# Oxide MBE—
# A Tool to Create Artificial Quantum Materials

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# Outline

- What is MBE and what is it good for?
  *Greatest hits of MBE*

- How to grow your favorite oxide quantum material by MBE?
  *Nuts and bolts of oxide MBE*

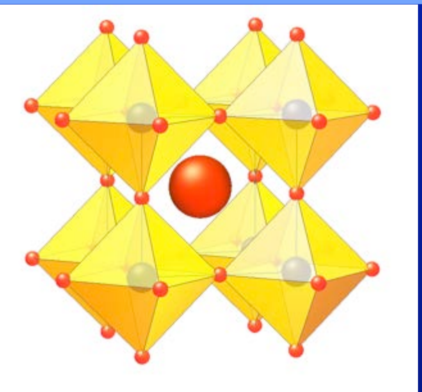
- Oxide MBE growth of quantum materials
  *Case studies—including $Sr_2RuO_4$*

- How can I gain access to an oxide MBE if I don't have one?
  *Use PARADIM's oxide MBE (+ ARPES + …)*

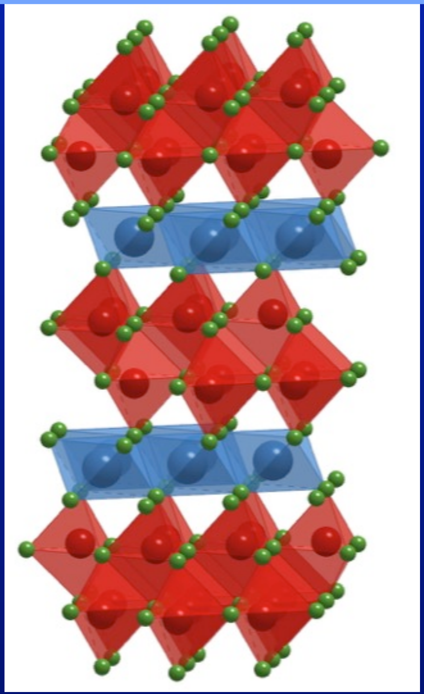
# Nuts and Bolts of Oxide MBE

- Mean Free Path (maximum $P_{O_2}$)
- Minimum $P_{O_2}$, need for $P_{O_3}$, Optimal $T_{sub}$
- MBE System, Sources, and Crucibles
- Composition Control
    - Adsorption-Controlled Growth
    - Flux-Controlled Growth
- Substrates

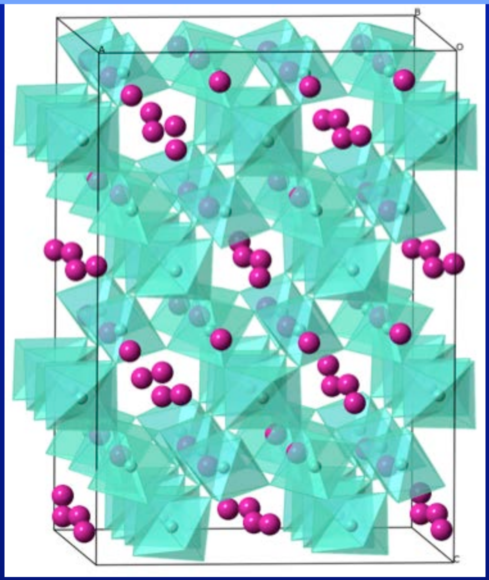
# Wacky Oxides we Grow



**$PbTiO_3$**
**or**
**$BiFeO_3$**
**or**
**$BiMnO_3$**



**$LuFe_2O_4$**



**$\alpha$-$Bi_2Sn_2O_7$**
**(352 atoms/unit cell)**
**or**
**$Bi_2Ru_2O_7$**

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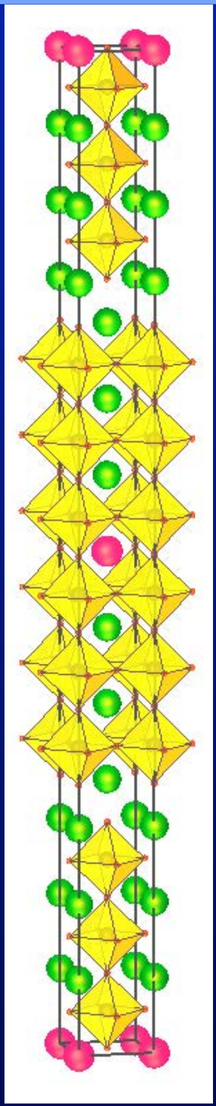
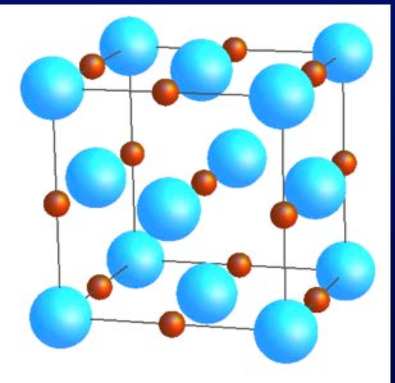
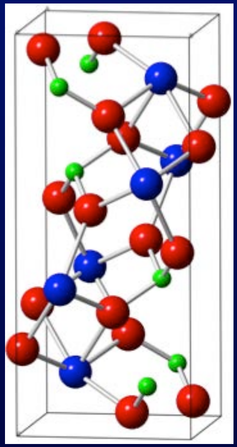
**$Sr_7Ti_6O_{19}$**



**$BaSr_6Ti_6O_{19}$**

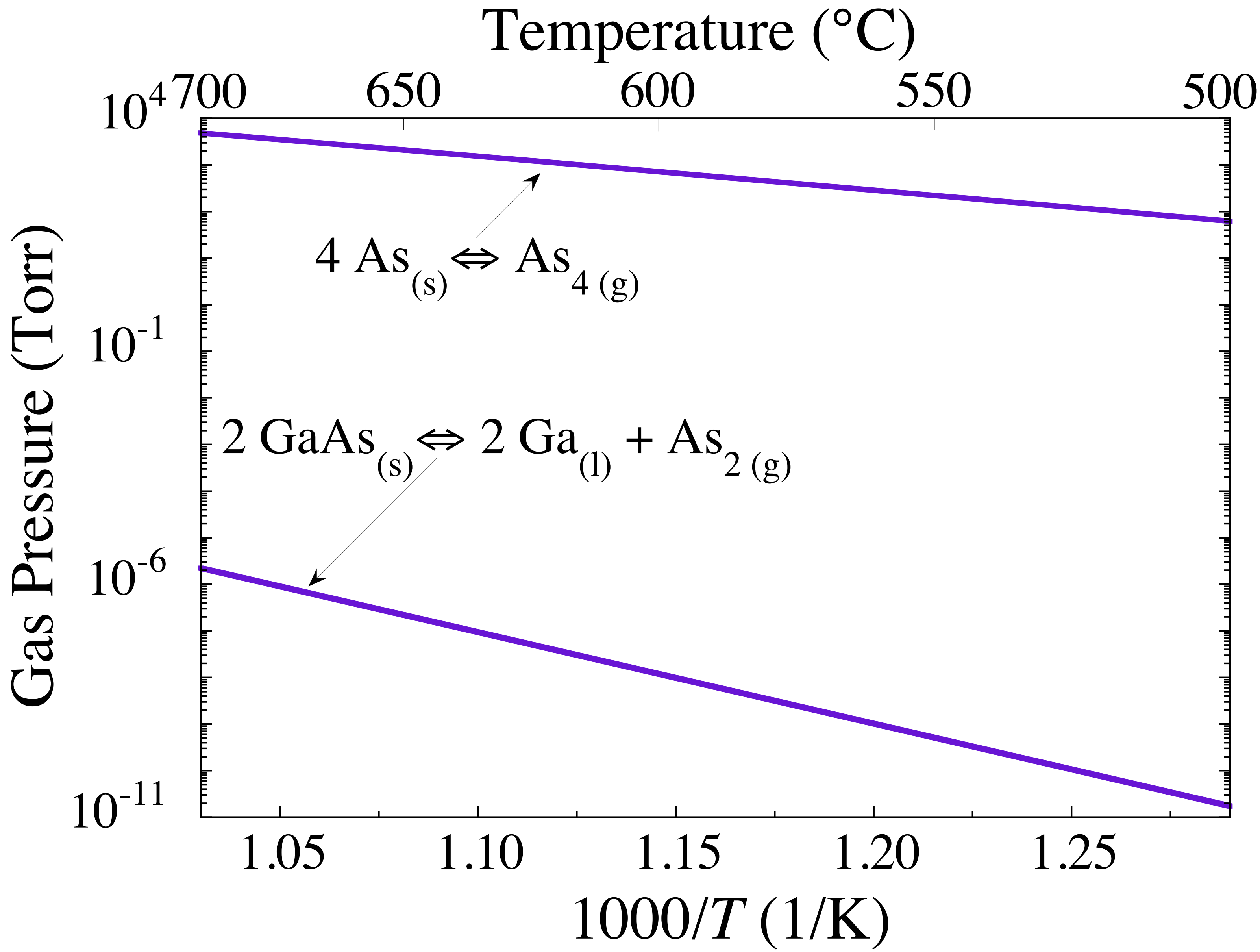


**EuO**



**$BiVO_4$**

# Adsorption-Controlled Growth of GaAs




C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown, "Adsorption-Controlled Growth of $PbTiO_3$ by Reactive Molecular Beam Epitaxy," *Thin Solid Films* **325** (1998) 107-114.

# Adsorption-Controlled Growth of

- **Plumbites**
  - **$PbTiO_3$** — C.D. Theis *et al*., *J. Cryst. Growth* **174** (1997) 473-479.
  - **$PbZrO_3$** — (unpublished)
- **Bismuthates**
  - **$Bi_2Sr_2CuO_6$** — S. Migita *et al*., *Appl. Phys. Lett.* **71** (1997) 3712-3714.
  - **$Bi_4Ti_3O_{12}$** — C.D. Theis *et al*., *Appl. Phys. Lett.* **72** (1998) 2817-2819.
  - **$BiFeO_3$** — J.F. Ihlefeld *et al*., *Appl. Phys. Lett.* **91** (2007) 071922.
  - **$BiMnO_3$** — J.H. Lee *et al*., *Appl. Phys. Lett.* **96** (2010) 262905.
  - **$BiVO_4$** — S. Stoughton *et al*., *APL Materials* **1** (2013) 042112.
  - **$Bi_2Sn_2O_7$** and **$Bi_2Ru_2O_7$** — (unpublished)
- **Titanates by MOMBE**
  - **$SrTiO_3$** — B. Jalan *et al*., *Appl. Phys. Lett*. 95 (2009) 032906.
  - **$GdTiO_3$** — P. Moetakef *et al*., *J. Vac. Sci. Technol. A* **31** (2013) 041503.
  - **$BaTiO_3$** — Y. Matsubara *et al*., *Appl. Phys. Express* **7** (2014) 125502.
  - **$CaTiO_3$** —R.C. Haislmaier *et al*., *Adv. Funct. Mater.* **26** (2016) 7271.

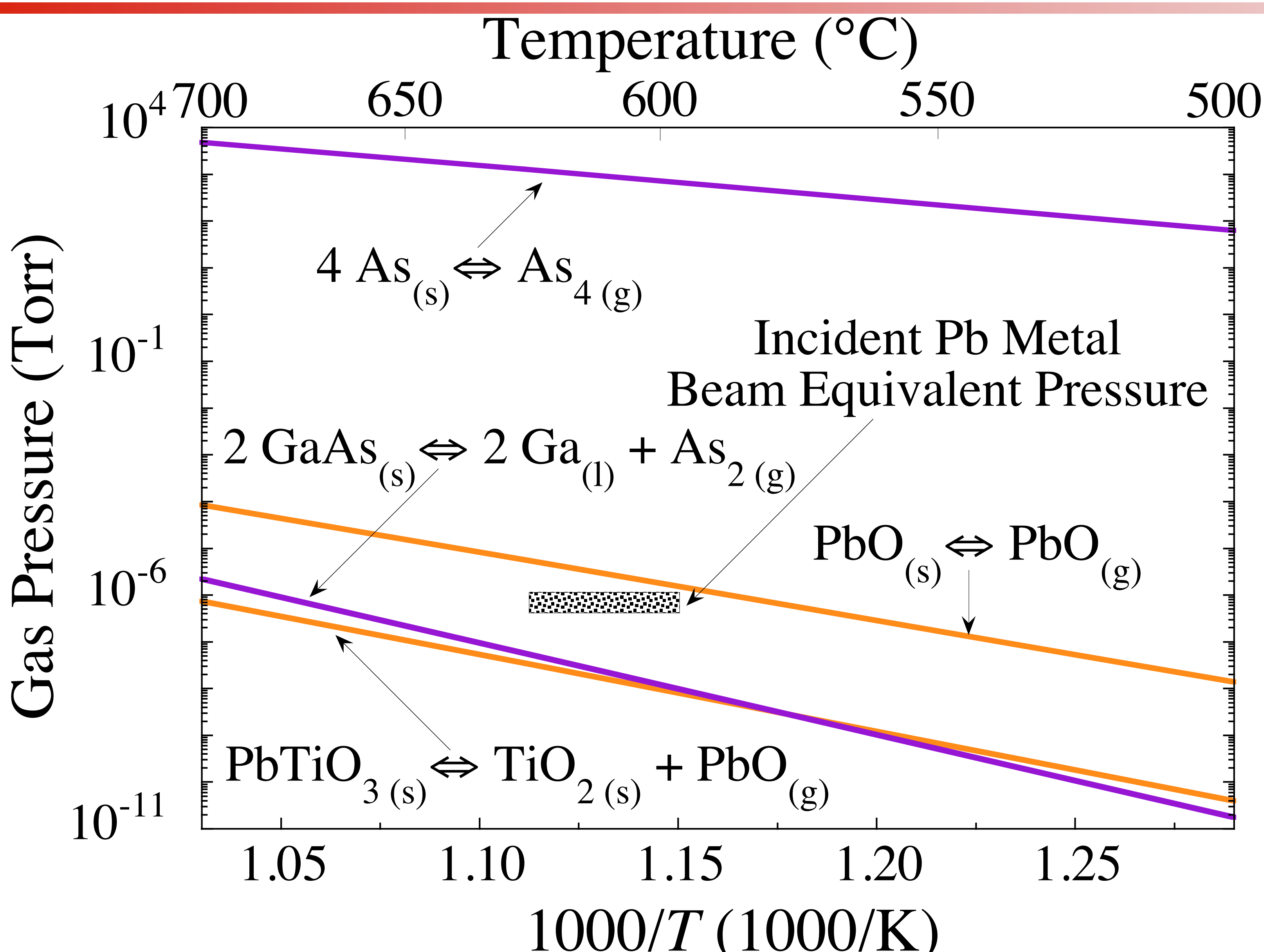
# Adsorption-Controlled Growth of

- **Ferrites**
  - **$LuFe_2O_4$** — C.M. Brooks *et al*., *Appl*. *Phys*. *Lett*. **101** (2012) 132907.
- **Vanadates by MOMBE**
  - **$LaVO_3$** —H.-T. Zhang *et al*., *Appl*. *Phys*. *Lett*. **106** (2015) 233102.
  - **$(La,Sr)VO_3$** —M. Brahlek *et al*., *Appl*. *Phys*. *Lett*. **109** (2016) 101903.
- **Ruthenates**
  - **$SrRuO_3$** — D.E. Shai *et al*., *Phys*. *Rev*. *Lett*. **110** (2013) 087004.
  - **$Sr_2RuO_4$** and **$Ba_2RuO_4$**— B. Burganov *et al*., *Phys*. *Rev*. *Lett*. **116** (2016) 197003.
  - **$CaRuO_3$** — H.P. Nair *et al*., *APL Mater*. **6** (2018) 046101.
  - **$Ca_2RuO_4$** — (unpublished)

# Adsorption-Controlled Growth of

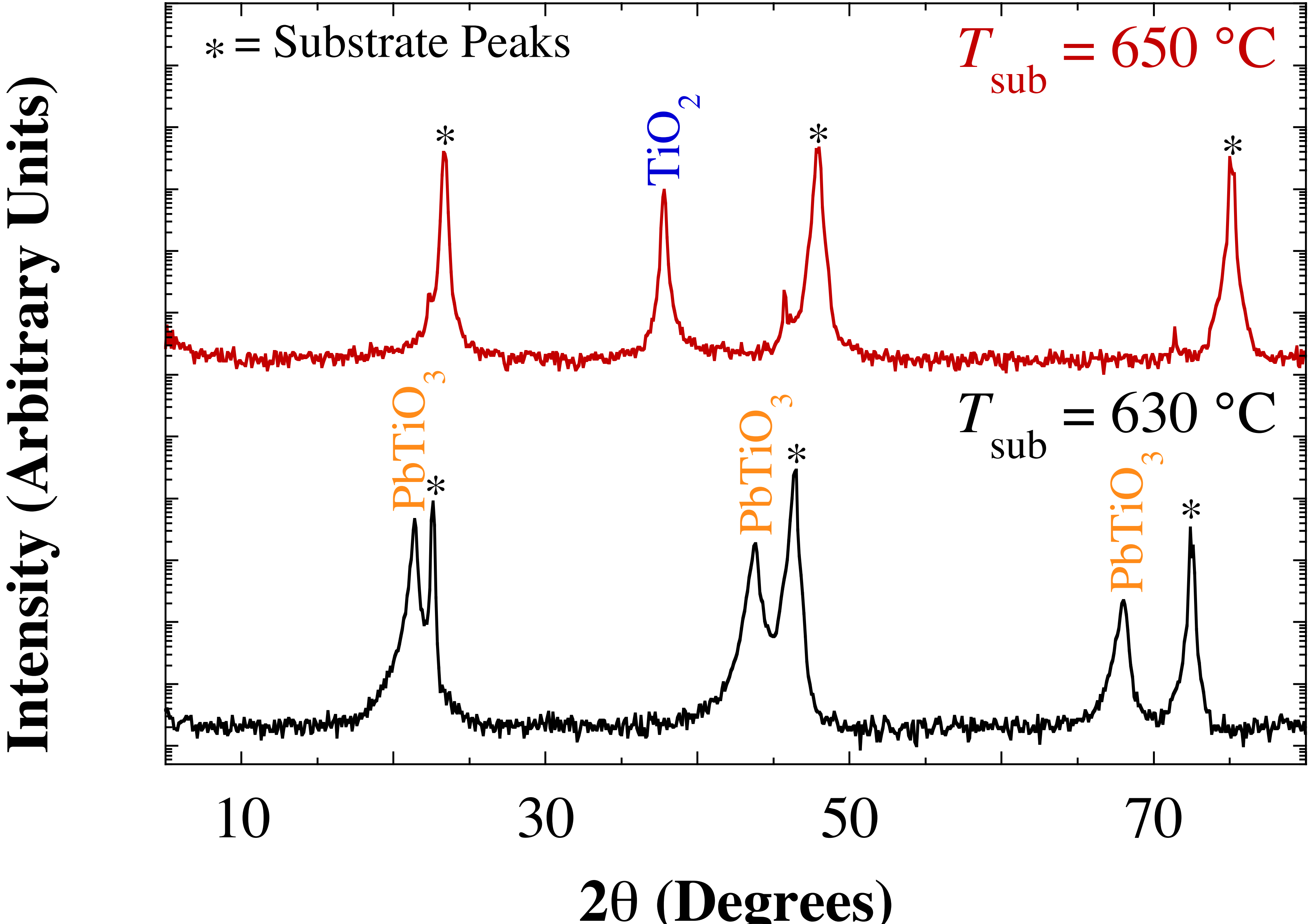
- **Iridates**
  - **$Ba_2IrO_4$** — M. Uchida *et al*., *Phys. Rev. B* **90** (2014) 075142.
  - **$SrIrO_3$** and **$Sr_2IrO_4$** — Y.F. Nie *et al*., *Phys. Rev. Lett*. **114** (2015) 016401.
- **Stannates by MOCVD**
  - **$BaSnO_3$** — A. Prakash *et al*., *J. Mater. Chem. C* **5** (2017) 5730 .
- **Stannates**
  - **$BaSnO_3$** — H. Paik *et al*., *APL Materials* **5** (2017) 116107.
- **Other**
  - **EuO** — R.W. Ulbricht *et al*., *Appl. Phys. Lett*. **93** (2008) 102105.

# Adsorption-Controlled Growth of $PbTiO_3$

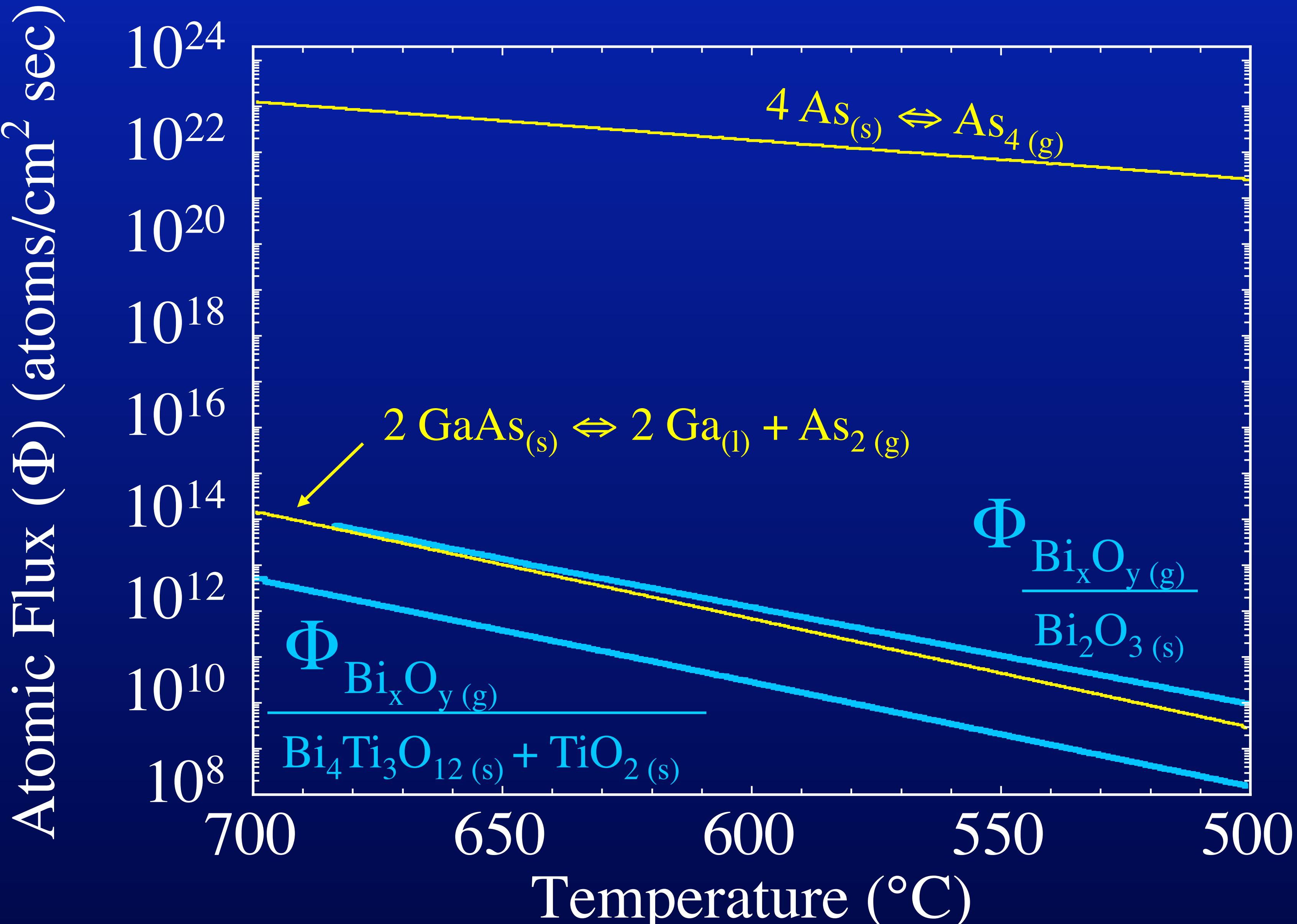



C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown,
"Adsorption-Controlled Growth of $PbTiO_3$ by Reactive Molecular Beam Epitaxy," *Thin Solid Films* **325** (1998) 107-114.

# Adsorption-Controlled Growth of $PbTiO_3$

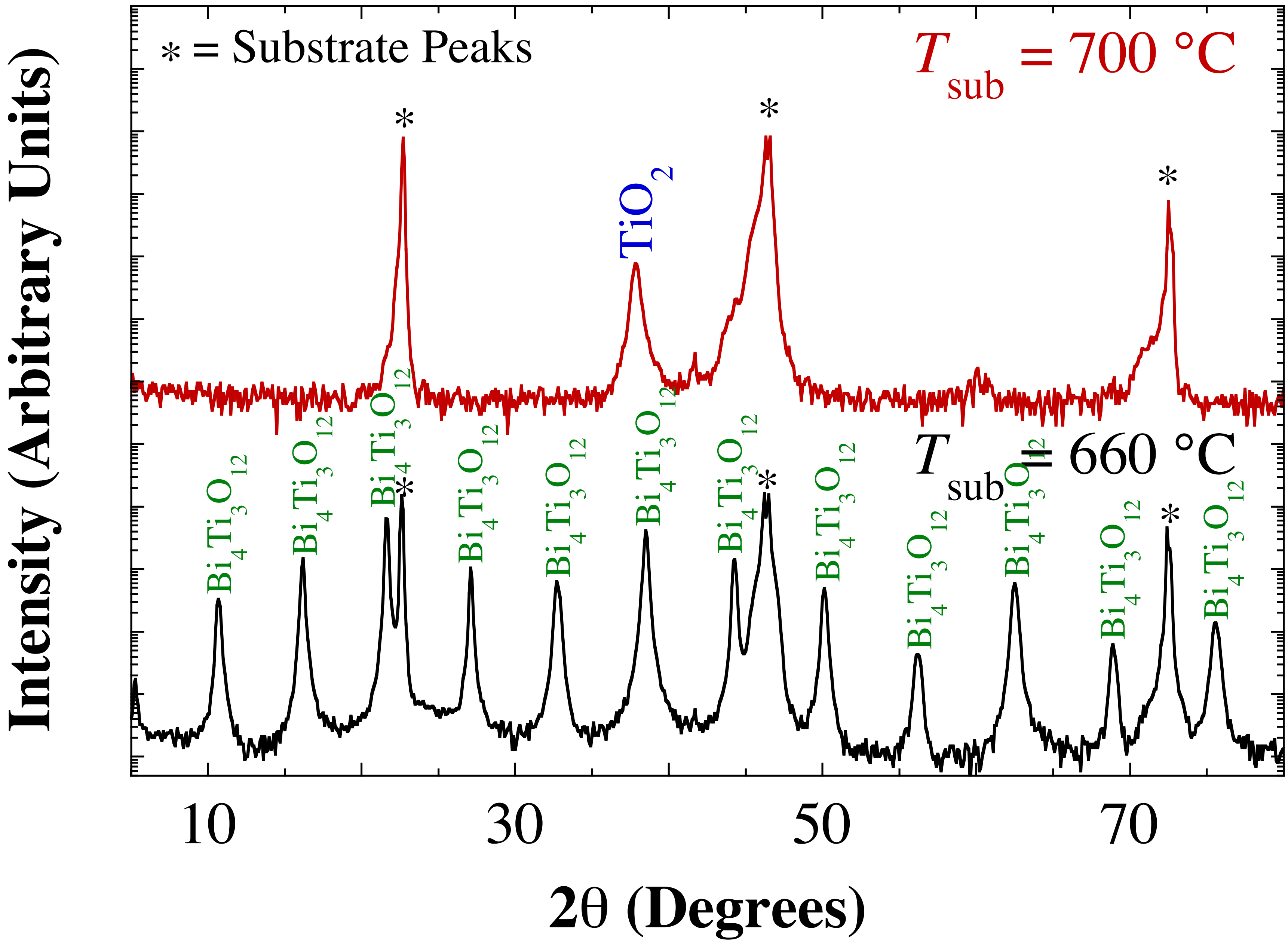


# Growth of $Bi_4Ti_3O_{12}$ by MBE

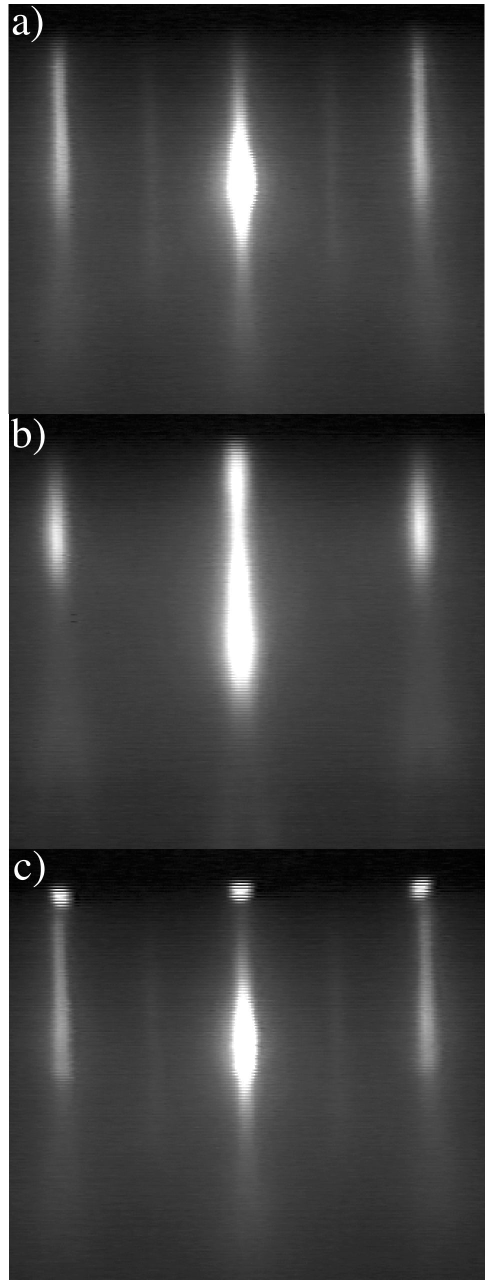



D.G. Schlom, J.H. Haeni, J. Lettieri, C.D. Theis, W. Tian, J.C. Jiang, and X.Q. Pan, *Mater. Sci. Eng. B* **87** (2001) 282-291.

# Adsorption-Controlled Growth of $Bi_4Ti_3O_{12}$



# Adsorption-Controlled Growth of $Bi_4Ti_3O_{12}$



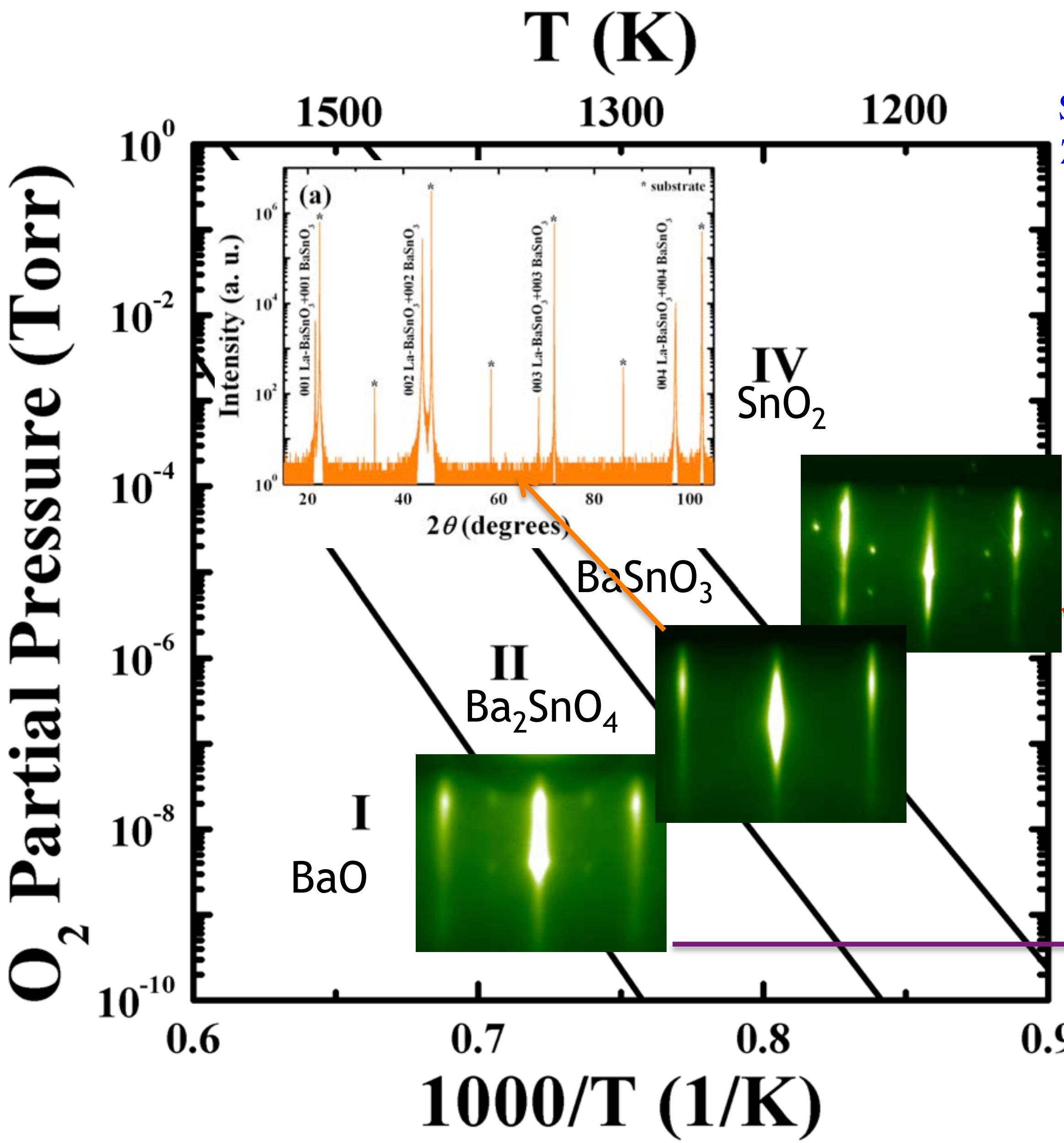

$Bi_4Ti_3O_{12}$

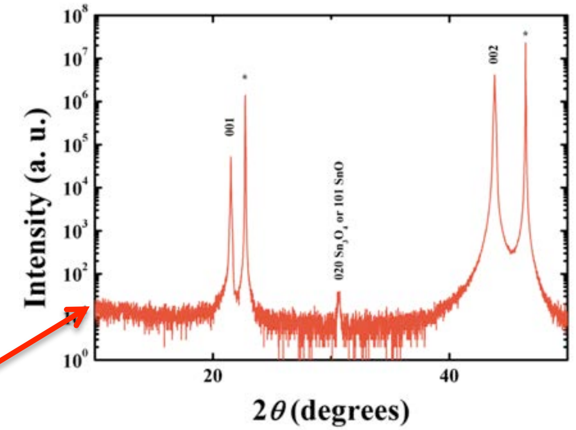
$TiO_2$

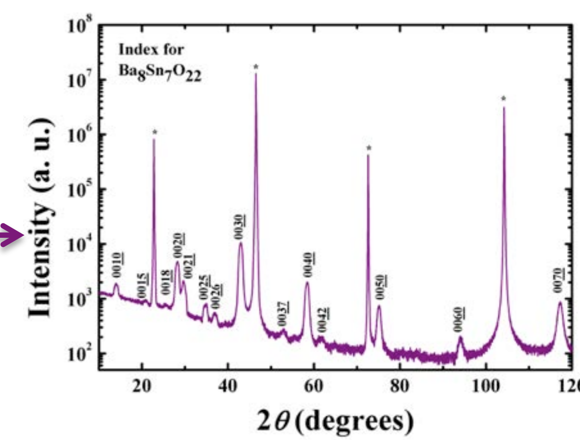
$Bi_2O_{2.33}$

# Growth of $BaSnO_3$ by MBE

H. Paik, Z. Chen, E. Lochocki, A. Seidner H., A. Verma, N. Tanen, J. Park, M. Uchida, S.L. Shang, B-C. Zhou, M. Brützam, R. Uecker, Z.K. Liu, D. Jena, K.M. Shen, D.A. Muller, and D.G. Schlom, *APL Materials* **5** (2017) 116107.

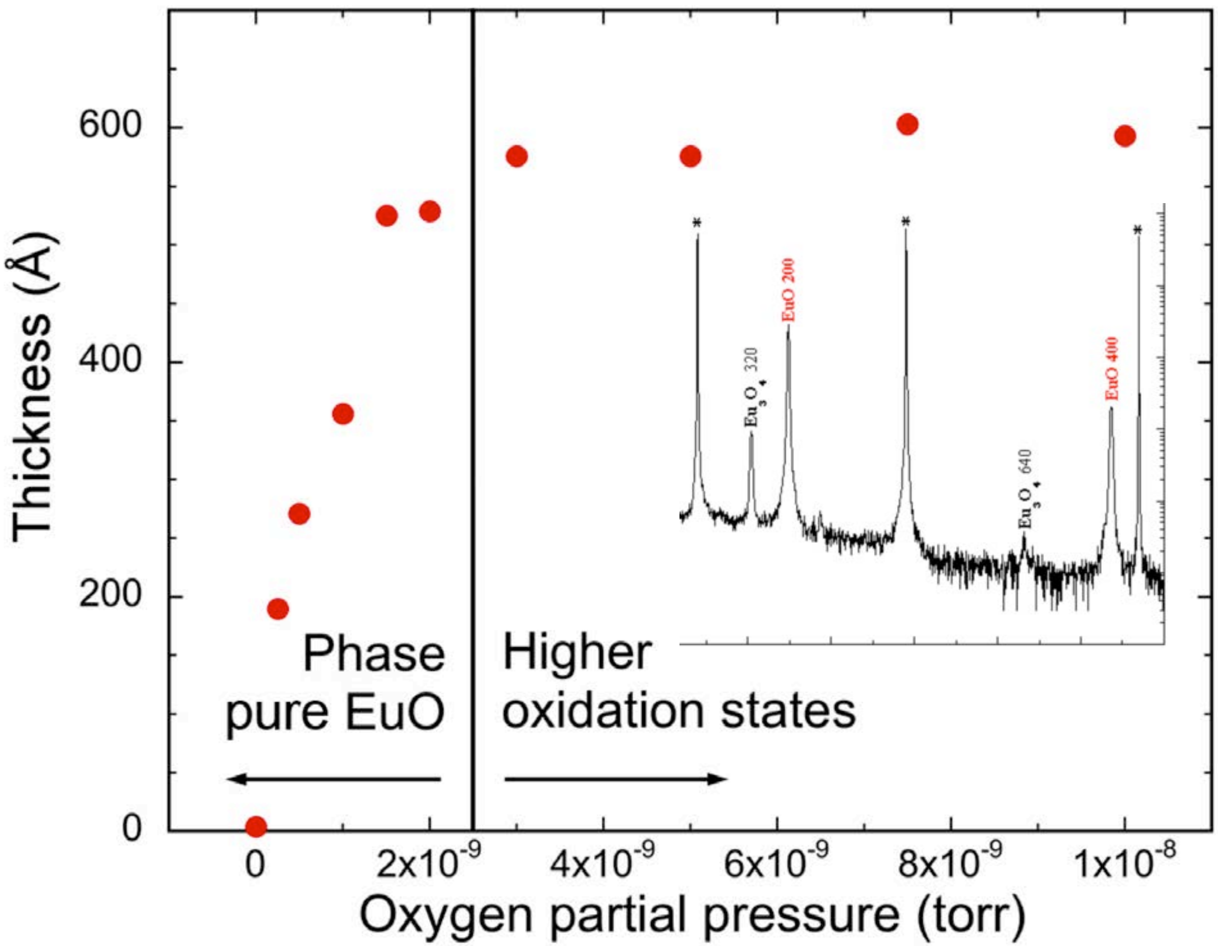


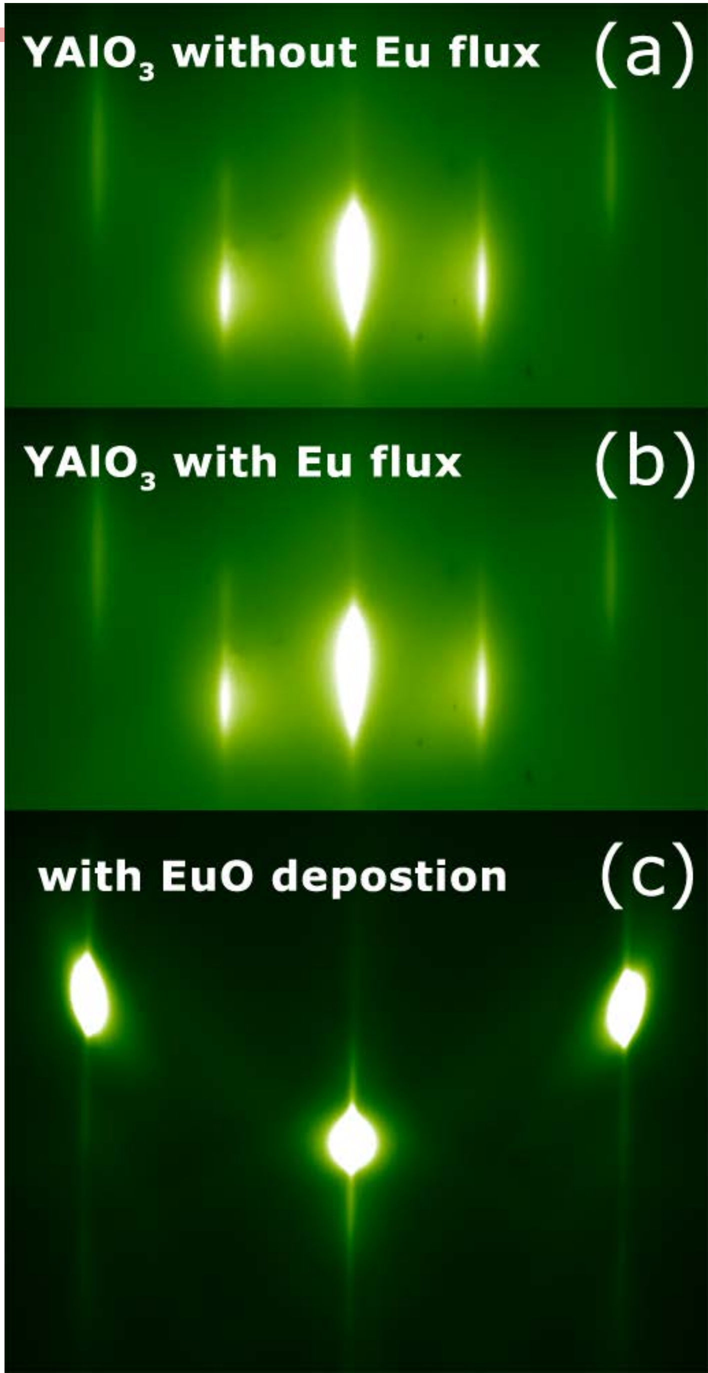



# Adsorption-Controlled Growth of EuO

Eu Flux = $1.1\times10^{14}$ Eu atoms/($cm^2$ s), $T_{sub}$ = 590 °C
EuO film thickness (from RBS) after 30 min




R.W. Ulbricht, A. Schmehl, T. Heeg, J. Schubert, and D.G. Schlom, *Applied Physics Letters* **93** (2008) 102105.

# Adsorption-Controlled $SrTiO_3$

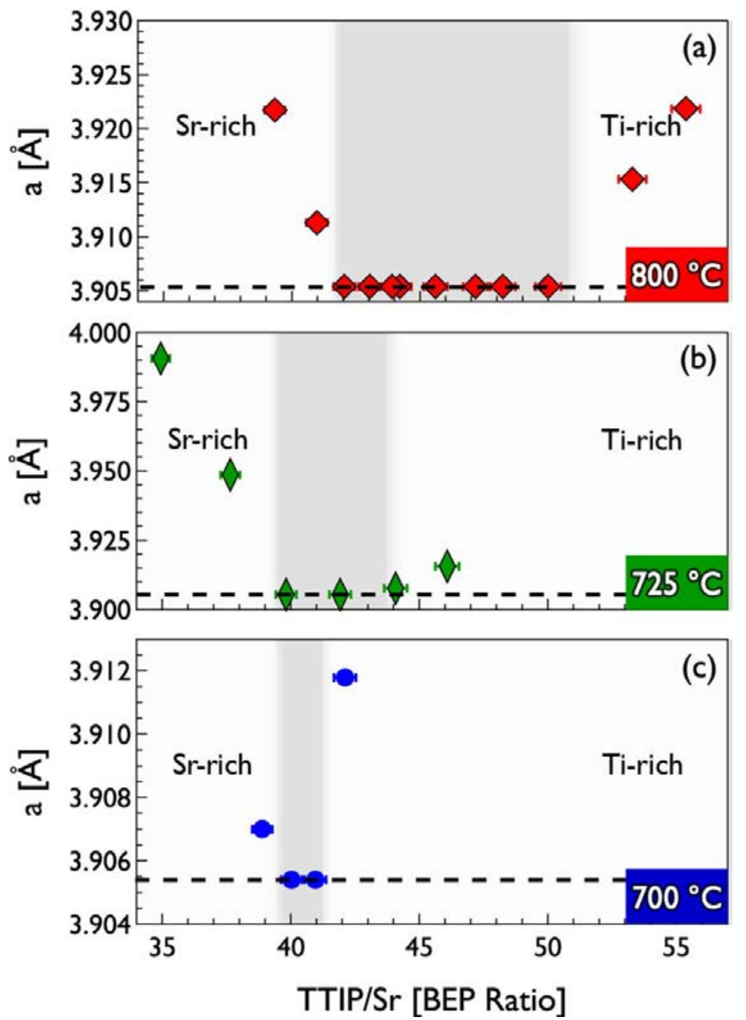



FIG. 3. (Color online) Out-of-plane lattice parameter as a function of TTIP/Sr BEP ratio for epitaxial $SrTiO_3$ films grown on (001)$SrTiO_3$ at (a) 800 °C, (b) 725 °C, and (c) 700 °C. All films were grown using an oxygen BEP of $8 \times 10^{-6}$ torr. The darker gray-shaded region shows the growth window for stoichiometric films with a lattice parameter that is equivalent to that of the substrate at each temperature.

**<u>MOMBE Sources</u>**

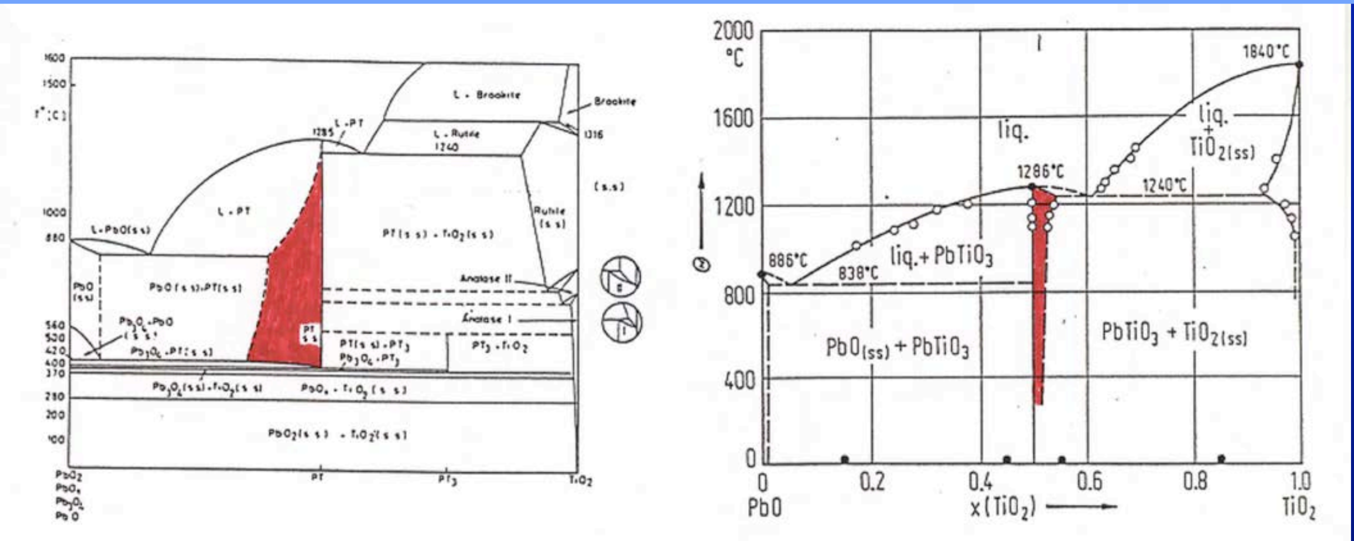
**Sr**

**$Ti(OC_3H_7)_4$**

**Oxygen Plasma**

B. Jalan, P. Moetakef, and S. Stemmer, *Applied Physics Letters* **95** (2009) 032906.

# Single-Phase Field of GaAs vs. $PbTiO_3$




$PbTiO_3$

GaAs

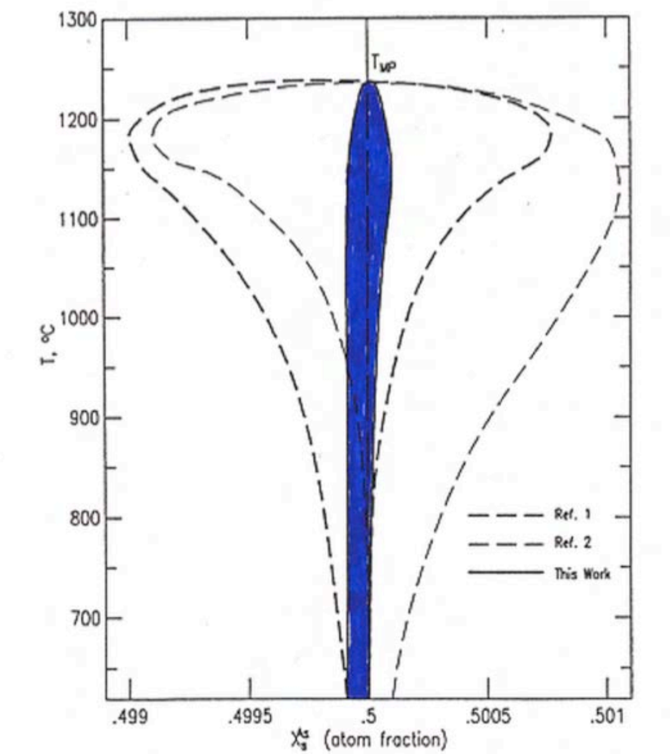



**Fig. 8337**—GaAs solidus curve. Curves represent the calculated deviations from stoichiometry for solid GaAs.
A. I. Ivashchenko, F. Ya. Kopanskaya, and G. S. Kuzmenko, *J. Phys. Chem. Solids*, 45 [8-9] 871-875 (1984).

Single-phase film does not imply stoichiometric film

# III-V Phase Diagrams



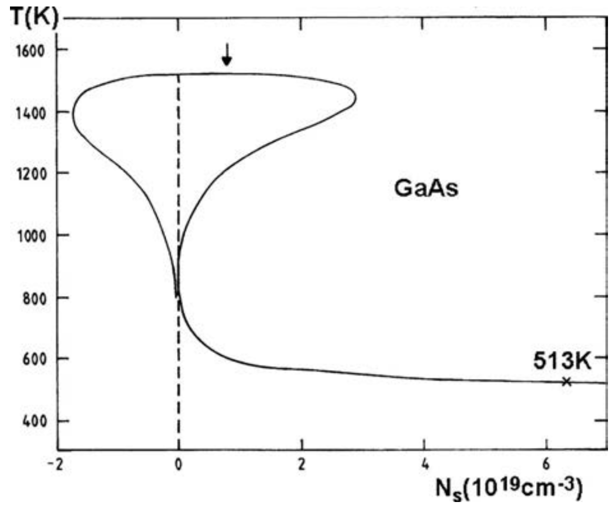



FIG. 2. The calculated solidus of gallium arsenide showing the catastrophic deviation from stoichiometry at low temperature under arsenic-rich conditions. Arrow marks the congruent point.

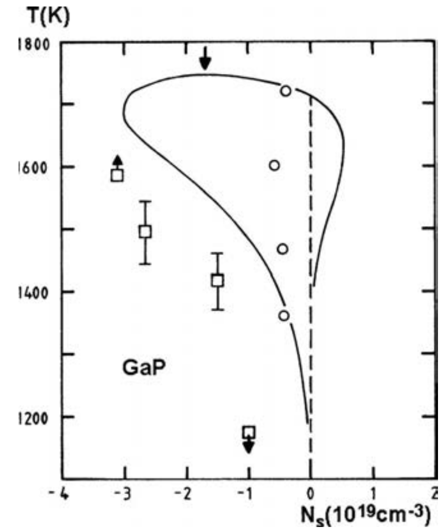



FIG. 3. Calculated GaP solidus. Arrow marks the congruent point. Experimental data: Jordan *et al.* (○); Morozov *et al.* (□).

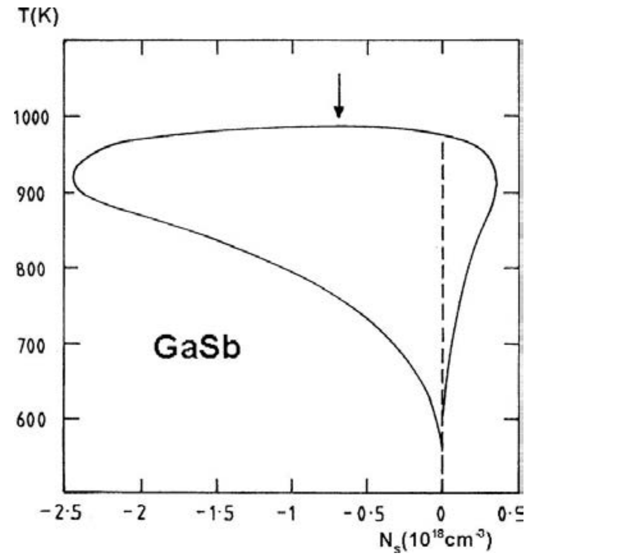



FIG. 5. Calculated GaSb solidus. Arrow marks the congruent point.

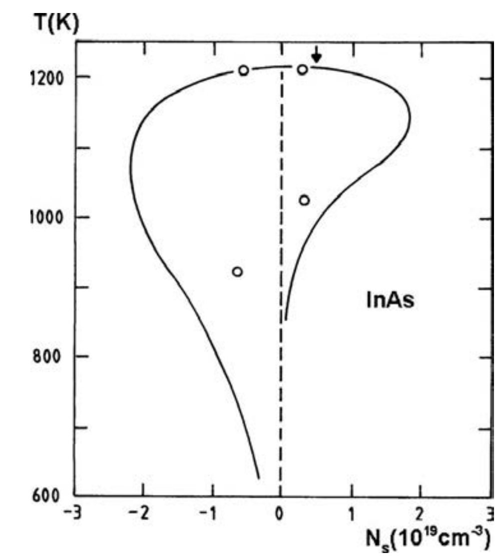



FIG. 7. Calcuated InAs solidus. Arrow marks the congruent point. Data points: Bublik *et al.* (○).

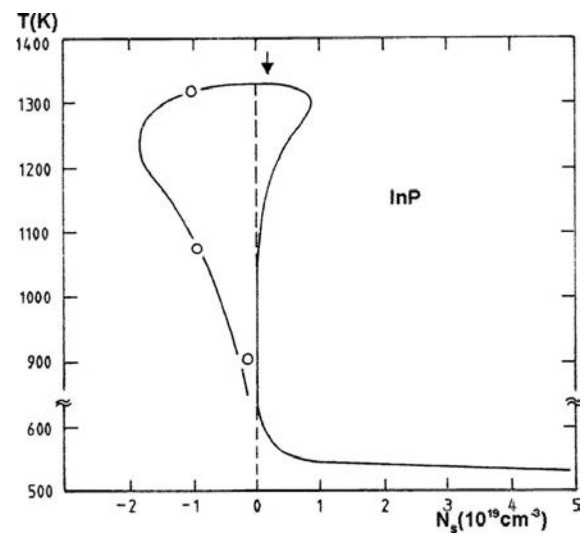



FIG. 8. Calculated InP solidus. Arrow marks the congruent point. Data points: Morozov *et al.* (Ref. 34) (○).

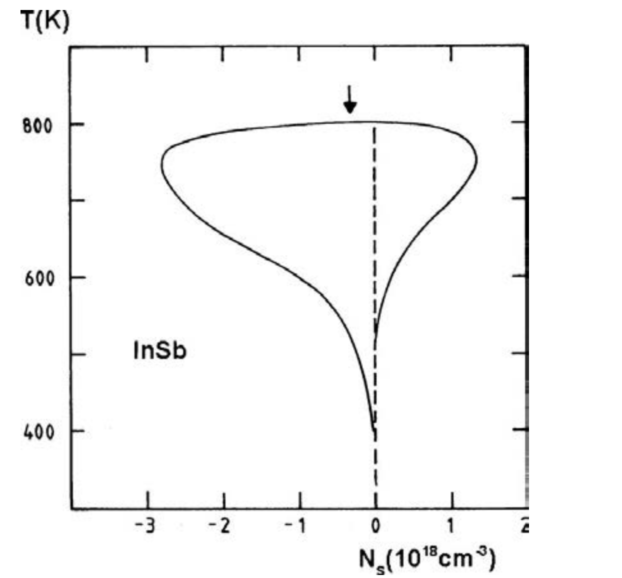
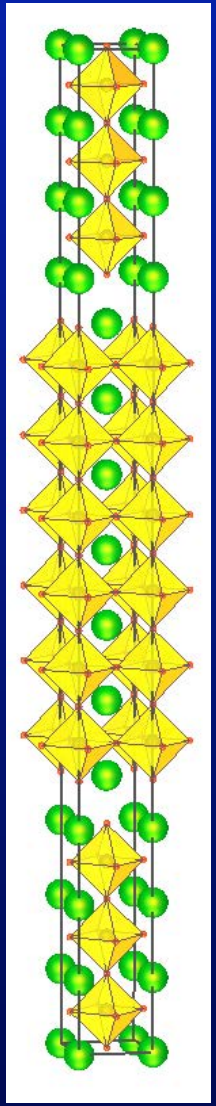


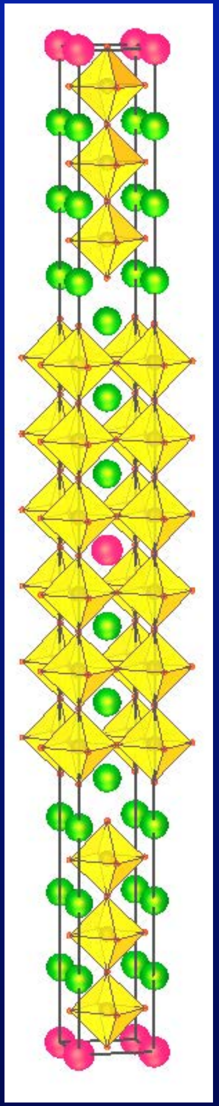

FIG. 9. Calculated InSb solidus. Arrow marks the congruent point.

# Challenge

**What if the wacky oxide you desire cannot be grown by adsorption-control?**



$Sr_7Ti_6O_{19}$



$BaSr_6Ti_6O_{19}$

# Nuts and Bolts of Oxide MBE

- Mean Free Path (maximum $P_{O_2}$)
- Minimum $P_{O_2}$, need for $P_{O_3}$, Optimal $T_{sub}$
- MBE System, Sources, and Crucibles
- Composition Control
  - Adsorption-Controlled Growth
  - Flux-Controlled Growth
- Substrates

# Reflection High-Energy Electron Diffraction (RHEED) Oscillations

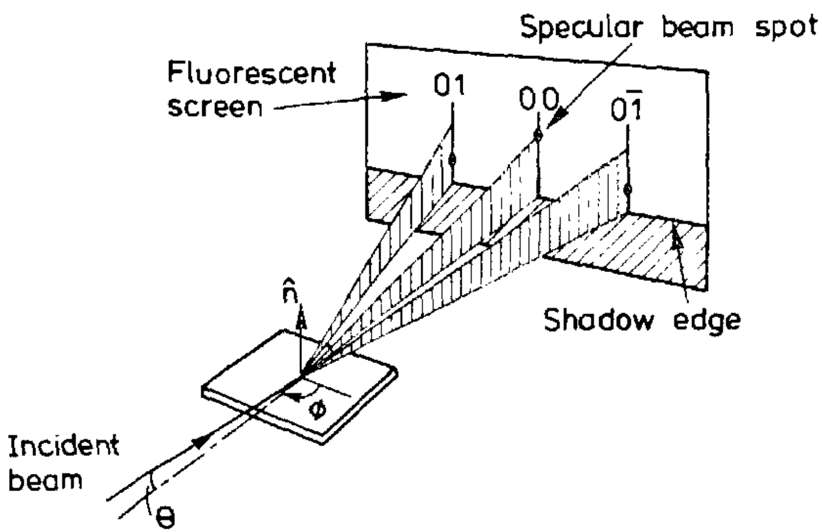
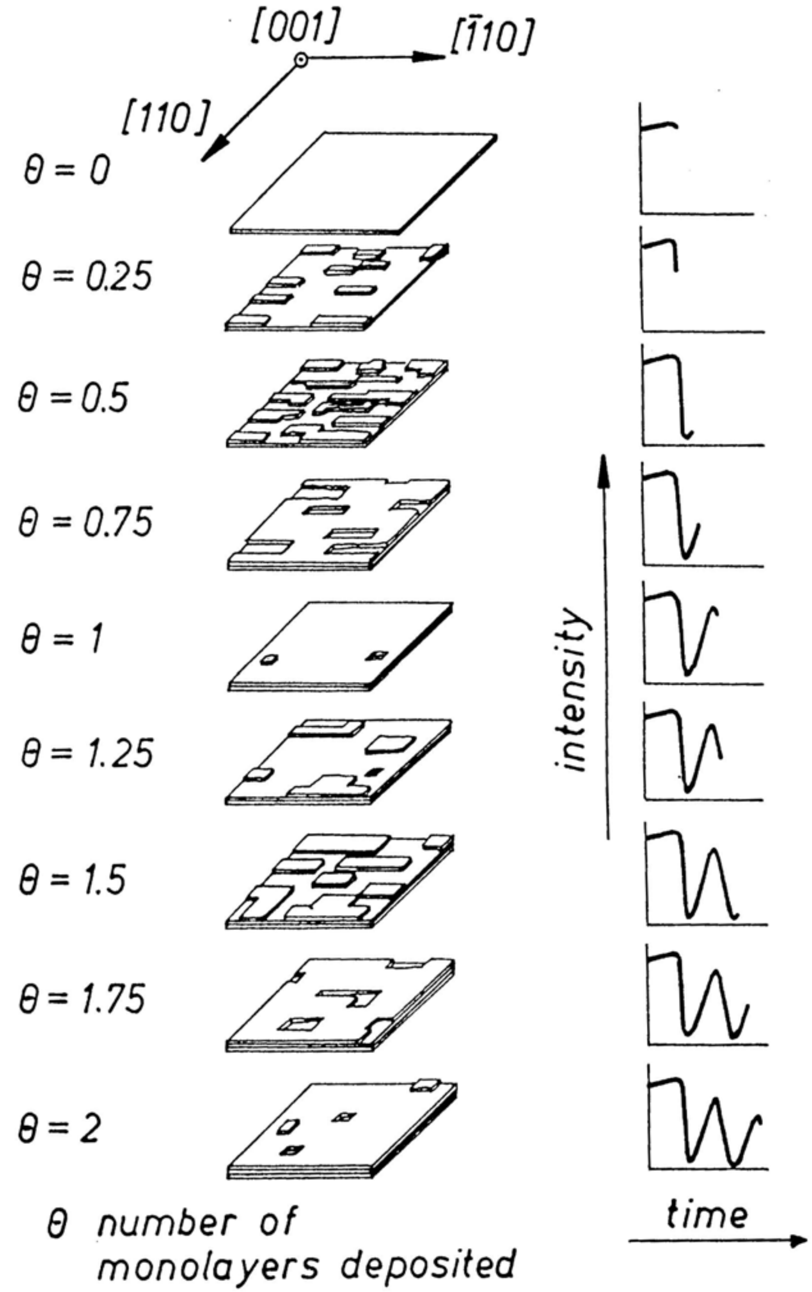


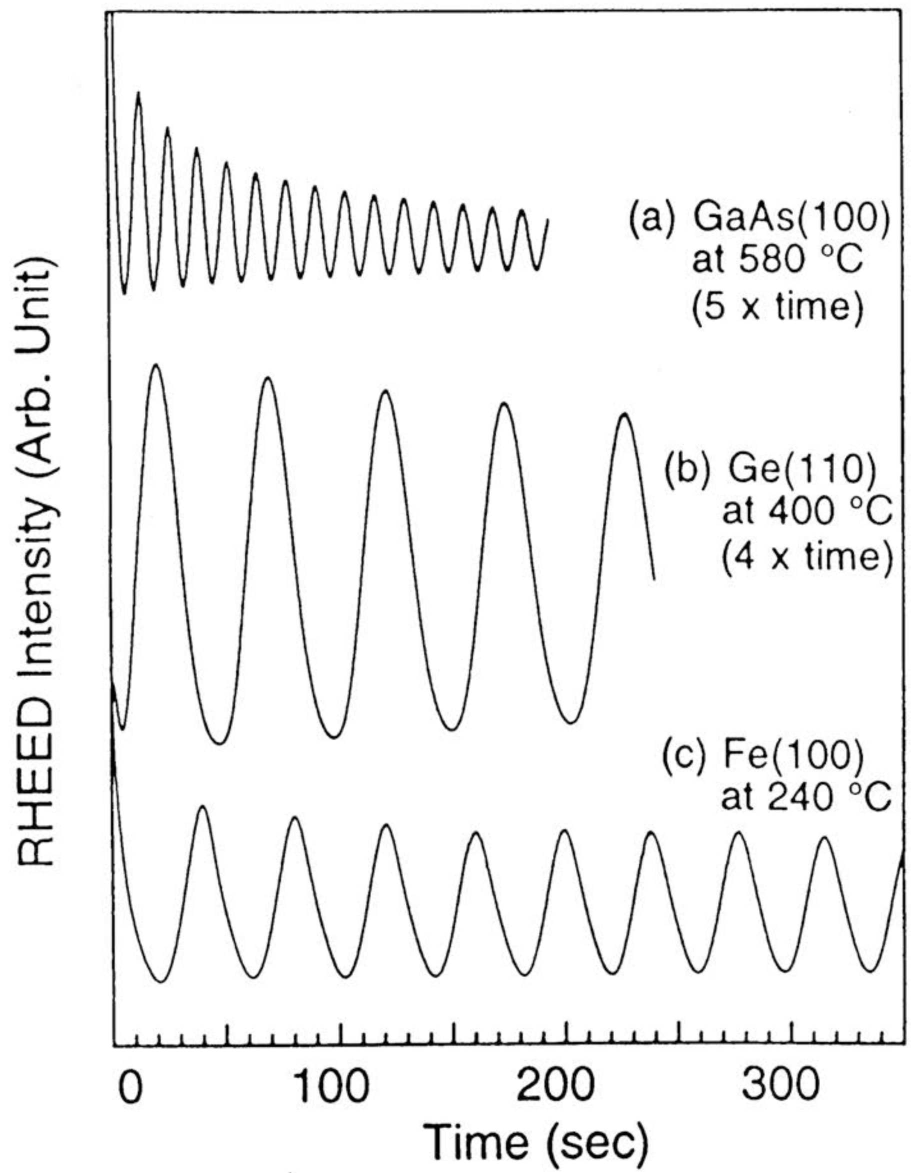

FIG. 1. Schematic diagram of RHEED geometry showing the incident beam at an angle $\theta$ to the surface plane; azimuthal angle $\varphi$. The elongated spots indicate the intersection of the Ewald sphere with the 01, 00, and 0$\bar{1}$ rods.

B. Bölger and P. K. Larsen, *Review of Scientific Instruments* **57** (1986) 1363-1367.




B.A. Joyce, P.J. Dobson, J.H. Neave, K. Woodbridge, J. Zhang, P.K. Larsen, and B Bölger, *Surface Science* **168** (1986) 423-438.

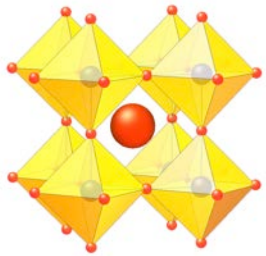
# Conventional RHEED Oscillations



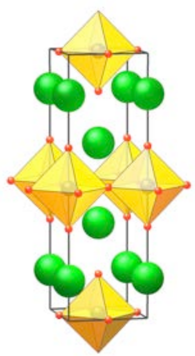

Molecular Beam Epitaxy: *Applications to Key Materials*, edited by R.F.C. Farrow (Noyes, Park Ridge, 1995), p. 694.

# Conventional RHEED Oscillations

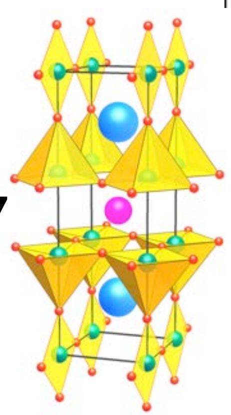
$BaTiO_3$

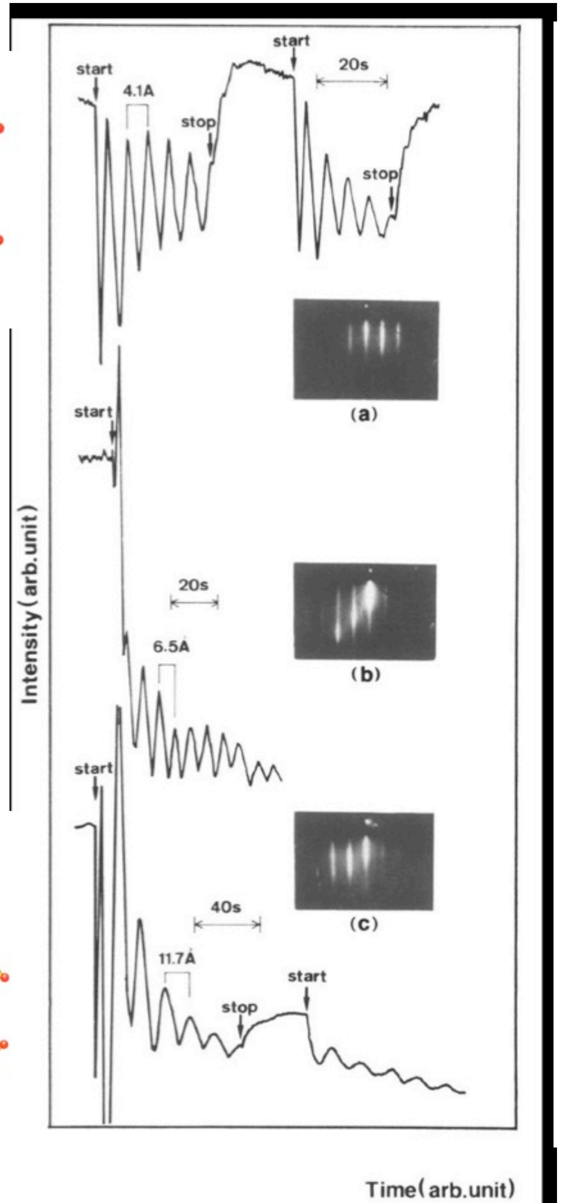


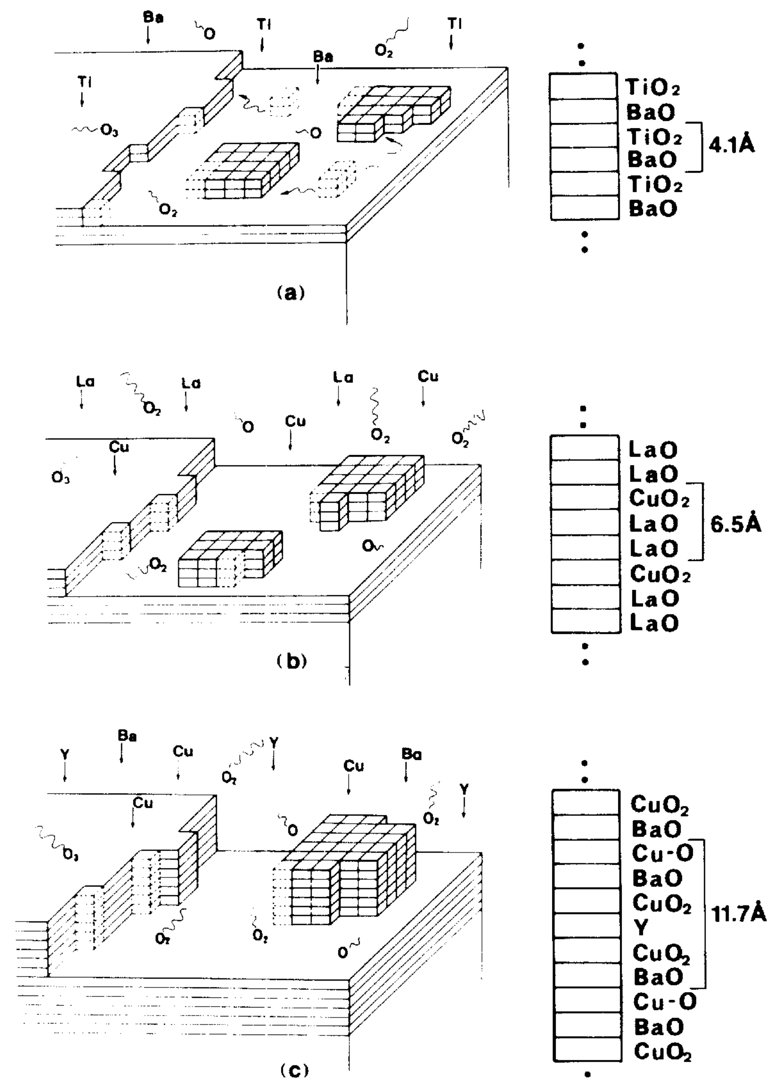
$La_2CuO_4$



$YBa_2Cu_3O_7$



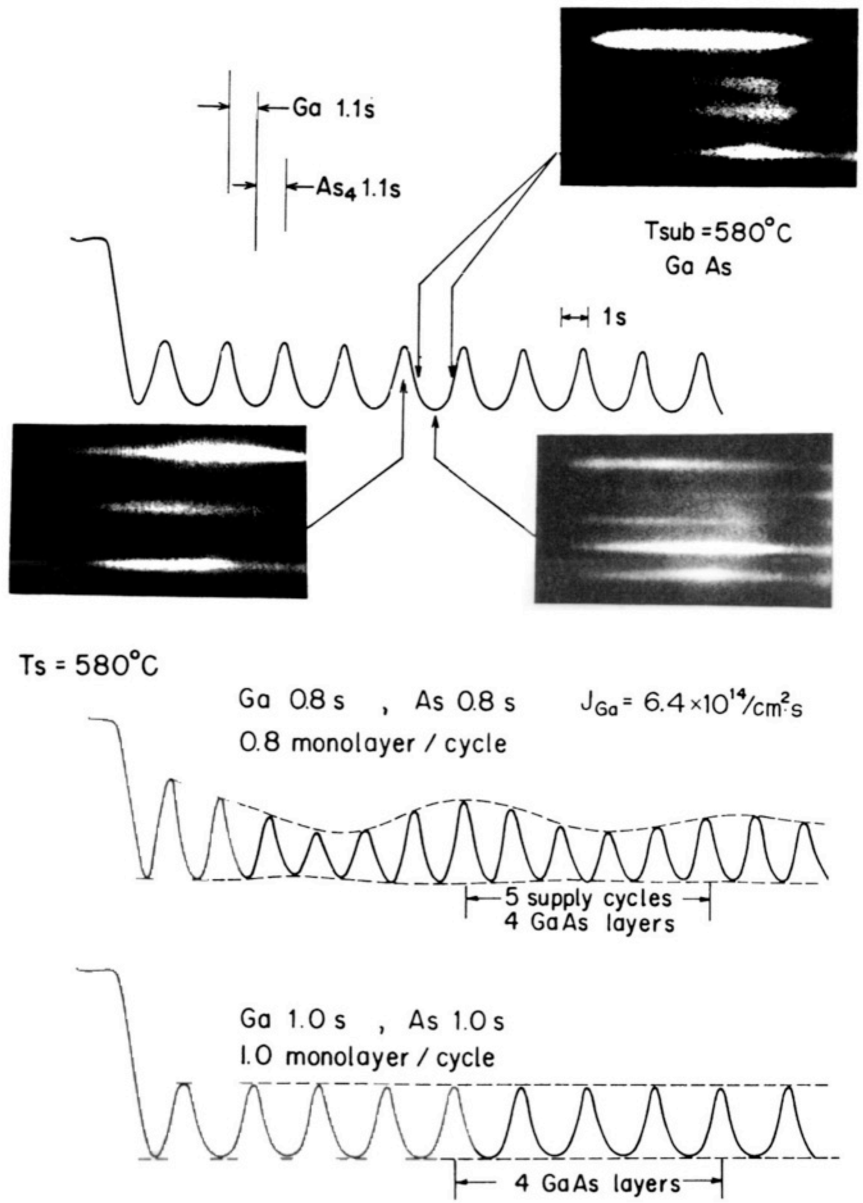



T. Terashima, Y. Bando, K. Iijima, K. Yamamoto, K. Hirata, K. Hayashi, K. Kamigaki, and H. Terauchi, *Physical Review Letters* **65** (1990) 2684–2687.

# Migration-Enhanced Epitaxy of GaAs and AlGaAs

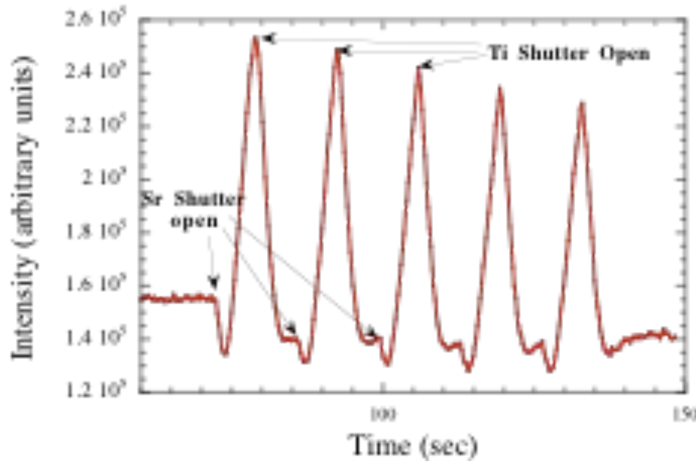
Yoshiji HORIKOSHI, Minoru KAWASHIMA and Hiroshi YAMAGUCHI



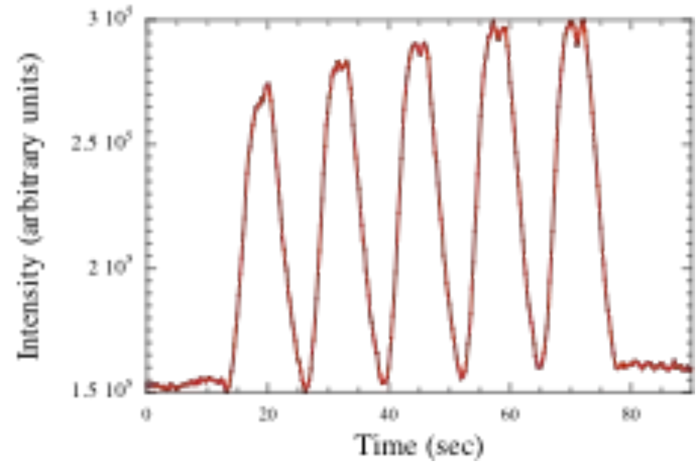

JAPANESE JOURNAL OF APPLIED PHYSICS
VOL. 27, NO. 2, FEBRUARY, 1988, pp. 169–179

# Shuttered RHEED to Get Sr:Ti = 1:1

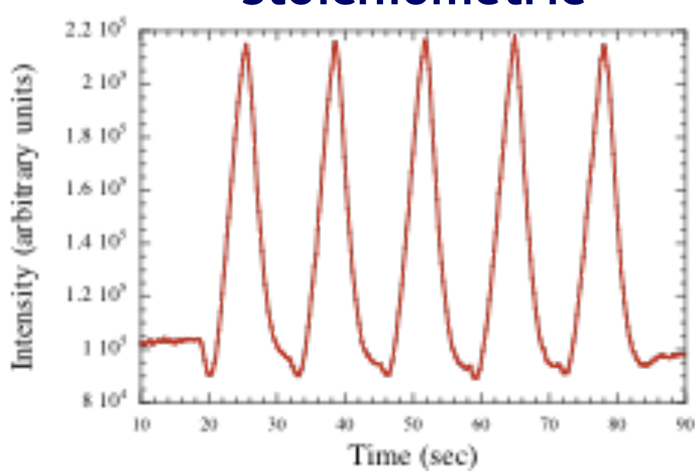
**3 % Ti Rich**



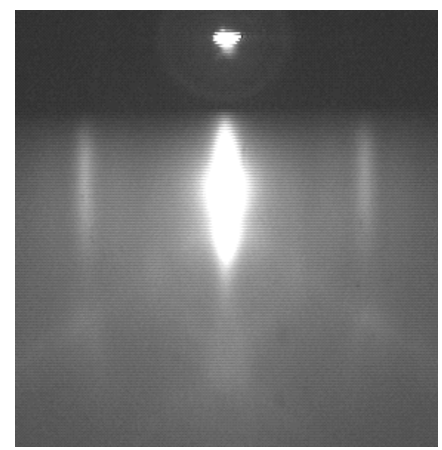

**3 % Ti Poor**




**Stoichiometric**



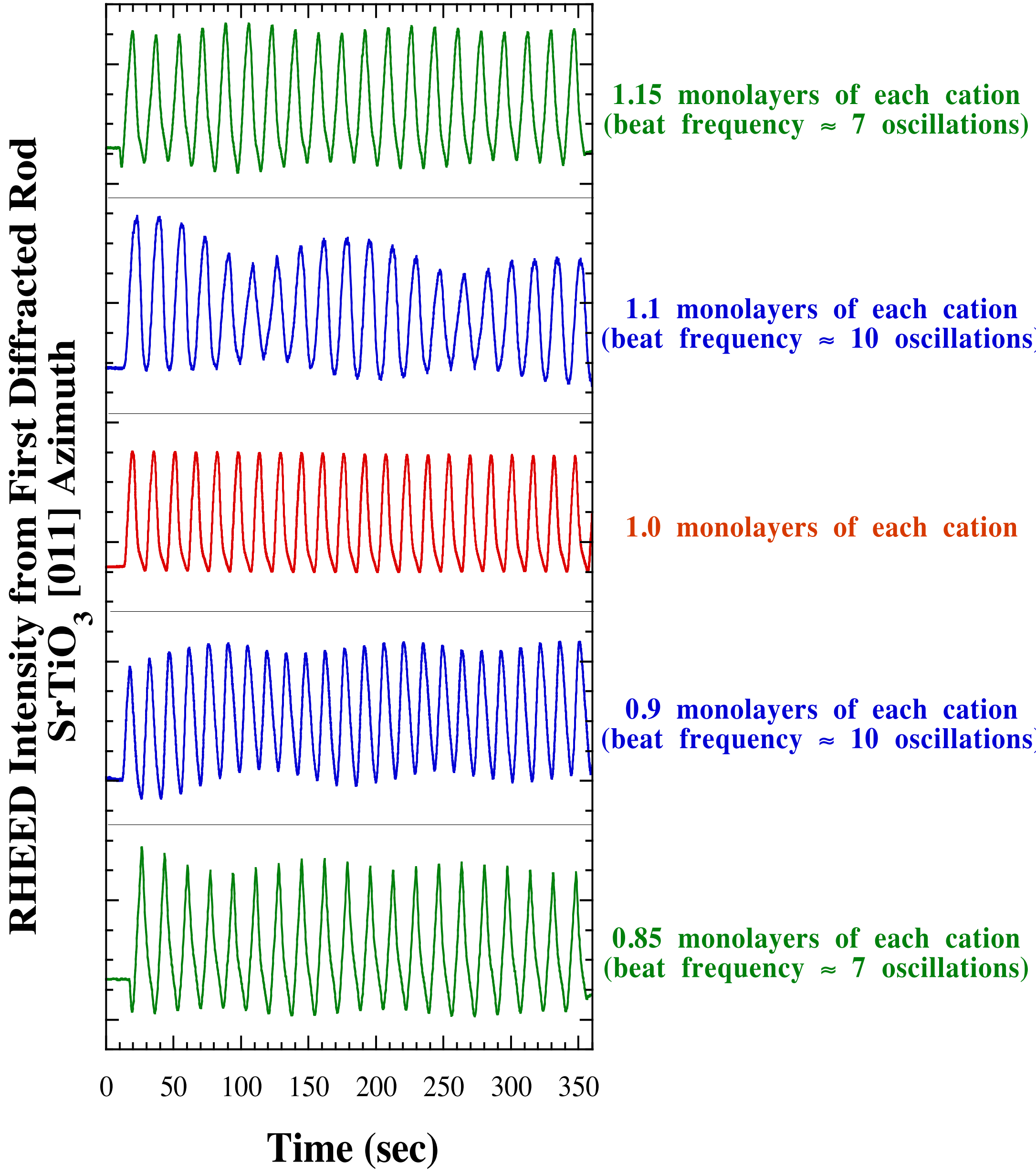

**$SrTiO_3$ [011] Azimuth**



Oscillations of the central diffracted rod as the Sr and Ti are deposited in a sequential manner

J.H. Haeni, C.D. Theis, and D.G. Schlom, *Journal of Electroceramics* **4** (2000) 385-391.

# Beat Frequency for Sr:Ti = 1:1 Absolute



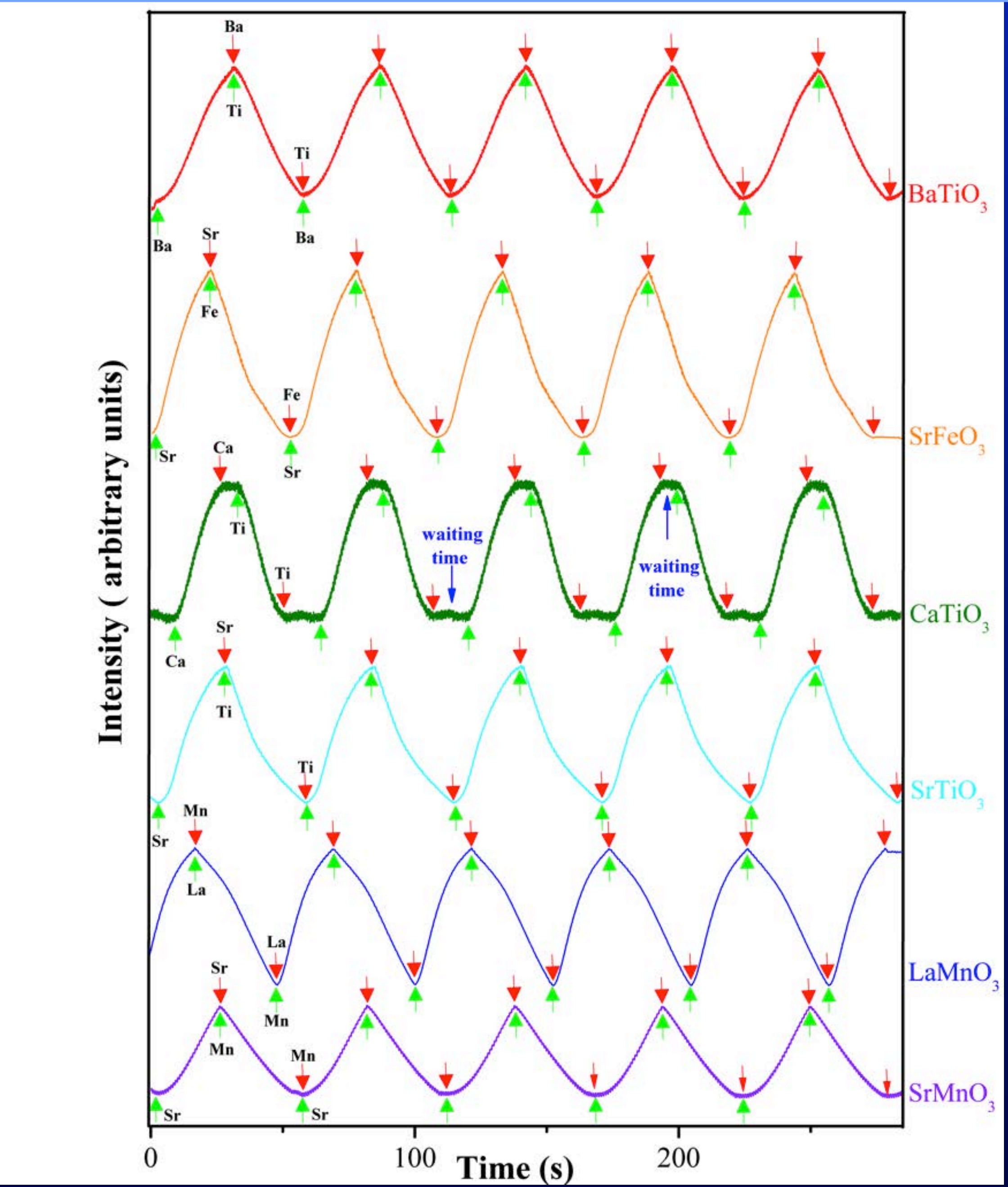

J.H. Haeni, C.D. Theis, and D.G. Schlom, *Journal of Electroceramics* **4** (2000) 385-391.

# How we do it

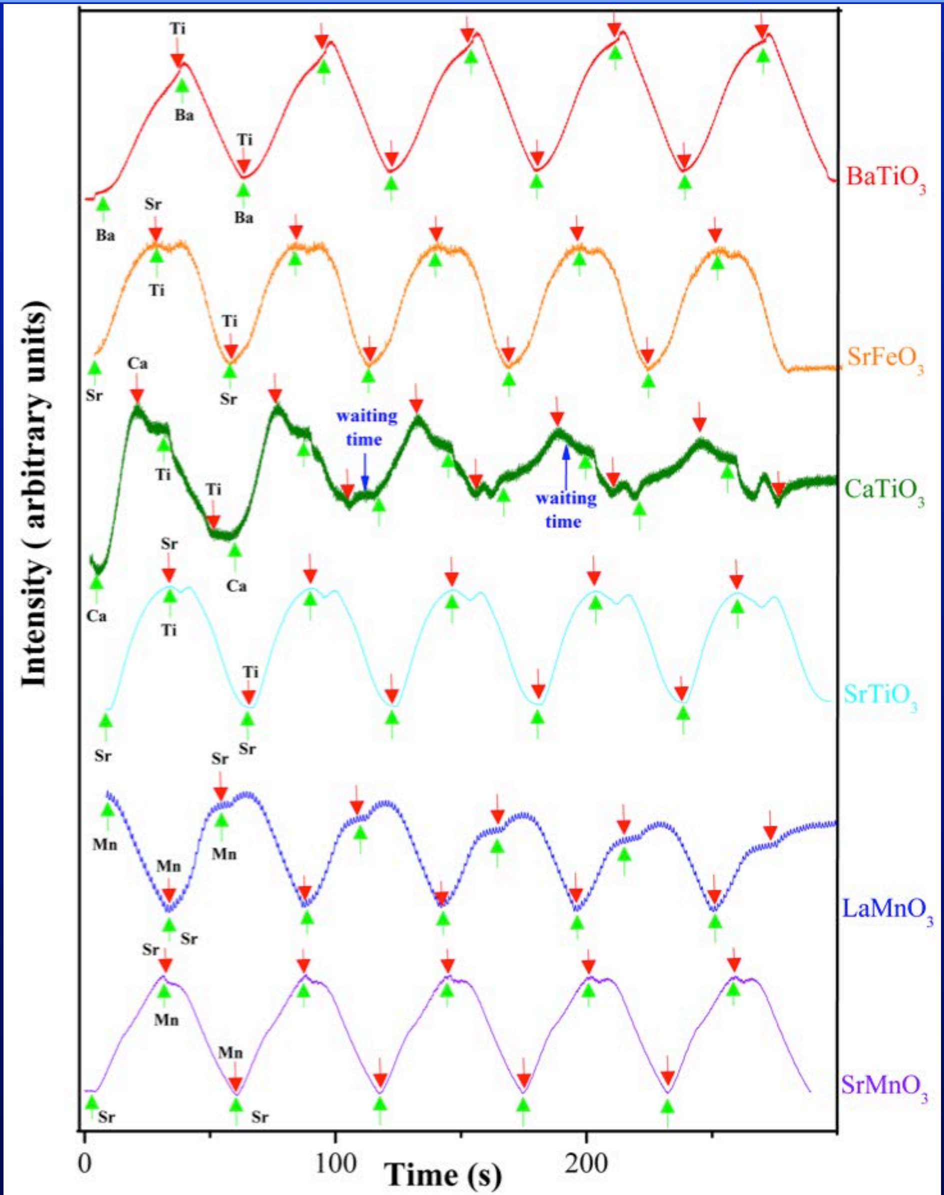
- Use Quartz Crystal Microbalance to Get Fluxes Close (~10% accuracy)
- Use Shuttered RHEED Oscillations (analogous to MEE of GaAs)
- Yields Sr:Ti *Relative* Incorporation Ratio (~1% accuracy)
- Yields *Absolute* Monolayer Dose for SrO and $TiO_2$ (~1% accuracy)
- Works for many Perovskites

J.H. Haeni, C.D. Theis, and D.G. Schlom, *Journal of Electroceramics* **4** (2000) 385-391.

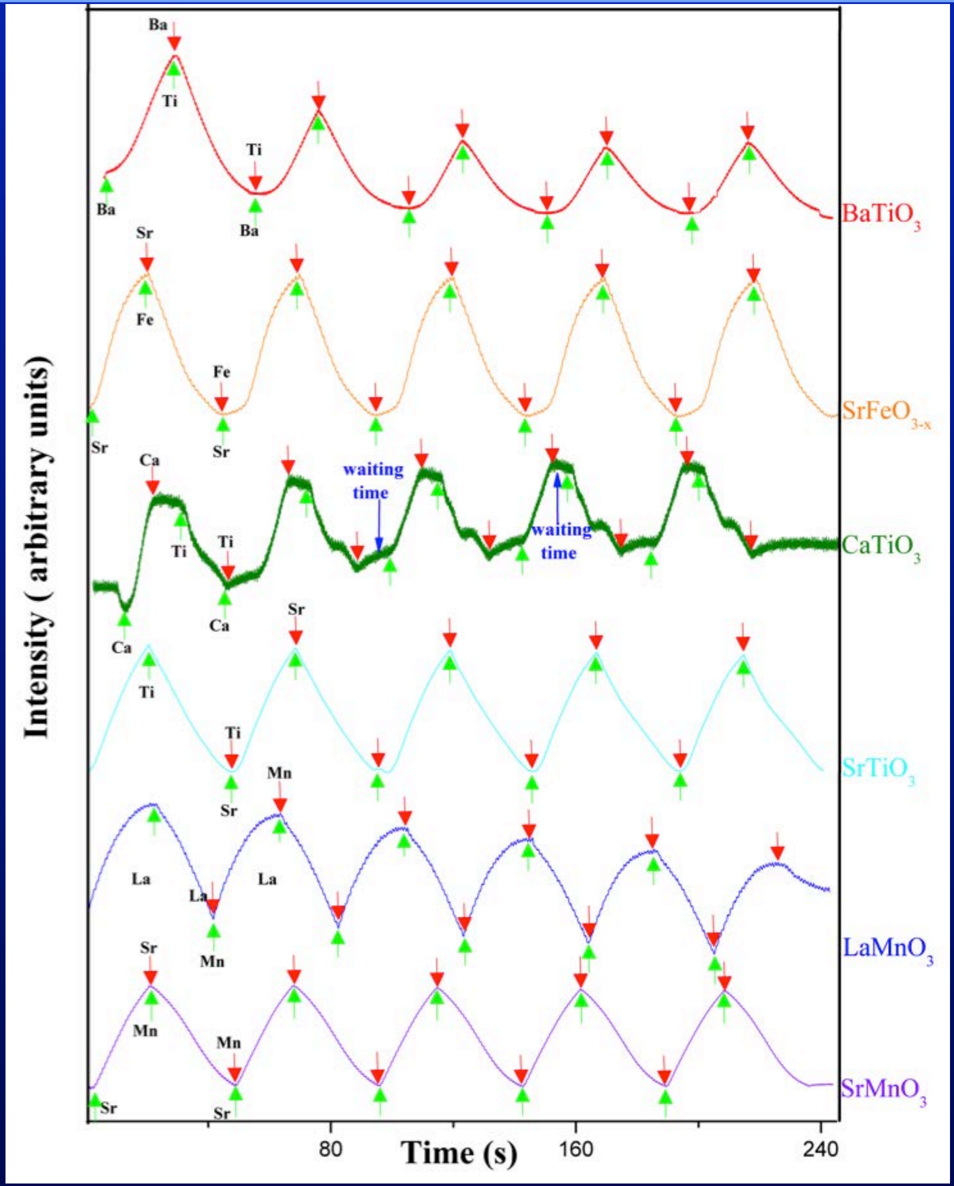
# Shuttered RHEED Oscillations



# Shuttered RHEED Oscillations



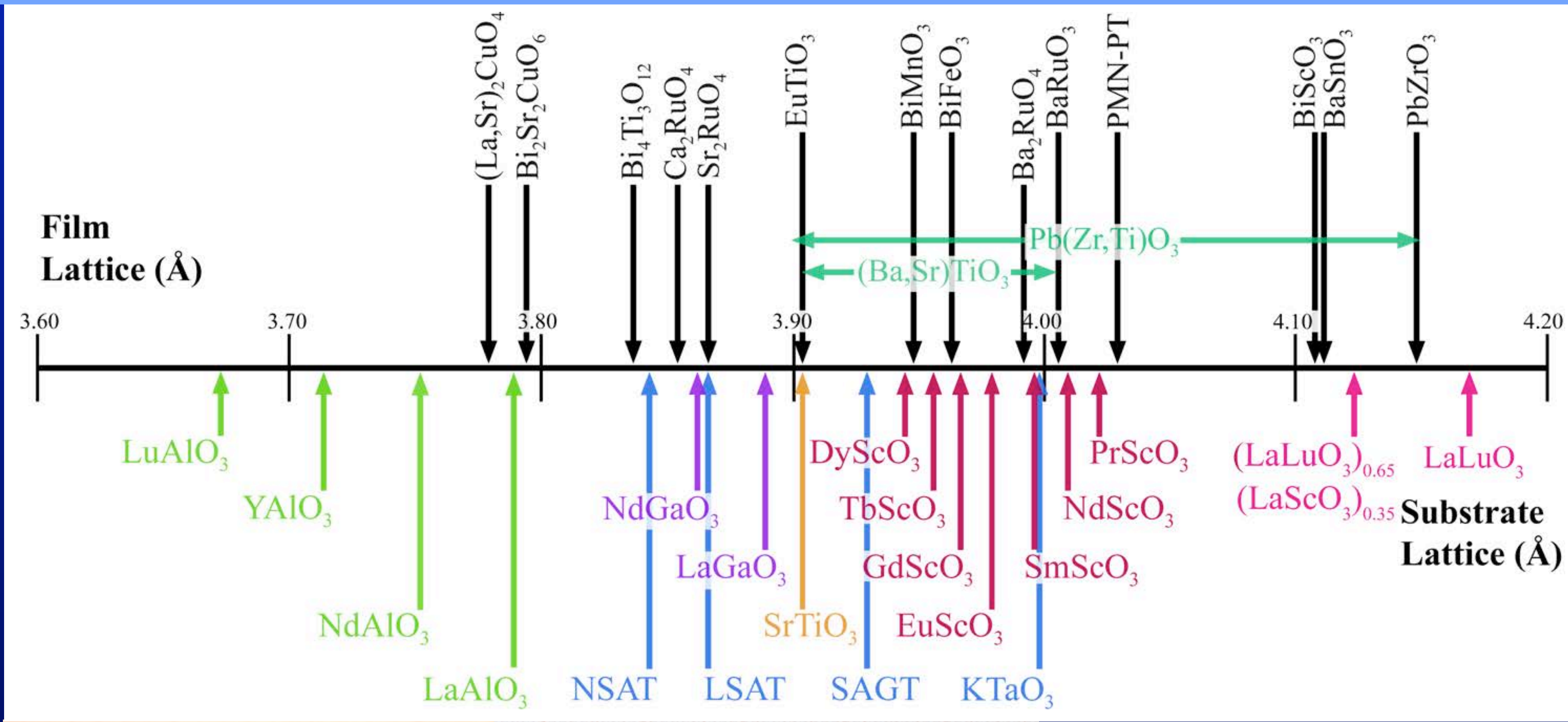

*A*-Site Rich

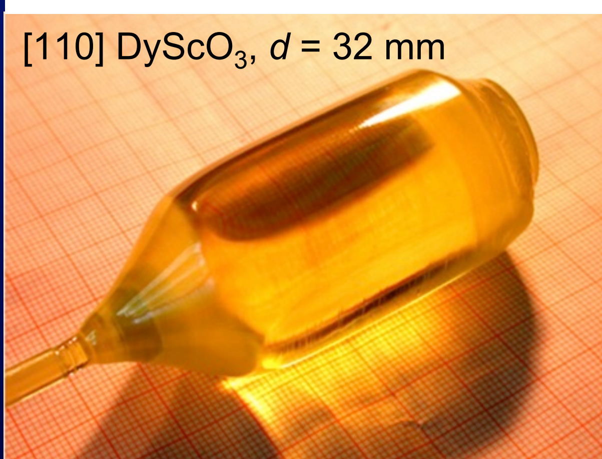


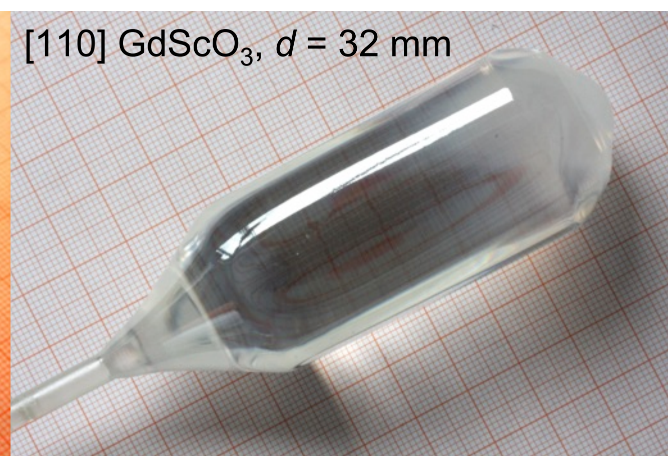

*B*-Site Rich

# Substrates are Key

# Commercial Perovskite Substrates




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.

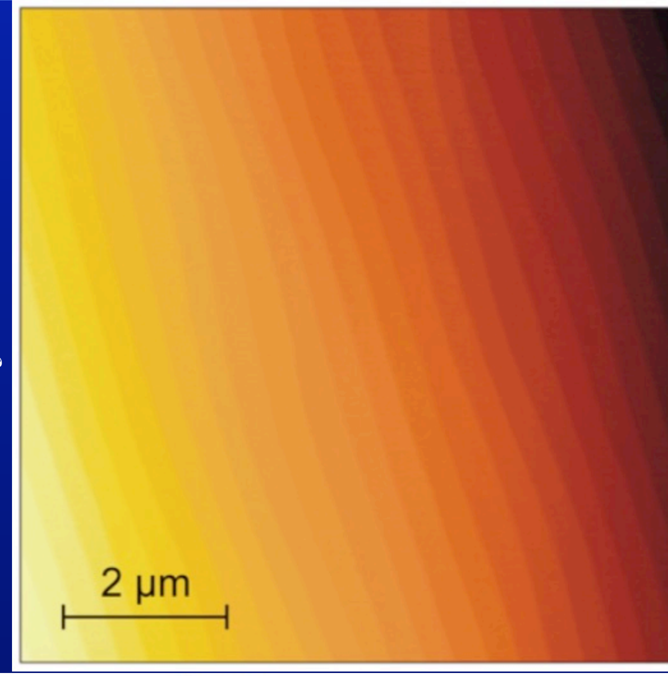
# Surface Termination Recipes

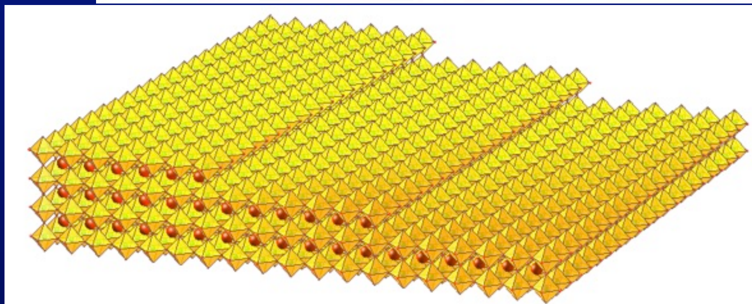
- **(100) and (111) $SrTiO_3$**
  G. Koster, B.L. Kropman, G.J.H.M. Rijnders, D.H.A. Blank, H. Rogalla, "Quasi-Ideal Strontium Titanate Crystal Surfaces through Formation of Strontium Hydroxide,"
  *Applied Physics Letters* **73** (1998) 2920-2922.

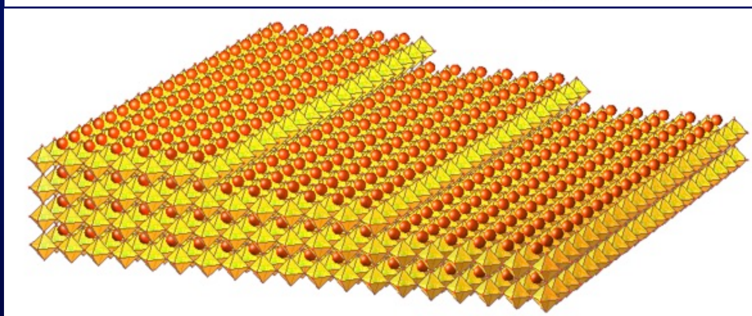
- **(110) *RE*$ScO_3$**
  J.E. Kleibeuker, G. Koster, W. Siemons, D. Dubbink, B. Kuiper, J.L. Blok, C-H. Yang, J. Ravichandran, R. Ramesh, J.E. ten Elshof, D.H.A. Blank, and G. Rijnders, "Atomically Defined Rare-Earth Scandate Crystal Surfaces,"
  *Advanced Materials* **20** (2010) 3490-3496.

- **$(100)_p$ 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 .

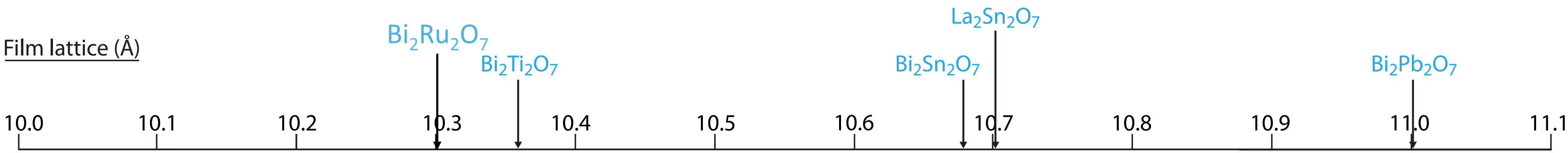
AFM (100) $SrTiO_3$—Jochen Mannhart



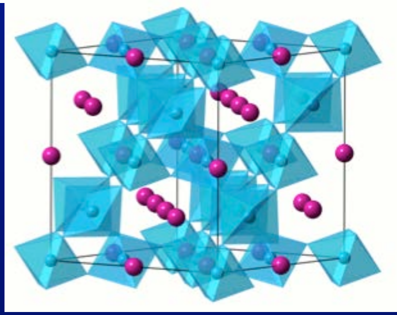


# Pyrochlores

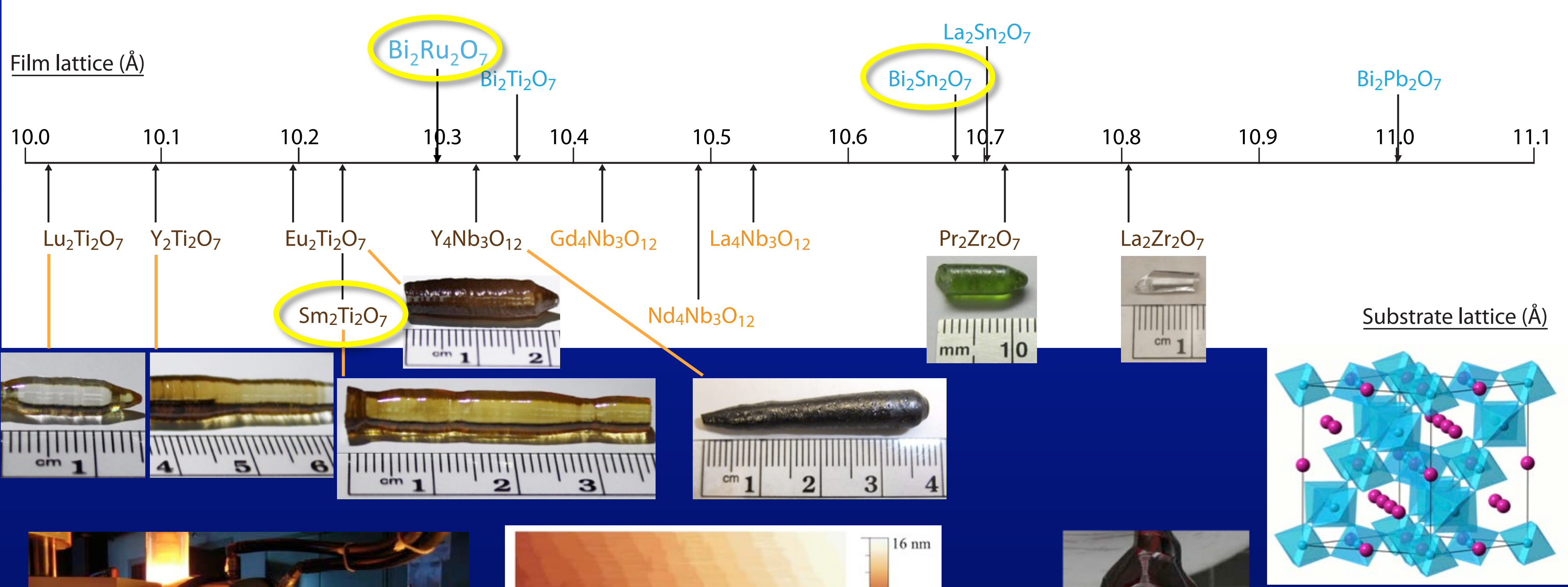


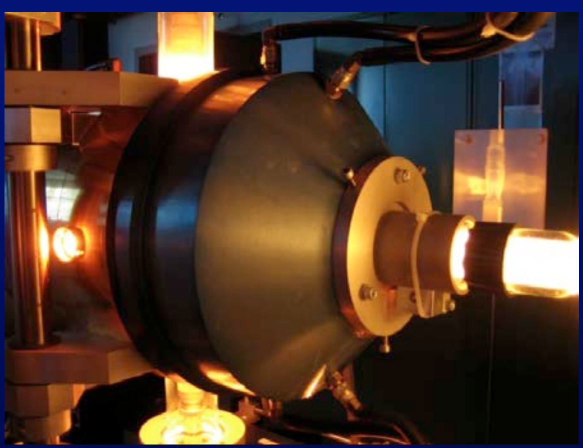

**No Commercial Pyrochlore Substrates!**

Substrate lattice (Å)

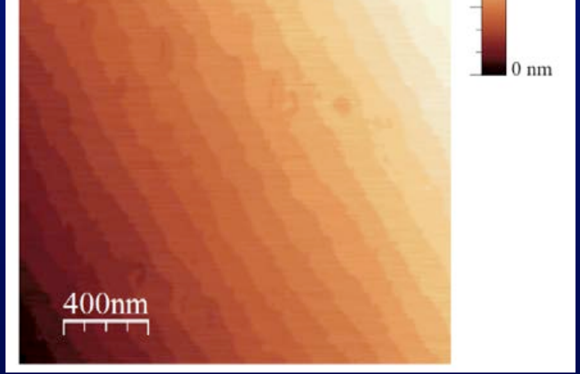


# Pyrochlore Substrates



Floating zone furnace (Augsburg)

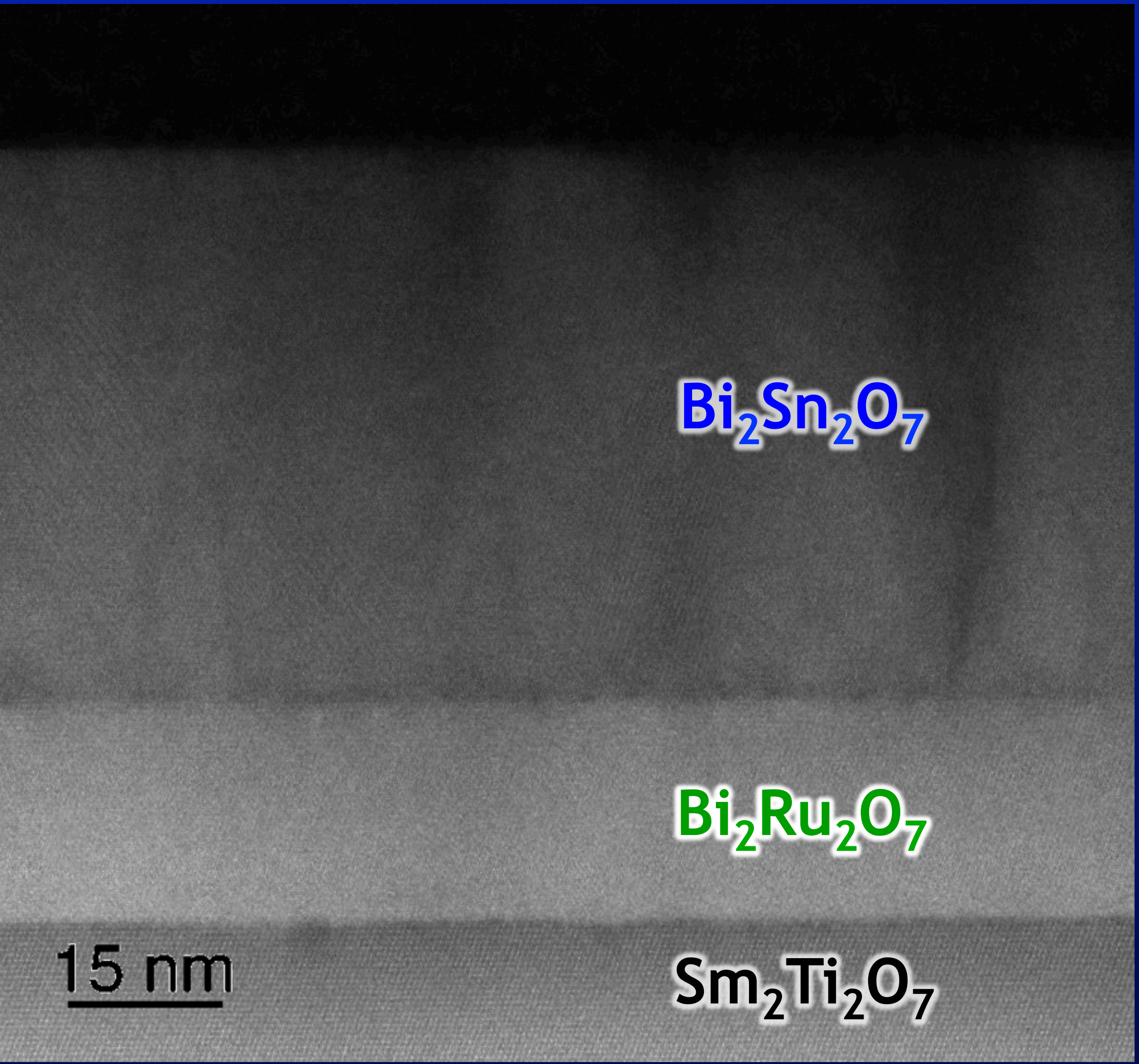


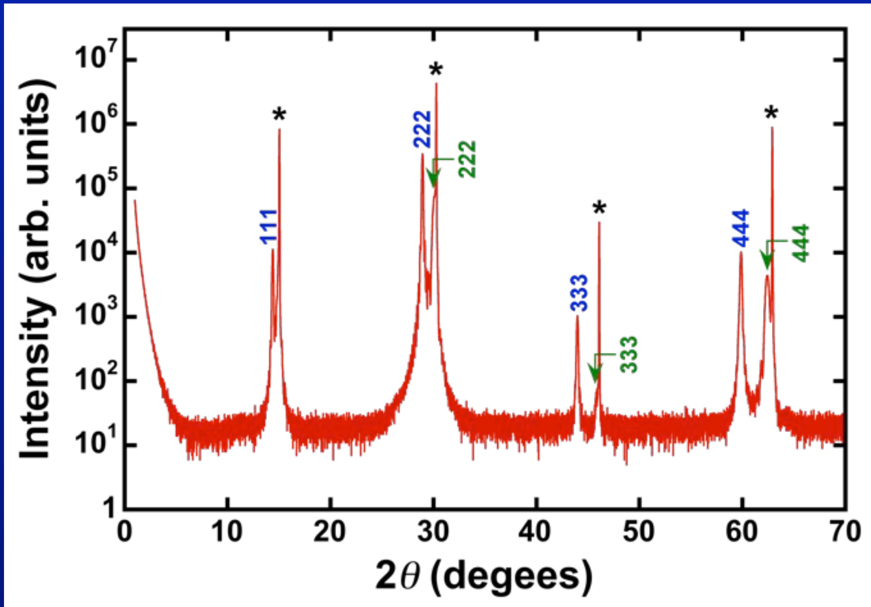

AFM: as-polished (111) $Sm_2Ti_2O_7$ (floating zone)

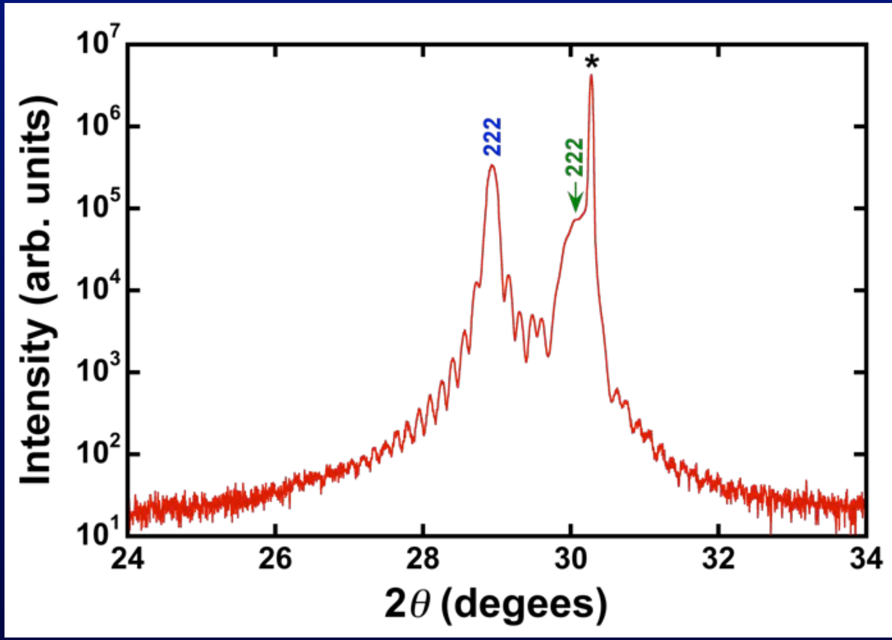
$Sm_2Ti_2O_7$ grown by Czochralski (IKZ, Berlin)

with
Tyrel McQueen
Jochen Mannhart
Reinhard Uecker

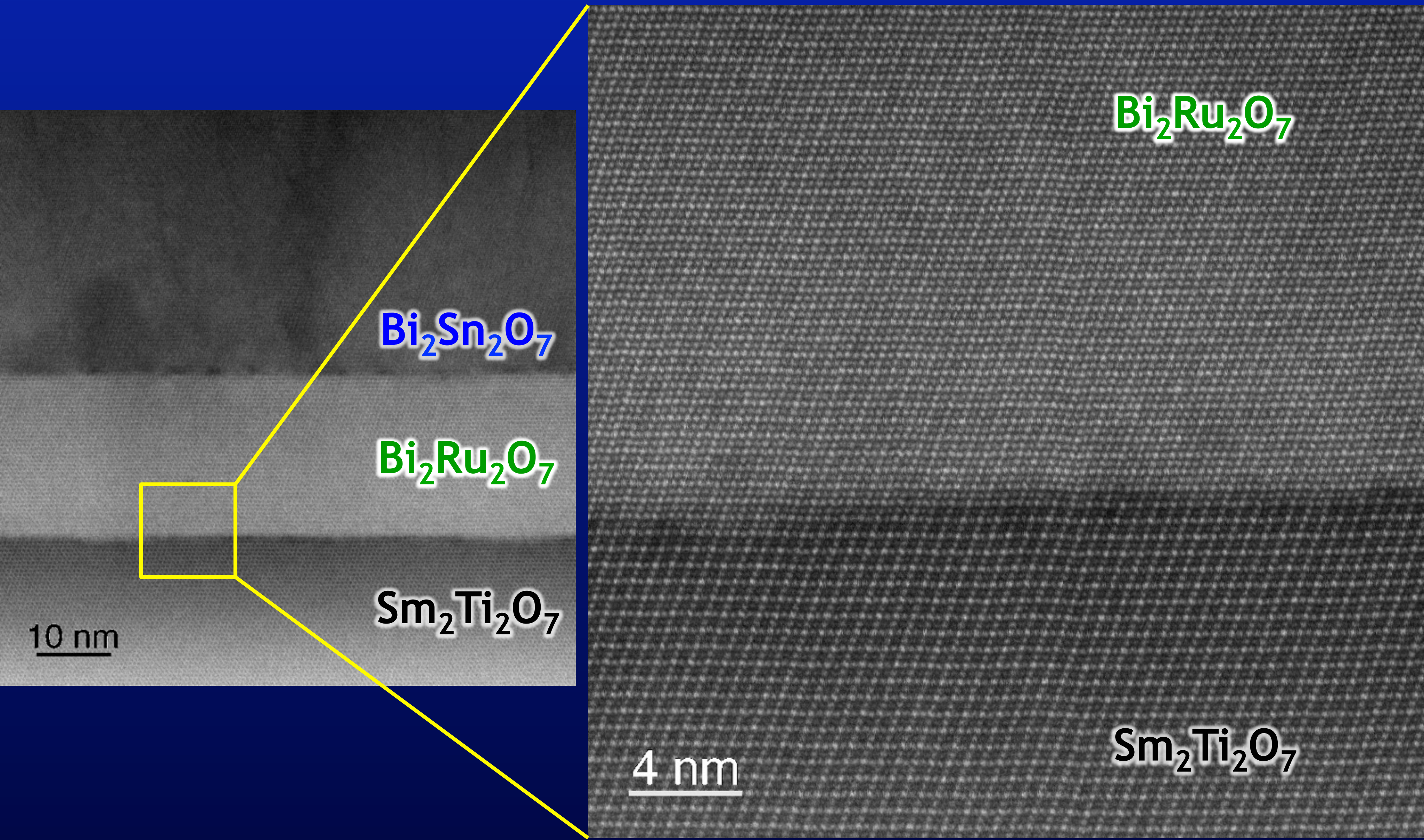
# MBE of Pyrochlores



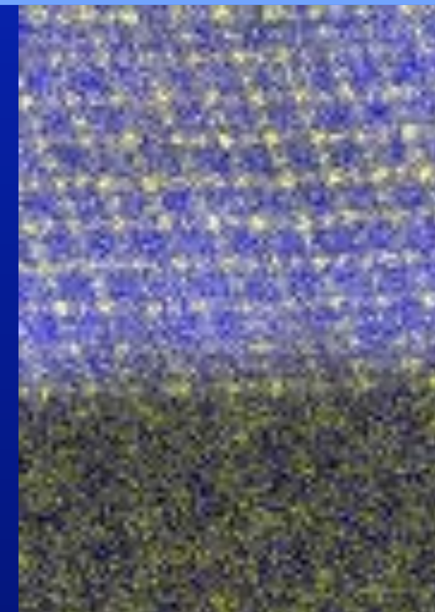



# MBE of Pyrochlores

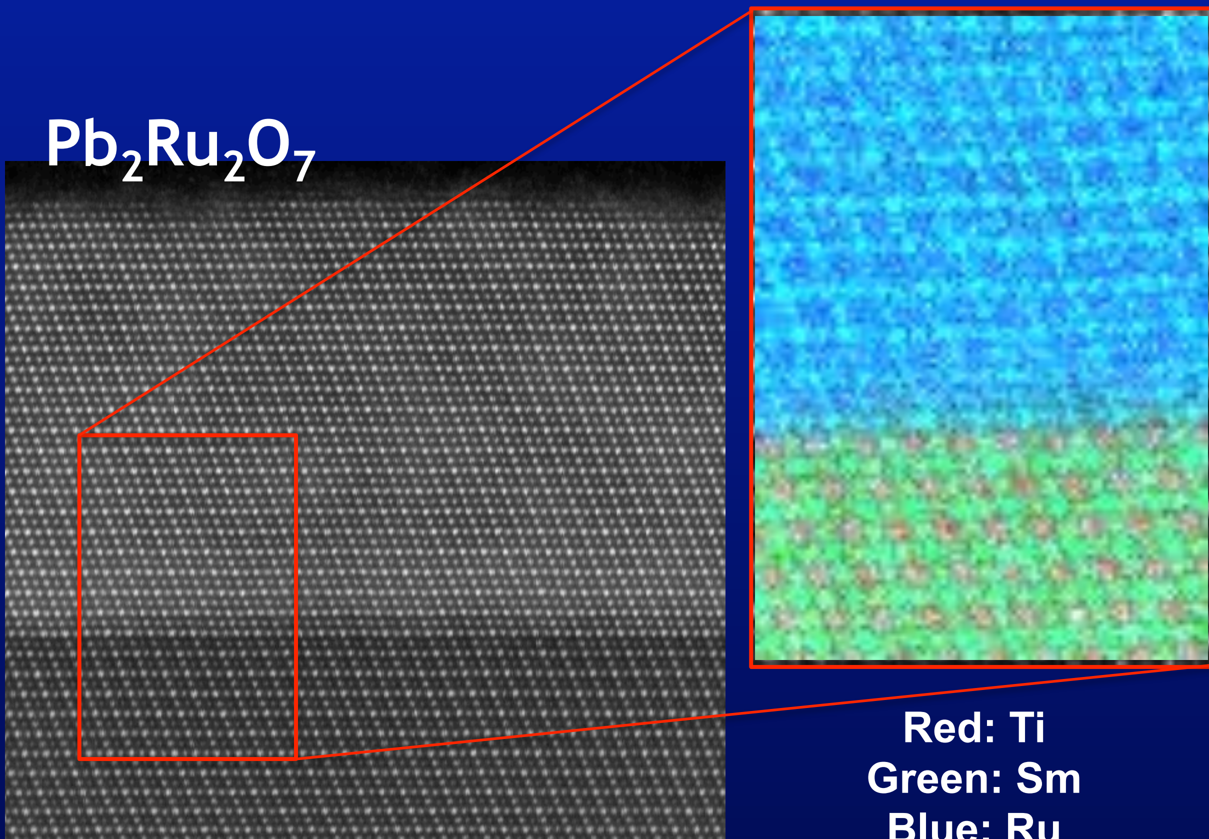


# MBE of Pyrochlores

Yellow: Pb, Blue: Ru

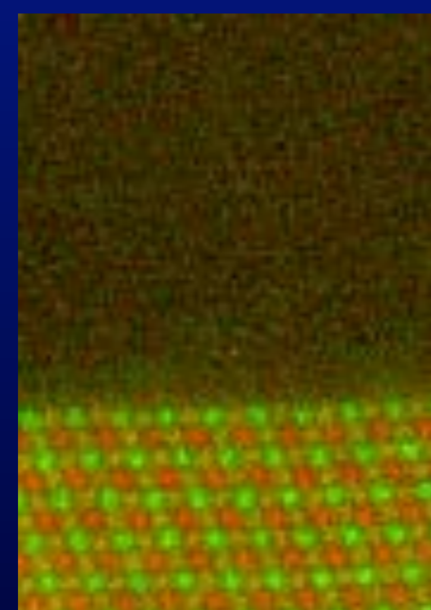


$Pb_2Ru_2O_7$



$Sm_2Ti_2O_7$

Red: Ti
Green: Sm
Blue: Ru
Cyan: Pb



Red: Sm, Green: Ti

# MBE Summary

## Advantages

- Extreme Flexibility
- Independent Growth Parameters
- Compatible with wide range of *in situ* Diagnostics
- Clean
- Gentle
- Precise Layering Control at the Atomic Level

## Disadvantages

- Extreme Flexibility (uncontrolled flexibility = chaos!)
- High Cost
- Long Set-up Time
- MBE (the other meanings…)