Can Halide Perovskites be *Ferroelectric*?

Yes, they can !

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It has been proposed that Methylammonium (MA) lead halide perovskites ($MAPbBr_3$ and $MAPbI_3$) are ferroelectric and that this property explains some of their excellent photovoltaic behaviour. Using the periodic temperature change (Chynoweth) technique and the more classical electric field (*E*)-dependent polarization (*P*) we showed that $MAPbBr_3$ cannot be ferroelectric in either the cubic or tetragonal phase. While for $MAPbI_3$ such experiments are much more challenging, we report here now definitive experimental evidence for pyroelectricity of this material in the PV-relevant tetragonal phase. Ultimate proof for ferroelectricity comes from the *P(E)* hysteresis loop, which could be measured at -60 C with minimal sample degradation.

Background

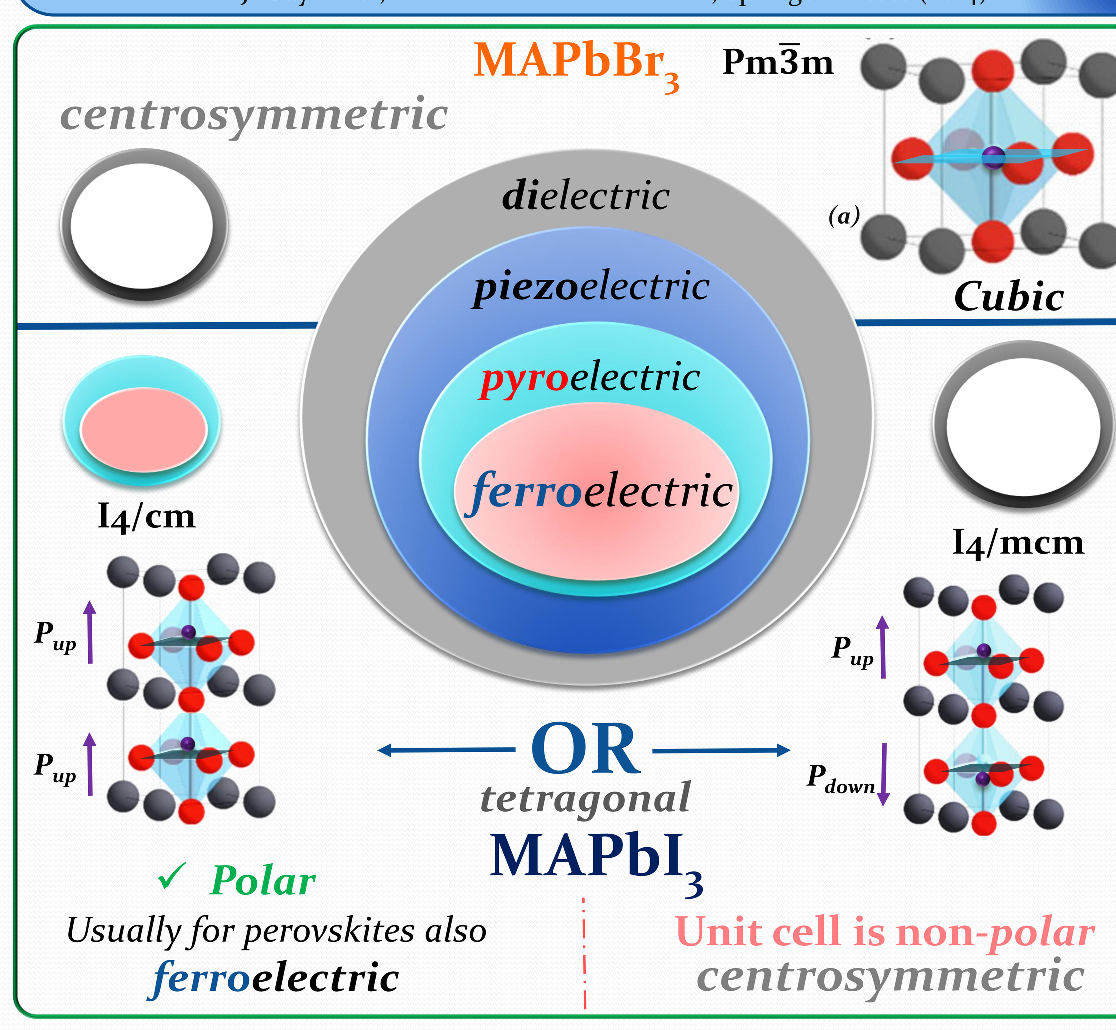
In $MAPbX_3$- based solar cells ferroelectricity could be responsible for :

- ❑ Long carrier lifetime
- ❑ Efficient charge separation
- ❑ Hysteresis

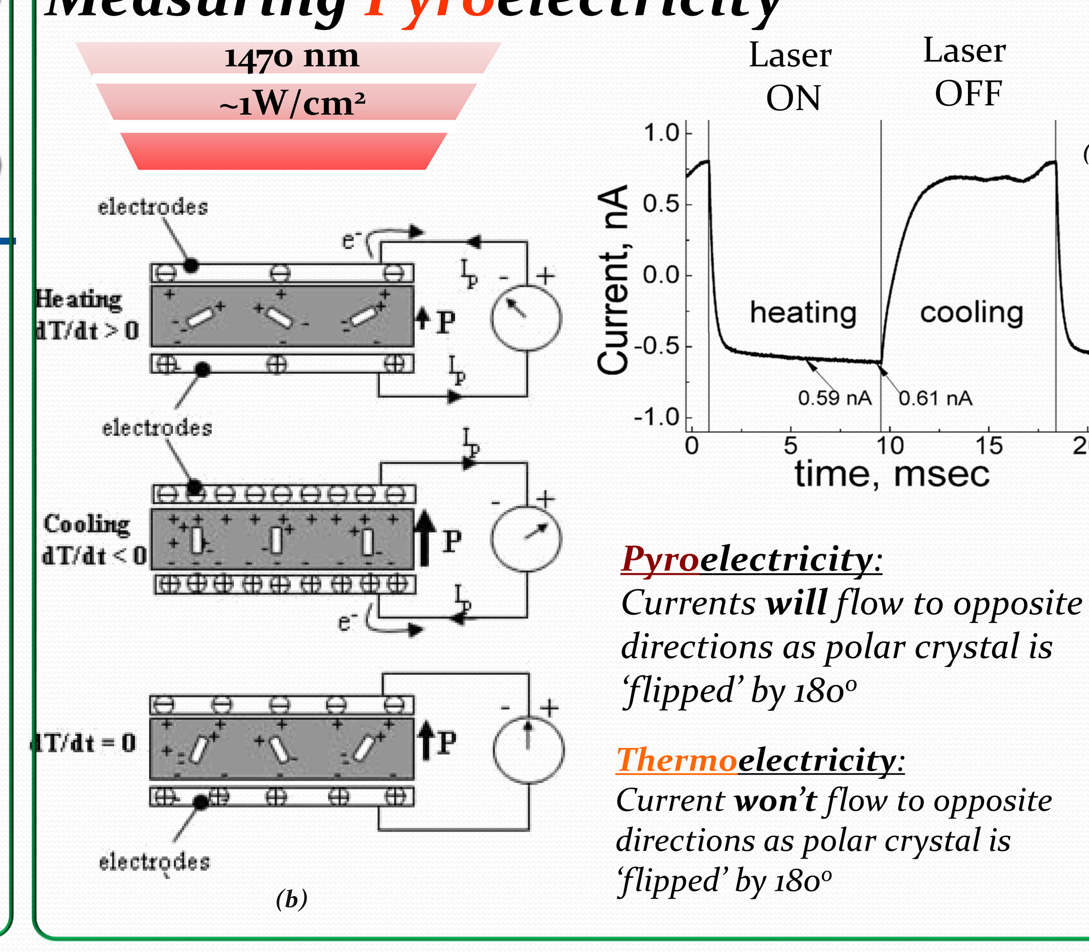
What is known so far ($MAPbI_3$)?

- ❑ Theoretical calculations (DFT, MD) support ferroelectricity
- ❑ Contradicting experimental evidence: Scanning probe suggests **piezo**electricity; absence of 2[nd] harmonic generation implies centrosymmetry; *cf. adjacent scheme* →
- ❑ ***P*** *vs.* ***E*** at **RT** (classical way to measure **ferro**electricity) did not provide evidence for existence of ferroelectricity.

(a) Crystal images are from: J. Guyonnet, *Ferroelectric Domain Walls*, Springer Theses (2014)
(b) Physics Today **2005**, 58 (8) 31-36
(c) I. Lubomirsky, O. Stafsudd, *Rev. Sci. Instrum.* **2012**, 83, 051101.



Measuring Pyroelectricity



Pyro*electricity:** *Currents* ***will *flow to opposite directions as polar crystal is 'flipped' by 180°*

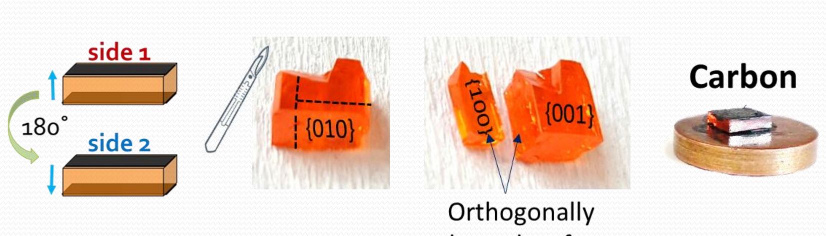
Thermo*electricity:** *Current* ***won't *flow to opposite directions as polar crystal is 'flipped' by 180°*

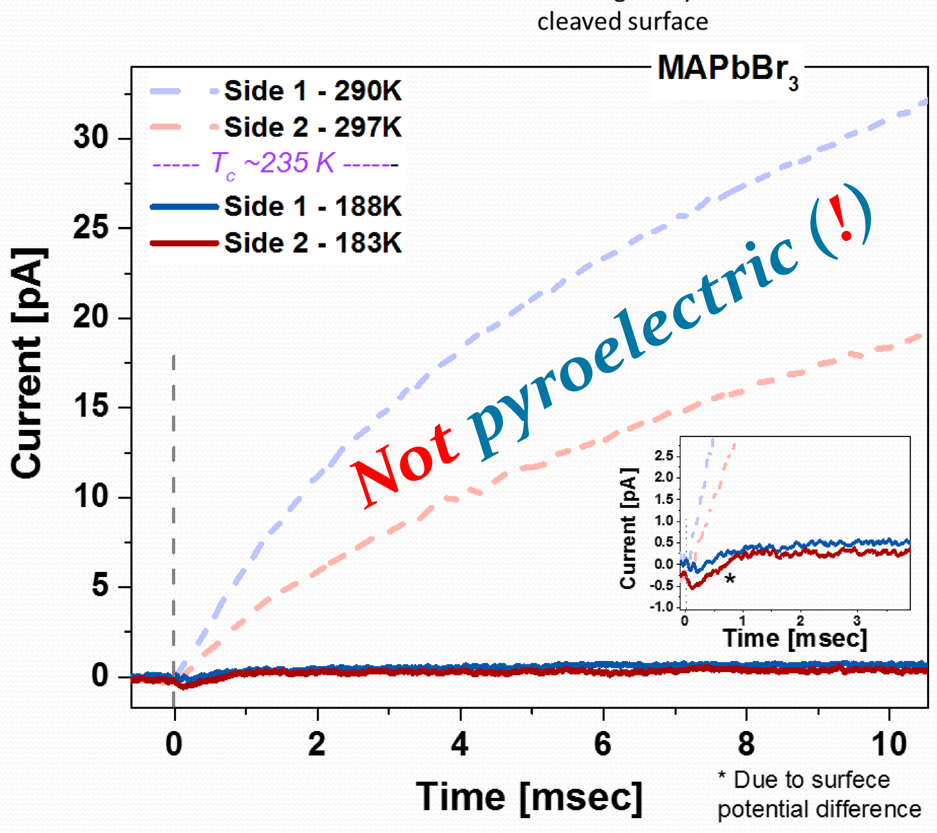
Results

Y. Rakita et al. *APL Mater.* **4**, 051101 (2016)

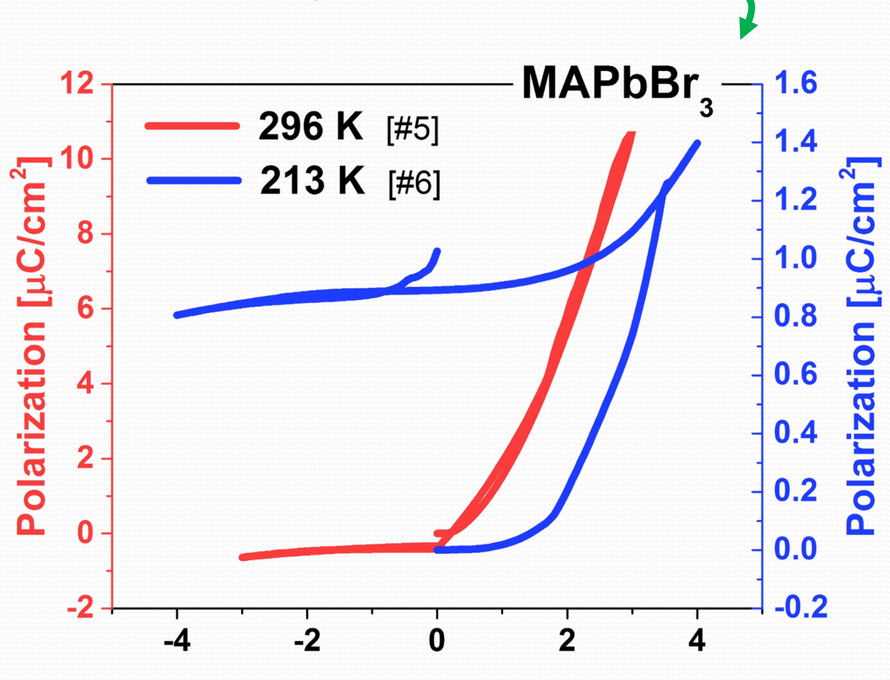
$MAPbBr_3$

- ✓ Eliminate thermoelectricity by cooling sample.
- ✓ After cooling **no** pyroelectric currents are observed.
- ✓ Also not in the tetragonal phase (<235 K)! *





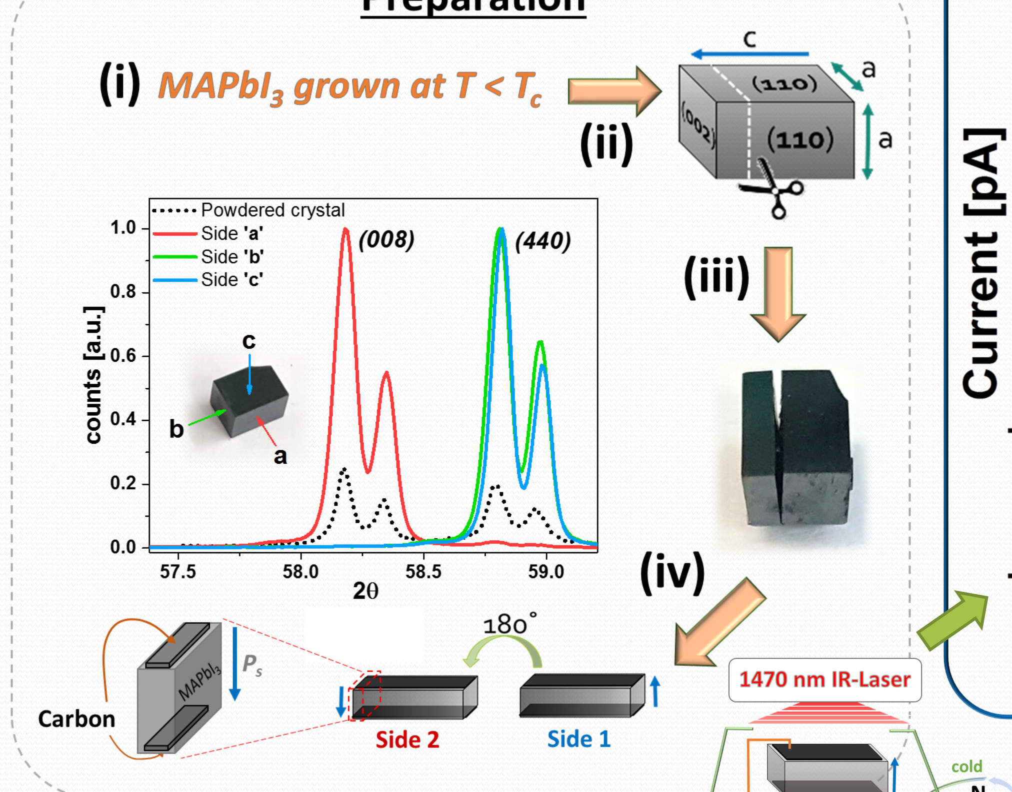
* This can be due to anti-parallel polar domain, creating zero net dipole.



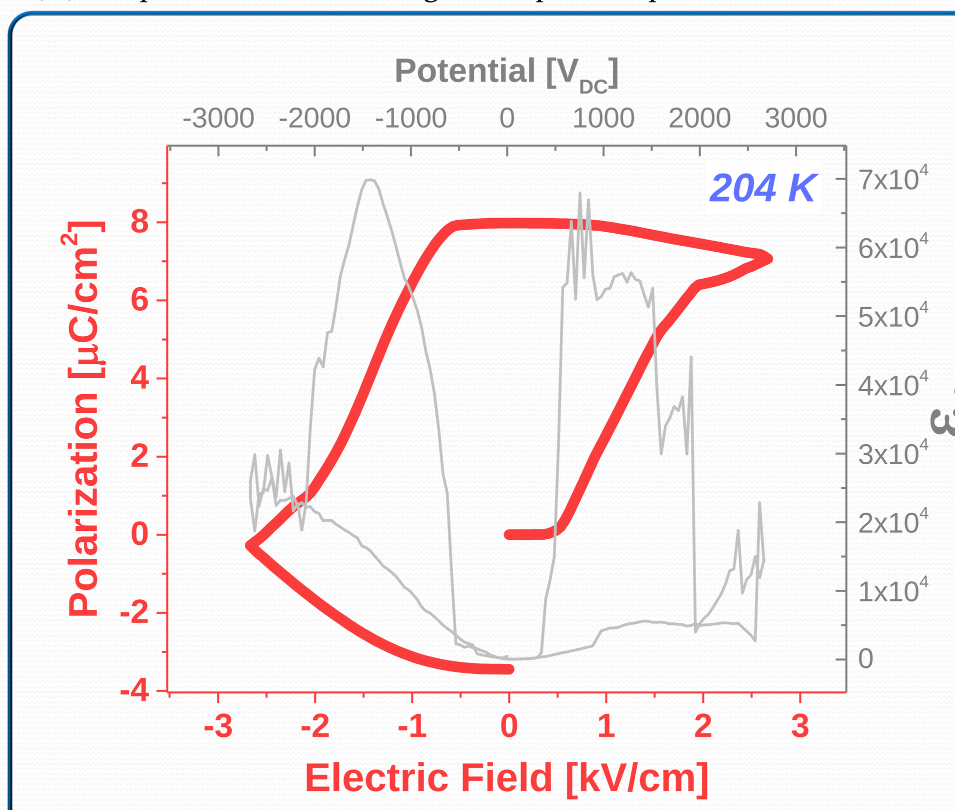
No ferroelectric-like hysteresis observed!

$MAPbI_3$

Preparation

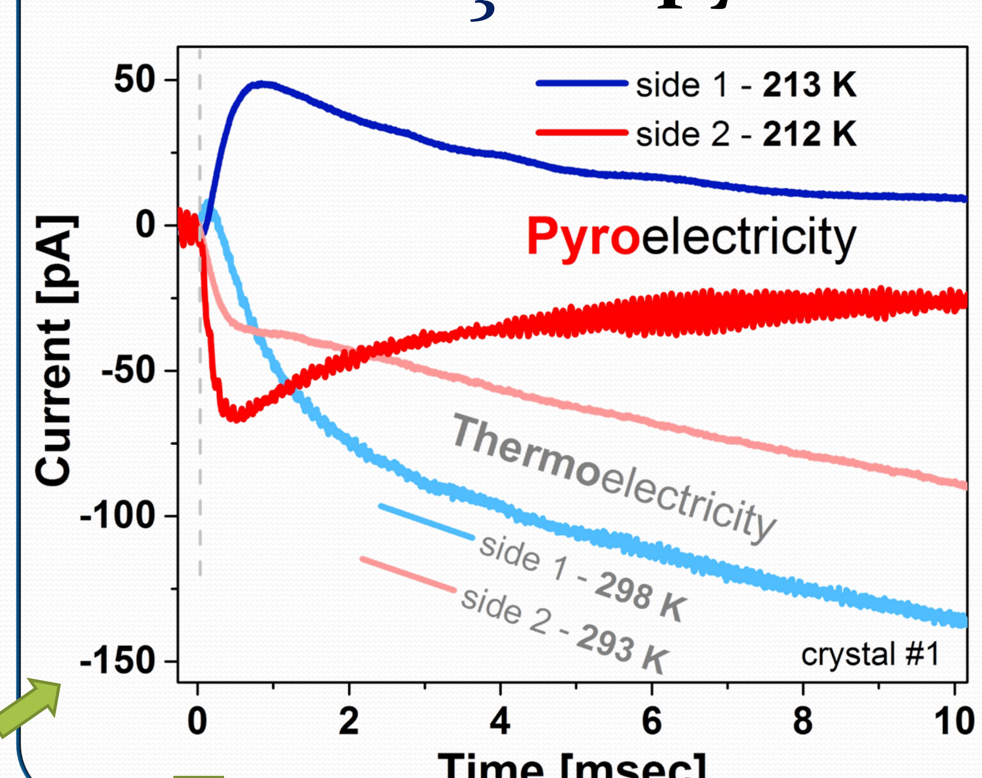


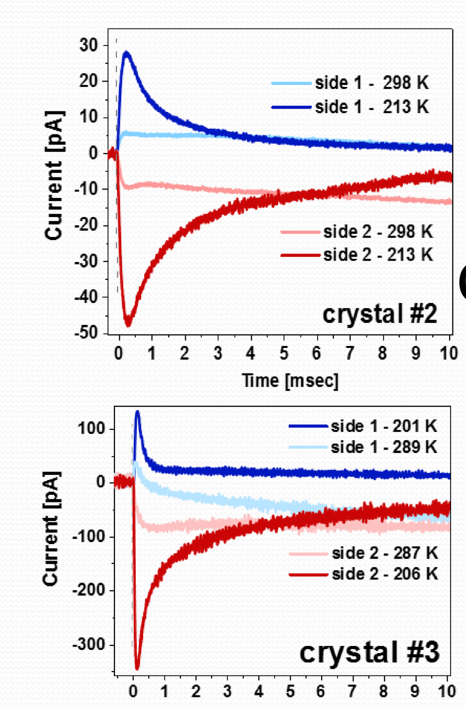
(i) – growth ; (ii) – face identification ;
(iii) – cleave orthogonally to possibly polar direction
(iv) – deposit electrodes orthogonal to possible polar direction



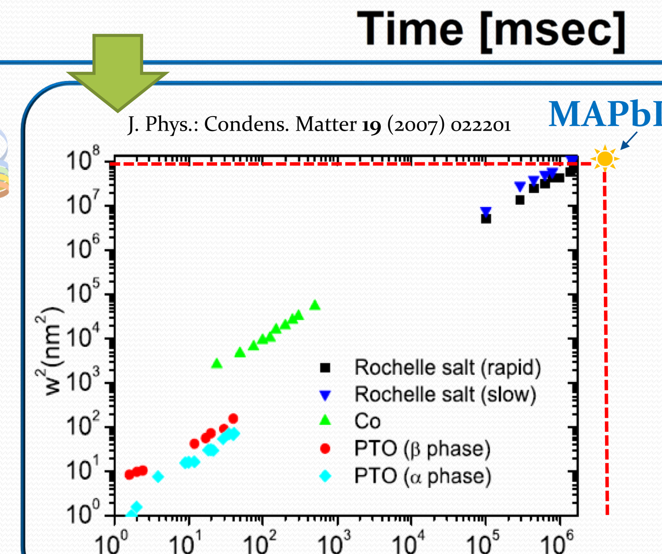
Hysteresis loop shows ferroelectric-like behavior!

$MAPbI_3$ – is pyroelectric = polar!





Observed for several crystals!



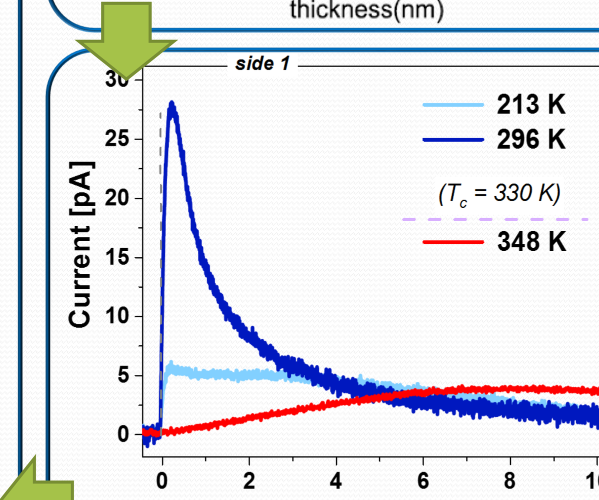
D. Ehre; *Ferroelectrics*, 472:41–49, 2014

The domain width (δ) using $I = I_0 \cdot erf\left(\frac{\delta}{2\sqrt{\alpha \cdot \tau}}\right)$

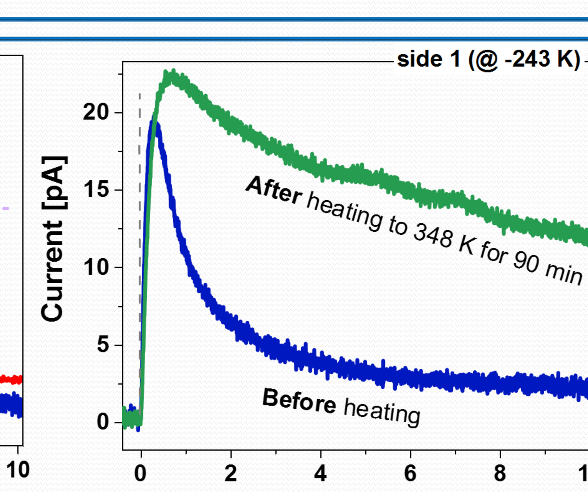
α – *thermal Diffusivity* ; τ – *half of the decay time*

Crystal #1 (L_z=10 mm) δ ≈ 38 µm
Crystal #3 (L_z=3 mm) δ ≈ 10 µm

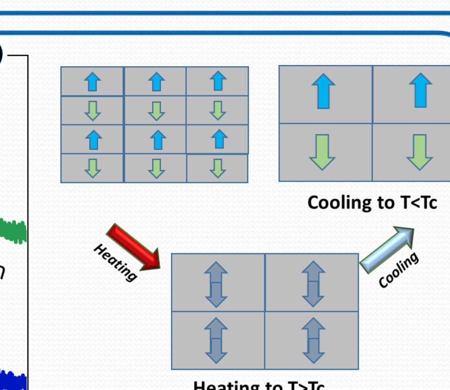
Domain size (w) scales with overall crystal width, as expected from theory!



Polar behavior disappears above T_c (330K)



Polarity is reversible



Suggested mechanism to post-heating domain growth

conclusions

$MAPbBr_3$

Both cubic and tetragonal $MAPbBr_3$ are *not* polar or ferroelectric! *

* Easily-trapped charges at the crystal surfaces and/or interfaces cause artificial pyroelectric-like behavior.

$MAPbI_3$

$MAPbI_3$ is *polar* and likely to have switchable ferroelectric domains (at least at 213 K)
The domain size scales similarly to other ferroelectric materials.