Karlsruhe Institute of Technology

Ferroelectric Domains in Perovskite Solar Cells

Holger Röhm, Tobias Leonhard, Alexander Schulz, Alexander Colsmann


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Karlsruhe Institute of Technology (KIT)

Founded 2009
- University of Karlsruhe 1825
- Nat'l Research Lab 1956

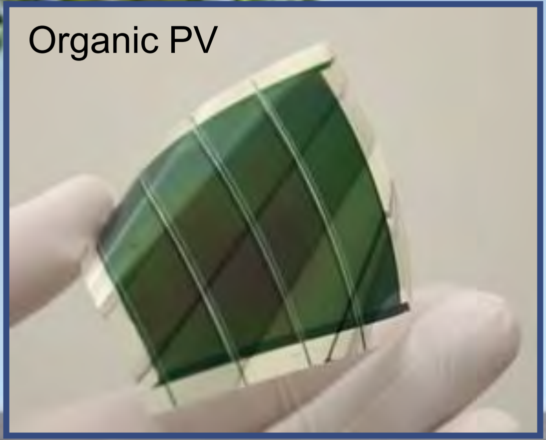
Employees	**9,783**
• Professors	385

Students	**22,275**
• Engineering	13,170
• Natural Sci.	3,805

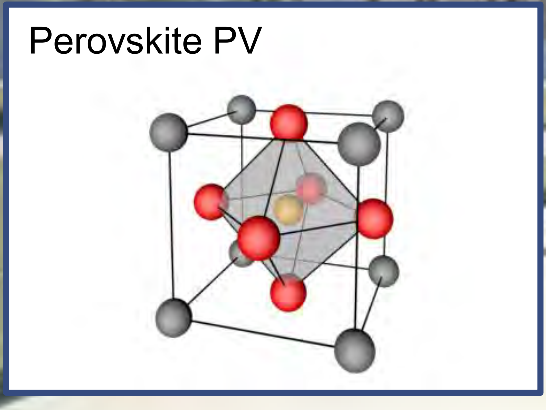
Material Research Center
for Energy Systems(MZE)

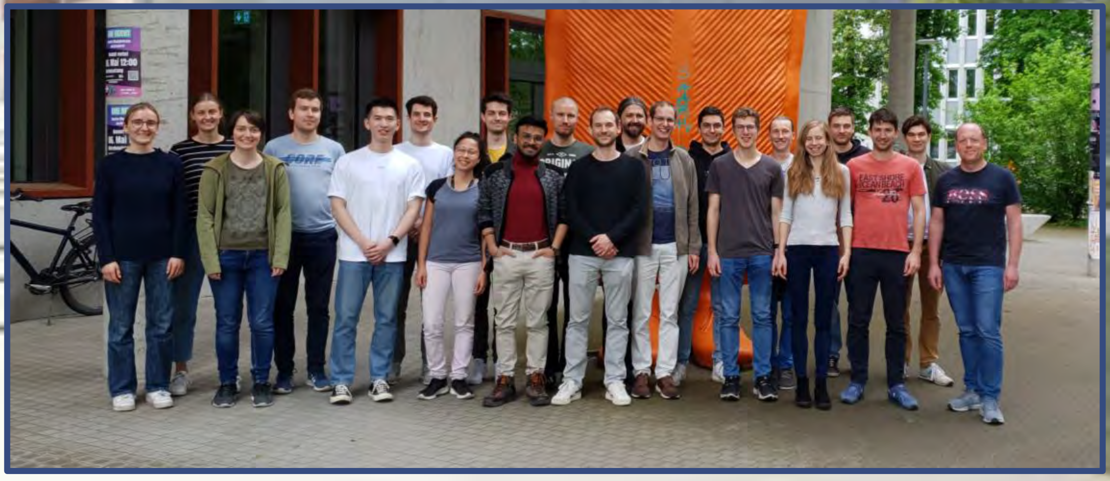
Building: 27,4 M€, Equipment: 8,4 M€
Foundation of the state of Baden-Württemberg (50%)
plus BMBF top-up according to §91b GG (50%)

Floor space: 4.174 m^2
Seats: ca. 180
Inauguration: November 2016


Organic PV


OLEDs


Perovskite PV

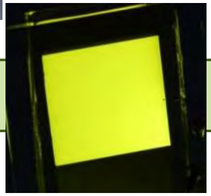


Research: Past – Present – Future

Today

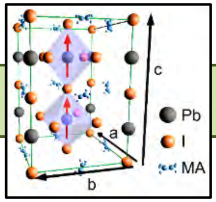
Organic PV

Photocatalysis

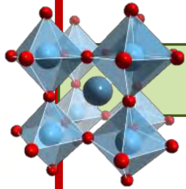


OLEDs

OTEGs



Perovskite PV



PV Beyond Perovskites

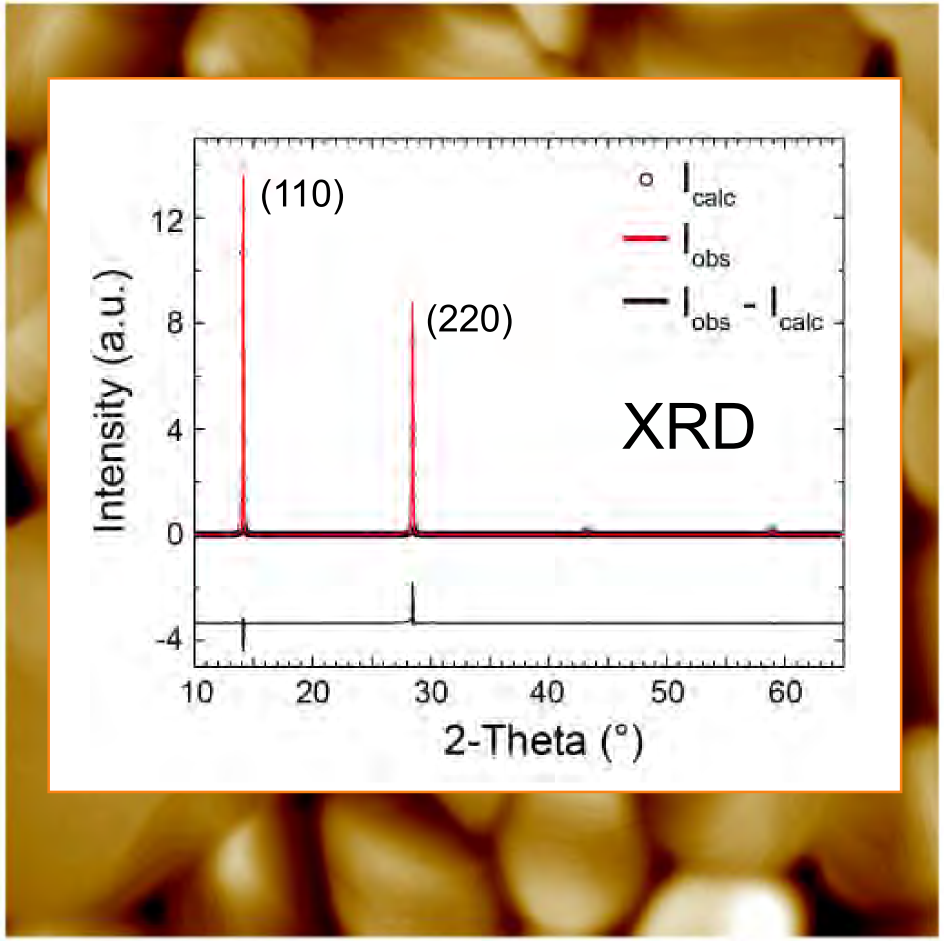
Batteries

Superconductors

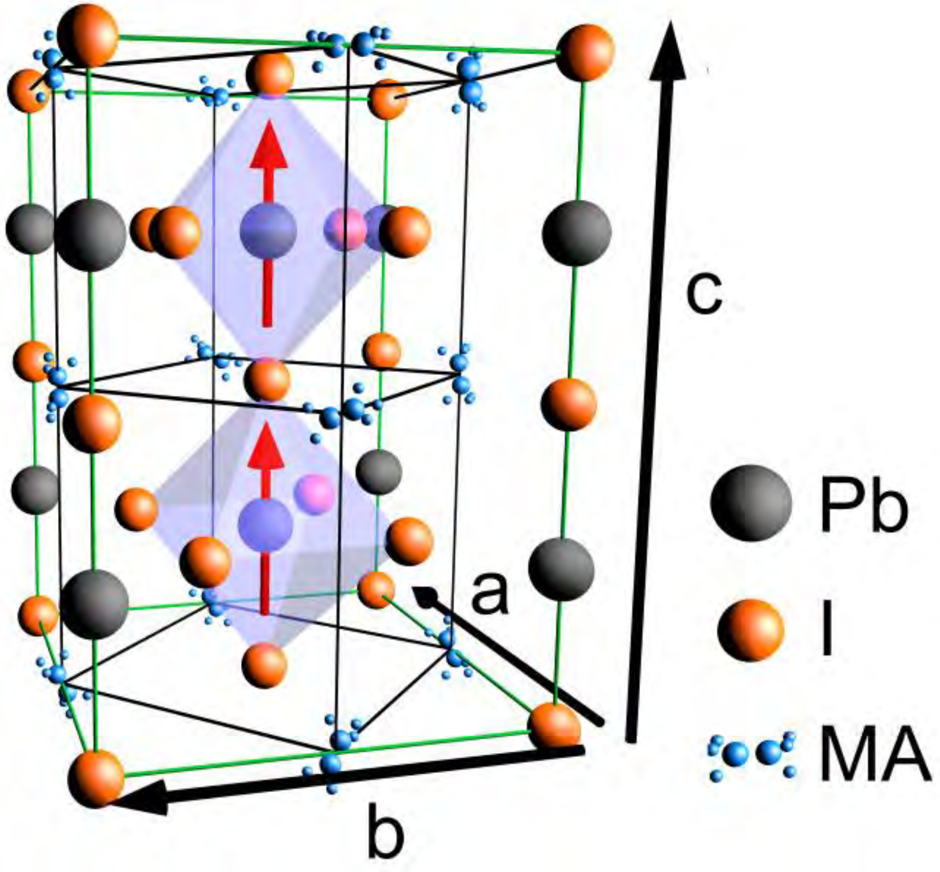
Cross-sectional topics

- Electrical doping
- Surfaces & interfaces
- Printable electrodes

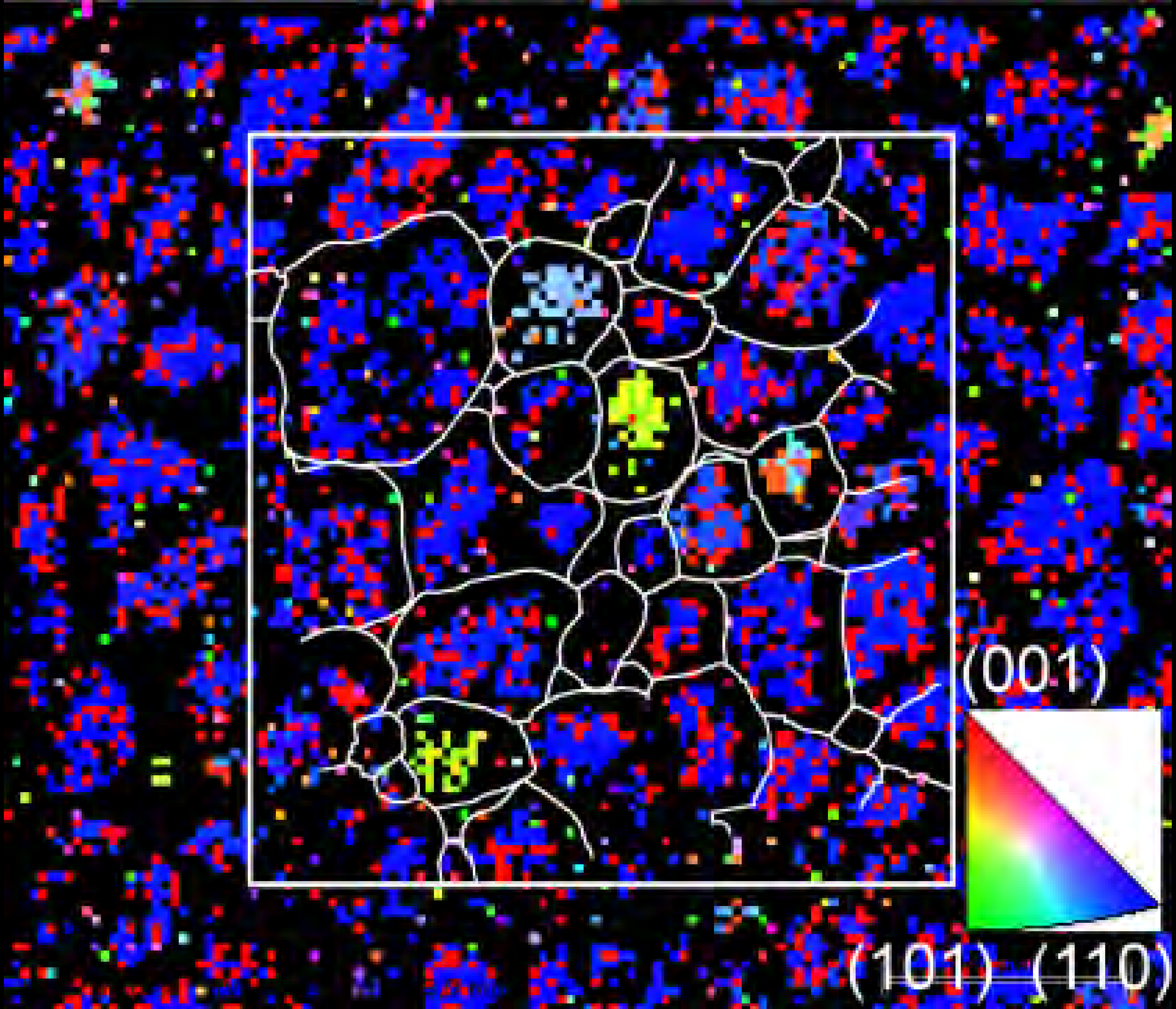
Microstructure of $MAPbI_3$ thin-films?



Topography 1.0 µm

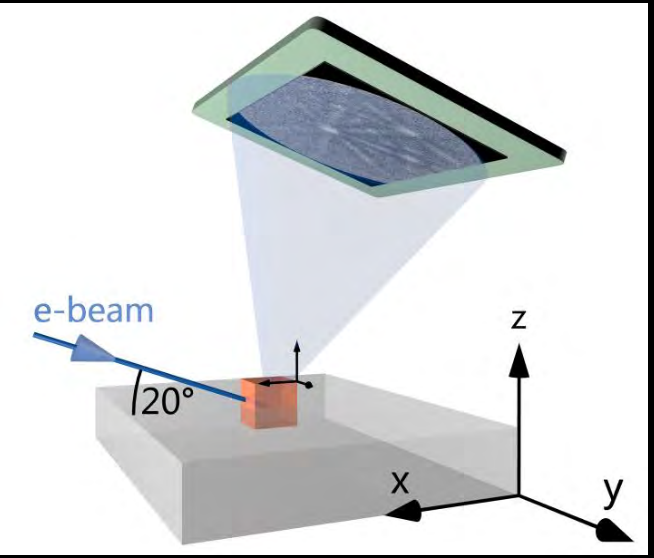


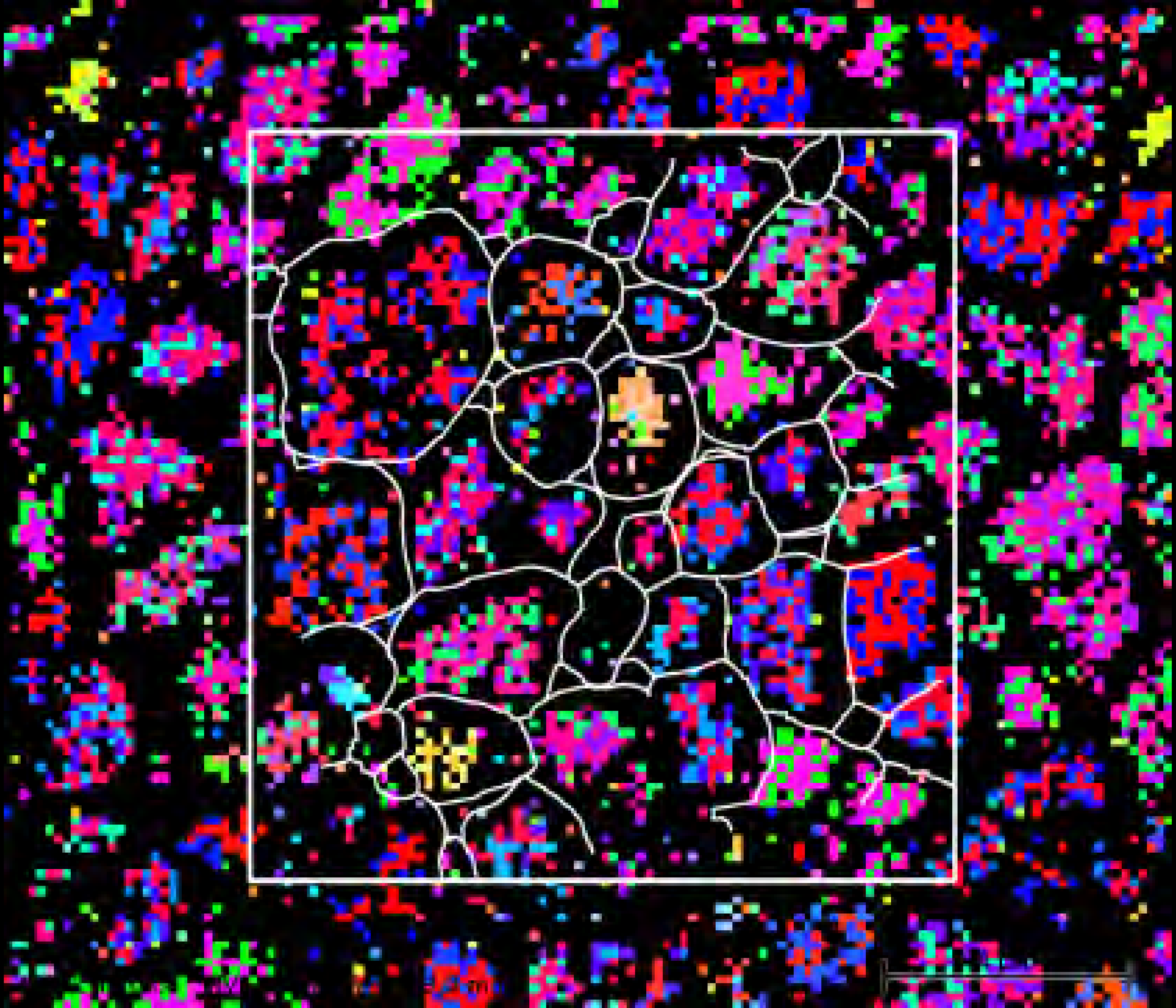
Large grains on PEDOT:PSS, PV η=16%



z - EBSD

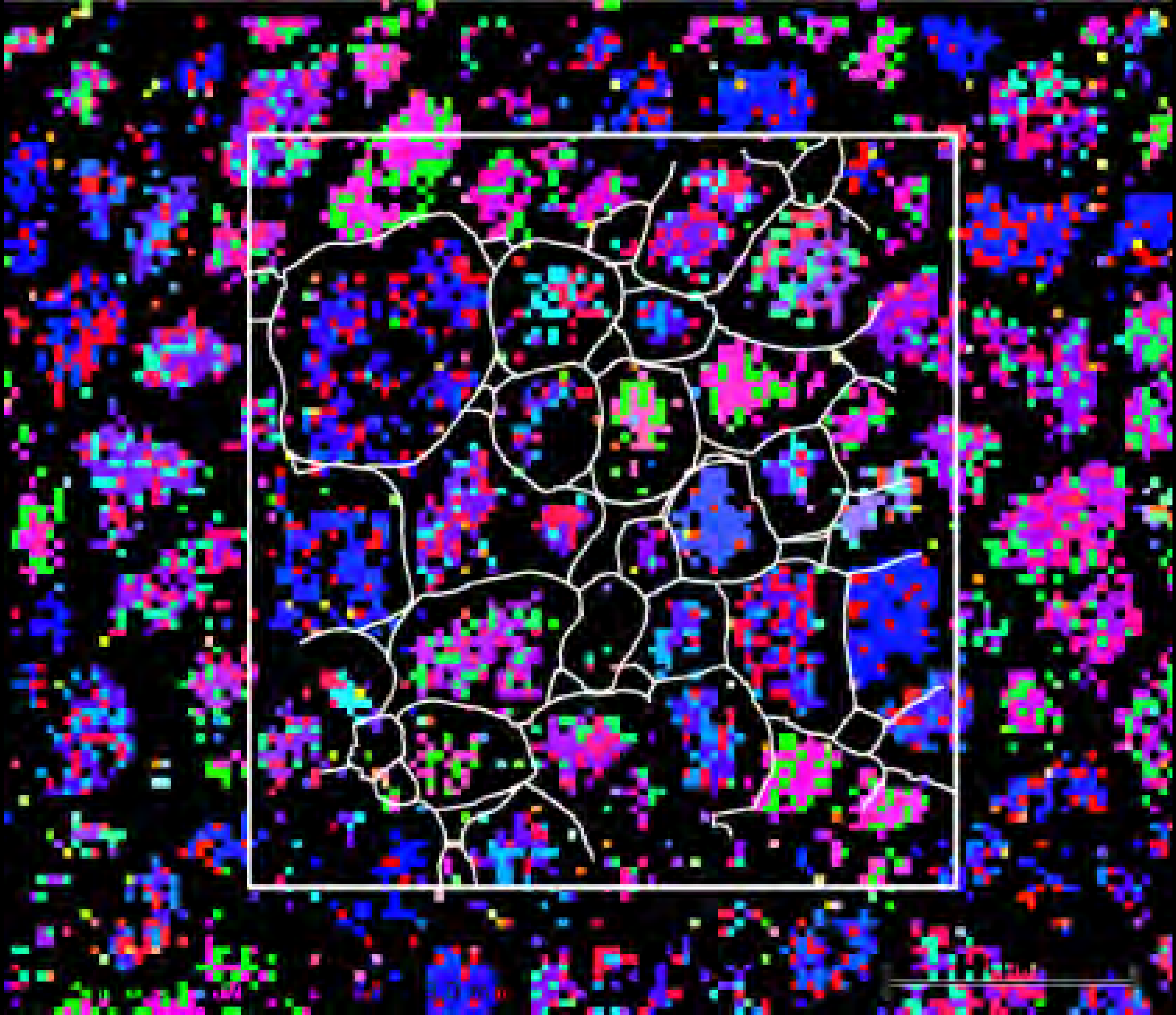
20×20 µm²





x - EBSD

20×20 μm²



y - EBSD

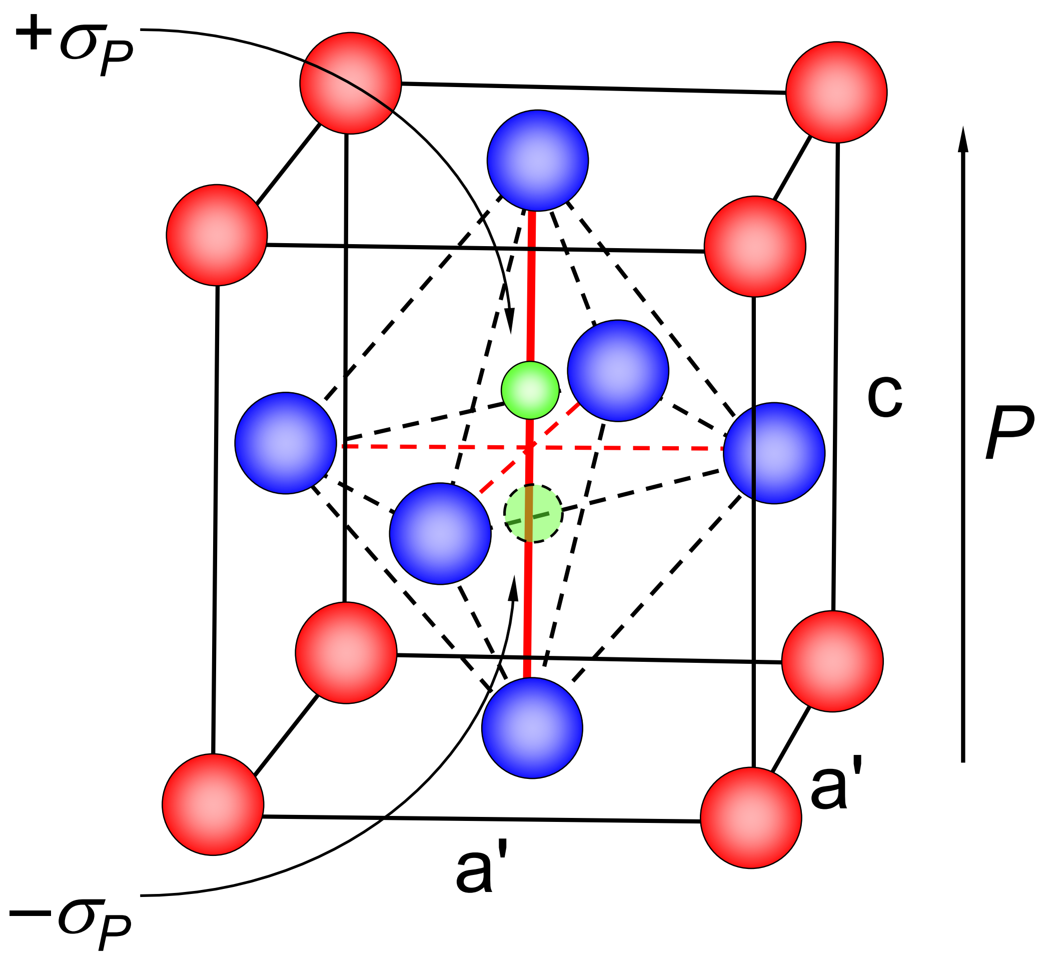
$20\times20\ \mu m^2$

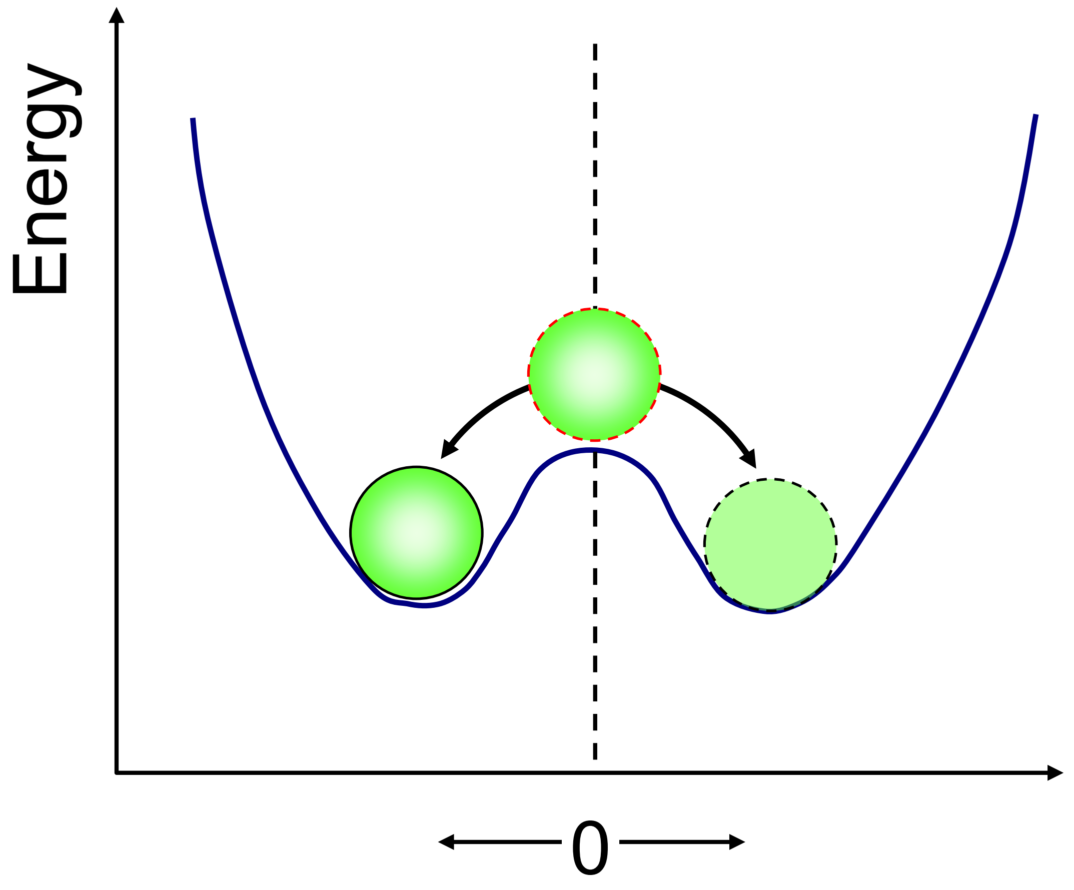
Ferroelectricity

<table>
<tr><td colspan="3">32 crystalline classes</td><td></td></tr>
<tr><td colspan="3">21 non-centrosymmetric</td><td>11 centrosymmetric</td></tr>
<tr><td colspan="3">20 piezoelectric</td><td rowspan="4">non-piezoelectric
[Wikipedia 2018]</td></tr>
<tr><td colspan="2">10 pyroelectric</td><td rowspan="2">non-pyroelectric</td></tr>
<tr><td>ferroelectric</td><td>non-ferroelectric</td></tr>
<tr><td>$PbZr/TiO_3$, $BaTiO_3$, $PbTiO_3$</td><td>Tourmaline, ZnO, AlN</td><td>Quartz, Langasite</td></tr>
</table>

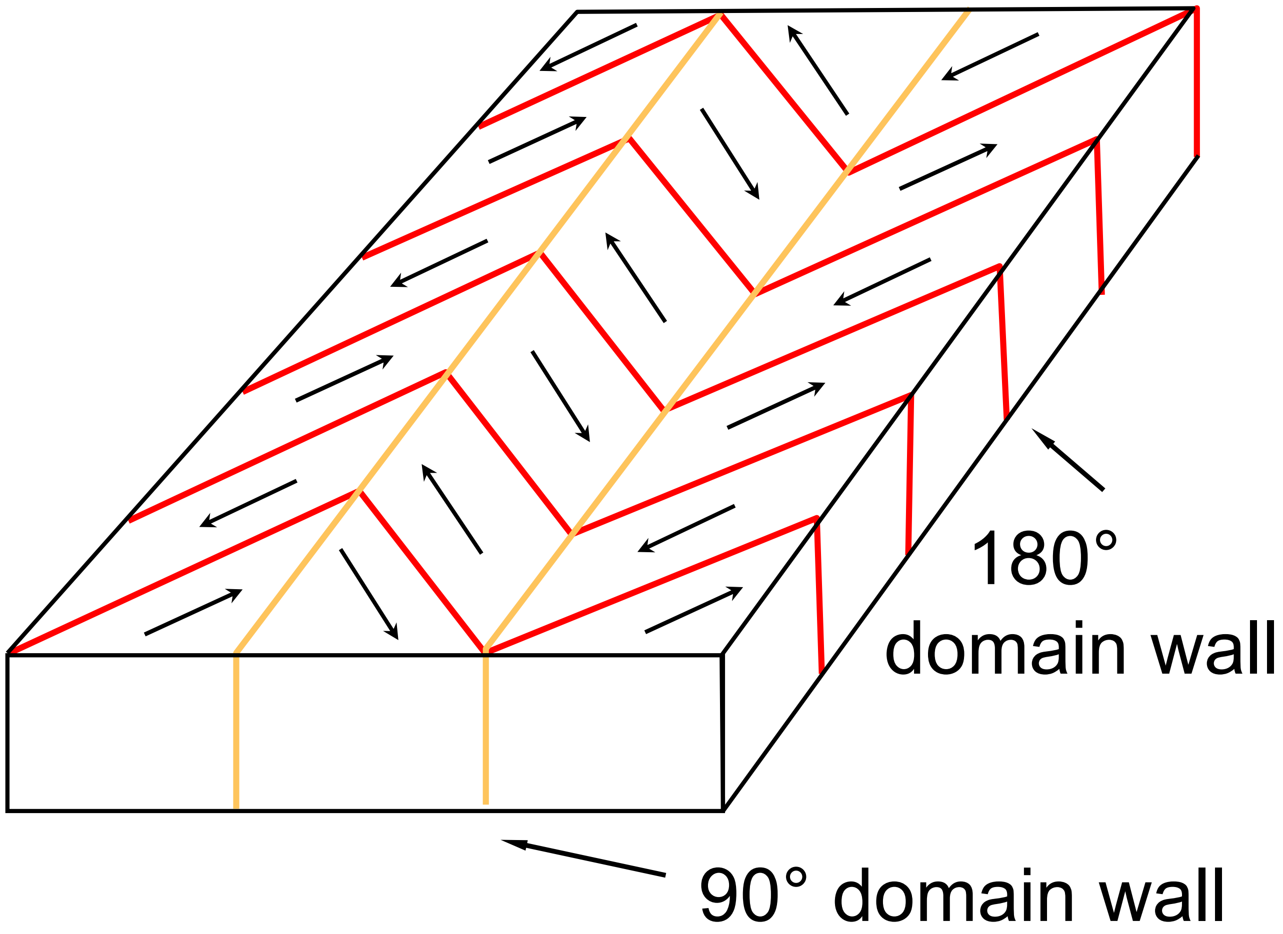
Ferroelectric materials exhibit a permanent dipole and hence form twin-domains.

Ferroelectricity





Ferroelectric Properties ?

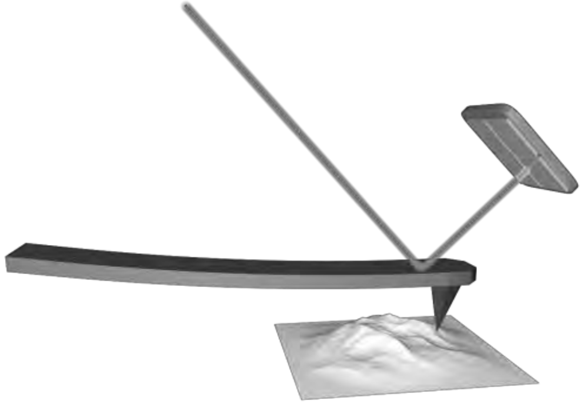


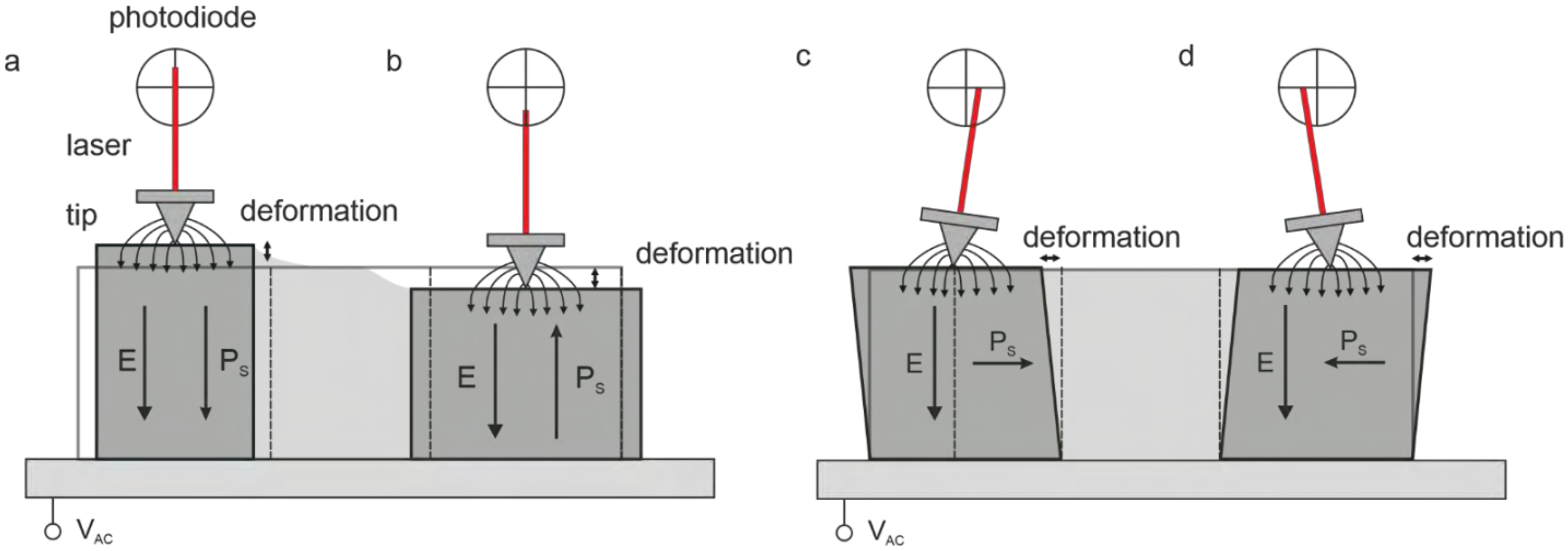
Formation of domains reduces stress …

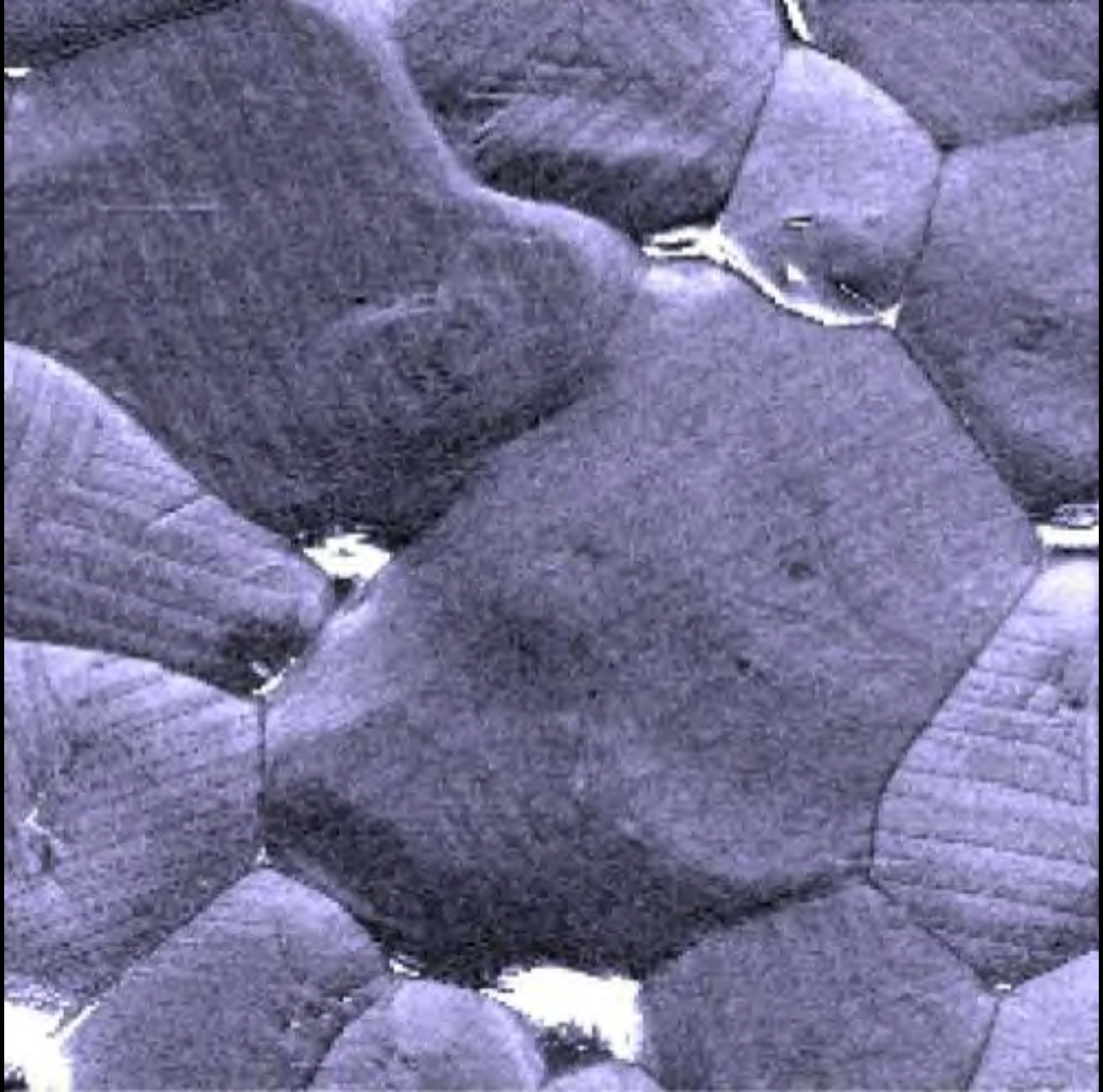
Ferroelectricity
Reduction of electrical stress

Ferroeleasticity
Reduction of mechanical stress

Piezoresponse Force Microscopy (PFM)

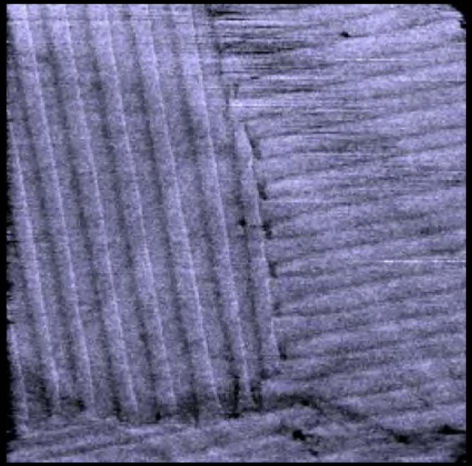


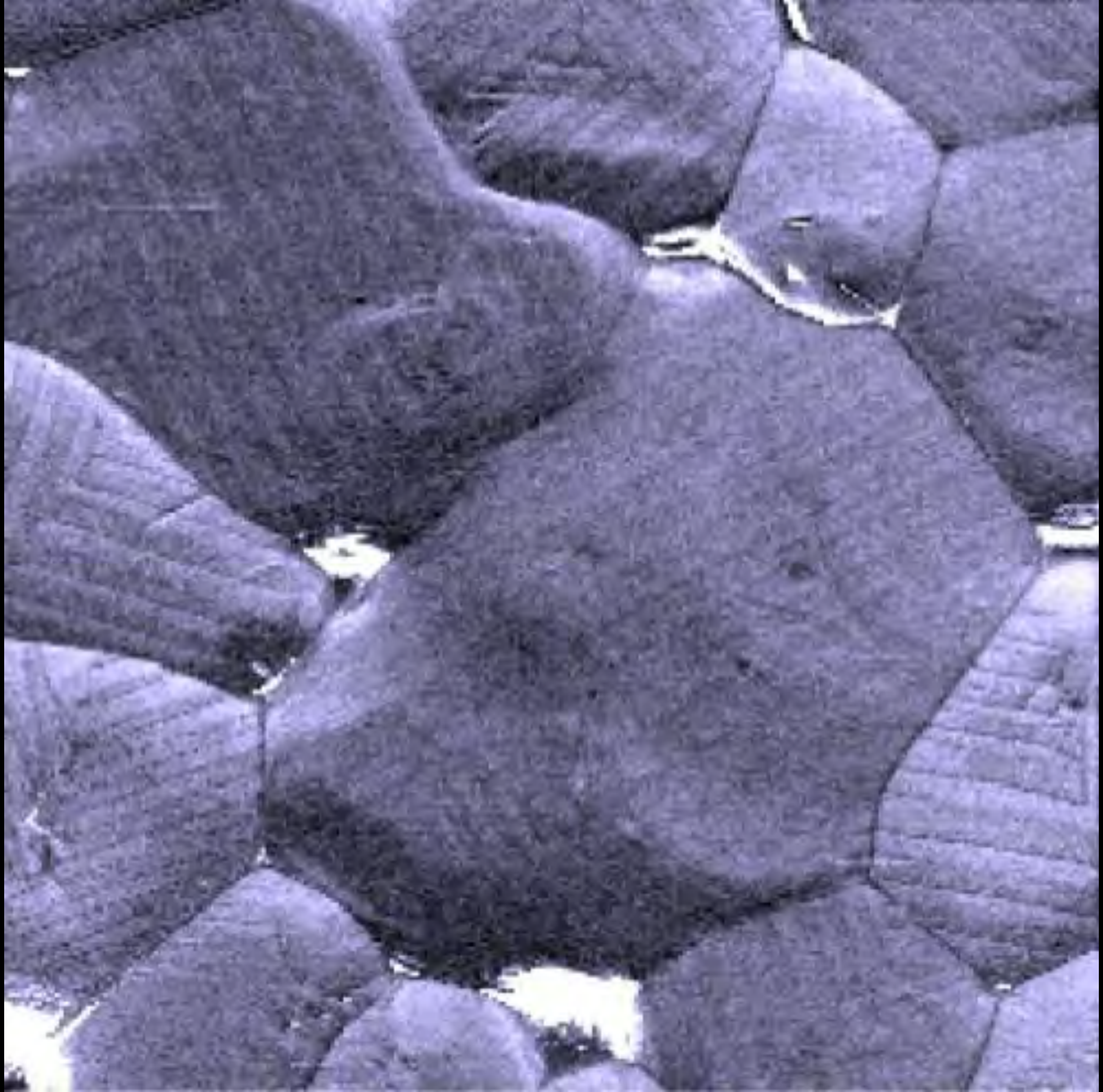




PFM, 4×4 μm²

Topography ?

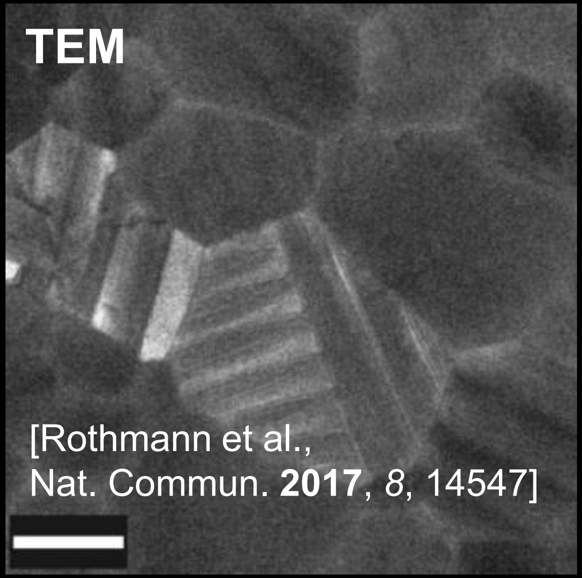


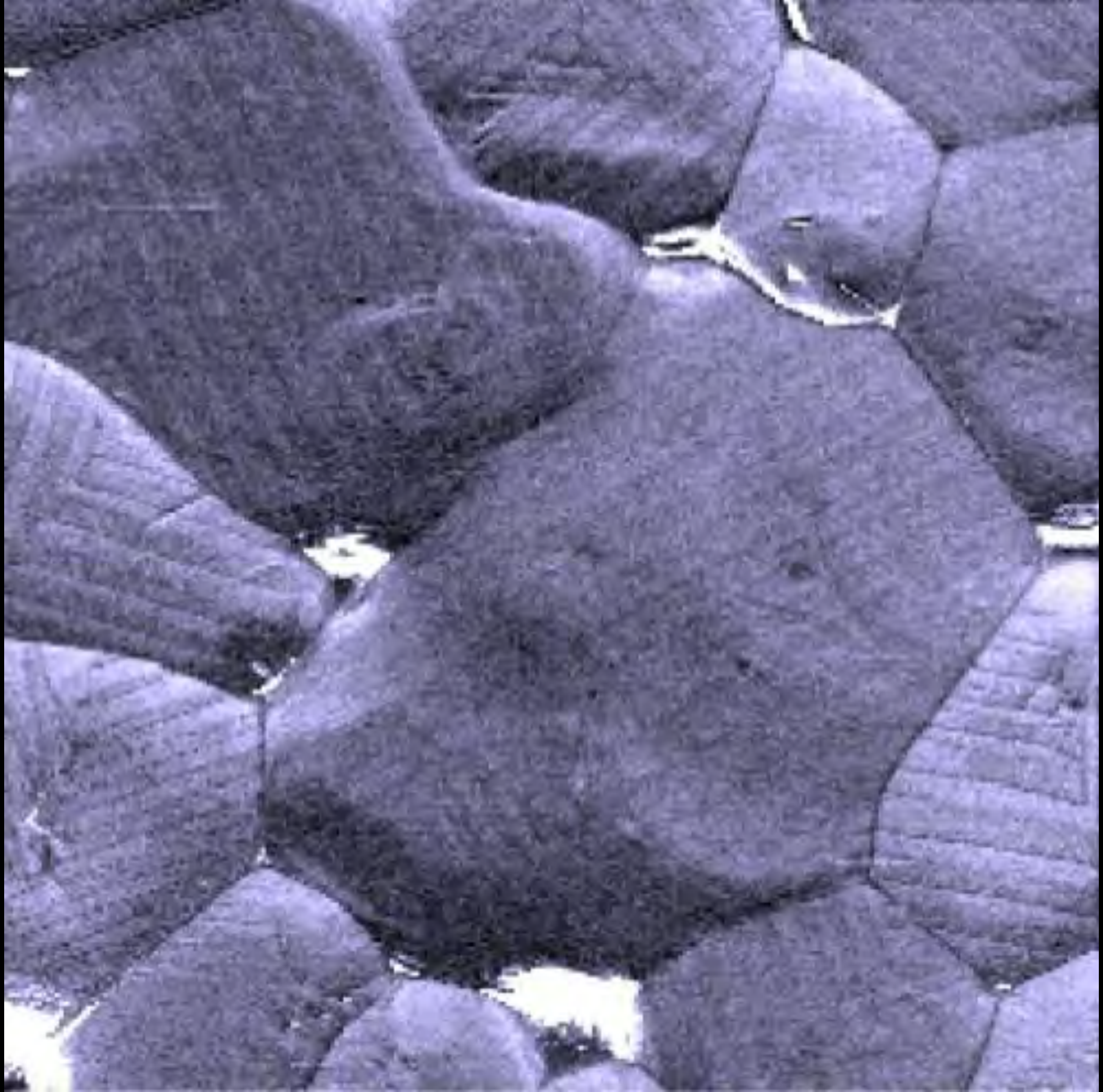


PFM, 4×4 μm²

Topography ?
No.

Surface effect ?
Bulk-property





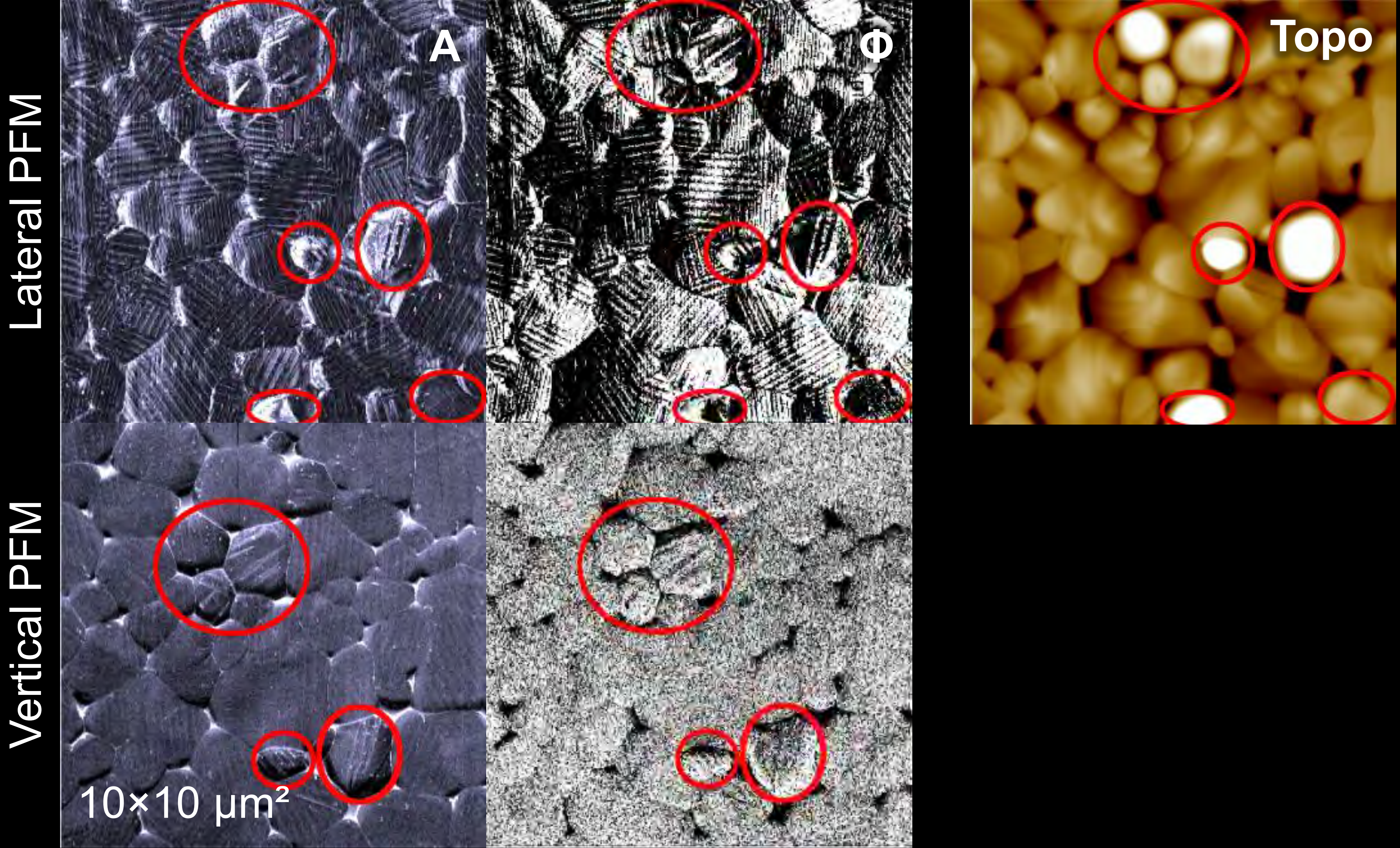
PFM, 4×4 µm²

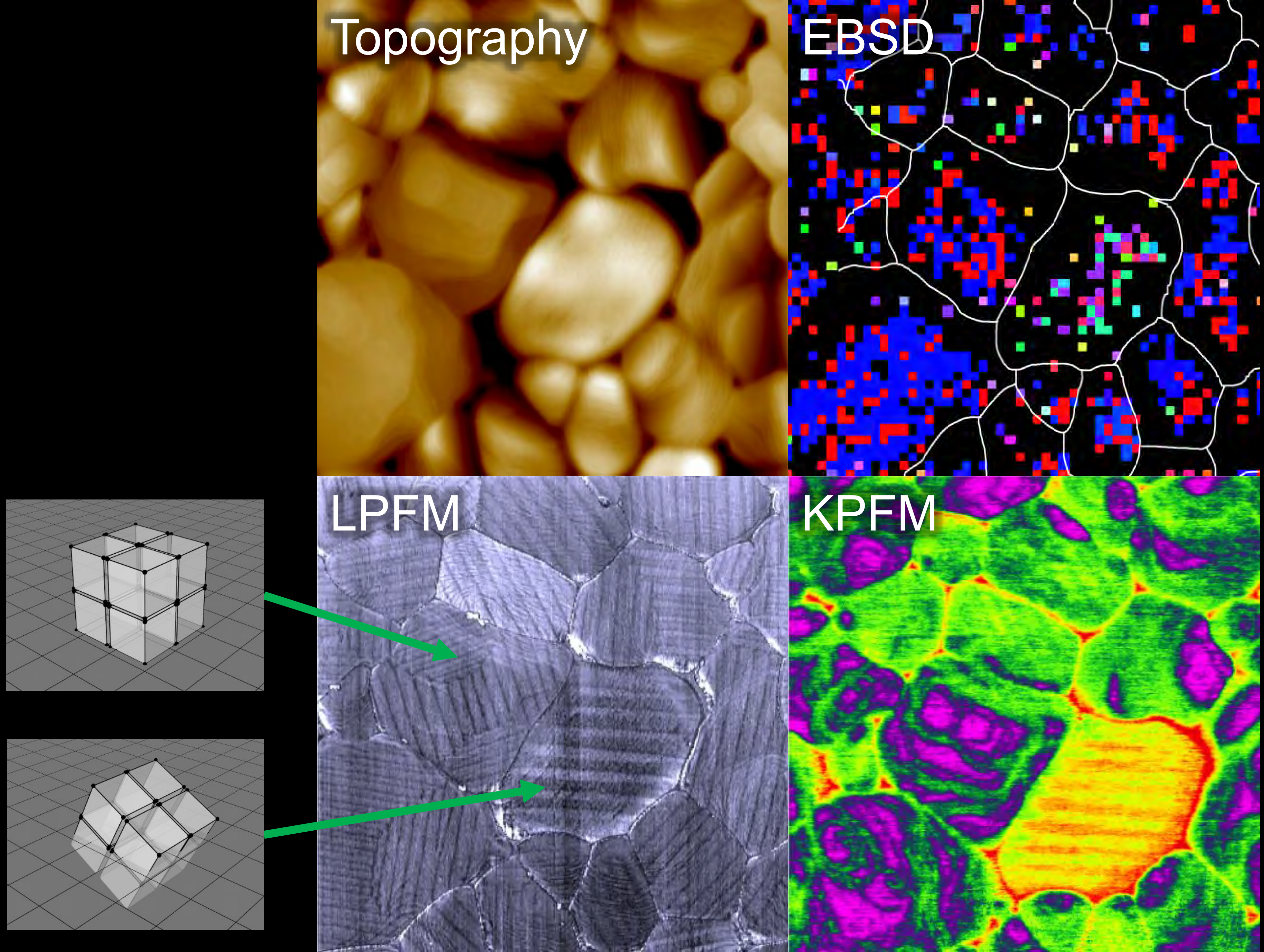
Topography ?
No.

Surface effect ?
Bulk-property

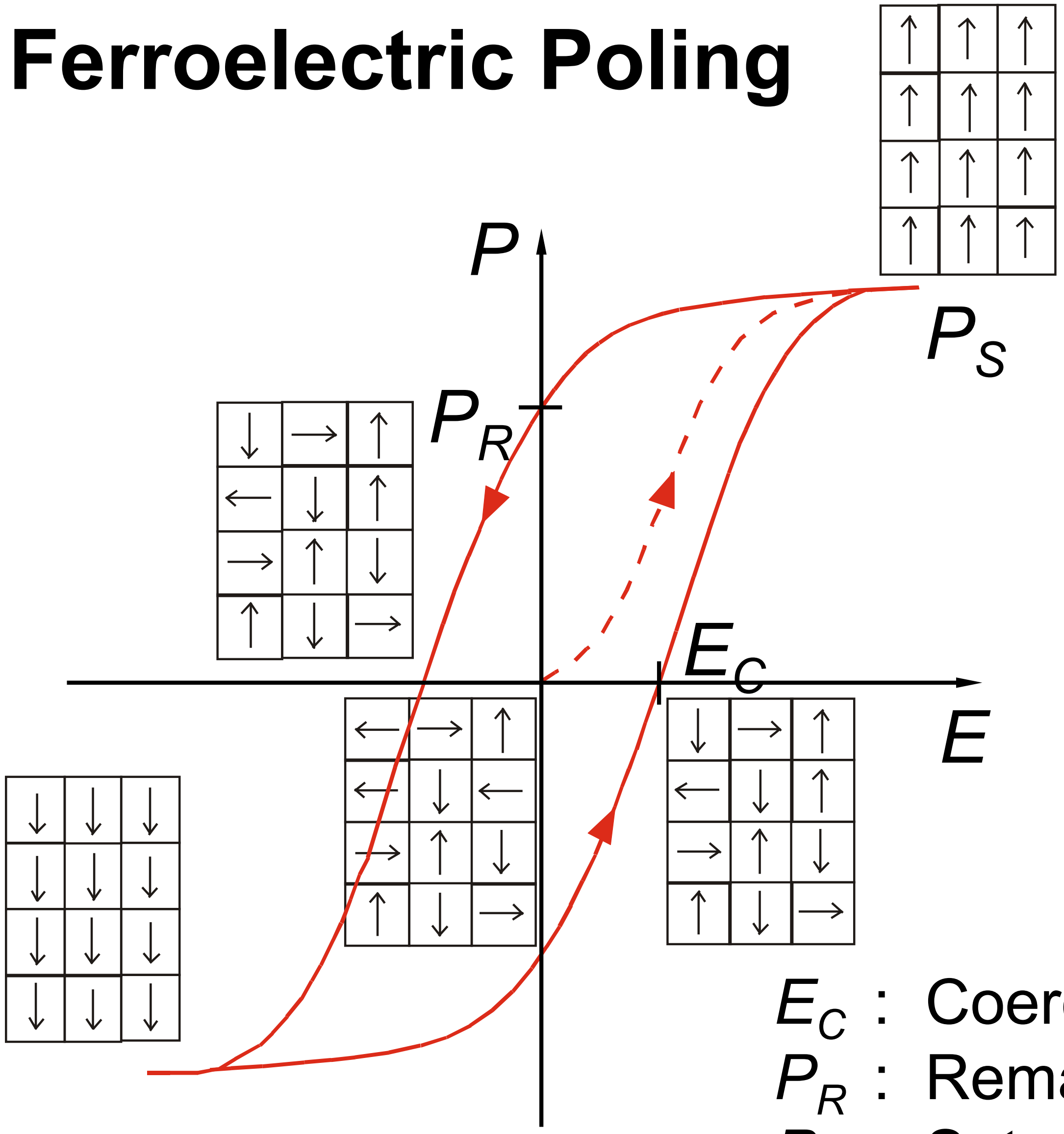
Ferroelasticity ?
Ferroelastic materials do not respond to PFM

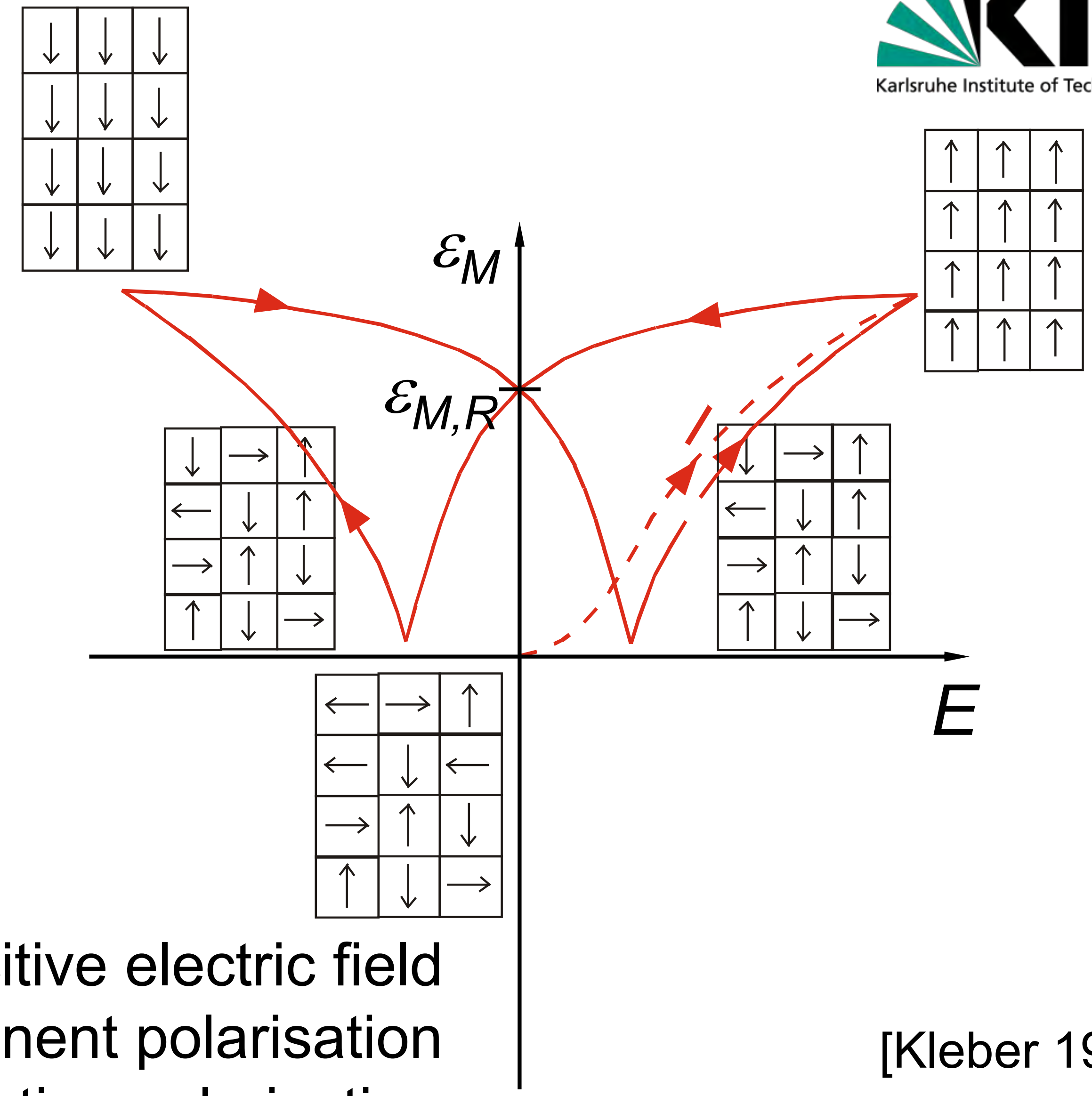
Ionic charges / migration?
Maybe, but …


Lateral PFM
Vertical PFM
A
Φ
Topo
10×10 μm²


Topography
EBSD
LPFM
KPFM

Ferroelectric Poling





E_C : Coercive electric field

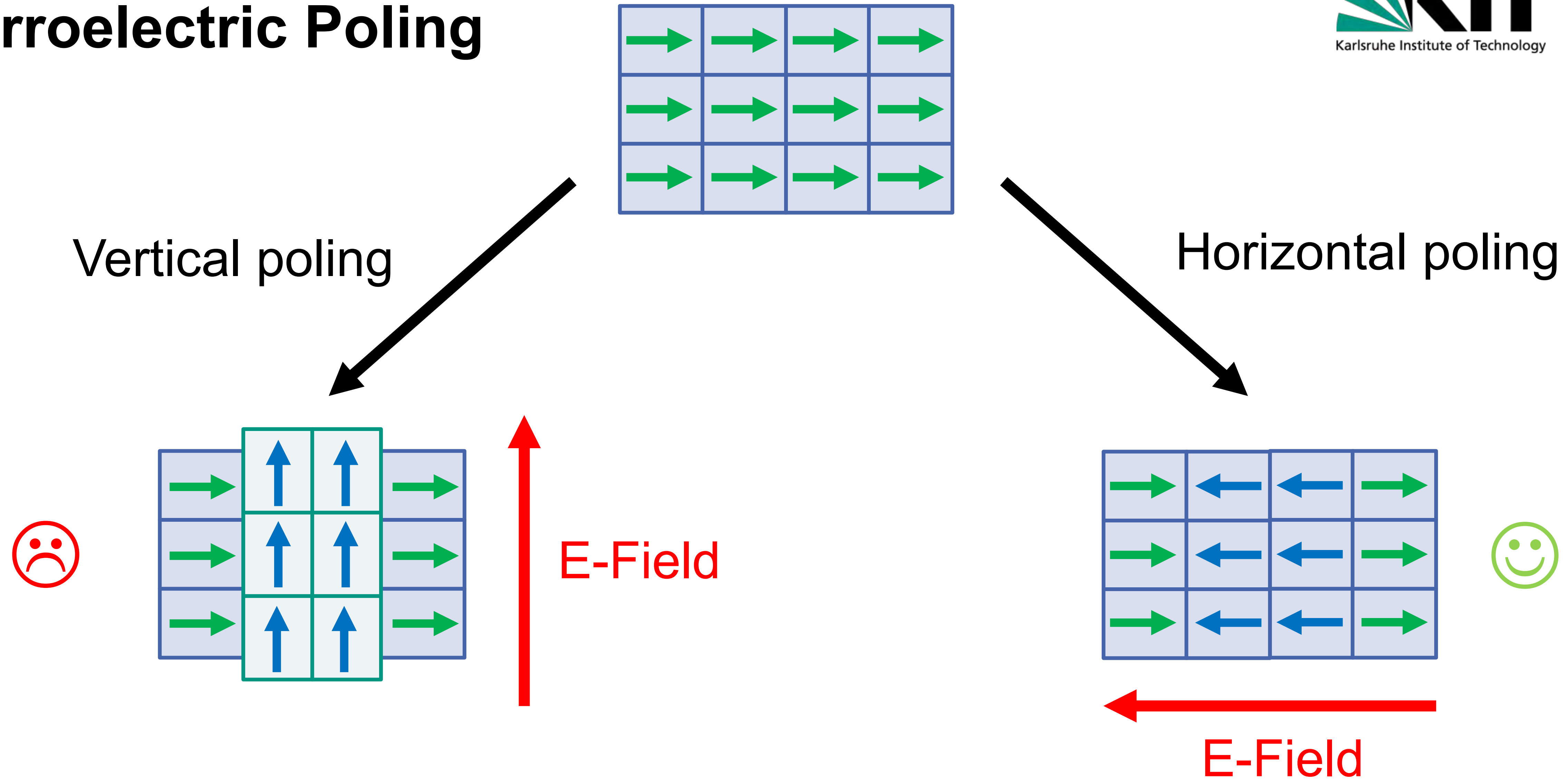
P_R : Remanent polarisation

P_S : Saturation polarisation

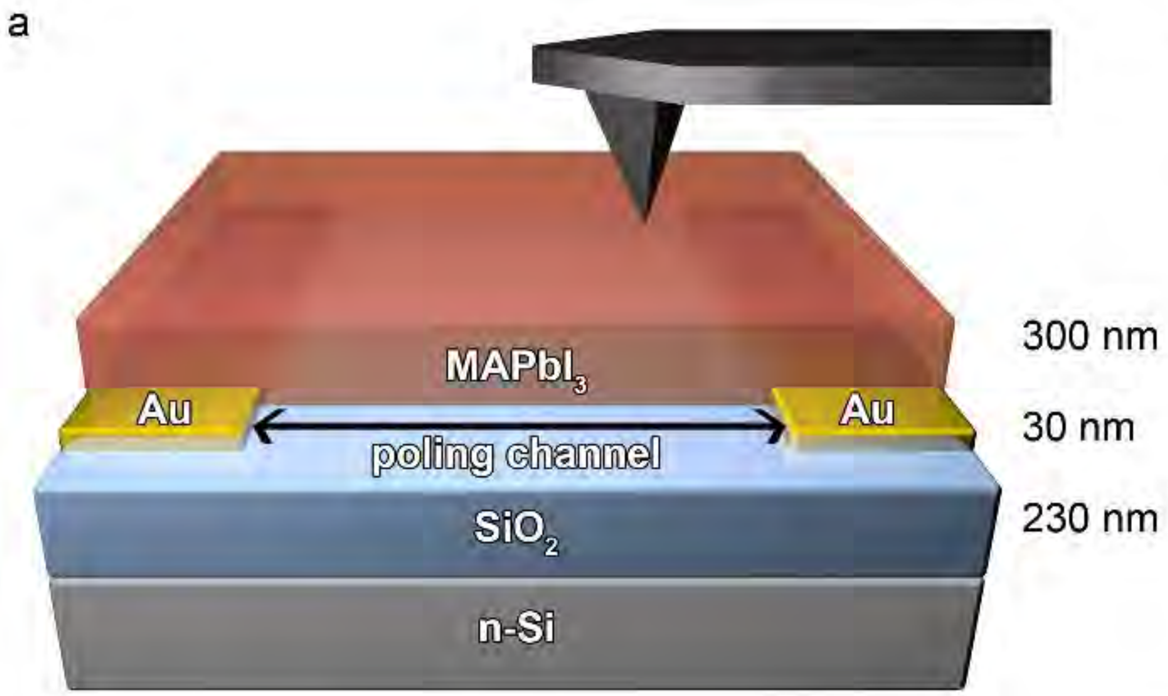
$\varepsilon_{M,R}$: Remanente Dehnung

[Kleber 1977]

Ferroelectric Poling



Ferroelectric Poling



[H. Röhm et al., Adv. Funct. Mater. **2019**, 1908657]

Ferroelectric Poling

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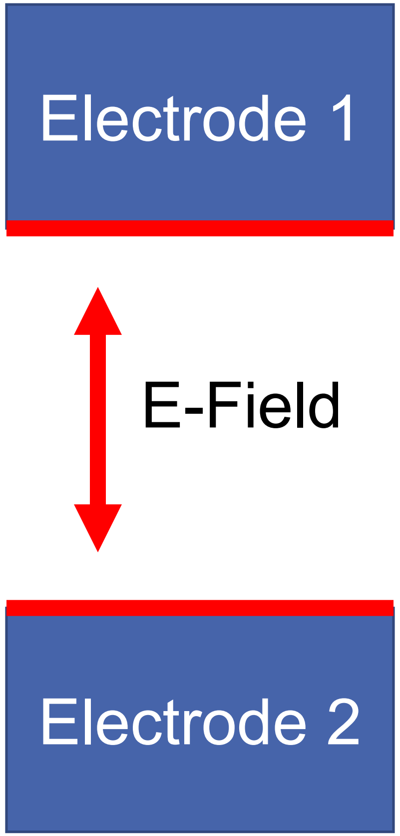
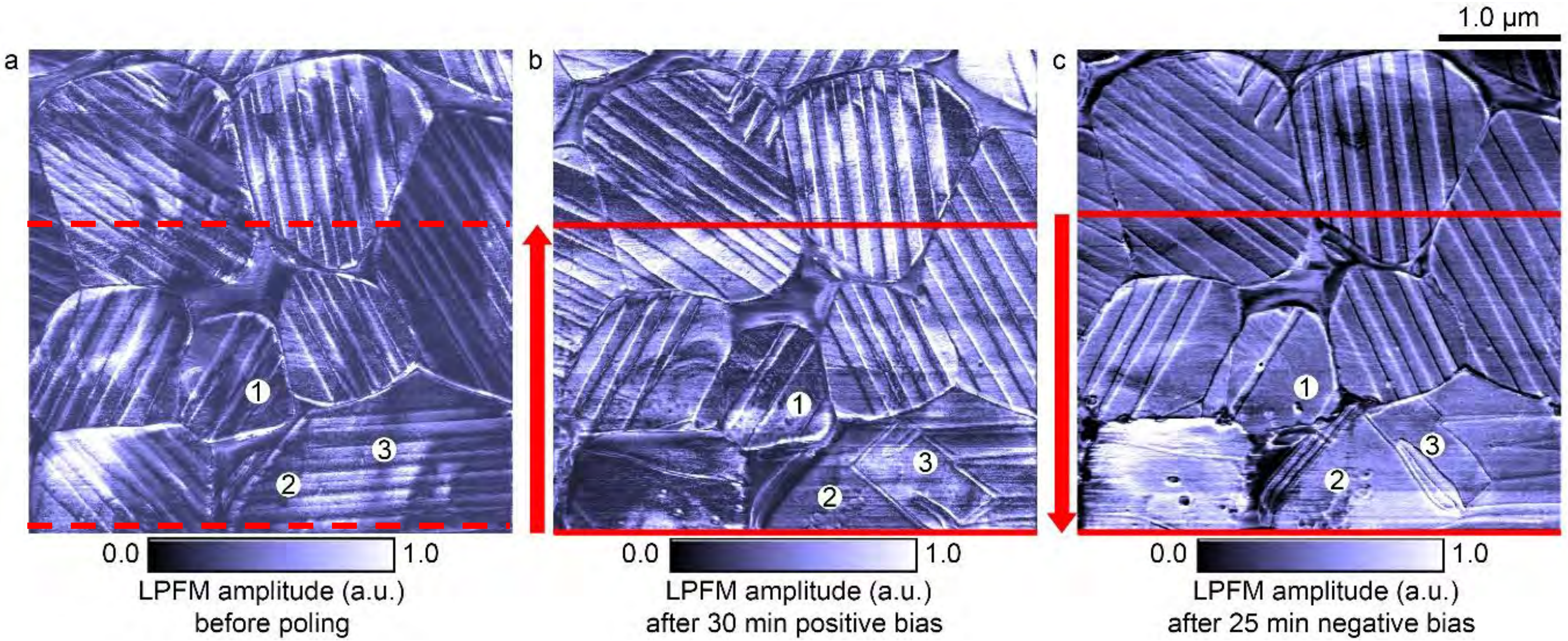
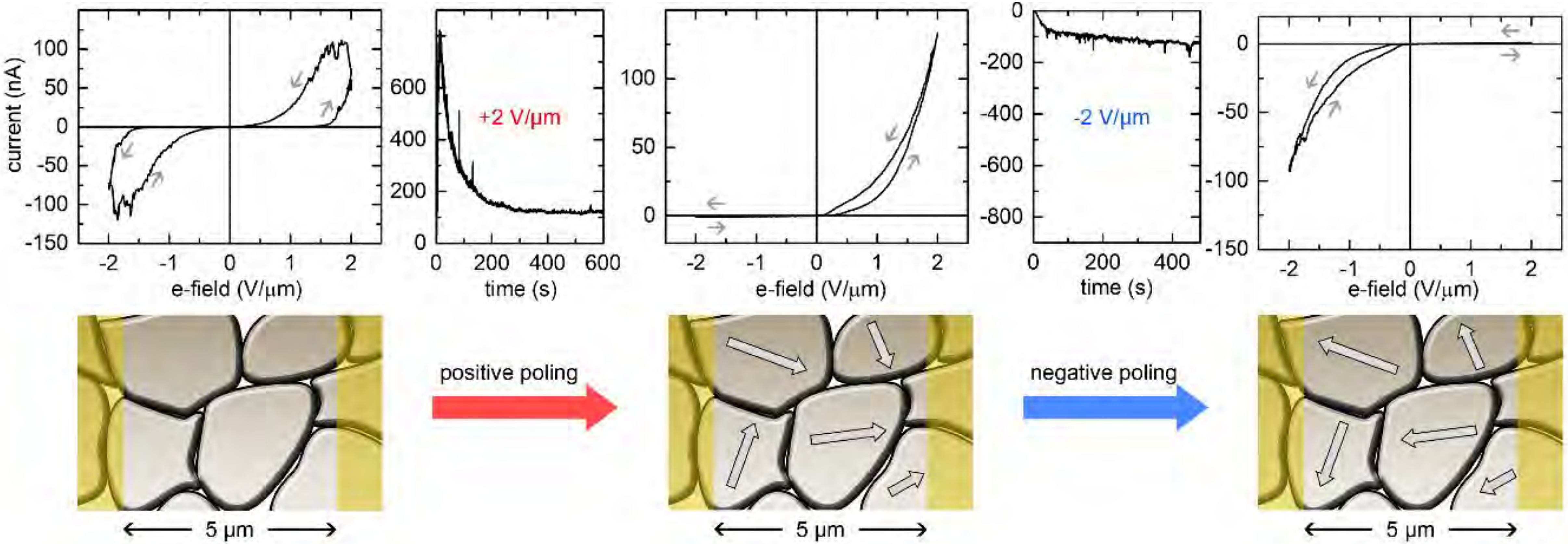




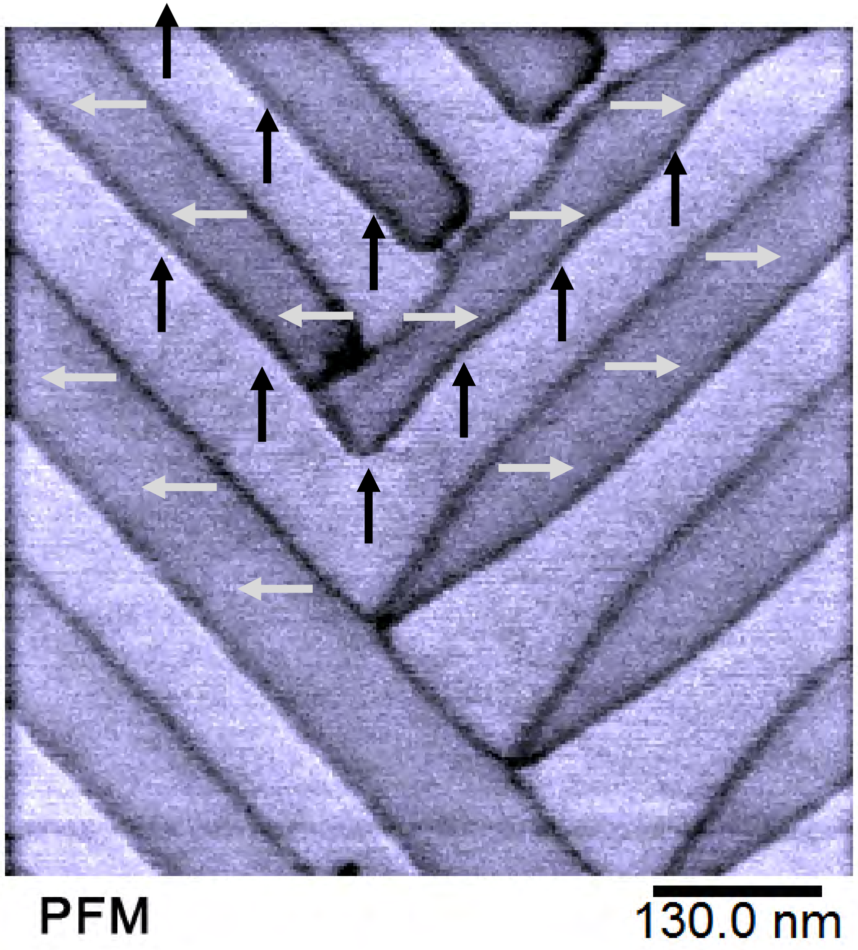
[H. Röhm et al., Adv. Funct. Mater. **2019**, 1908657]

Ferroelectric Poling



[H. Röhm et al., Adv. Funct. Mater. **2019**, 1908657]

What have we learned about the domains?



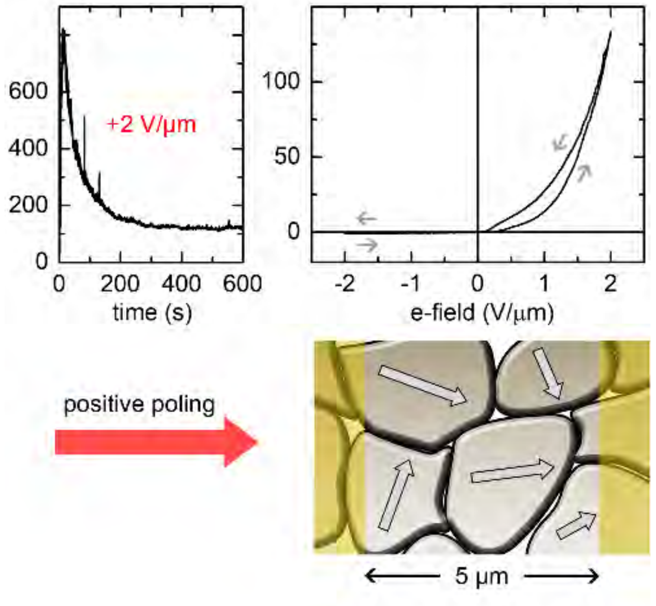
[H. Röhm et al., Adv. Mater., **2019**, *26*, 1806661]

- Domains are ferroelectric
  - Polarizable in E-field
  - LPFM/VPFM contrast
  - 180° phase contrast
  - Surface potential modulation

- The c- axis is oriented in-plane
- Polarization is oriented 45° towards domain walls
- Poling voltages are on the order of measurement voltages

$MAPbI_3$ is ferroelectric – so what?

1. Influence on J-V measurements?

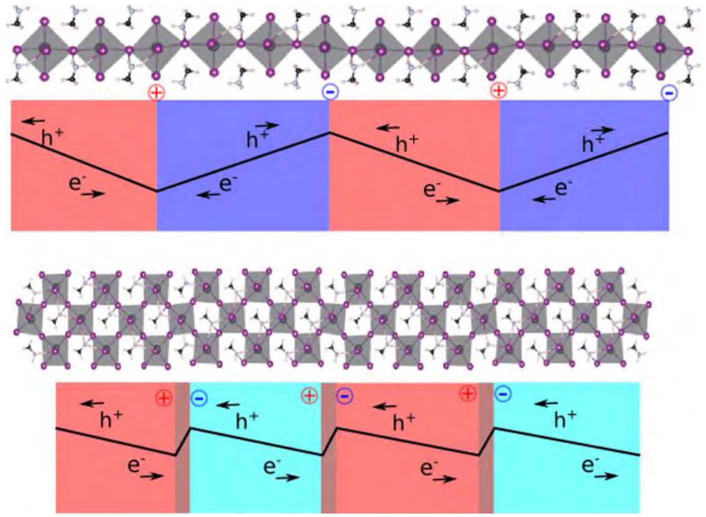


[H. Röhm et al., Adv. Funct. Mater. **2019**, 1908657]
[A. Colsmann et al., IOP J. Phys. Energy, **2019**, doi:10.1088/2515-7655/ab5b71]

2. Influence on excitons

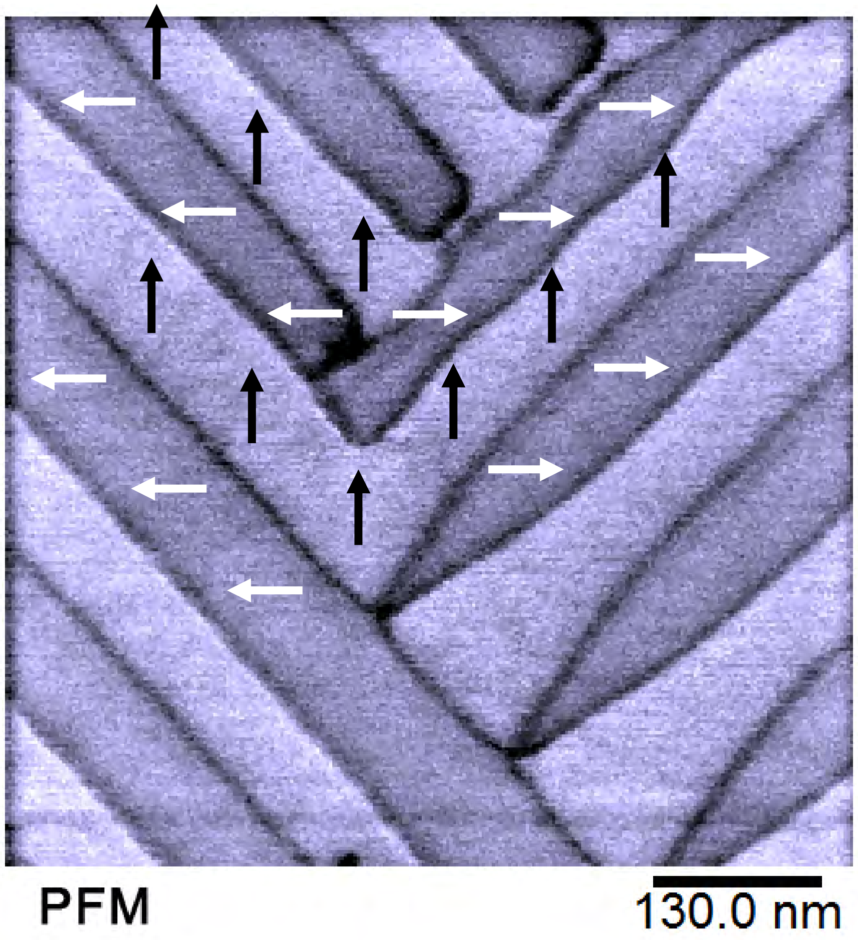
High ε, non-excitonic

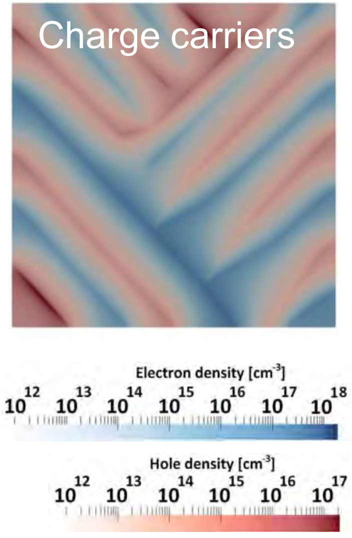
3. Influence on charge carrier separation & extraction

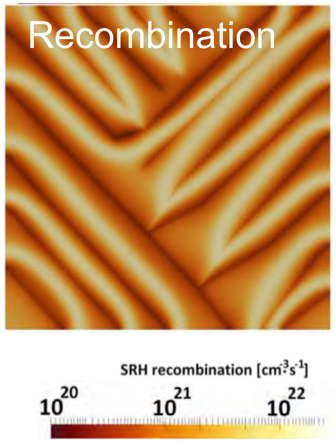


[S. Liu et al., J. Phys. Chem. Lett. **2015**, *6*, 693−699]

Importance of Ferroelectric Domains







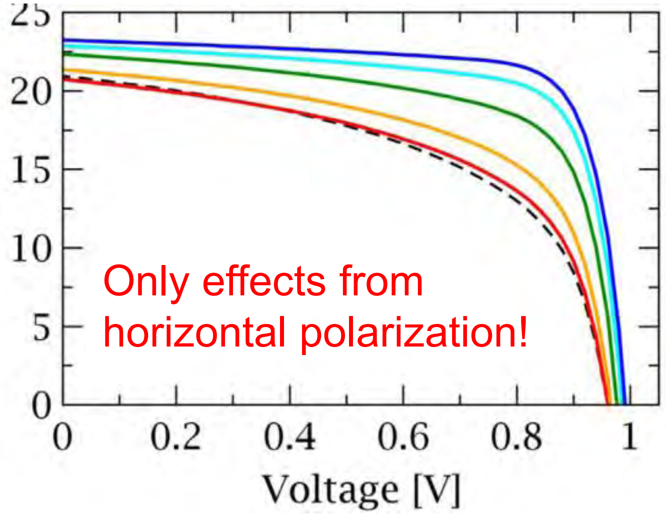
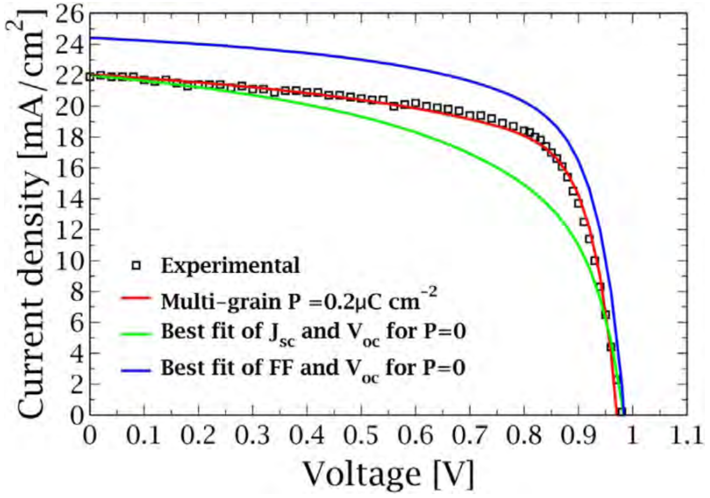


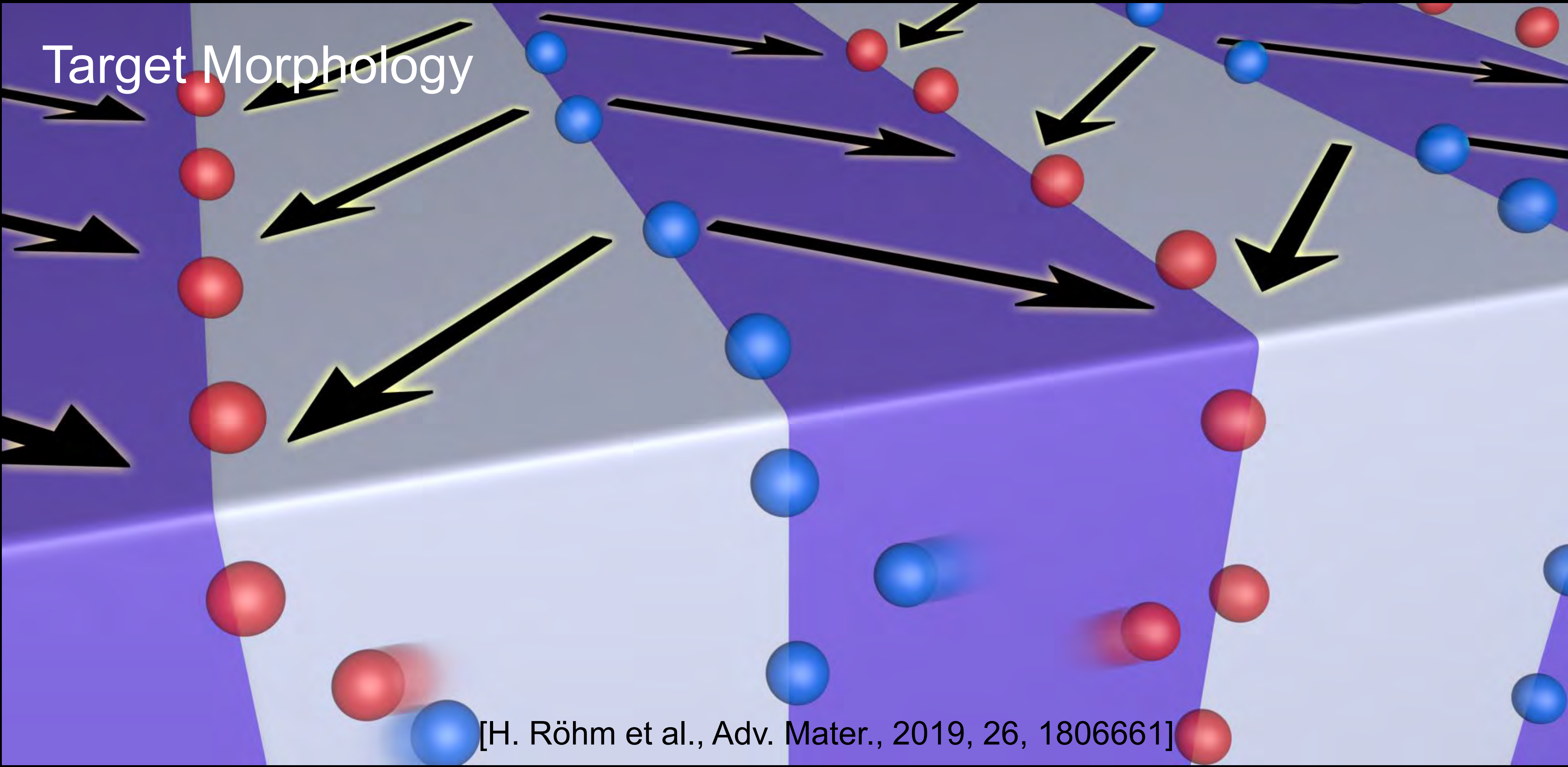
Table S1 Parameters used in the device simulations.

Parameter	**Symbol**	**Value**
Relative permittivity	ε	40
Hole and electron mobility	μ_n, μ_p	1 cm^{2}V^{-1} s^{-1}
Direct recomb. constant	k_2	10^{-9} cm^3 s^{-1}
SRH carrier lifetimes	τ_n, τ_p	$5 \cdot 10^{-10}$ s

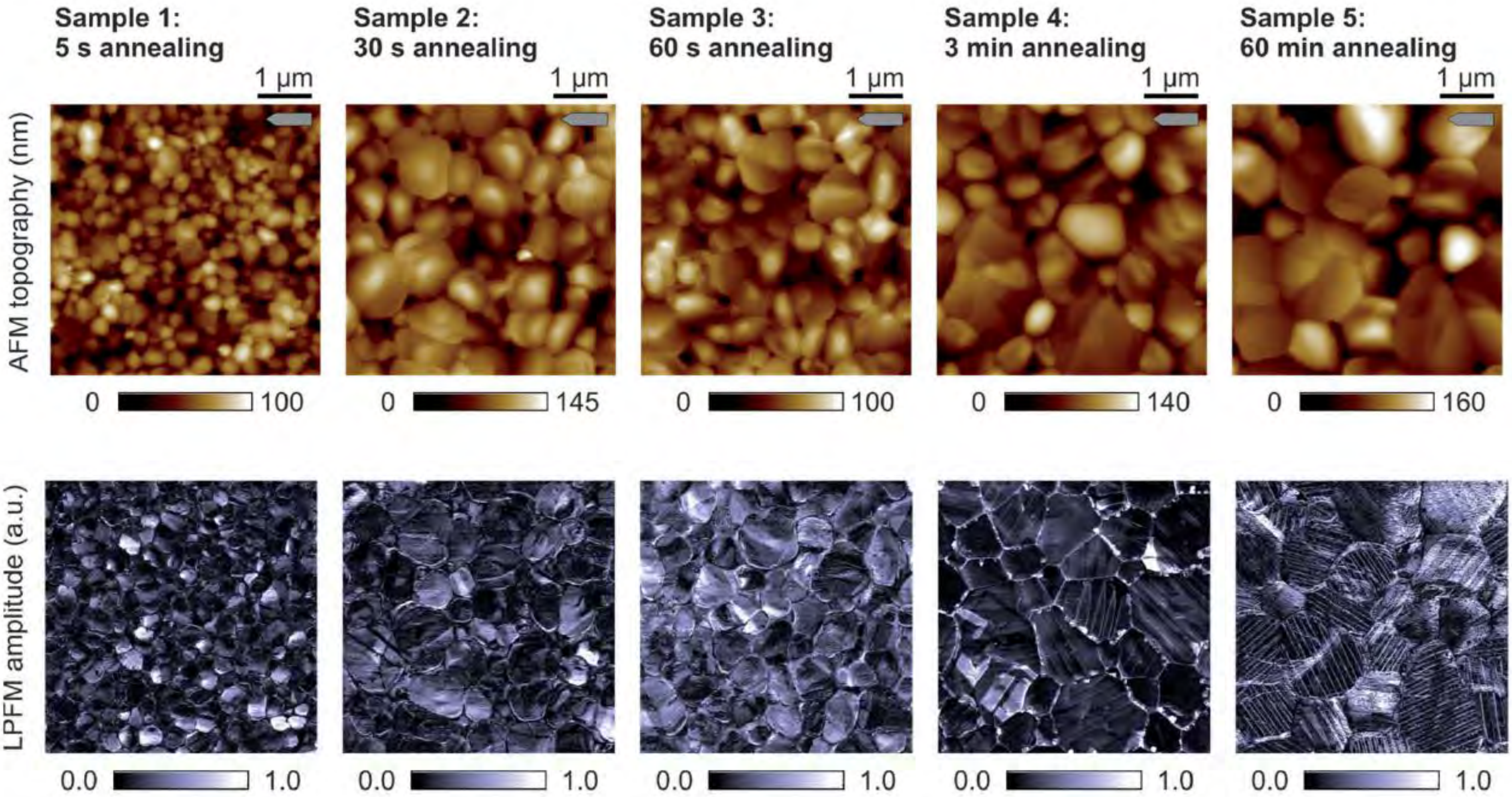


[D. Rossi, A. Colsmann, A. Di Carlo et al., Nano Energy **2018**, *48*, 20-26]

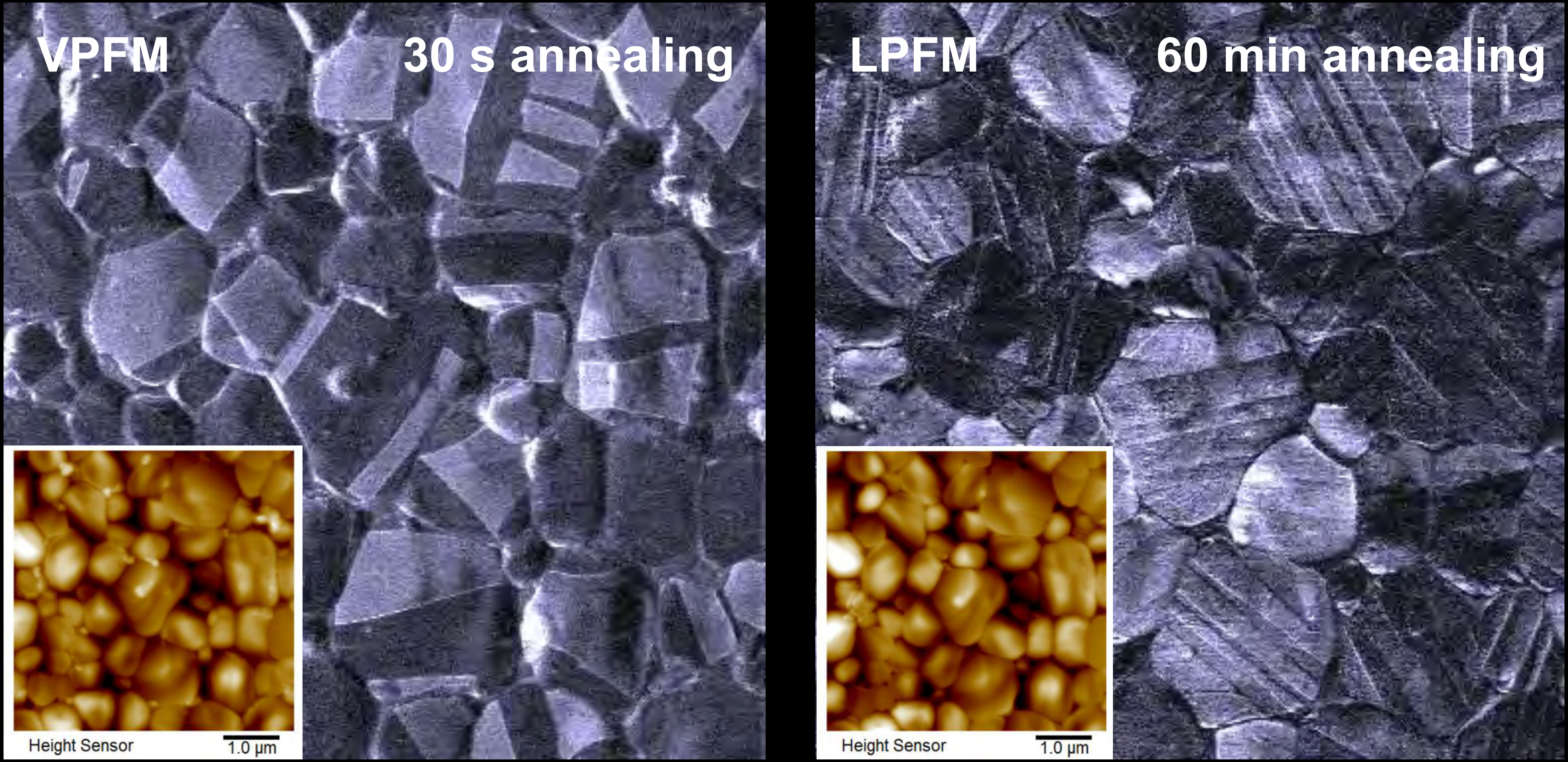
Target Morphology



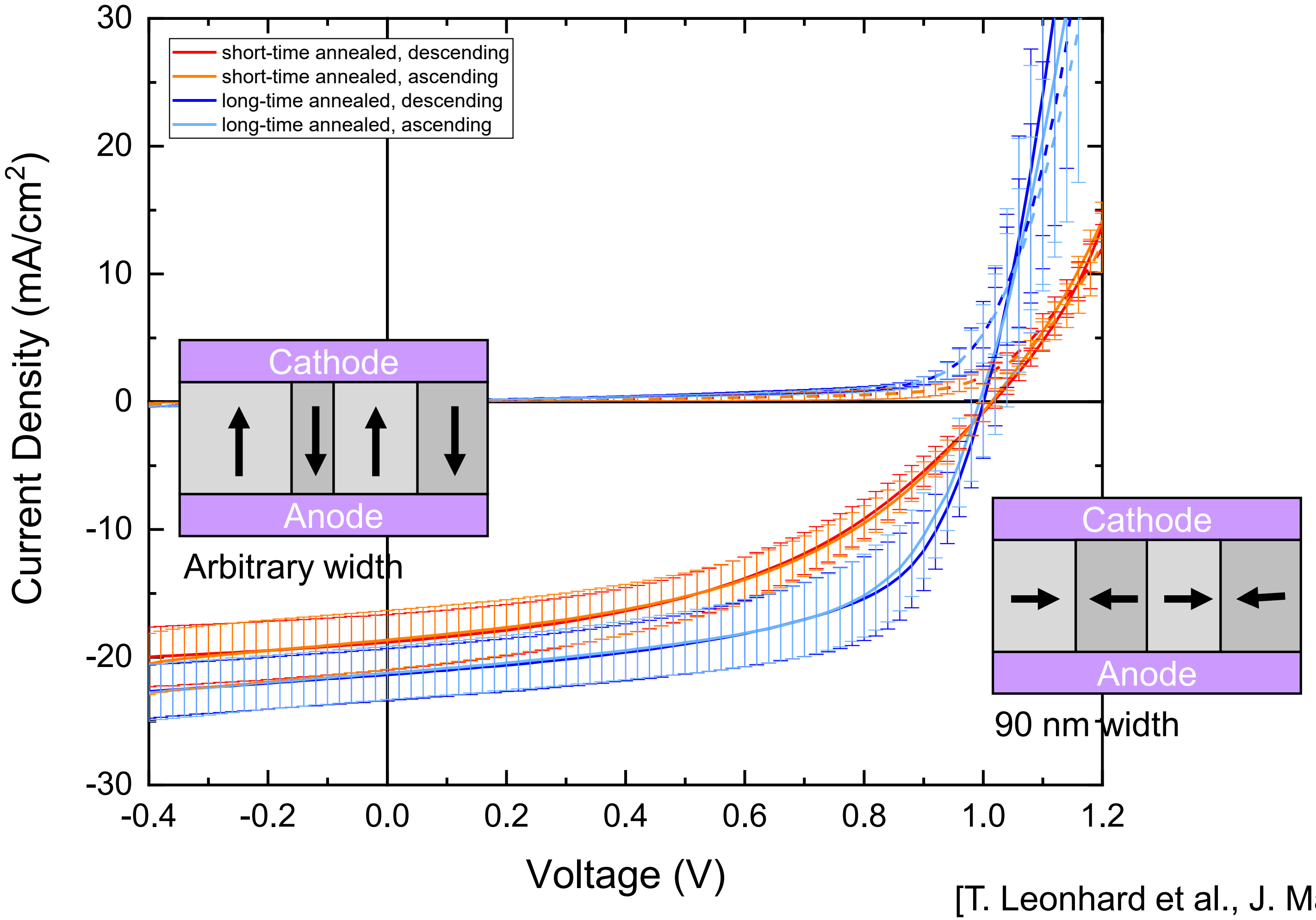
[H. Röhm et al., Adv. Mater., 2019, 26, 1806661]



Sample 1:
5 s annealing
Sample 2:
30 s annealing
Sample 3:
60 s annealing
Sample 4:
3 min annealing
Sample 5:
60 min annealing
1 µm
AFM topography (nm)
0
100
145
140
160
LPFM amplitude (a.u.)
0.0
1.0

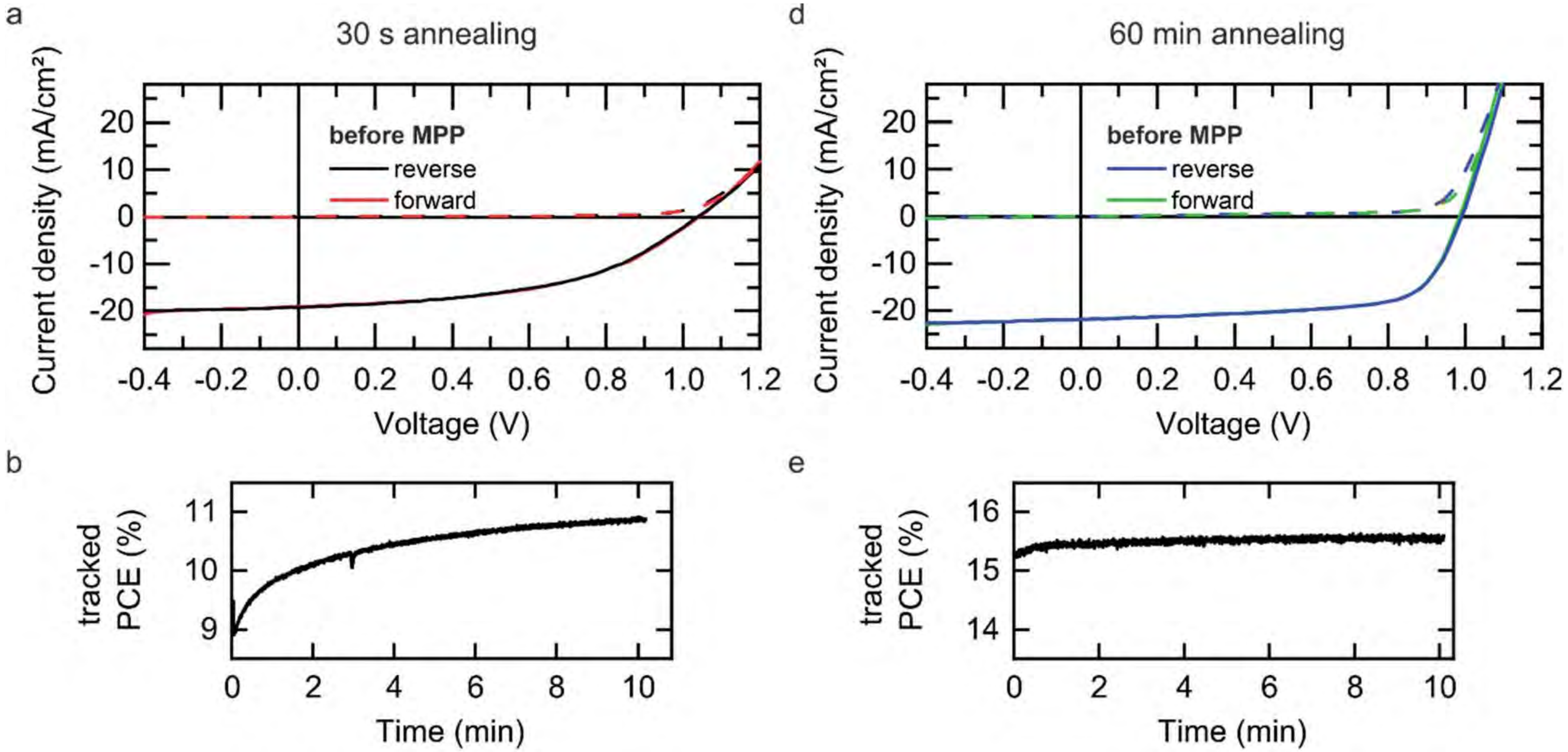

VPFM
30 s annealing
Height Sensor
1.0 µm
LPFM
60 min annealing
Height Sensor
1.0 µm

Importance of Ferroelectric Domains



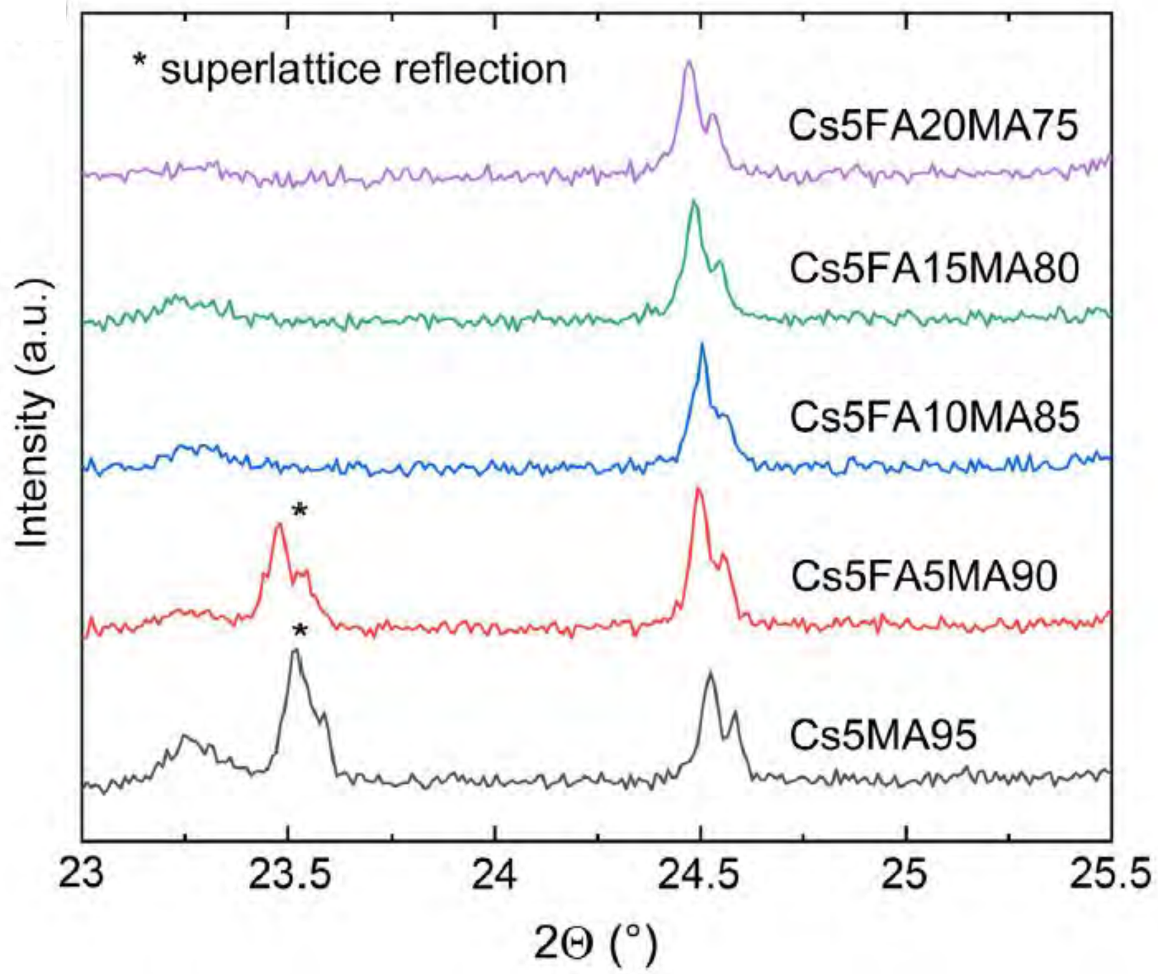
[T. Leonhard et al., J. Mater. Chem. A 2021, 9, 21845]

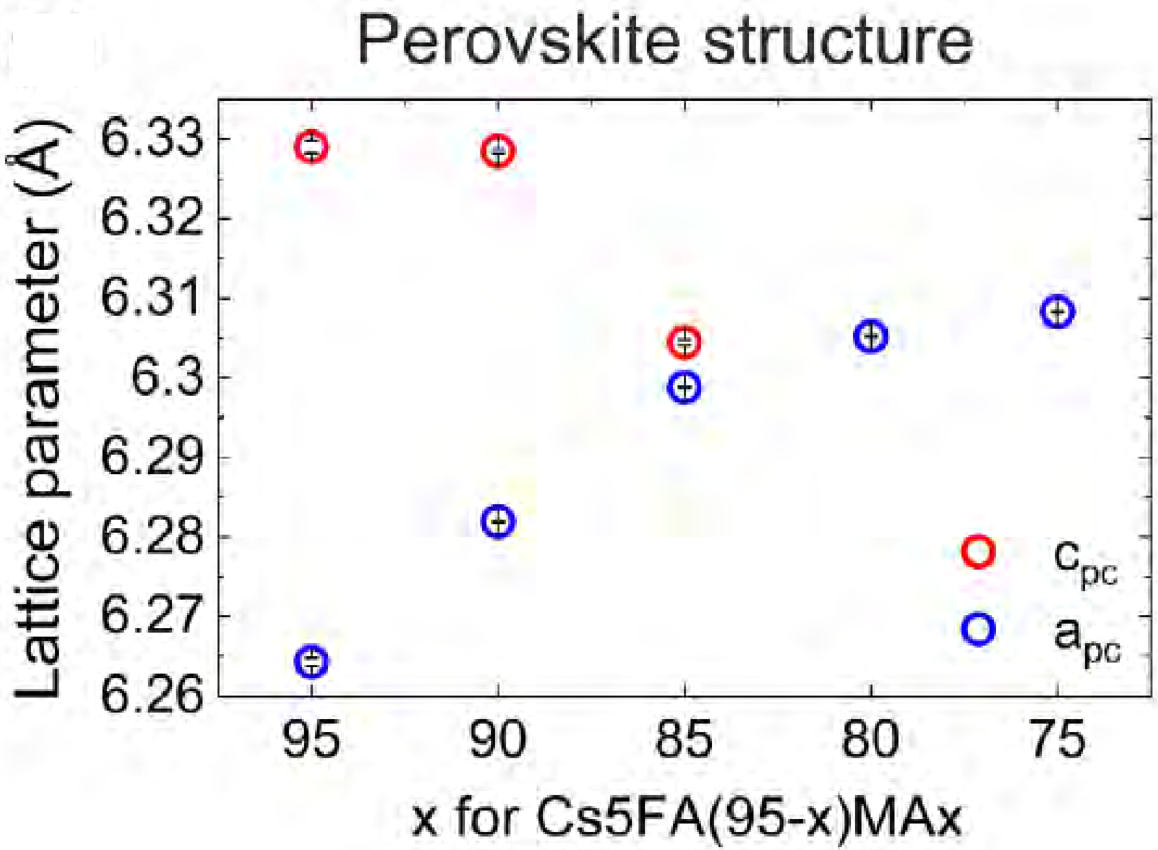
Importance of Ferroelectric Domains



[T. Leonhard et al., J. Mater. Chem. A 2021, 9, 21845]

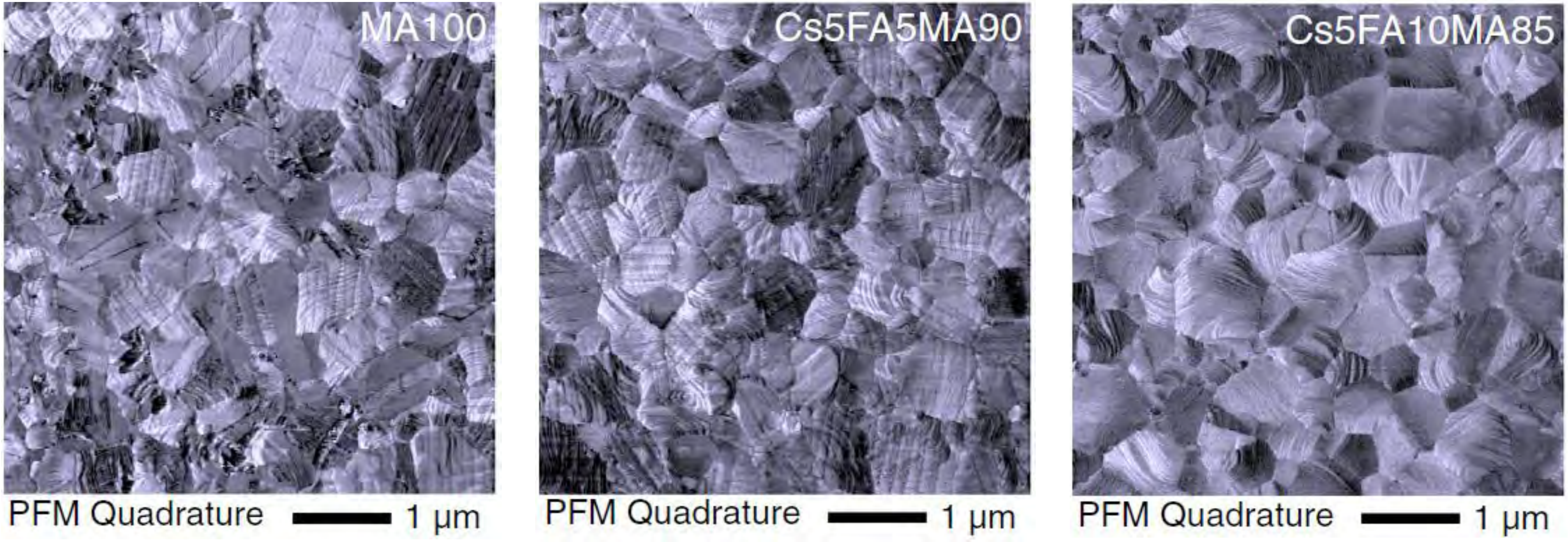
From $MAPbI_3$ to Triple-Cation Perovskites





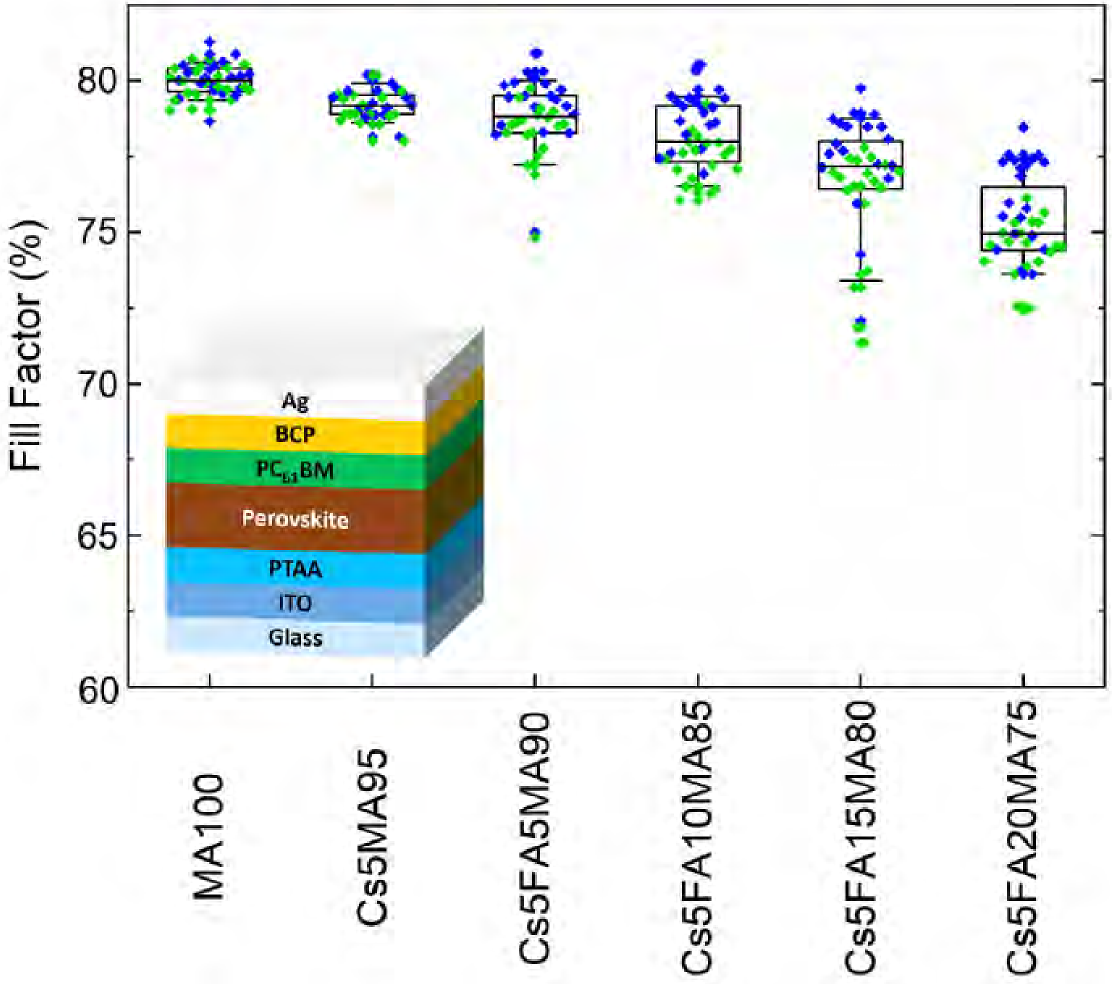
[A. Schulz et al., Solar RRL 2022, 2200808]

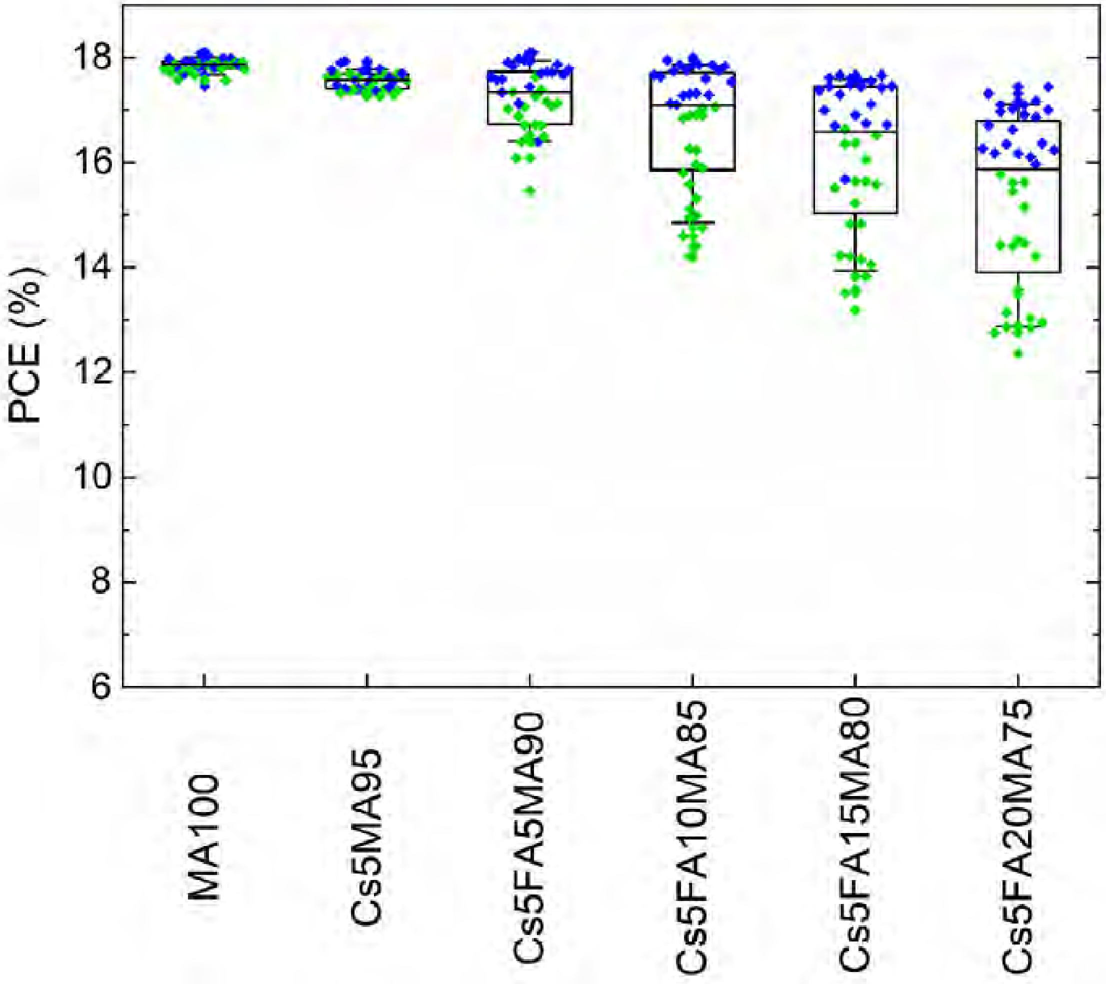
From $MAPbI_3$ to Triple-Cation Perovskites



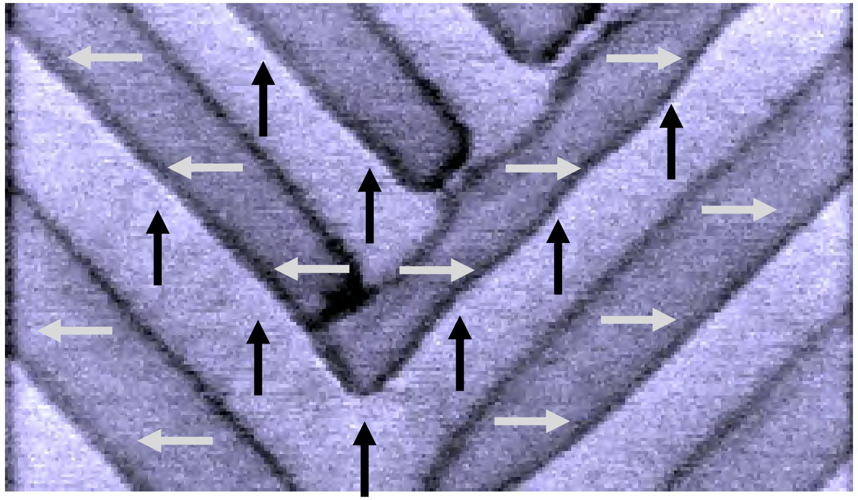
[A. Schulz et al., Solar RRL 2022, 2200808]

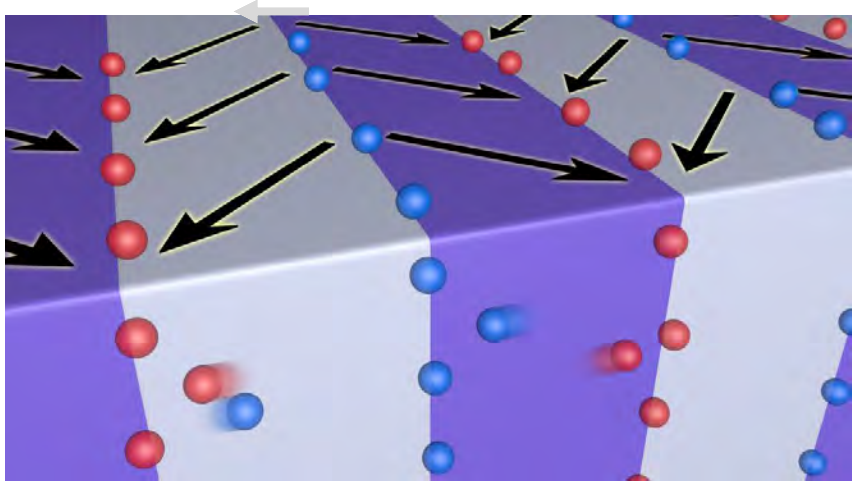
From $MAPbI_3$ to Triple-Cation Perovskites





Take-home message: $MAPbI_3$ is ferroelectric





- Domains are ferroelectric
  - Polarizable in E-field
  - LPFM/VPFM contrast
  - 180° phase contrast
  - Surface potential modulation

- c-Axis is oriented in-plane
- Polarization 45° towards domain walls
- Horizontal polarization helps cc extraction
- Orientation change upon ann.
- $V_{pol} \approx V_{J-V}$
- Ferroelectricity does not occur in TC-perovskites
- Design criterium for future PV materials ?

Contact

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Bundesministerium für Bildung und Forschung
BADEN-WÜRTTEMBERG STIFTUNG Wir stiften Zukunft

Erwin-Schrödinger-Preis 2019

HELMHOLTZ GEMEINSCHAFT

The perfect solar cell: How ferroelectricity improves power harvesting in perovskite solar cells

PD Dr. Alexander Colsmann, Holger Röhm (M.Sc.),
Prof. Dr. Dr. h.c. Michael J. Hoffmann, Tobias Leonhard (M.Sc.),
Dr. Susanne Wagner, Alexander D. Schulz (M.Sc.)

H. Röhm et al., Energy Environ. Sci. **2017**, *10*, 950-955
D. Rossi et al., Nano Energy **2018**, *48*, 20-26
T. Leonhard et al., Energy Technol. **2019**, *7*, 1800989
H. Röhm et al., Advanced Materials **2019**, *26*, 1806661
A. Schulz et al., Nature Materials **2019**, no. NM18124010B
H. Röhm et al., Adv. Funct. Mater. **2019**, 1908657
A. Colsmann, J. Phys. Energy **2019**, *2*, 011003
A. Colsmann et al., Energy Environ. Sci. **2020**, *13*, 1888
T. Leonhard et al., J. Mater. Chem. A **2021**, *9*, 21845
A. Schulz et al., Solar RRL **2022**, 2200808