Direct experimental evidence for absence of polarity in $CH_3NH_3PbBr_3$ crystals

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Experiments to detect pyroelectricity in methylammonium lead bromide ($CH_3NH_3PbBr_3$), using periodic temperature change, show that any pyro response is not due to intrinsic polarity of the material, but to (easily) trapped charges. This result excludes ferro- (and possibly piezo-) electricity and "evidence" for such is due to charge trapping.

Why is it important?

In $CH_3NH_3PbX_3$-based solar cells ferroelectricity could be responsible for :

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

} nm- to µm-scale depleted zones between ferroelectric domains

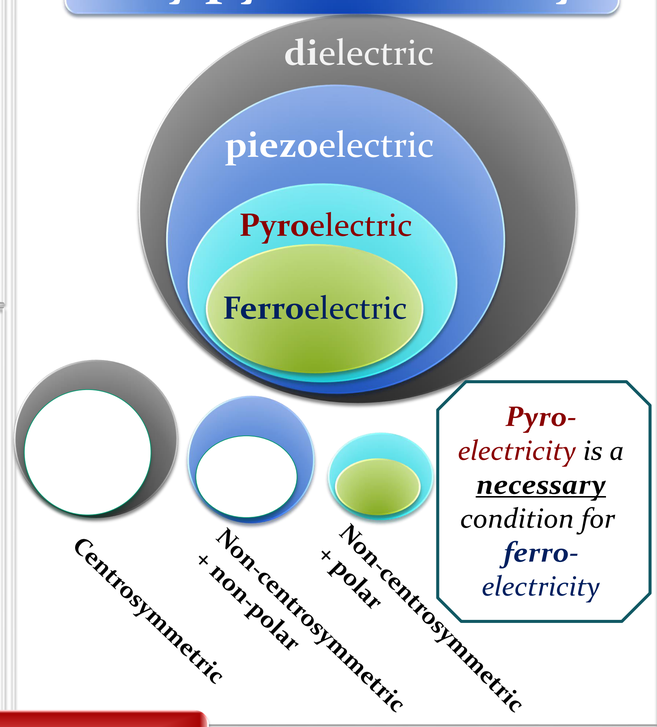
- ❑ **Hysteresis →** ferroelectric domain dynamic polarization

What is known?

- ❑ Several theoretical calculations (DFT, MD) support ferroelectricity
- ❑ Experimental evidence is contradictary (for **$CH_3NH_3PbI_3$**):
  - Piezoforce microscopy – observed **piezo**electric domains of ~100 nm
  - Cyclic voltammetry (classical way to measure **ferro**electricity) does not provide evidence for existence of ferroelectricity
- ❑ Neutron diffraction symmetries:

$CH_3NH_3PbI_3$	Tetragonal - I4cm	*both are **NON-polar** space groups*
$CH_3NH_3PbBr_3$	Cubic – Pm-3m	

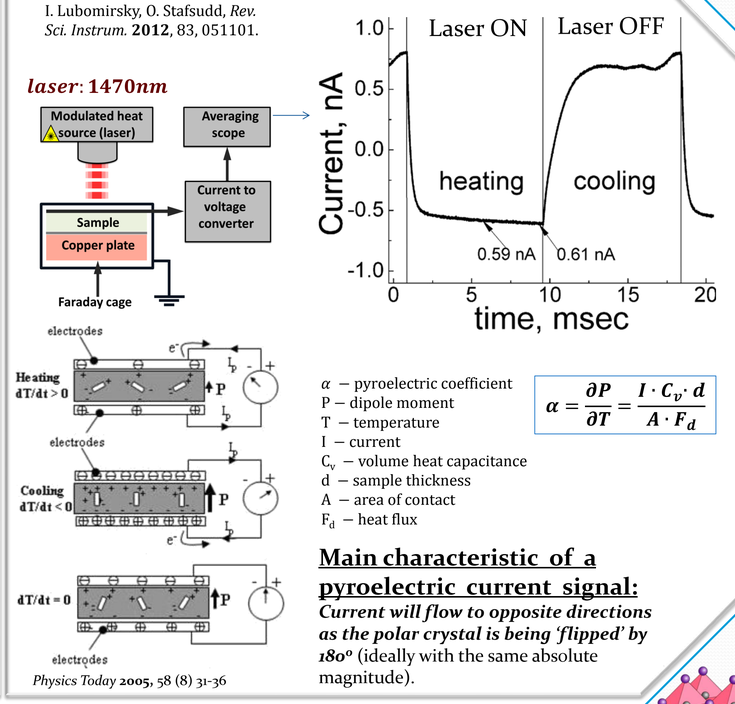
Why pyroelectricity?



***Pyro-**electricity is a **necessary** condition for **ferro-**electricity*

Experimental

I. Lubomirsky, O. Stafsudd, *Rev. Sci. Instrum.* **2012**, 83, 051101.

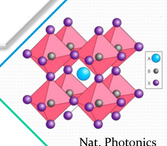


Physics Today **2005**, 58 (8) 31-36

α – pyroelectric coefficient
P – dipole moment
T – temperature
I – current
C_v – volume heat capacitance
d – sample thickness
A – area of contact
F_d – heat flux

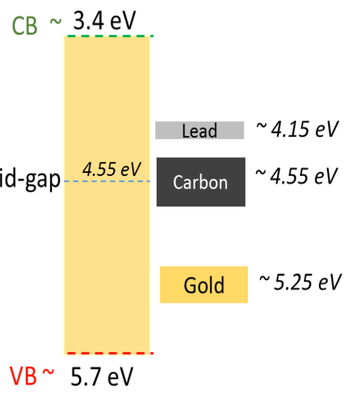
$$\alpha = \frac{\partial P}{\partial T} = \frac{I \cdot C_v \cdot d}{A \cdot F_d}$$

Main characteristic of a pyroelectric current signal:
Current will flow to opposite directions as the polar crystal is being 'flipped' by 180° (ideally with the same absolute magnitude).



Nat. Photonics **2014**, 8, 506–514

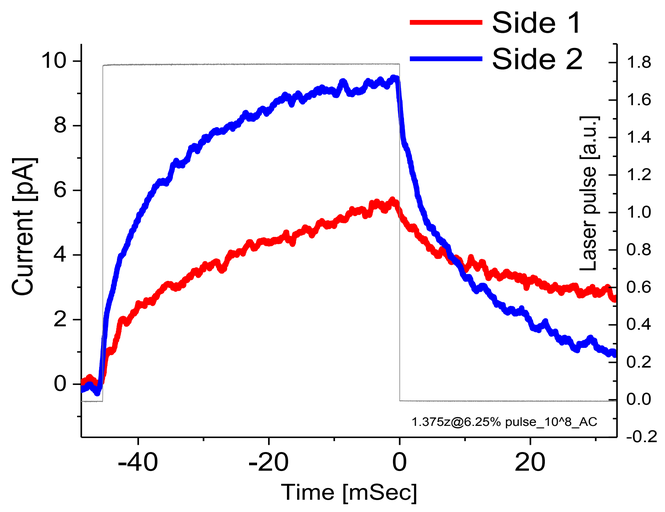
Results



The difference in work functions, which creates a different Schottky barrier, correlates with the polarization of the material.

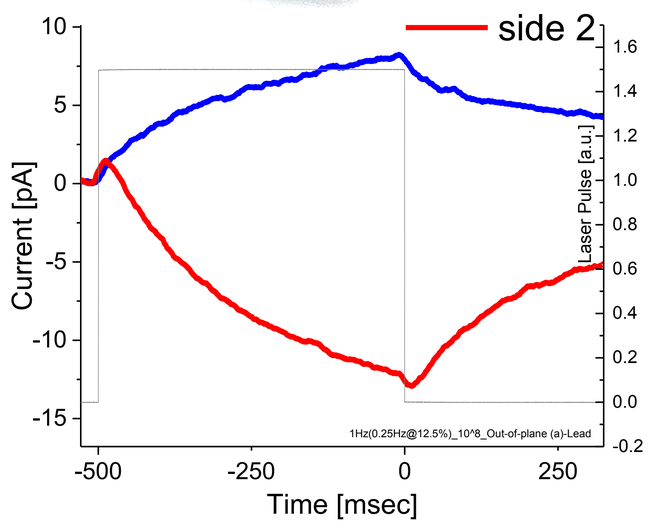
Carbon - Carbon

Carbon paste



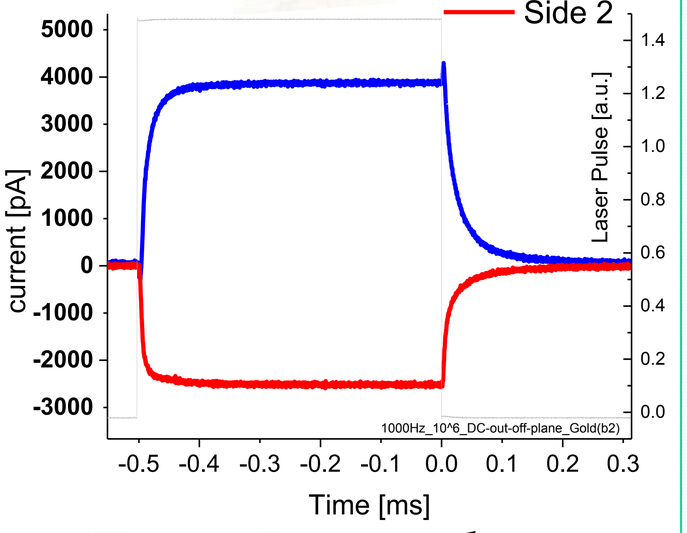
Lead – Lead

By thermal evaporation



Gold-Gold

By thermal evaporation



Heating

✓ Heating should release **trapped charges**.

✓ After flipping of the crystal the current did not change direction. Only thermoelectric currents remained.

✓ Making sure not to exceed the Curie temperature during the laser pulse

Poling

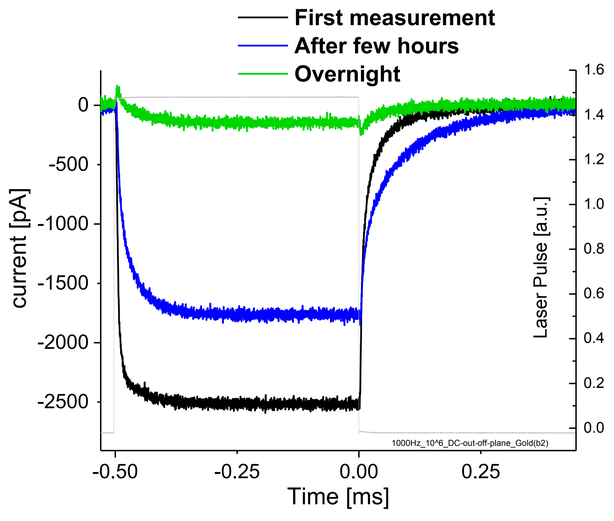
✓ **Trapped charges** can be stored. We see how poling changes the amount of trapped charges (battery-like).

Pole for 120 minutes
Short-circuit for 15 minutes
then measure

Time Dependence

x A natural pyroelectric signal will not change – **imbedded material property.**

✓ **Trapped charges** will de-trap and decrease the signal intensity.



Conclusions:

- ❑ **While we find evidence for polarity in $CH_3NH_3PbBr_3$, 'control' experiments support the existence of *trapped charges*, rather than of pyroelectricity.**
- ❑ **The easily-trapped charges at the crystal surfaces & interfaces can give rise to artificial signs of piezoelectricity, even though the symmetry of the crystal does not allow it.**