Are Halide-Perovskites Ferroelectric?

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Halide perovskite (HaP) semiconductors are revolutionizing photovoltaic (PV) solar energy conversion by showing remarkable performance of solar cells made with HaPs. In particular, the low voltage loss of these cells implies a remarkably low recombination rate of photogenerated carriers. It was suggested that low recombination can be due to the spatial separation of electrons and holes, a possibility if HaPs are semiconducting ferroelectrics, which, however, requires clear experimental evidence. As a first step, we show that **cubic methylammonium lead bromide ($MAPbBr_3$) is not pyroelectric and therefore cannot be ferroelectric**. In contrast, **tetragonal methylammonium lead iodide ($MAPbI_3$) is pyroelectric**, which implies it can be ferroelectric. The next step, proving $MAPbI_3$ is (not) ferroelectric, is challenging, because of the material's relatively high electrical conductance and low stability under high applied bias voltage. This excludes normal measurements of a ferroelectric hysteresis loop, to prove ferroelectricity's hallmark switchable polarization. By adopting an approach suitable for electrically leaky materials as tetragonal $MAPbI_3$, we show here ferroelectric hysteresis from well-characterized single crystals at low temperature. By chemical etching, we also can image the structural fingerprint for ferroelectricity, polar domains, periodically stacked along the polar axis of the crystal. We also succeeded in detecting clear second harmonic generation, direct evidence for the material's noncentrosymmetry. The dielectric anomaly at the tetragonal-cubic phase transition also supports the conclusion that **tetragonal $MAPbI_3$ is ferroelectric**.