Establishing How Oxide Films Grow: An Essential Part of the Materials-by-Design Dream

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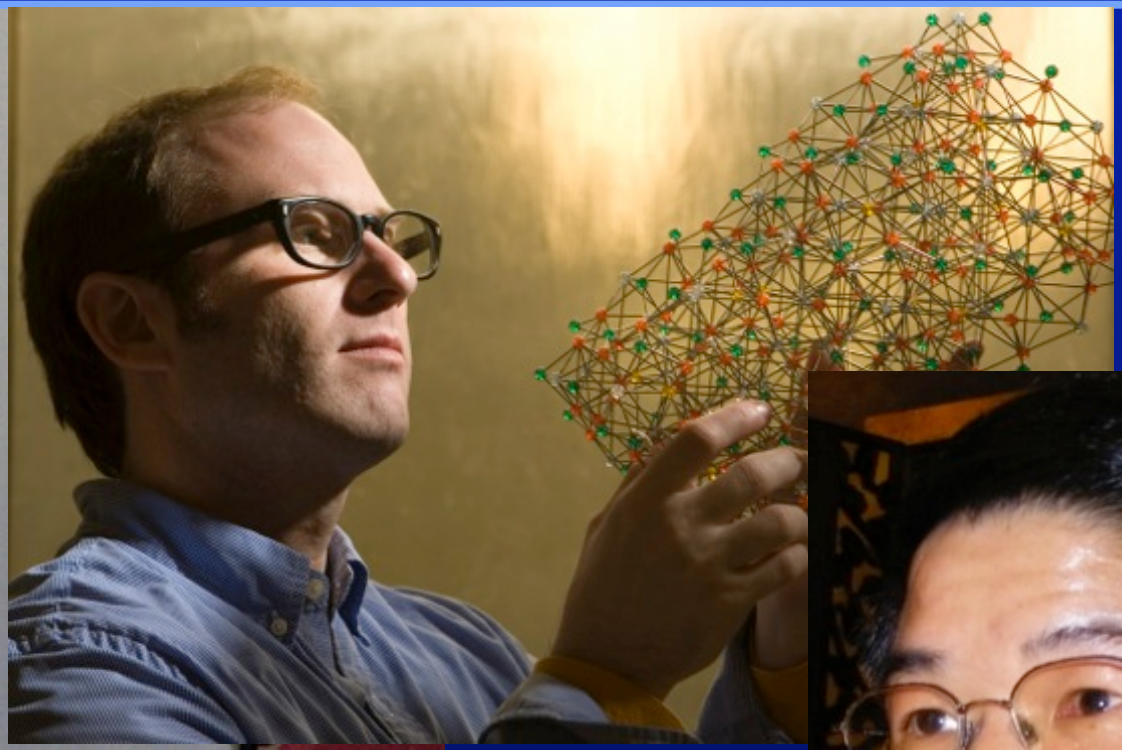
Outline

- **Examples of Oxide Materials by Design**
- **Surprise that Highlights Importance of Understanding How different Oxides Grow**
- **What Oxide MBE on APS can bring**
  - ***Understanding How Oxides Grow***
  - ***Composition Control—Measure Film Stoichiometry During Growth with 100 ppm Accuracy***
  - ***Interface Evolution (including buried interfaces)—Structure, Local Magnetism, Oxidation State, Electronic Reconstruction, Imaging***
  - ***Realization of the "Materials by Design" Dream!***

Oxide Designers

Karin Rabe (Rutgers)



Craig Fennie (Cornell)

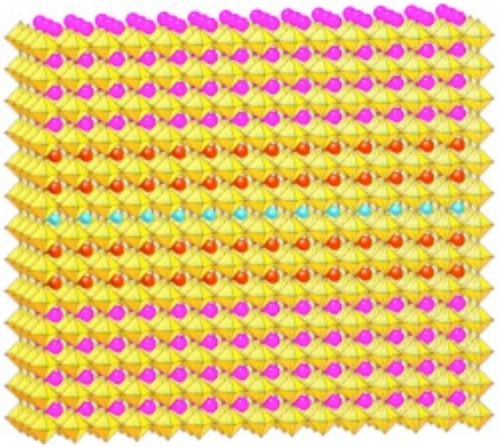
LongQing Chen (Penn State)

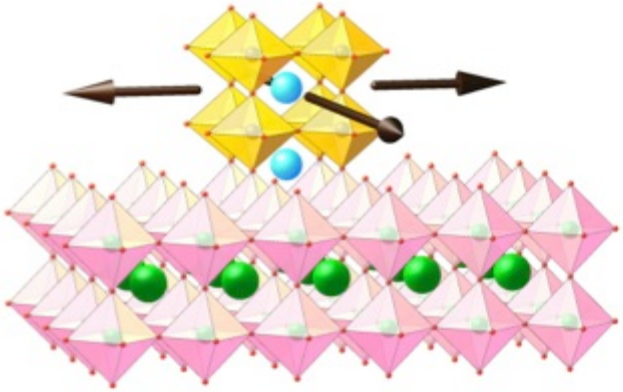
Materials by Design

- **Enhancing Existing Ground States**
  - **$BaTiO_3$**
- **Unleashing Hidden Ground States**
  - **$EuTiO_3$**
    strongest ferromagnetic ferroelectric
  - **$Sr_7Ti_6O_{19}$**
    highest performance tunable dielectric
- **Toolkit and Synthesis Science enabling Materials-by-Design of Oxide Thin Films**

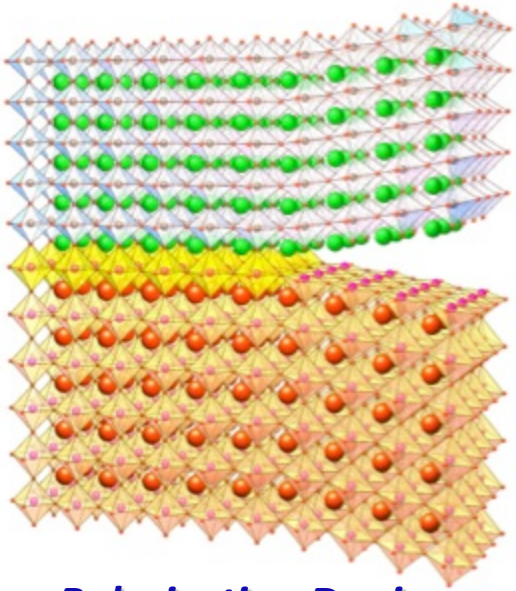
Oxide Thin-Film Toolbox

Interface Engineering



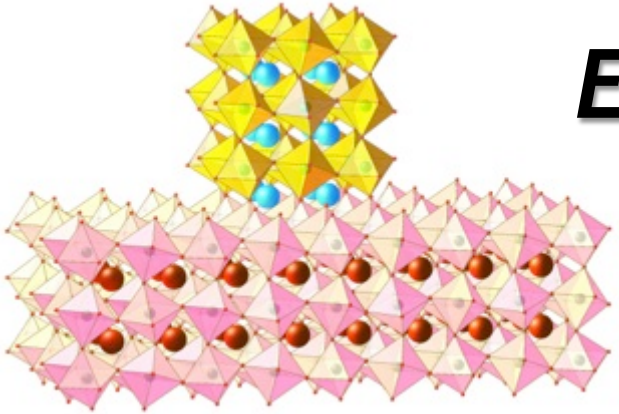


Strain Engineering

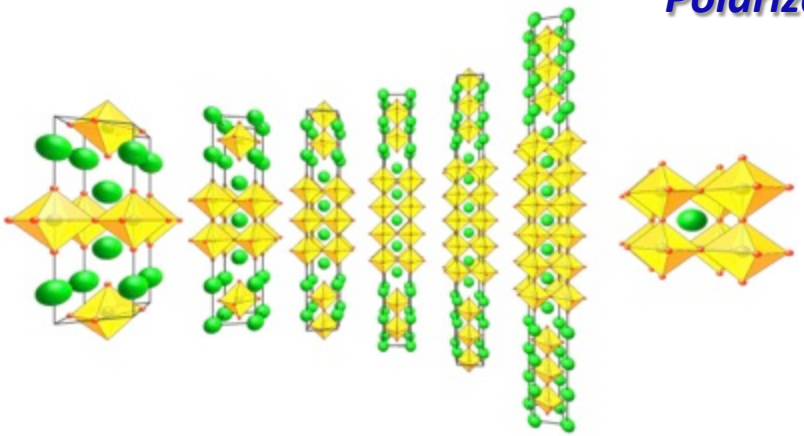


Polarization Doping

Epitaxial Engineering

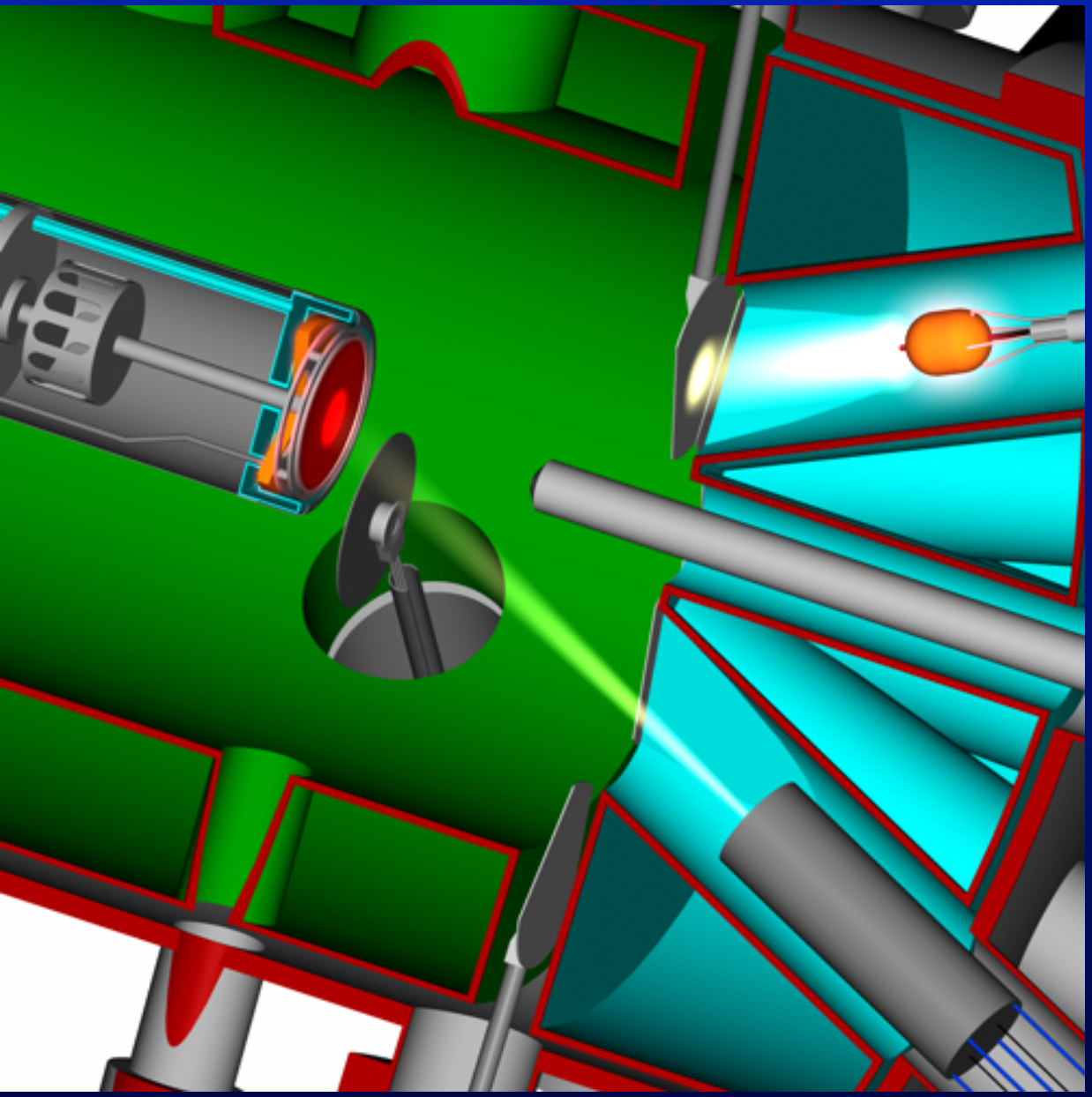


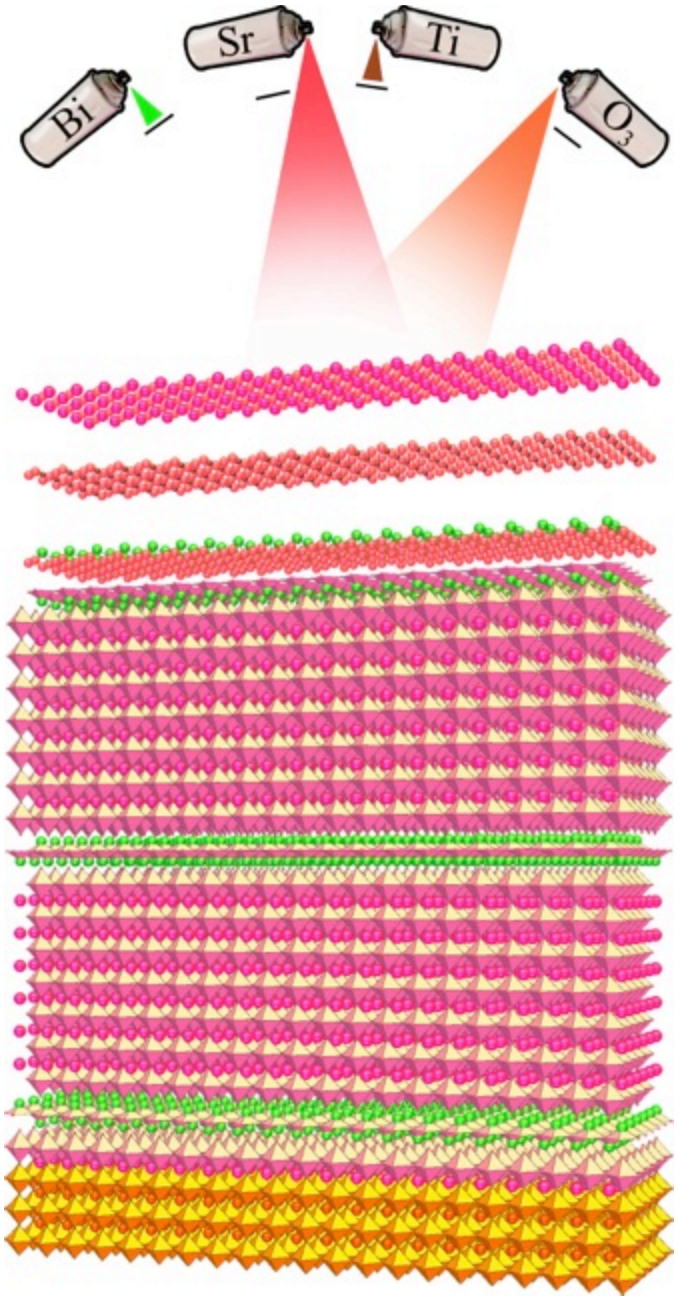
Epitaxial Stabilization



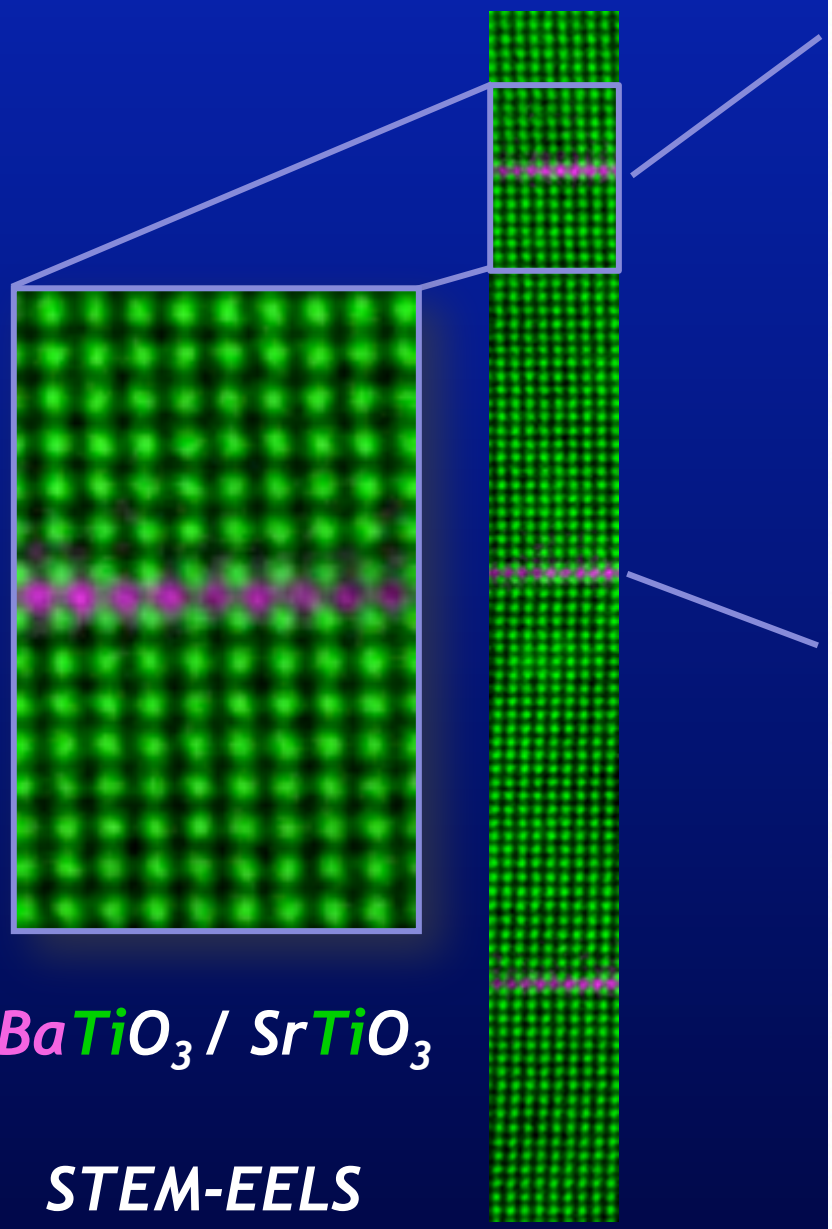
Dimensional Confinement

MBE ≈ Atomic Spray Painting



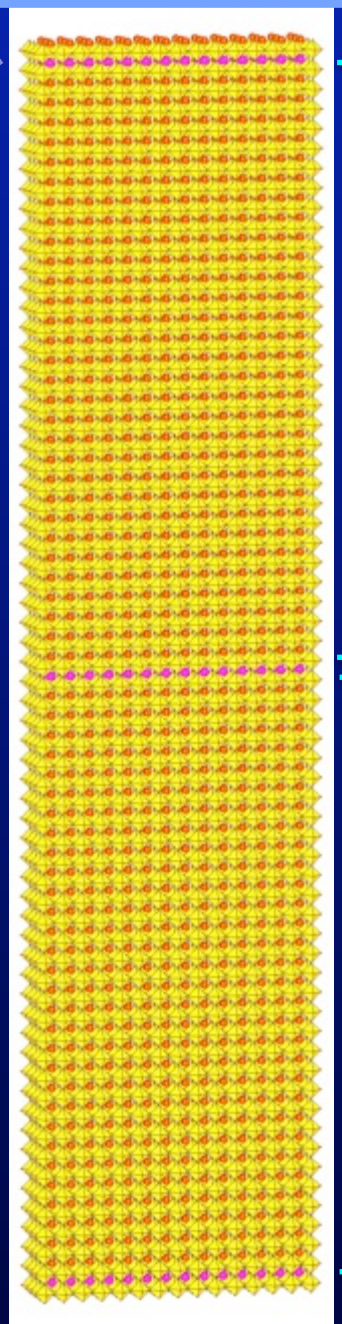


Creating New Oxides



$BaTiO_3$ / $SrTiO_3$

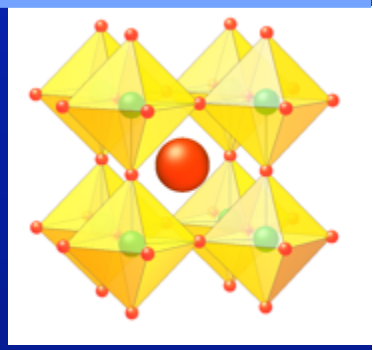
STEM-EELS



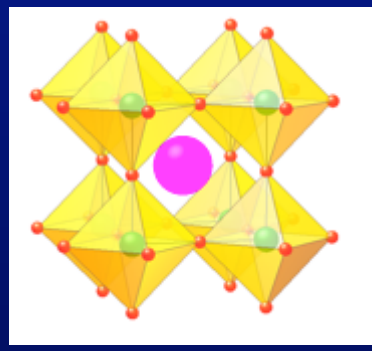
$(SrTiO_3)_{30}$

$(BaTiO_3)_1$

$(SrTiO_3)_{30}$



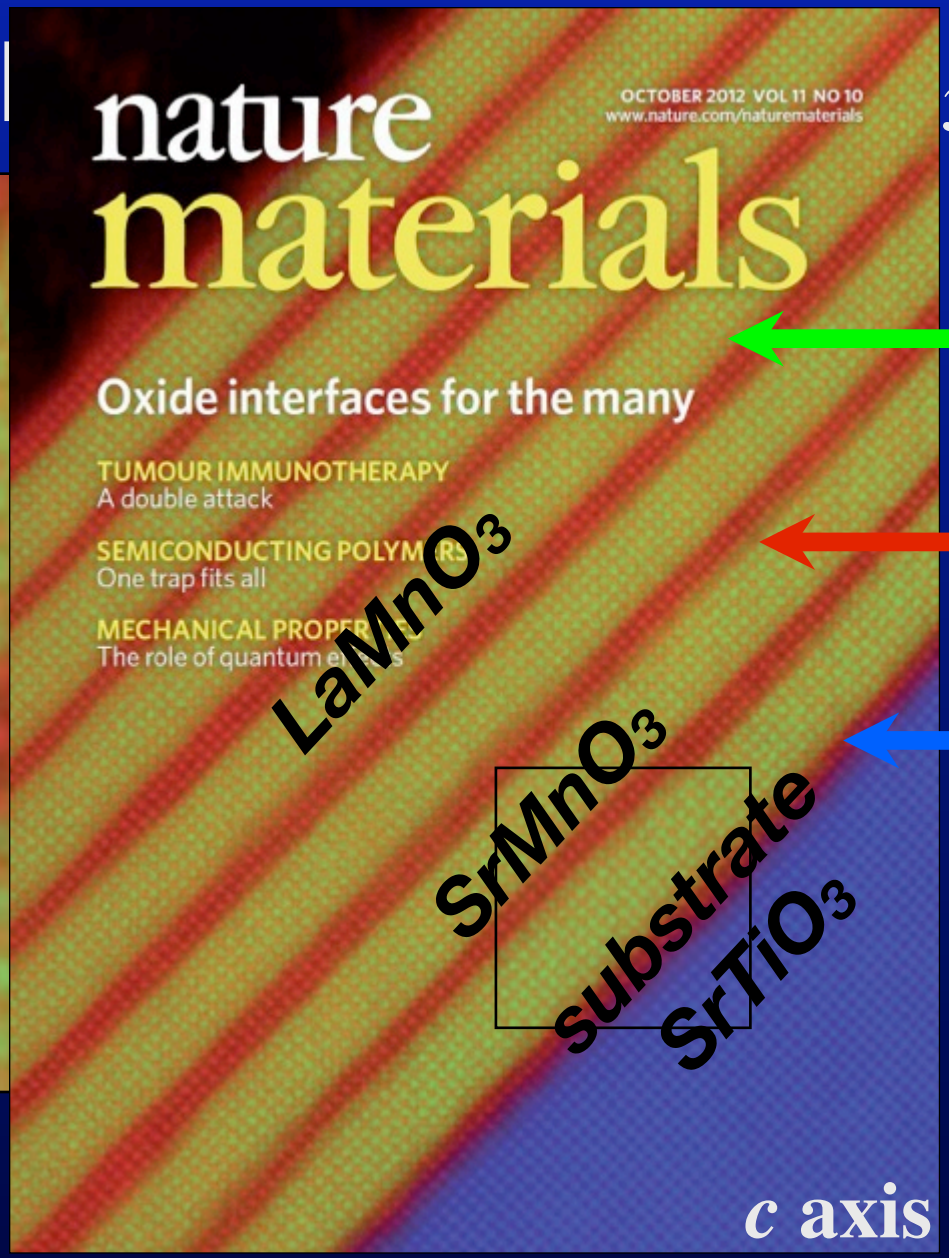
$SrTiO_3$



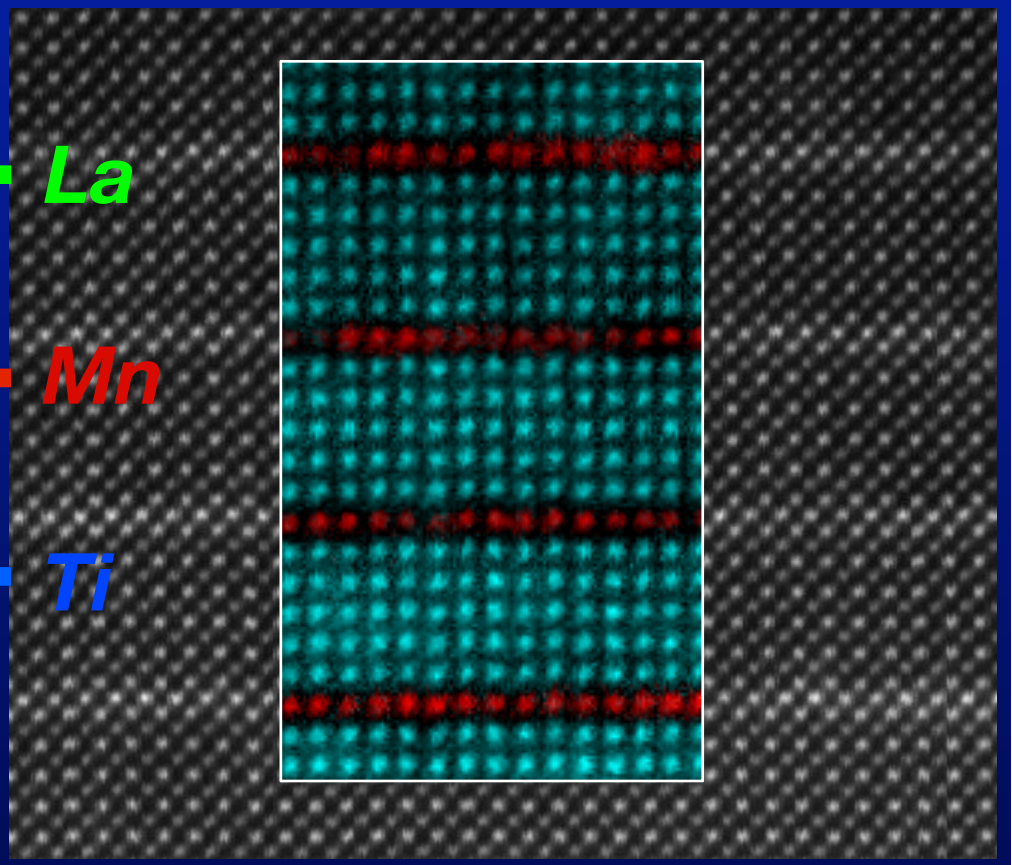
$BaTiO_3$

J. Ravichandran, A.K. Yadav, R. Cheaito, P.B. Rossen, A. Soukiassian, S.J. Suresha, J.C. Duda, B.M. Foley, C.H. Lee, Y. Zhu, A.W. Lichtenberger, J.E. Moore, D.A. Muller, D.G. Schlom, P.E. Hopkins, A. Majumdar, R. Ramesh, and M.A. Zurbuchen *Nature Materials* **13** (2014) 168-172.

Creating New Oxides



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

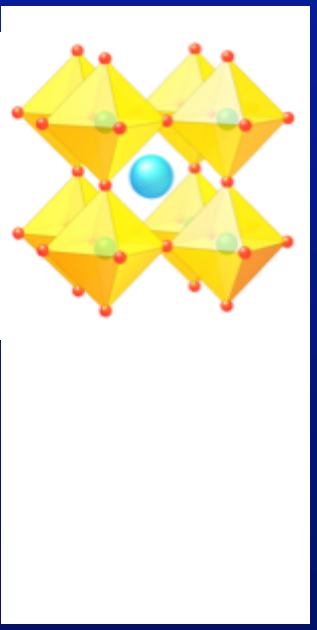


Red = Ru **Teal = Ti**

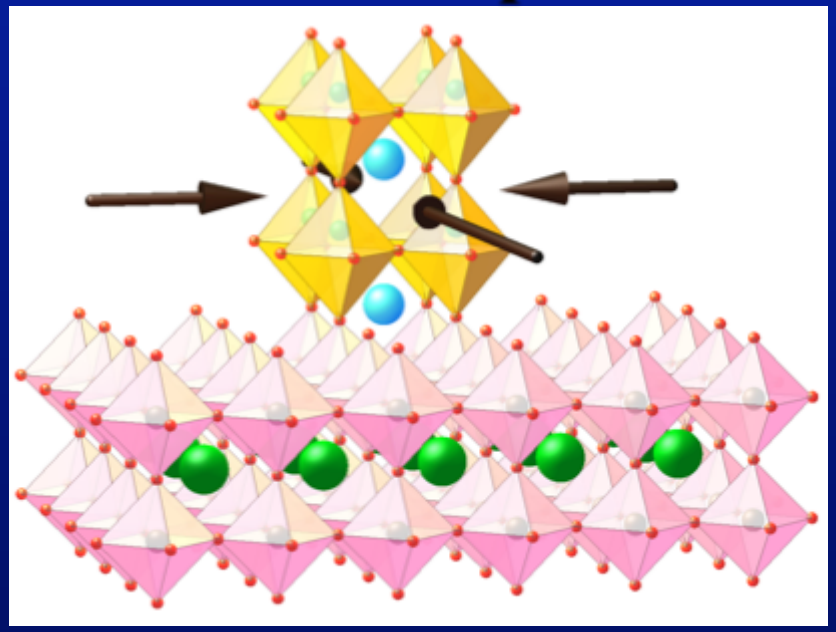
E.J. Monkman, C. Adamo, J.A. Mundy, D.E. Shai, J.W. Harter, D. Shen, B. Burganov, D.A. Muller, D.G. Schlom, and K.M. Shen, *Nature Materials* **11** (2012) 855-859.

Biaxial Strain via Epitaxy

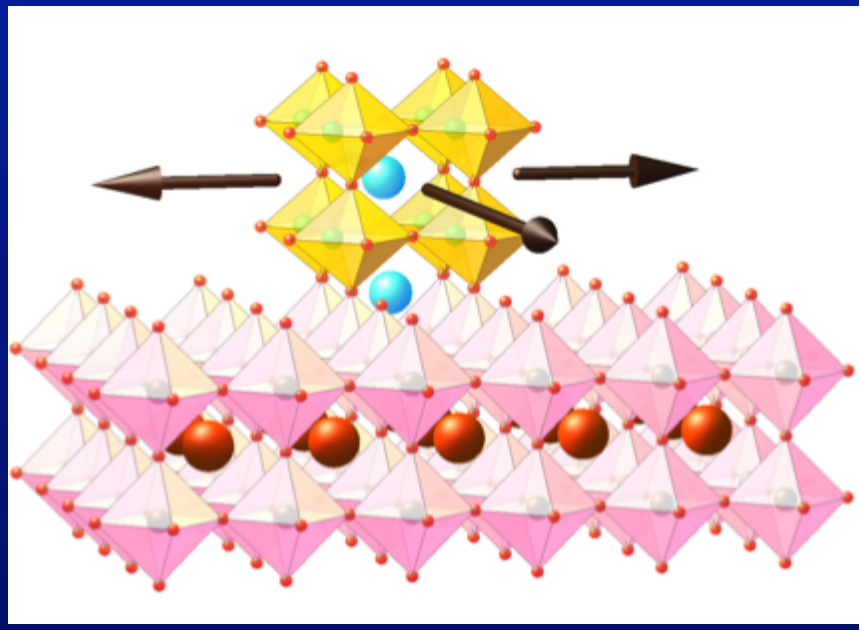
No Strain



Biaxial Compression

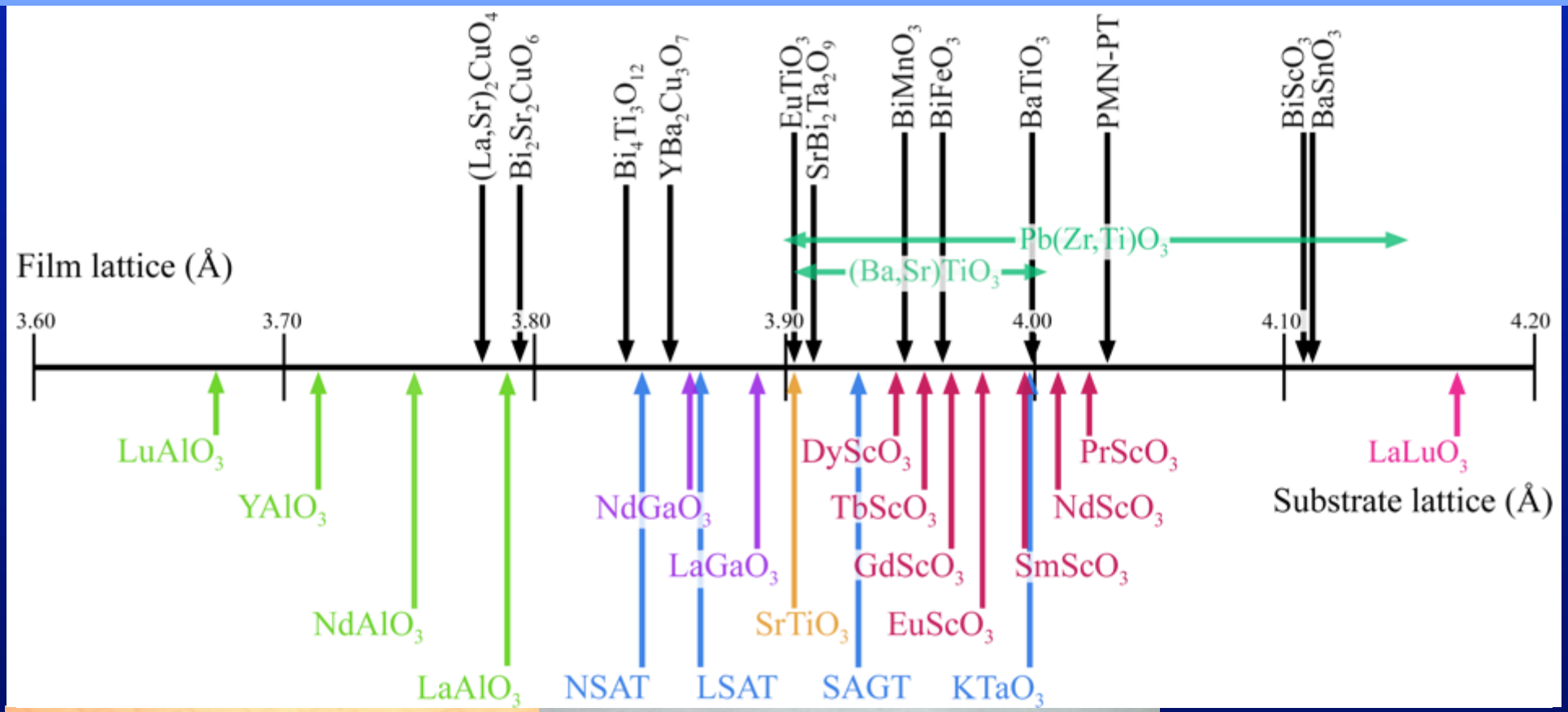


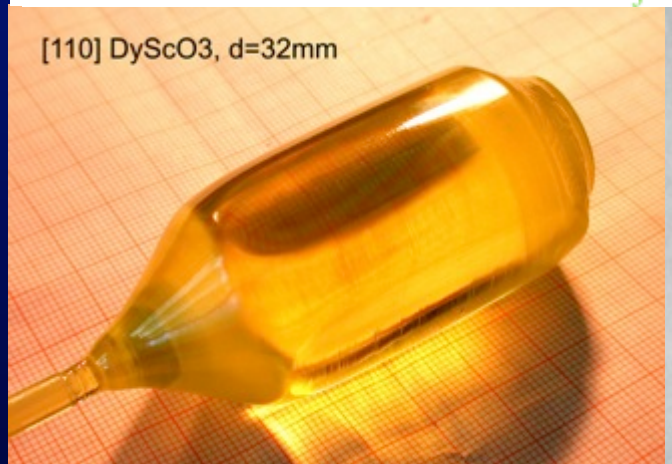
Biaxial Tension



The **Strain** *Game*

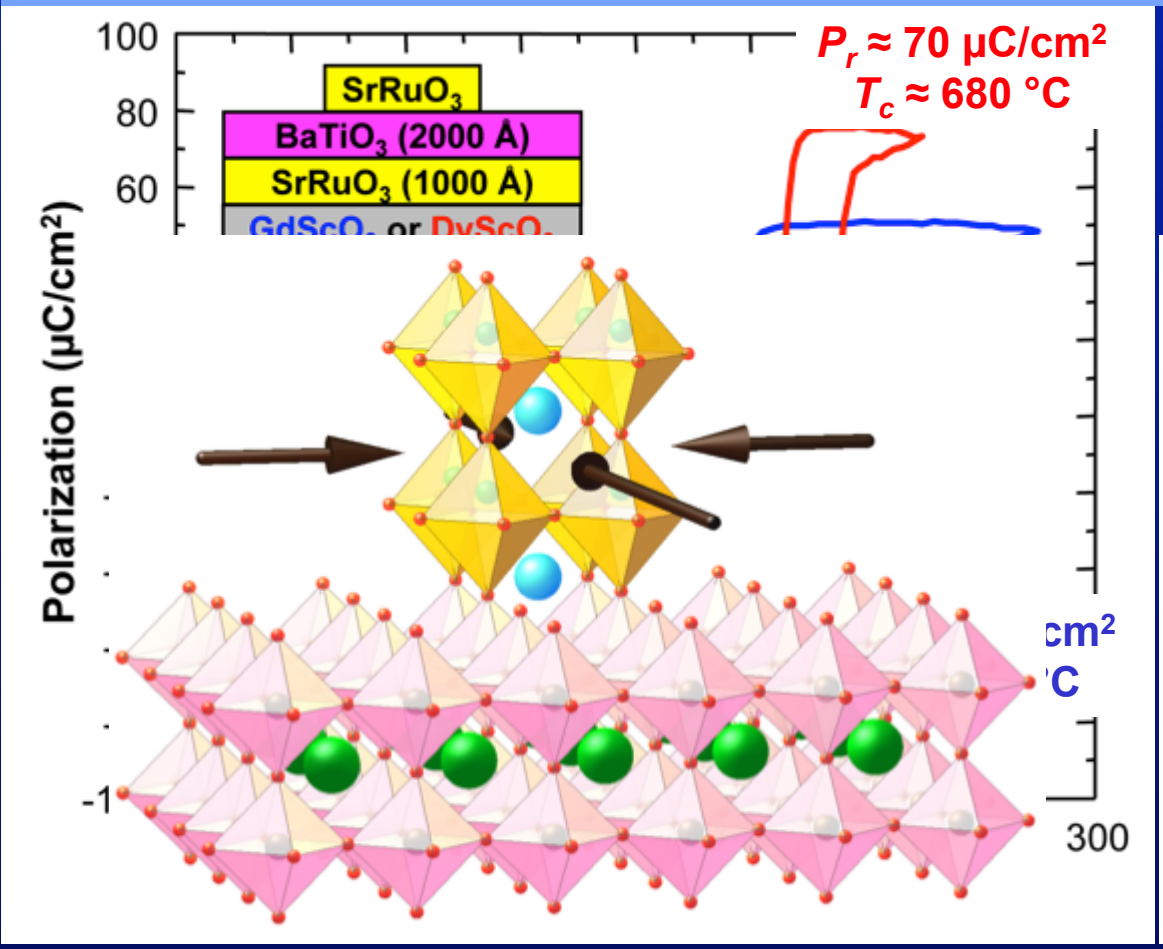
Perovskite Substrates — Today



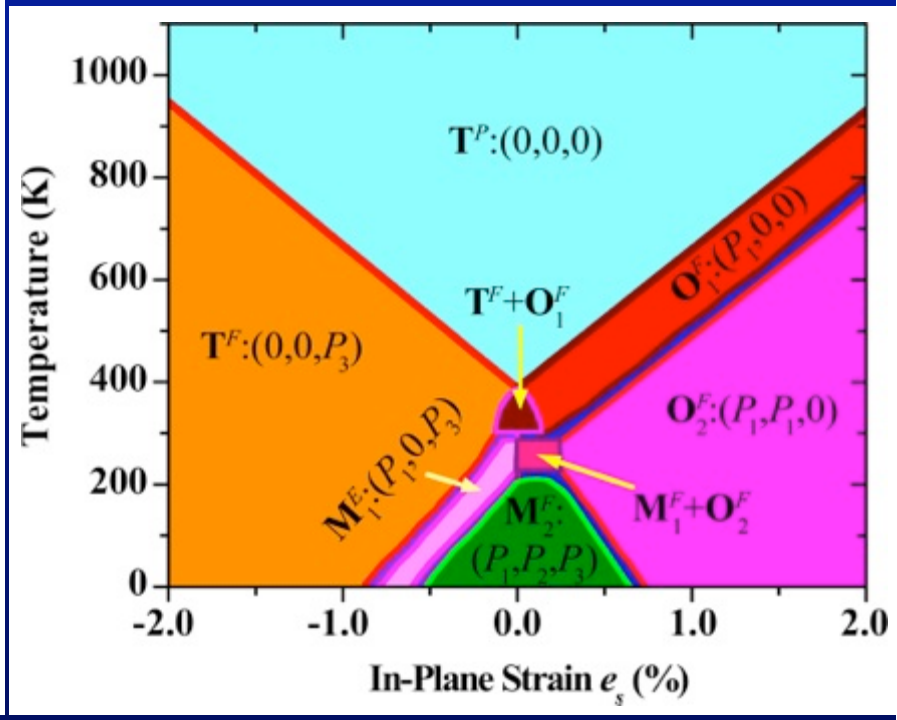


D.G. Schlom, L.Q. Chen, C.J. Fennie, V. Gopalan, D.A. Muller, X.Q. Pan, R. Ramesh, and R. Uecker, "Elastic Strain Engineering of Ferroic Oxides," *MRS Bulletin* **39** (2014) 118-130.

Enhancing Pb-Free Ferroelectrics



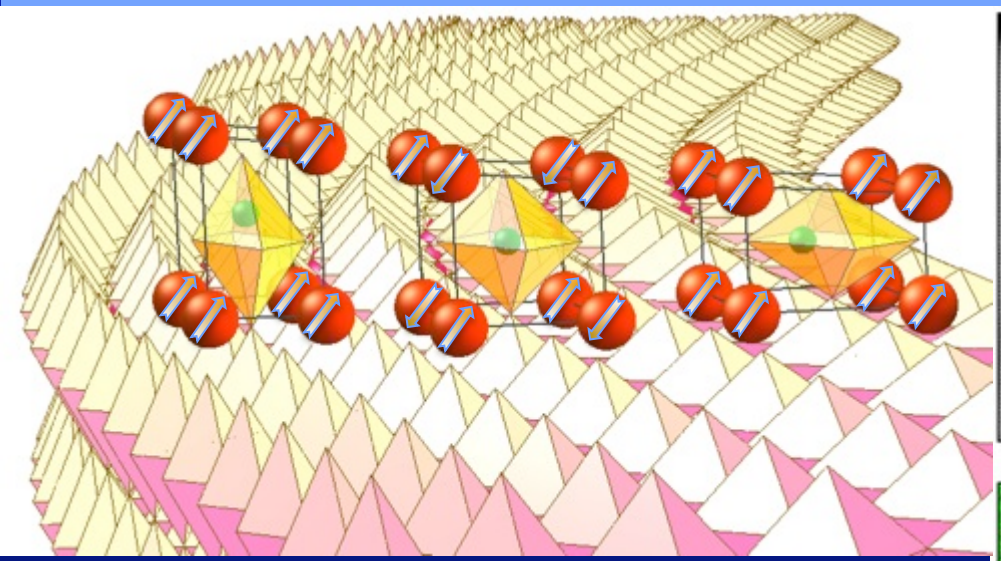
Predicted Effect of Strain on $BaTiO_3$

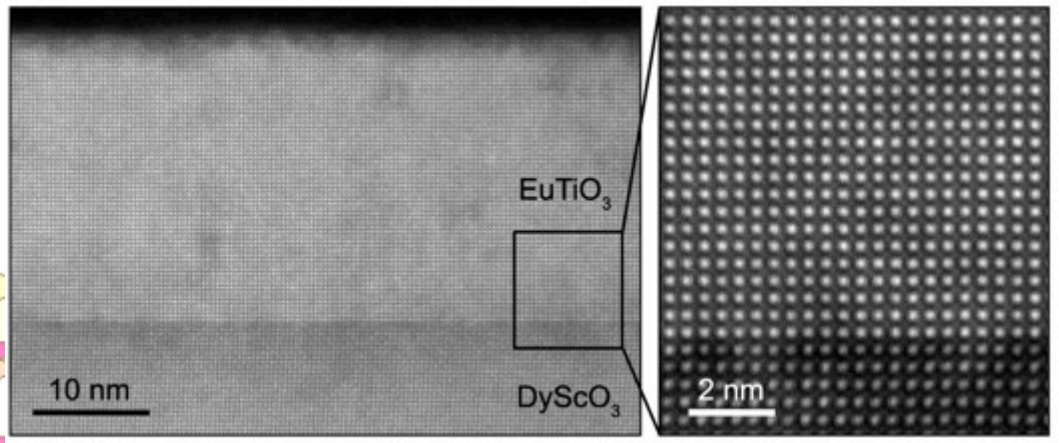


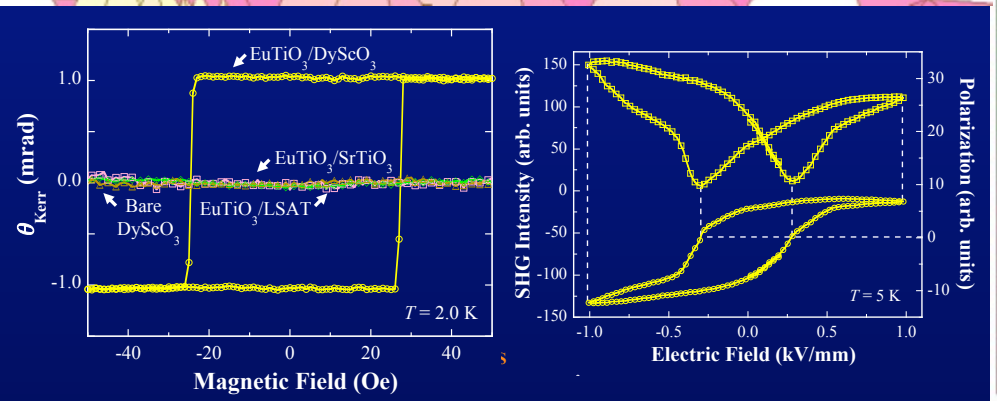
$BaTiO_3$ (a model ferroelectric) **+** **1.7% Strain** (by growing it commensurately) **=** **Pb-Free Ferroelectric** (with properties comparable to best leaded ferroelectric)

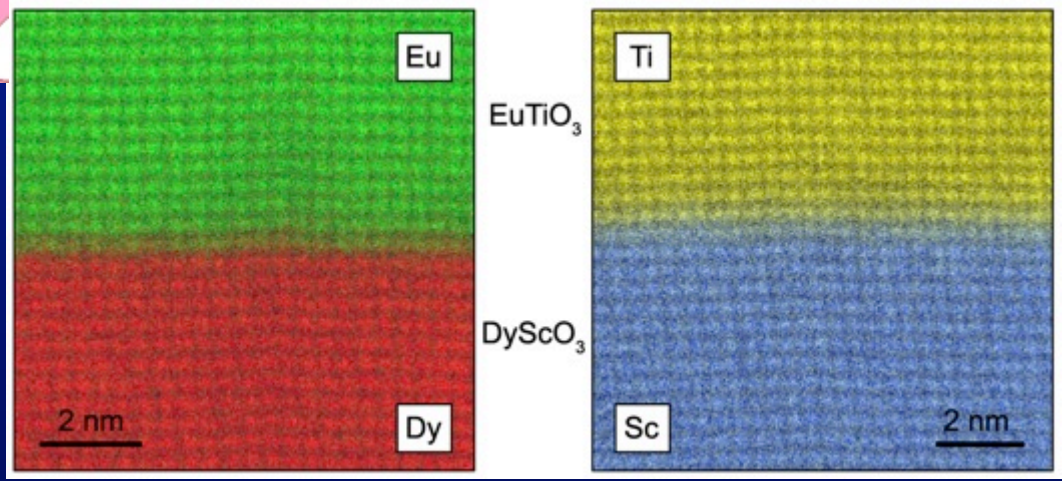
K.J. Choi, M. Biegalski, Y.L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y.B. Chen, X.Q. Pan, V. Gopalan, L.-Q. Chen, D.G. Schlom, and C.B. Eom, *Science* **306** (2004) 1005-1009.

Strongest Ferromagnetic Ferroelectric





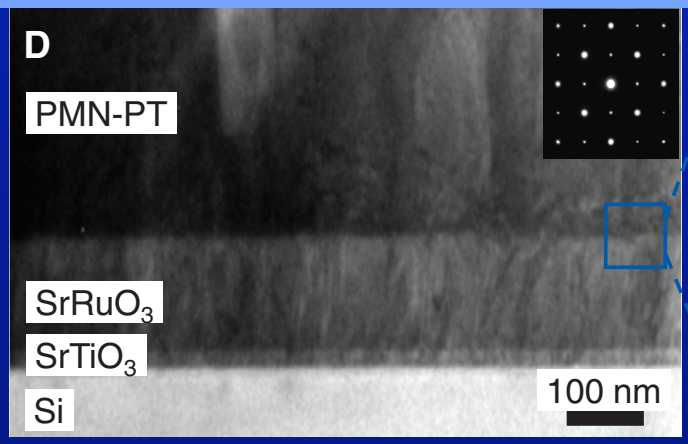


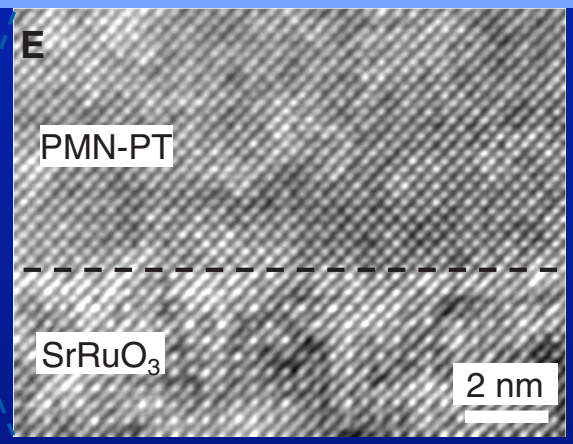


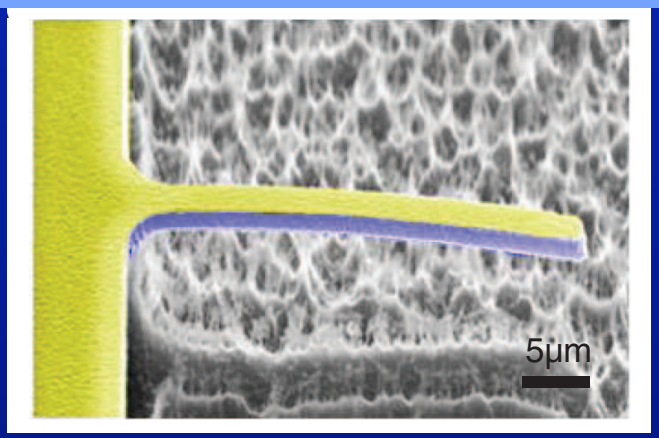
22 nm thick $EuTiO_3$ (a boring dielectric) + **1.1% Strain (by growing it commensurately)** = **Multiferroic (1000× stronger than prior ferromagnetic ferroelectrics)**

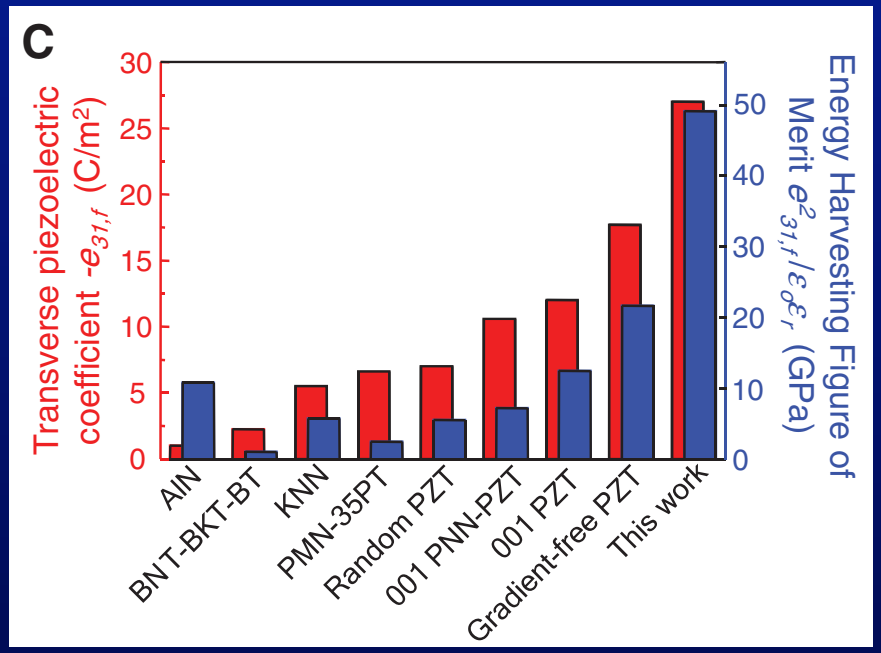
J.H. Lee, L. Fang, E. Vlahos, X. Ke, Y.W. Jung, L.F. Kourkoutis, J-W. Kim, P.J. Ryan, T. Heeg, M. Roeckerath, V. Goian, M. Bernhagen, R. Uecker, P.C. Hammel, K.M. Rabe, S. Kamba, J. Schubert, J.W. Freeland, D.A. Muller, C.J. Fennie, P. Schiffer, V. Gopalan, E. Johnston-Halperin, and D.G. Schlom, *Nature* **466** (2010) 954-958.

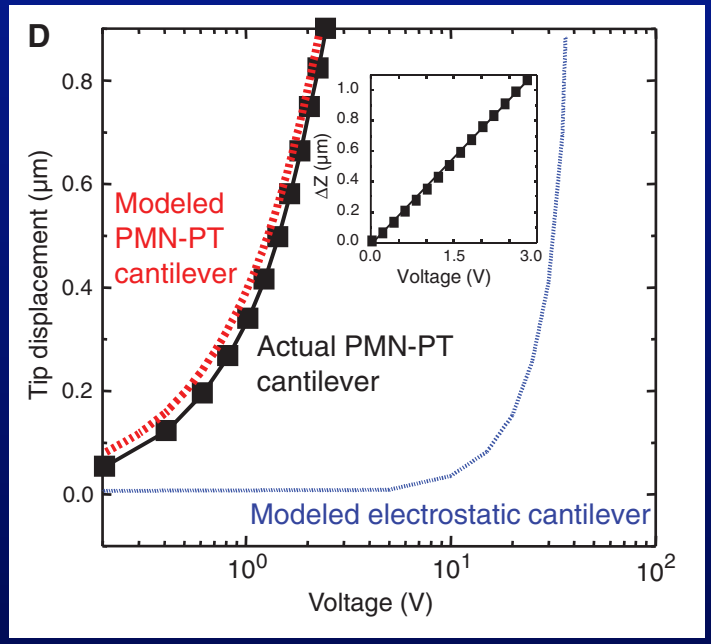
Piezoelectric PMN-PT on Silicon





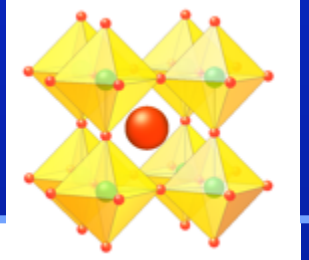






S.H. Baek, J. Park, D.M. Kim, V.A. Aksyuk, R.R. Das, S.D. Bu, D.A. Felker, J. Lettieri, V. Vaithyanathan, S.S.N. Bharadwaja, N. Bassiri-Gharb, Y.B. Chen, H.P. Sun, C.M. Folkman, H.W. Jang, D.J. Kreft, S.K. Streiffer, R. Ramesh, X.Q. Pan, S. Trolier-McKinstry, D.G. Schlom, M.S. Rzchowski, R.H. Blick, and C.B. Eom, "Giant Piezoelectricity on Si for Hyperactive MEMS," *Science* **334** (2011) 958-961.

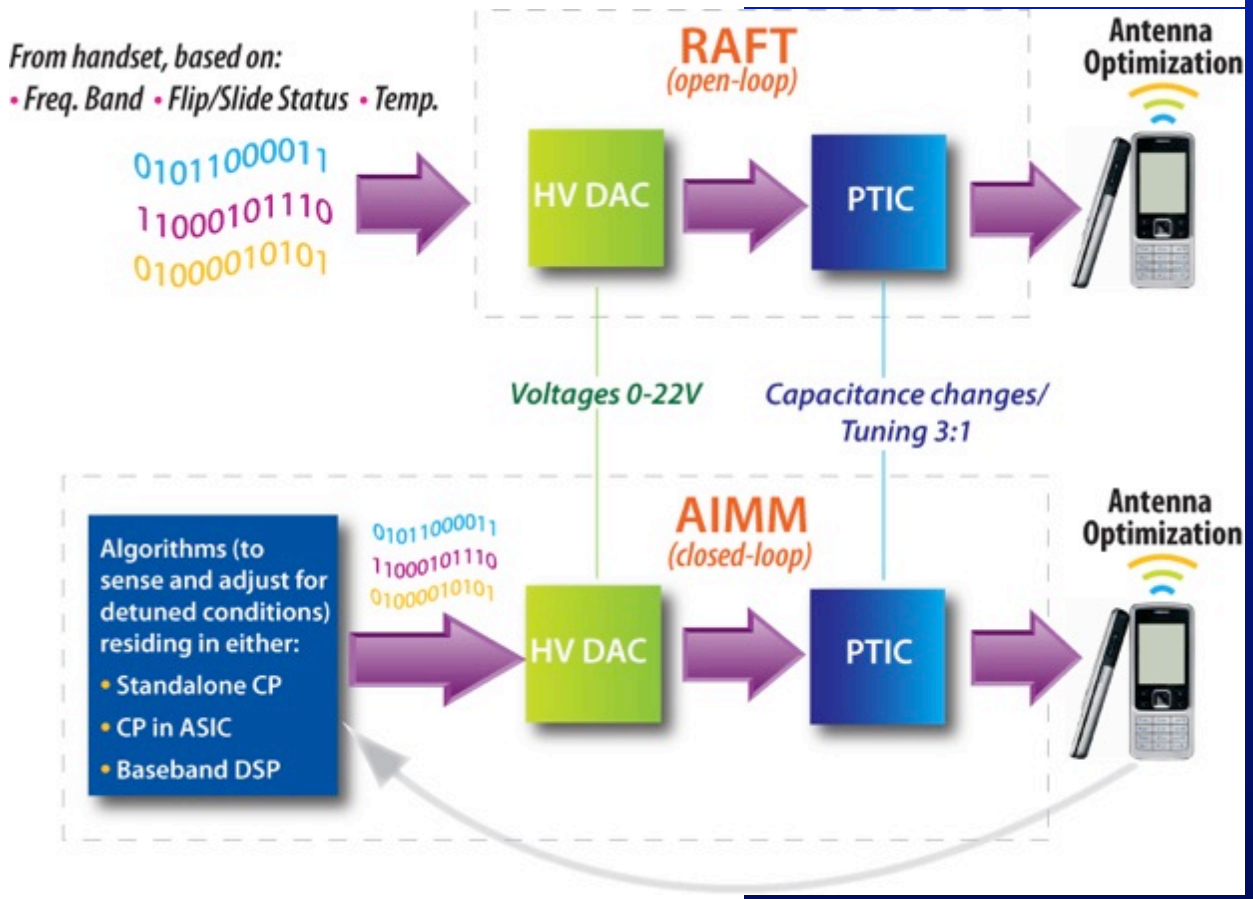
Tunable Dielectric $(Ba,Sr)TiO_3$



TUNABLE ICs

PARATEK NEWS

Research In Motion acquires Paratek



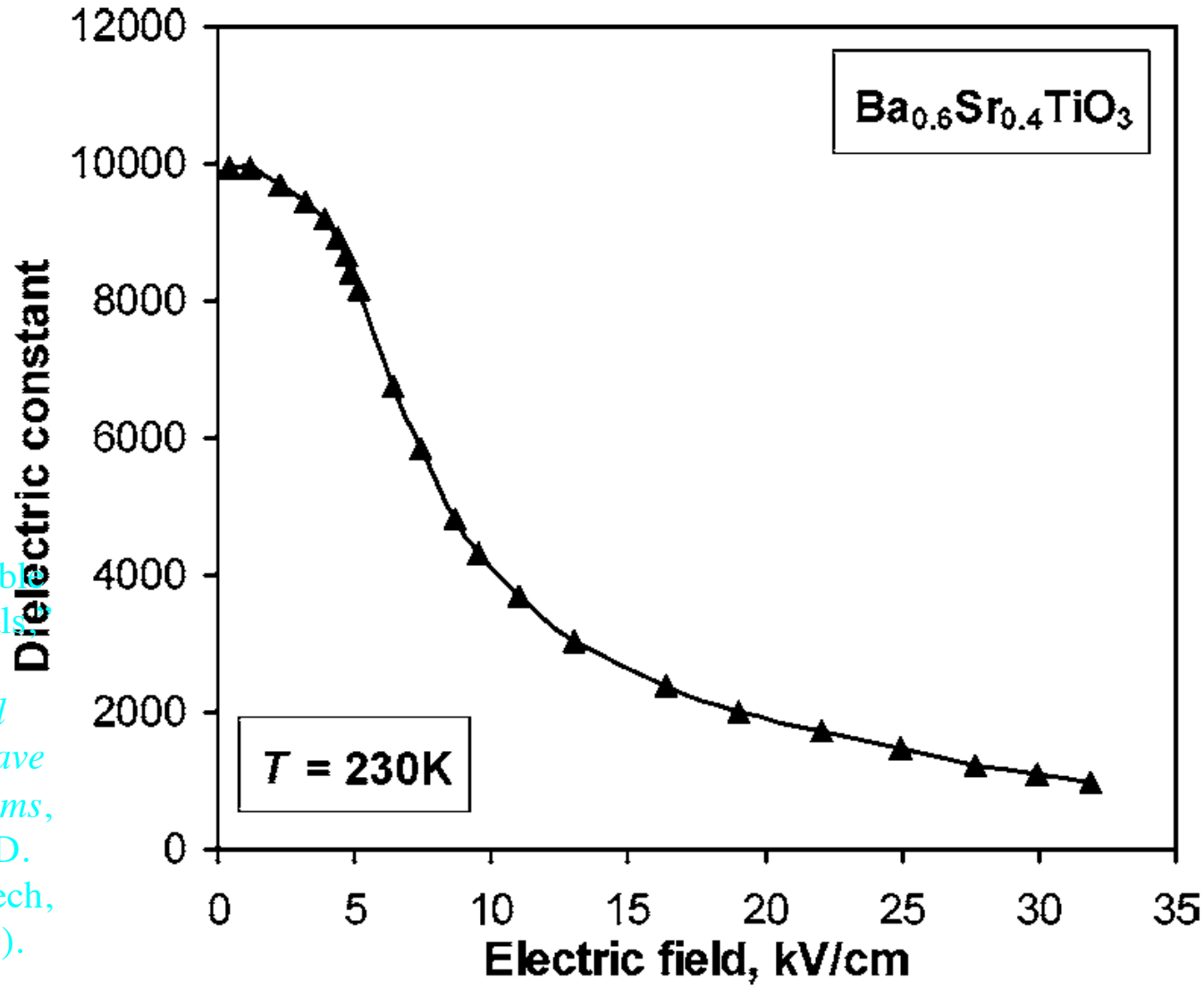
ParaTune ™ Tunable ICs!

Using its patented ParaScan ™ material as the foundational technology, Paratek has developed the **ParaTune ™** family of tunable ICs. These remarkable circuits offer the wireless industry a pathway to RF tuning for mobile handset antennas. Having the ability to tune, antennas can be made smaller *and* more efficient!

ParaScan is a proprietary doped BST-based material that exhibits exceptionally broad tuning characteristics with high linearity and high Q (exceeding 100 at 1 GHz and greater than 80 at 2 GHz). Other technologies such as varactor or PIN diodes, MEMS, and GaAS switches can all be used to improve the tuning function, but they all impose penalties. Some are too 'lossy,' or too costly, or too large to integrate seamlessly into a highly miniaturized mobile phone.

http://
www.paratek.com

What is a Tunable Dielectric?



R.A. York, "Tunable Dielectric Materials," Chapter 4 of *Multifunctional Adaptive Microwave Circuits and Systems*, M. Steer and W.D. Palmer, eds. (Scitech, New York 2009).

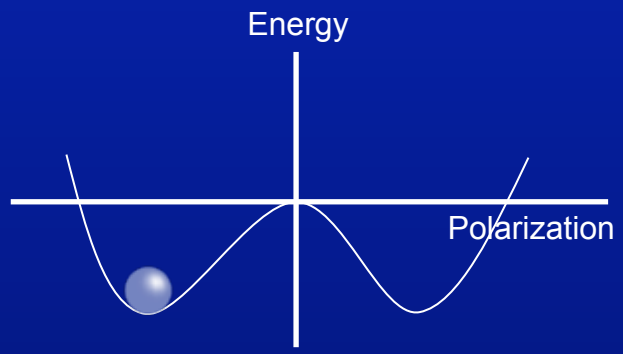
High-κ Capacitors & Varactors

c Field

O.G. Vendik, *Ferroelectrics for Microwave Applications* (Soviet Radio, Moscow, 1979).

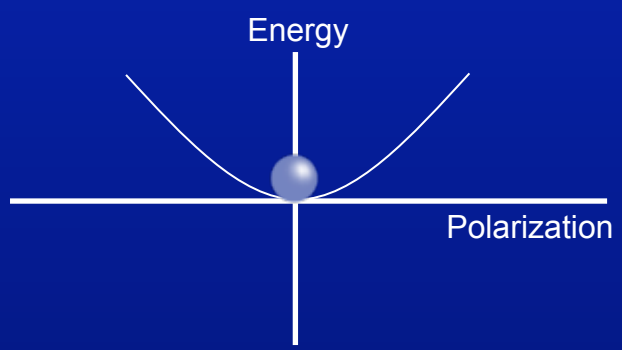
What is a Tunable Dielectric?

Ferroelectric



$P \neq 0$ when $E = 0$

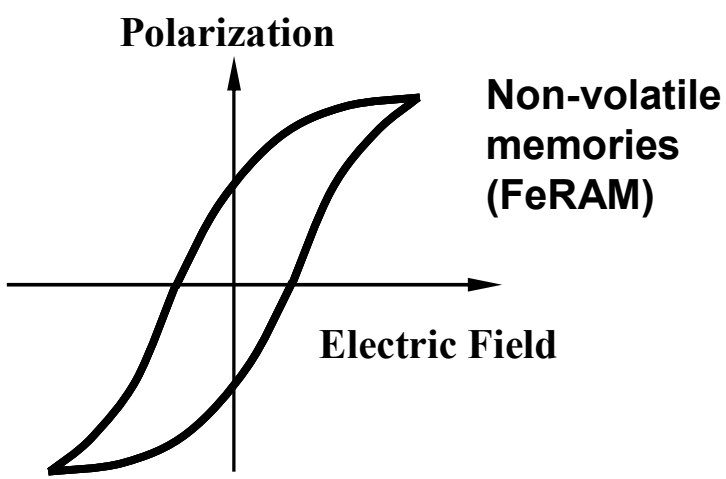
Paraelectric



$P \propto E$

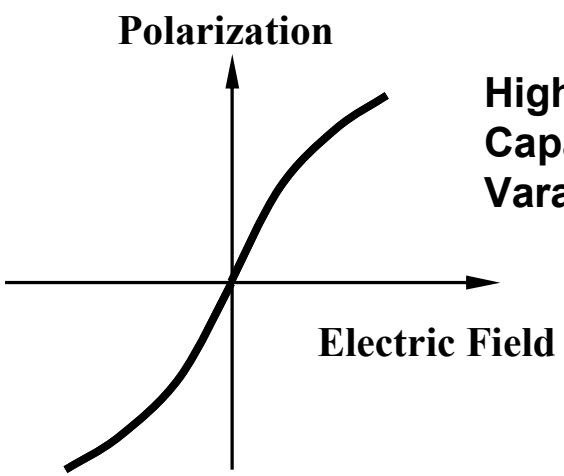
R.A. York, "Tunable Dielectric Materials," Chapter 4 of *Multifunctional Adaptive Microwave Circuits and Systems*, M. Steer and W.D. Palmer, eds. (Scitech, New York 2009).

Ferroelectric $T < T_c$



Non-volatile memories (FeRAM)

Paraelectric $T > T_c$



High-κ Capacitors & Varactors

$$D_i = \varepsilon_0 K_{ij} E_j + \varepsilon_{ijk} E_j E_k + \varepsilon_{ijk\ell} E_j E_k E_\ell + \ldots$$

Tunable $(Ba,Sr)TiO_3$

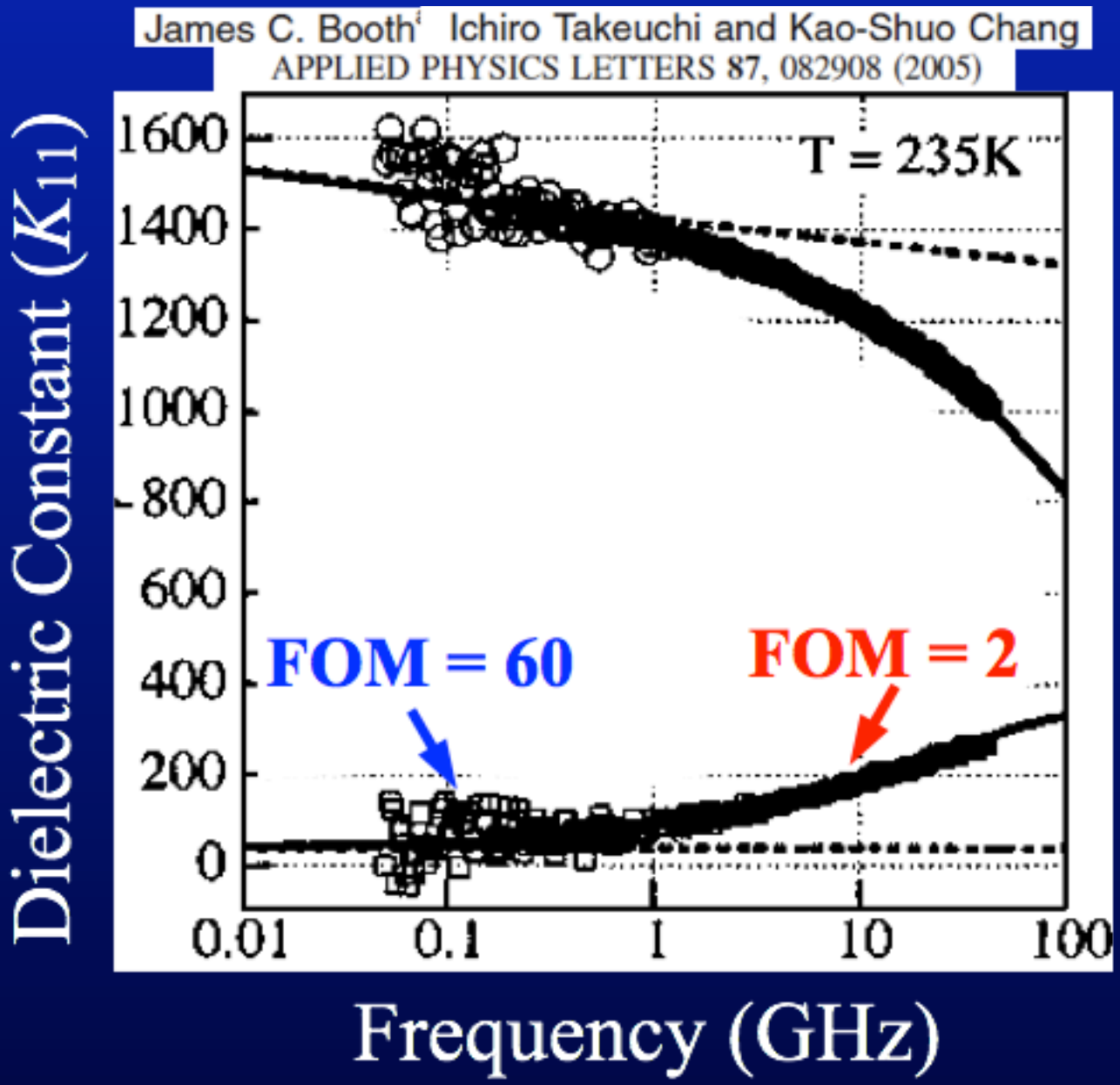


Figure of Merit $= \dfrac{\Delta K}{K \tan \delta}$

The big problem

Loss!

Issue with $(Ba,Sr)TiO_3$ Thin Films

- ***Dielectric Loss*** **in best $(Ba,Sr)TiO_3$ Films is 10× Higher than best Bulk $(Ba,Sr)TiO_3$**

Why?

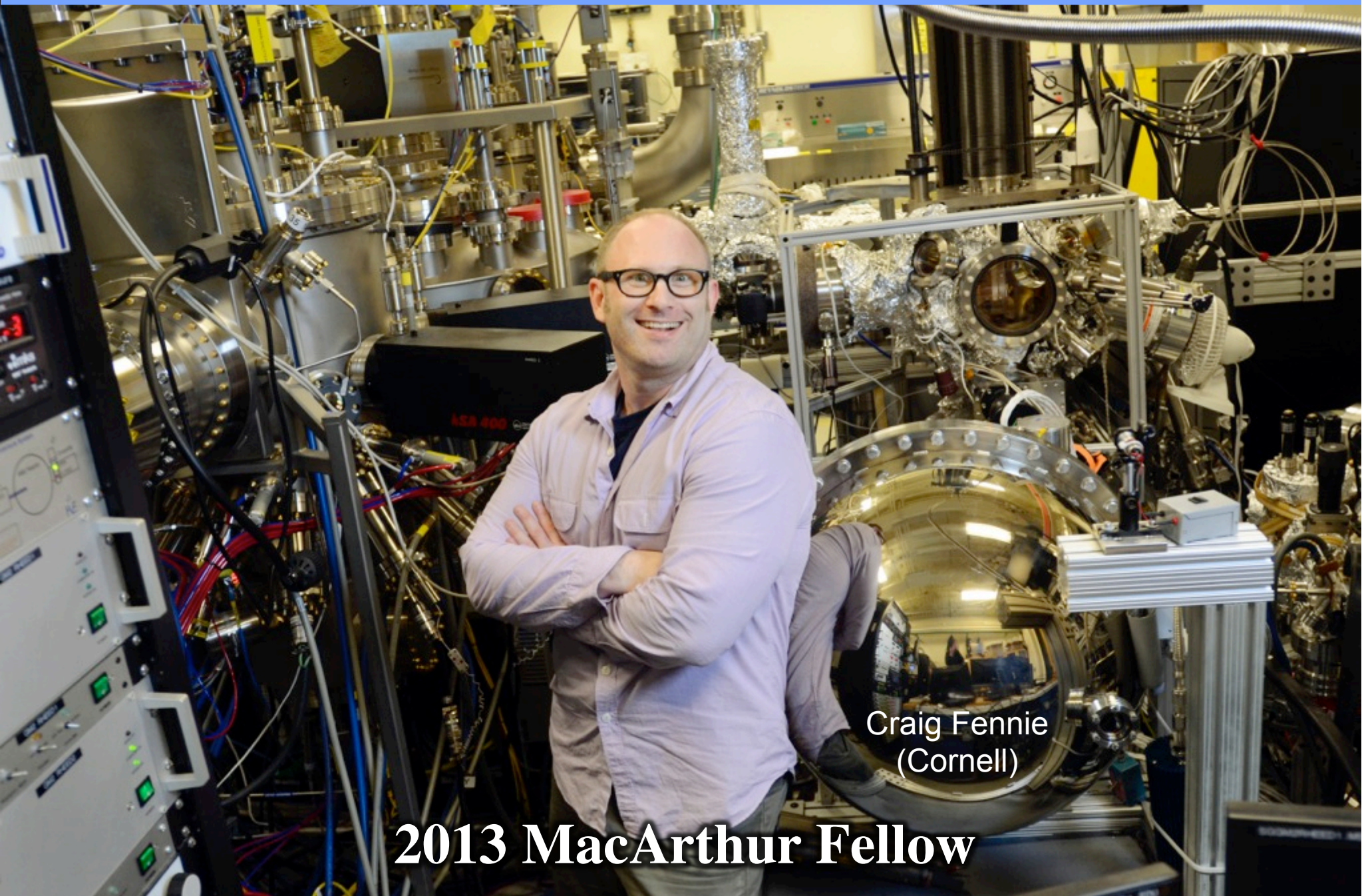
Low T_{sub} for Film vs. Bulk

Challenge of Composition Control in Films

Inhomogeneous Strain in Films

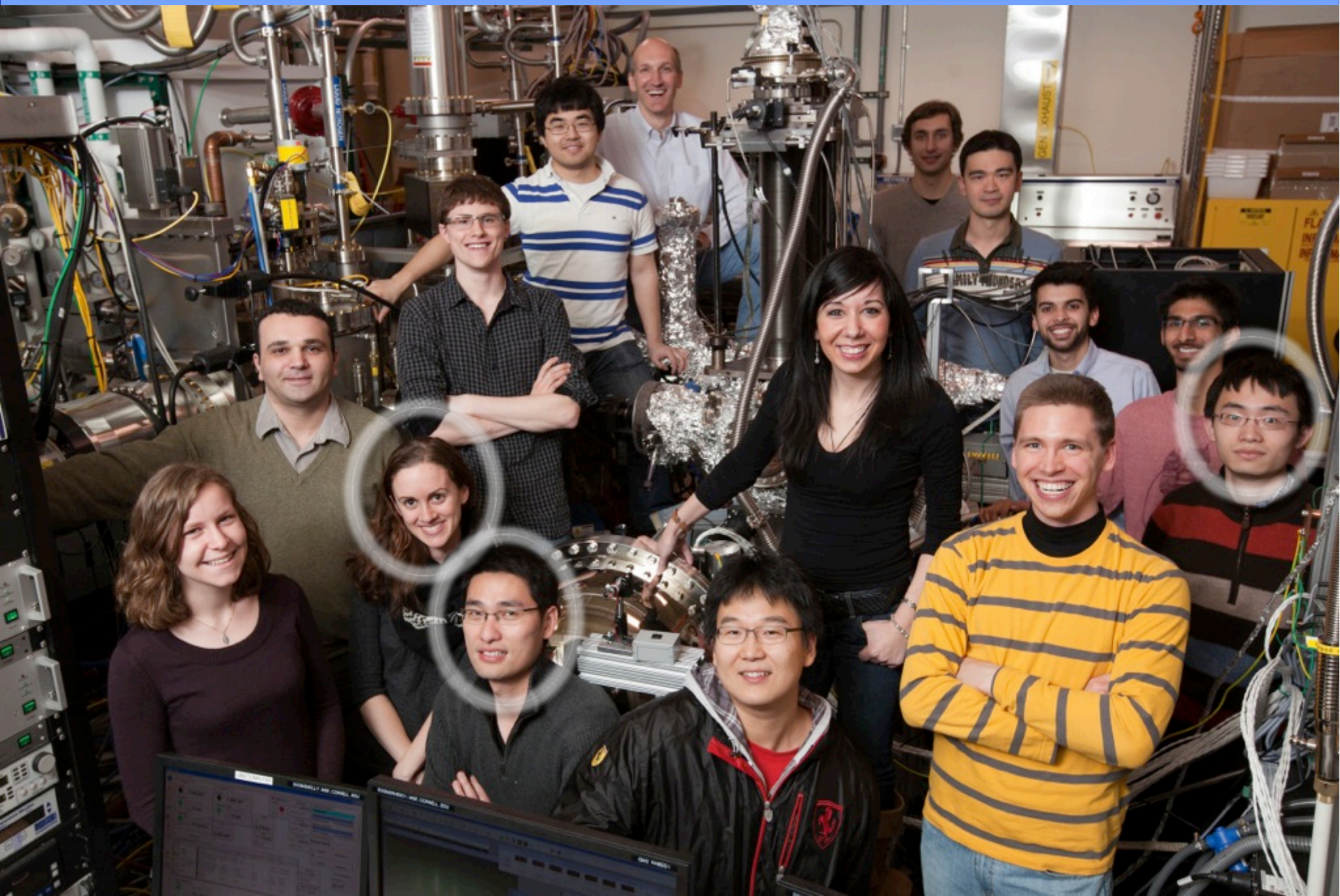
…

The Sorcerer

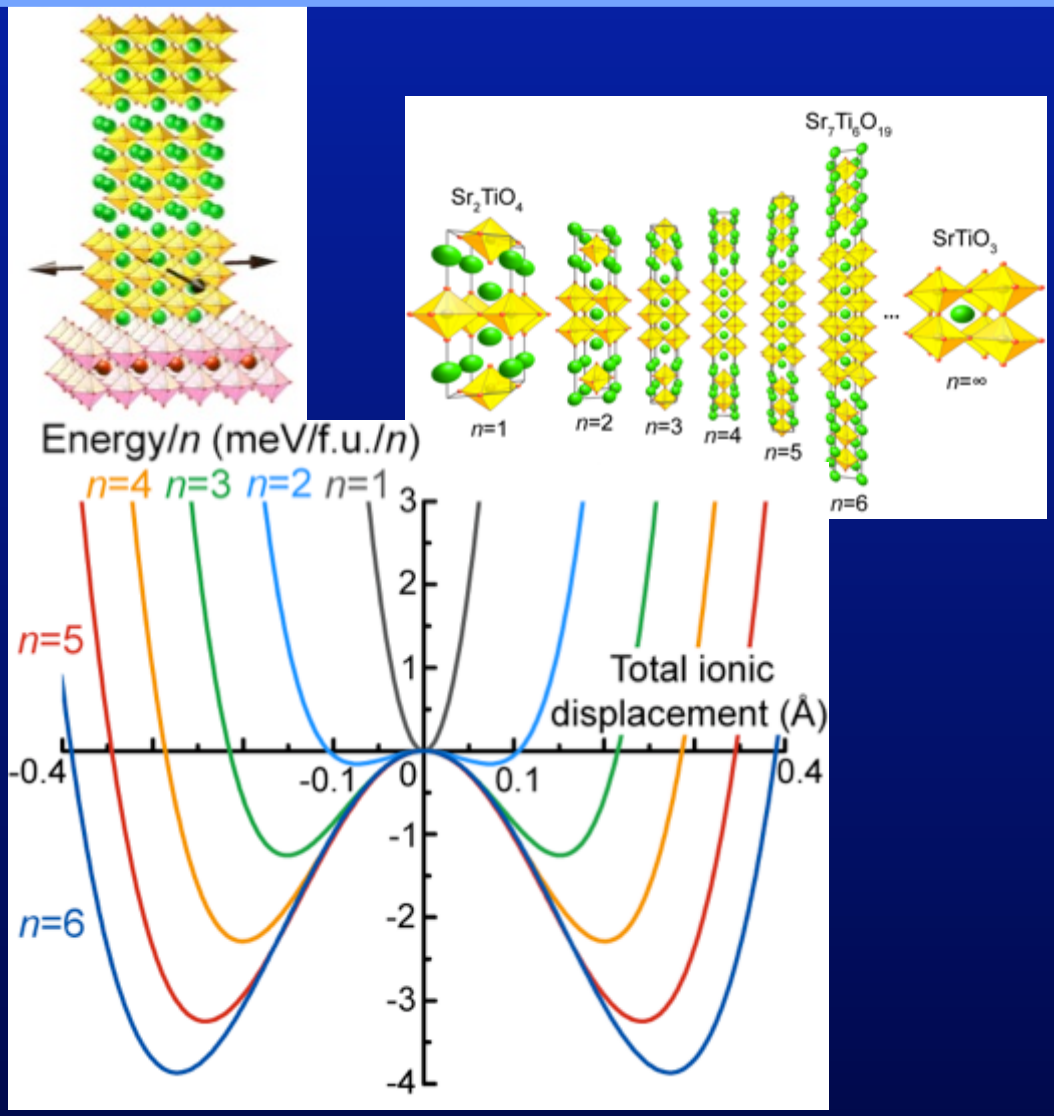


2013 MacArthur Fellow

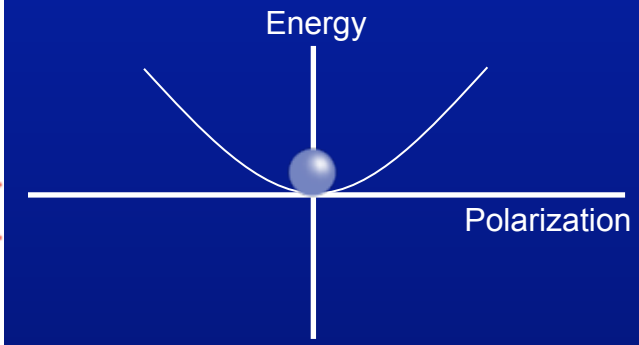
The Sorcerer's Apprentices



Ferroelectric Instability in *Strained* $Sr_{n+1}Ti_nO_{3n+1}$ / $DyScO_3$ Depends on n

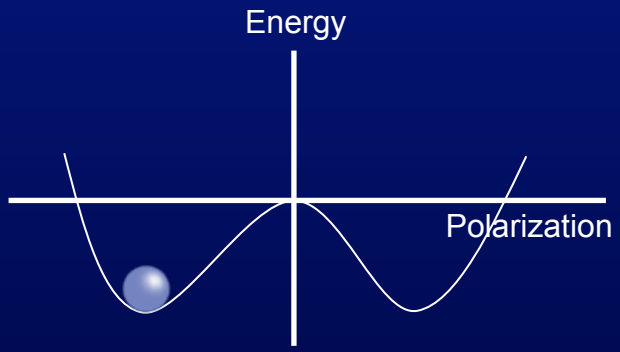


Dielectric



$P = 0$ when $E = 0$

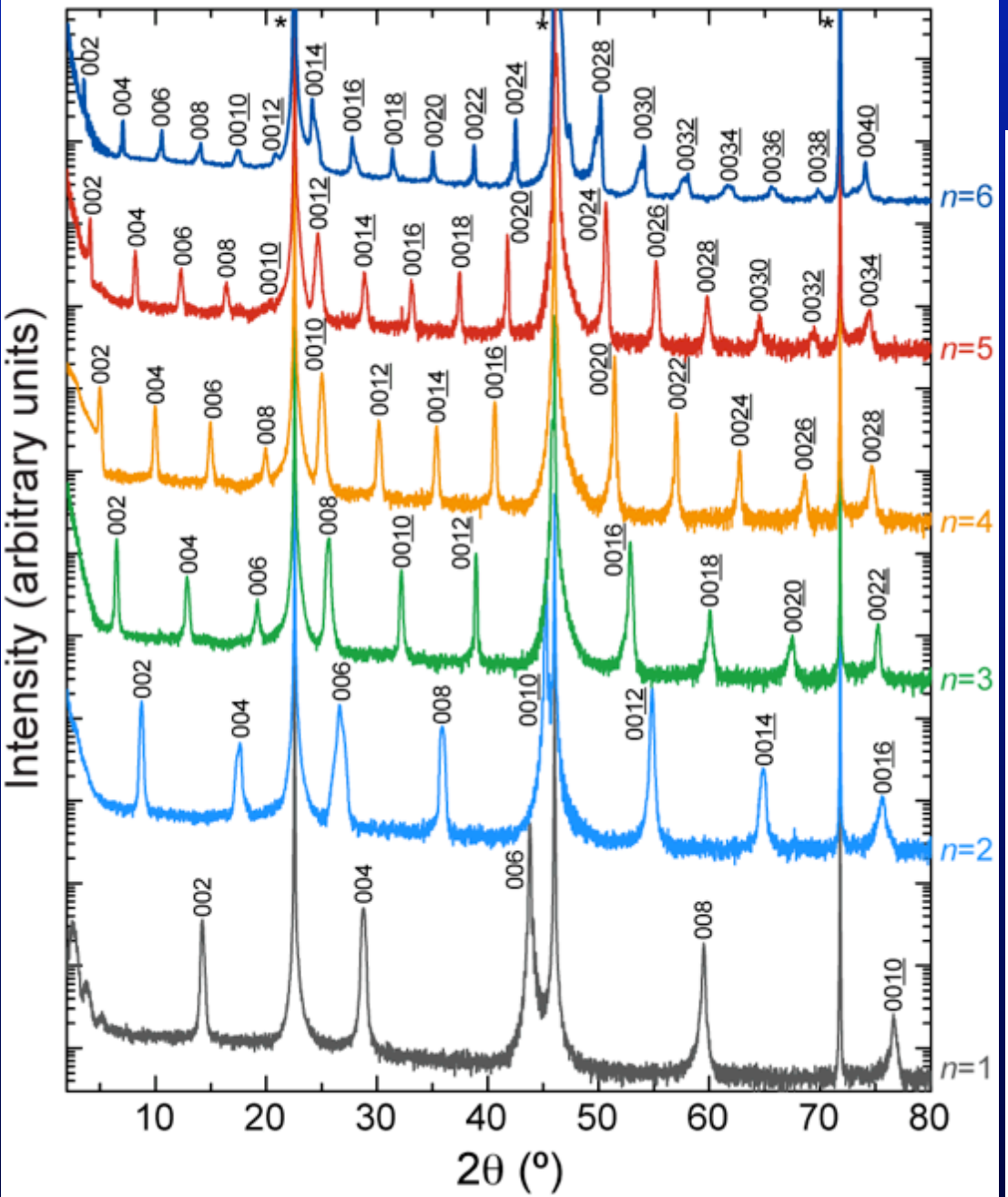
Ferroelectric



$P \neq 0$ when $E = 0$

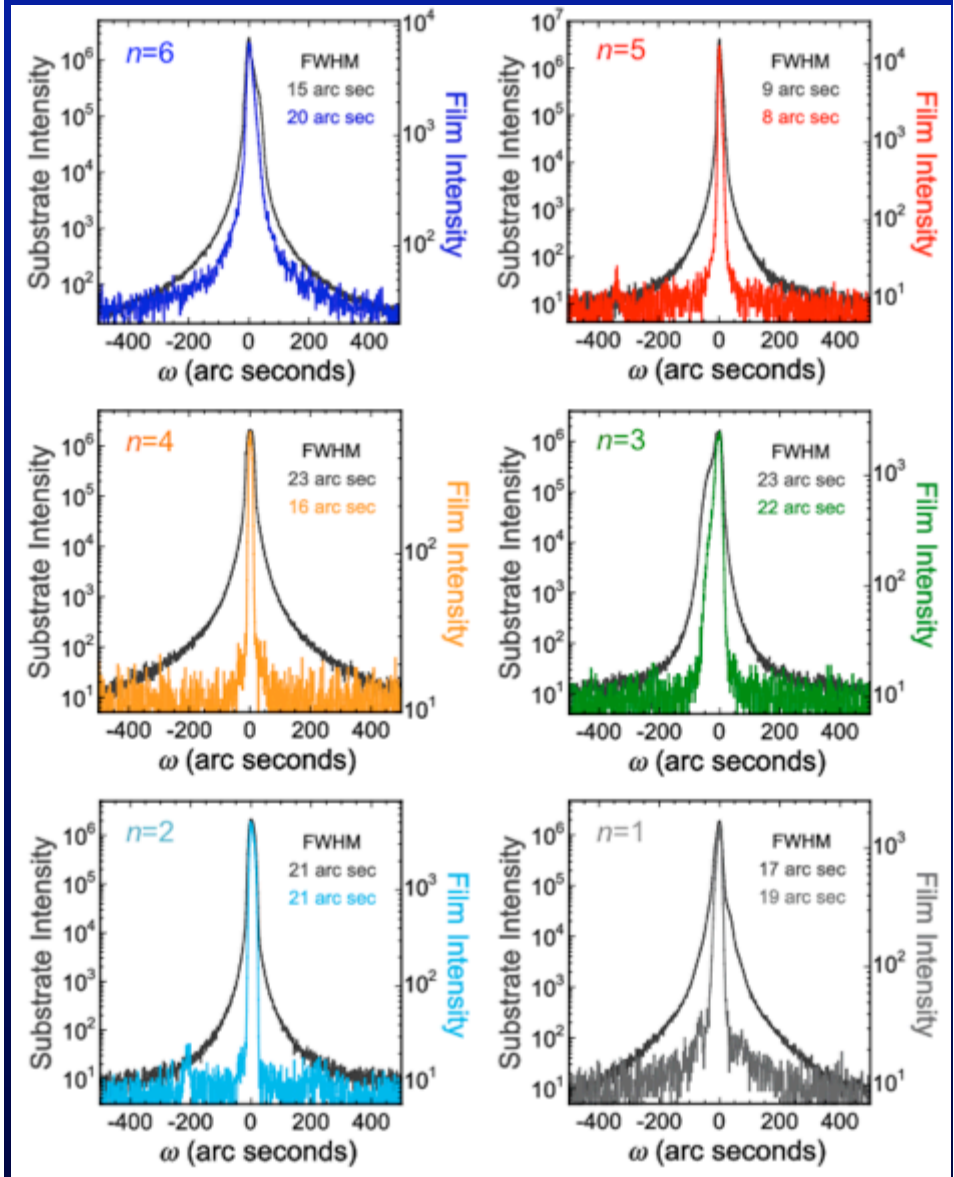
T. Birol, N.A. Benedek, and C.J. Fennie, *Physical Review Letters* **107** (2011) 257602.

50 nm $Sr_{n+1}Ti_nO_{3n+1}$ / (110) $DyScO_3$ (n = 1 to 6)



Rocking Curves

FWHM ≤ 22 arcsec (0.006°)

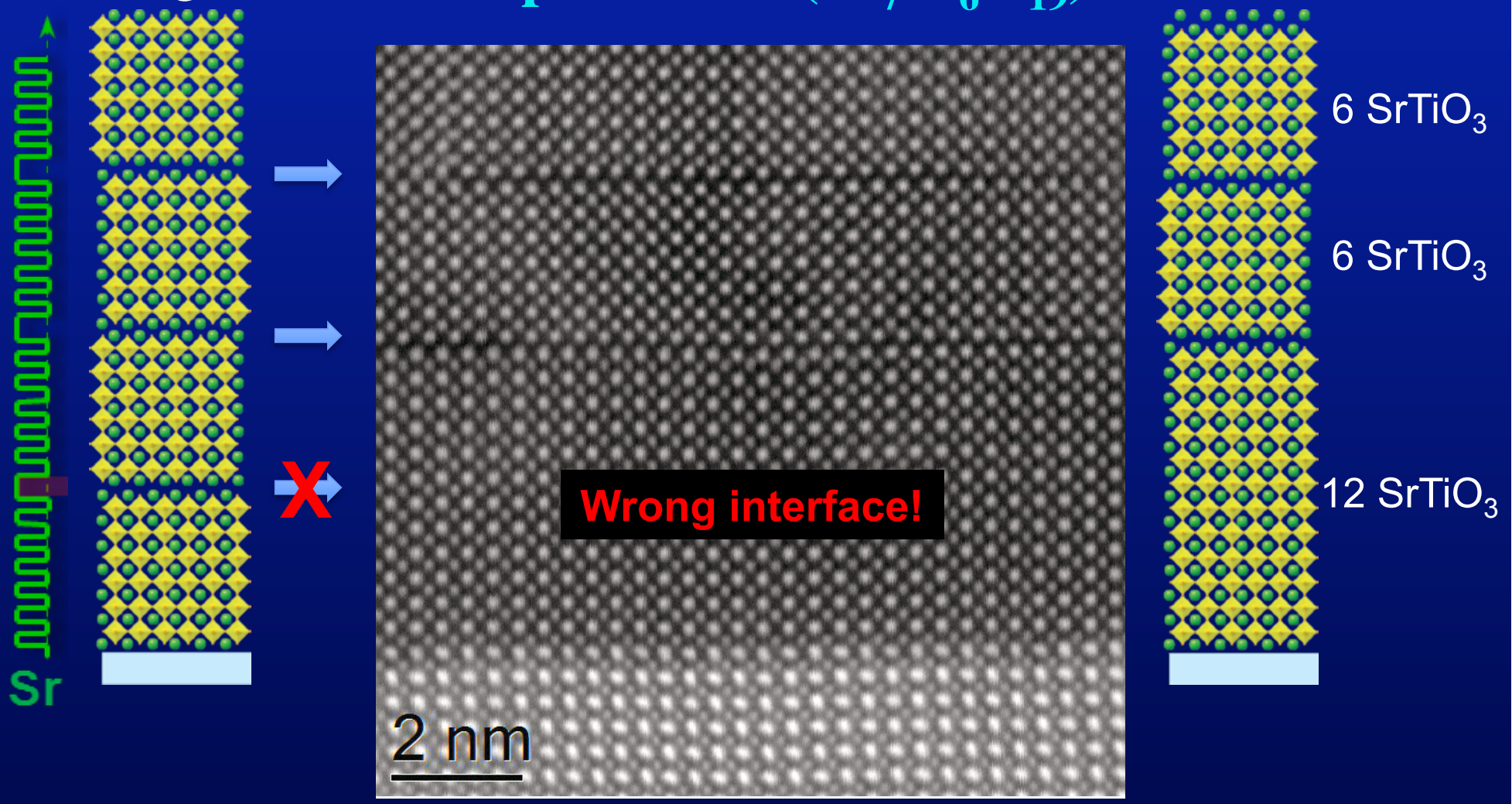


Initial SrO Double-Layer Missing!

Target

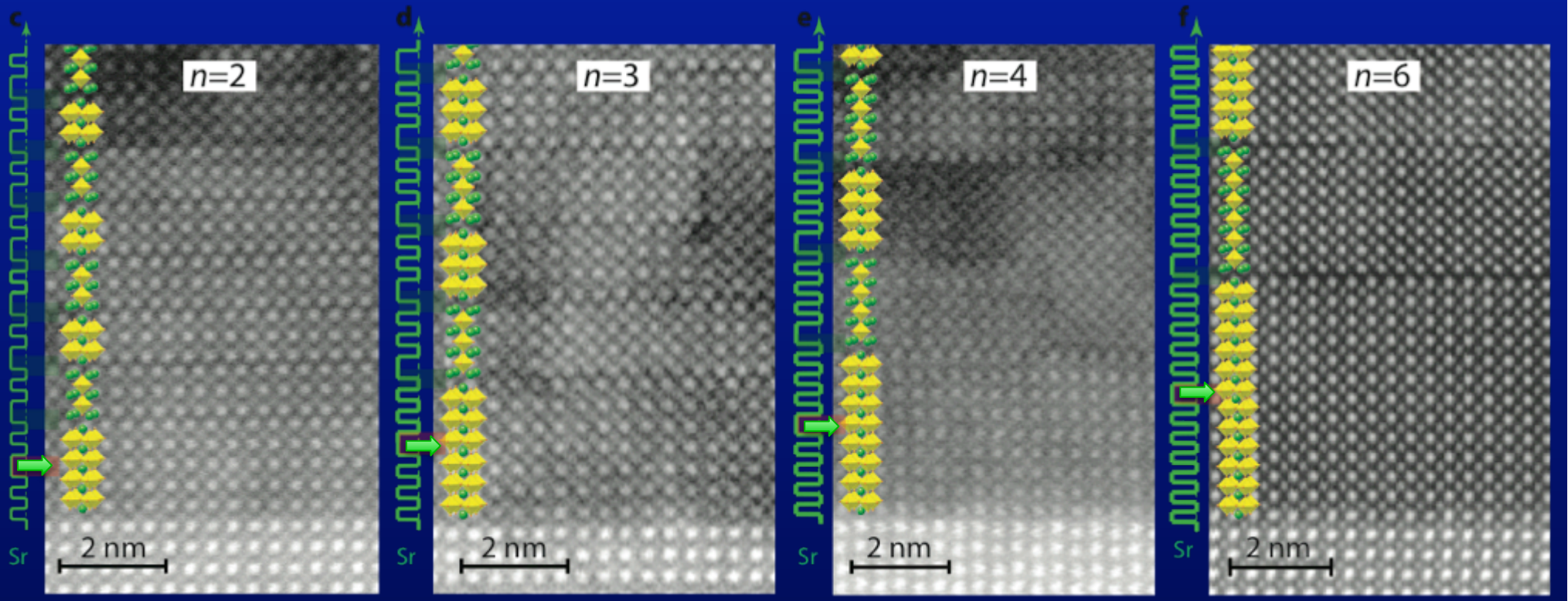
Example: $n = 6$ ($Sr_7Ti_6O_{19}$)

Result



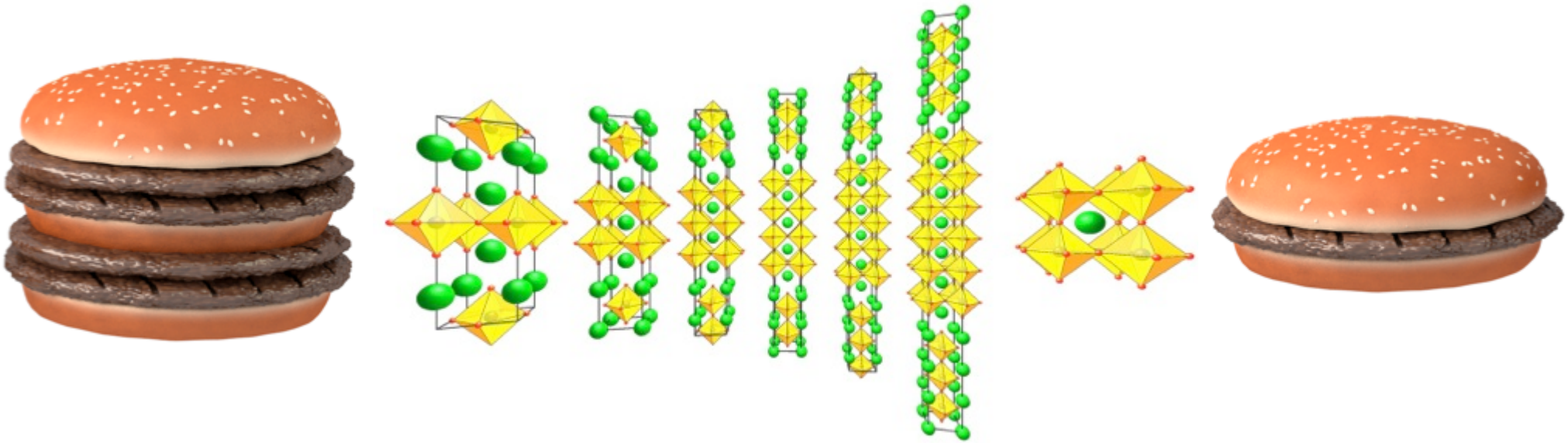
Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X.X. Xi, K.M. Shen, D.A. Muller, and D.G. Schlom, *Nature Communications* **5** (2014) 4530 .

Initial SrO Double-Layer Always Missing!

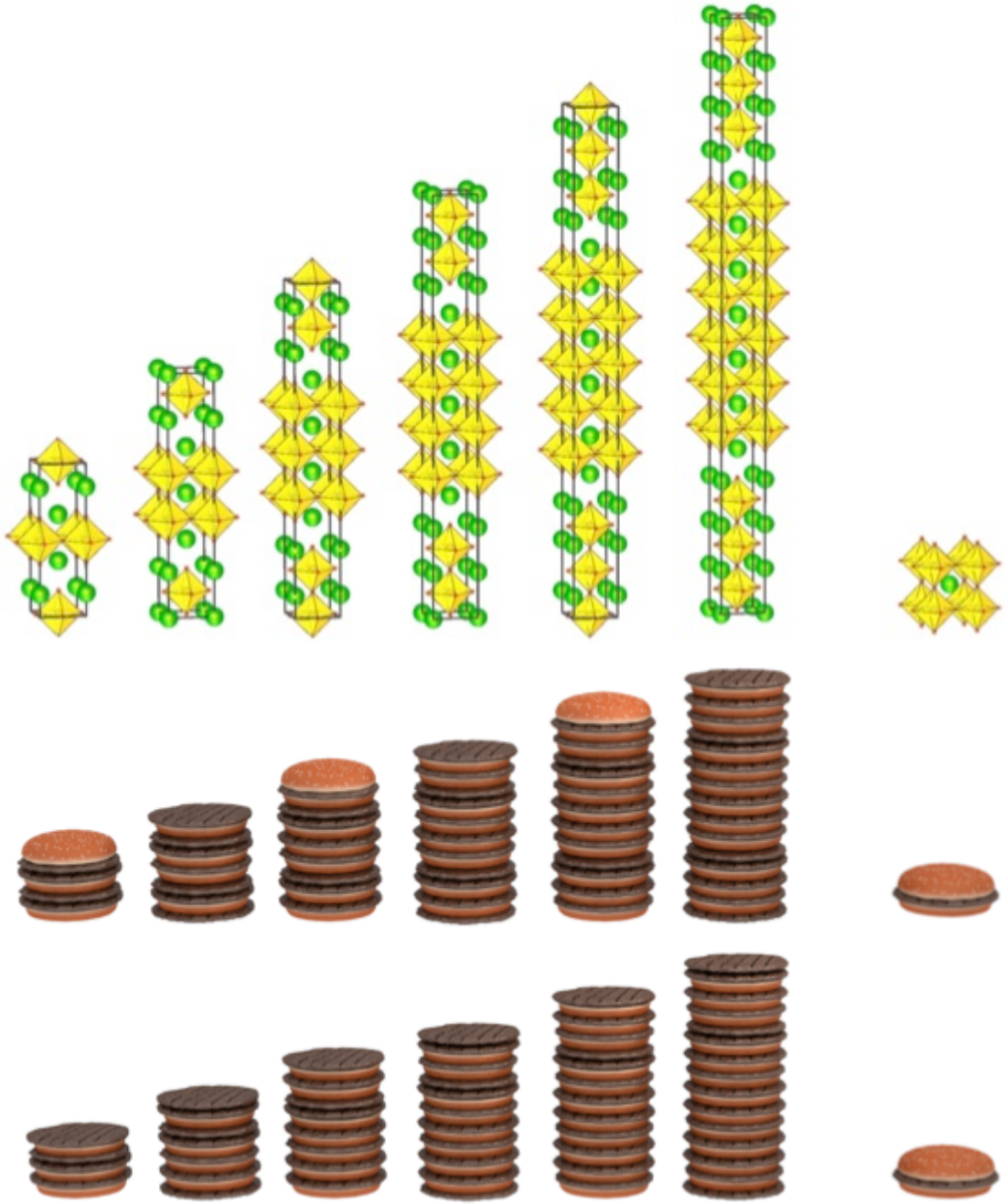


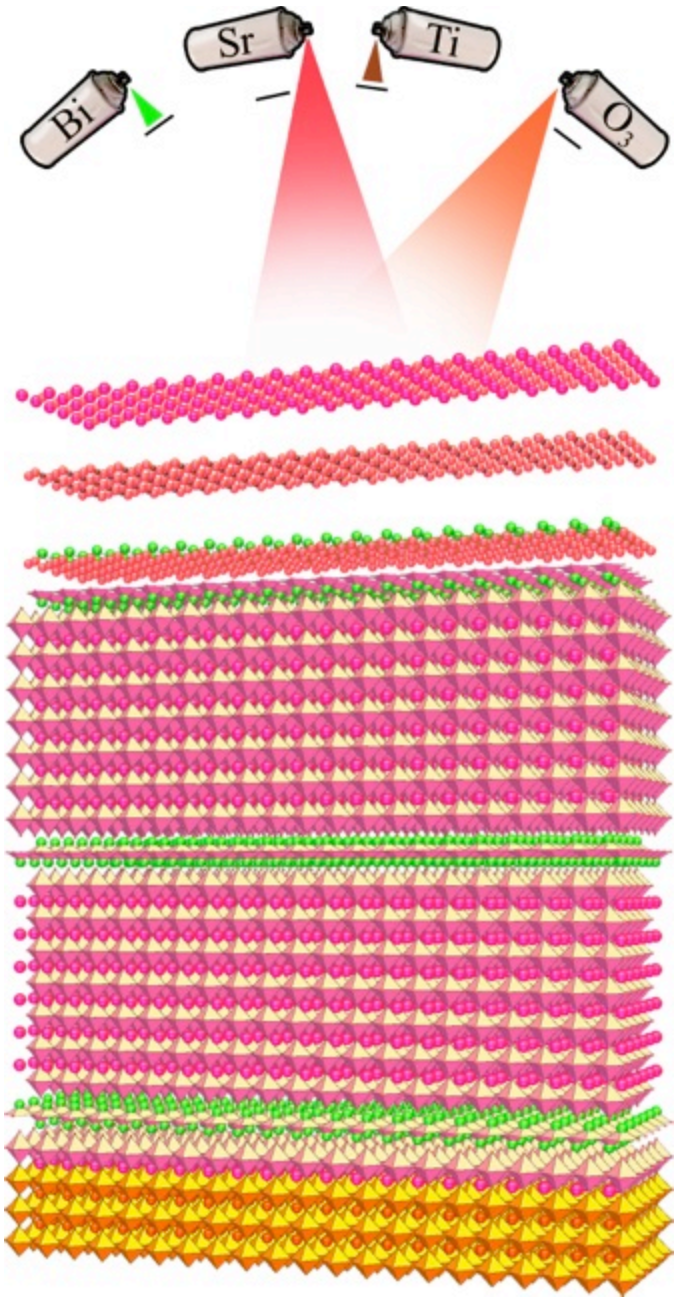
Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X.X. Xi, K.M. Shen, D.A. Muller, and D.G. Schlom, *Nature Communications* **5** (2014) 4530 .

How to Grow Oxide Superlattices?

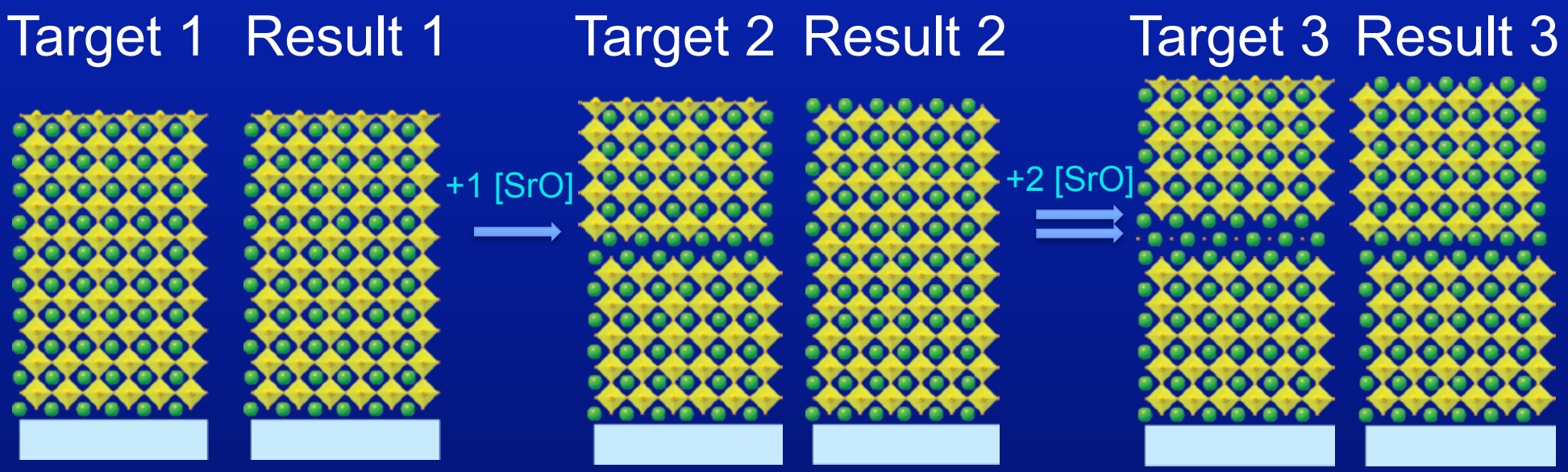


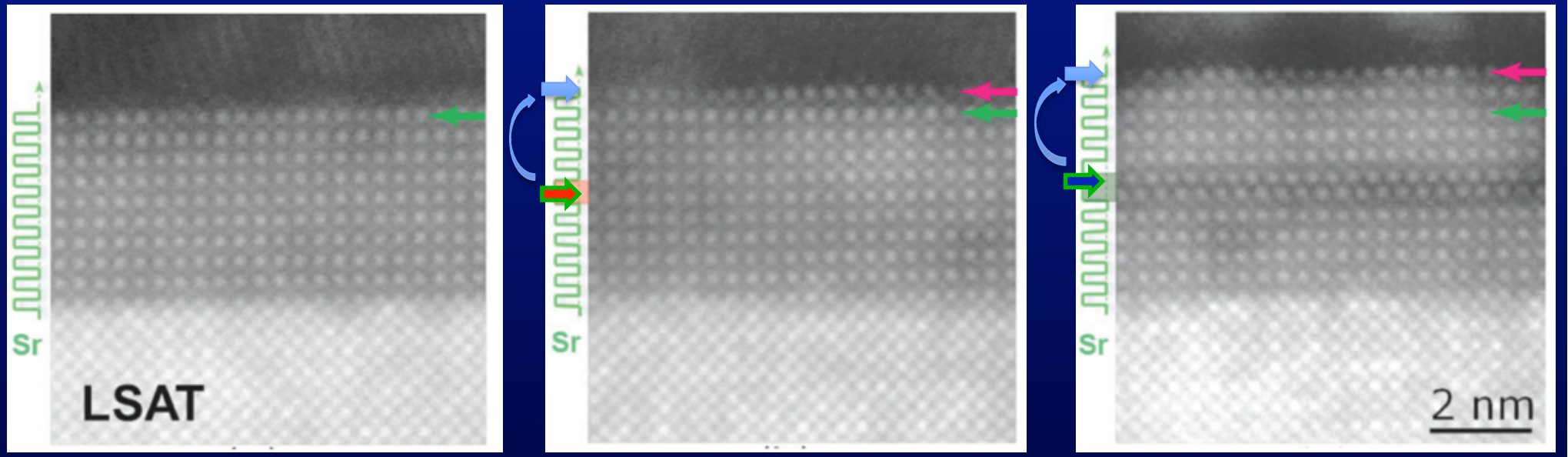
Growth does *not* Follow Cartoon





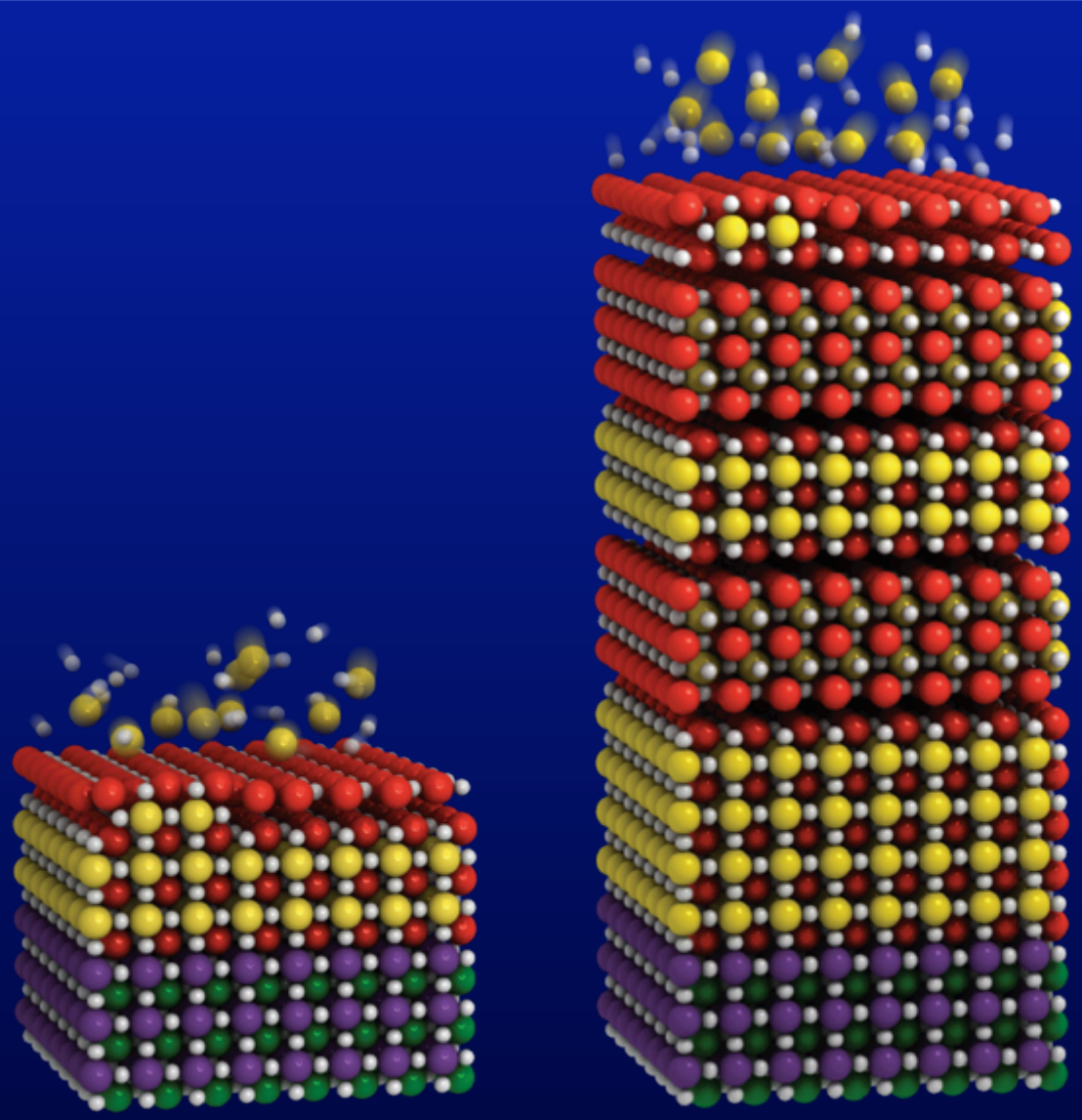
Missing SrO Layer Rides the Surface



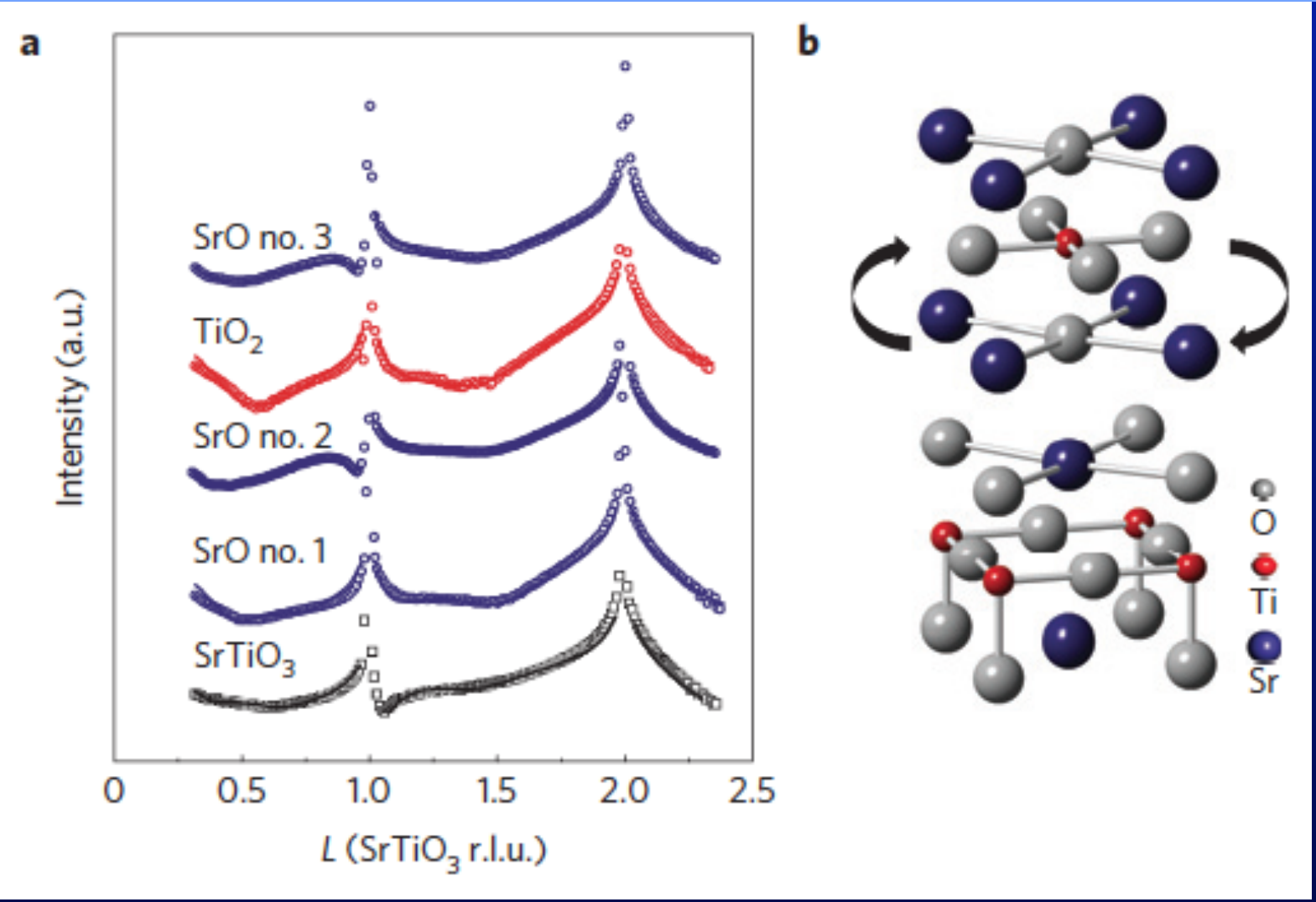


Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X.X. Xi, K.M. Shen, D.A. Muller, and D.G. Schlom, *Nature Communications* **5** (2014) 4530 .

Switching of SrO and TiO_2 Layers during Growth

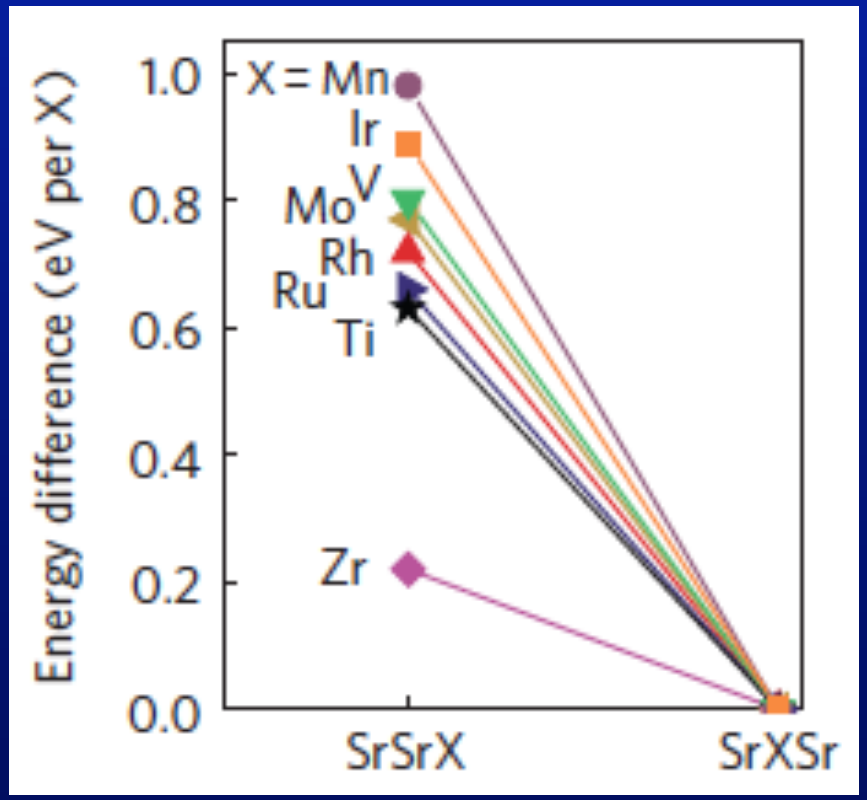


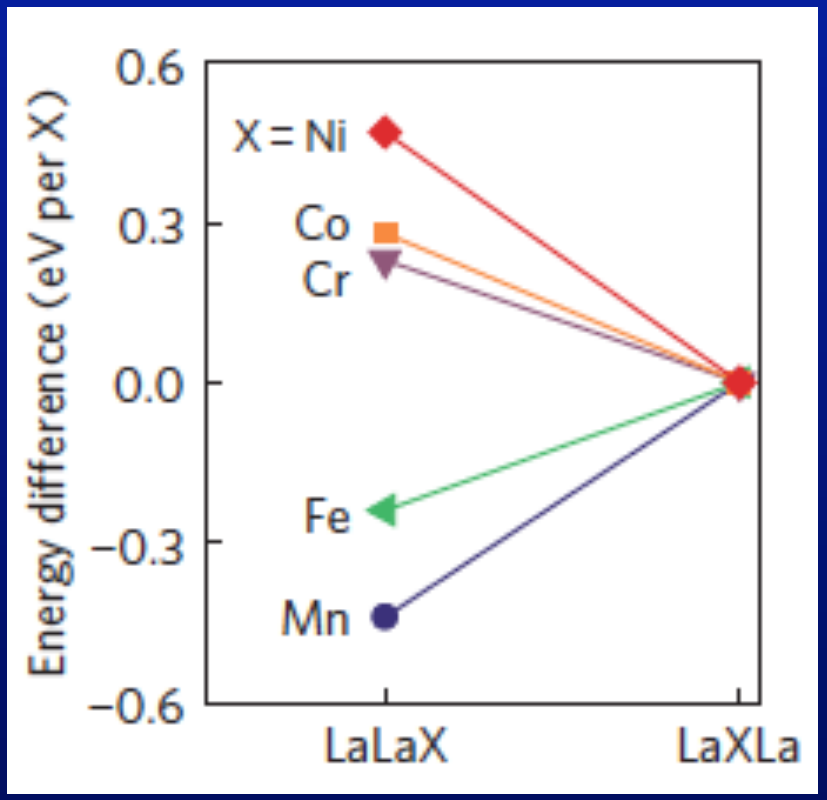
In situ Synchrotron X-ray Scattering during Oxide MBE



J.H. Lee, G. Luo, I.C. Tung, S.H. Chang, Z. Luo, M. Malshe, M. Gadre, A. Bhattacharya, S. M. Nakhmanson, J.A. Eastman, H. Hong, J. Jellinek, D. Morgan, D.D. Fong, and J.W. Freeland, *Nature Materials* **13** (2014) 879-883.

Theory Shows Applicable to Other Families of $A_{n+1}B_nO_{3n+1}$ Phases

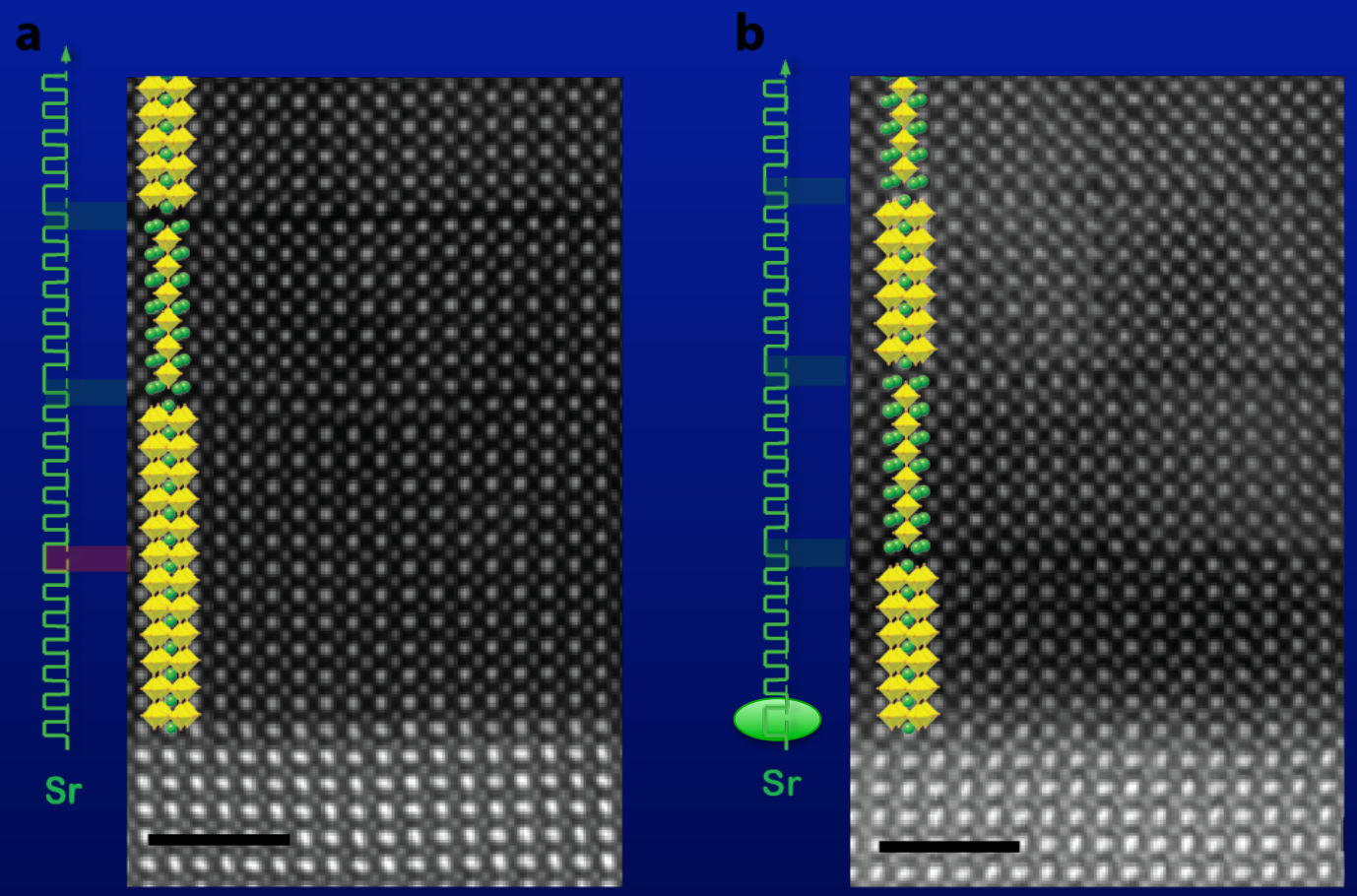




J.H. Lee, G. Luo, I.C. Tung, S.H. Chang, Z. Luo, M. Malshe, M. Gadre, A. Bhattacharya, S. M. Nakhmanson, J.A. Eastman, H. Hong, J. Jellinek, D. Morgan, D.D. Fong, and J.W. Freeland, *Nature Materials* **13** (2014) 879-883.

Achieve Desired Interface by Precisely Non-Stoichiometric Growth

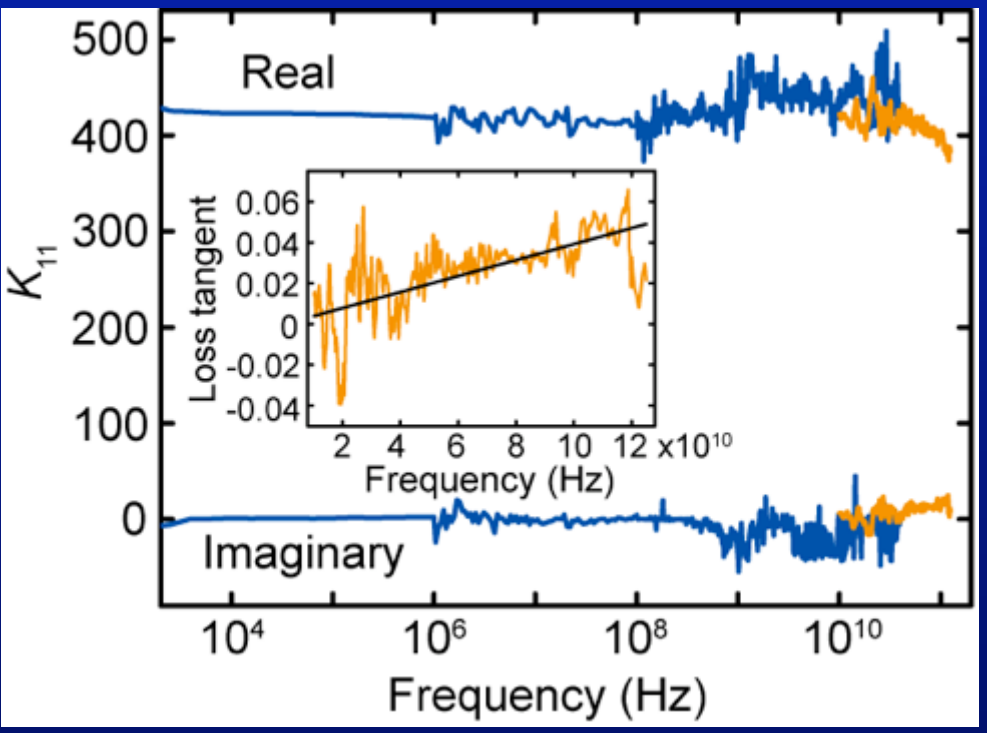
Deposit one extra SrO layer at the beginning!



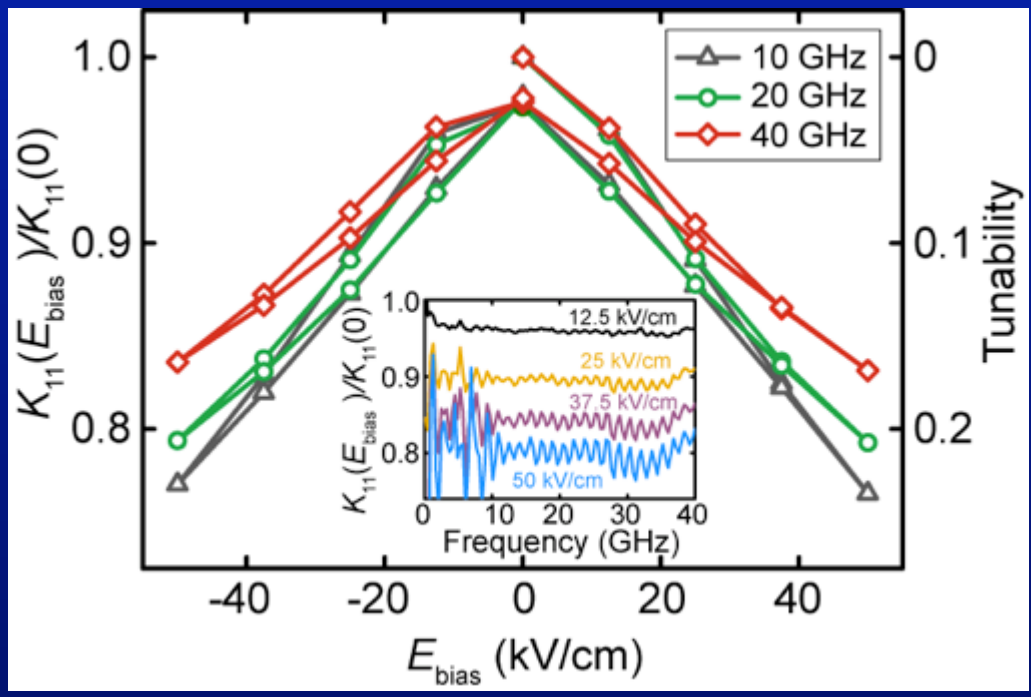
Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X.X. Xi, K.M. Shen, D.A. Muller, and D.G. Schlom, *Nature Communications* **5** (2014) 4530 .

50 nm $Sr_{n+1}Ti_nO_{3n+1}$ / (110) $DyScO_3$ (n = 6)

Broadband K_{11}



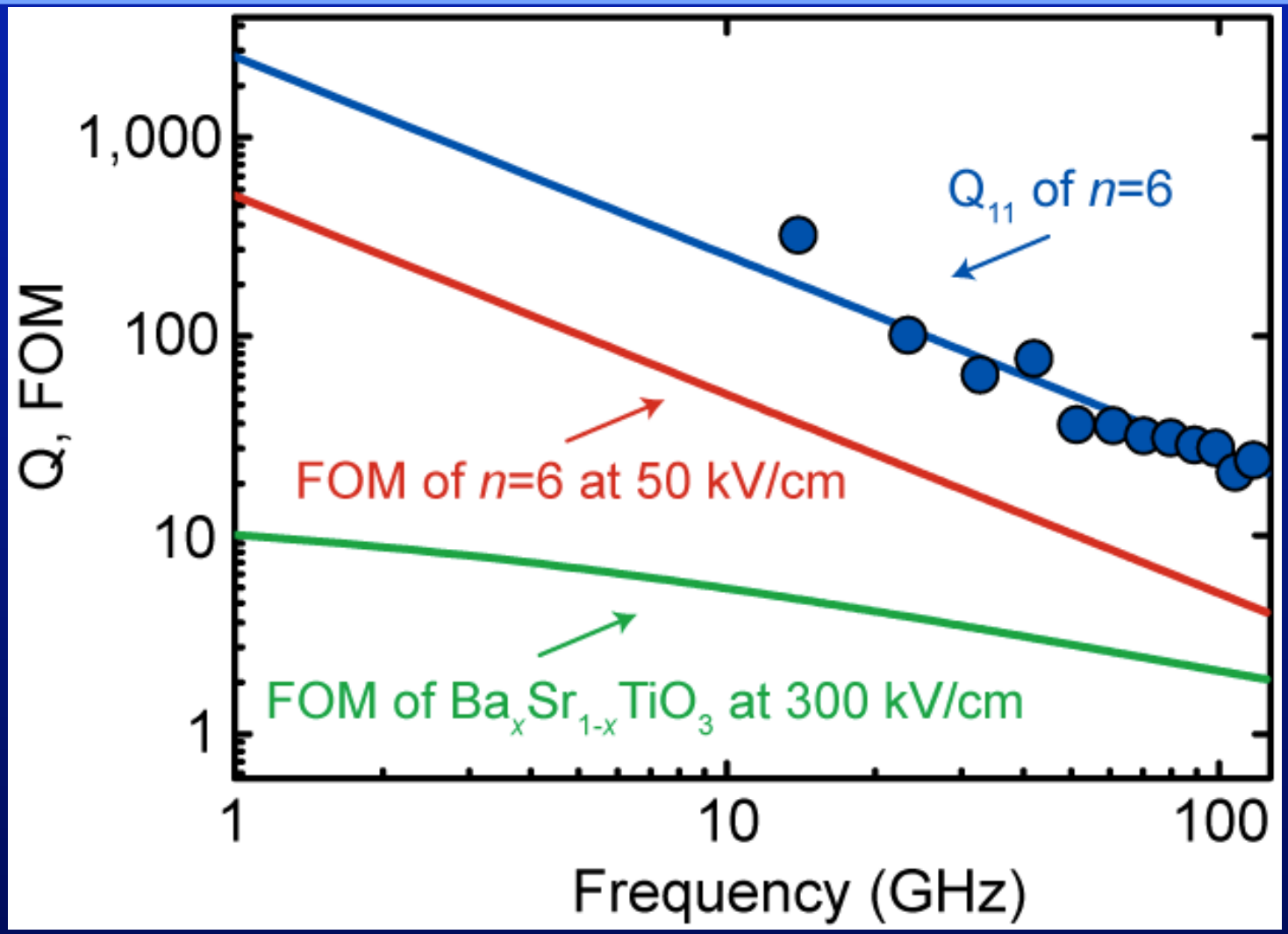
E-Field Tunable K_{11}



- Measurements span 8 order of magnitude (1 kHz - 125 GHz)
- Loss is fit to a line above 10 GHz
- ~ 20% tuning at 50 kV/cm

C.H. Lee, N.D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J.A. Mundy, L.F. Kourkoutis, Y. Nie, M.D. Biegalski, J. Zhang, M. Bernhagen, N.A. Benedek, Y. Kim, J.D. Brock, R. Uecker, X.X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D.A. Muller, I. Takeuchi, J.C. Booth, C.J. Fennie, and D.G. Schlom, *Nature* **502** (2013) 532-536.

Tunability of $(Ba,Sr)TiO_3$ vs. $Sr_7Ti_6O_{19}$



$Sr_7Ti_6O_{19}$ (n = 6) has highest FOM of any known material

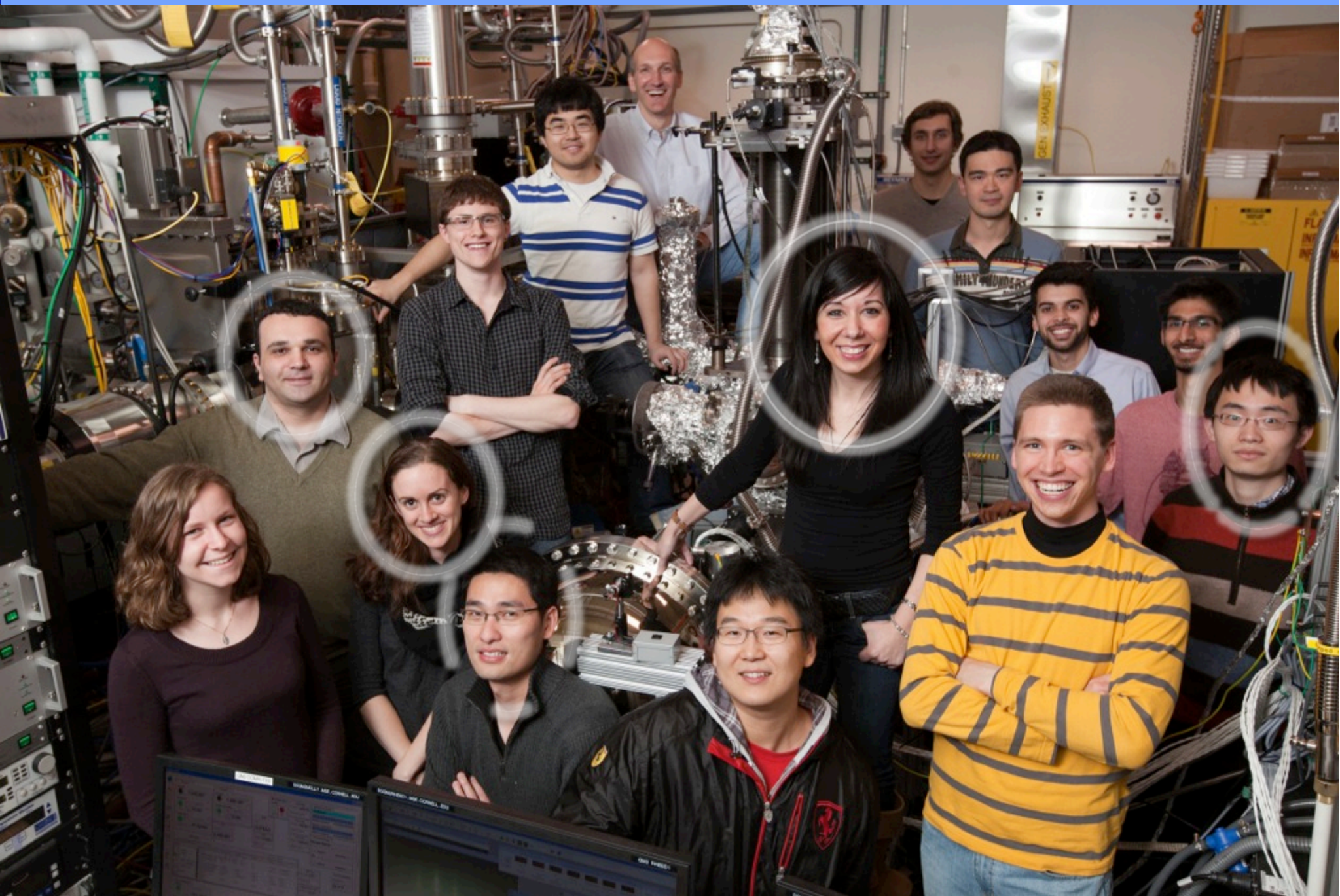
What's different?

Loss!

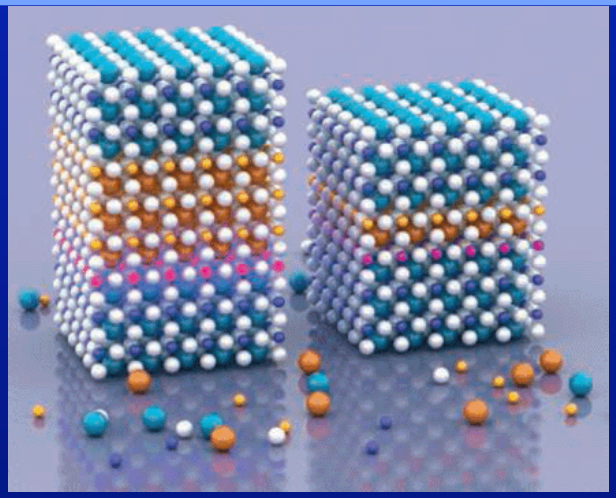
$Ba_{0.5}Sr_{0.5}TiO_3$ results from G. Houzet, L. Burgnies, G. Velu, J-C. Carru, and D. Lippens, *Applied Physics Letters* **93** (2008) 053507.

$$\text{Figure of Merit} = \frac{\Delta K}{K \tan \delta}$$

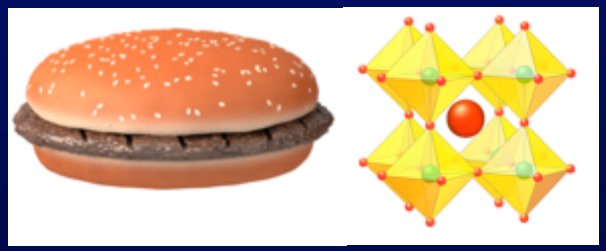
Oxide NanoSandwich Makers



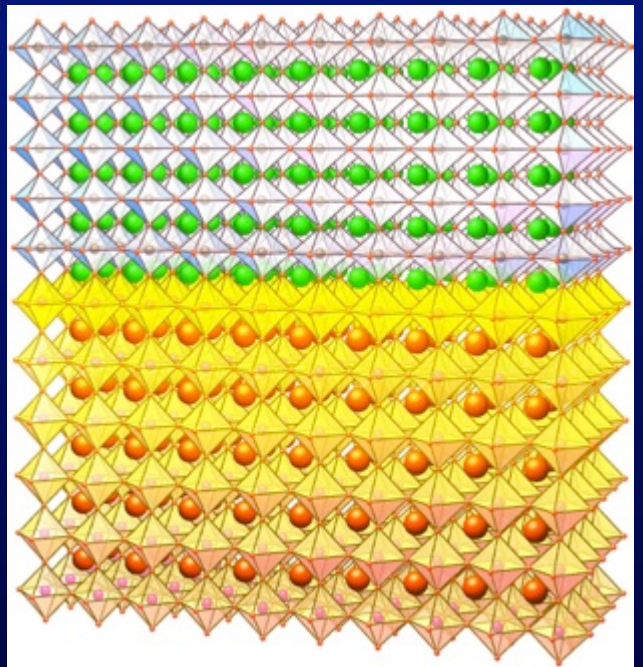
2DEL at $SrTiO_3$ / $LaAlO_3$ Interface



M. Huijben *et al.*, *Nature Mater.* **5**, 556 (2006).



electronic reconstruction



⋮
AlO_2
LaO
TiO_2
SrO
⋮

Interfaces between Ruddlesden-Poppers

Outlook for Oxides by Design

- **Lots of Emerging Opportunities for both Fundamentals and Technology**
- **Exploit Exceptional Known Properties of Oxides**
- **Use Thin Film Tricks to Access Hidden Properties of Oxides**
- **Need to Create Interfaces and Heterostructures with Atomic-Layer Precision**
- **Huge Opportunity for Materials-by-Design (provided can understand how oxide films grow!)**