Defeating depolarizing fields with artificial flux closure in ultrathin ferroelectrics

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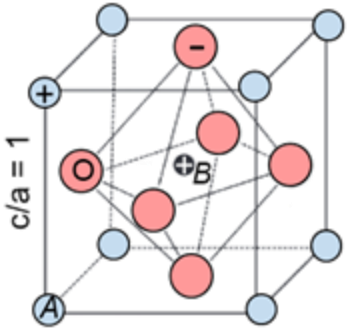
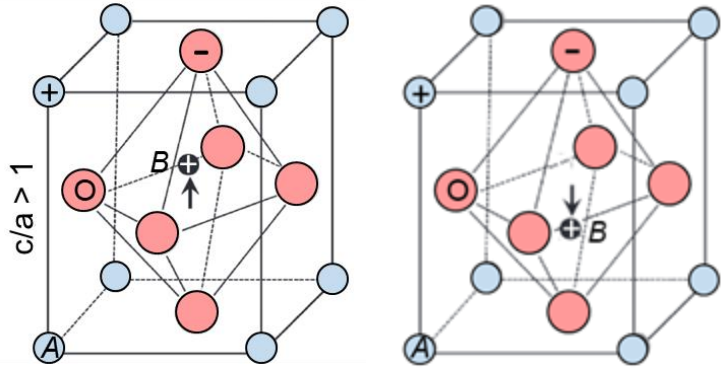
Ferroelectricity: remains challenging when ultrathin

Ferroelectrics: electrically ordered oxides

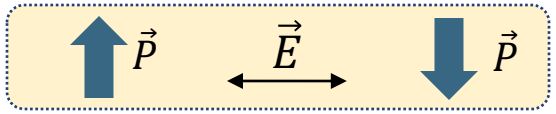
$A\,B\,O_3$ perovskites (e.g. $BaTiO_3$ - BTO)

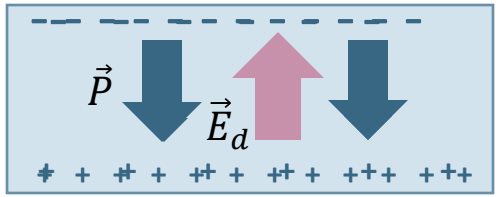


Paraelectric

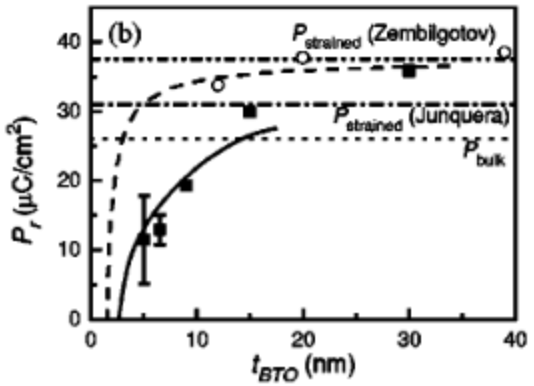


Ferroelectric





→ Ultrathin regime:
Suppressed polarization, dead layers



Y. S. Kim et al., *Appl. Phys. Lett.* **86**, 102907, 2005.

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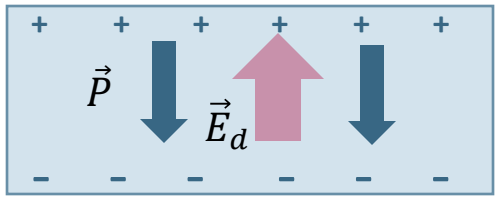
Initial motivation: stabilization of ultrathin ferroelectricity

Dead layers in ultrathin ferroelectrics

Increasing role of depolarizing field



Hinders integration into nanoscale devices

→ Suppressed polarization

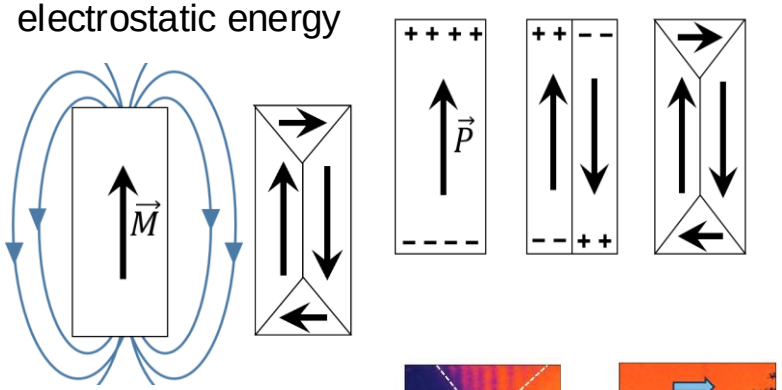
Below **critical thickness:**
Complete loss of ferroelectricity

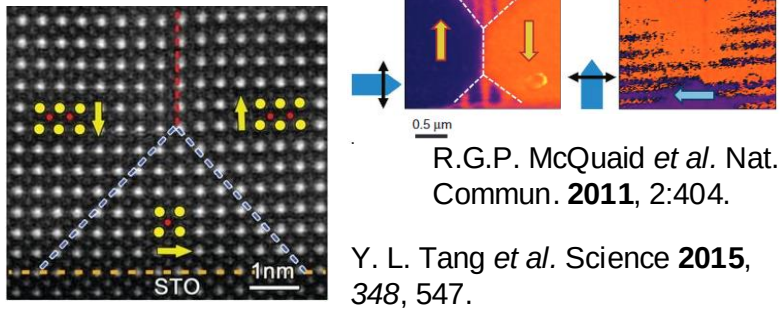
J. Junquera *et al.* Nature **2003**, *6931*, 506.

So far material-specific solutions only…

Spontaneous domain formation

Flux closure to minimize magneto/ electrostatic energy





R.G.P. McQuaid *et al.* Nat. Commun. **2011**, 2:404.

Y. L. Tang *et al.* Science **2015**, *348*, 547.

Can we create flux-closure artificially while maintaining net $\vec{P}$?

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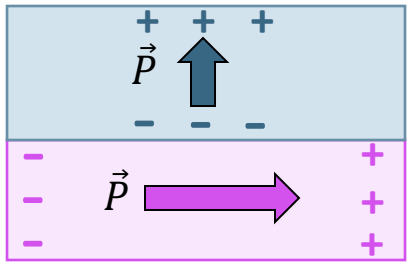
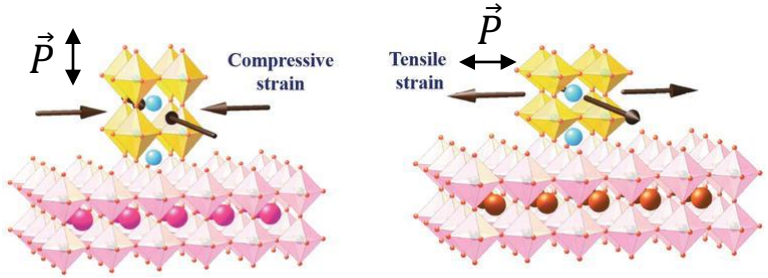
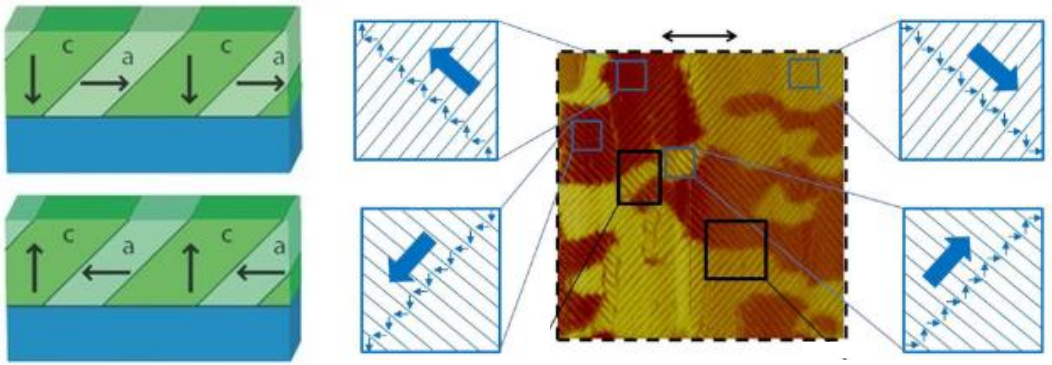
Epitaxial layers with perpendicular polar anisotropies



Epitaxial layers with in-plane and out-of-plane polarization?

Epitaxial strain:





ac ferroelastic domains

A. S. Everhardt *et al.*,
Adv. Electron.Mater. **2016**, *2*, 1500214.

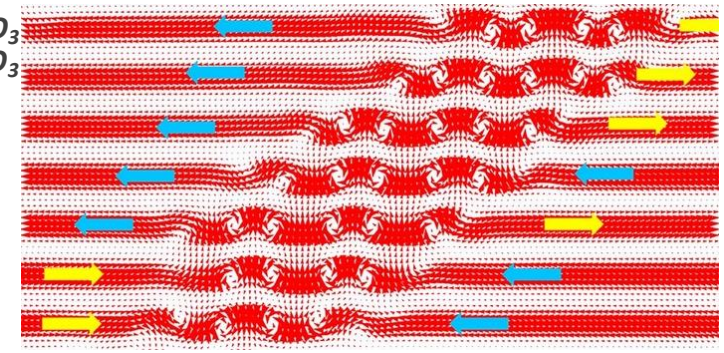
aa, a "superdomains"

S.Matzen *et al.*,
Nat. Commun. **2014**, *5*, 4415.

Electrostatics:

$[dielectric/ferroelectric]_N$ superlattices

a domains stabilized with no tensile strain



P. Zubko *et al.*,
Ferroelectrics **2014**, *433:1*, 127.

Z. Hong *et al.*, *Nano Lett.* **2021**, *21*, 3533.

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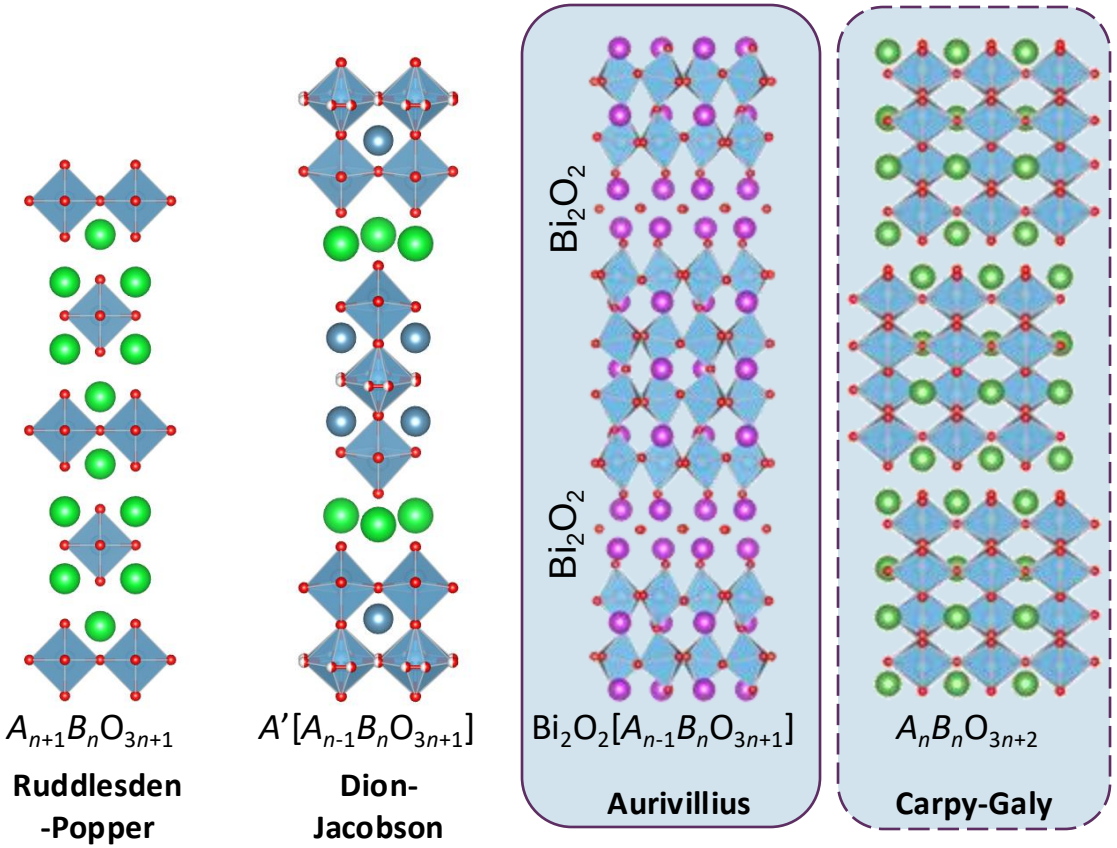
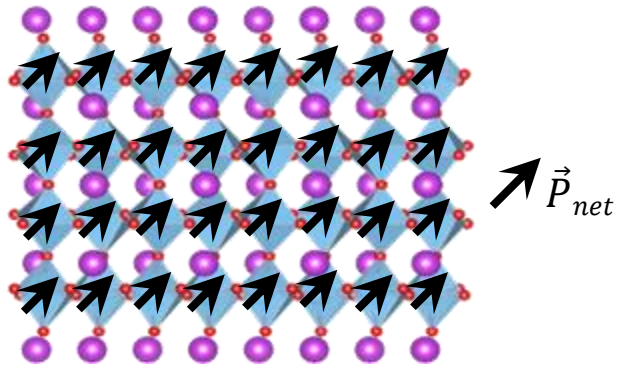
Natural superlattices with polarization in plane



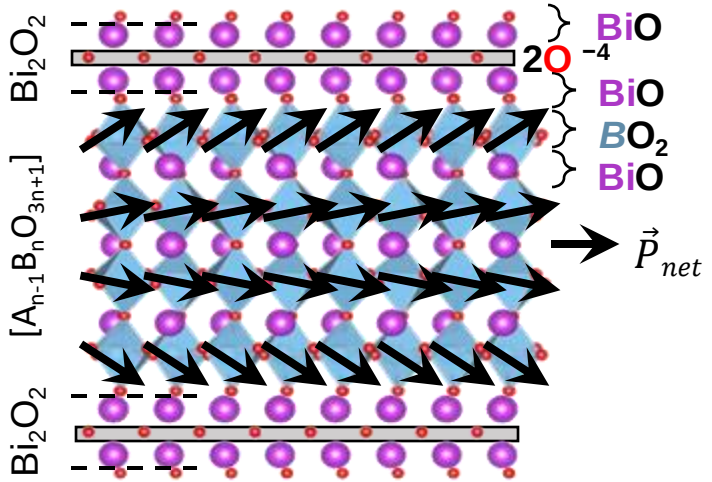
Layered perovskite-related ferroelectrics

- Form spontaneously
- Uniaxial in-plane polarization
- No epitaxial strain needed

ABO_3 films (e.g. $BiFeO_3$):



Additional layers create "frustration":



N. A. Benedek *et al.*, *Dalt. Trans.* **2015**, *44*, 10543.

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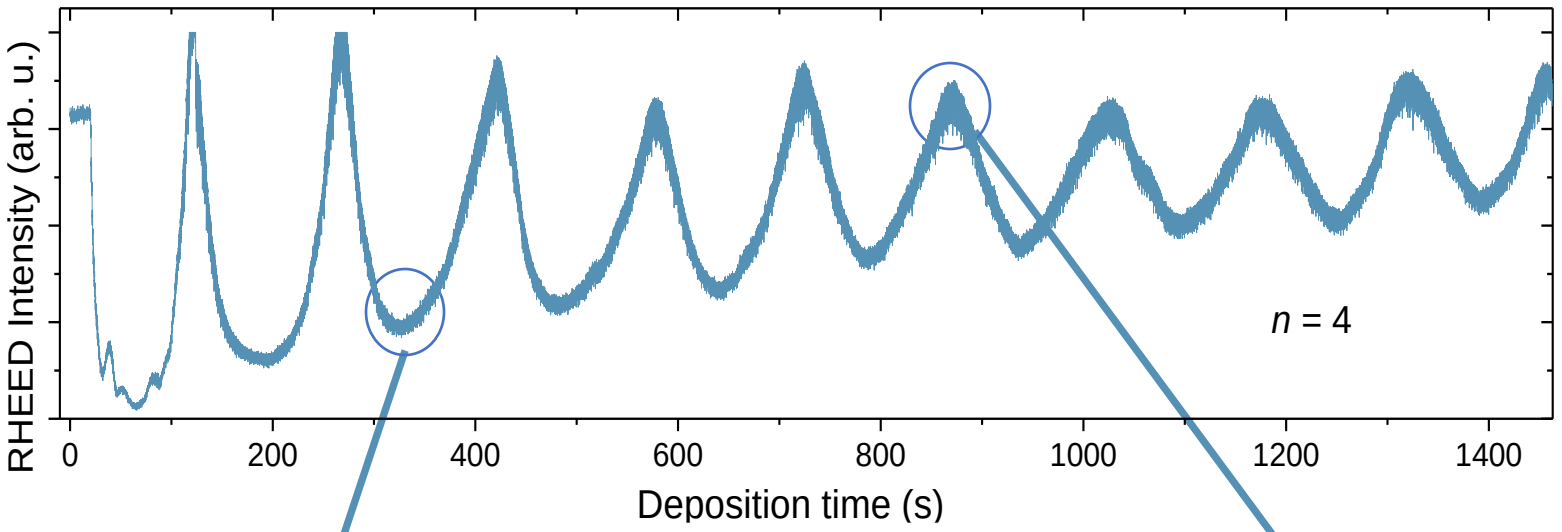
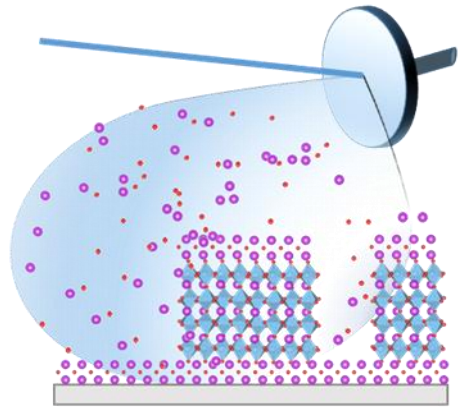
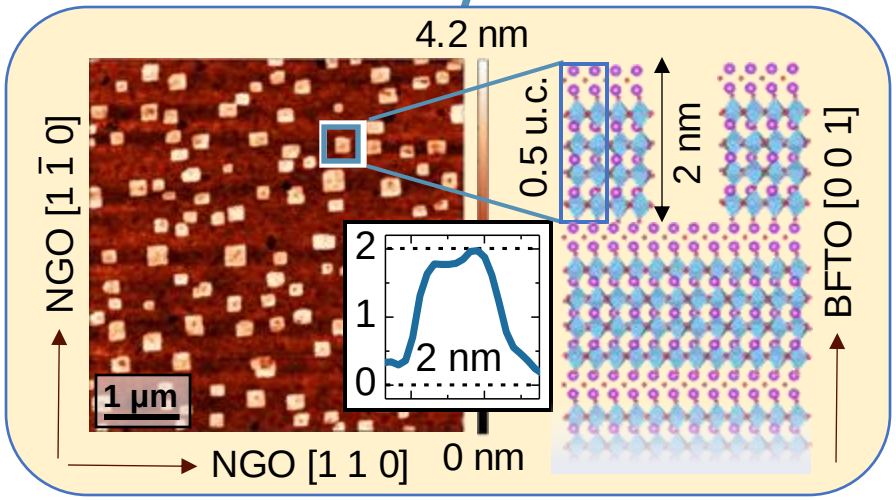
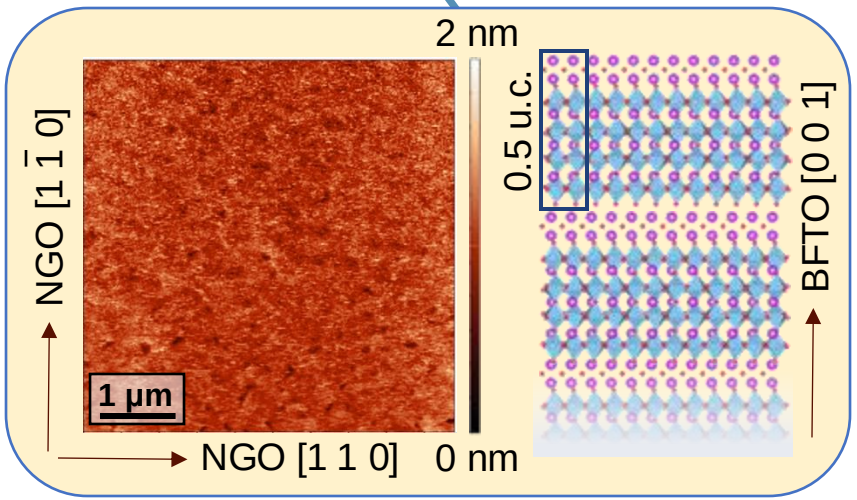
Aurivillius BFTO ($Bi_5FeTi_3O_{15}$, n=4)





Stabilization of the coalescent layer-by-layer growth





E. Gradauskaite *et al., Adv. Mater. Inter.* **2020**, *7*, 2000202.
E. Gradauskaite *et al., Chem. Mater.* **2021**, *33*, 9439.

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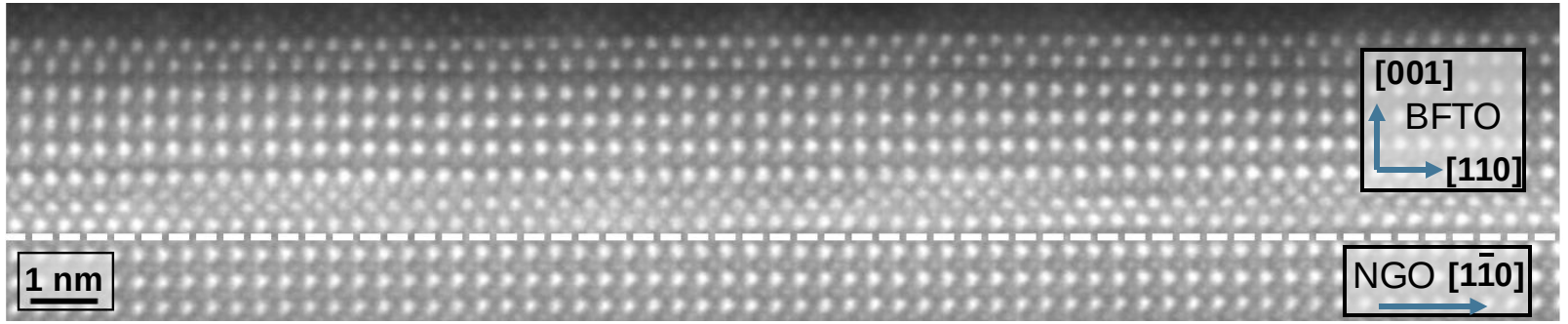
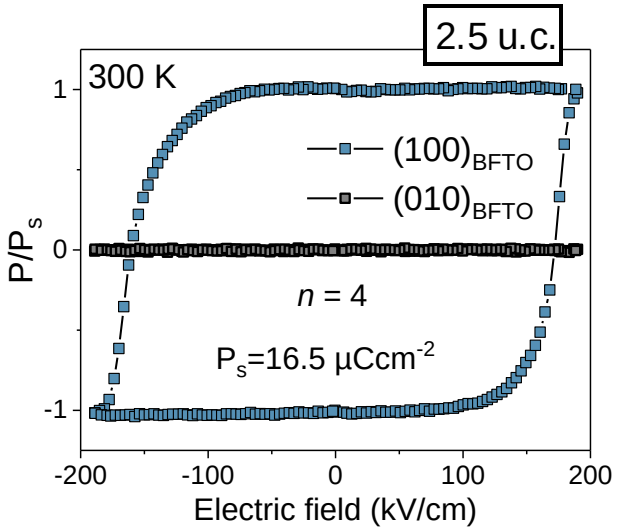
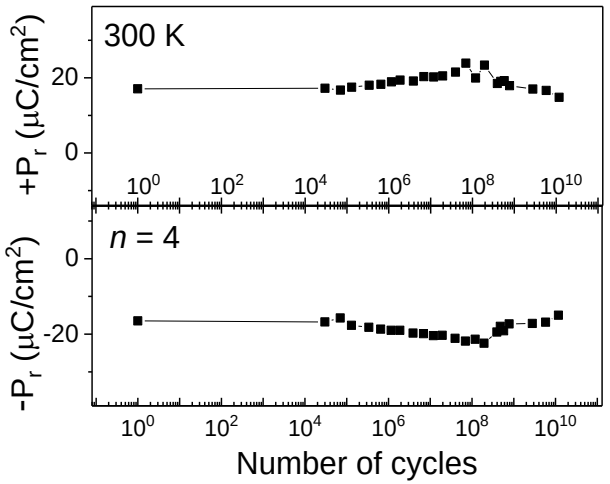
Robust uniaxial in-plane polarization in BFTO films



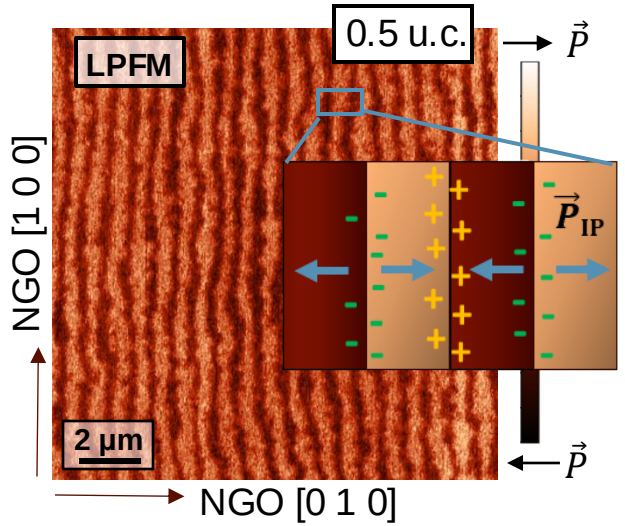
Uniform sub-unit-cell coverage



Uniaxial in-plane polarization



Robust against ferroelectric fatigue



HH and TT stripe domains

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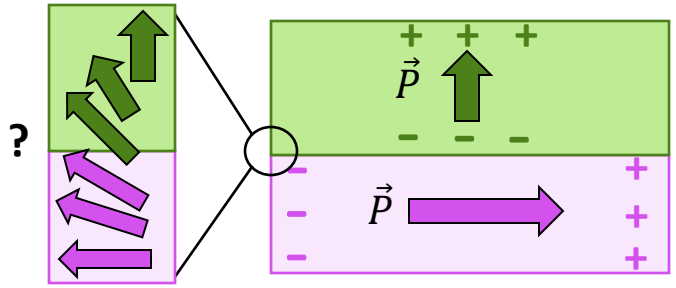
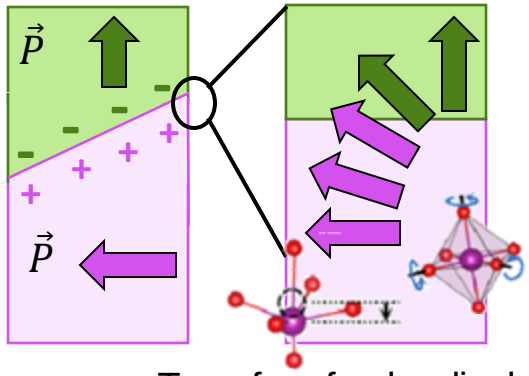
Heterostructures with perpendicular polar anisotropy: BTO on BFTO



Any out-of-plane polarized perovskite
…$BaTiO_3$ (BTO)?

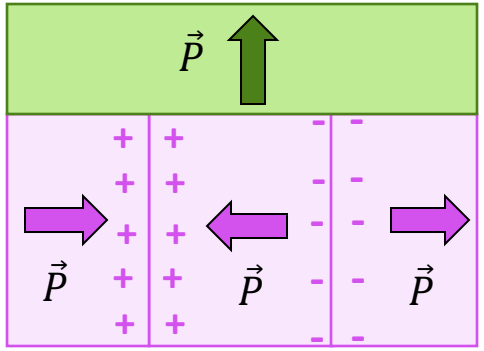
In-plane polarized Aurivillius BFTO ($Bi_5FeTi_3O_{15}$, n=4)

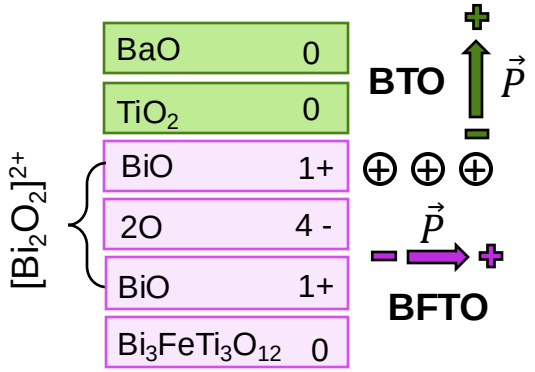
Minimized stray field



Transfer of polar displacements

Available screening charges





Discontinuity in layer polarization

Need to be able to probe emergence of polarization real-time: use in-situ SHG

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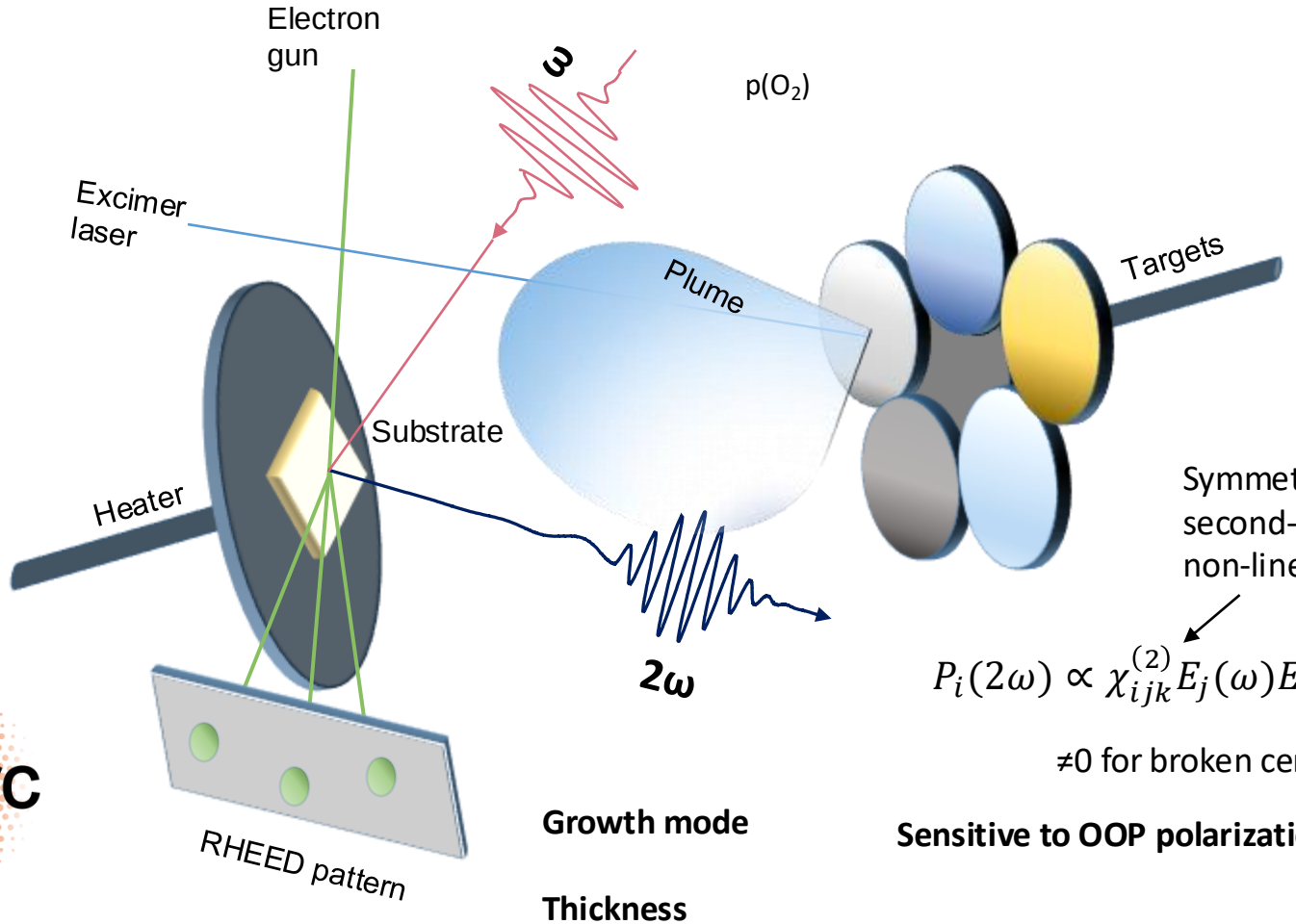
Real-time monitoring of polarization during the growth: in-situ second harmonic generation (ISHG)



Symmetry dependent second-order non-linear susceptibility

$$P_i(2\omega) \propto \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega)$$

≠0 for broken centrosymmetry

Sensitive to OOP polarization emergence

$I_{ISHG} \propto |P|^2$

Growth mode

Thickness

G. De Luca *et al., Nat. Commun.* **2017**, *1*, 8:1419

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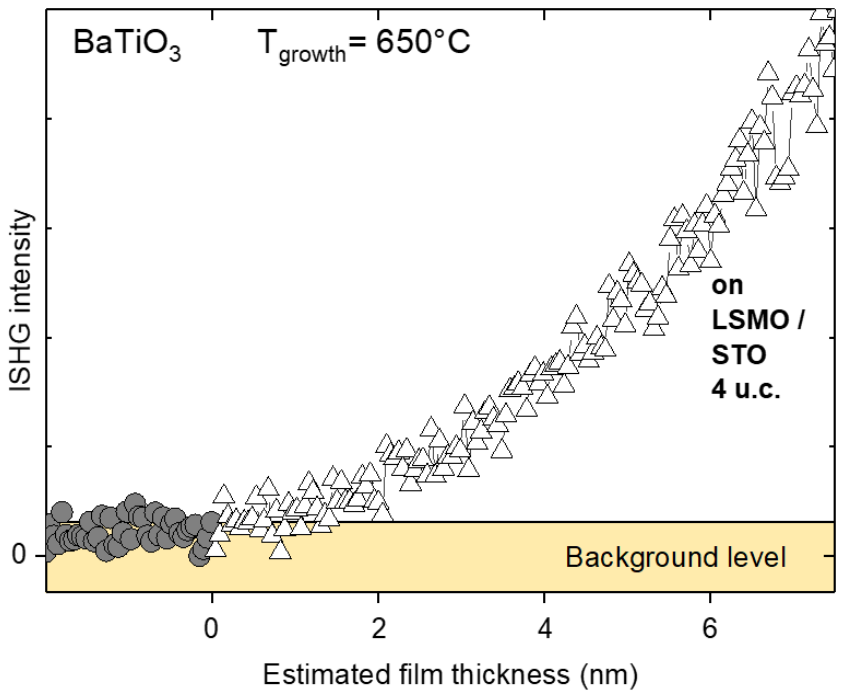
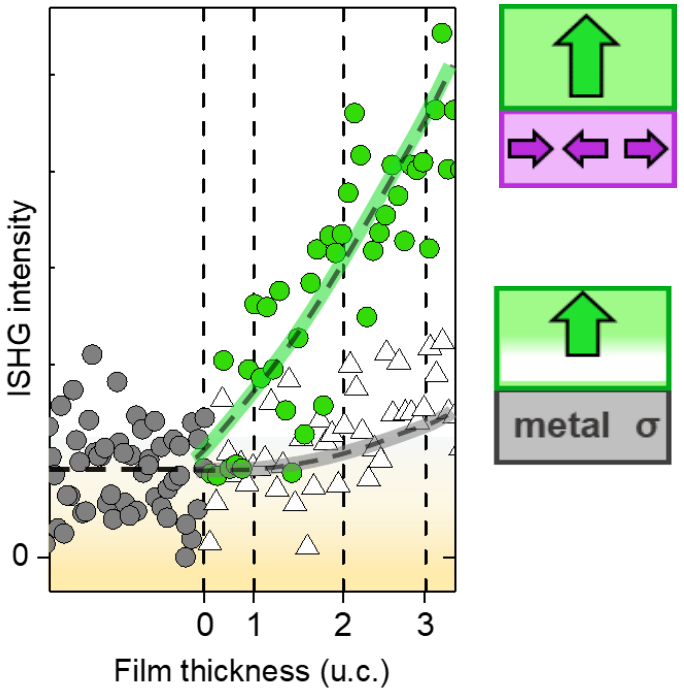
Aurivillius-perovskite epitaxy: BTO on BFTO

BTO polarization emergence during the growth





BTO unchanged: fully OOP, single domain, but…

No critical thickness for ferroelectricity on 0.5 u.c. in-plane-polarized BFTO buffer

E. Gradauskaite *et al. Nat. Mater.* **2023**, *22*, 1492–1498.

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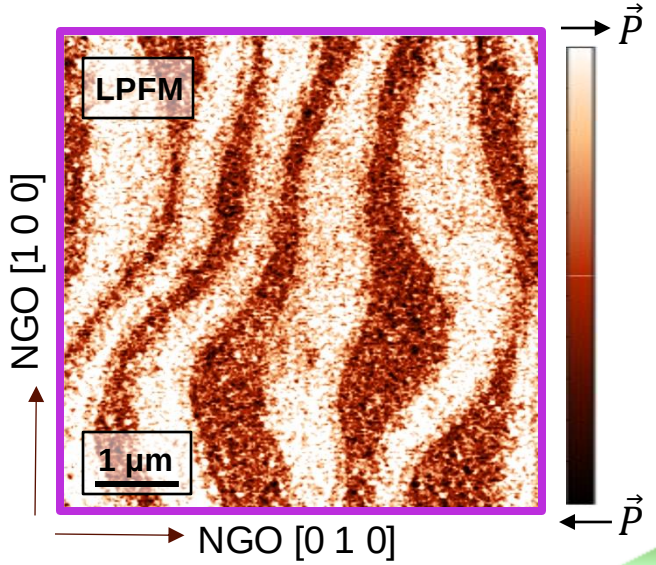
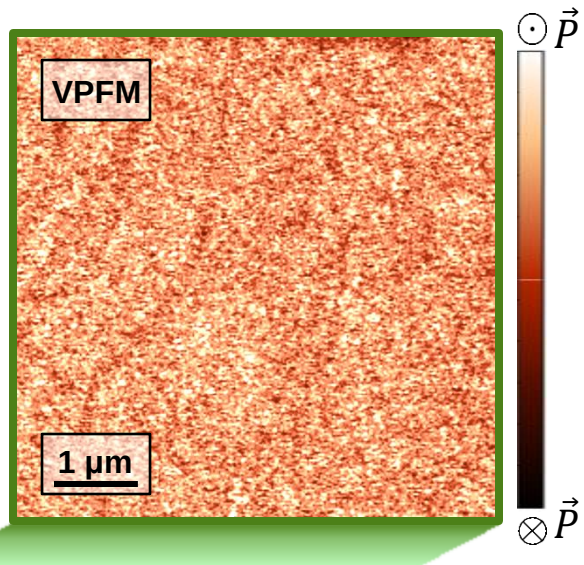
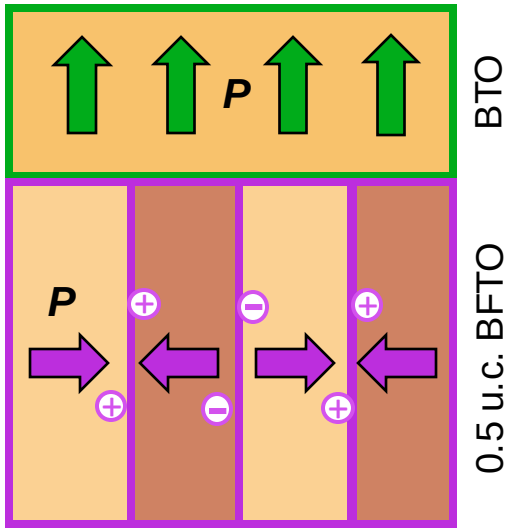
Perpendicular polar anisotropies preserved

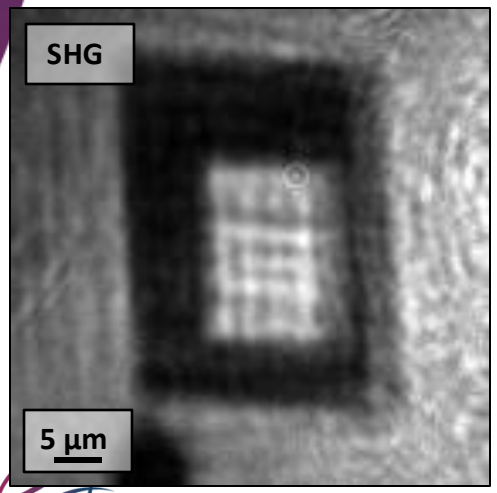


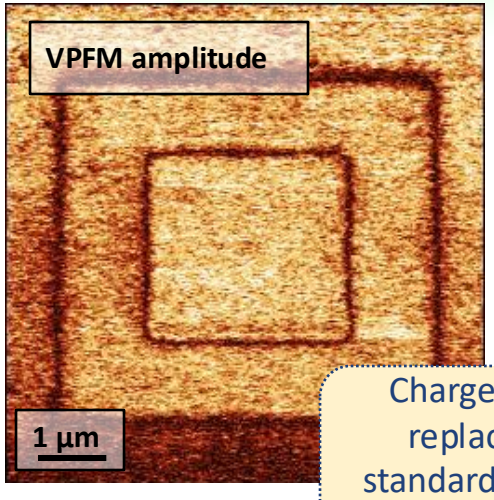
Stripe domains + uniaxial $\vec{P}_{IP}$
= charged DWs

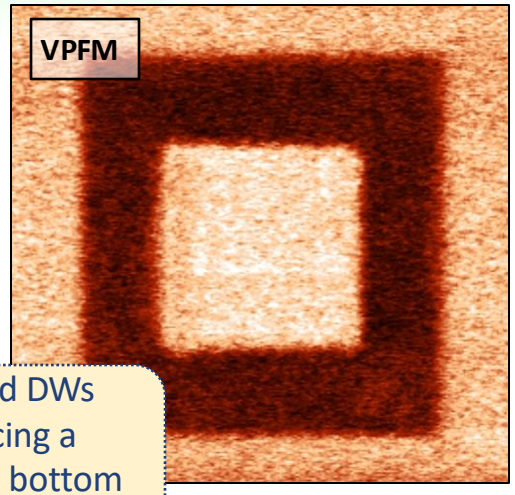


Single domain, out-of-plane polarized

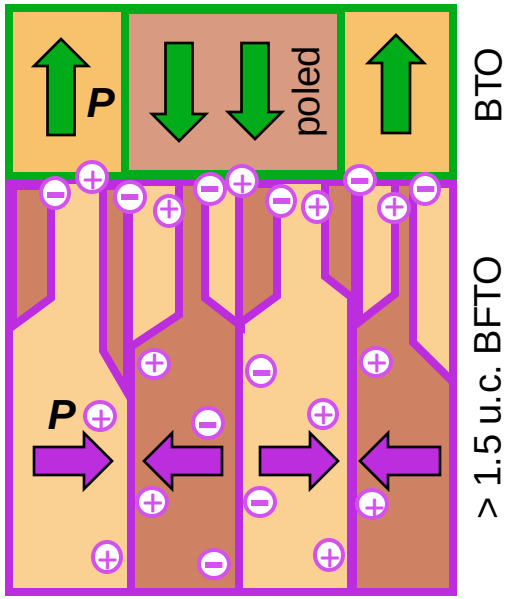








Charged DWs replacing a standard bottom electrode



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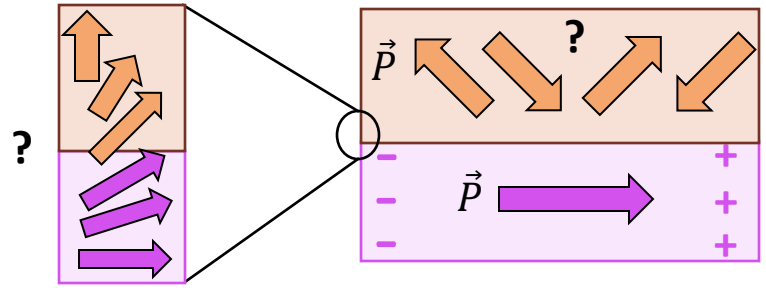
E. Gradauskaite *et al. Nat. Mater.* **2023**, *22*, 1492–1498.

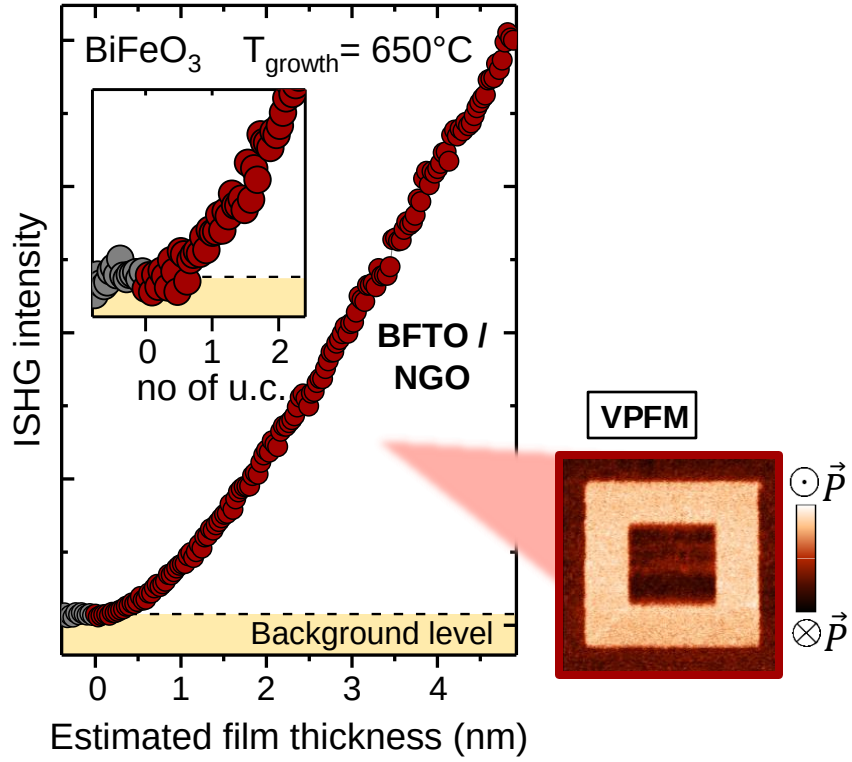
Domain engineering with Aurivillius buffers: BFO on BFTO



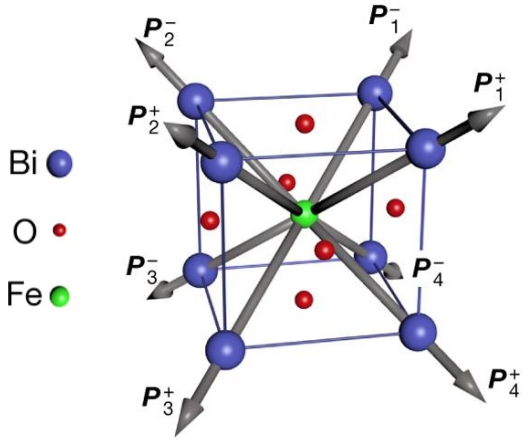
Perovskite with in-plane and out-of-plane $\vec{P}$

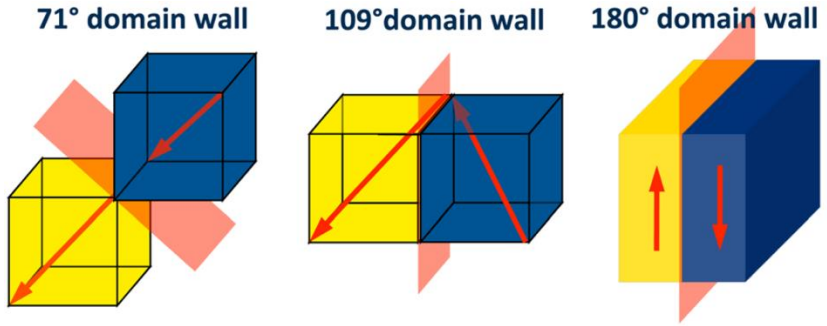
In-plane polarized Aurivillius BFTO ($Bi_5FeTi_3O_{15}$, n=4)

? No critical thickness **?** Selectivity of allowed domains and domain walls



Magnetoelectric multiferroic $BiFeO_3$ (BFO)





J. T. Heron *et al., Appl. Phys. Rev.*, **2014**, *1*, 021303

Universal approach to zero critical thickness in out-of-plane-polarized perovskites

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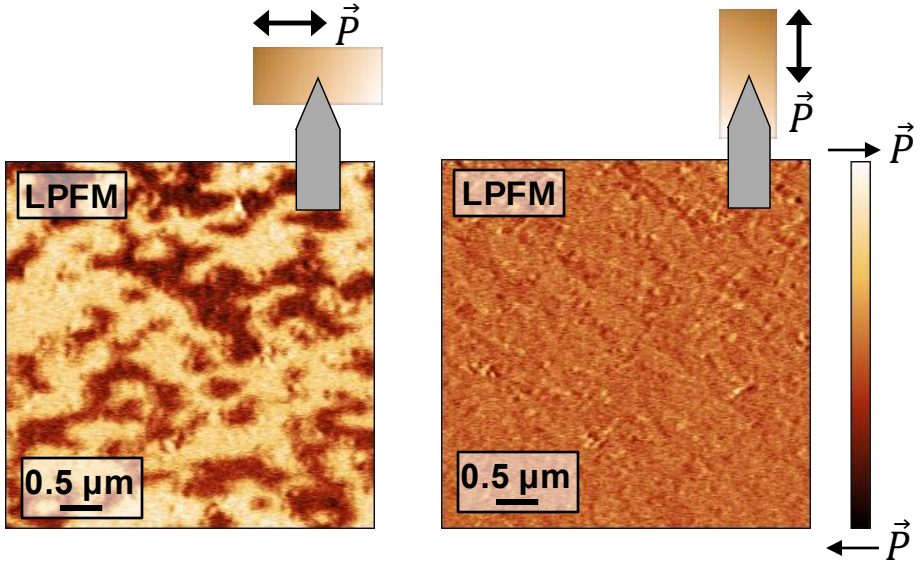
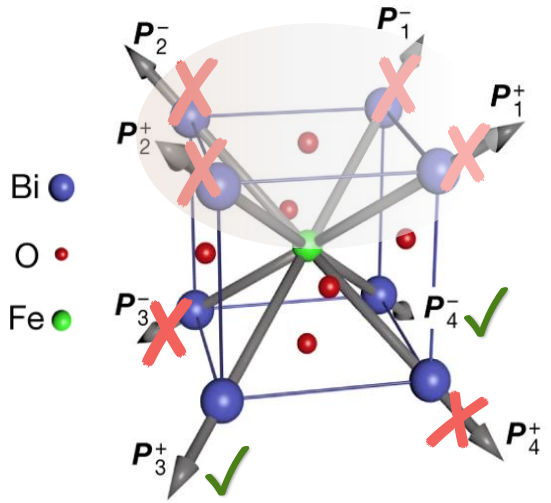
Selection of two allowed *P* components in BFO

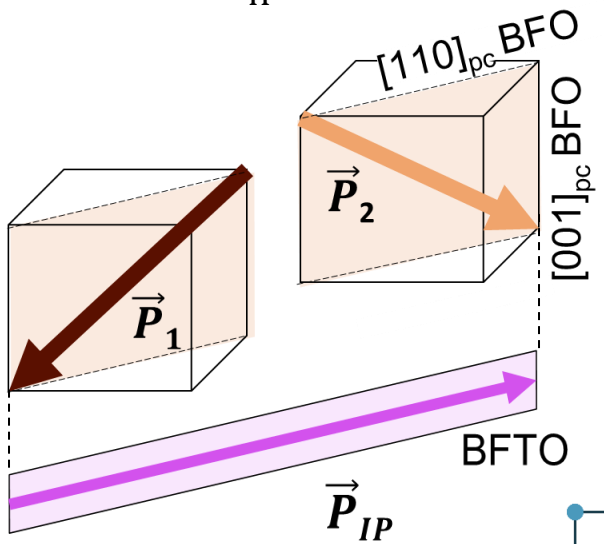


Uniaxial $\vec{P}_{IP}$

In-plane polarization components in BFO?



Only 2 out of 8 $\vec{P}$ components in pristine BFO on BFTO



Uniaxial in-plane polarization in BFO parallel to BFTO polarization

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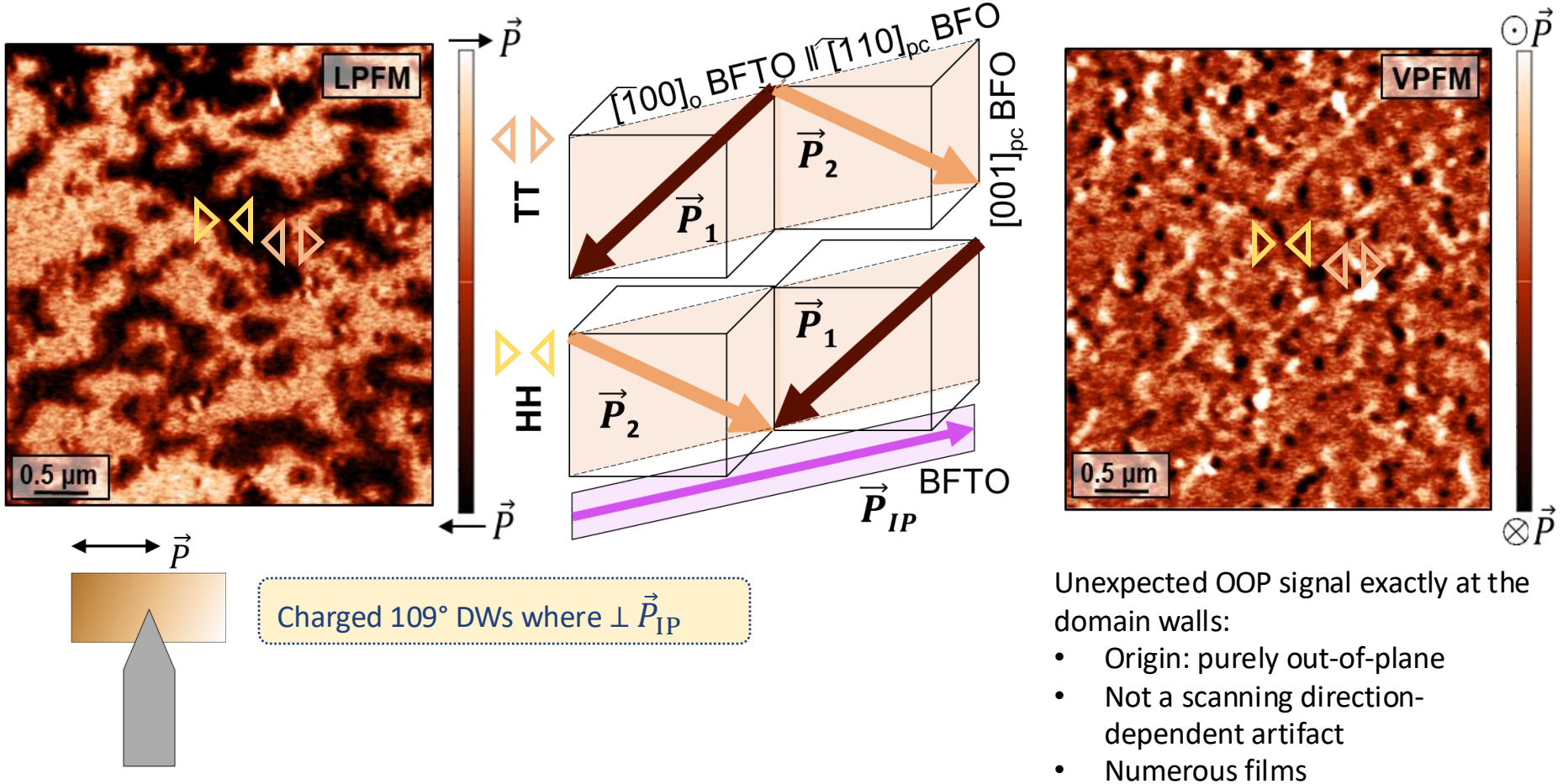
Unexpected OOP signal at the domain walls



Charged 109° DWs where ⊥ $\vec{P}_{IP}$

Unexpected OOP signal exactly at the domain walls:

- Origin: purely out-of-plane
- Not a scanning direction-dependent artifact
- Numerous films

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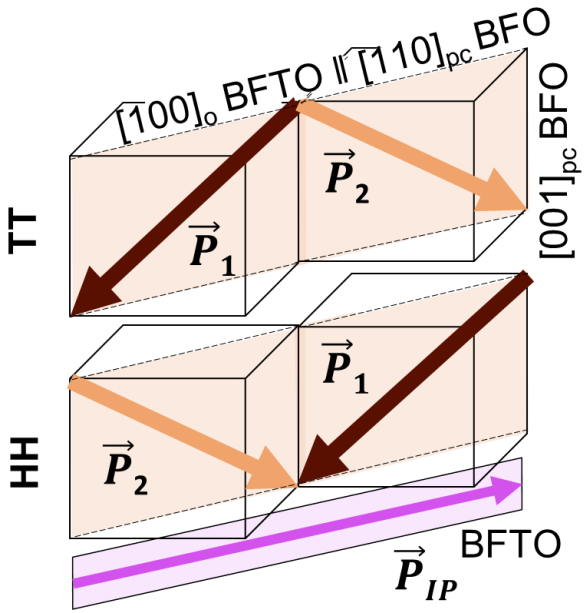
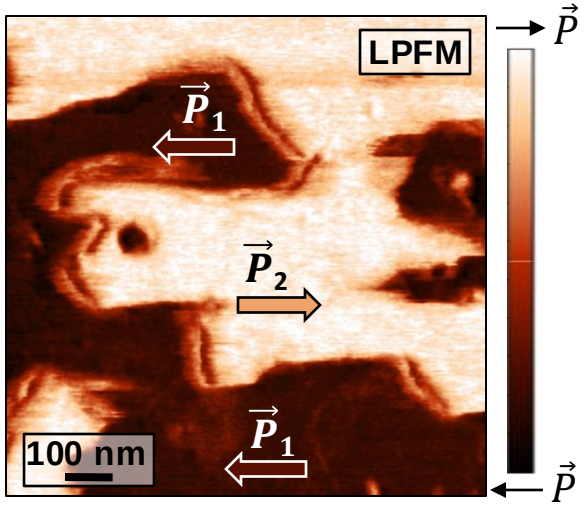
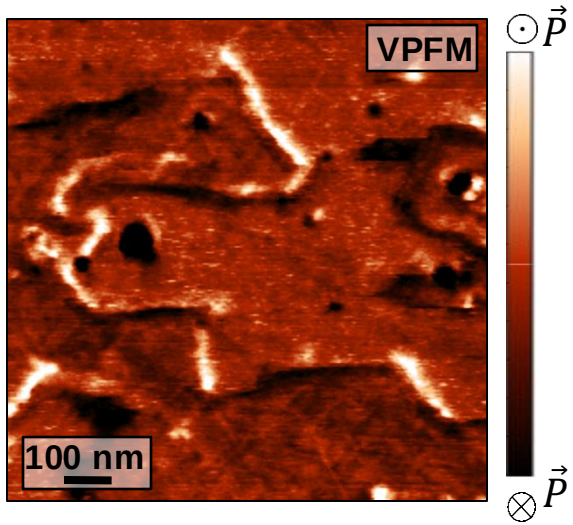
Ferroelectric Homochiral Néel walls



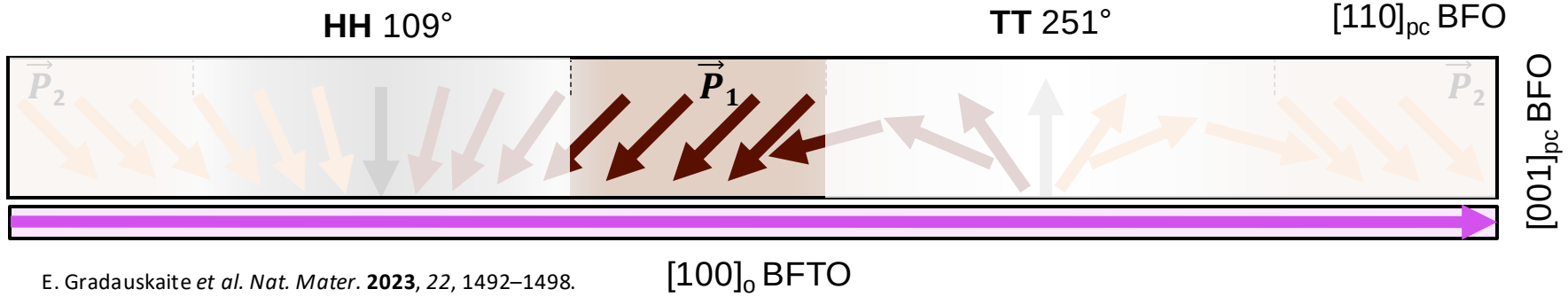




- OOP signal systematically appears at all charged DW sections. $\vec{P}$ rotation in the plane of DW
- Deterministic sense of rotation: up for TT and down for HH

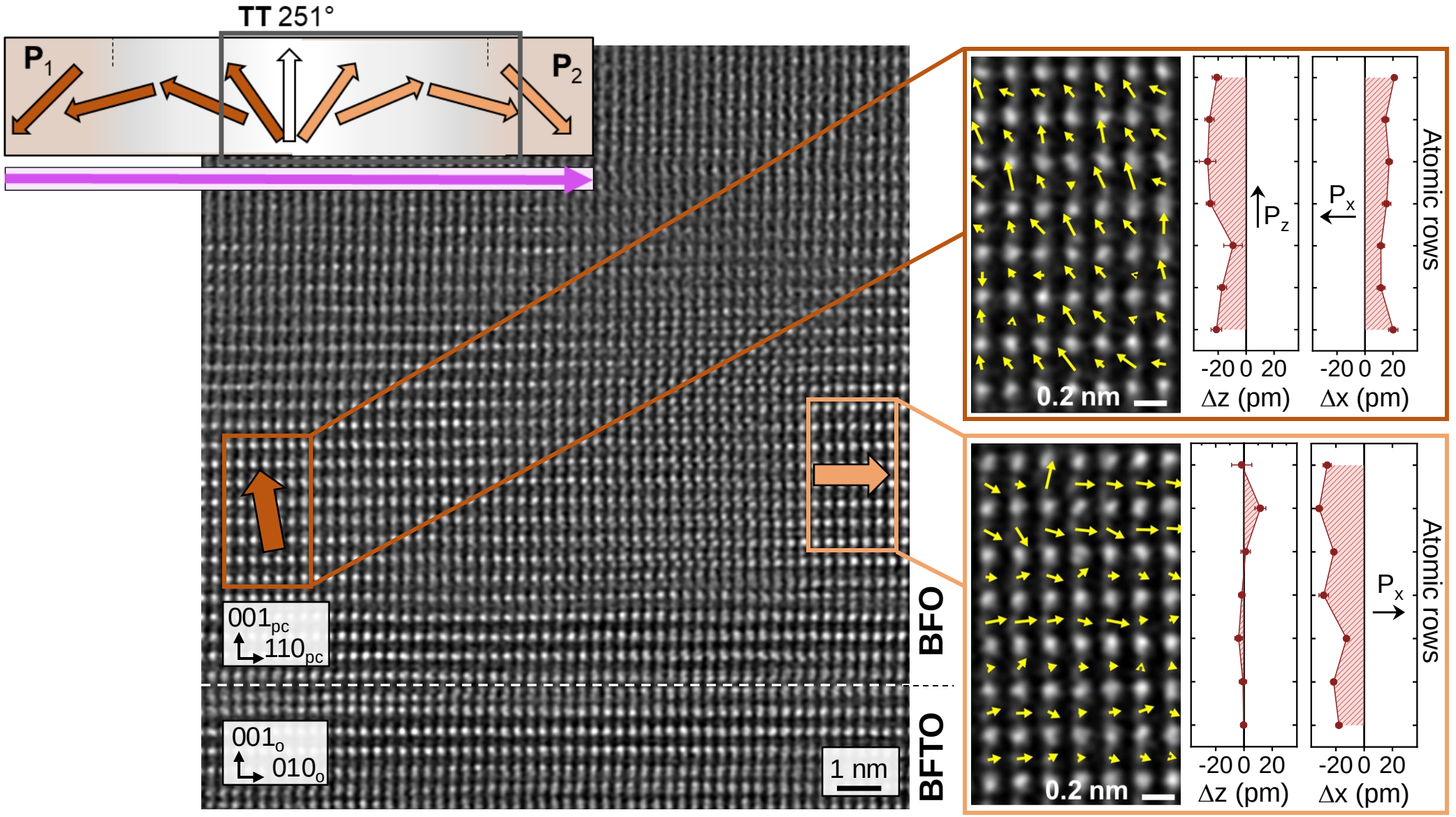
Néel DWs

Net chirality in the film



E. Gradauskaite *et al. Nat. Mater.* **2023**, *22*, 1492–1498.

Mapping of atomic displacements at the 251° TT wall



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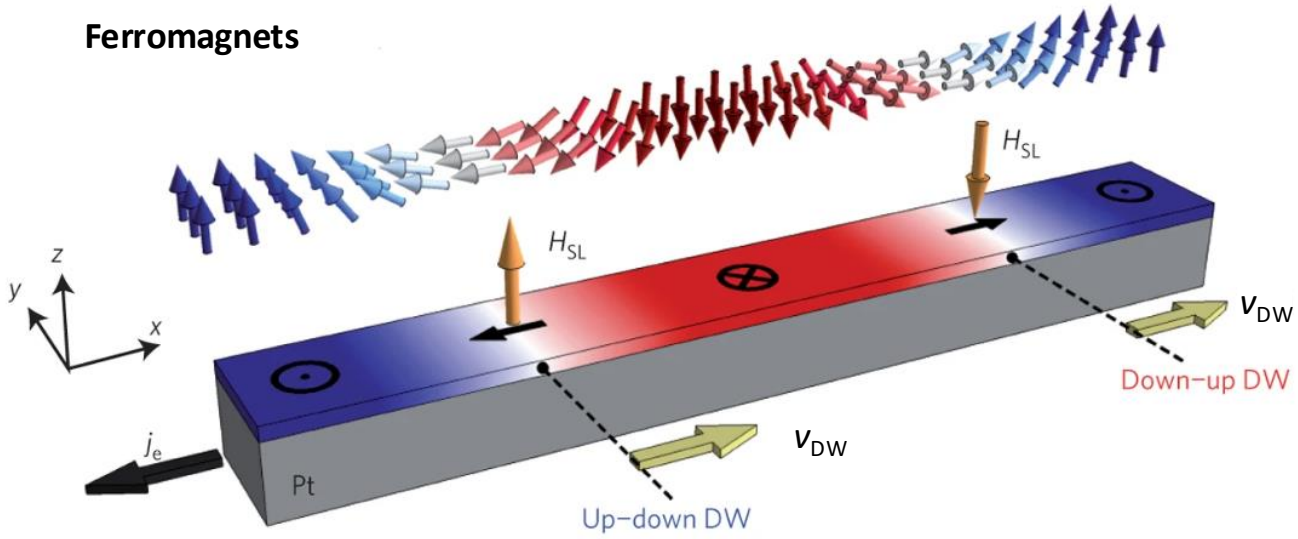
Homochiral domain walls in ferroics

Ferromagnets

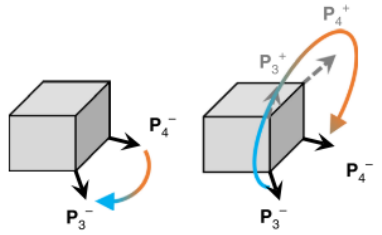


Homochiral domain walls in ferromagnets stabilized by interfacial DMI.

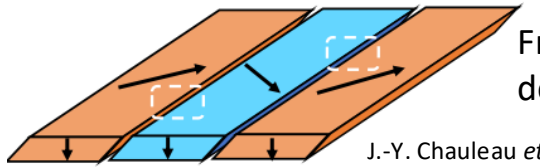
Unidirectional current-driven motion.

S. Emori *et al., Nat. Mater,* **2013,** *7*, 611.

Ferroelectrics



Net chirality of polarization in BFO: Synchrotron X-ray resonant scattering



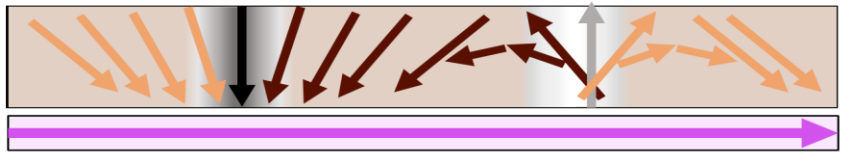
Frustration induced by dense stripe domains

J.-Y. Chauleau *et al., Nat. Mater.,* **2020,** *19*, 386.
S. Fusil *et al., Adv. Electron. Mater.,* **2022,** *8*, 2101155.

Our case:
IP BFTO buffer → symmetry breaking
Chirality pronounced → SPM

Electric DMI counterpart

H. J. Zhao *et al., Nat. Mater.,* **2021**, *20*, 341.



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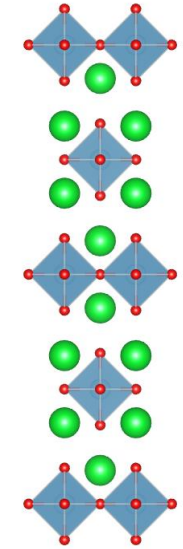
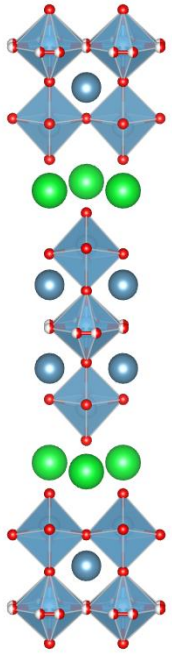
Outlook: layered Carpy-Galy ferroelectrics as polar metals



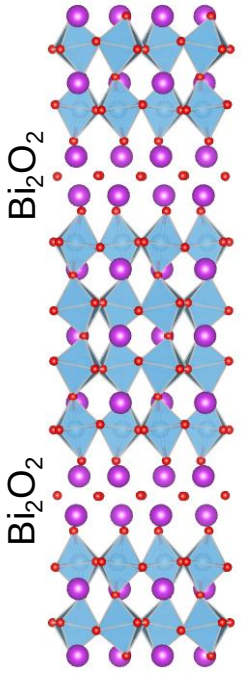
$A_{n+1}B_nO_{3n+1}$

Ruddlesden -Popper



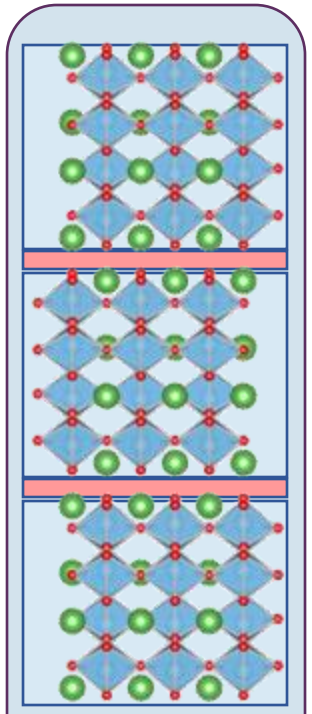
$A'[A_{n-1}B_nO_{3n+1}]$

Dion-Jacobson



$Bi_2O_2[A_{n-1}B_nO_{3n+1}]$

Aurivillius



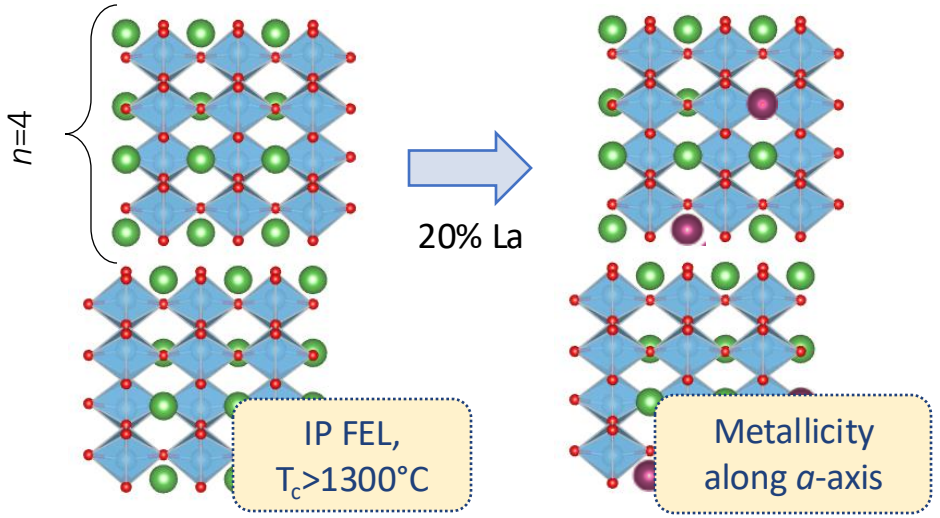
$A_nB_nO_{3n+2}$

Carpy-Galy

110-oriented perovskites

Additional oxygen layers

Quasi-metallic layered ferroelectrics:
1D metallicity in $A_2B_2O_7$ Carpy-Galy phases



$Sr_2Nb_2O_7$ *n*=4
Nb^{5+} / $4d^0$

$Sr_{1..6}La_{0.4}NbO_7$ *n*=4
$Nb^{4.8+}$ / $4d^{0.2}$

Optical conductivity:
survival of phonon modes + FEL soft mode.

Layered perovskite-related ferroelectrics

- Form spontaneously
- Uniaxial in-plane polarization
- No epitaxial strain needed

C. A. Kuntscher *et al.*, *Phys. Rev. B.* **2004**, *70*, 245123.
F. Lichtenberg *et al.*, *Prog. Solid State Chem.* **2008**, *36*, 253.

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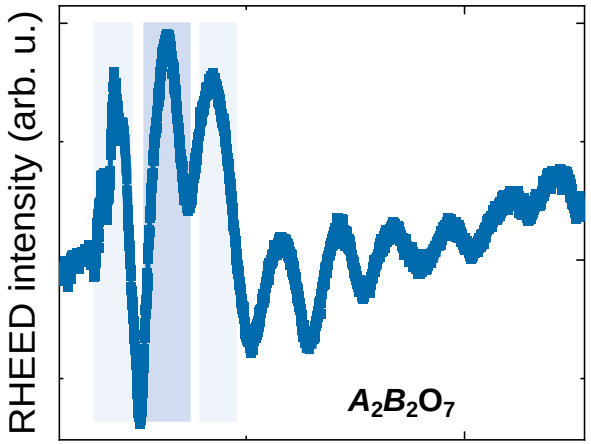
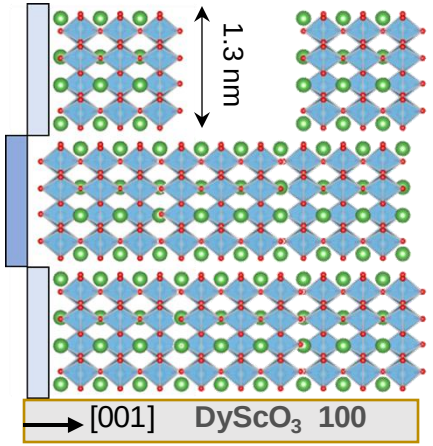
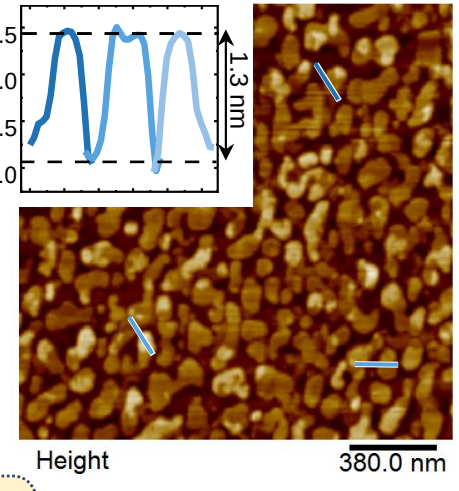
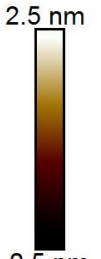
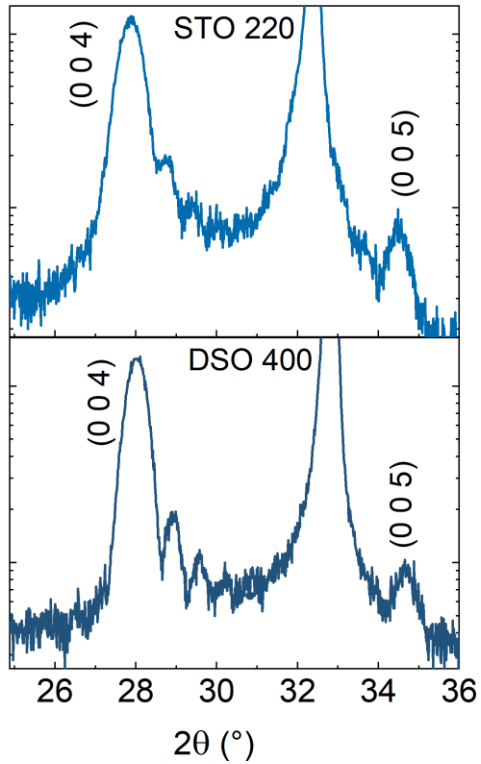
Epitaxial $A_2B_2O_7$ (n=4) Carpy-Galy ferroelectrics





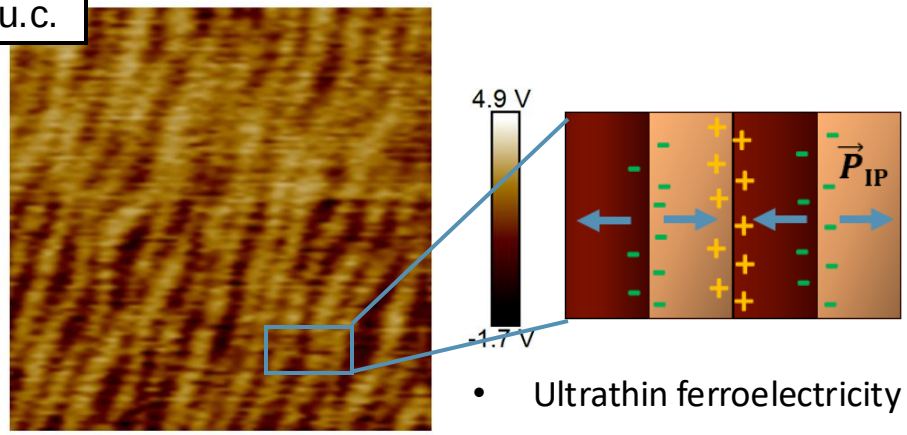






The same coalescent layer-by-layer growth mode seen for the Aurivillius phases

1 u.c.

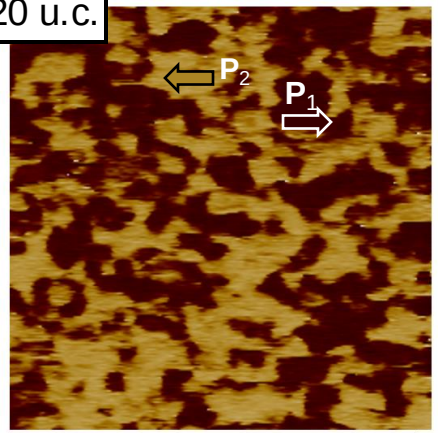


lateral phase

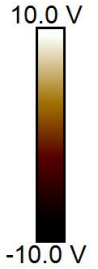
→ DSO [0 1 0]

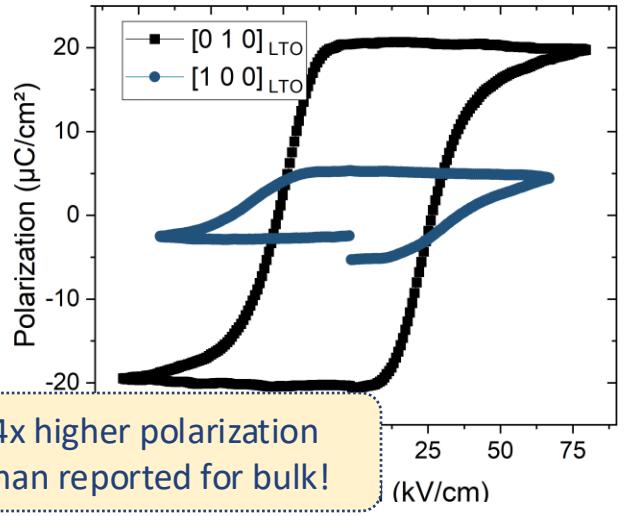
- Ultrathin ferroelectricity
- HH and TT stripe domains

20 u.c.



lateral phase





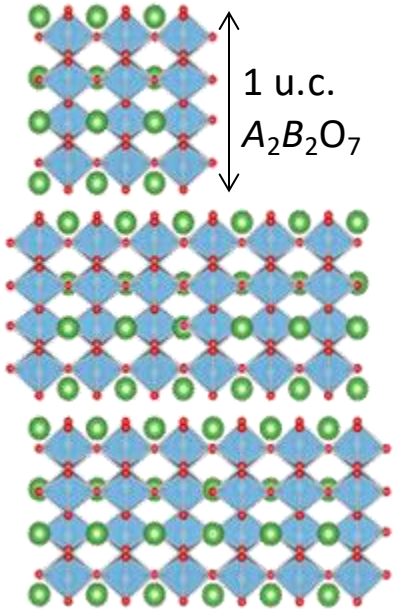
4x higher polarization than reported for bulk!

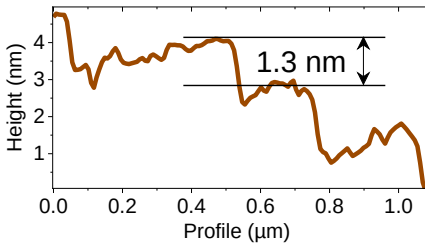
- Uniaxial IP polarization

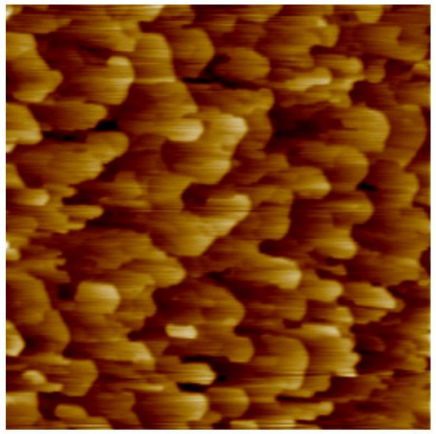
Ferroelectricity vs metallicity in the parent perovskite

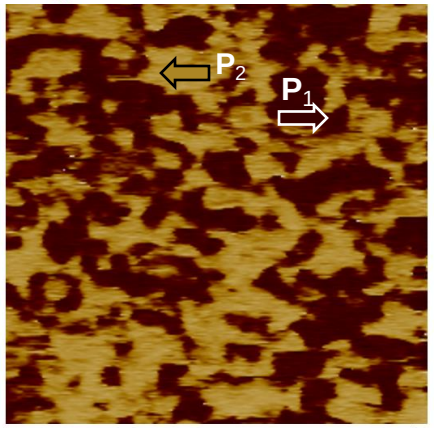
$A_2B_2O_7$ (insulating+FEL) → [110] ABO_3 (metallic+paraelectric) e.g. Ti [4+] → Ti [3+] Nb [5+] → Nb [4+] Ta [5+] → Ta [4+]

$A_2B_2O_7$



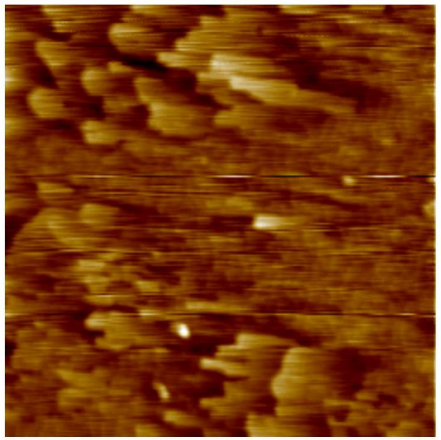


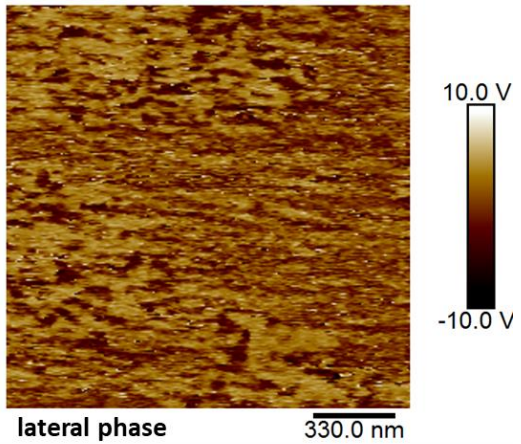


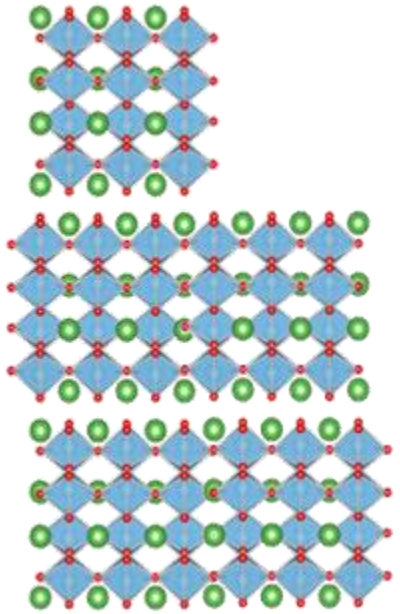


lateral phase

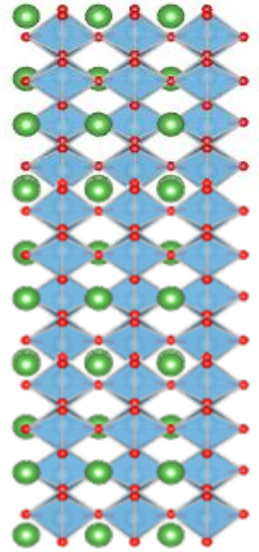
$A_2B_2O_7 + ABO_3$







+



$A_2B_2O_7$ (insulating+FEL)

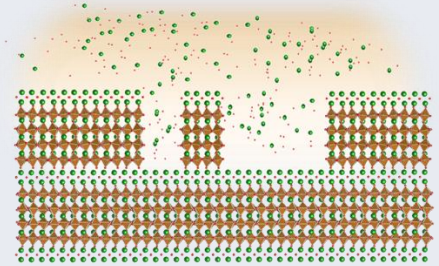
[110] ABO_3 (metallic+paraelectric)

→ ?? Polar metal ?? →

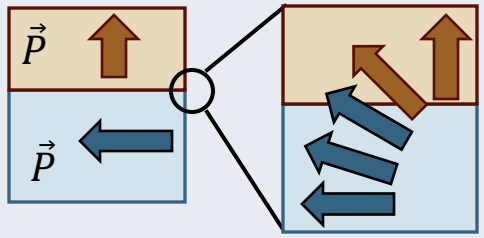
Ti [4+] → Ti [3+] Nb [5+] → Nb [4+] Ta [5+] → Ta [4+]

Summary

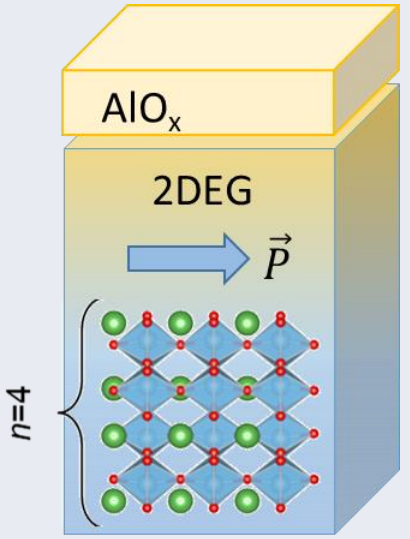
Sub-unit-cell control of emerging oxide phases



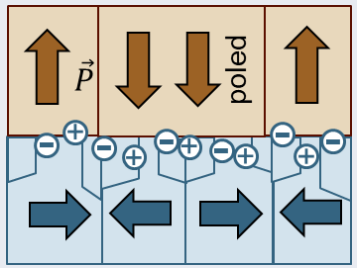
Zero critical thickness for ferroelectricity



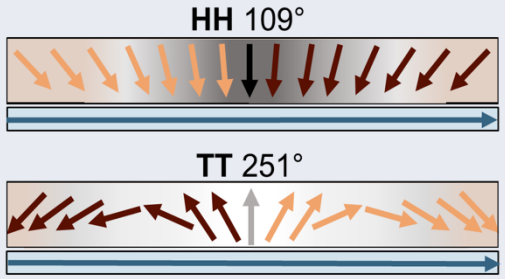
Towards polar metals



Electrode-free poling



Design of domains and domain-wall chirality



Thank you!

E. Gradauskaite *et al. Nat. Mater.* **2023**, *22*, 1492–1498.
E. Gradauskaite *et al., Chem. Mater.* **2022**, 34, 14, 6468–6475.
E. Gradauskaite *et al., Chem. Mater.* **2021**, *33*, 9439.

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