Direct experimental evidence for absence of polarity in CH$_3$NH$_3$PbBr$_3$ crystals

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Experiments to detect pyroelectricity in methylammonium lead bromide (CH$_3$NH$_3$PbBr$_3$), 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?
- Long carrier lifetime
- Efficient charge separation
- Hysteresis ➔ ferroelectric domain dynamic polarization

What is known?
- Several theoretical calculations (DFT, MD) support ferroelectricity
- Experimental evidence is contradictory (for CH$_3$NH$_3$PbI$_3$):
  - Piezoforce microscopy – observed piezoelectric domains of ~100 nm
  - Cyclic voltammetry (classical way to measure ferroelectricity) does not provide evidence for existence of ferroelectricity
- Neutron diffraction symmetries:
  - CH$_3$NH$_3$PbI$_3$: Tetragonal - 14cm
  - CH$_3$NH$_3$PbBr$_3$: Cubic – Pm-3m
  - both are NON-polar space groups

Results

Carbon - Carbon
- Carbon paste
- Lead - Lead
- 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
- 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$_3$NH$_3$PbBr$_3$, ‘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.