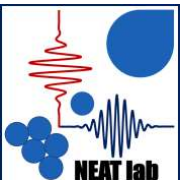
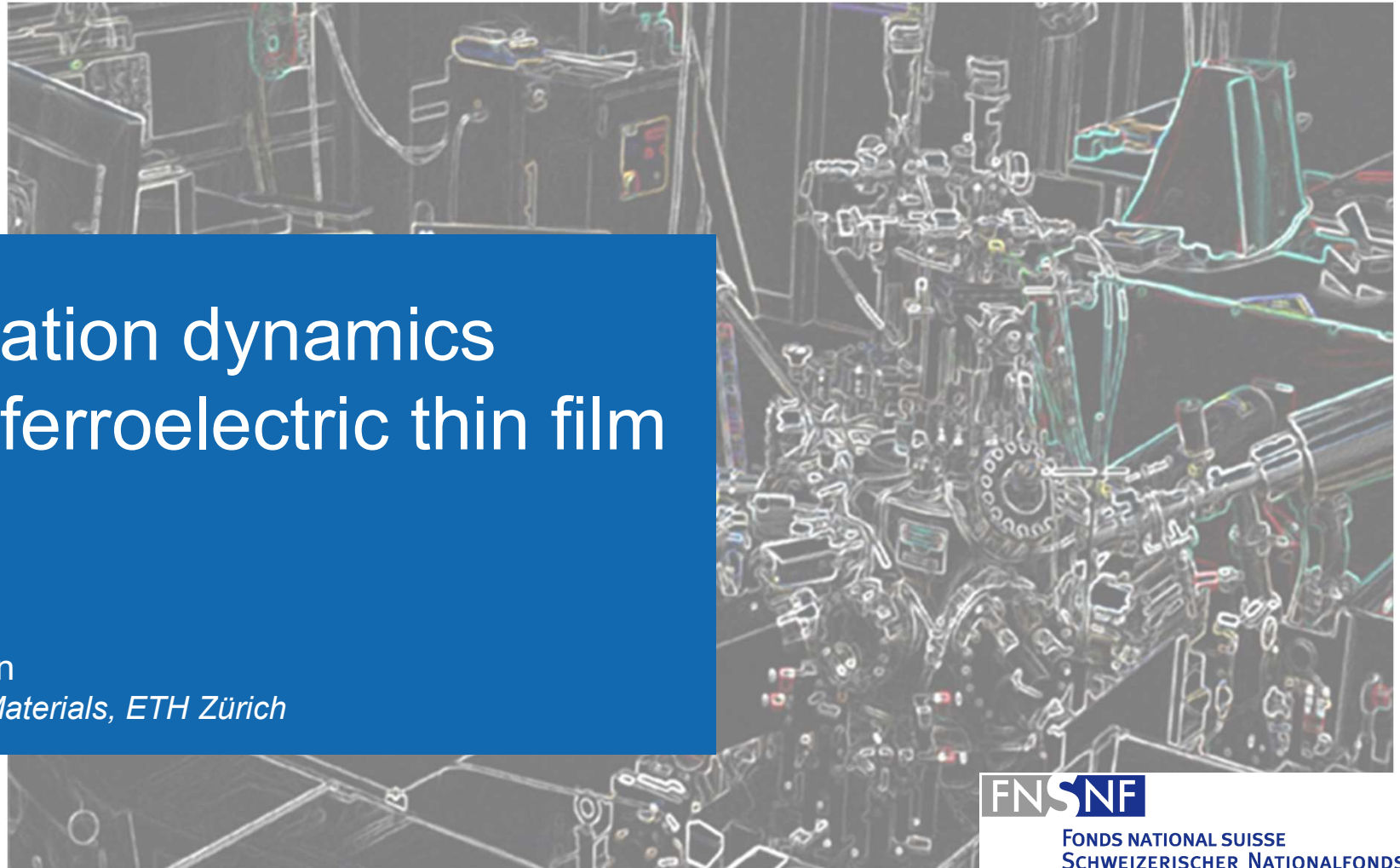


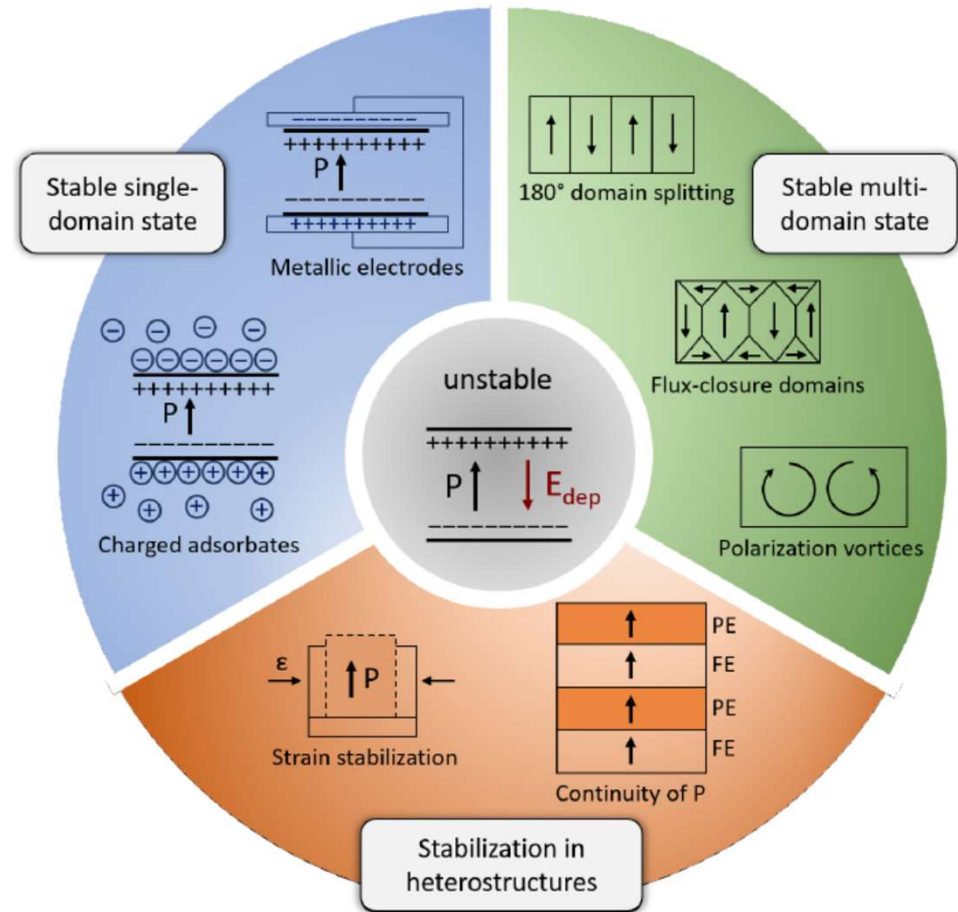
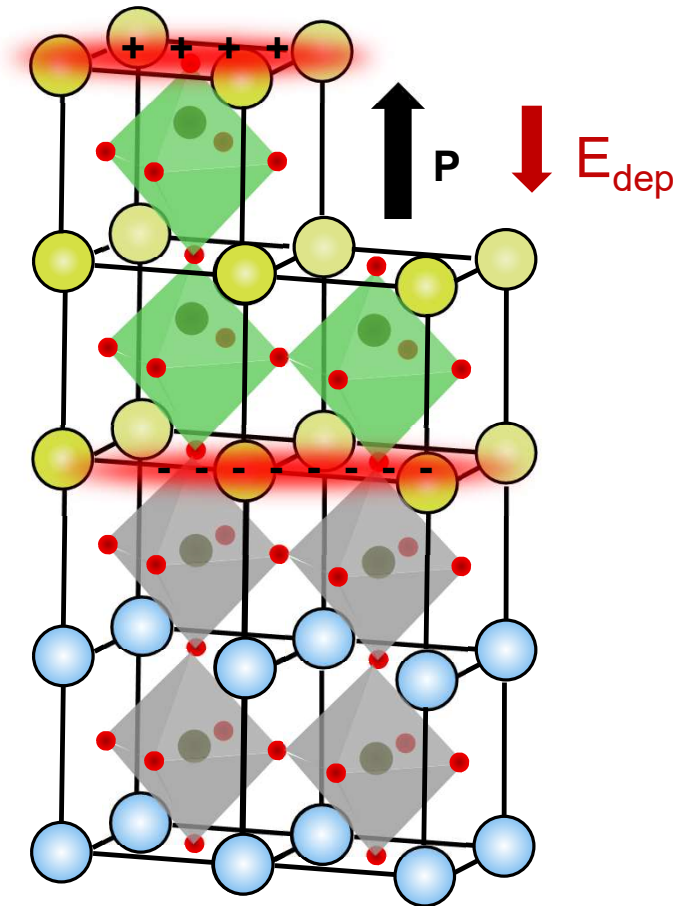
# Polarization dynamics during ferroelectric thin film growth

Morgan Trassin  
*Department of Materials, ETH Zürich*



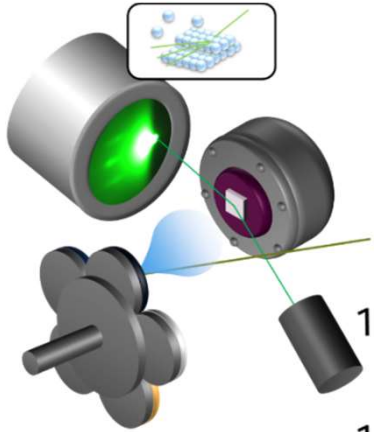
FONDS NATIONAL SUISSE  
SCHWEIZERISCHER NATIONALFONDS  
FONDO NAZIONALE SVIZZERO  
SWISS NATIONAL SCIENCE FOUNDATION

# Ferroelectric Thin Films



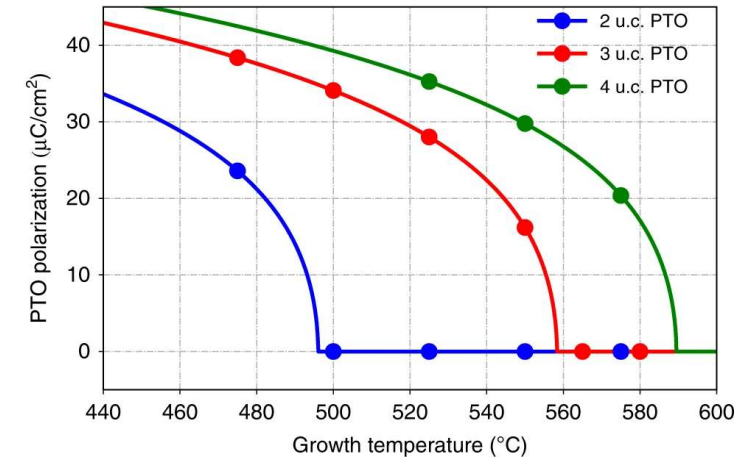
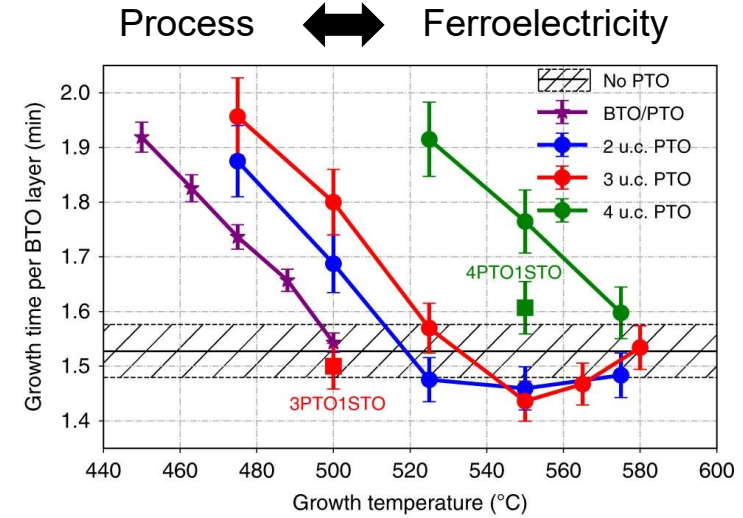
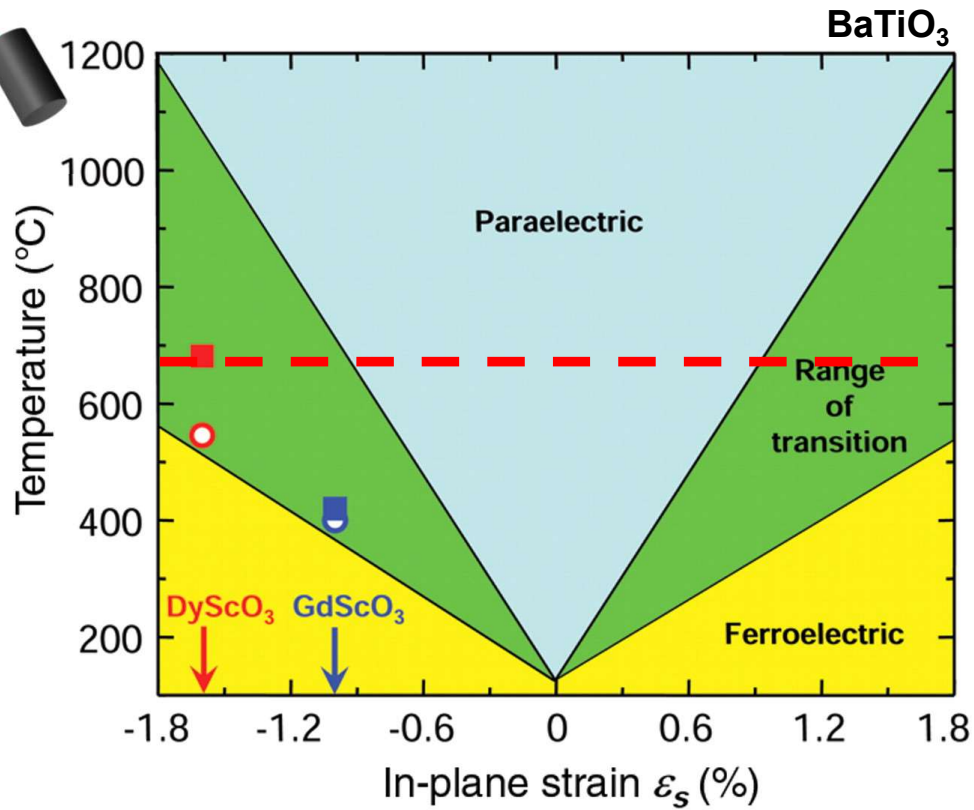
Lichtensteiger, C. et al., Nano Lett. 14, 4205 (2014)  
 Pacchioni, G. Oxide Ultrathin Films, Wiley (2012)

# Ferroelectric Epitaxial Growth



500-700 °C  
 $10^{-2} - 10^{-1}$   
 $O_2$  mbar

**Epitaxy and ferroelectricity**

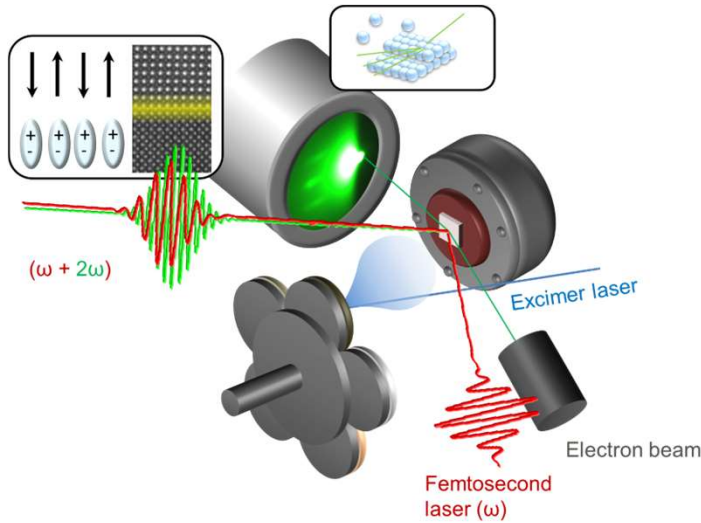


Liu, R., et al. Nat. Commun. 11, 2630 (2020)

Choi, K. J. et al. Science 306, 1005 (2004)

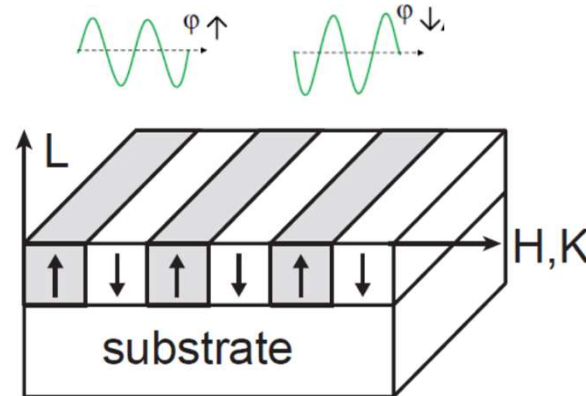
Sarott, M. F., MT, et al. J. Phys.: Condens. Matter 33 293001 (2021)

# Monitoring Ferroelectricity in-situ



Optical second harmonic generation (SHG)

$$P_i(2\omega) = \epsilon_0 \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega)$$



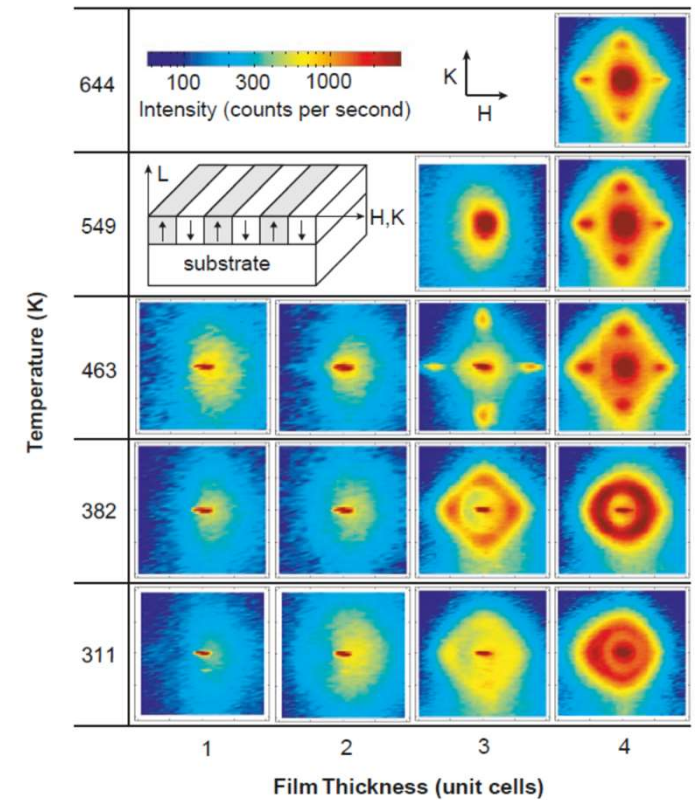
- De Luca, G., MT, et al. *Adv. Mater.* 27, 4871. (2015)
- De Luca, G., MT, et al. *Nat. Commun* 8, 1419 (2017)
- Nordlander, J., MT, et al. *Appl. Sci.*, 8, 570 (2018)
- Strkalj, N., MT, et al. *Materials*, 12, 3108 (2019)
- Nordlander, J., MT, et al. *Nat. Commun* 10, 5591 (2019)
- Sarott, M. F., MT, et al. *J. Phys.: Condens. Matter* 33 293001 (2021)
- Mueller, M. MT, et al. *ACS Appl. Electron. Mater.* (2023)

## Ferroelectricity in Ultrathin Perovskite Films

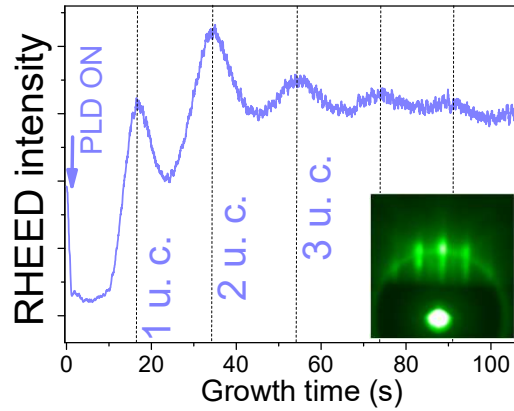
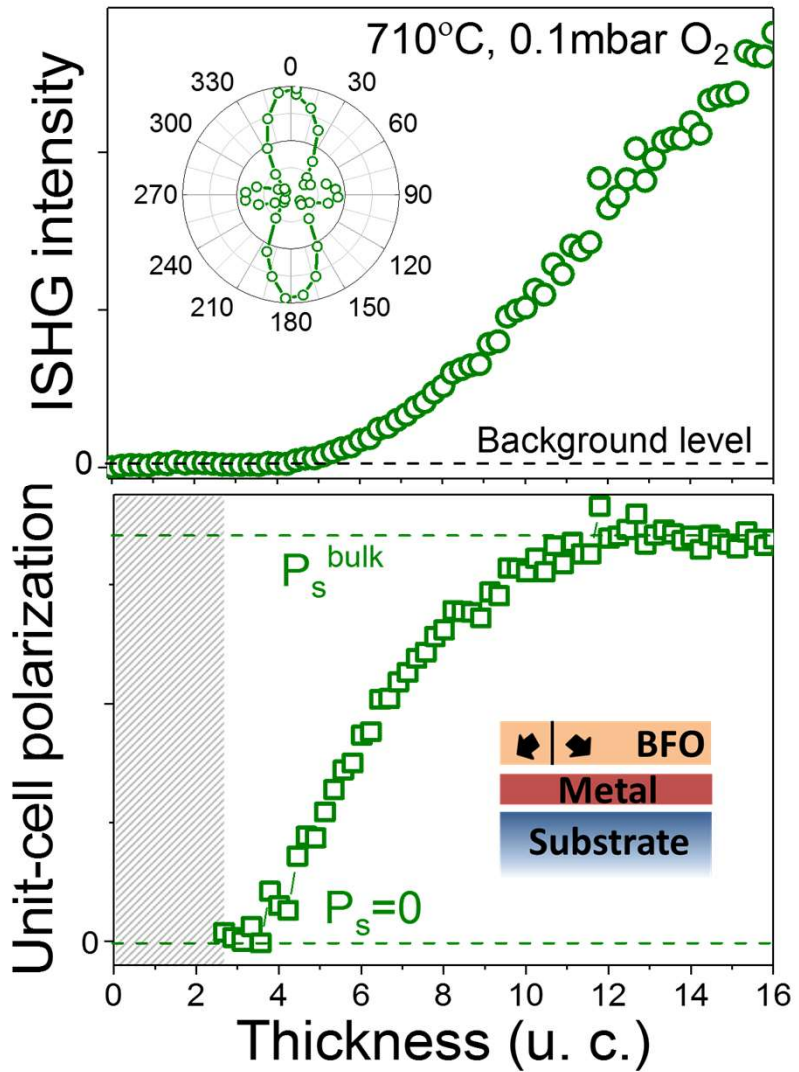
Dillon D. Fong,<sup>1</sup> G. Brian Stephenson,<sup>1\*</sup> Stephen K. Streiffer,<sup>1</sup>  
 Jeffrey A. Eastman,<sup>1</sup> Orlando Auciello,<sup>1</sup> Paul H. Fuoss,<sup>1</sup>  
 Carol Thompson<sup>2</sup>

1650

11 JUNE 2004 VOL 304 SCIENCE

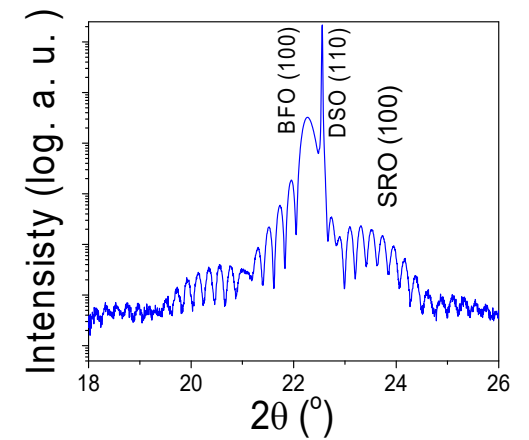
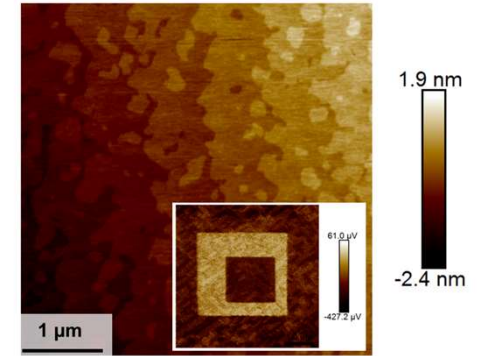


# Monitoring Ferroelectricity in-situ



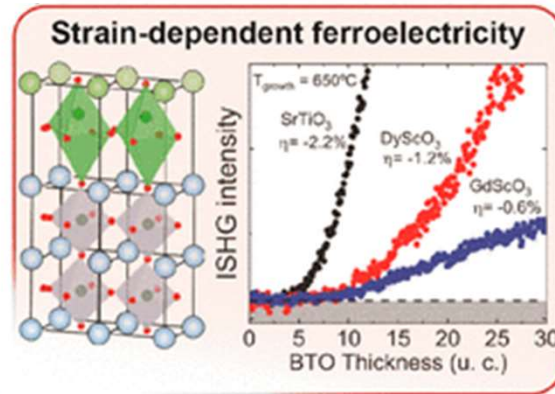
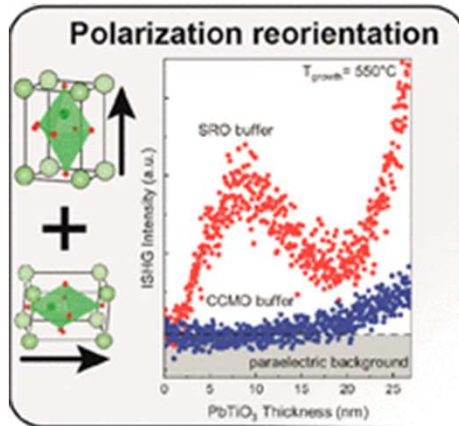
**Real-time monitoring of the evolution of the ferroelectric polarization**

**Determination of the critical thickness with u.c. accuracy**



# Monitoring Ferroelectricity in-situ

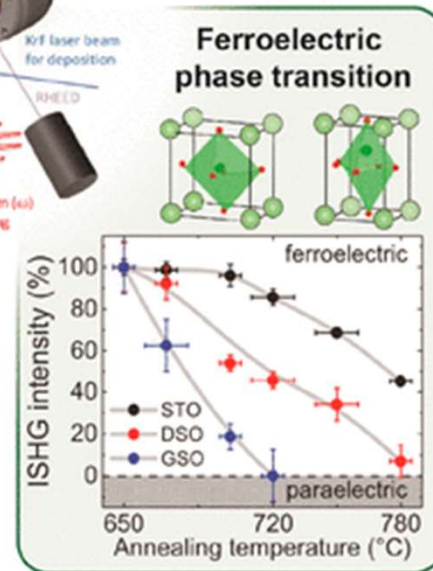
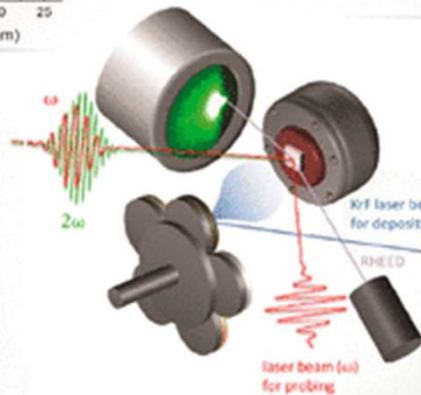
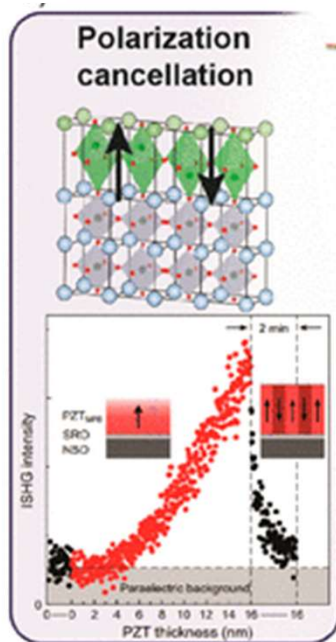
## Monitoring domain formation



Strkalj, N., MT, et al. Phys. Rev. Lett. 123, 147601 (2019)

Sarott, M. F., MT, et al. APL 117, 132901 (2020)  
 Sarott, M. F., MT, et al. Nat. Commun. 13, 3159 (2022)  
 Strkalj, N., MT, et al. Phys. Rev. Lett. 123, 147601 (2019)

## Sub-unit cell symmetry breaking



## Direct access to Tc

Nordlander, J., MT et al. Nano Lett. 21, 2780 (2021)

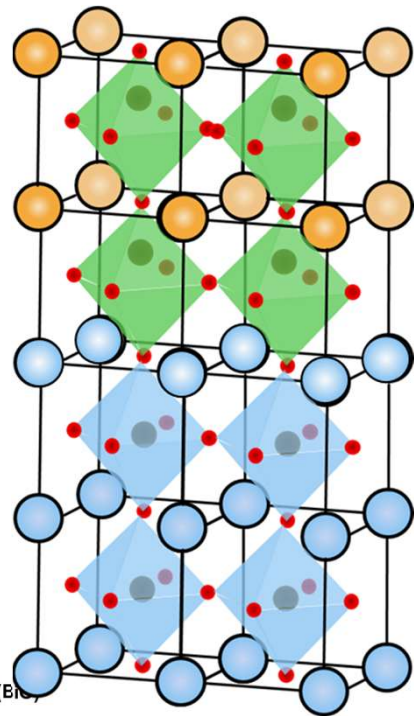
Sarott, M. F., MT, et al. Nat. Commun. 13, 3159 (2022)  
 Strkalj, N., MT, et al. Phys. Rev. Lett. 123, 147601 (2019)

Strkalj, N., MT, et al. Phys. Rev. Lett. 123, 147601 (2019)  
 Nordlander, J., MT, et al. Nat. Commun. 10, 5591 (2019)

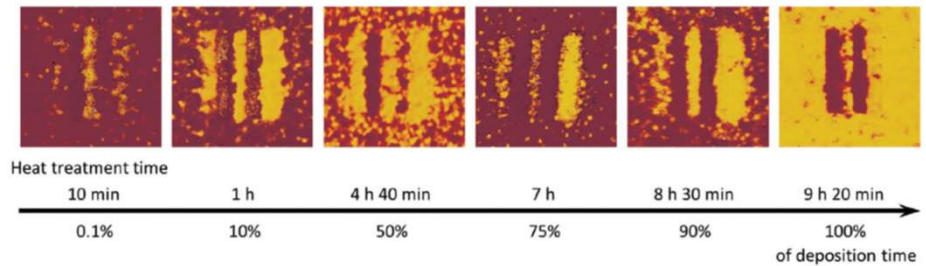
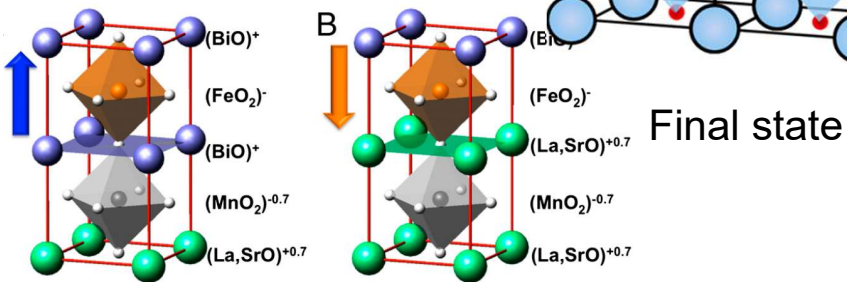
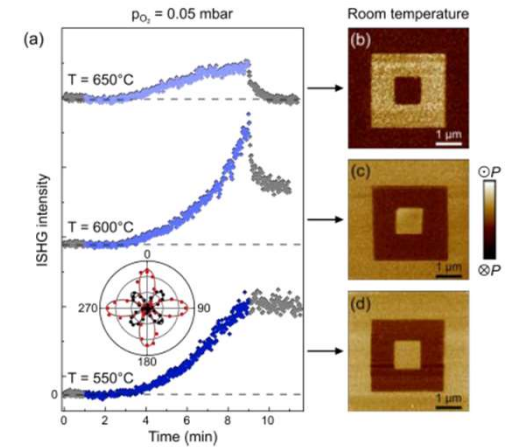
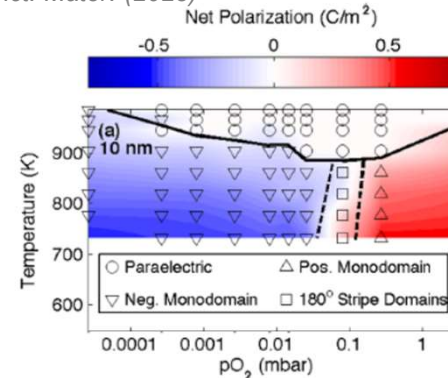
# The Power of in-situ Monitoring

**Direct access to transient states  
(evolving electrostatics, surface reconstructions, ...)**

De Luca, G., MT, et al.  
Nat. Commun 8, 1419 (2017)  
Yu, P., et al.  
PNAS 109 9710 (2012)  
Strkalj, N., MT, et al.  
Nat. Commun. 11, 5815 (2020)  
Gattinoni, C., MT, et al.  
PNAS. 117, 28589 (2020)

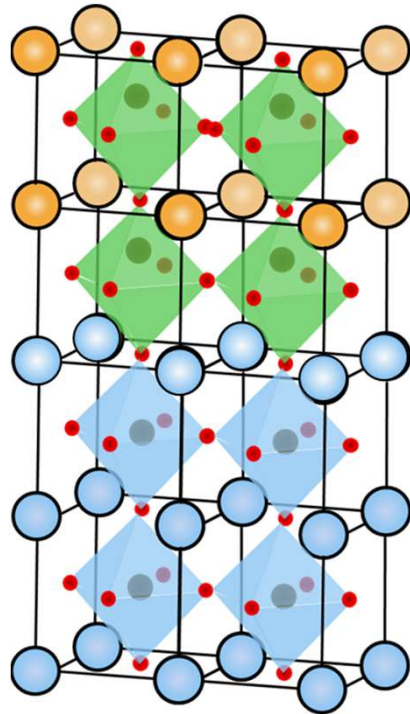


Highland, M. J., et al.  
PRL. 107, 187602 (2011)  
Tian, Y., et al.  
Nat Commun. 9, 3809 (2018)  
Weymann, C. et al.  
Adv. Electron. Mater. 6, 2000852 (2020)  
Sarott, M. F., MT, et al.  
Adv. Funct. Mater. (2023)



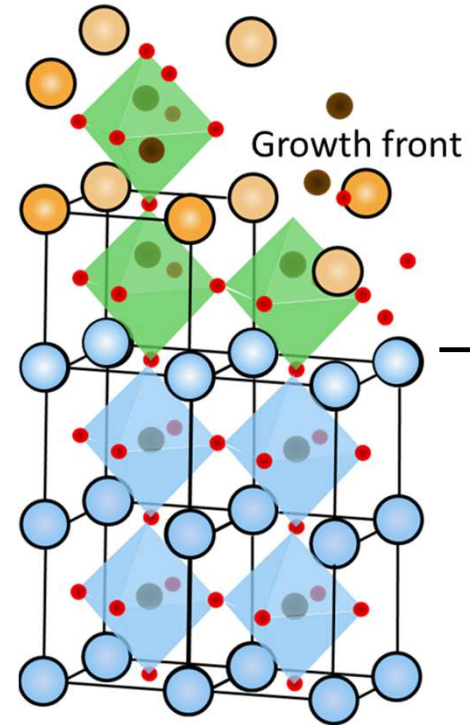
# The Power of in-situ Monitoring

**Direct access to transient states  
(evolving electrostatics, surface reconstructions, ...)**



Final state

**“2 interfaces contributing”**



During growth

**“single interface contributing”**

De Luca, G., MT, et al.  
*Nat. Commun* 8, 1419 (2017)  
Yu, P., et al.  
*PNAS* 109 9710 (2012)  
Strkalj, N., MT, et al.  
*Nat. Commun.* 11, 5815 (2020)  
Gattinoni, C., MT, et al.  
*PNAS.* 117, 28589 (2020)

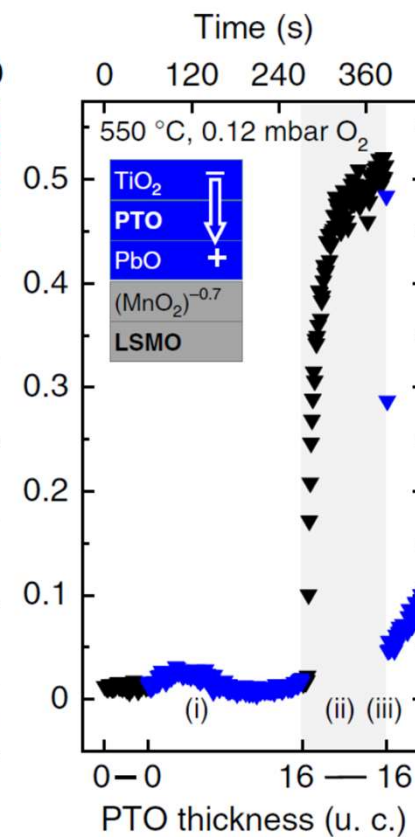
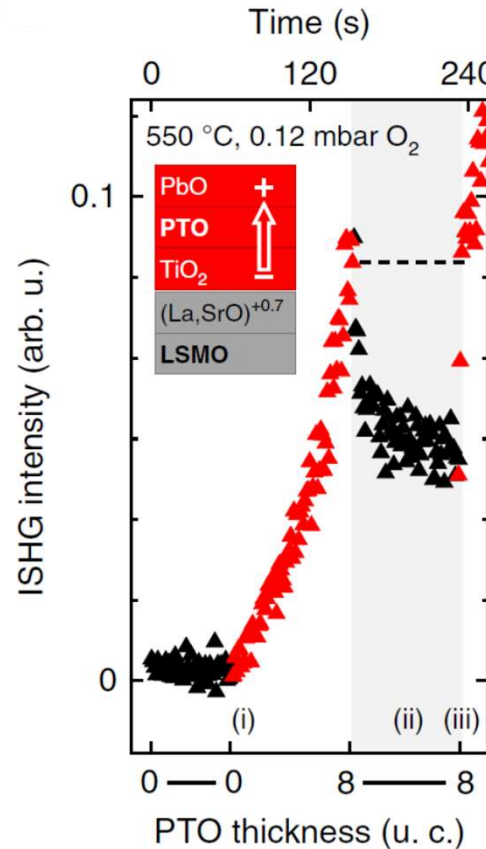
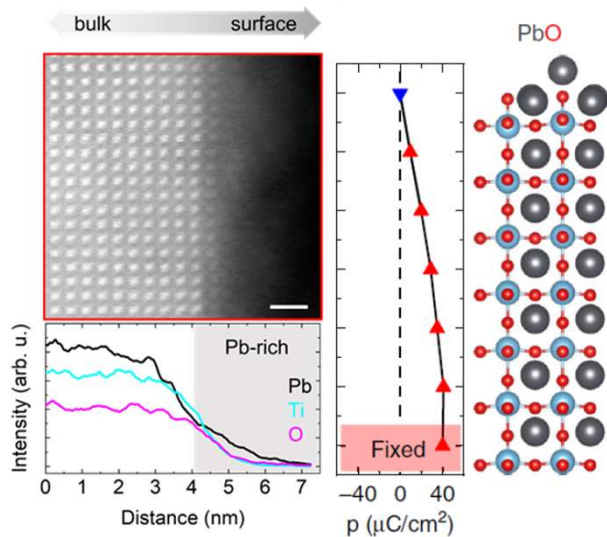


# Interface Contribution in the Final Polarization State

**A-site volatile compound:  
Charged defect gradient**

**Switching the atomic termination to trigger  
interface cooperation**

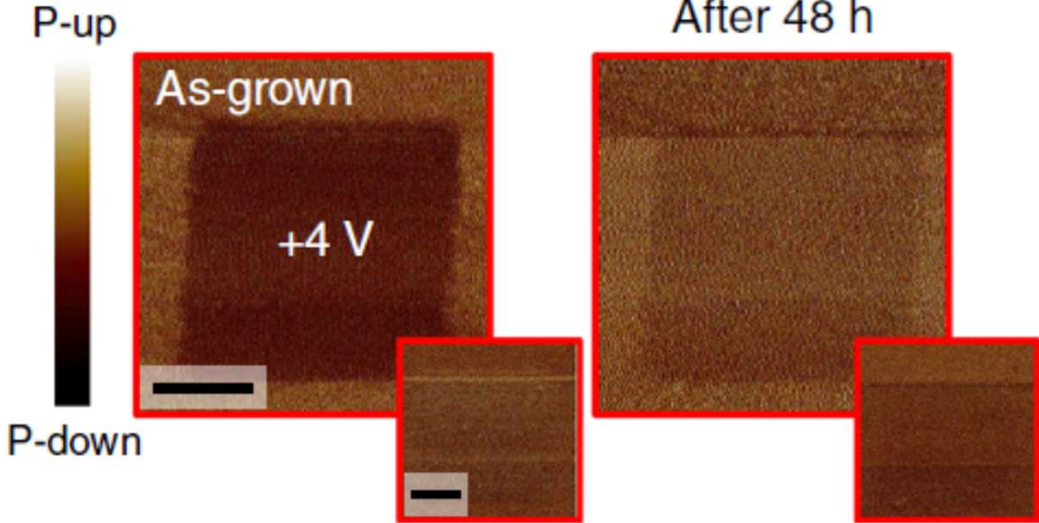
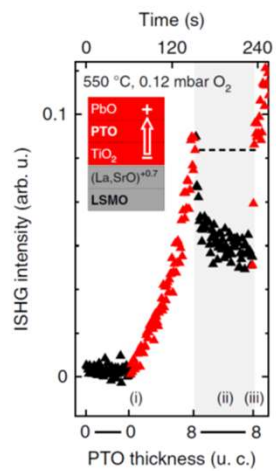
Top surface preferentially screens negative bound charges



Strkalj, N., MT, et al.  
*Nat. Commun.* 11, 5815 (2020)  
 Gattinoni, C., MT, et al.  
*PNAS.* 117, 28589 (2020)  
 Weymann, C. et al.  
*Adv. Electron. Mater.* 6, 2000852 (2020)  
 Sarott, M. F., MT, et al.  
*Adv. Funct. Mater.* (2023)

Strkalj, N., MT, et al.  
*Nat. Commun.* 11, 5815 (2020)

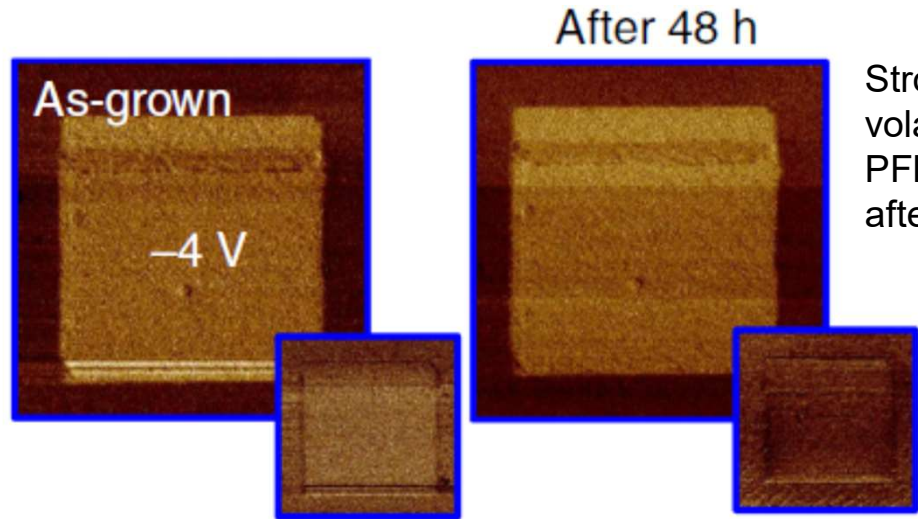
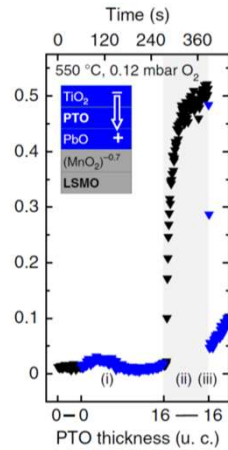
# Interface Contribution in the Final Polarization State



Weak and vanishing PFM contrast after poling

**Drastic enhancement of the polarization & Ferroelectric performance**

Strkalj, N., MT, et al. Nat. Commun. 11, 5815 (2020)

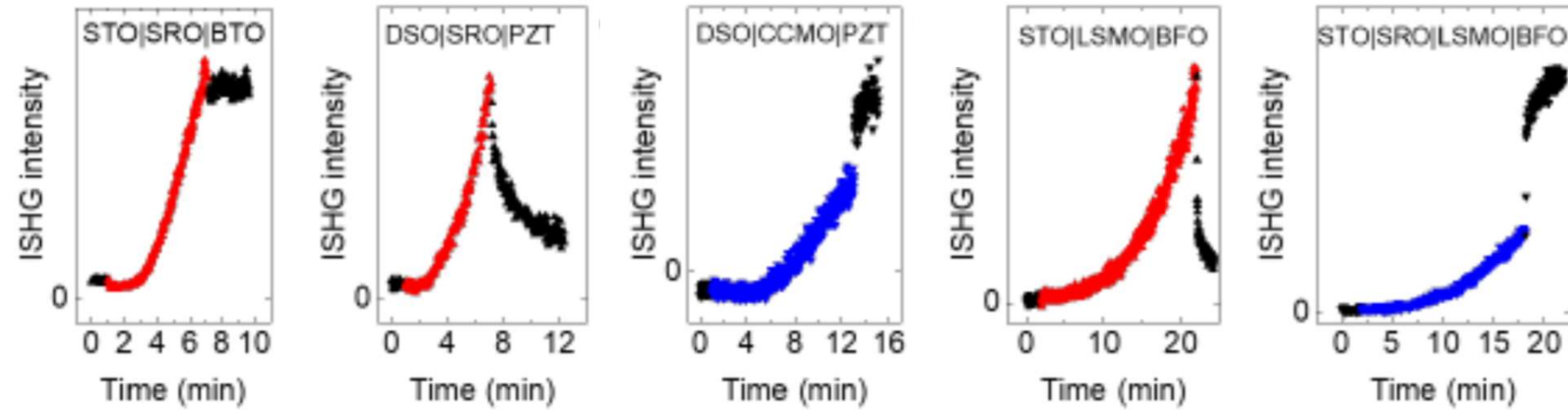


Strong and non volatile PFM contrast after poling

P-left  
P-right

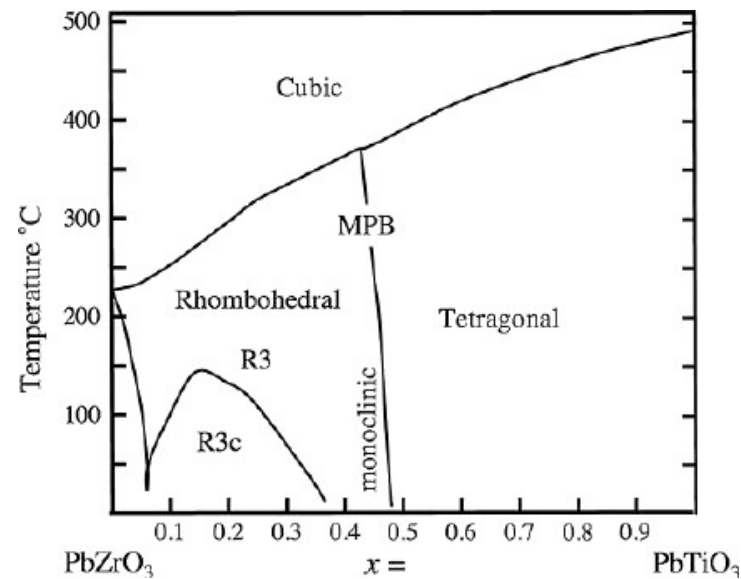
# Interface Contribution in the Final Polarization State

Strkalj, N., MT, et al.  
*Nat. Commun.* 11, 5815 (2020)



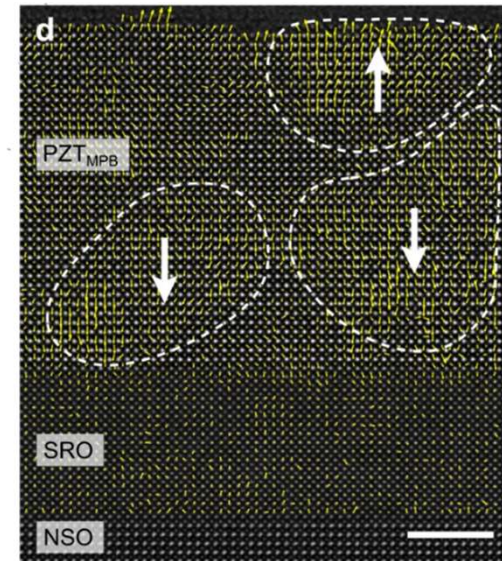
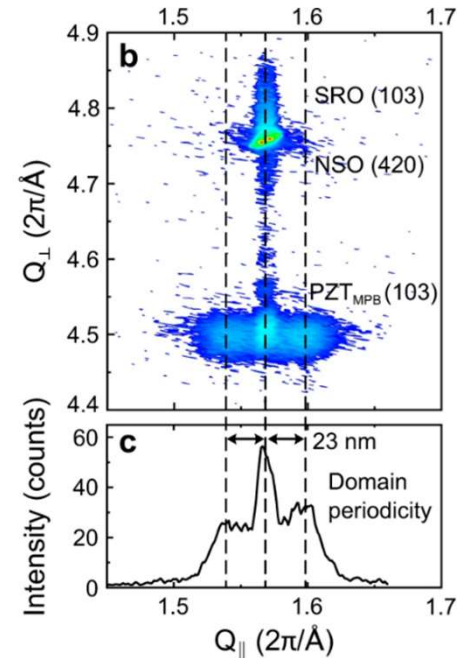
Interface proximity effect in A-site volatile compounds < 40 unit cells.

Sarott, M. F., MT, et al.  
*Nat. Commun.* 13, 3159 (2022)

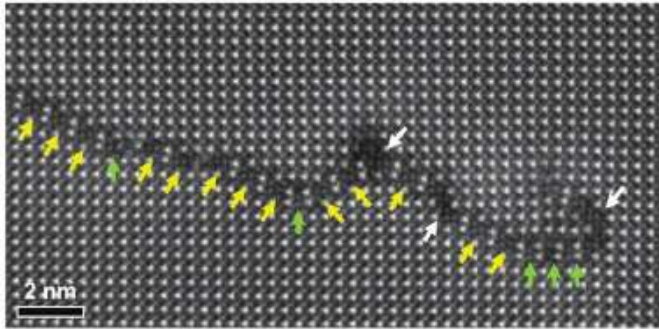


**Interface competition triggers functionality**

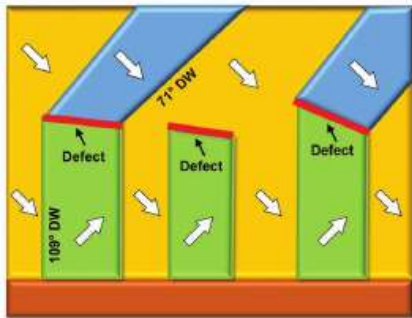
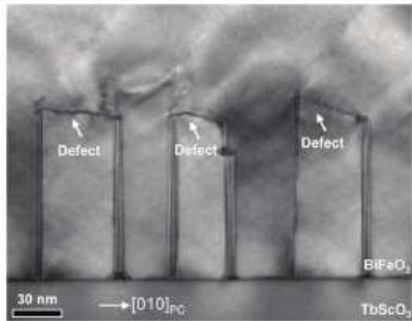
Piezoelectric Ceramics (Academic Press, 1971).



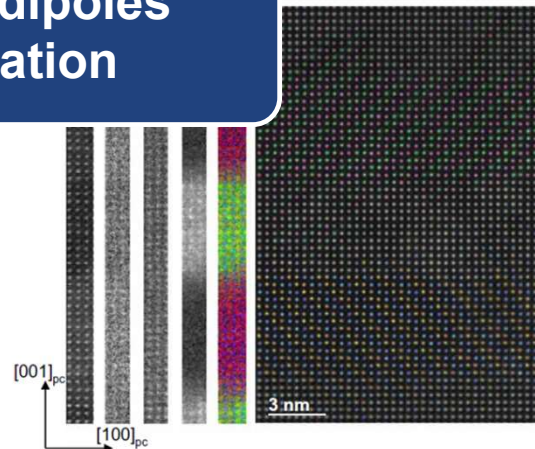
# Interface Contribution in the Final Polarization State



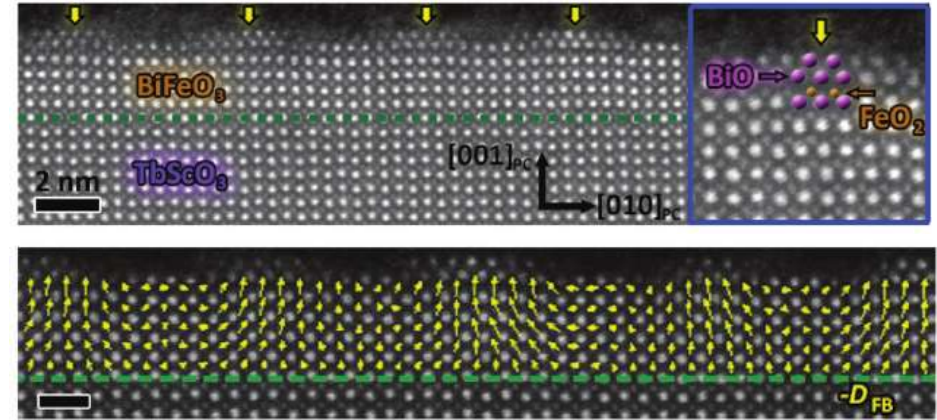
Li, L. et al., *Adv. Mater.* 30, 1802737 (2018)



**Using chemistry at the interface for the design of electric dipoles configuration**

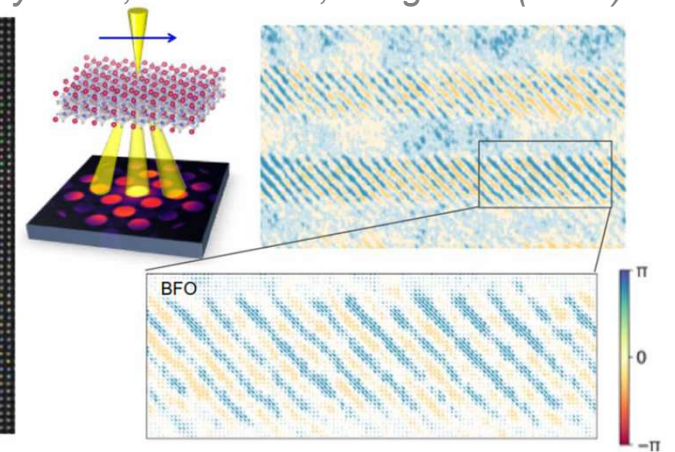


Xie, L. et al., *Adv. Mater.* 29, 1701475 (2017)



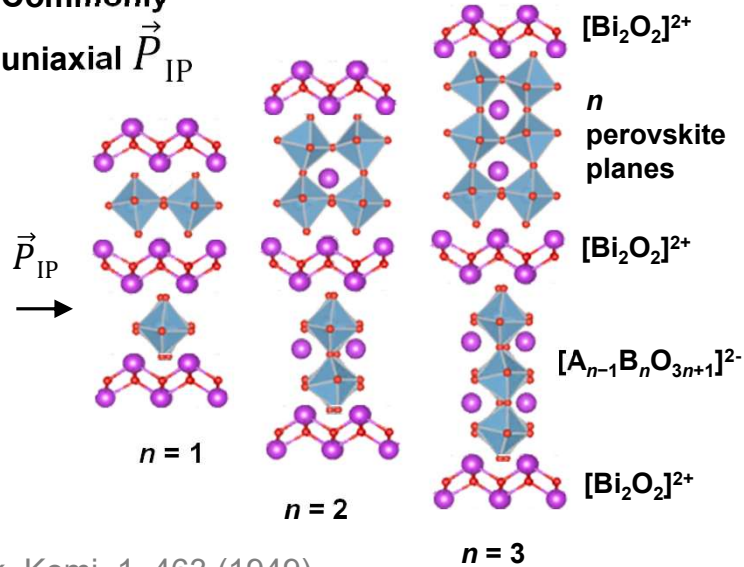
Spontaneous surface reconstruction

Mundy et al., *Sci. Adv.* 8, eabg5860 (2022)



# Layered Ferroelectric Aurivillius Thin Films

Commonly uniaxial  $\vec{P}_{IP}$



Ark. Kemi. 1, 463 (1949)

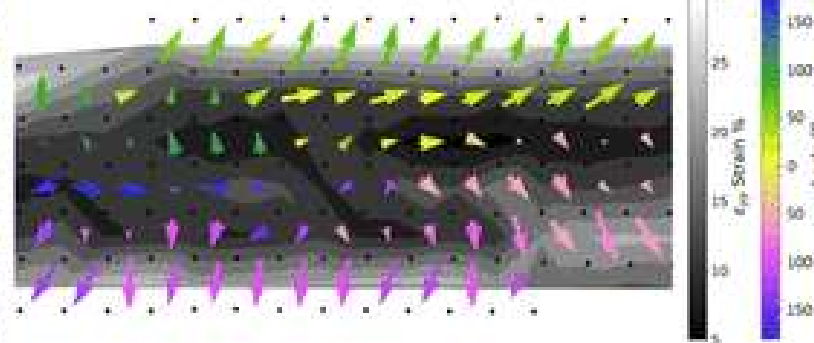
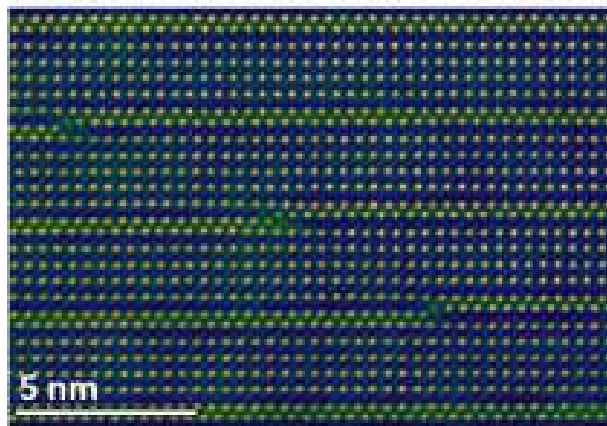
$\text{SrBi}_2\text{Ta}_2\text{O}_9$

Fatigue free layered ferroelectrics

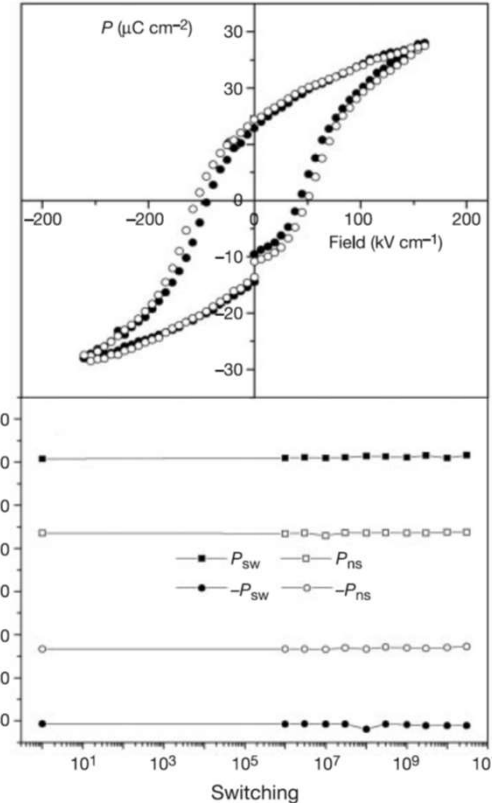
de Araujo, C. A. P, et al. Nature, 374, 627. (1995)  
 Ding, Y. et al., Appl. Phys. Lett., 78, 4175 (2001)  
 Zurbuchen M. A. et al., J. Mater. Res., 22, 1439 (2007)

Strain at Out-of-Phase Boundaries

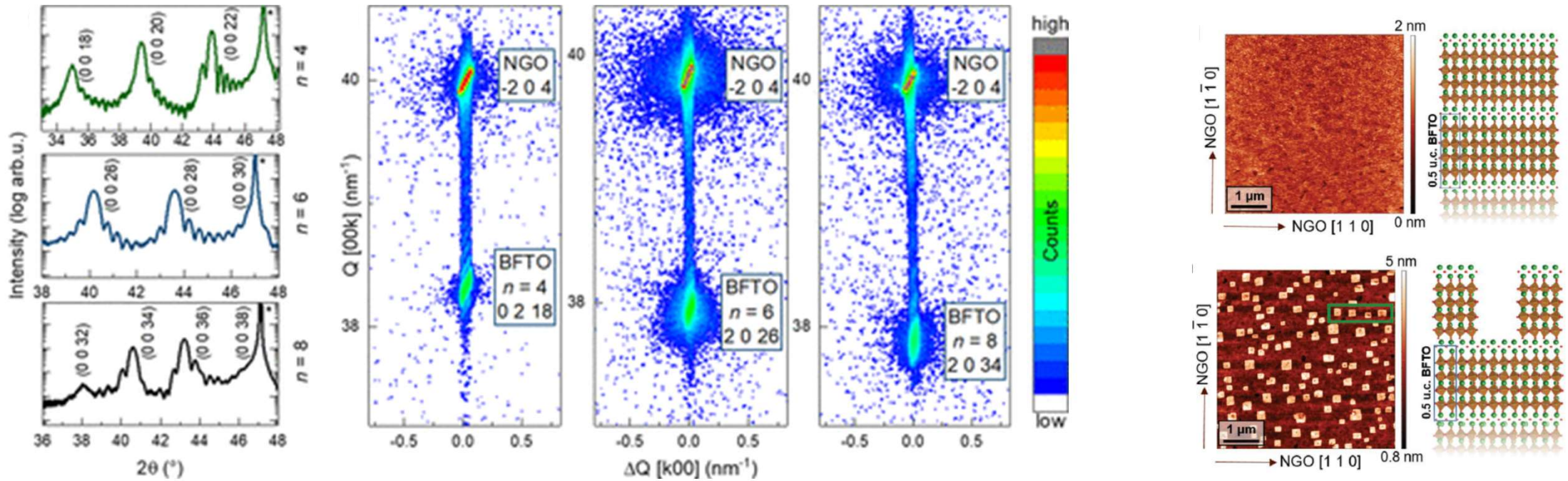
Multiferroic Vortex Topologies



Moore, K. et al. ACS Appl. Mater. Int. 14, 5525 (2022)

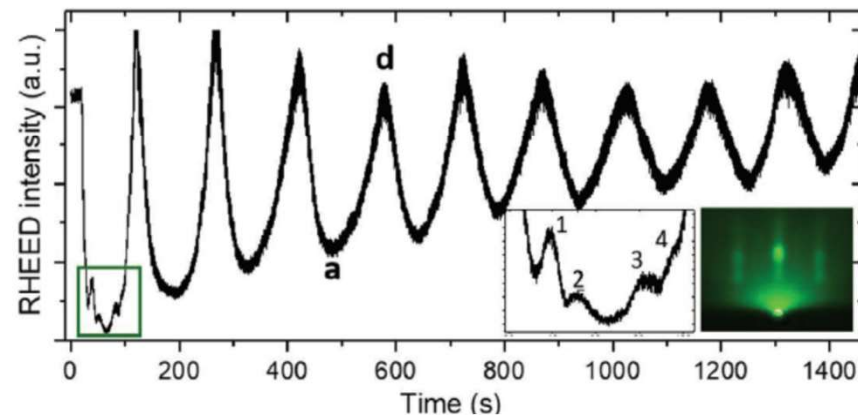


# Layered Ferroelectric Aurivillius Thin Films

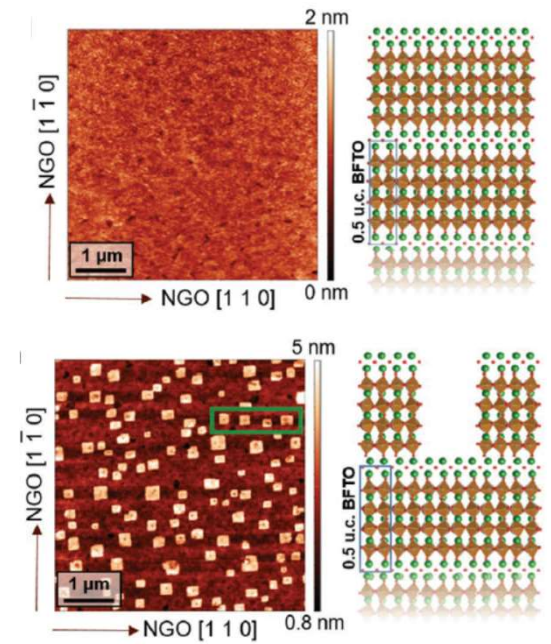
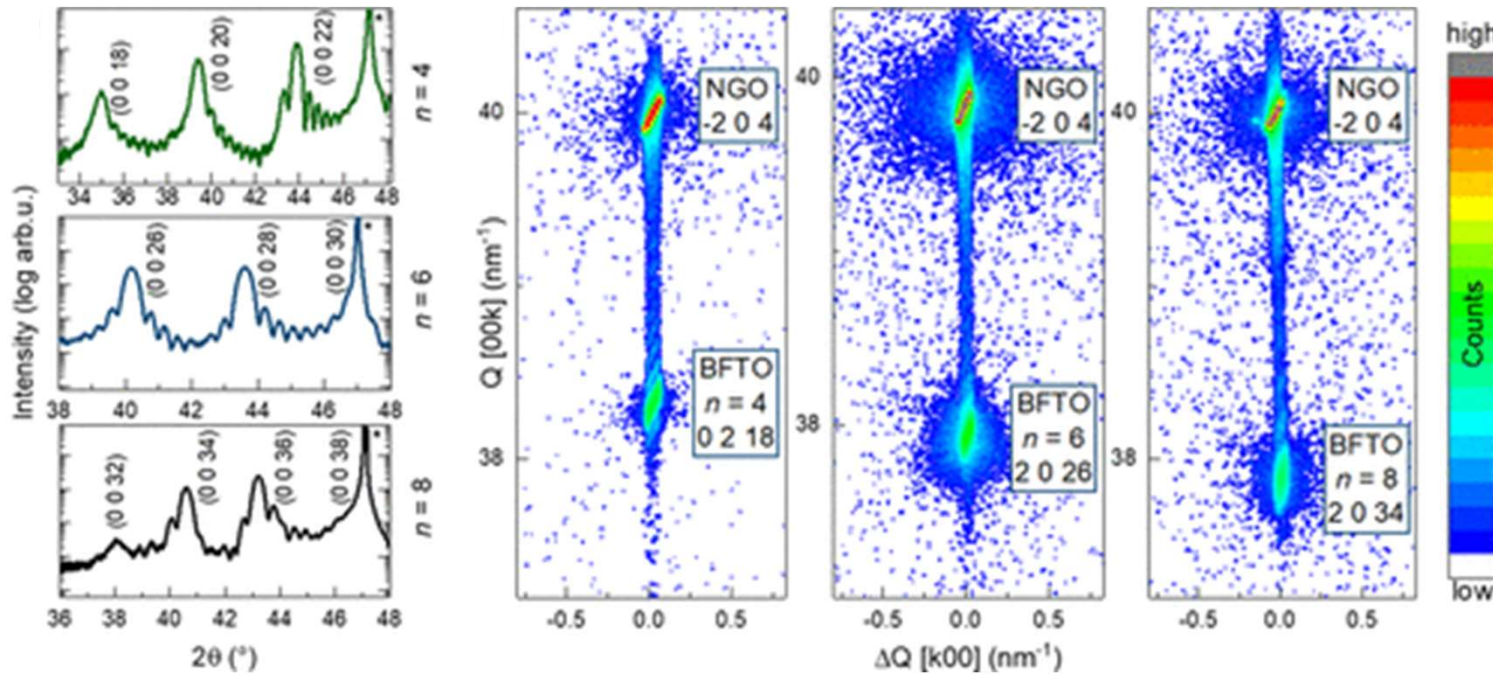


Gradauskaite, E., MT, et al. *Adv. Mater. Inter.* 7, 2000202 (2020)  
 Gradauskaite, E., MT, et al. *Chem. Mater.* 2021, 33 9439 (2021).  
 Campanini, M., MT, et al. *ACS Appl. Electr. Mater.* 1, 1019 (2019)  
 Gradauskaite, E., MT, et al. *Chem. Mater.* 34, 6468 (2022)

**Layer-by-layer growth, twin-free, single crystalline films**

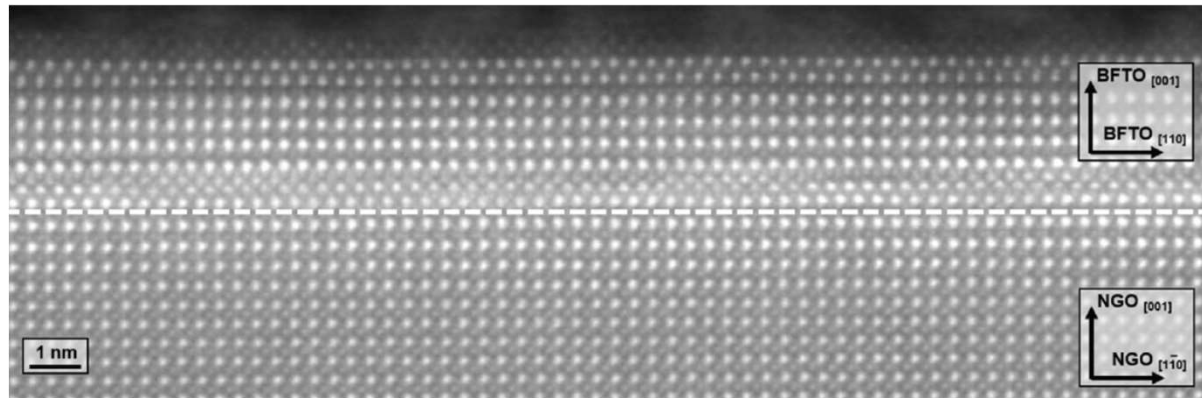


# Layered Ferroelectric Aurvillius Thin Films



Gradauskaite, E., MT, et al. *Adv. Mater. Inter.* 7, 2000202 (2020)  
 Gradauskaite, E., MT, et al. *Chem. Mater.* 2021, 33 9439 (2021).  
 Campanini, M., MT, et al. *ACS Appl. Electr. Mater.* 1, 1019 (2019)  
 Gradauskaite, E., MT, et al. *Chem. Mater.* 34, 6468 (2022)

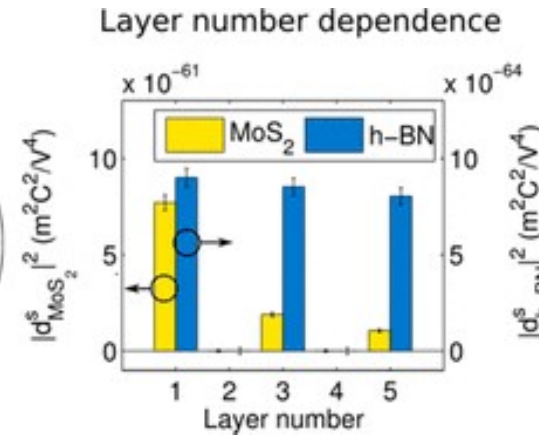
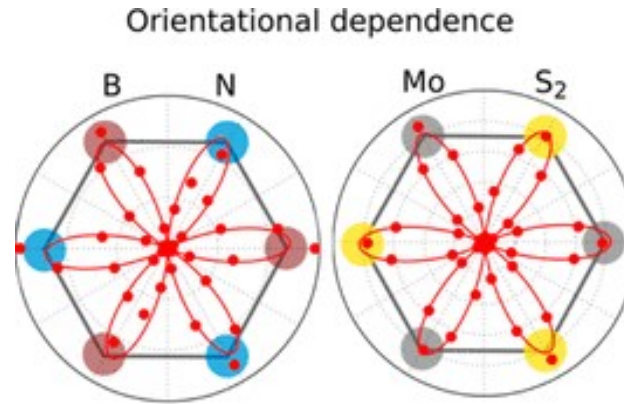
**Layer-by-layer growth, twin-free, single crystalline films**



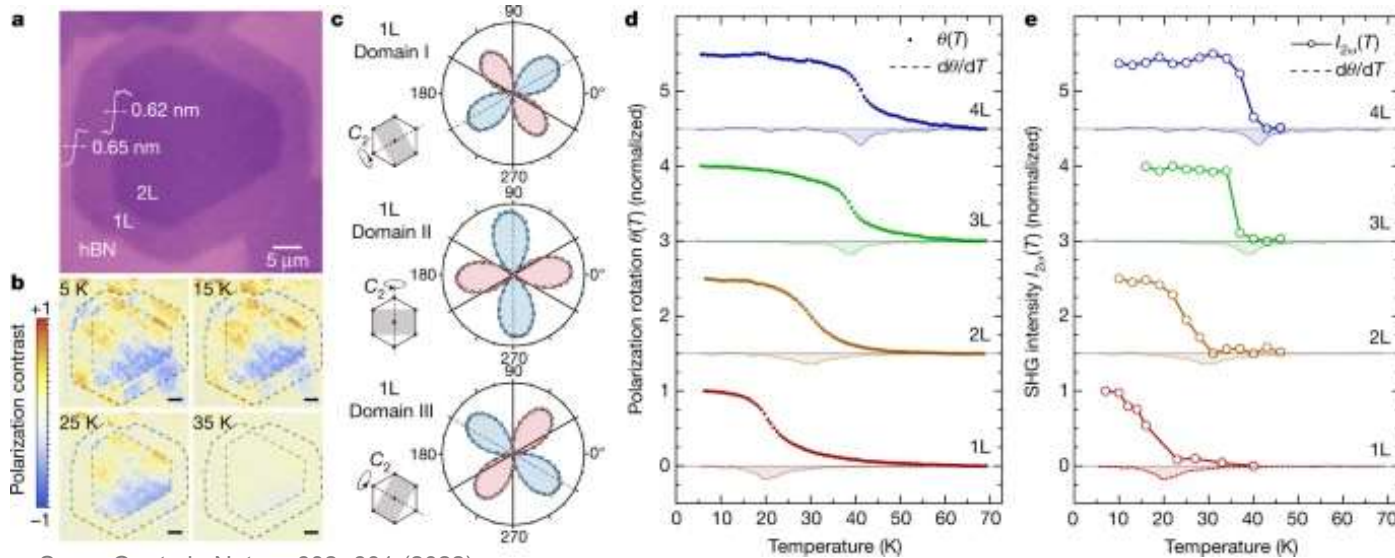
# Probing Ferroelectricity in 2D

**Small polarization values  
&  
Increased leakage**

Mueller M, MT, et al. ACS Appl. Electron. Mater. 5, 1314(2023)

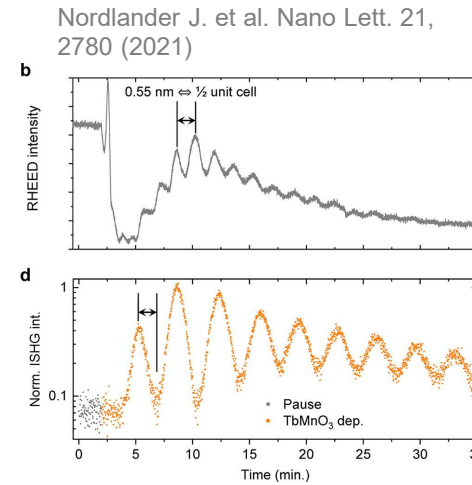
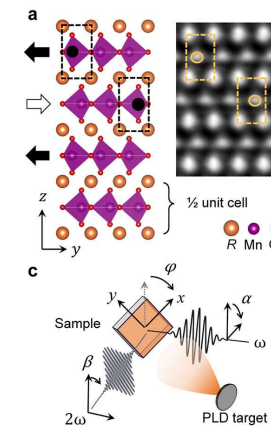


Li Y. et al. Nano Lett. 13, 3329 (2013)



Song, Q. et al., Nature 602, 601 (2022)

type-II multiferroic in van der Waals  $\text{NiI}_2$

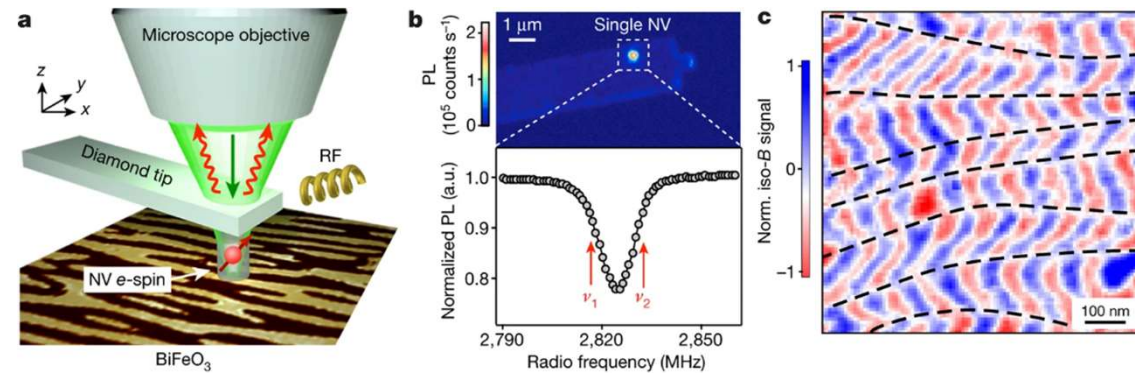
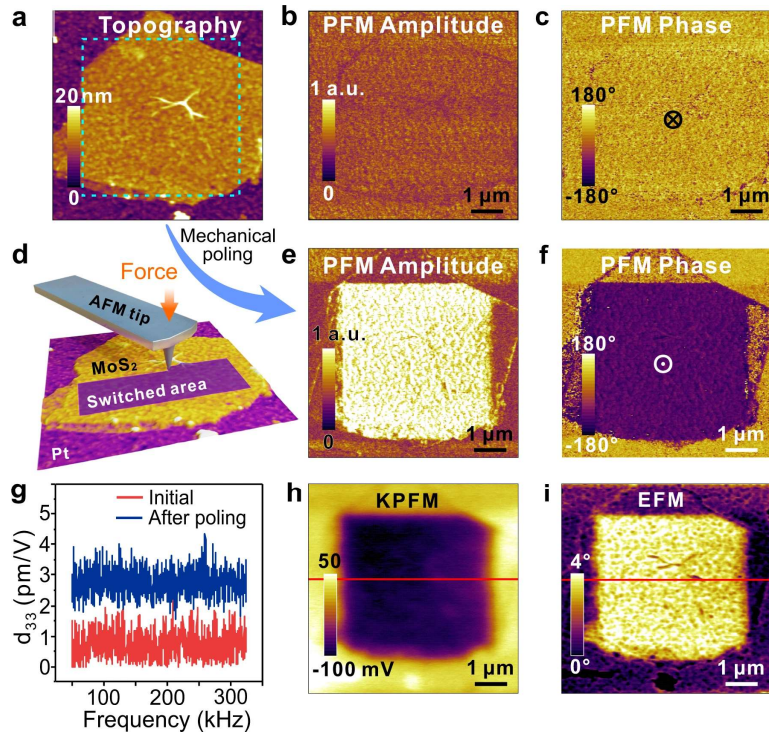




# Probing Ferroelectricity in 2D

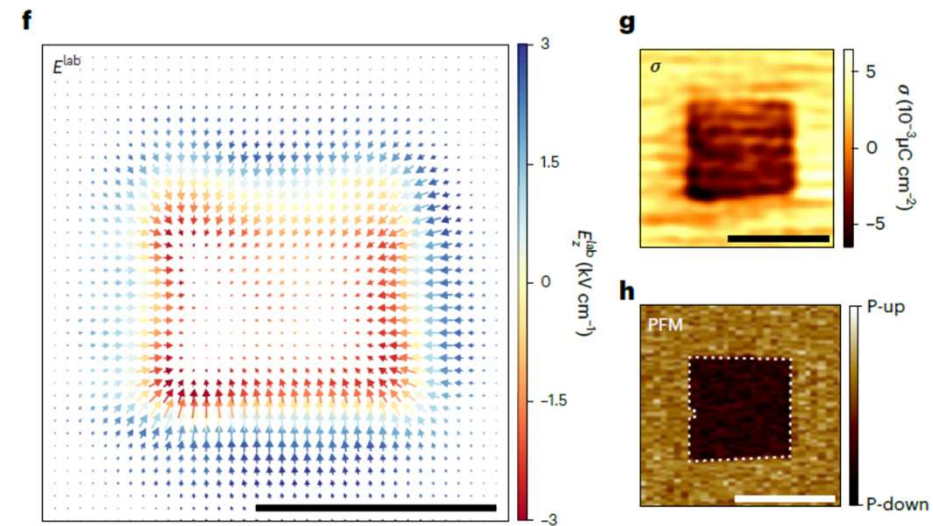
Small polarization values  
&  
Increased leakage

Mueller M, MT, et al. ACS Appl. Electron. Mater. 5, 1314(2023)  
 Tsymbol E. Y., et al. science 372, 1389 (2021)  
 Li, Y. et al. Nano Lett. 13, 3329 (2013)  
 Lipatov A. et al, npj 2D Mater. Appl. 6, 18 (2022)



Gross, I. et al. Nature 549, 252 (2017)

NV electrometry for quantitative, non-invasive investigations



Huxter, W, MT, et al. Nat. Phys. 19, 644 (2023)  
 Huxter, W, MT et al Nat Commun 13, 3761 (2022)



D MATL.

HAADF-STEM analysis by  
A. Vogel & M. D. Rossell



 **Empa**  
Materials Science and Technology

**FNSNF**

FONDS NATIONAL SUISSE  
SCHWEIZERISCHER NATIONALFONDS  
FONDO NAZIONALE SVIZZERO  
SWISS NATIONAL SCIENCE FOUNDATION

**ETH zürich**

DFT  
N. A. Spaldin, C. Gattinoni

M. Fiebig, N. Strkalj, M. Sarott,  
E. Gradauskaite, I. Efe,  
J. Lehman, M. Mueller

XPS  
A. Rossi

R. Ramesh



PAUL SCHERRER INSTITUT  
**PSI**

C. W. Schneider

B. Huey



UNIVERSITY OF TWENTE.

G. Koster