Lecture #3—

NUTS AND BOLTS OF OXIDE MBE:

Composition Control and Calibration

Darrell G. Schlom

Nuts and Bolts of Oxide MBE

How to grow your favorite oxide by MBE?

- Lecture #2—*Growth Conditions, Sources, and Crucibles*
- Lecture #3—*Composition Control and Calibration*
- Lecture #4—*Epitaxy, Substrates, and Crystal Growth*

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How to Calibrate Growth Rate

- Shadow Mask and Surface Profilometer
- Quartz Crystal Microbalance
- Ion Gauge
- RHEED Oscillations
- Shuttered RHEED Oscillations
- Rutherford Backscattering Spectrometry
- Mass Spectrometer
- Atomic Absorption Spectroscopy
- Atomic Emission Spectroscopy
- X-Ray Reflectivity, Ellipsometry, ⋯

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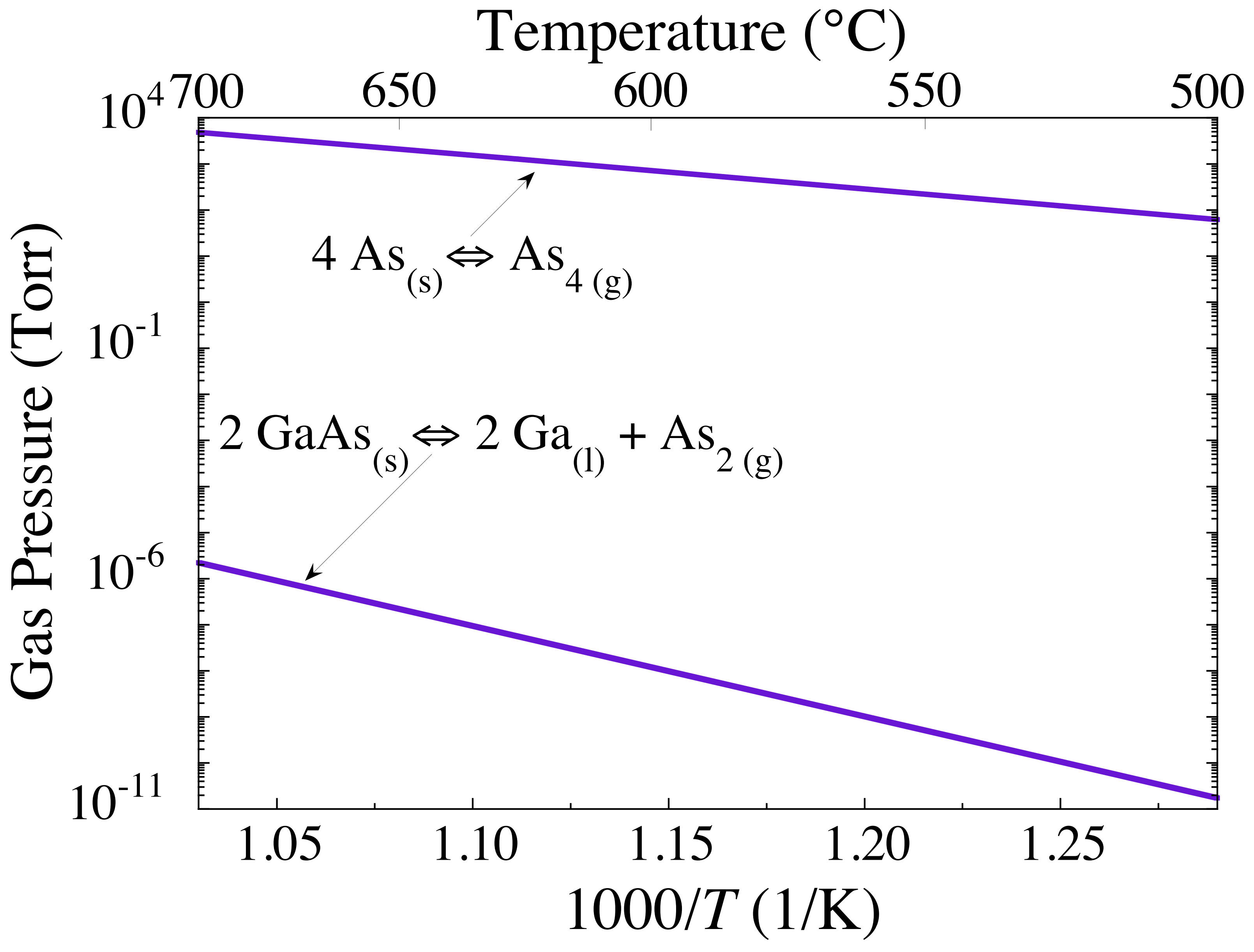
Composition Control

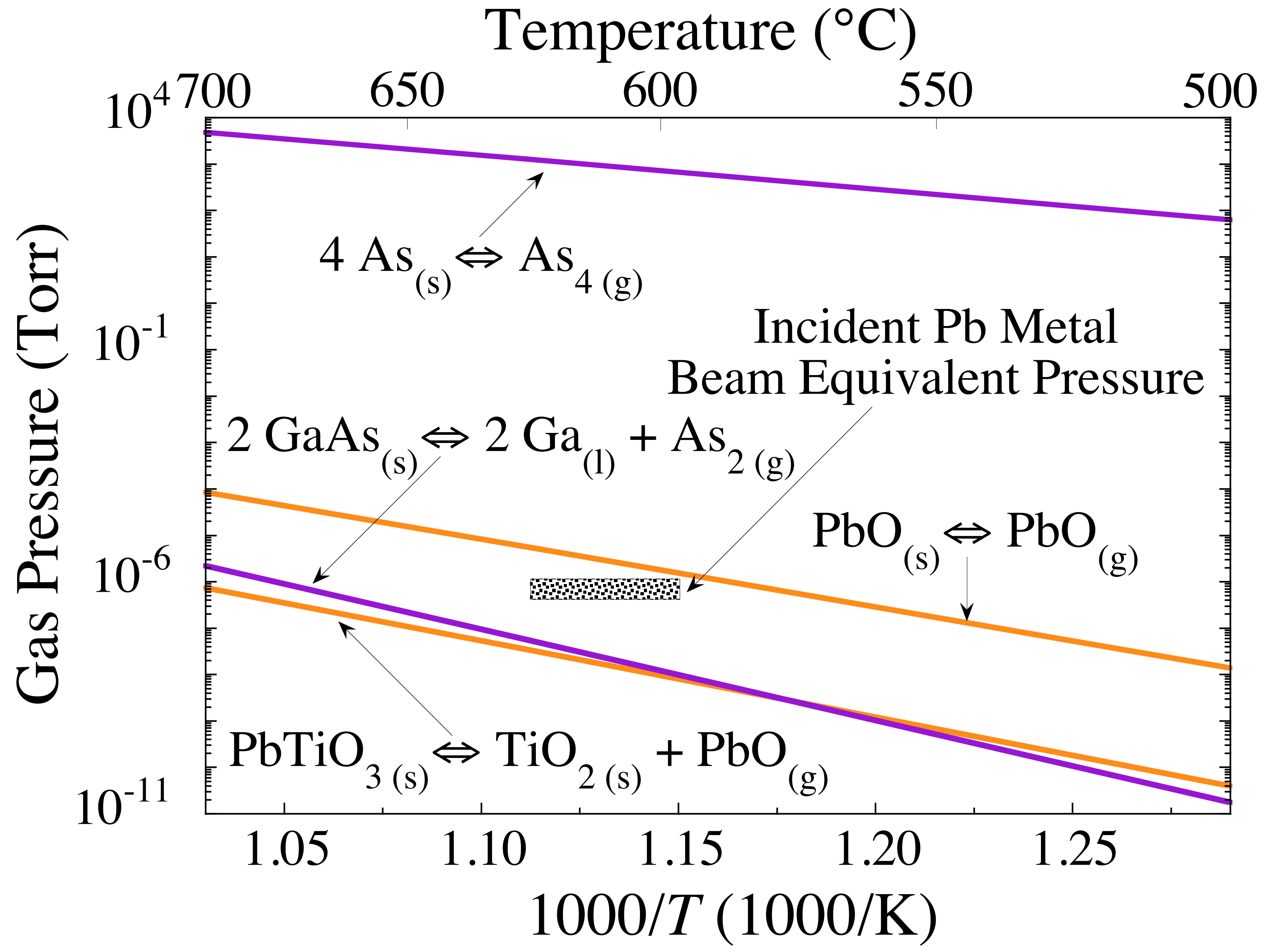
- Adsorption-Controlled Growth
- Flux-Controlled Growth

Adsorption-Controlled Growth of GaAs



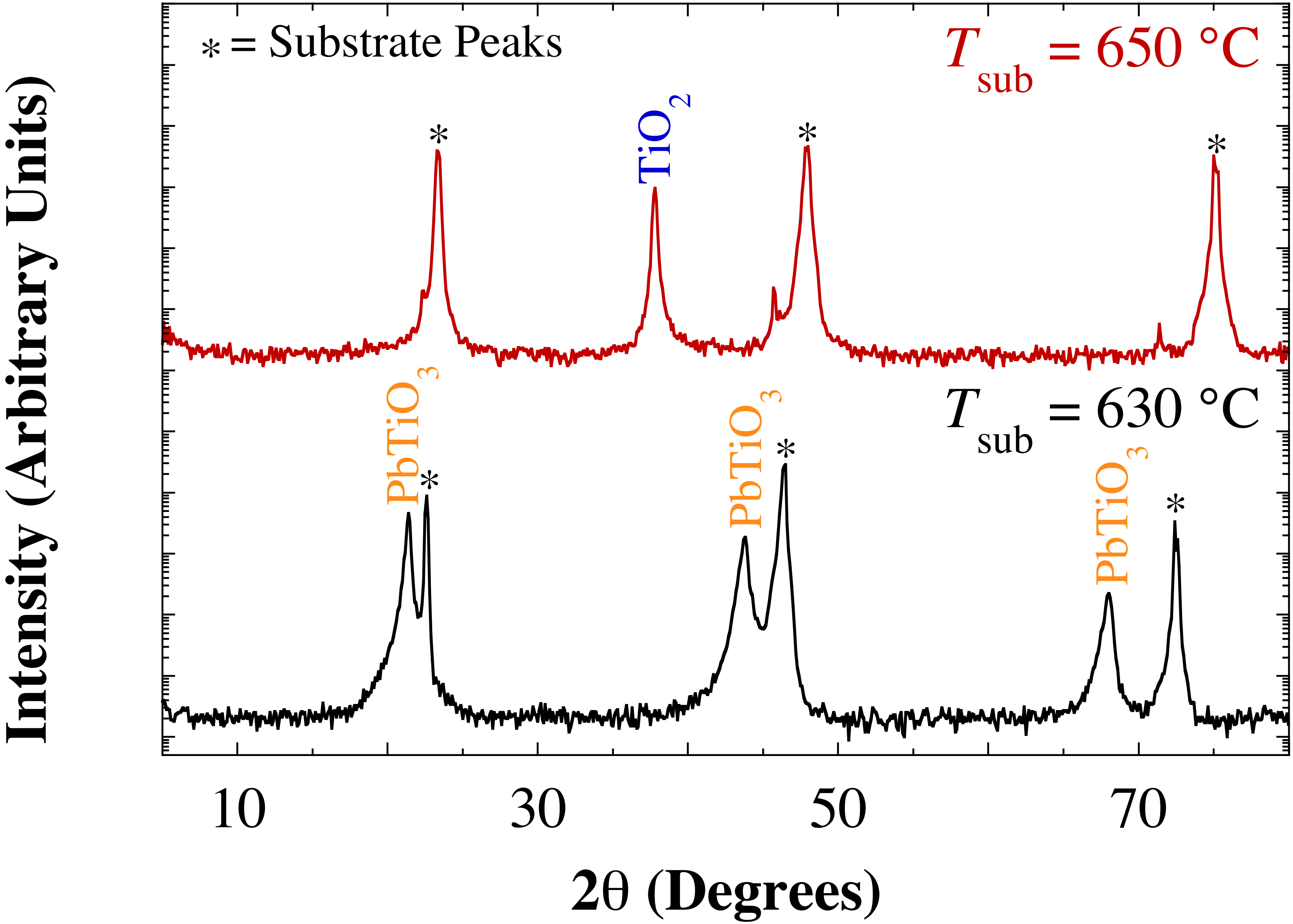
C.D. Theis, J. Yeh, D.G. Schlom, M.E. Hawley, and G.W. Brown, "Adsorption-Controlled Growth of $PbTiO_3$ by Reactive Molecular Beam Epitaxy," *Thin Solid Films* **325** (1998) 107-114.

Adsorption-Controlled Growth of $PbTiO_3$



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 $PbTiO_3$



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  - $PbZrO_3$ — (unpublished)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)
- Ferrites
  - $LuFe_2O_4$ — C.M. Brooks *et al.*, *Appl. Phys. Lett.* **101** (2012) 132907.

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NSF

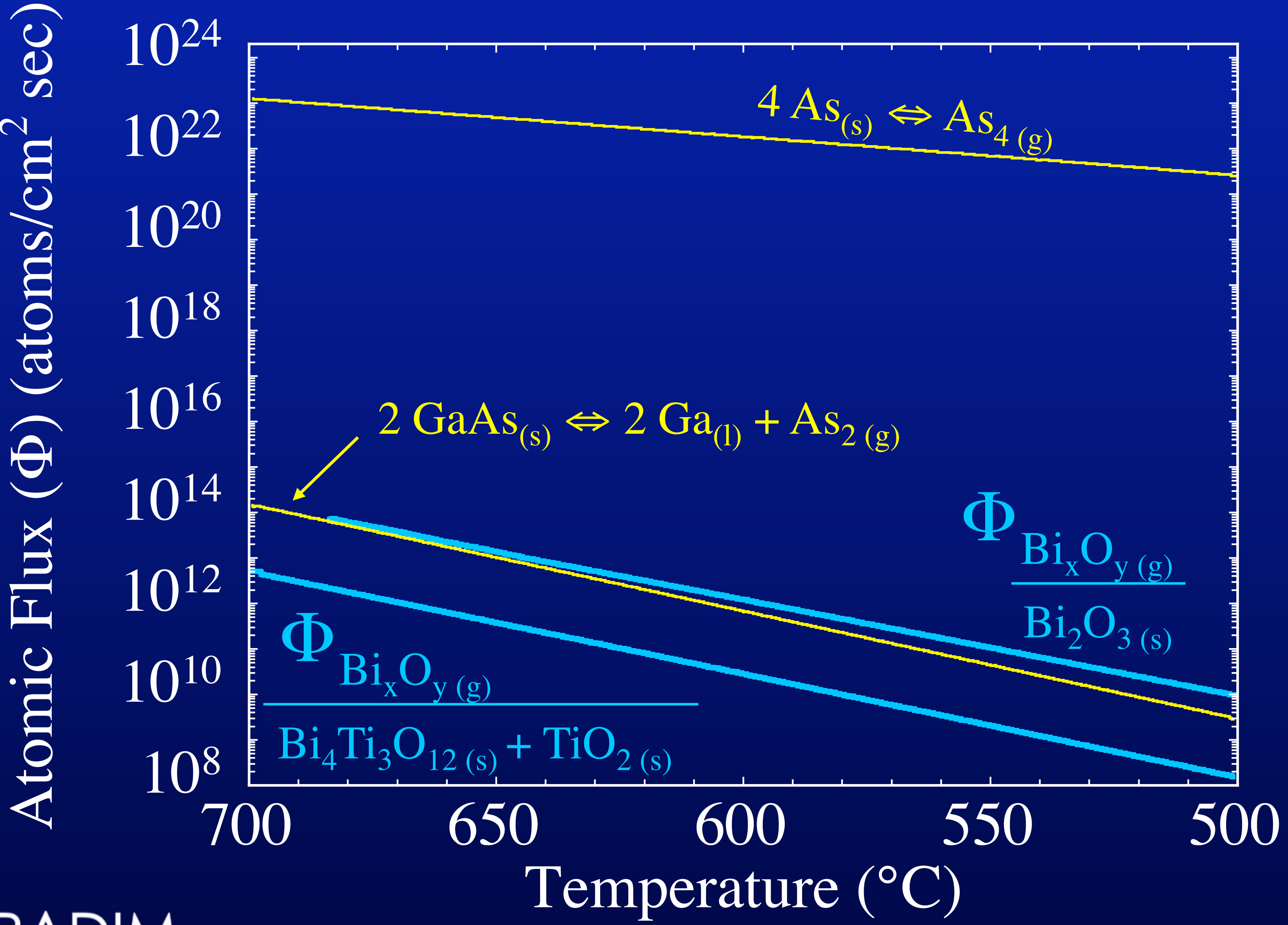
Adsorption-Controlled Growth of

- 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. H.P. Nair *et al.*, *APL Mater.* **6** (2018) 101108.
  - $CaRuO_3$ — H.P. Nair *et al.*, *APL Mater.* **6** (2018) 046101.
  - Ca_2RuO_4 — (unpublished)
- 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
  - $BaSnO_3$ — 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

- 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.
- 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.
- Stannates by MOMBE
  - **$BaSnO_3$** — A. Prakash *et al.*, *J. Mater. Chem. C* **5** (2017) 5730 .

Growth of $Bi_4Ti_3O_{12}$ by MBE

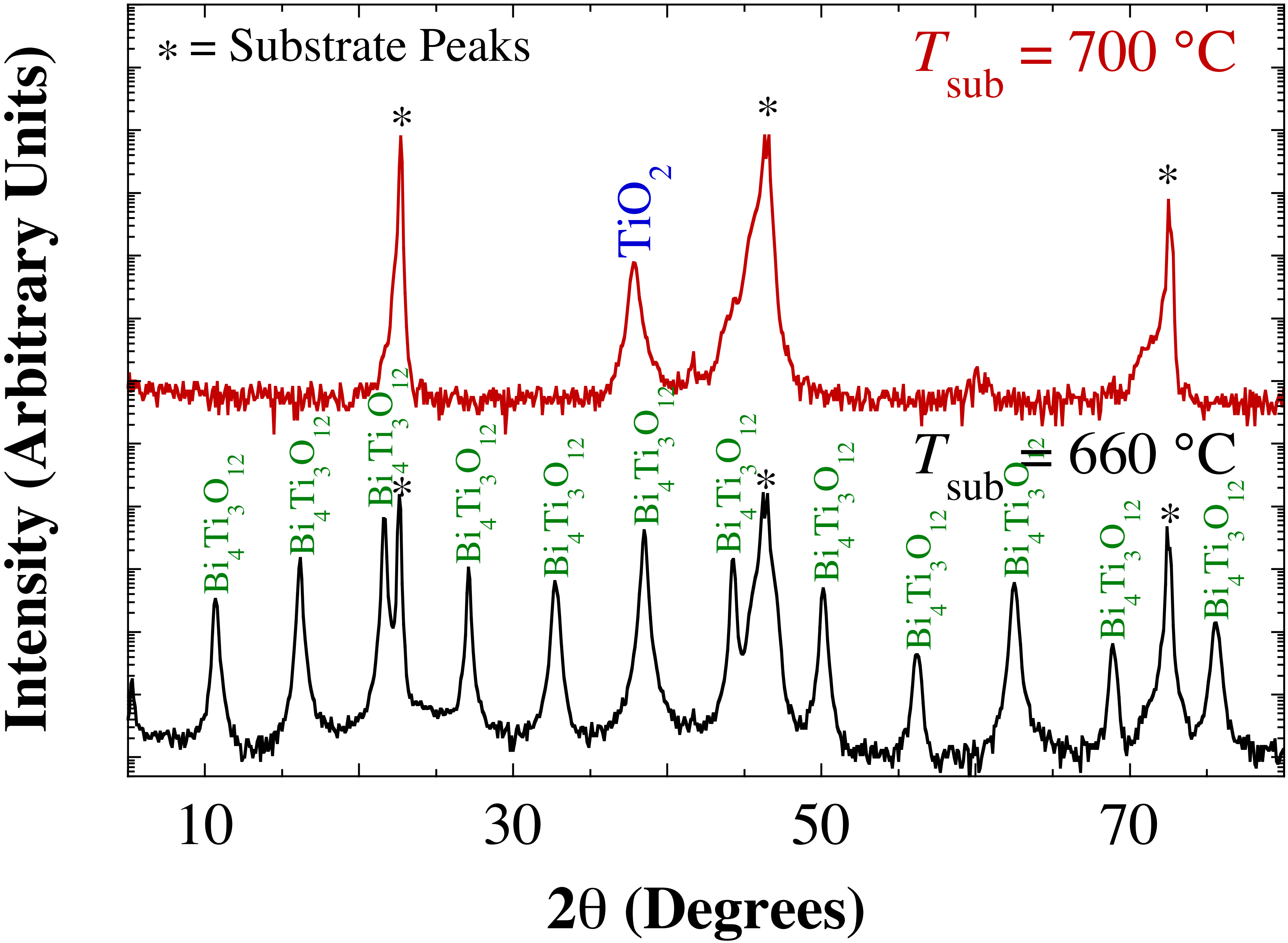


D.G. Schlom, J.H. Haeni, J. Lettieri, C.D. Theis, W. Tian, J.C. Jiang, and X.Q. Pan, *Mater. Sci. Eng. B* **87** (2001) 282-291.

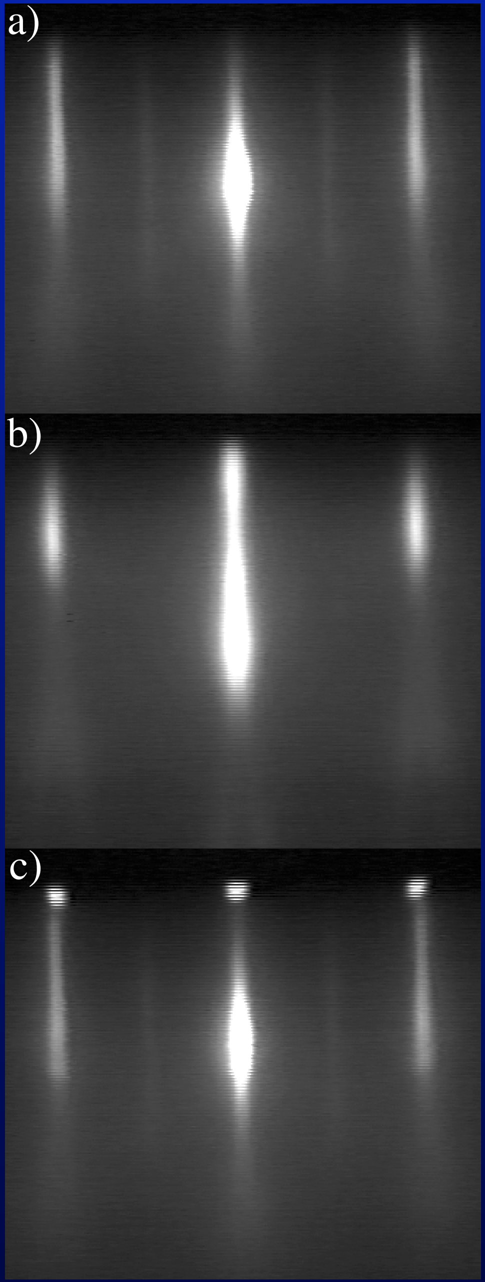
PARADIM

NSF

Adsorption-Controlled Growth of $Bi_4Ti_3O_{12}$



Adsorption-Controlled Growth of $Bi_4Ti_3O_{12}$

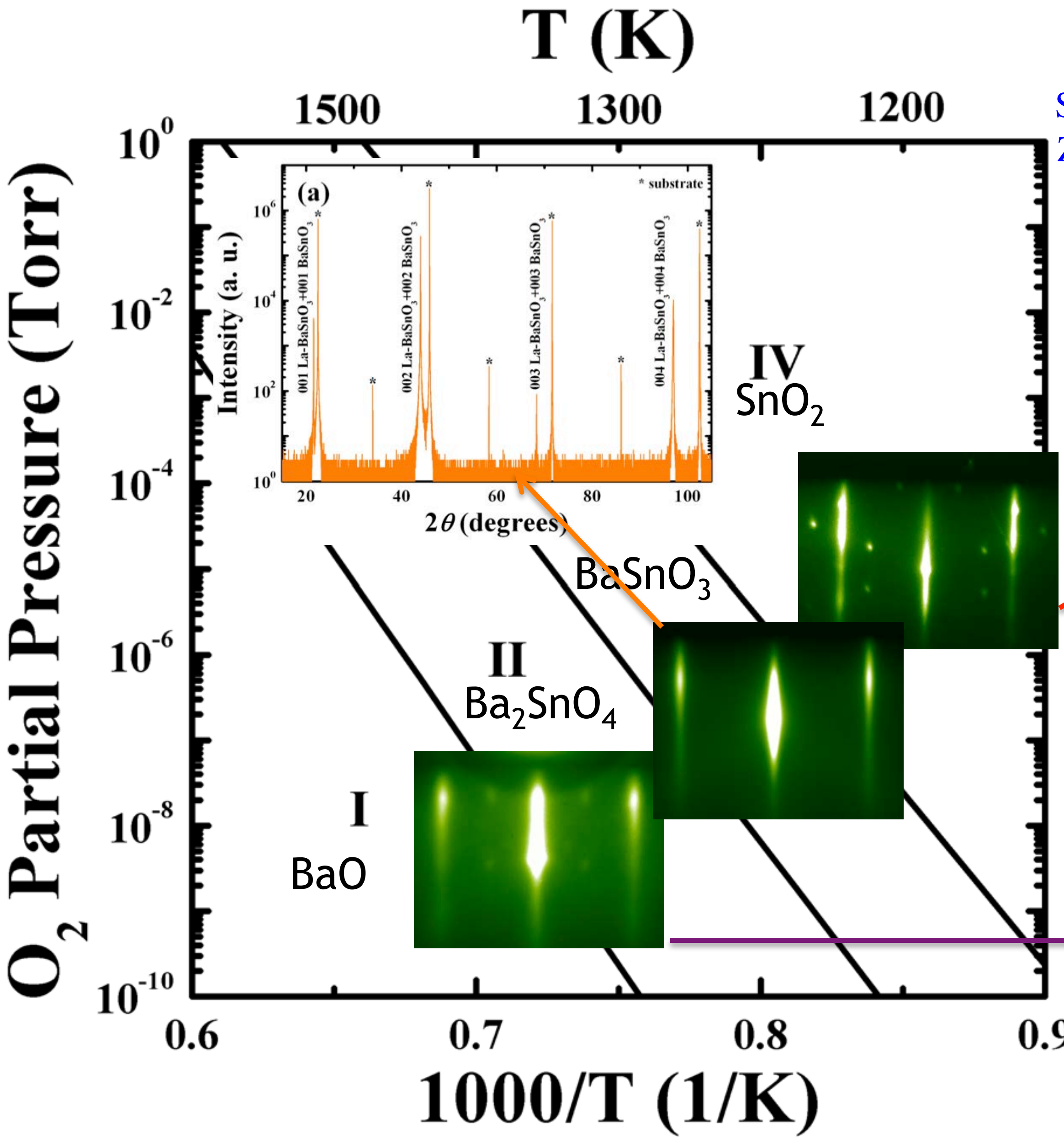


$Bi_4Ti_3O_{12}$

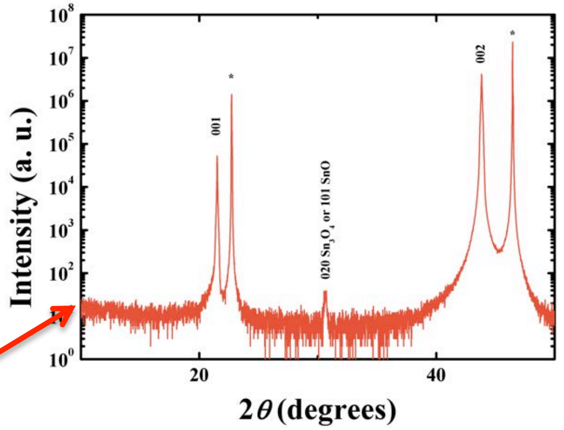
TiO_2

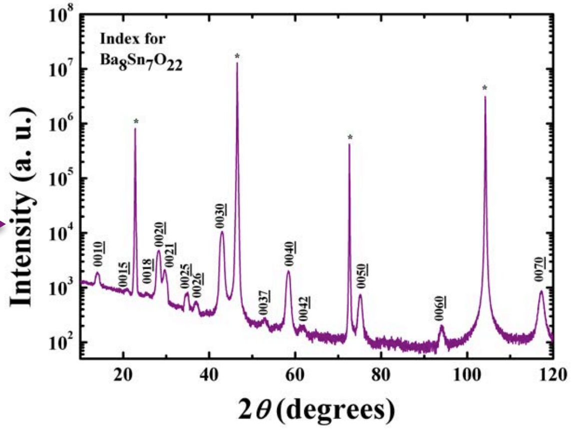
$Bi_2O_{2.33}$

Adsorption-Controlled Growth of $BaSnO_3$



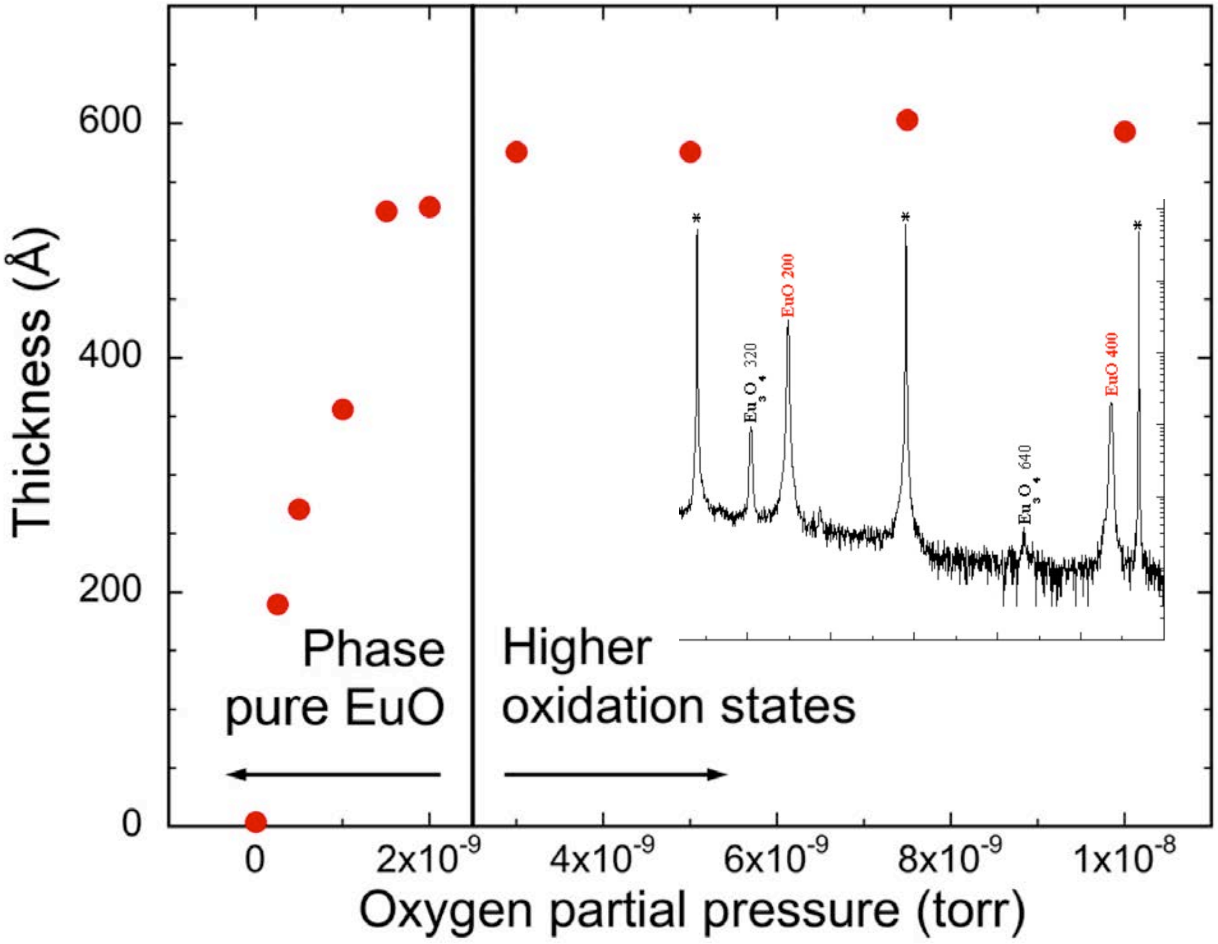
H. Paik, Z. Chen, E. Lochocki, A. Seidner H., A. Verma, N. Tanen, J. Park, M. Uchida, S.L. Shang, B-C. Zhou, M. Brützam, R. Uecker, Z.K. Liu, D. Jena, K.M. Shen, D.A. Muller, and D.G. Schlom, *APL Materials* **5** (2017) 116107.

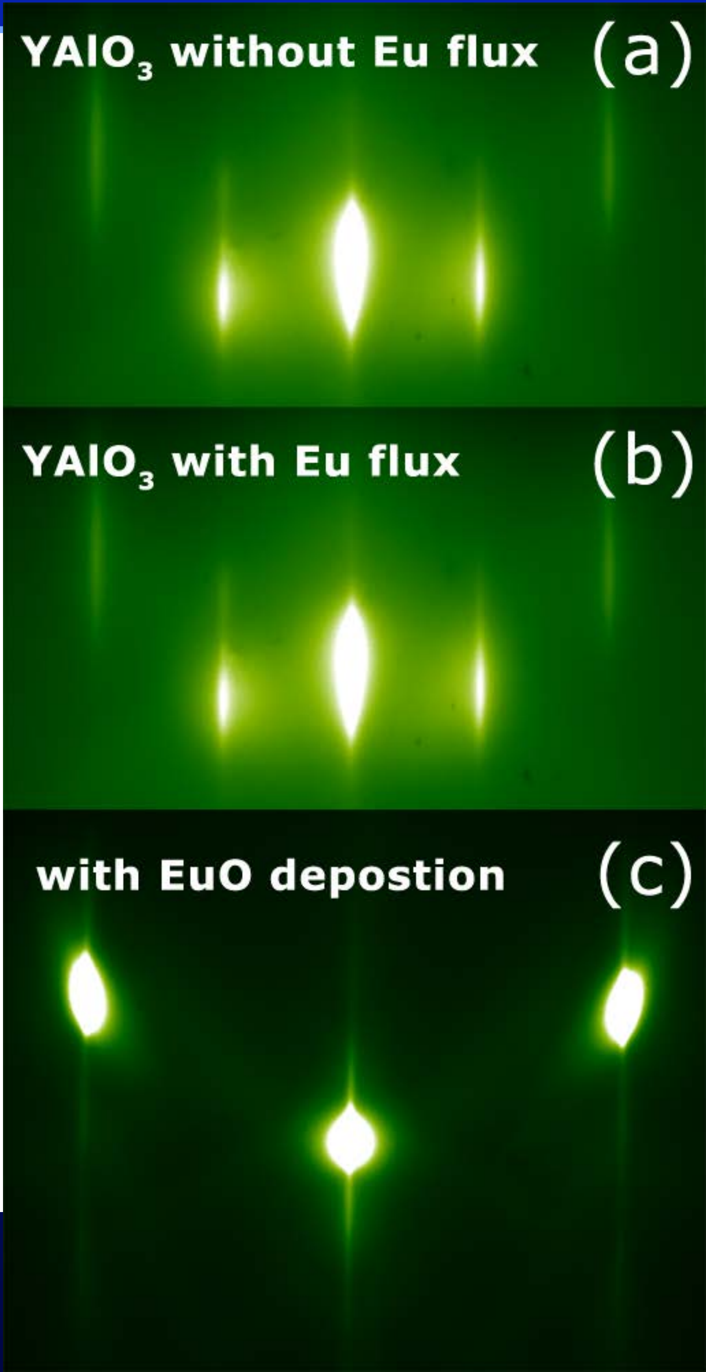




Adsorption-Controlled Growth of EuO

Eu Flux = 1.1×10^{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$_3$

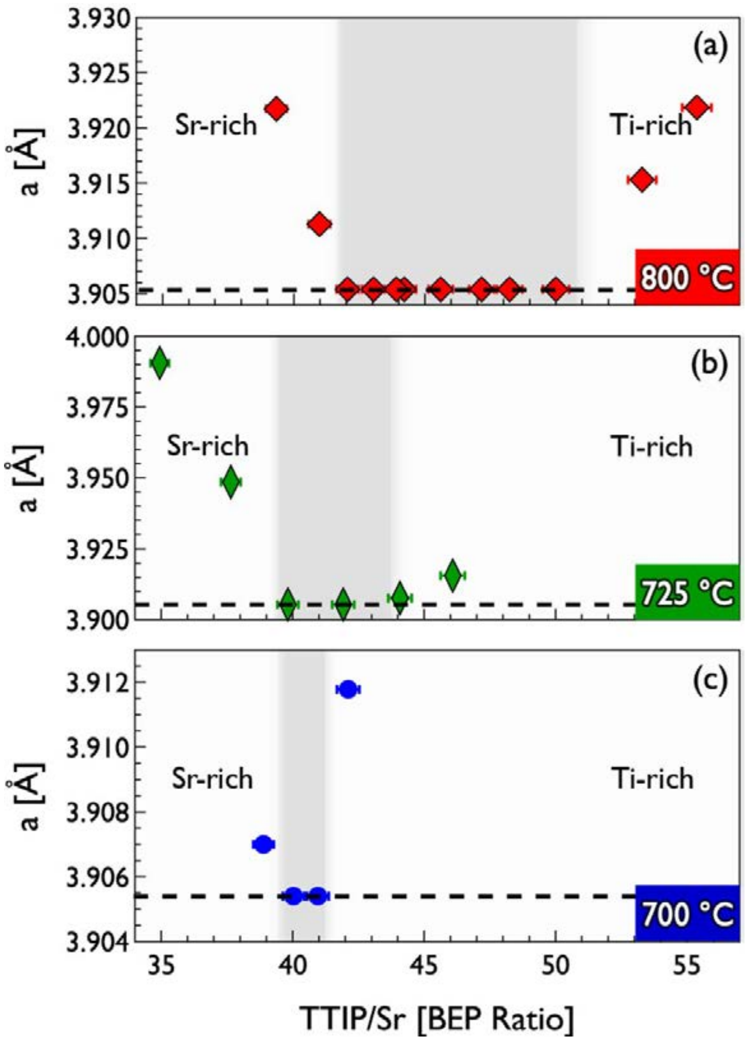


FIG. 3. (Color online) Out-of-plane lattice parameter as a function of TTIP/Sr BEP ratio for epitaxial SrTiO$_3$ films grown on (001)SrTiO$_3$ at (a) 800 °C, (b) 725 °C, and (c) 700 °C. All films were grown using an oxygen BEP of 8×10^{-6} torr. The darker gray-shaded region shows the growth window for stoichiometric films with a lattice parameter that is equivalent to that of the substrate at each temperature.

MOMBE Sources

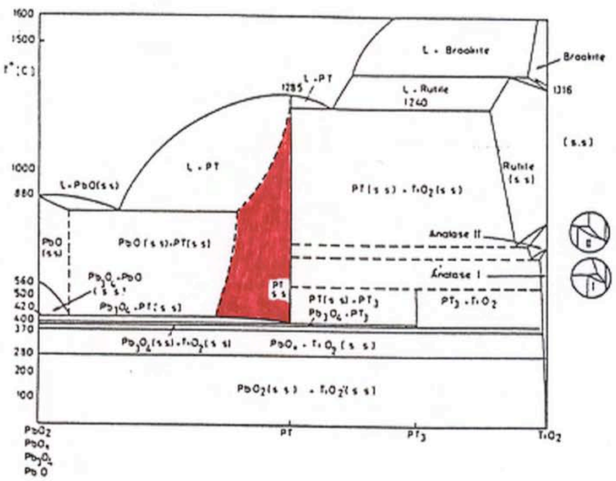
Sr

Ti(OC$_3$H$_7$)$_4$

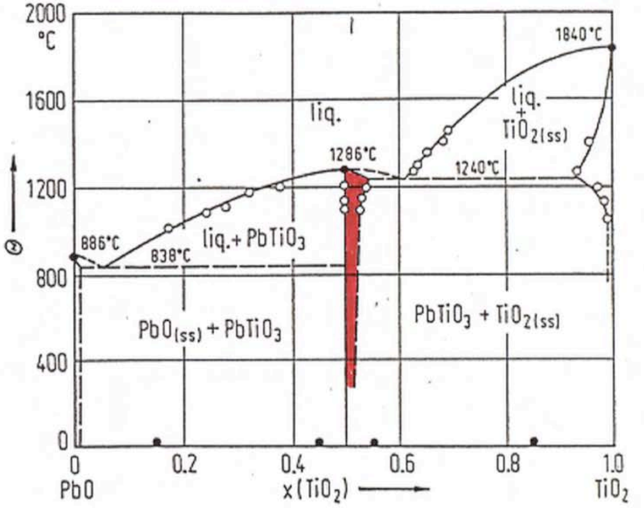
Oxygen Plasma

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

Single-Phase Field of GaAs vs. $PbTiO_3$



M.A. Eisa, M.F. Abadir, and A.M. Gadalla, *Transactions and Journal of the British Ceramic Society* **79** (1980) 100–104.



R.L. Holman, *Ferroelectrics* **14** (1976) 675–678.

$PbTiO_3$

GaAs

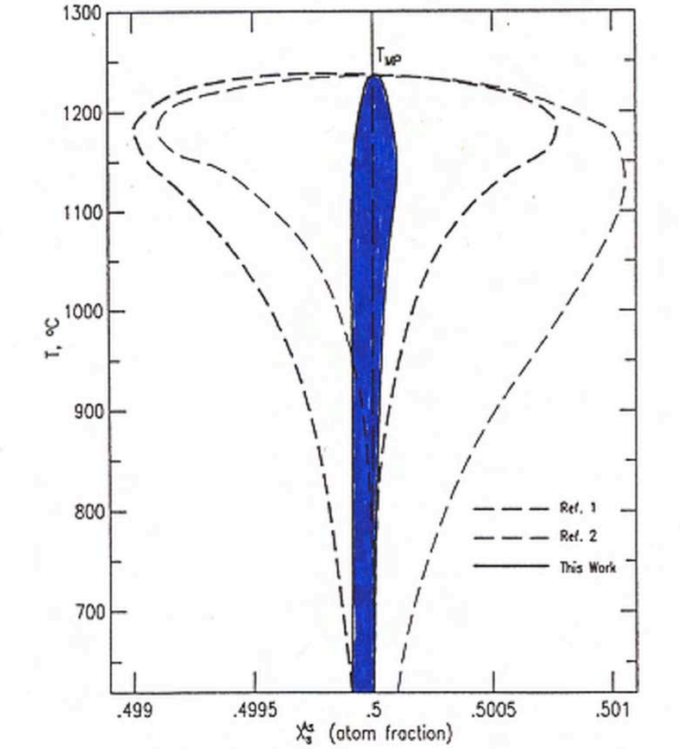


Fig. 8337—GaAs solidus curve. Curves represent the calculated deviations from stoichiometry for solid GaAs.
A. I. Ivashchenko, F. Ya. Kopanskaya, and G. S. Kuzmenko, *J. Phys. Chem. Solids*, **45** [8-9] 871-875 (1984).

Single-phase film does not imply stoichiometric film

Phase Diagrams for Ceramists, Vol. 9, edited by G.B. Stringfellow (American Ceramic Society, Westerville, 1992) p. 126.

III-V Phase Diagrams

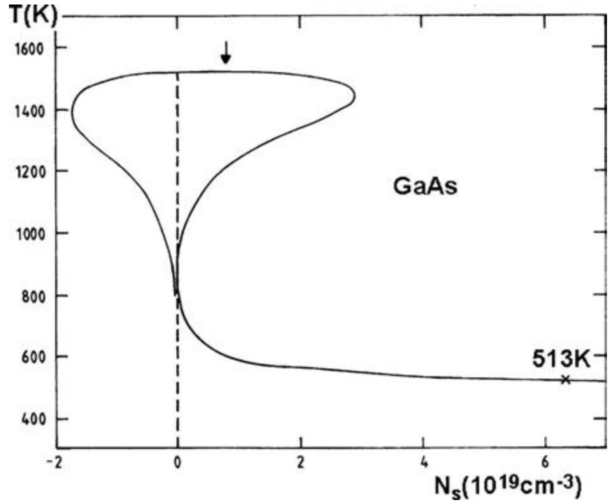


FIG. 2. The calculated solidus of gallium arsenide showing the catastrophic deviation from stoichiometry at low temperature under arsenic-rich conditions. Arrow marks the congruent point.

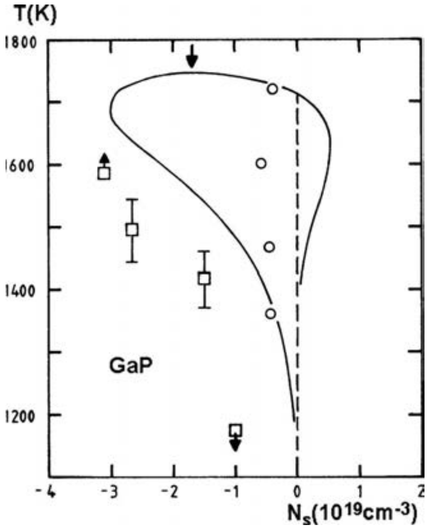


FIG. 3. Calculated GaP solidus. Arrow marks the congruent point. Ex
mental data: Jordan *et al.* (○); Morozov *et al.* (□).

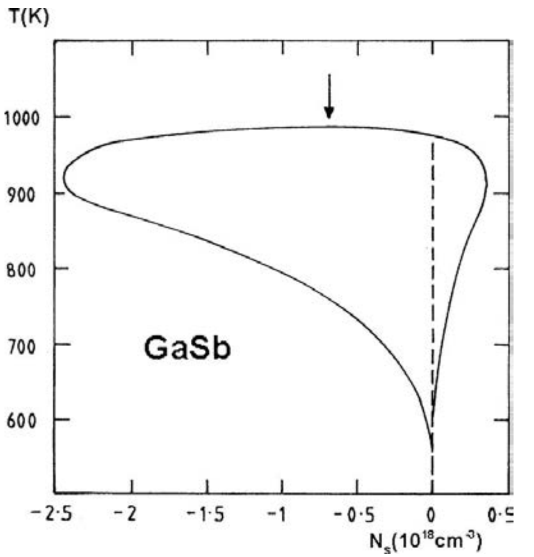


FIG. 5. Calculated GaSb solidus. Arrow marks the congruent point.

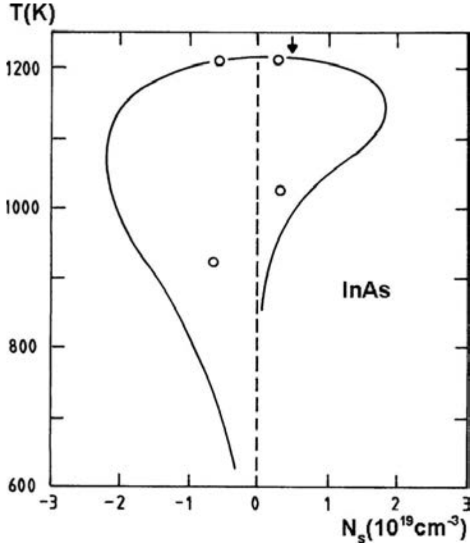


FIG. 7. Calcuated InAs solidus. Arrow marks the congruent point. Data points: Bublik *et al.* (○).

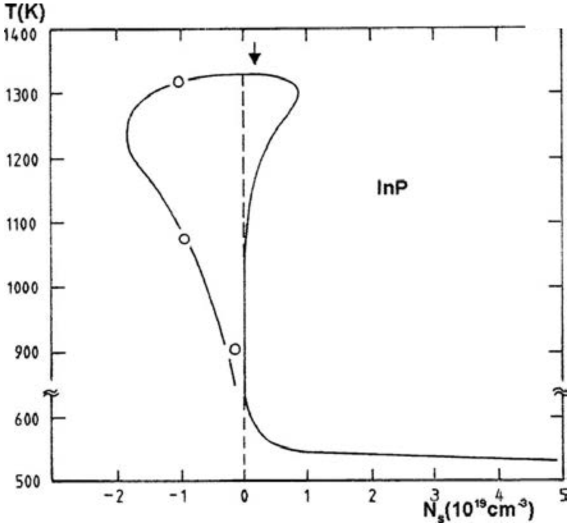


FIG. 8. Calculated InP solidus. Arrow marks the congruent point. Data points: Morozov *et al.* (Ref. 34) (○).

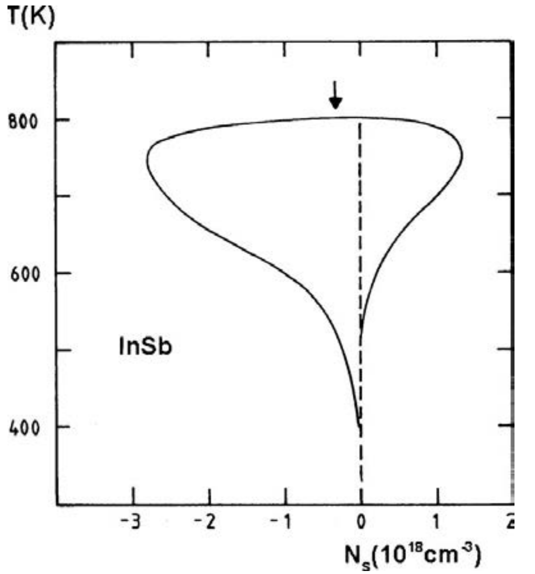


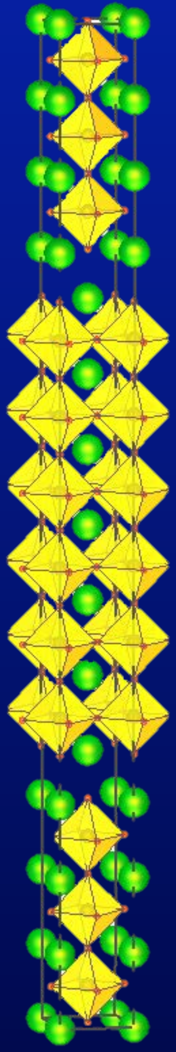
FIG. 9. Calculated InSb solidus. Arrow marks the congruent point.

D.T.J. Hurle, *Journal of Applied Physics* **107** (2010) 121301.

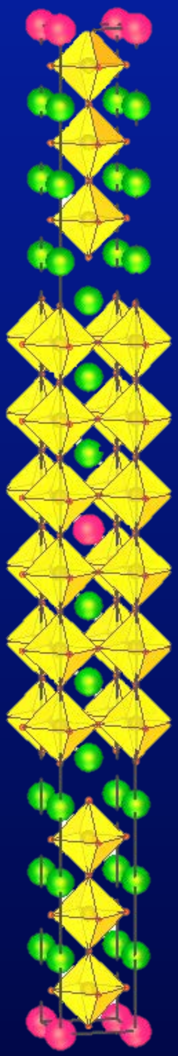
Challenge

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

$Sr_7Ti_6O_{19}$



$BaSr_6Ti_6O_{19}$



Composition Control

- Adsorption-Controlled Growth
- Flux-Controlled Growth

Reflection High-Energy Electron Diffraction (RHEED) Oscillations

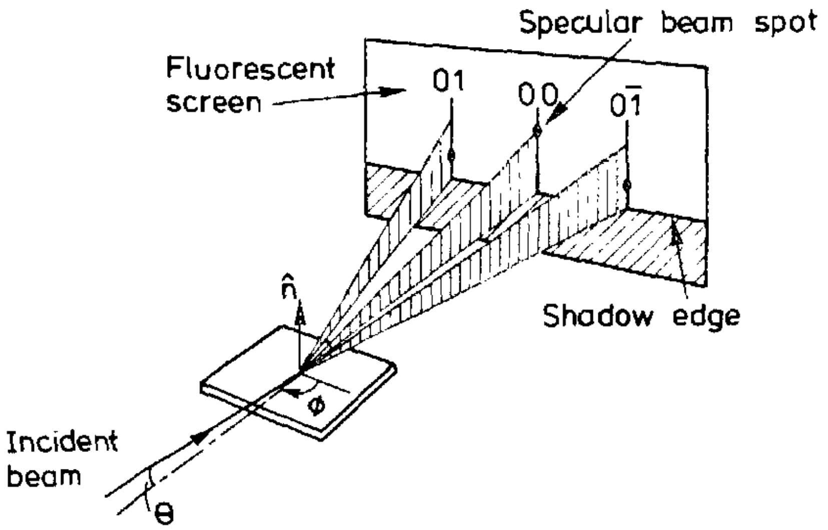
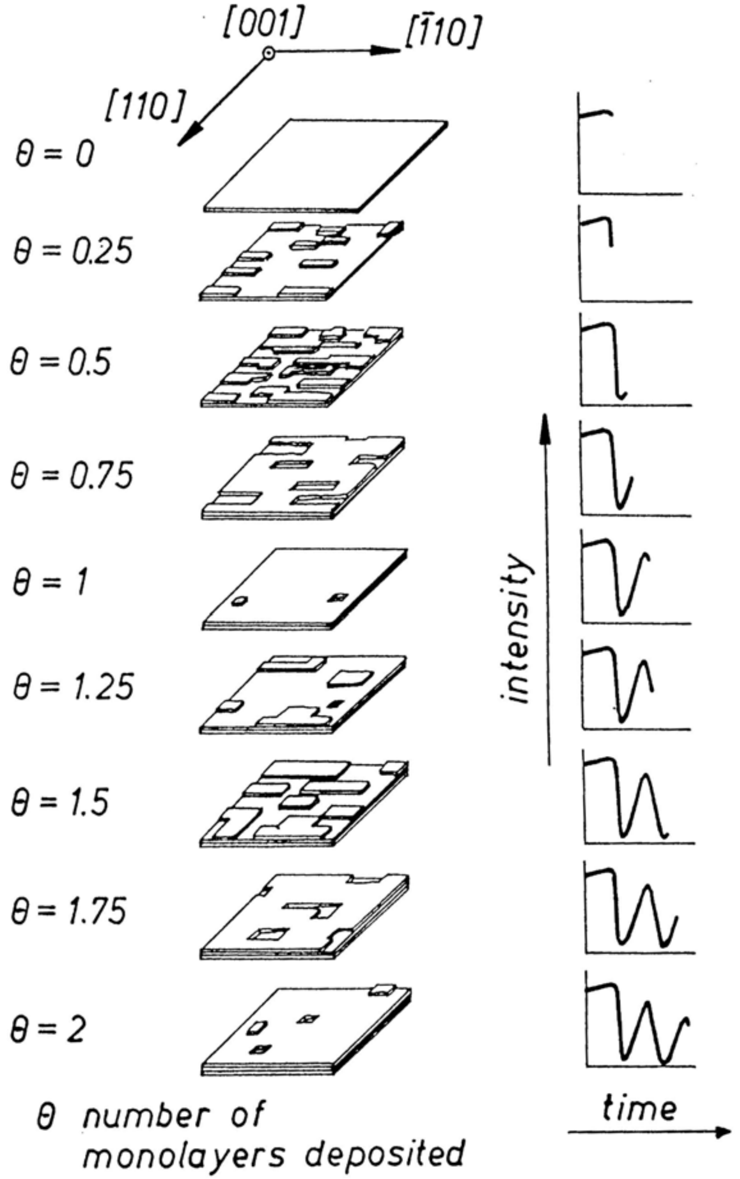


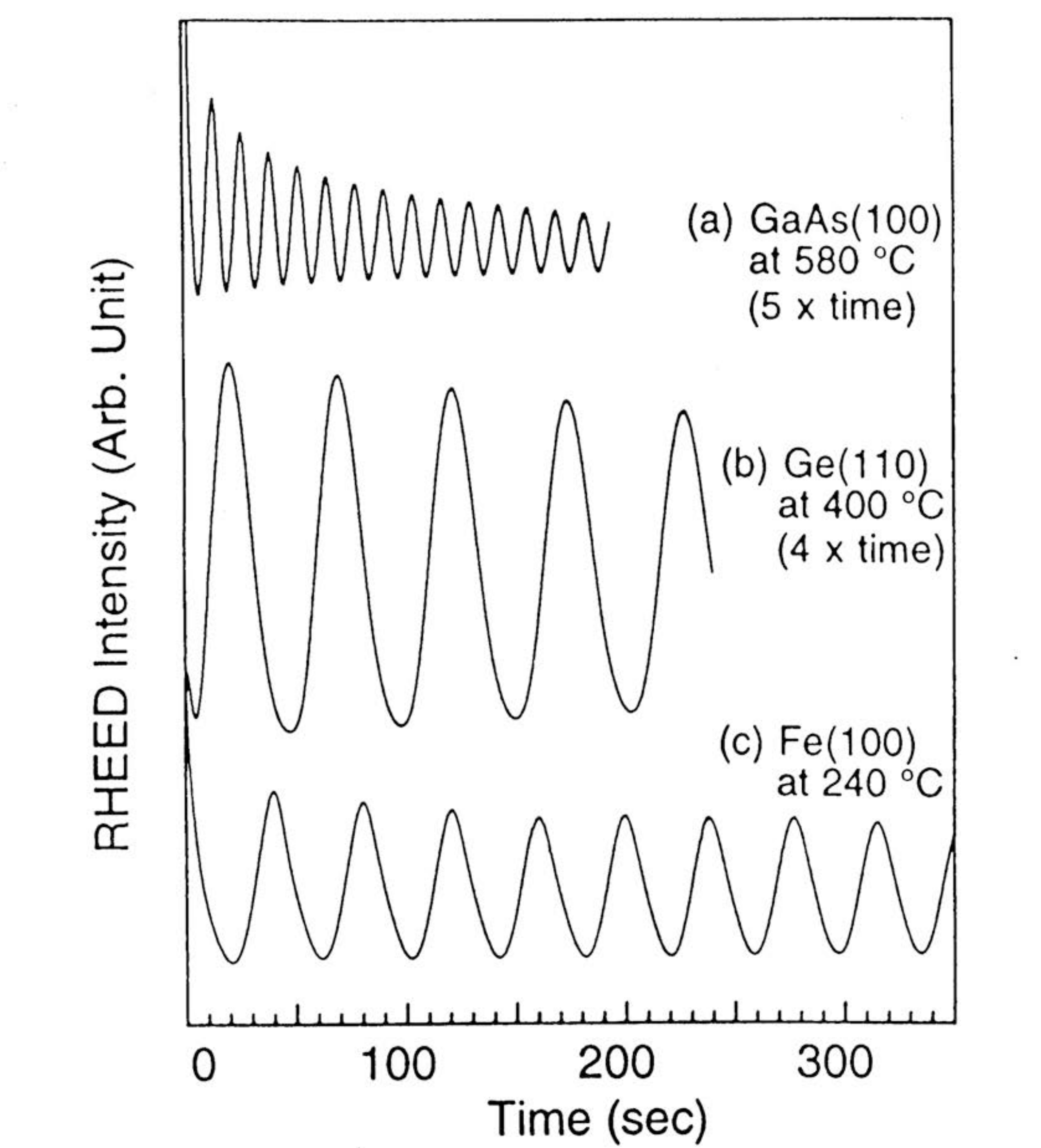
FIG. 1. Schematic diagram of RHEED geometry showing the incident beam at an angle θ to the surface plane; azimuthal angle φ. The elongated spots indicate the intersection of the Ewald sphere with the 01, 00, and $0\bar{1}$ rods.

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.

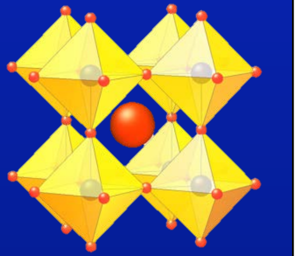
Conventional RHEED Oscillations



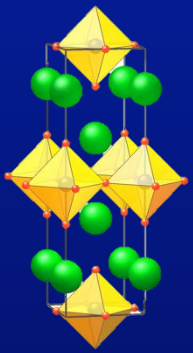
Molecular Beam Epitaxy: Applications to Key Materials, edited by R.F.C. Farrow (Noyes, Park Ridge, 1995), p. 694.

Conventional RHEED Oscillations

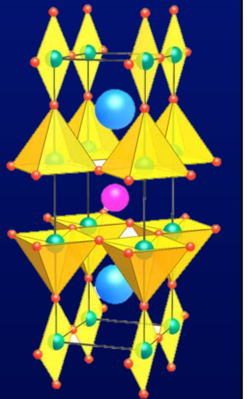
$BaTiO_3$

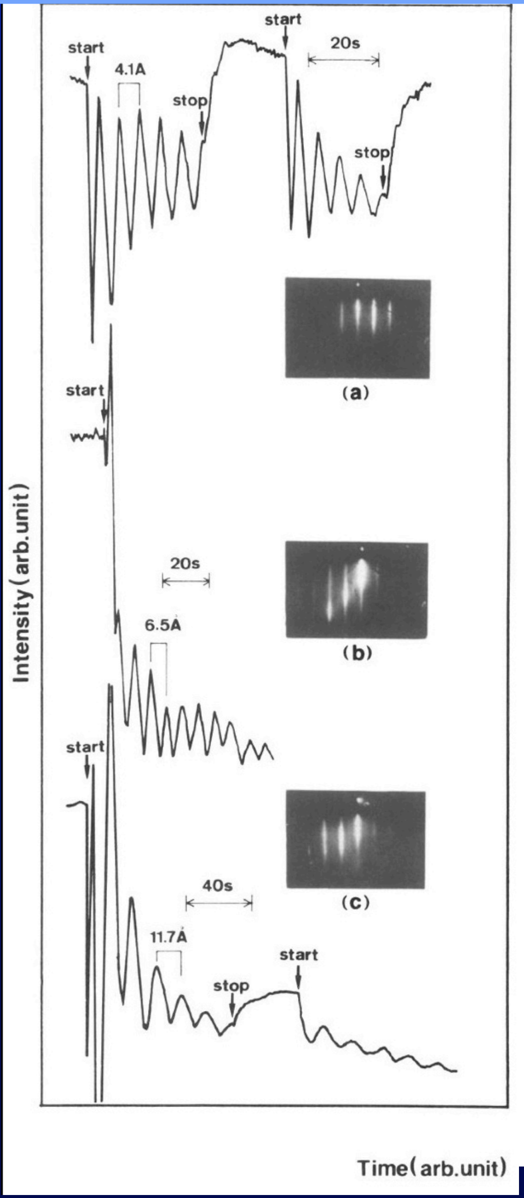


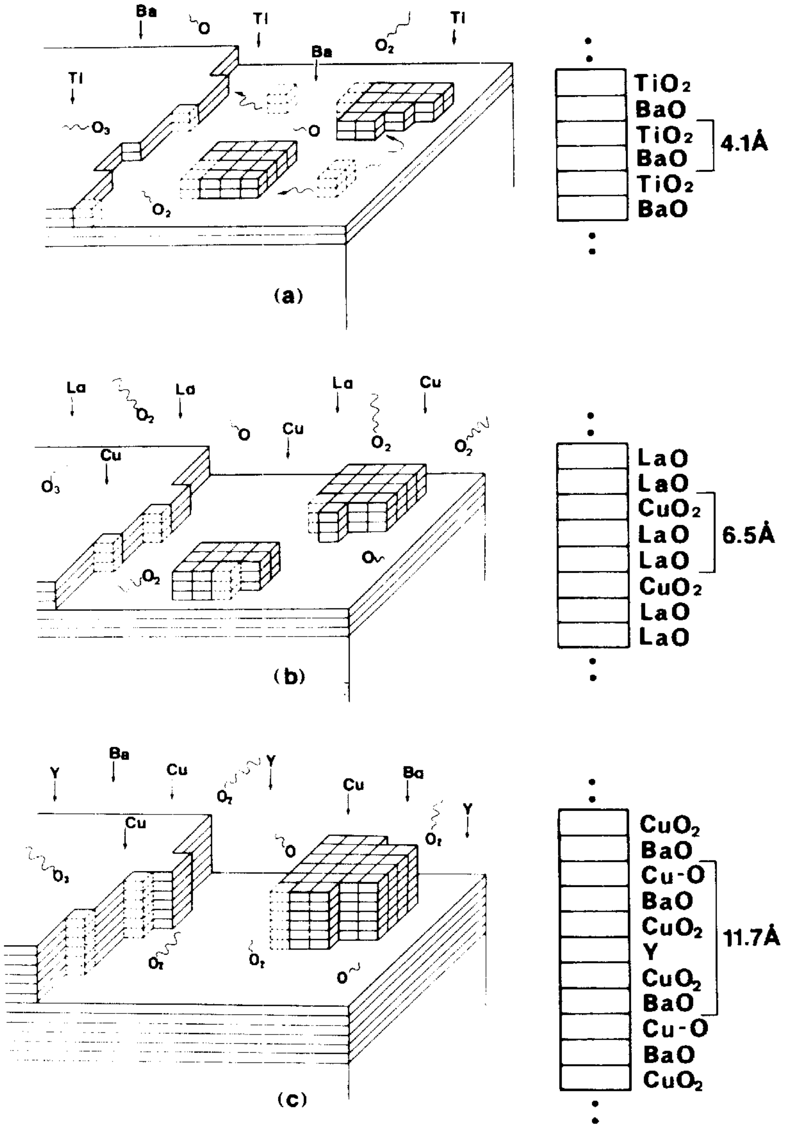
La_2CuO_4



$YBa_2Cu_3O_7$



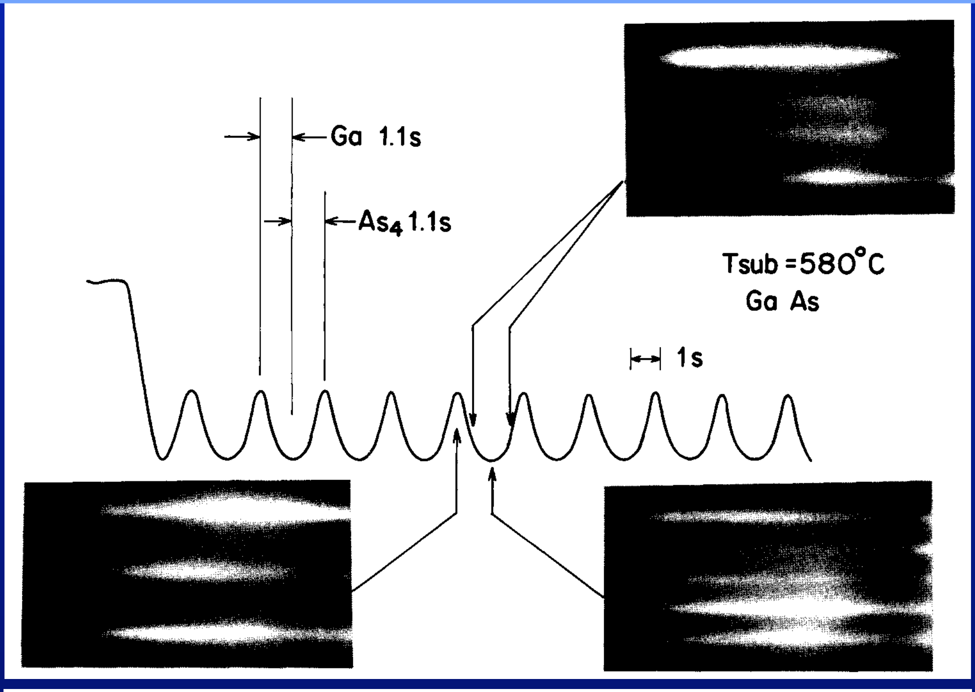


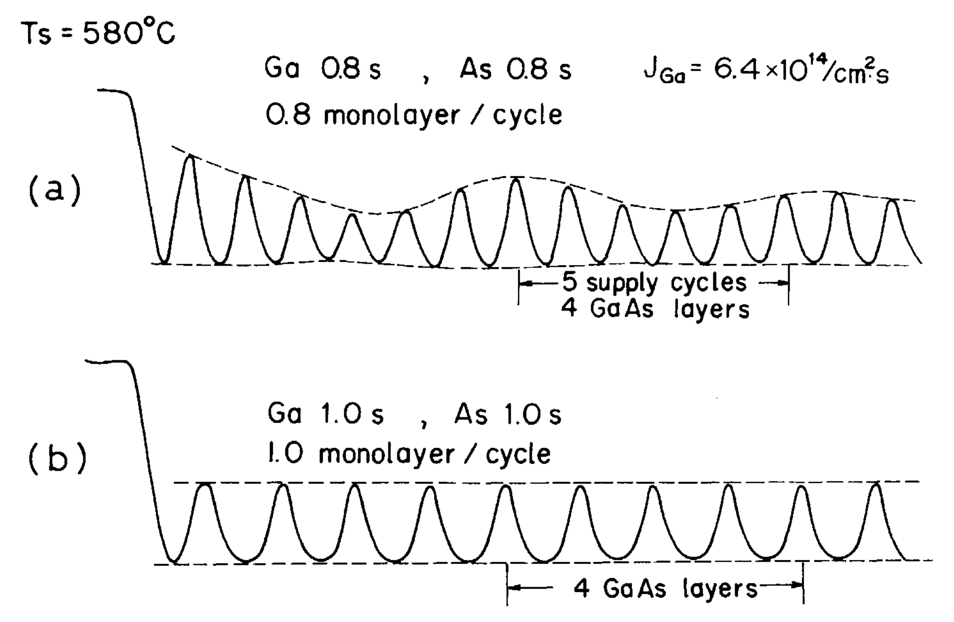


T. Terashima, Y. Bando, K. Iijima, K. Yamamoto, K. Hirata, K. Hayashi, K. Kamigaki, and H. Terauchi, *Physical Review Letters* **65** (1990) 2684–2687.

Migration-Enhanced Epitaxy

Y. Horikoshi, M. Kawashima, and H. Yamaguchi
"Migration-Enhanced Epitaxy of GaAs and AlGaAs"
Japanese Journal of Applied Physics **27** (1988) 169–179.



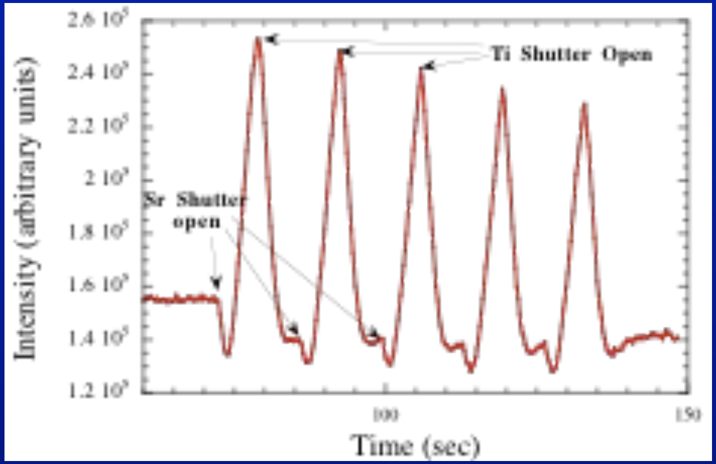


GaAs
or
(Al,Ga)As

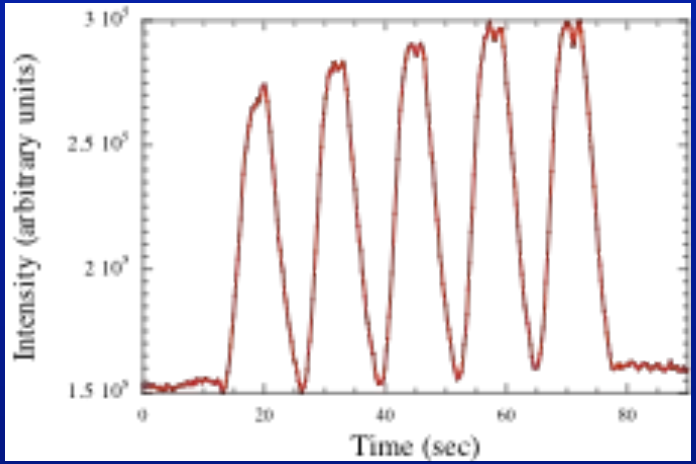
Shuttered RHEED to get Sr:Ti = 1:1

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

3 % Ti Rich

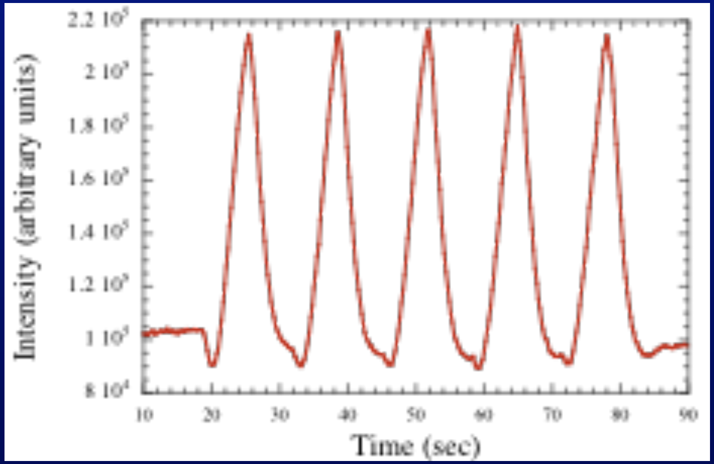


3 % Ti Poor

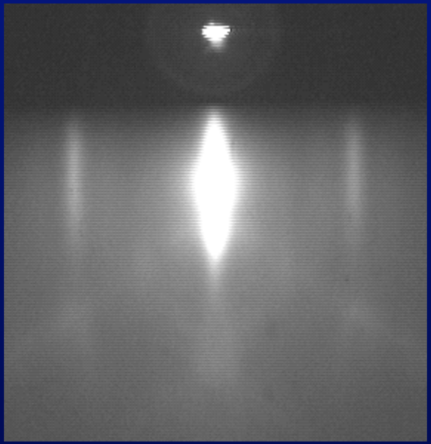


$SrTiO_3$

Stoichiometric



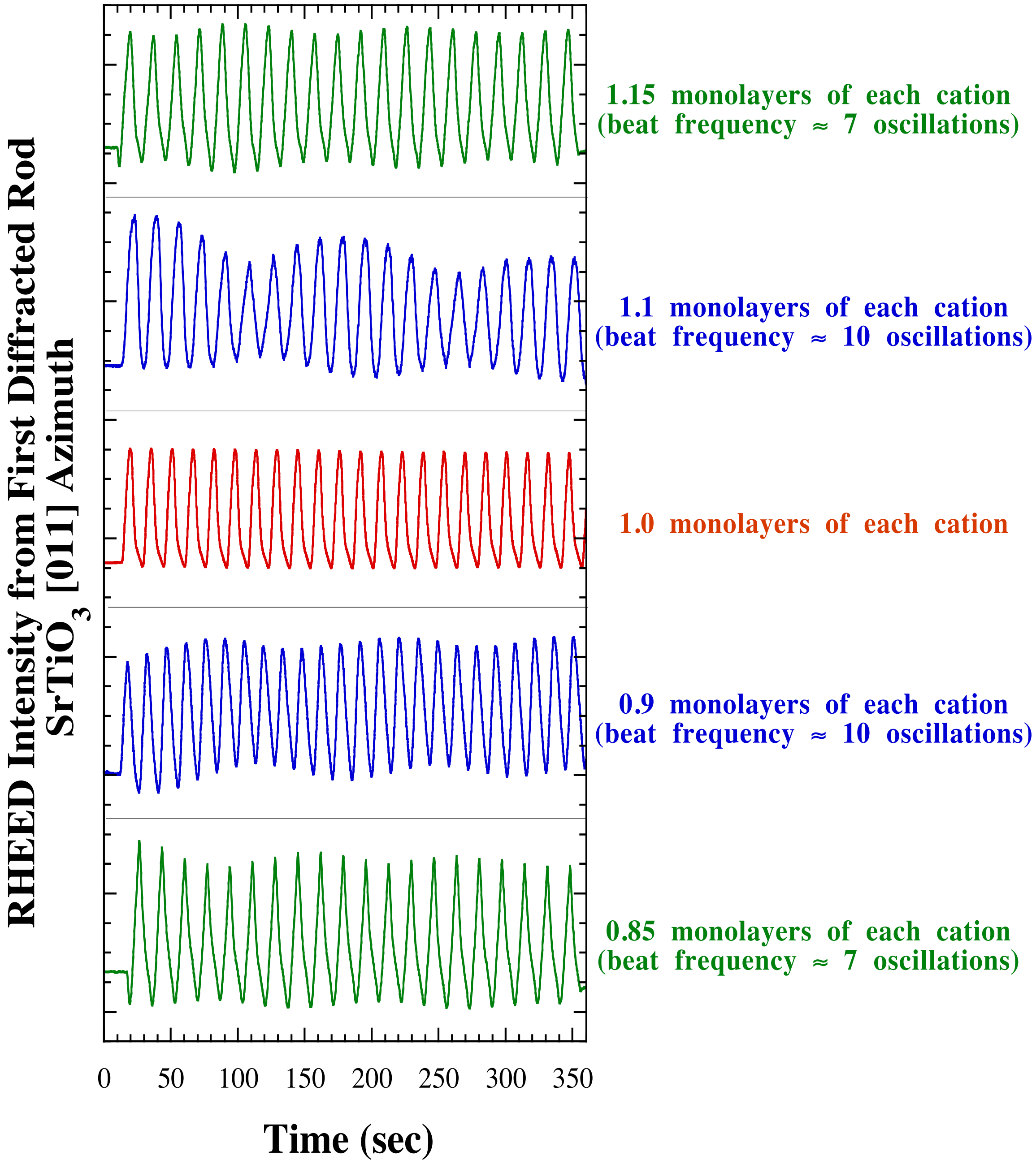
$SrTiO_3$ [011] Azimuth



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

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.



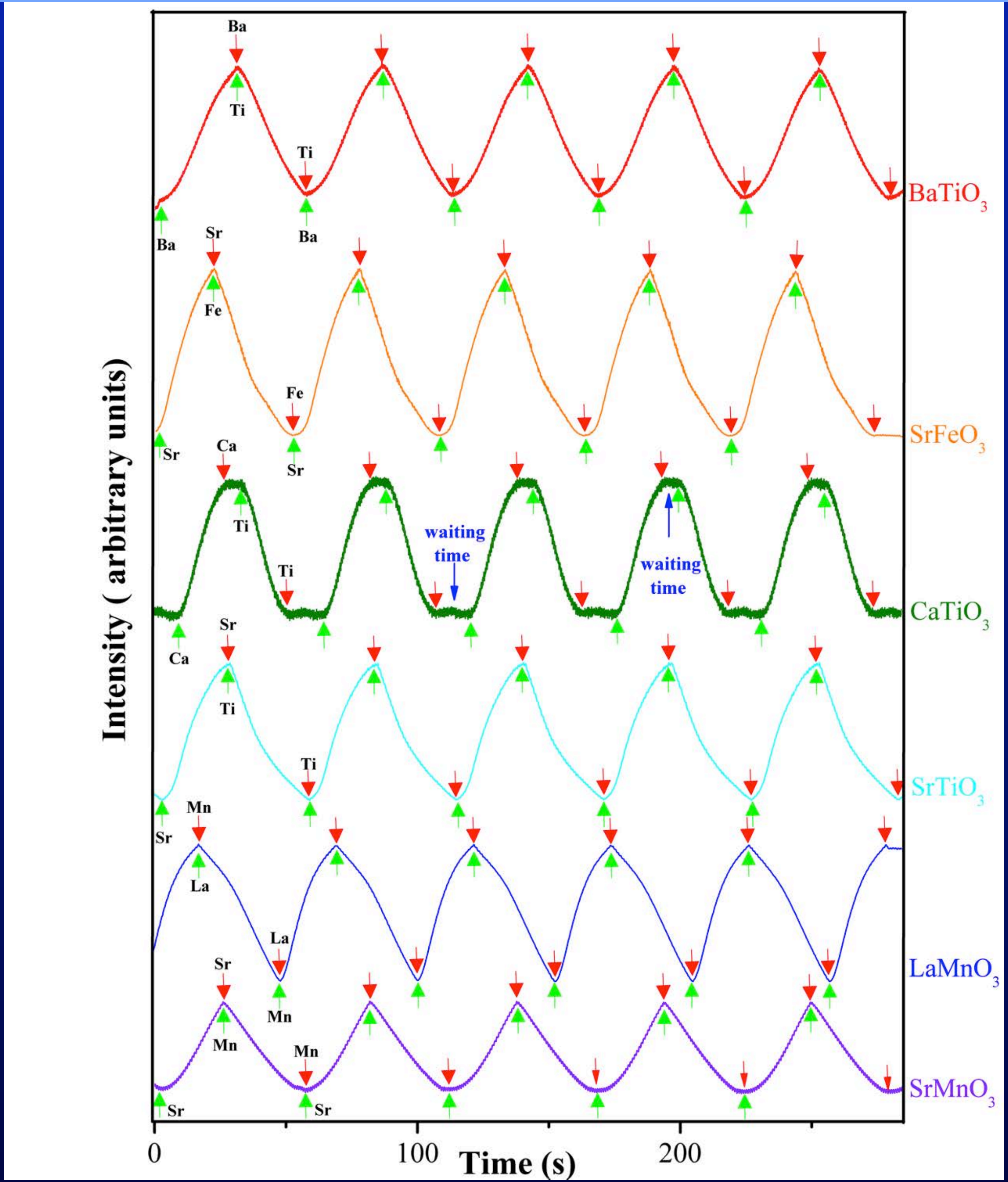
$SrTiO_3$

How we do it

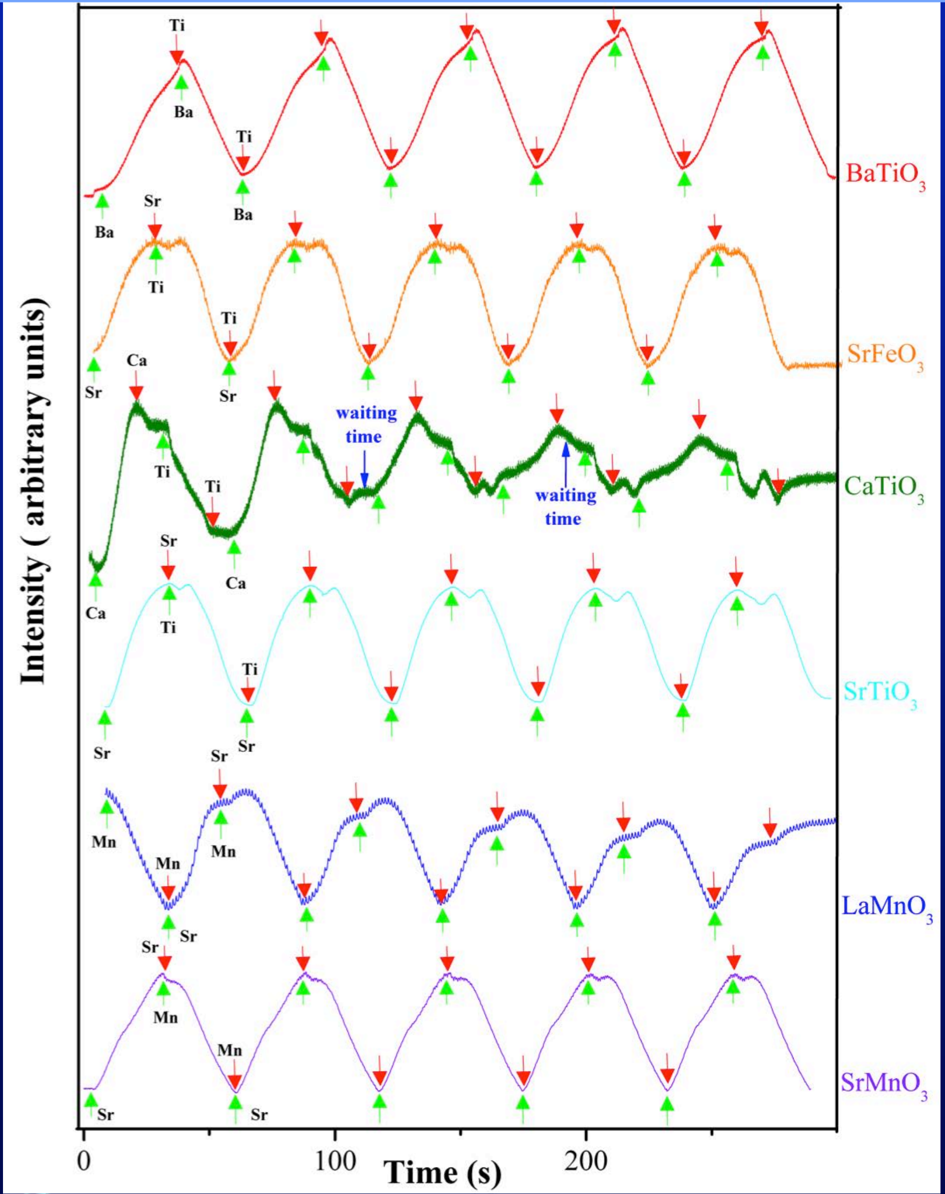
- Use Quartz Crystal Microbalance to Get Fluxes Close (~10% accuracy)
- Use Shuttered RHEED Oscillations (analogous to MEE of GaAs)
- Yields Sr:Ti *Relative* Incorporation Ratio (~1% accuracy)
- Yields *Absolute* Monolayer Dose for SrO and TiO_2 (~1% accuracy)
- Works for many Perovskites

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

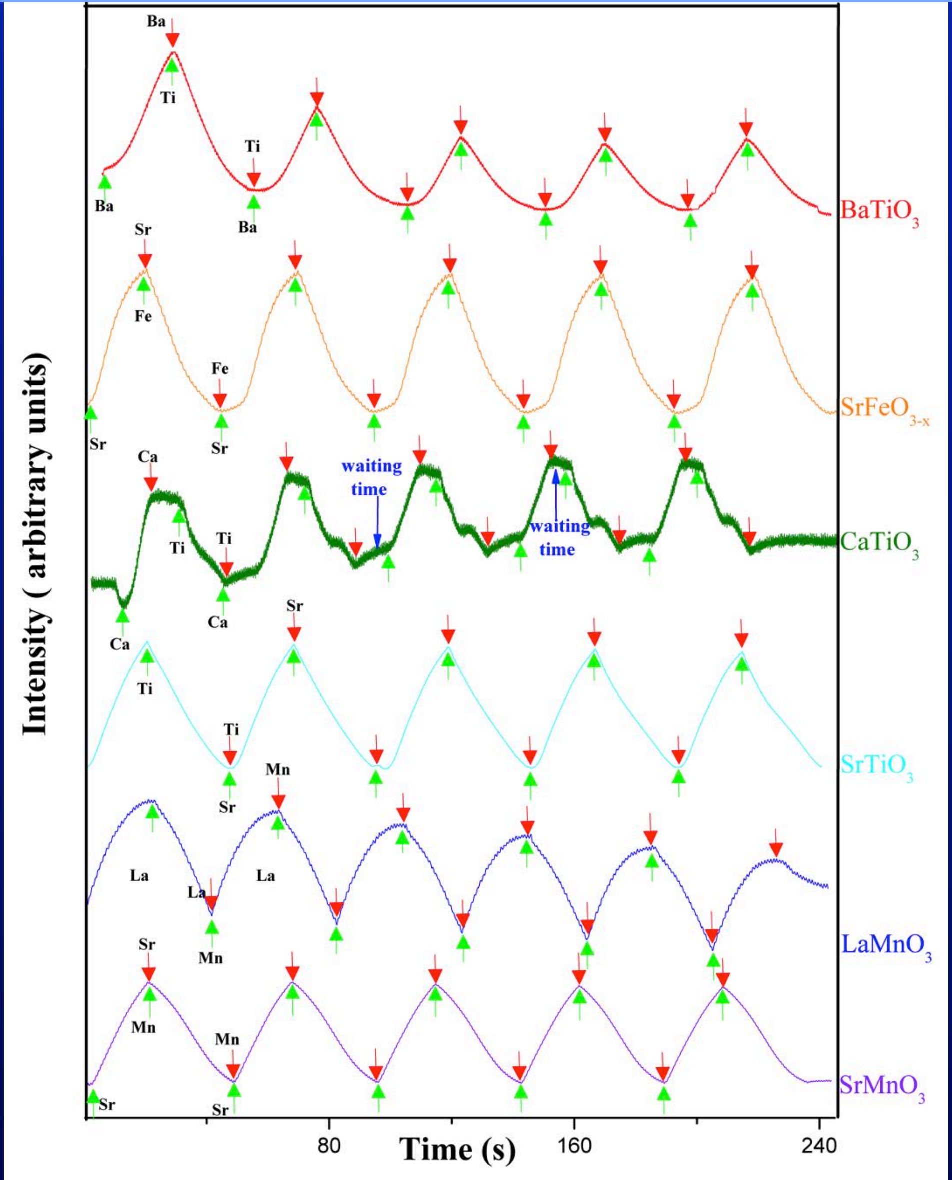
Shuttered RHEED Oscillations



Shuttered RHEED Oscillations



A-Site Rich



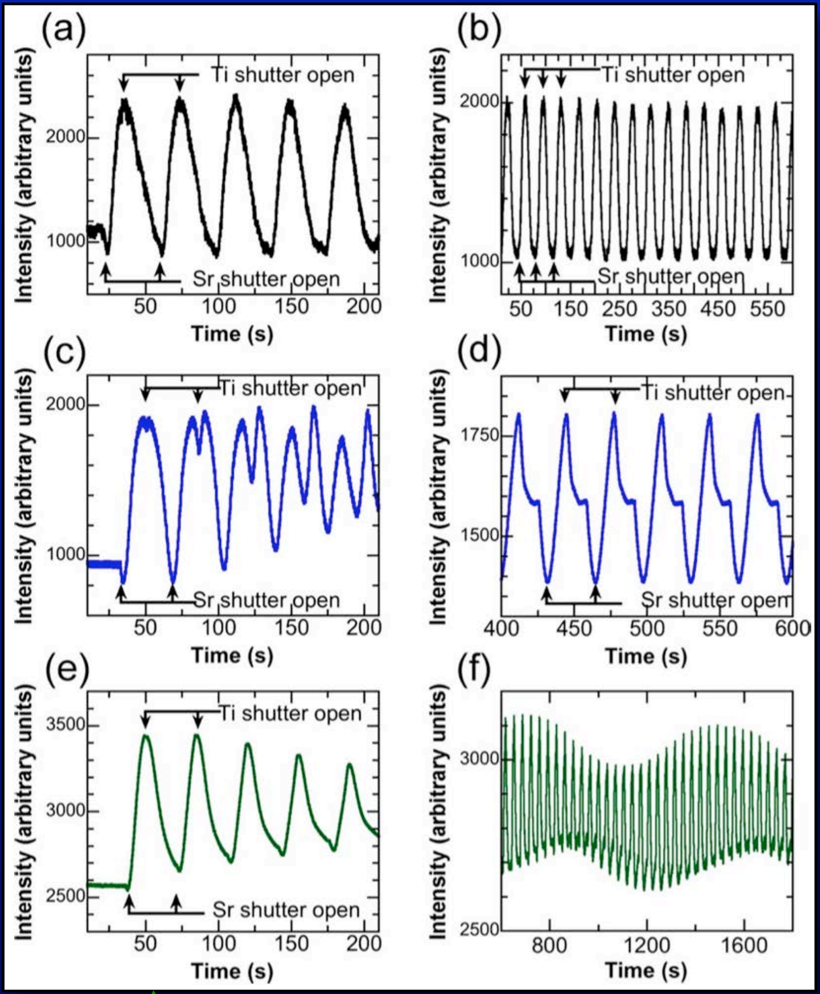
B-Site Rich

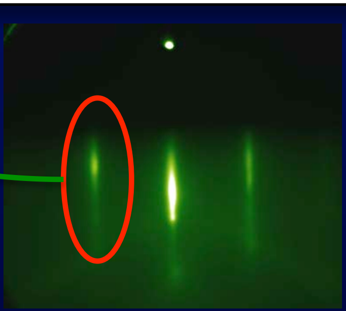
Shuttered RHEED Calibration

$SrTiO_3$

+10% Sr

–10% Sr

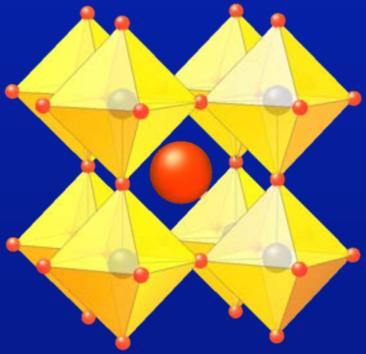




- Deposition of superlattices and layered structures requires precise control to achieve perfect layer termination
- Calibration of beam flux with quartz crystal monitor not precise enough
- Intensity variation of electron diffraction (RHEED) pattern during deposition of one unit cell can be used for flux calibration
- Very time-consuming process, calibration can easily take 8 hours

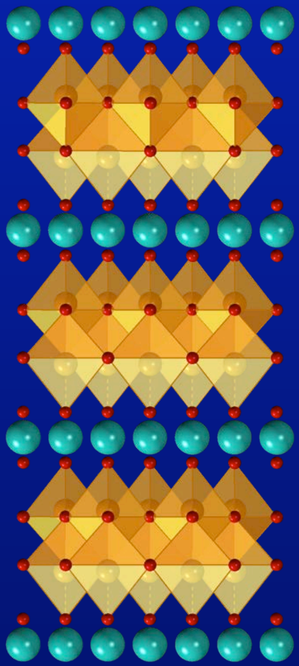
PARADIM

Examples of Oxides we Grow

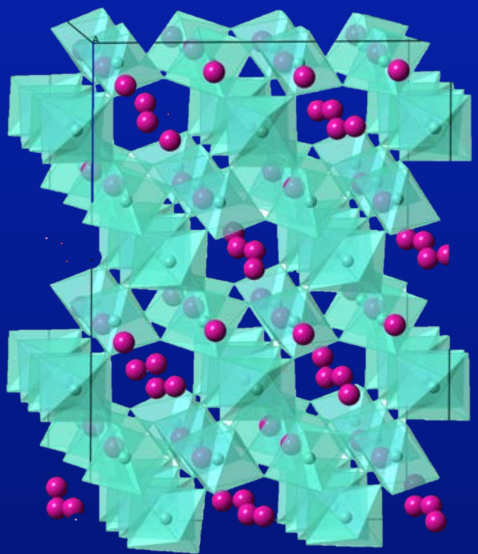


$BaSnO_3$

today's record
transparent transistors

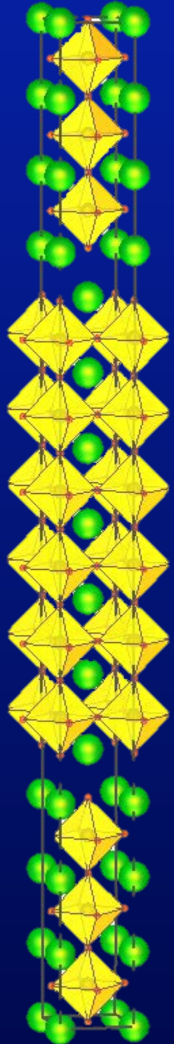


$LuFe_2O_4$

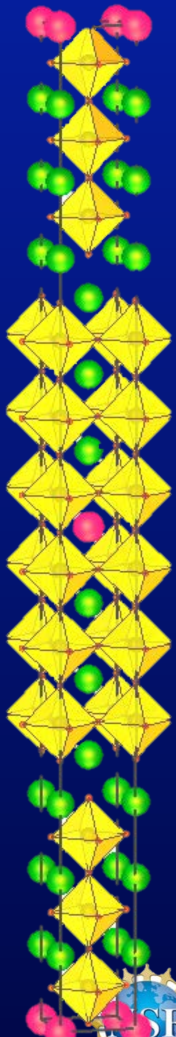


α-$Bi_2Sn_2O_7$
(352 atoms/unit cell)

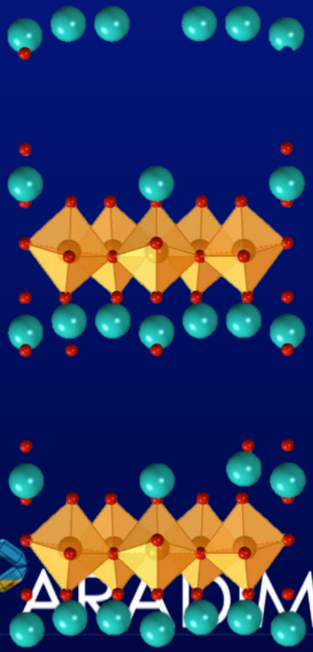
$Sr_7Ti_6O_{19}$



$BaSr_6Ti_6O_{19}$

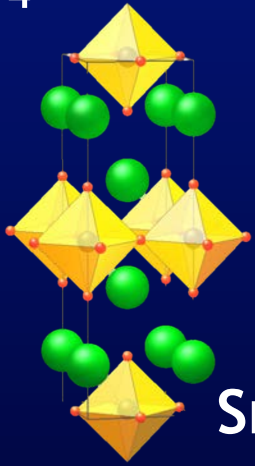


today's record
tunable microwave dielectric



today's record
room-temperature
multiferroic
(superlattices)

$LuFeO_3$



leading
candidate
odd-parity
topological
superconductor

Sr_2RuO_4