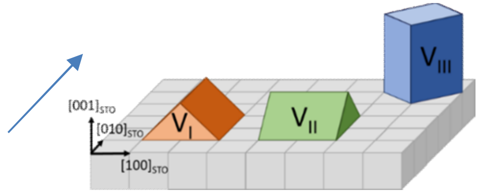


STEM HAADF
[010] STO Zone axis

X_5^-







X_5^- displacements of La (11-12pm) and Pr (14-15pm) atoms
Transition region from the substrate (≈ 6 pc cells)

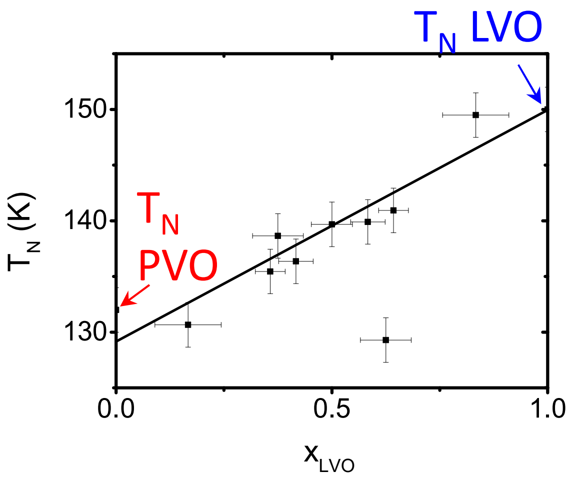
Conclusion

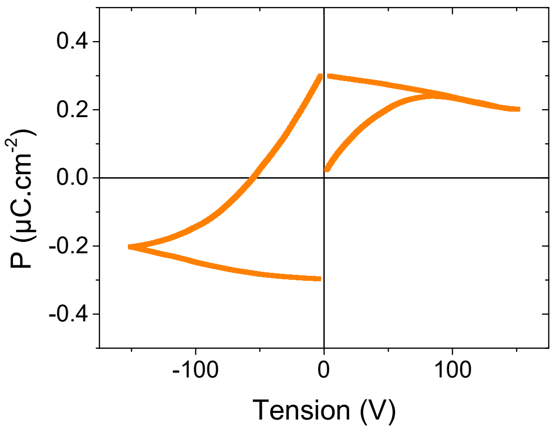
Ultimate control of elementary sources by ozone-MBE

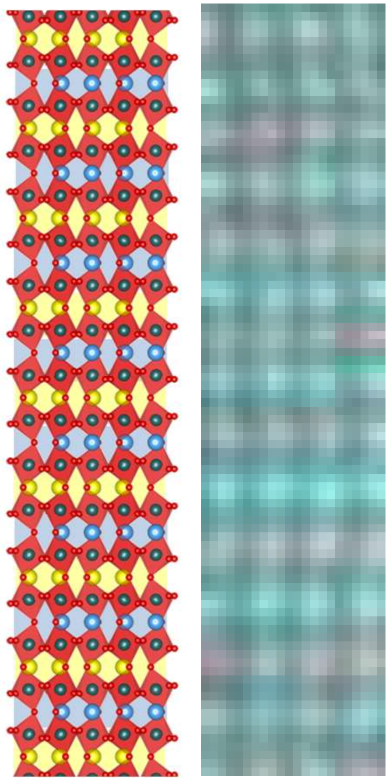
Ultimate design at the atomic plane level

order, confinement, dimensionality, proximity…

new functionalities







$[(LVO)_1 / (PVO)_1]_{110}$

Thank you

Gauthier Masset

Olivier Copie

Ludovic Pasquier

Jaafar Ghanbaja

Stéphane Andrieu

Sébastien Petit-Watelot