Exploring the Limits of Epitaxy to further Materials by Design

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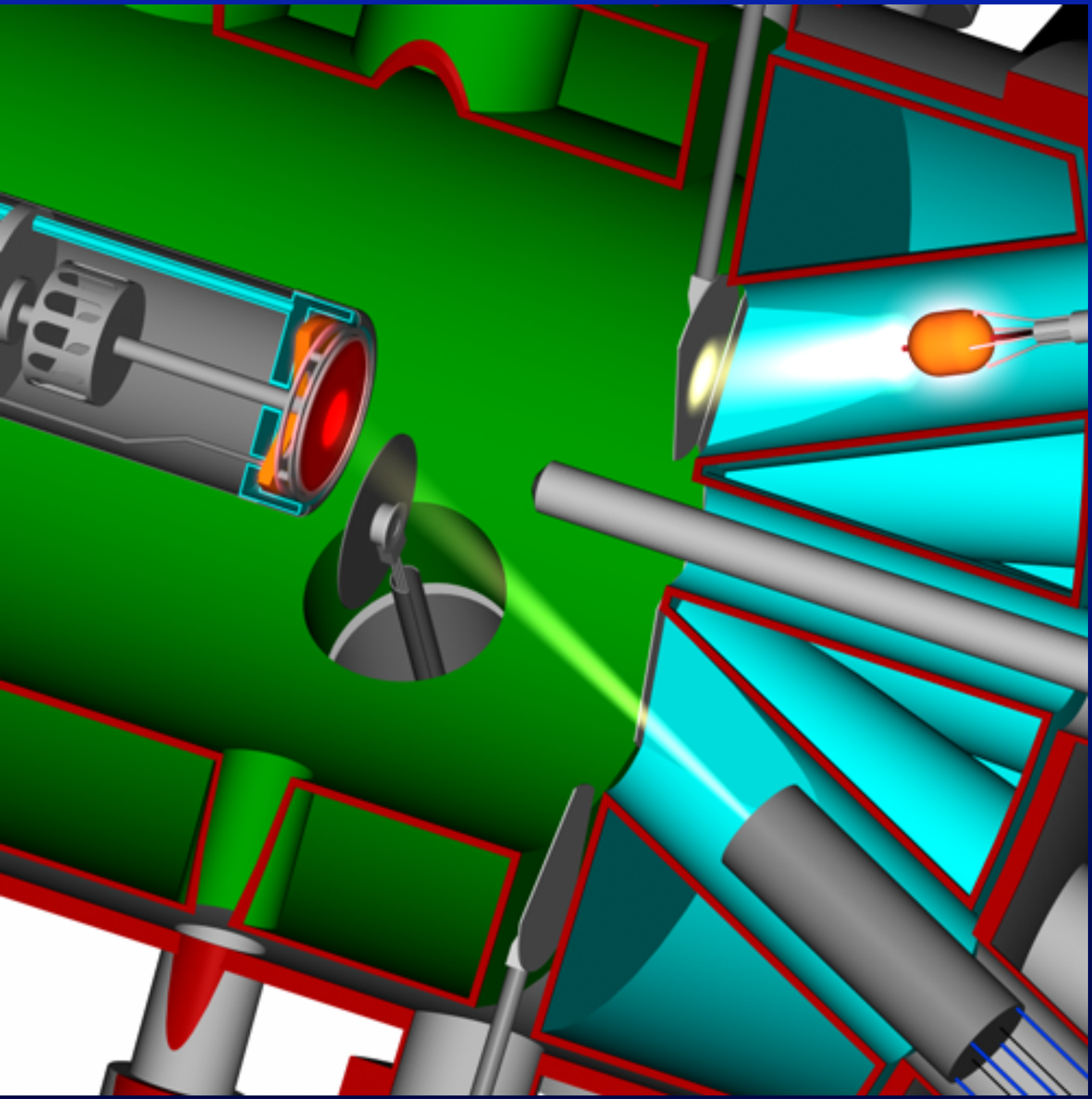
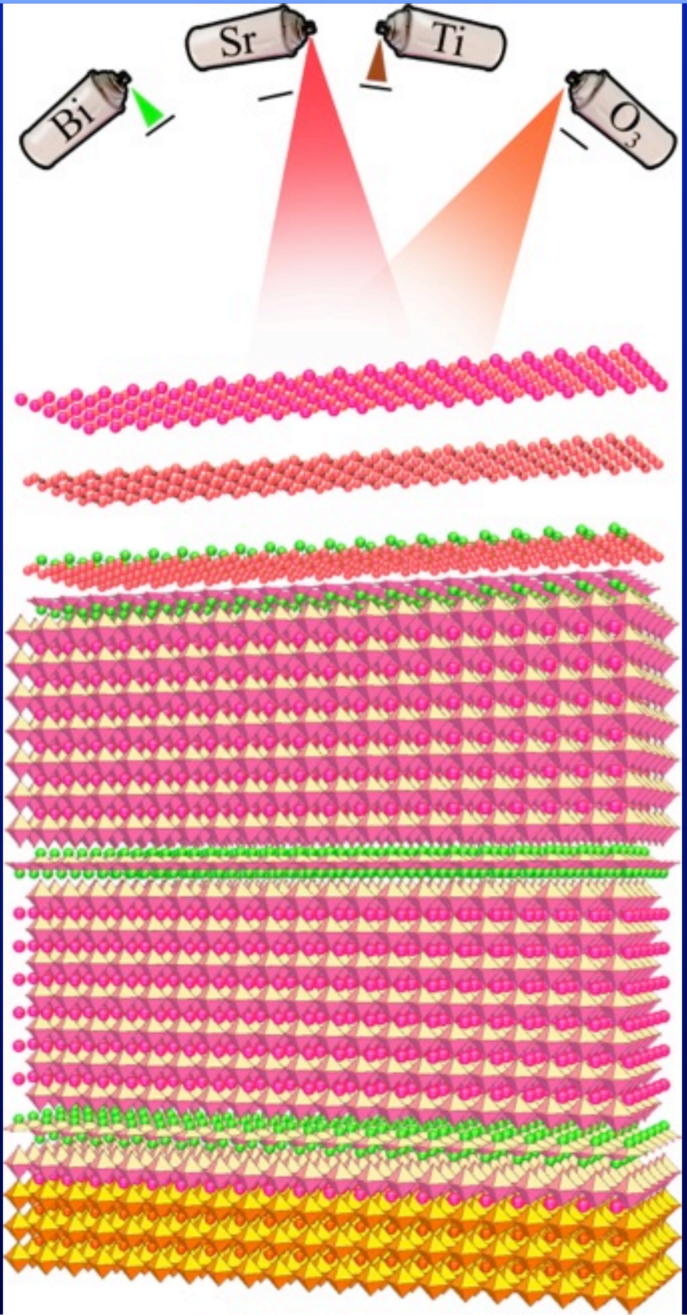
Sandwich Maker

Outline

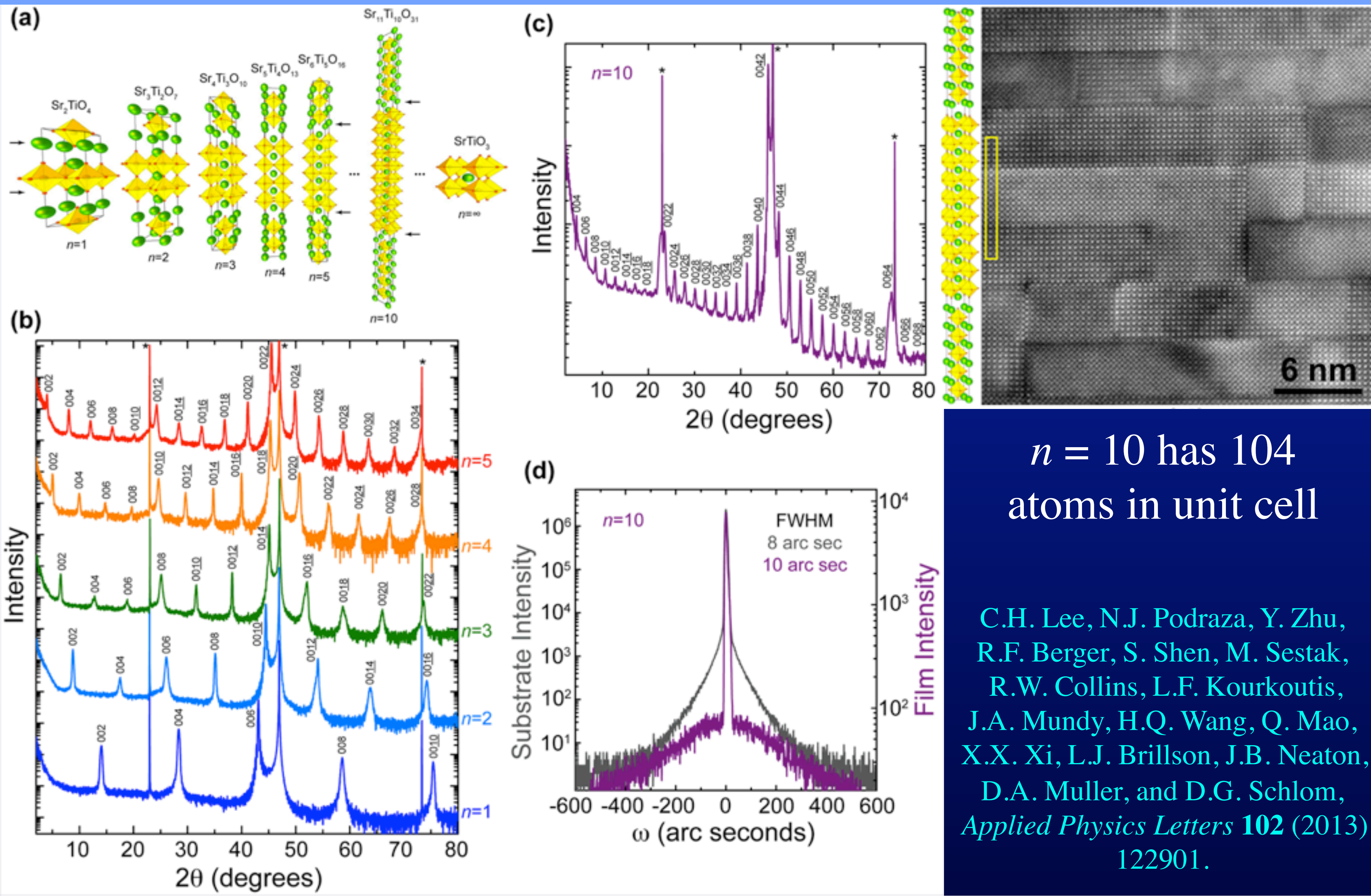
- **What can be synthesized**
  - **Ruddlesden Popper ($A_{n+1}B_nO_{3n+1}$) with *n* up to 10**
  - **Aurivillius ($Bi_2O_2(A_{n-1}B_nO_{3n+1})$) with *n* up to 8**
  - **Superlattices**
  - **Strain Game with $\varepsilon_{11} \approx \varepsilon_{22}$ up to 6%**
  - **Epitaxial Stabilization**
  - ***in situ* ARPES**
- **Challenges**

MBE ≈ Atomic Spray Painting





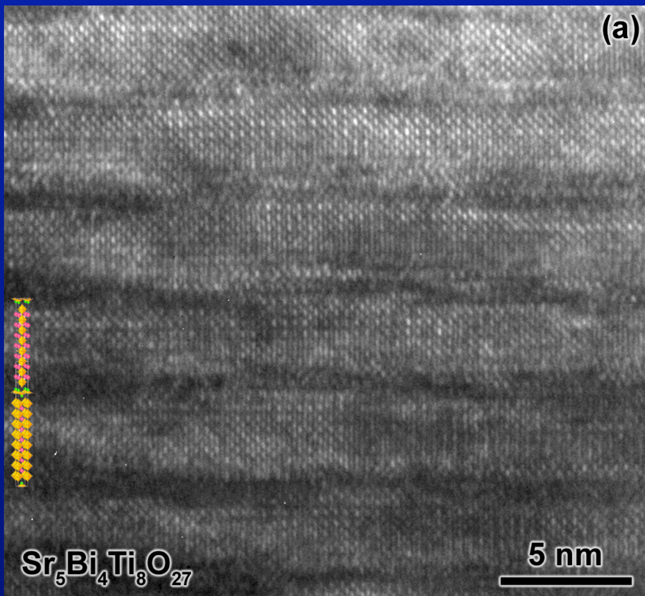
Ruddlesden-Popper $A_{n+1}B_nO_{3n+1}$ with $n \leq 10$

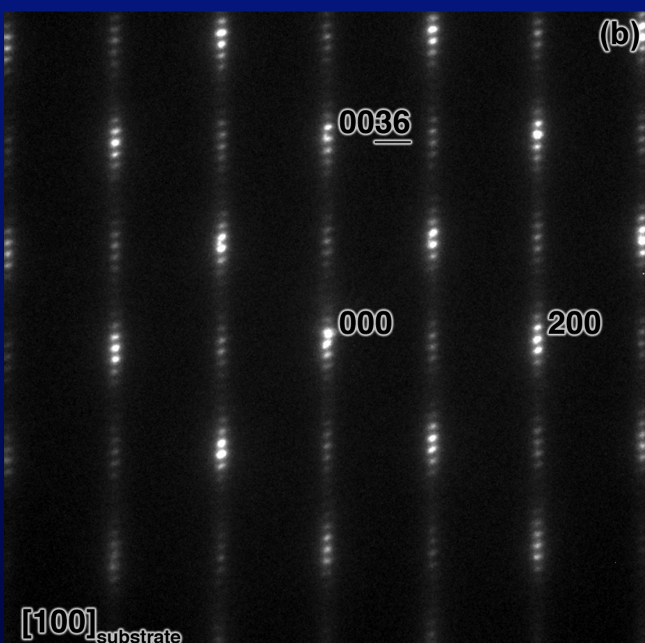


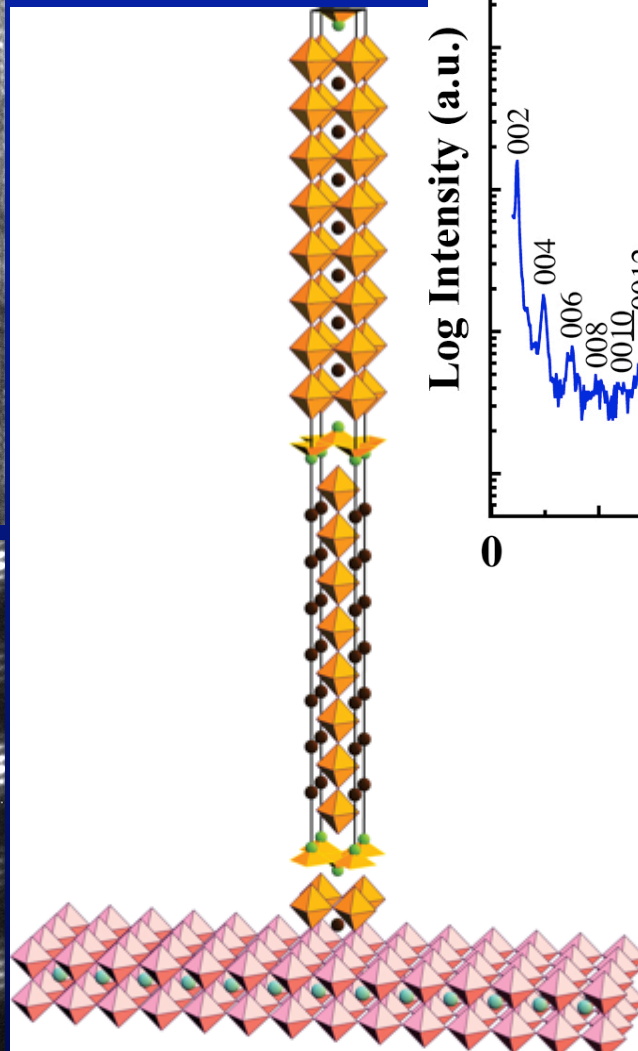
n = 10 has 104 atoms in unit cell

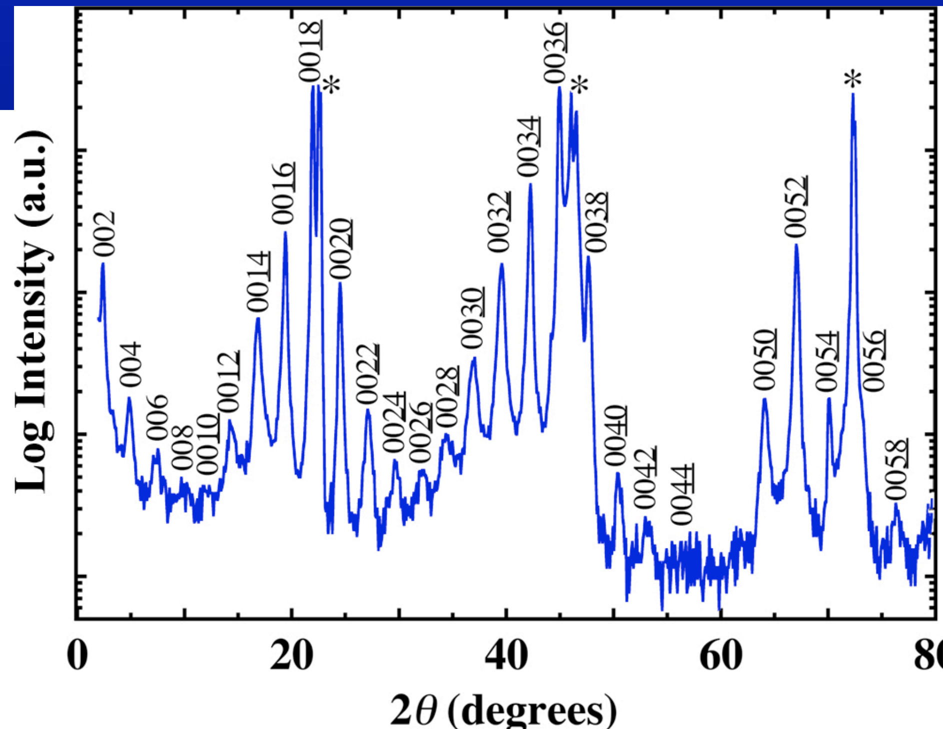
C.H. Lee, N.J. Podraza, Y. Zhu, R.F. Berger, S. Shen, M. Sestak, R.W. Collins, L.F. Kourkoutis, J.A. Mundy, H.Q. Wang, Q. Mao, X.X. Xi, L.J. Brillson, J.B. Neaton, D.A. Muller, and D.G. Schlom, *Applied Physics Letters* **102** (2013) 122901.

$n = 8$ Aurivillius Phase [$Bi_4Ti_3O_{12}$—$(SrTiO_3)_5$]





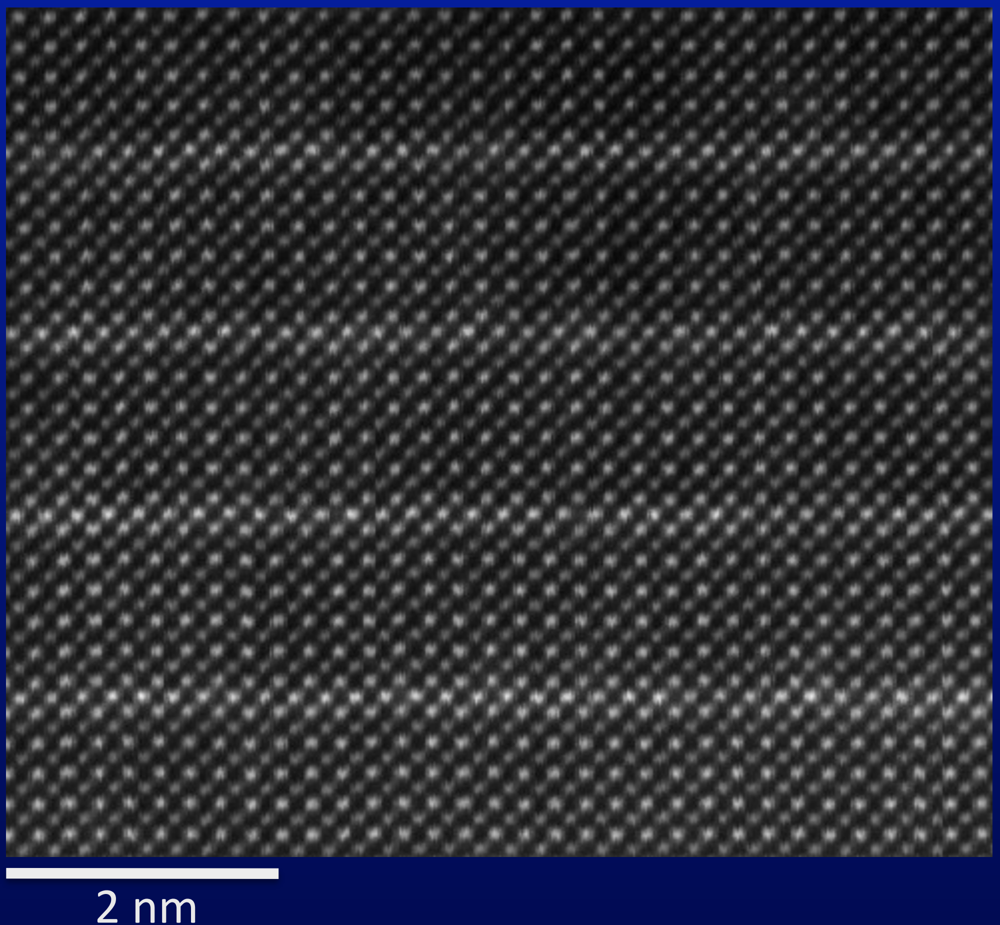




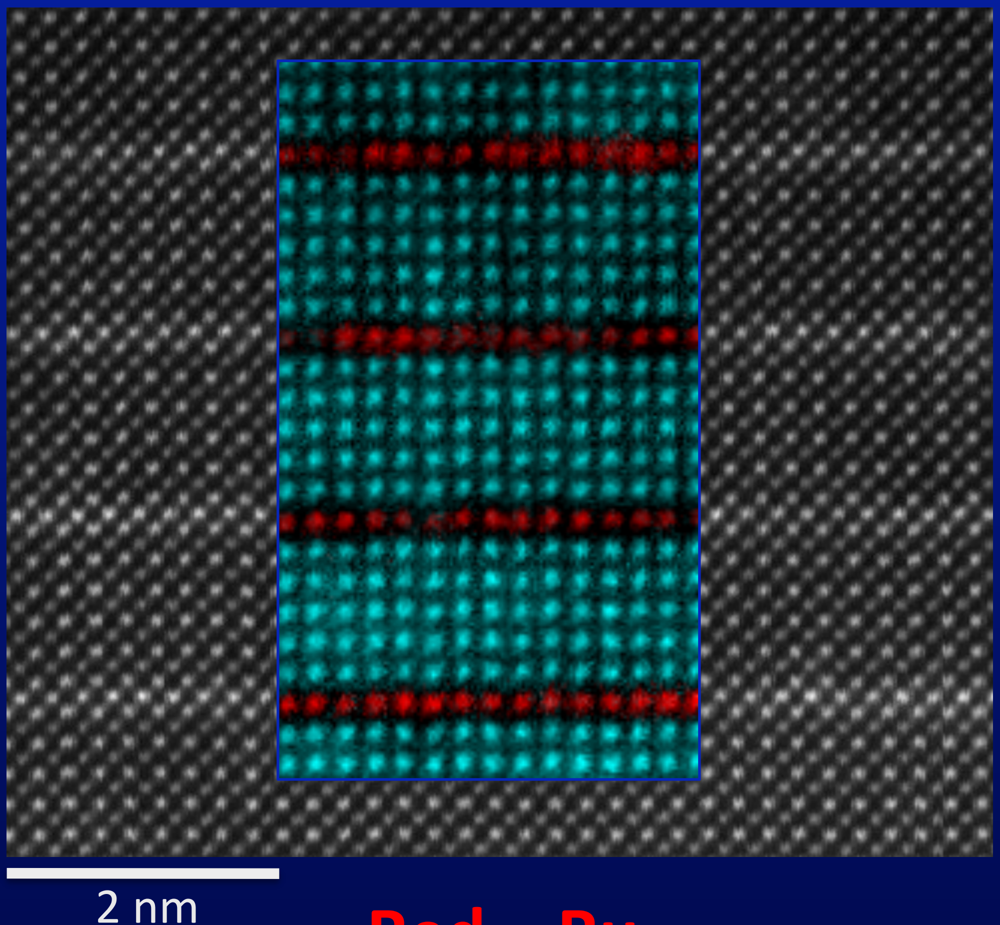
M.A. Zurbuchen, N.J. Podraza, J. Schubert, Y. Jia, and D.G. Schlom, *Applied Physics Letters* **100** (2012) 223109.

$(SrRuO_3)_1$ / $(SrTiO_3)_5$ Superlattice

ADF-STEM



STEM-EELS

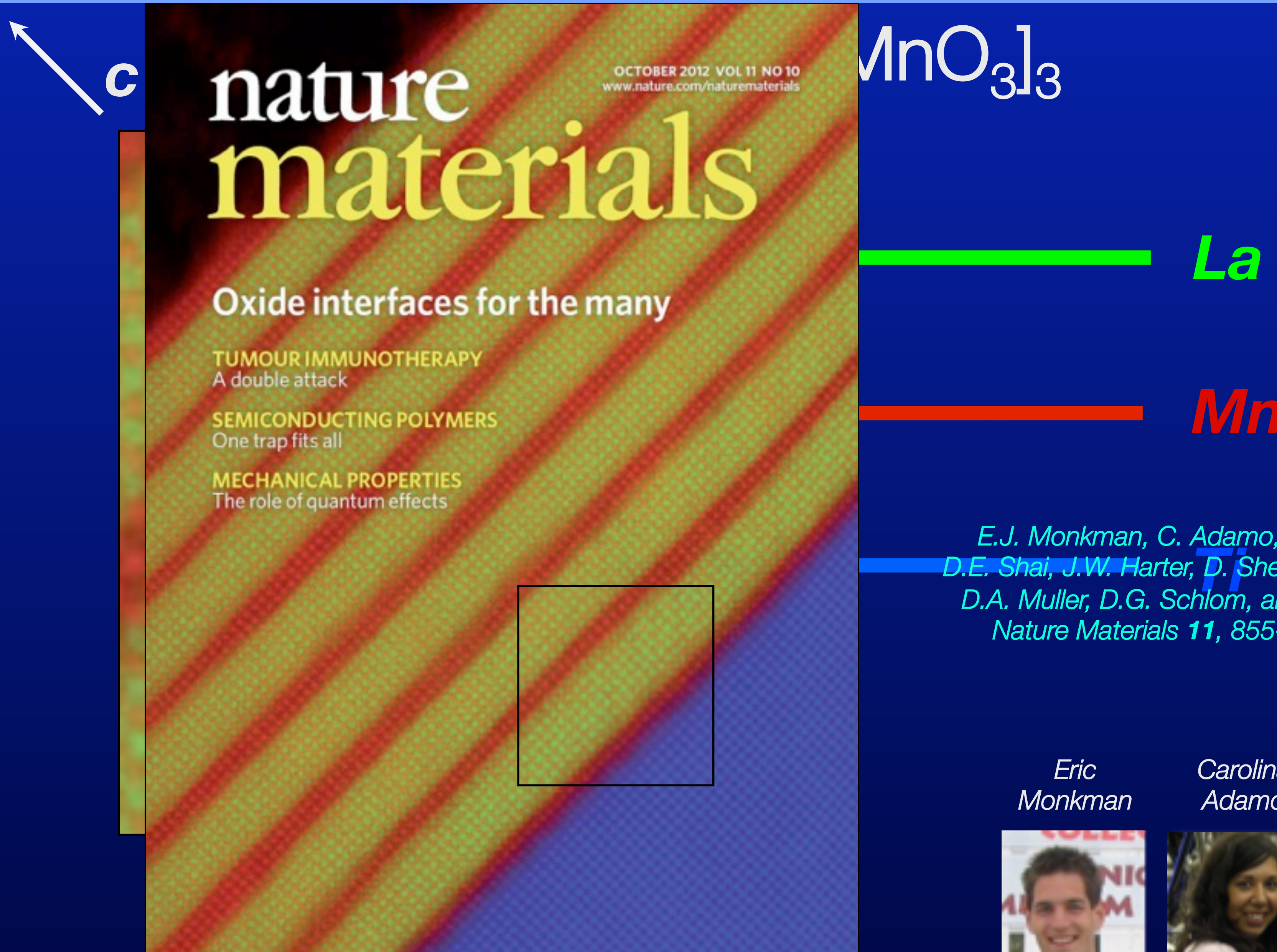


Red = Ru

Teal = Ti

David Muller's group (Cornell)

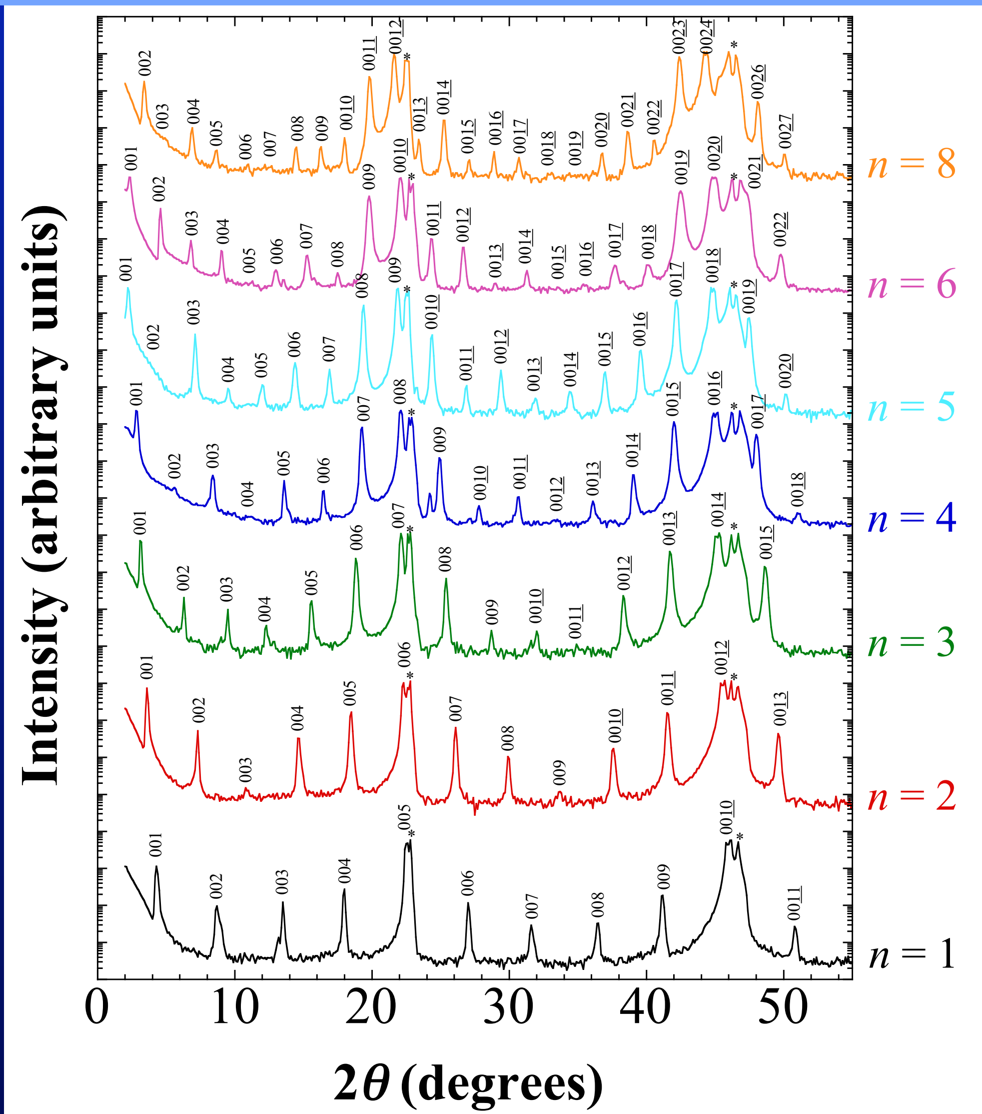
Scanning Transmission Electron Microscopy



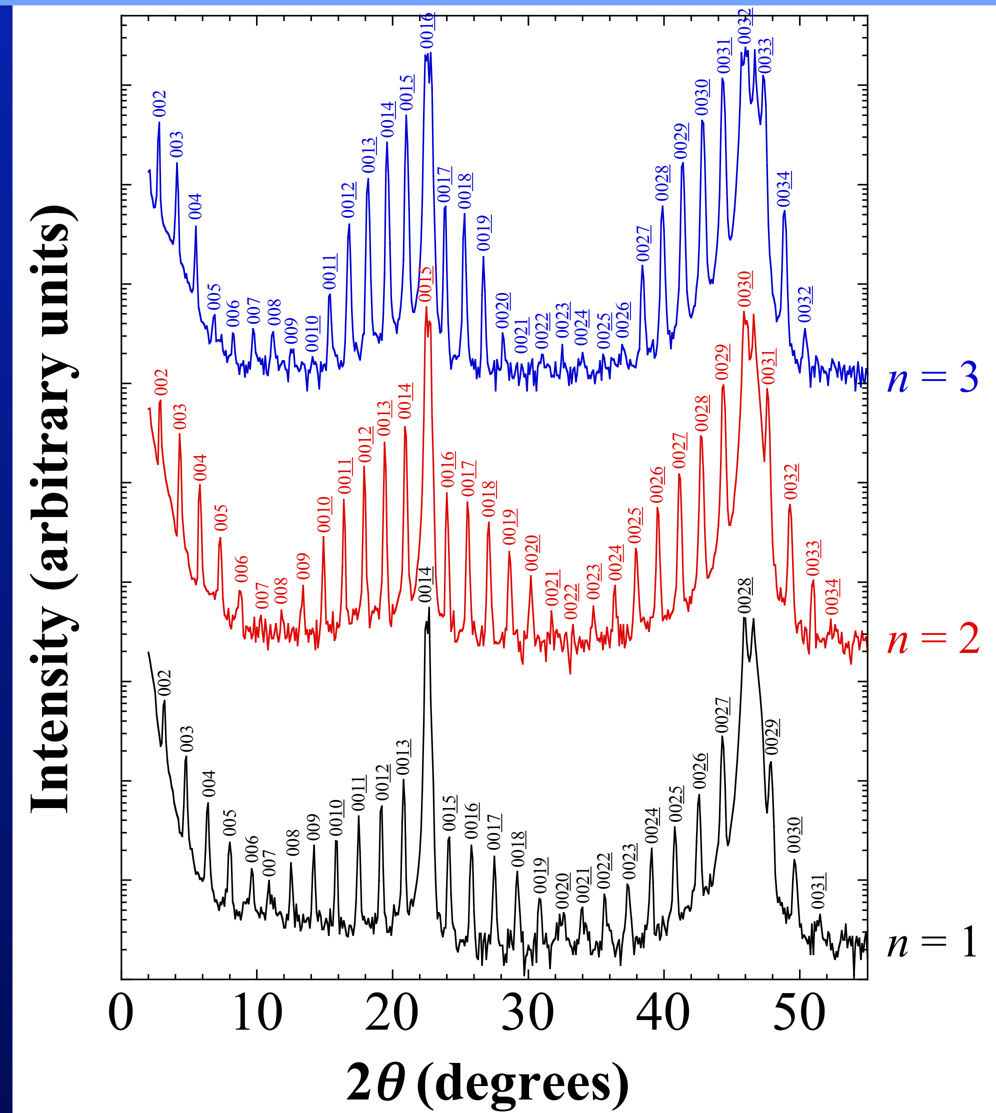
E.J. Monkman, C. Adamo, J.A. Mundy, D.E. Shai, J.W. Harter, D. Shen, B. Burganov, D.A. Muller, D.G. Schlom, and K.M. Shen, Nature Materials ***11****, 855-859 (2012)*

Eric Monkman | *Carolina Adamo* | *Julia Mundy, Muller Group*

XRD of $(BaTiO_3)_n$ / $(SrTiO_3)_m$ Superlattices



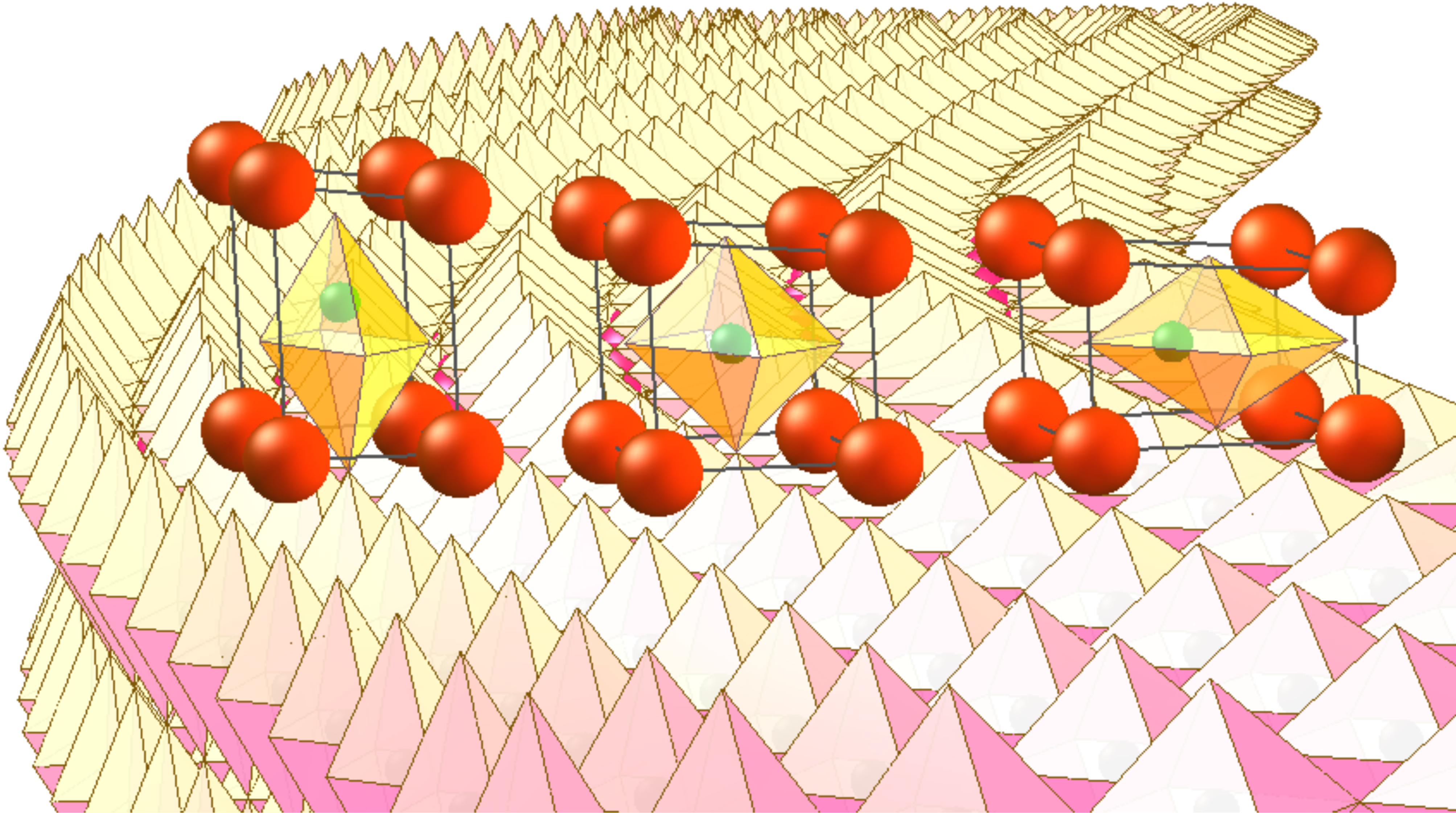
$m = 4$



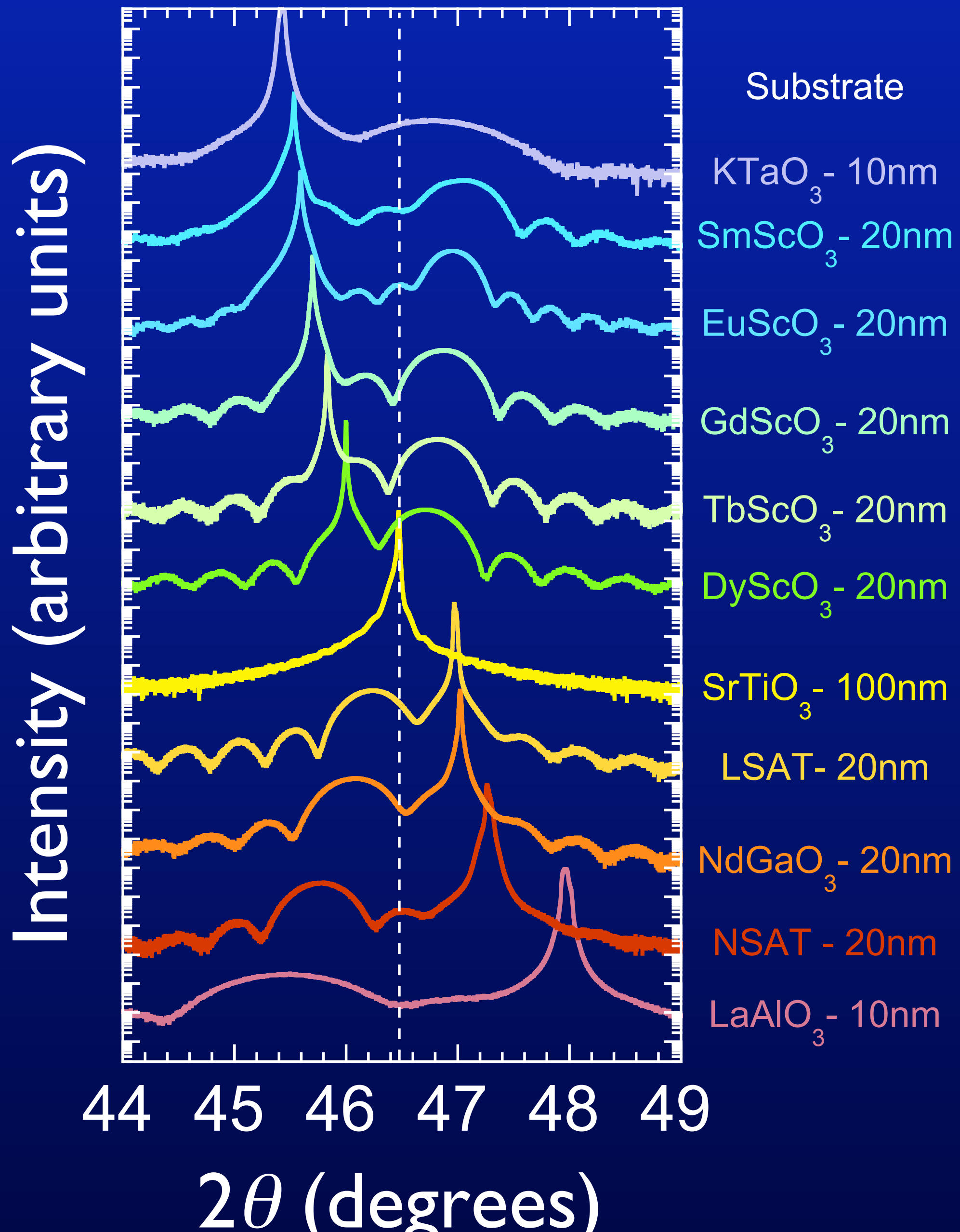
$m = 13$

A. Soukiassian, W. Tian, V. Vaithyanathan, J.H. Haeni, L.Q. Chen, X.X. Xi, D.G. Schlom, D.A. Tenne, H.P. Sun, X.Q. Pan, K.J. Choi, C.B. Eom, Y.L. Li, Q.X. Jia, C. Constantin, R.M. Feenstra, M. Bernhagen, P. Reiche, and R. Uecker, *Journal of Materials Research* **23** (2008) 1417-1432.

The *Strain* Game

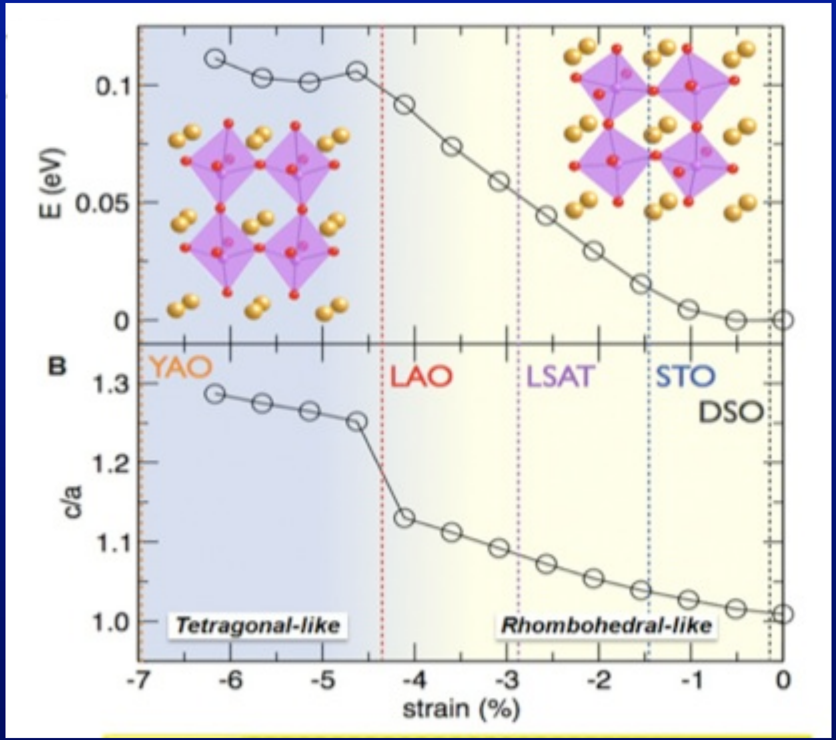


Strained (001) Perovskite Films



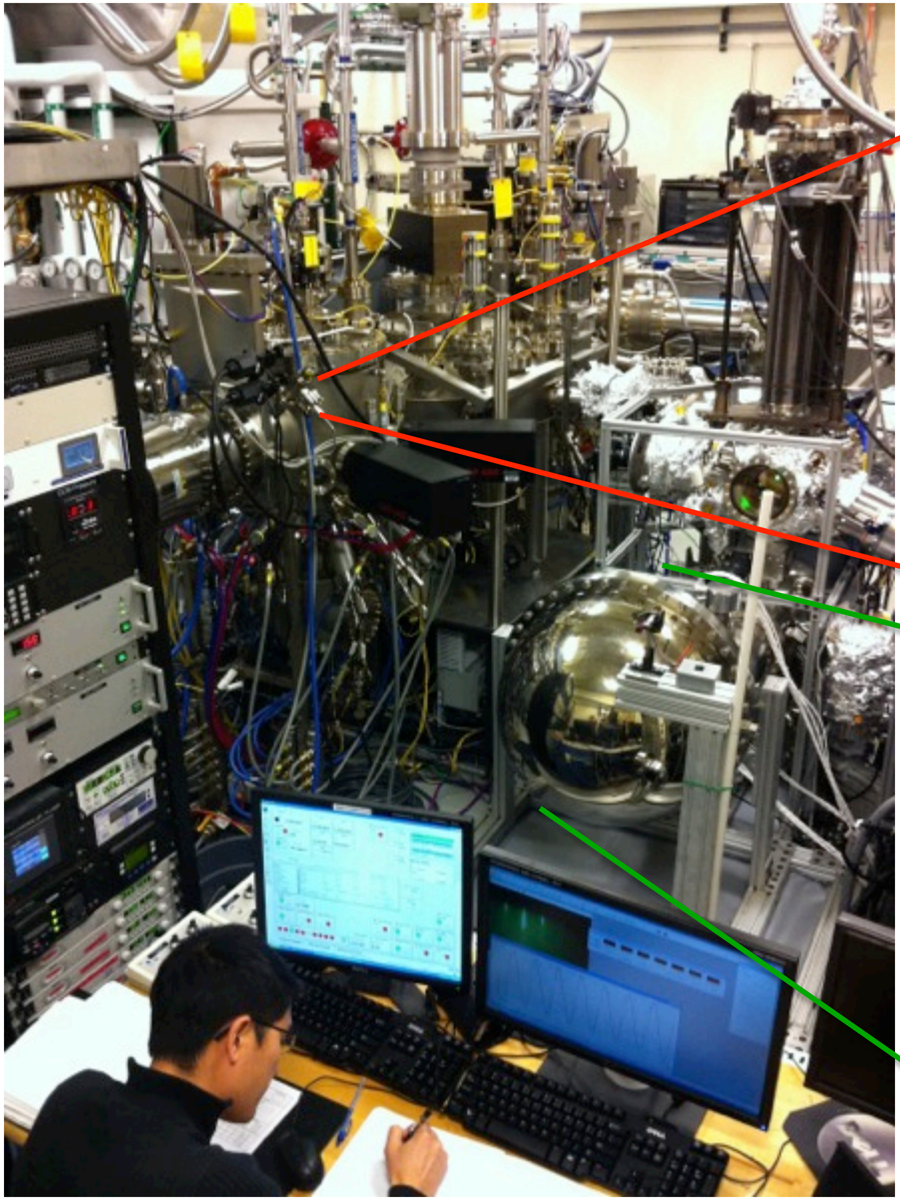
$\varepsilon_{11} \approx \varepsilon_{11} \leq 3\%$ typical

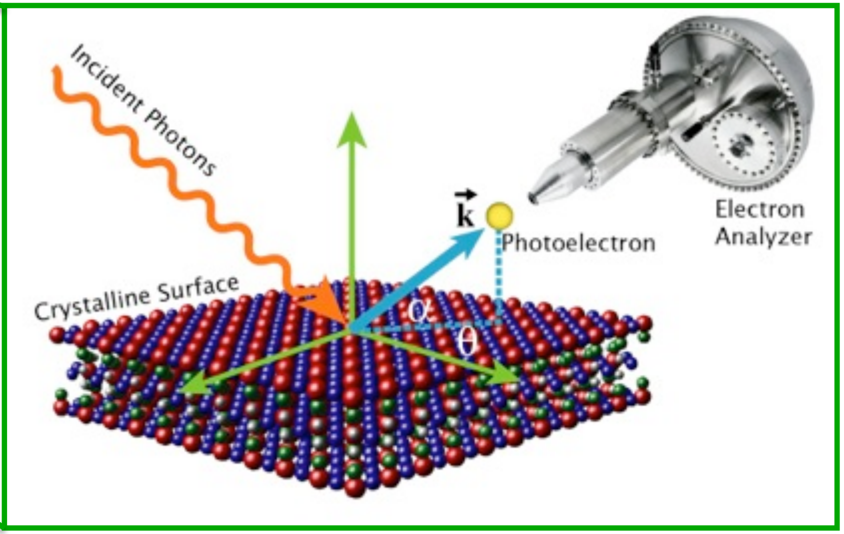
max to date 6.6% in $BiFeO_3$

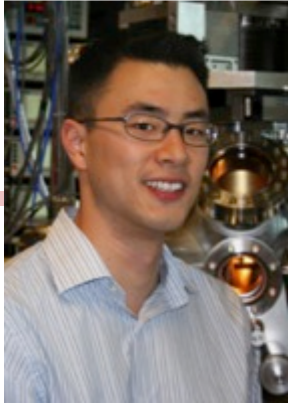


R.J. Zeches, M.D. Rossell, J.X. Zhang, A.J. Hatt, Q. He, C.-H. Yang, A. Kumar, C.H. Wang, A. Melville, C. Adamo, G. Sheng, Y.-H. Chu, J.F. Ihlefeld, R. Erni, C. Ederer, V. Gopalan, L.Q. Chen, D.G. Schlom, N.A. Spaldin, L.W. Martin, and R. Ramesh, *Science* **326** (2009) 977-980 .

MBE + ARPES

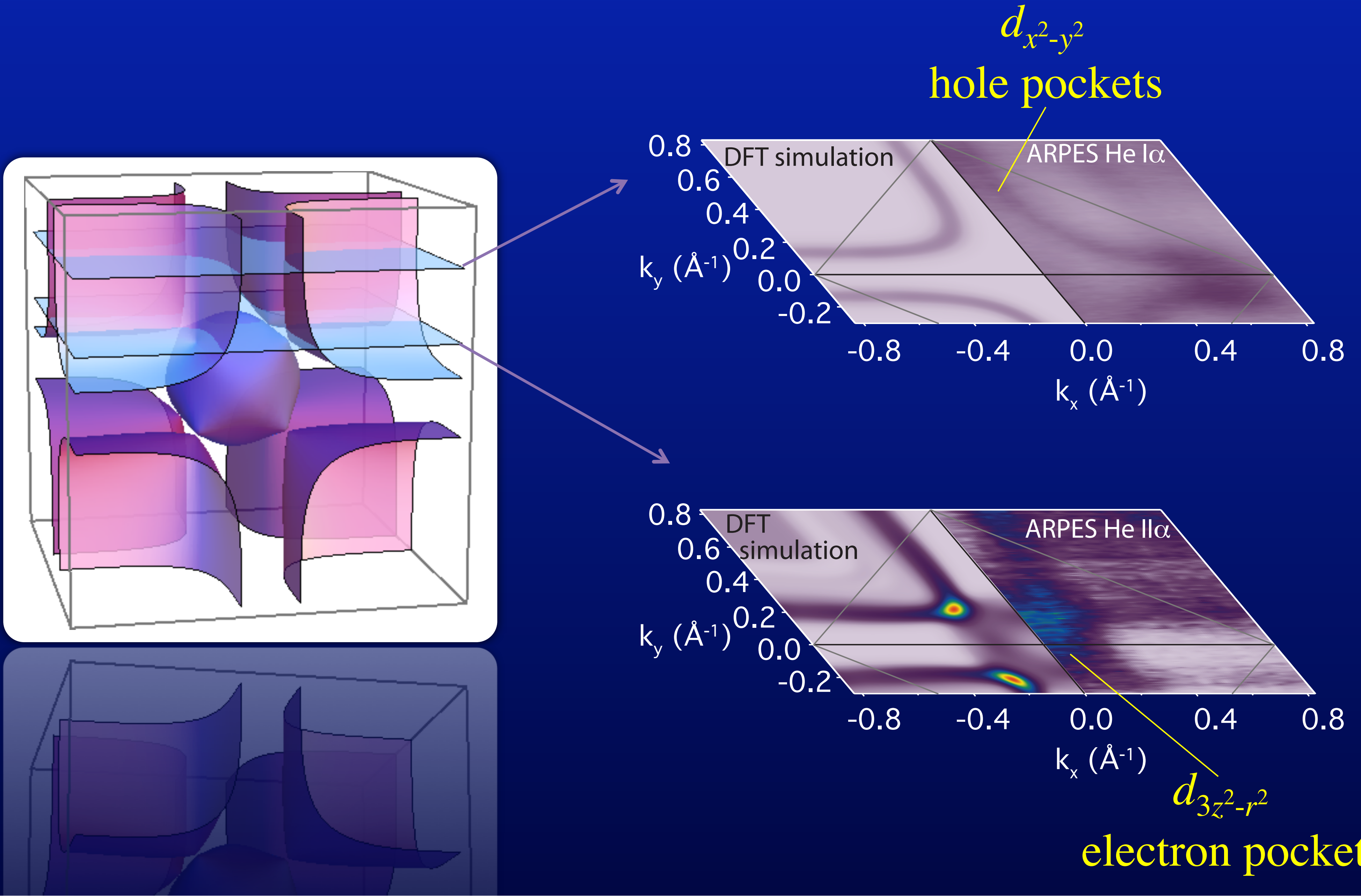




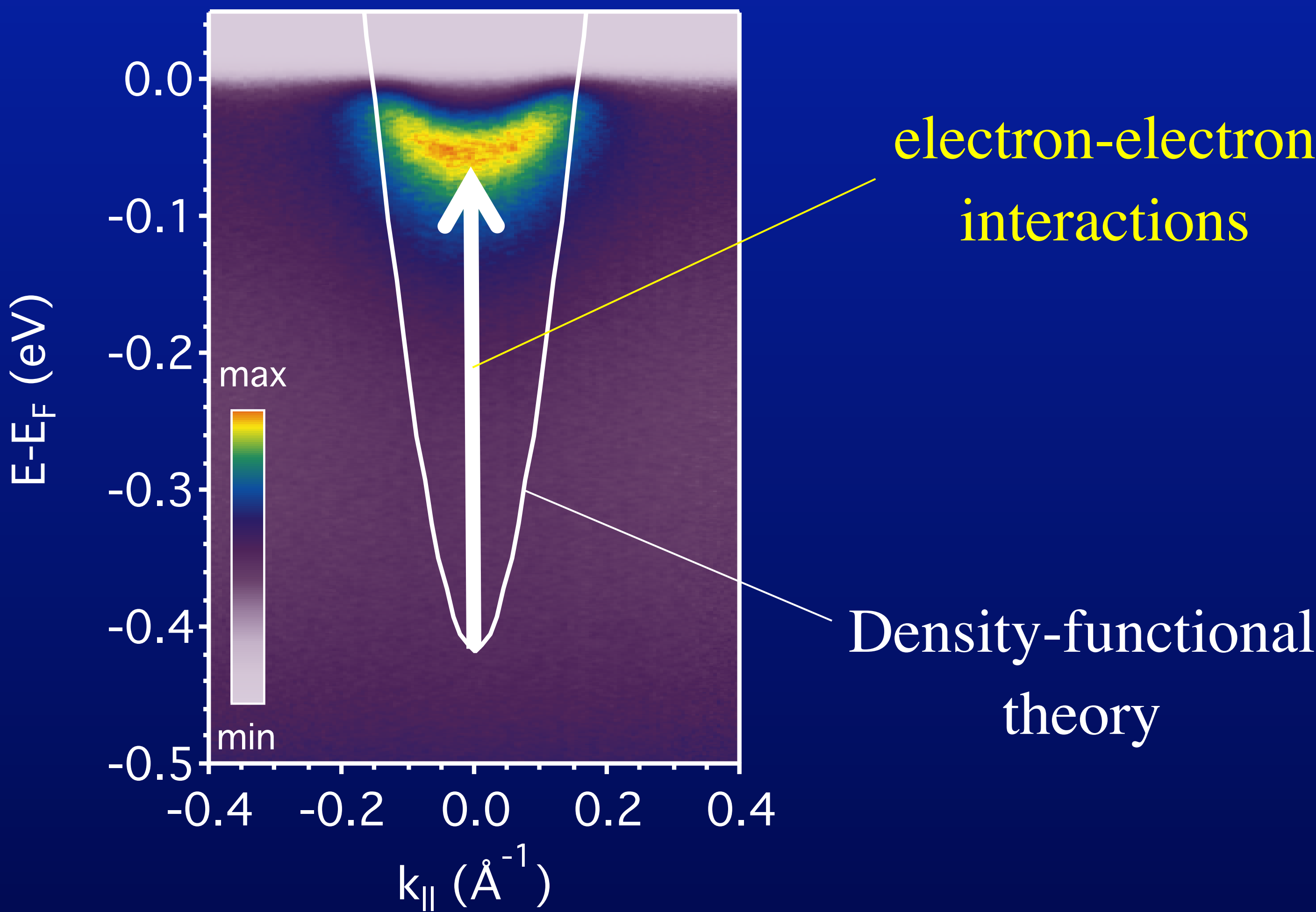


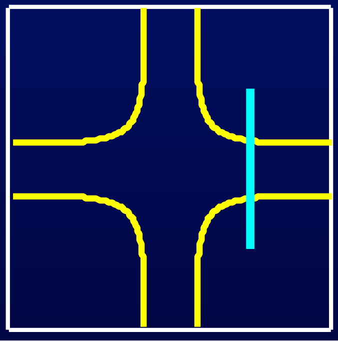
***Angle-Resolved Photoemission Spectroscopy* (*Kyle Shen*)**

ARPES of $LaNiO_3$: e_g Fermi Surface



Giant Quasiparticle Mass Renormalization

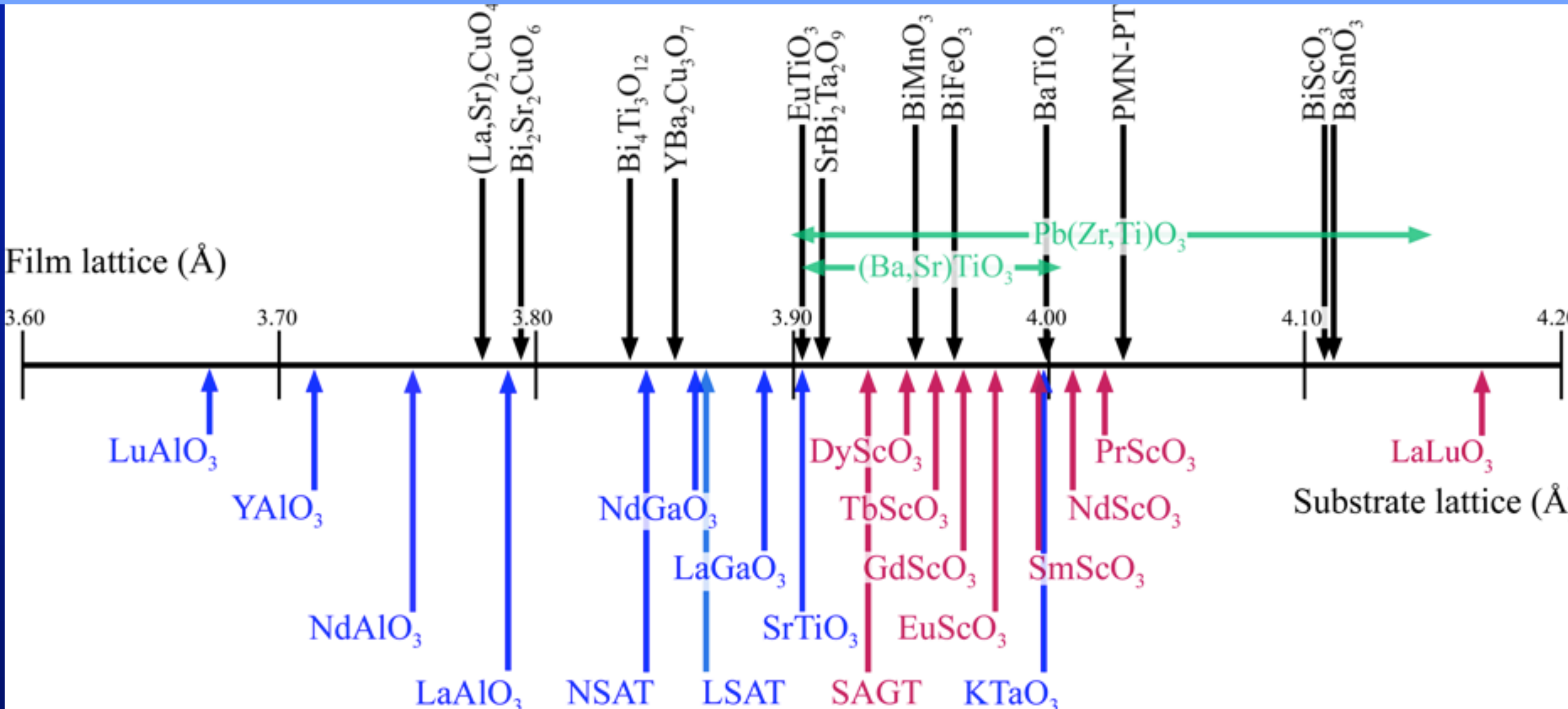


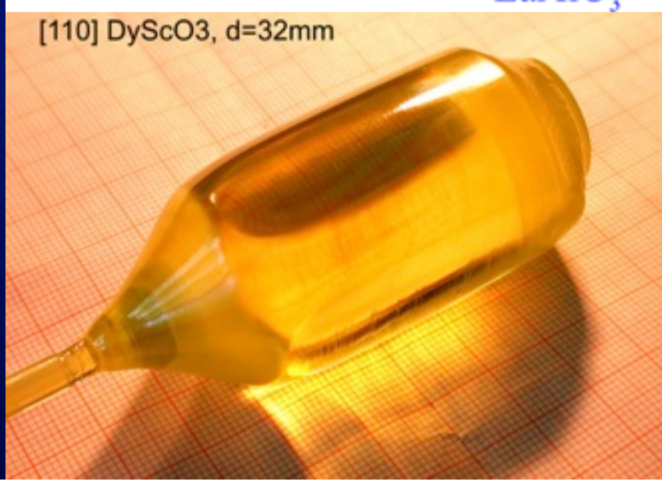


Outline

- What can be done
- Challenges
  - Substrates (isostructural, high perfection, desired lattice constant, desired octahedral rotations, …)
  - Substrate Termination
  - Details of Growth Richer than Simple Cartoon
  - Point Defects (including defect complexes)

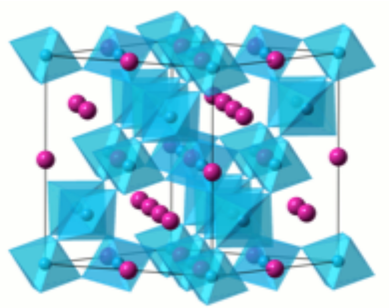
Commercial Perovskite Substrates

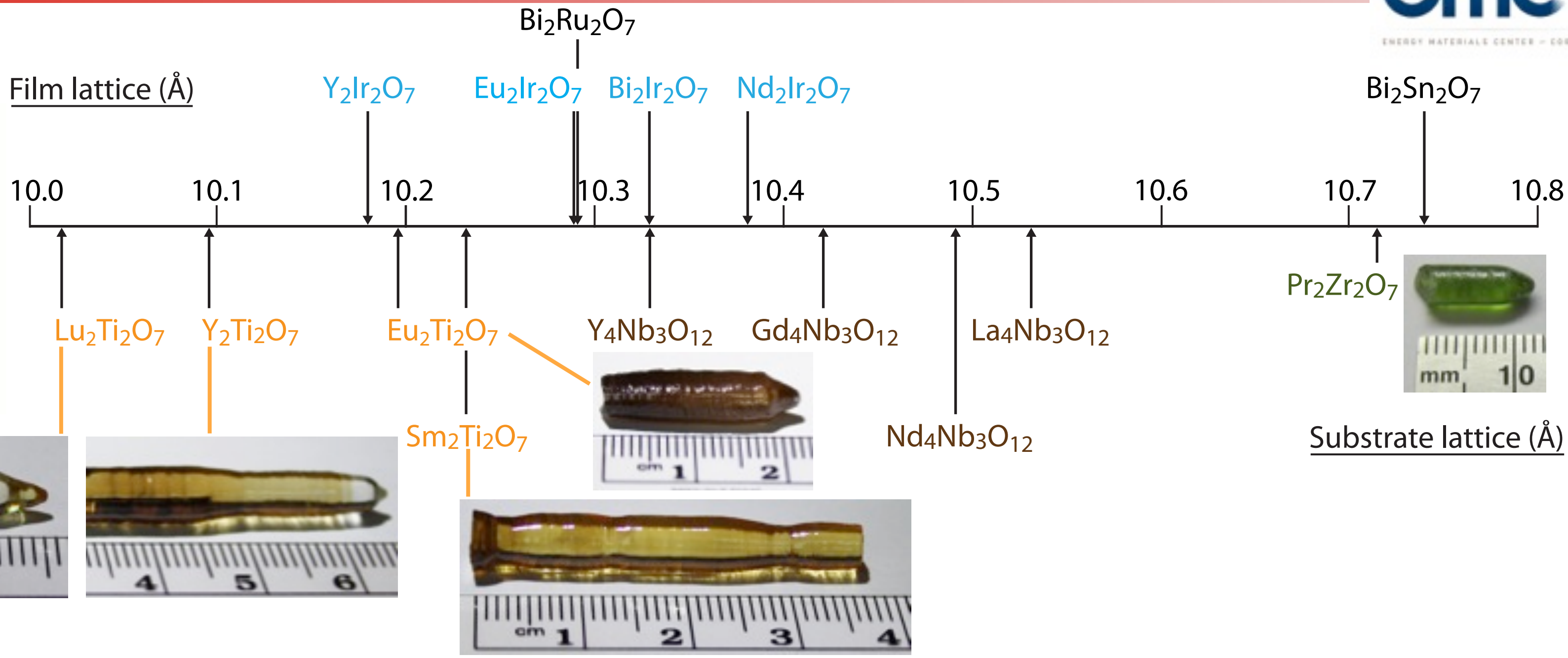


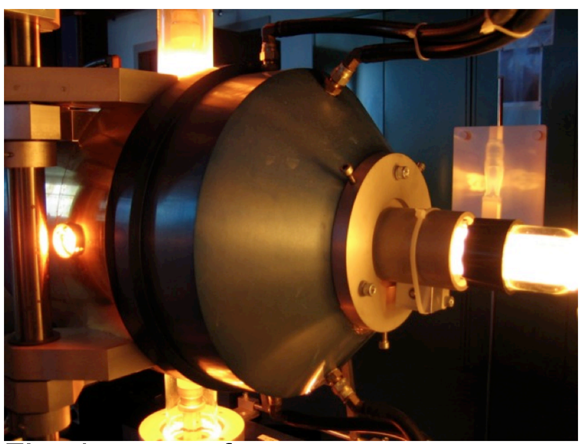


Reinhard Uecker's Group
Leibniz Institute
for Crystal Growth
Berlin, Germany

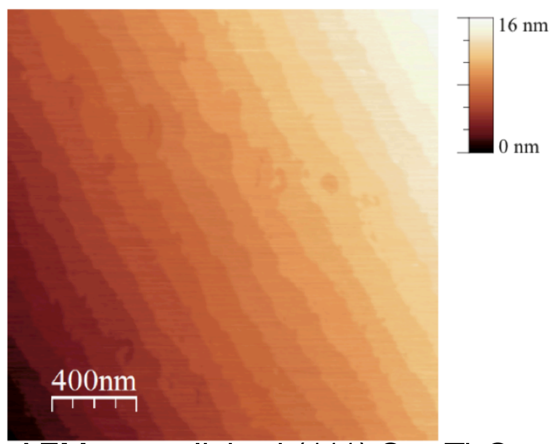
Pyrochlore Substrates







Floating zone furnace (Augsburg)



AFM: as-polished (111) $Sm_2Ti_2O_7$ (floating zone)

- New, large $Sm_2Ti_2O_7$ crystals (Czochralski)
- Suitable for fabrication of 1 cm x 1 cm substrates
- Annealing in O_2 removes oxygen vacancies

Collaboration with University of Augsburg (Jochen Mannhart's Group), Leibniz Institute for Crystal Growth (Reinhard Uecker's Group) and Johns Hopkins University (Tyrel McQueen's Group)

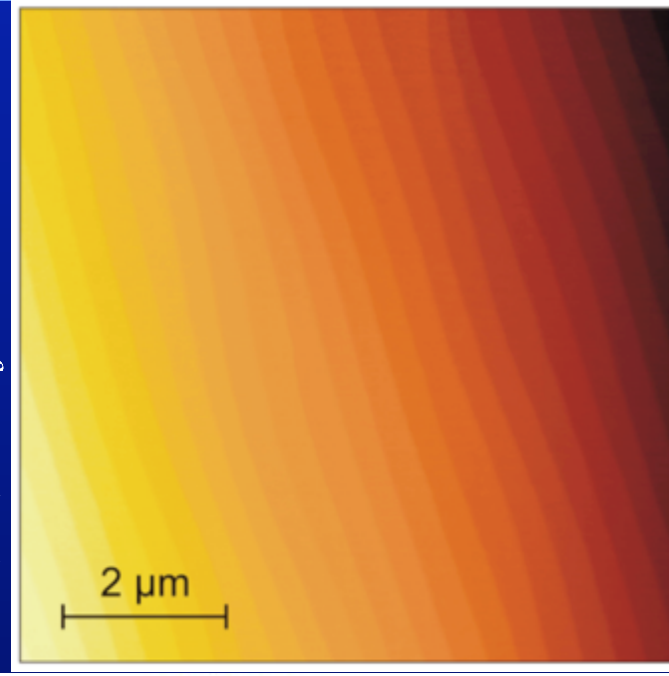
Surface Termination Recipes

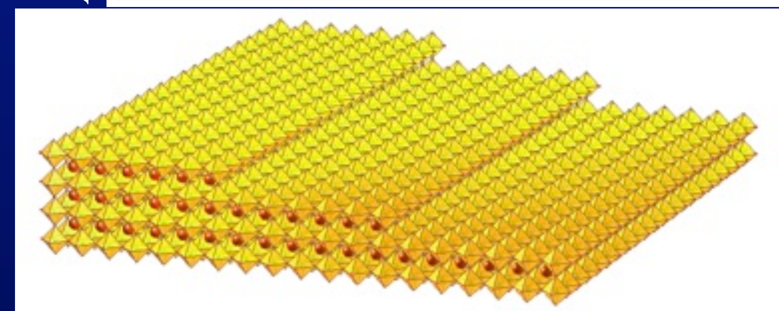
- **(100) and (111) $SrTiO_3$**
  G. Koster, B.L. Kropman, G.J.H.M. Rijnders, D.H.A. Blank, H. Rogalla, "Quasi-Ideal Strontium Titanate Crystal Surfaces through Formation of Strontium Hydroxide," *Applied Physics Letters* **73** (1998) 2920-2922.

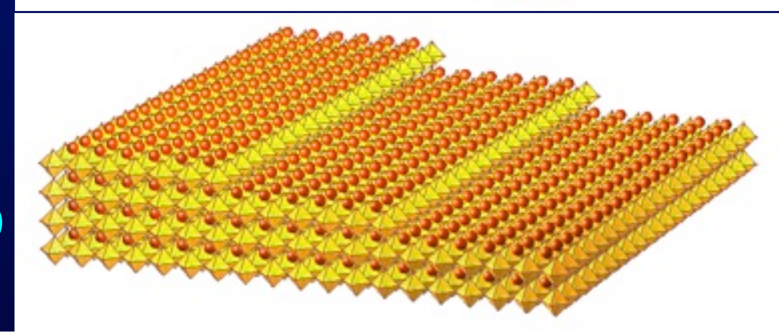
- **(110) *RE*ScO_3**
  J.E. Kleibeuker, G. Koster, W. Siemons, D. Dubbink, B. Kuiper, J.L. Blok, C-H. Yang, J. Ravichandran, R. Ramesh, J.E. ten Elshof, D.H.A. Blank, and G. Rijnders, "Atomically Defined Rare-Earth Scandate Crystal Surfaces," *Advanced Materials* **20** (2010) 3490-3496.

- **$(100)_p$ and $(111)_p$ $LaAlO_3$**
  J.L. Blok, X. Wan, G. Koster, D.H.A. Blank, and G. Rijnders, "Epitaxial Oxide Growth on Polar (111) Surfaces ," *Applied Physics Letters* **99** (2011) 151917 .

AFM (100) $SrTiO_3$—Jochen Mannhart

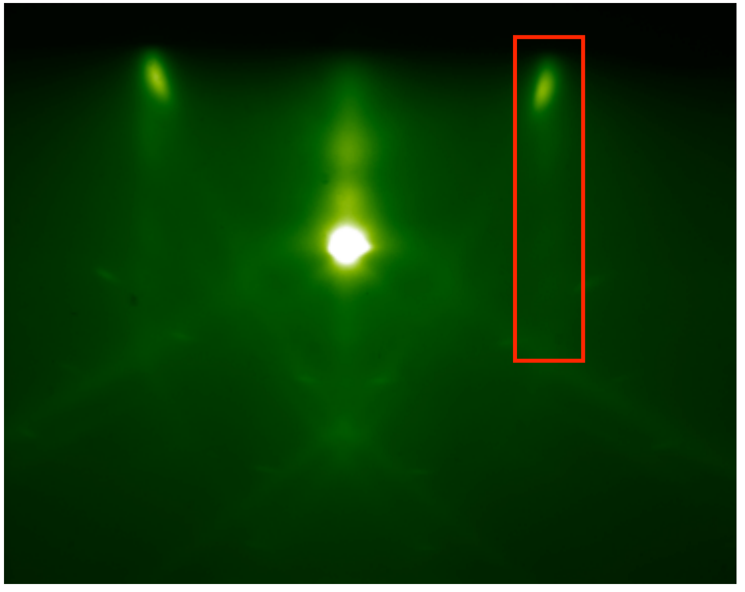


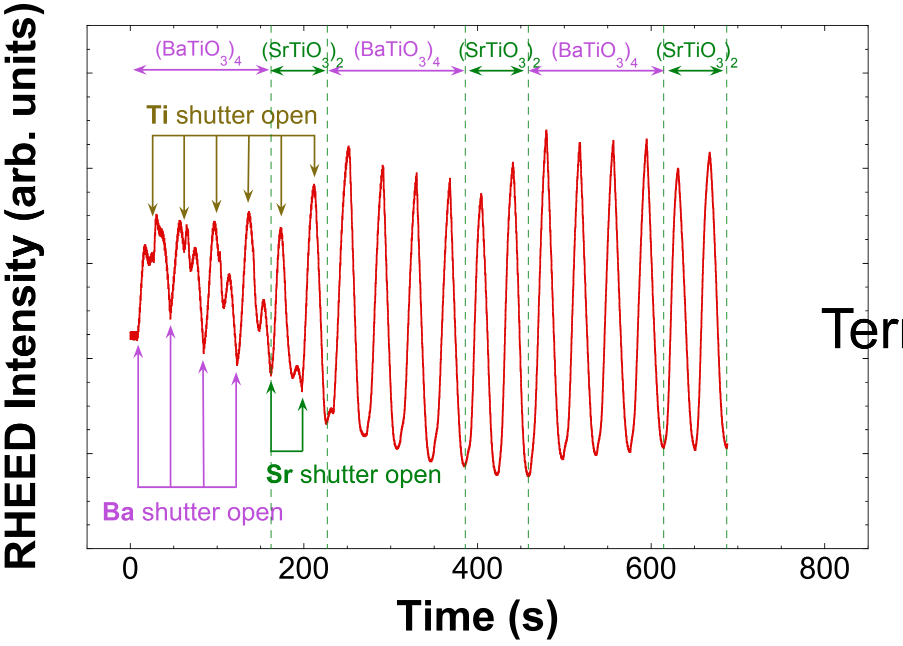




Terminated vs. Unterminated $SrTiO_3$

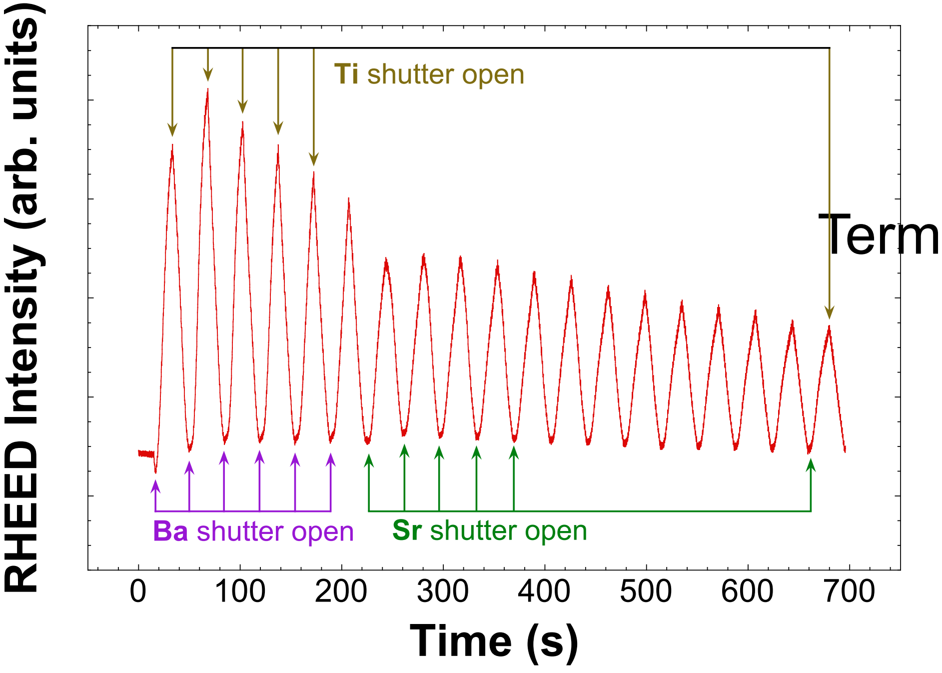
[110] azimuth





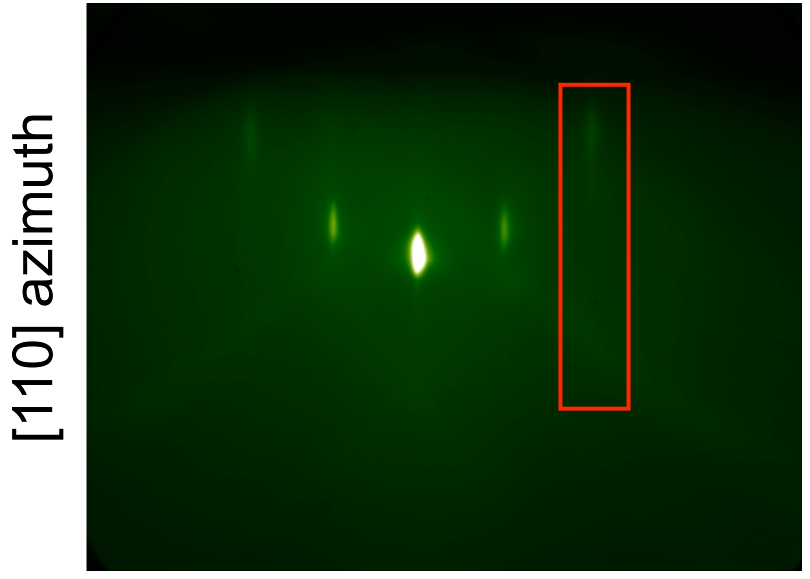
Not Terminated

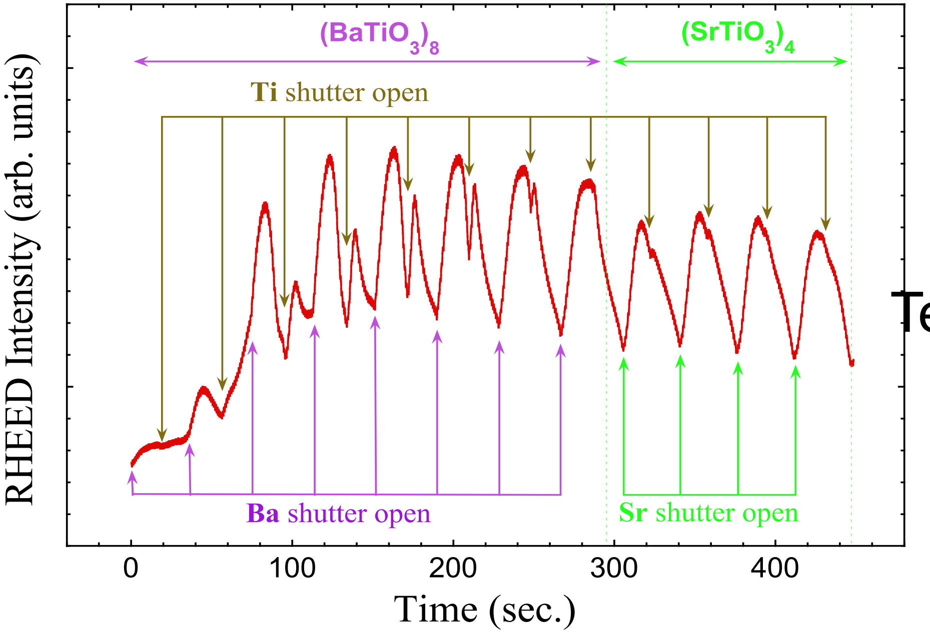
[100] azimuth



Terminated

Terminated vs. Unterminated $DyScO_3$





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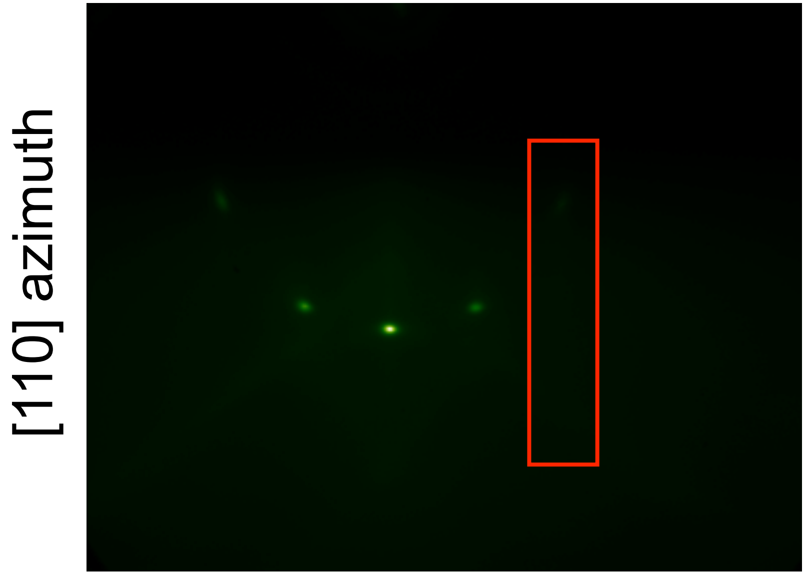
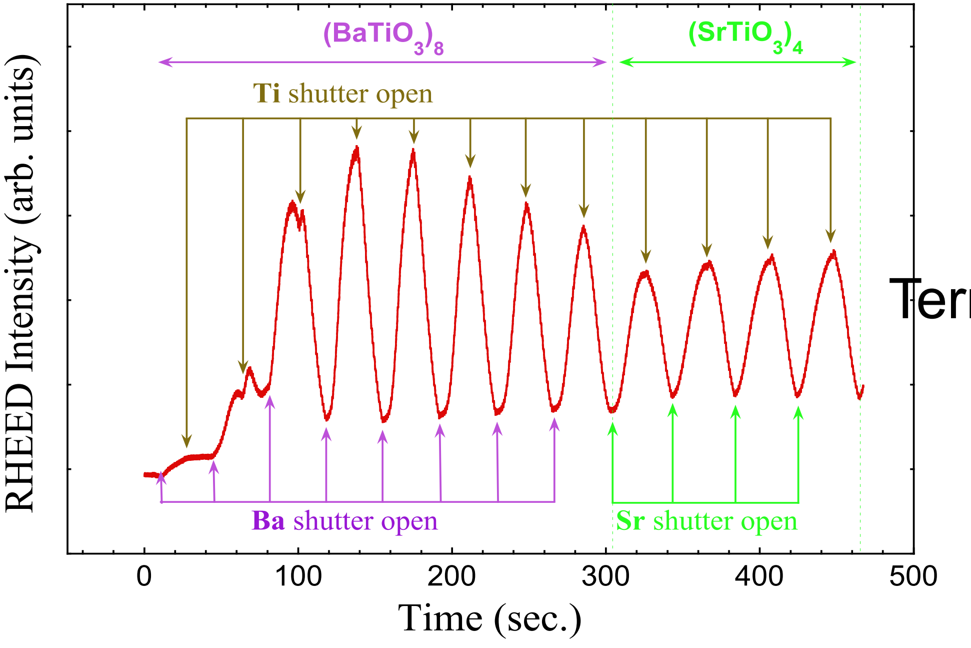
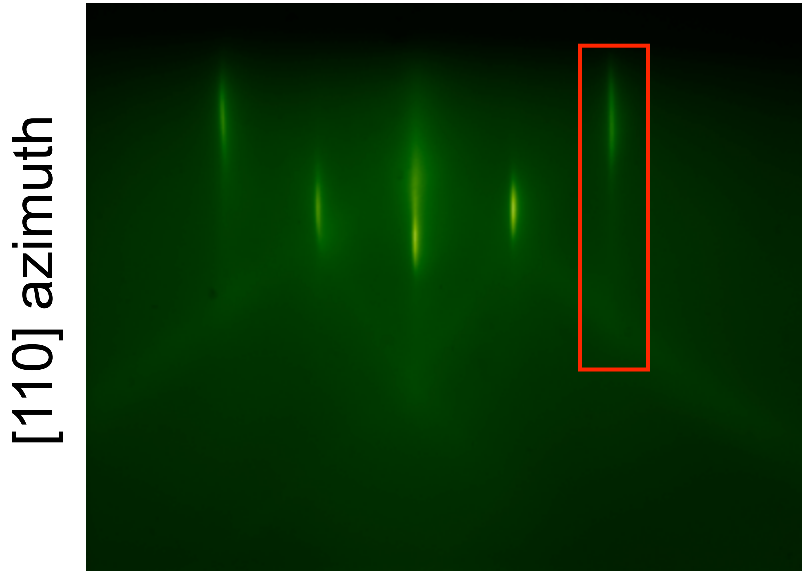
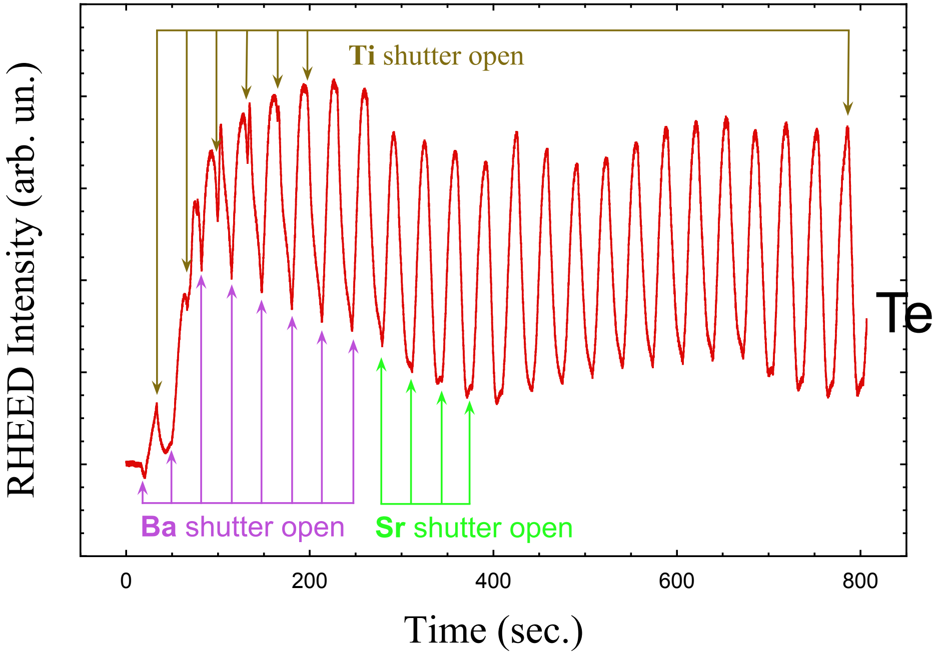




Terminated

Terminated vs. Unterminated $GdScO_3$





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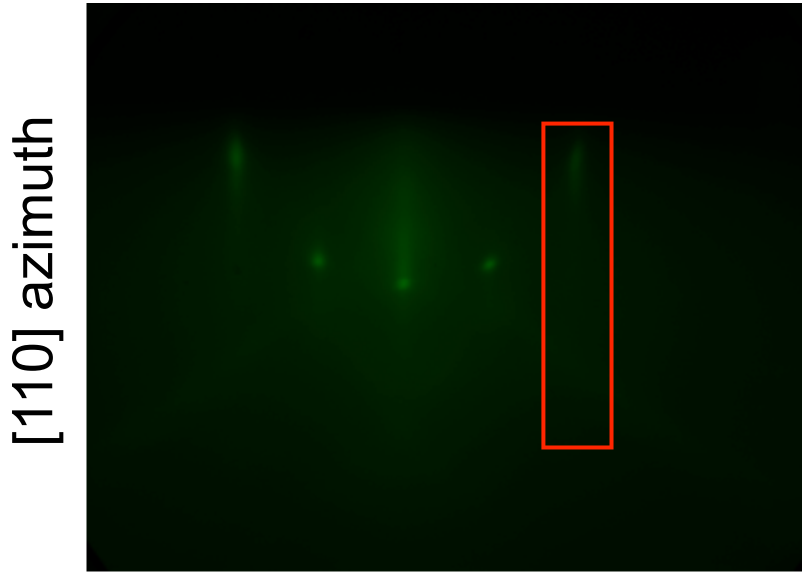
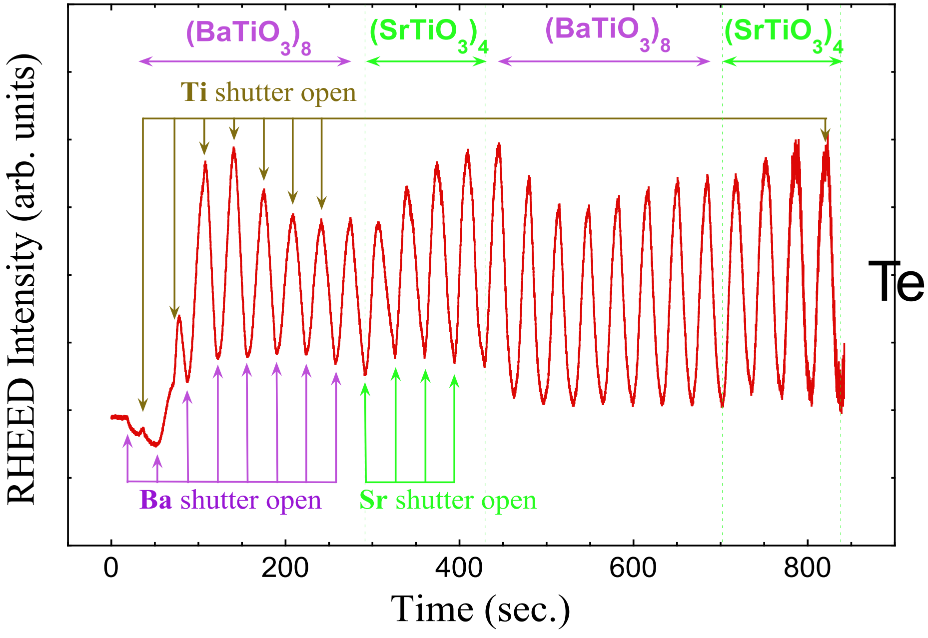
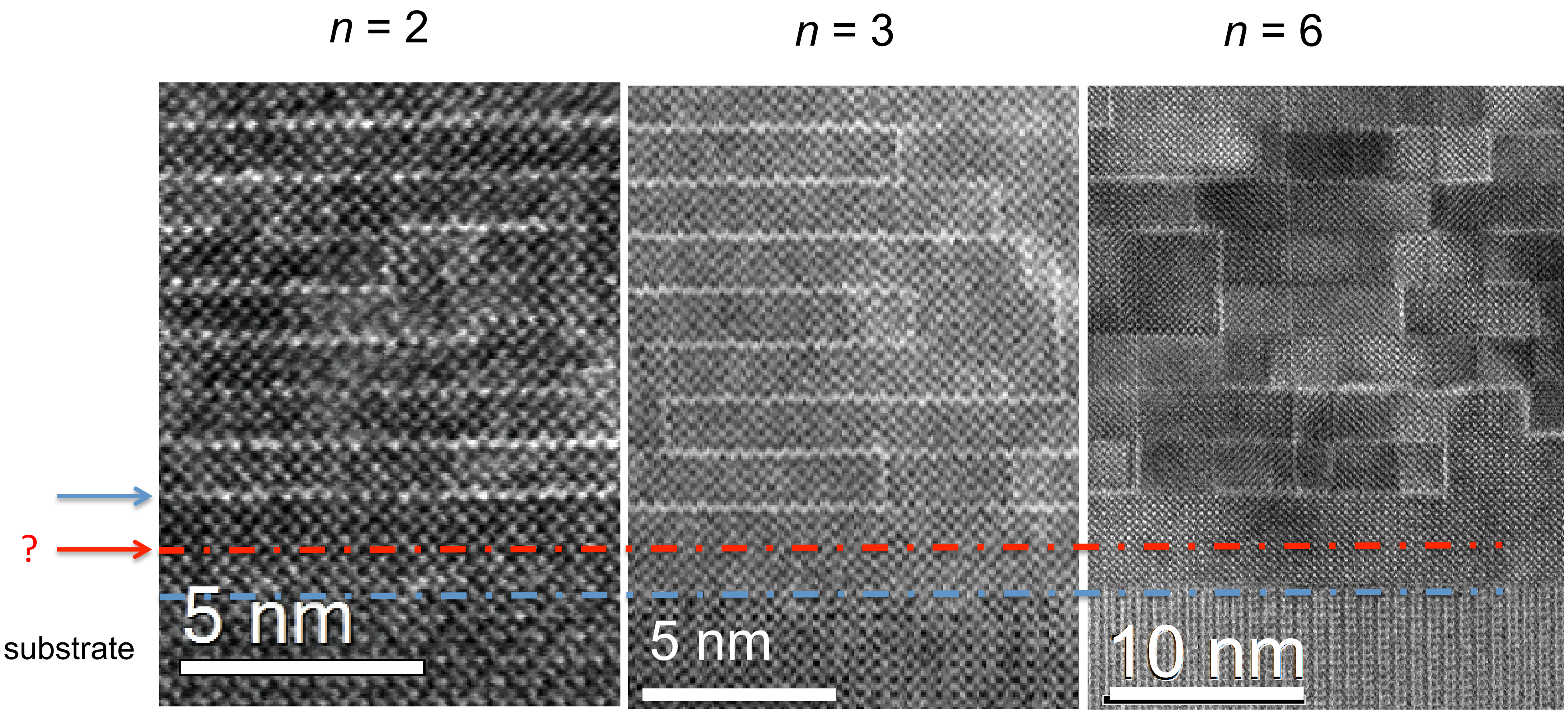


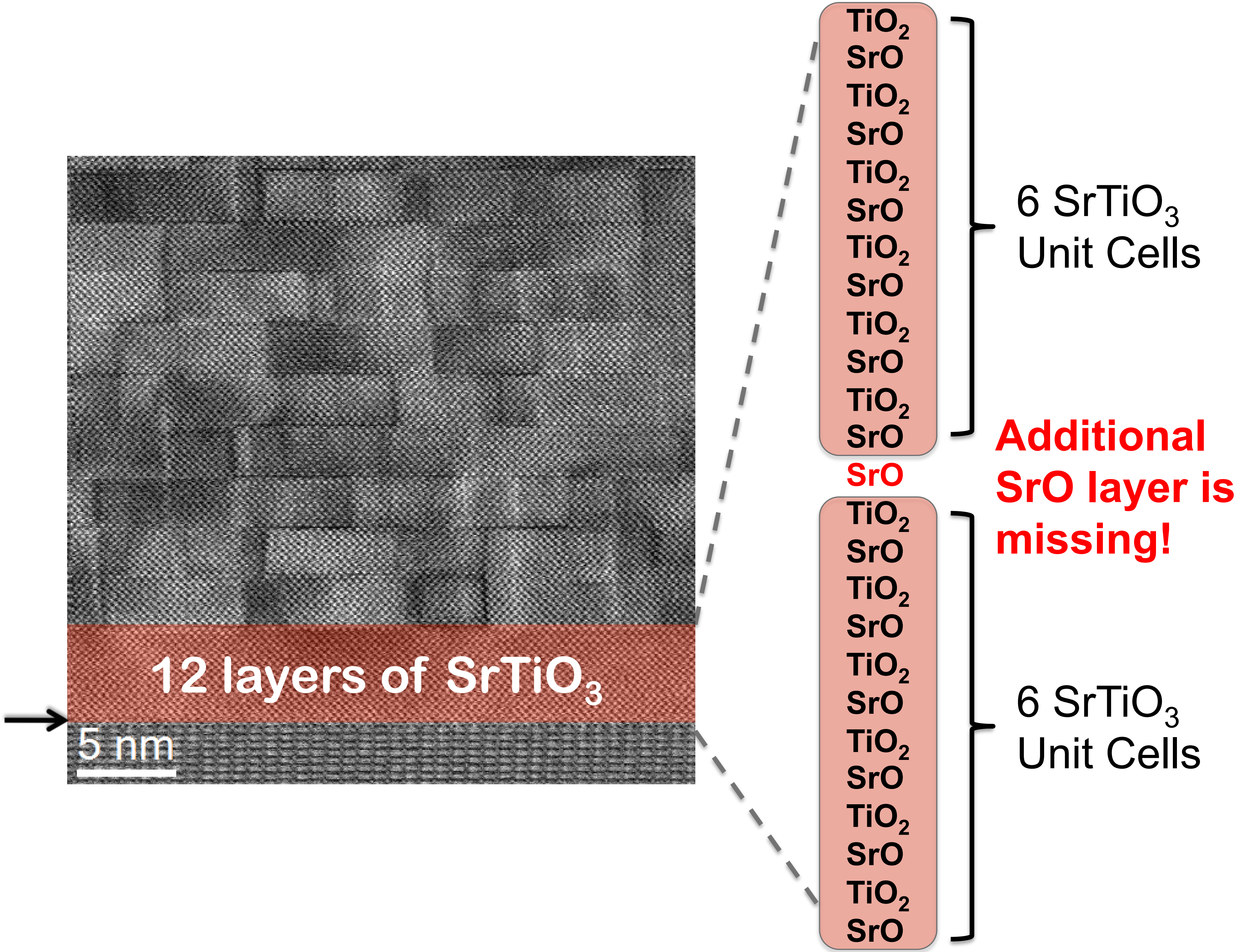


Terminated

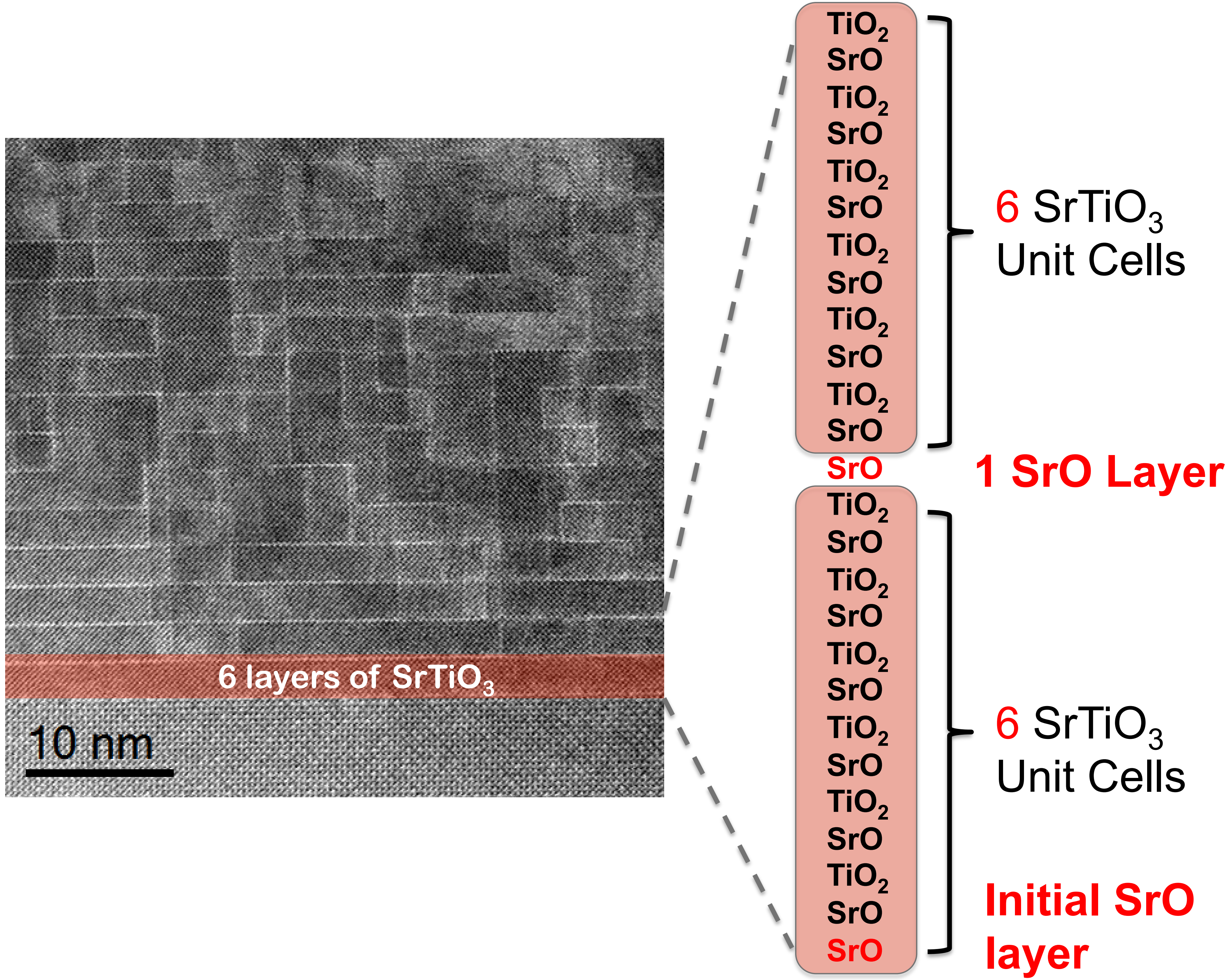
BF-STEM of n = 2, 3, 6 $(SrO)(SrTiO_3)_n$



In each case, the first SrO fault is missing – independent of *n*!



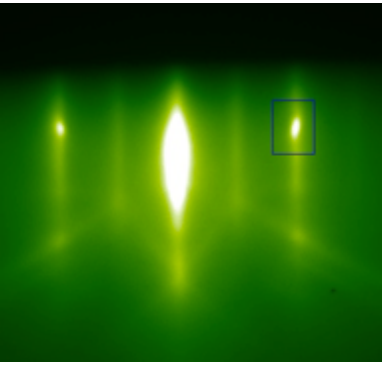
12 layers of $SrTiO_3$
5 nm
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
6 $SrTiO_3$ Unit Cells
SrO
Additional SrO layer is missing!
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
6 $SrTiO_3$ Unit Cells

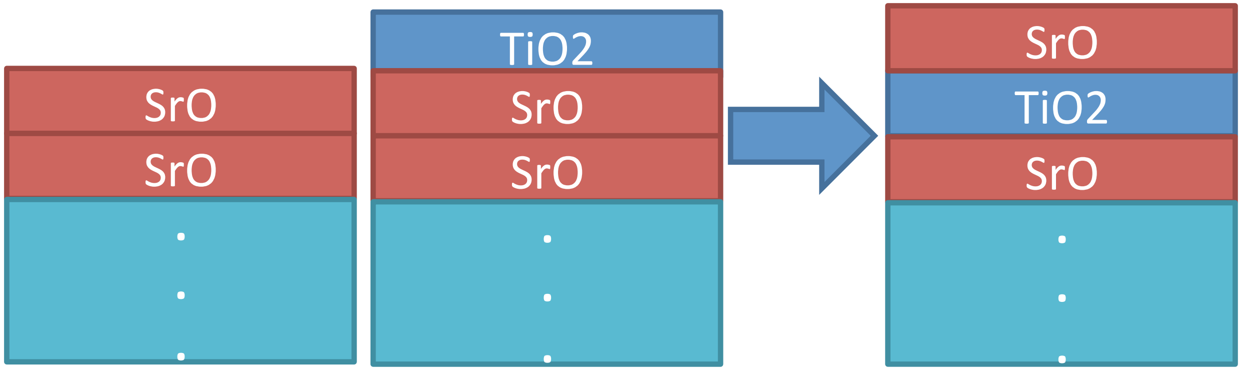


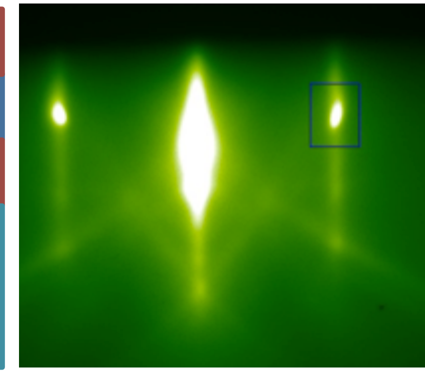
6 layers of $SrTiO_3$
10 nm
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
TiO_2
SrO
SrO
6 $SrTiO_3$ Unit Cells
1 SrO Layer
6 $SrTiO_3$ Unit Cells
Initial SrO layer

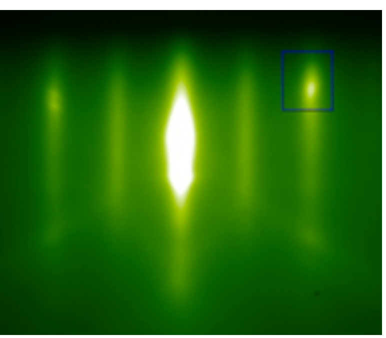
≥ 1 SrO Layer Yields RHEED Half-Order

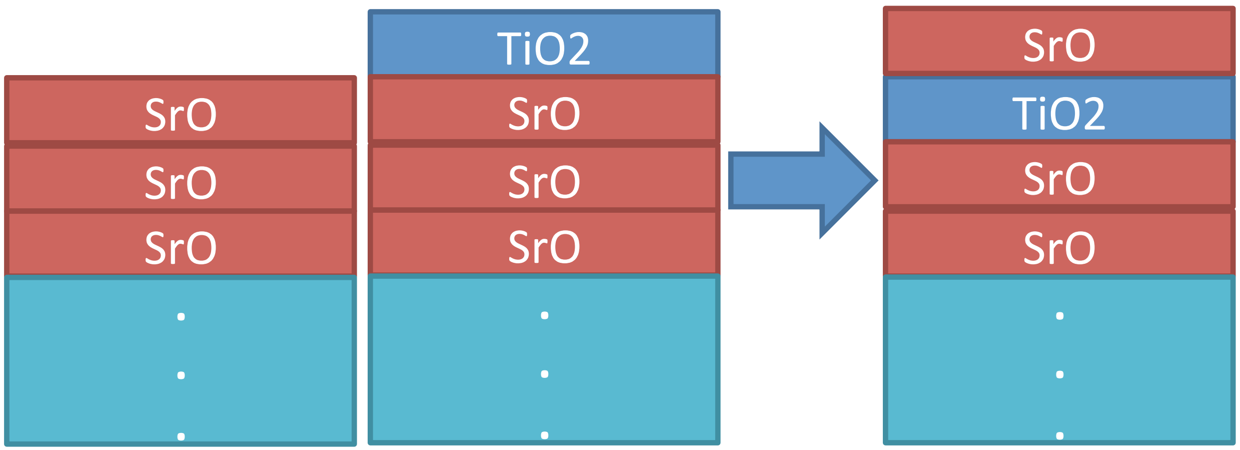
Unstable
double SrO layer

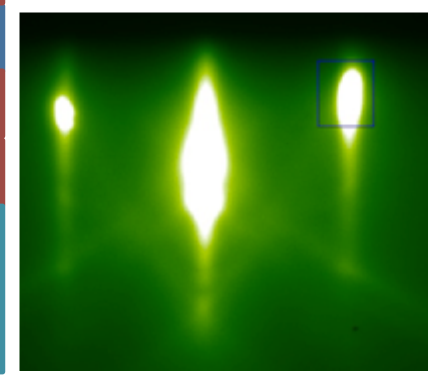












[110] Azimuth

3 layers of SrO is needed in forming double Sr layer

[110] Azimuth

Oxide MBE + ARPES Team