# Lead halide perovskites are not ferroelectric

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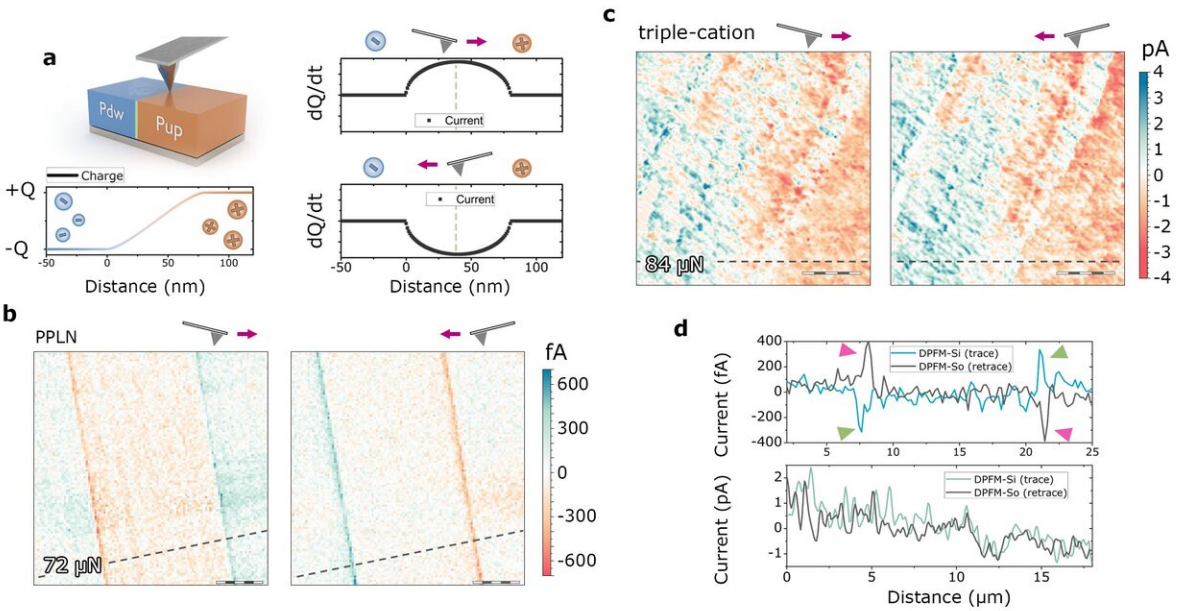


Scan direction dependence of the DPFM signals. (a) Scheme of the DPFM measurement of a ferroelectric sample (top left panel), with an antiparallel domain configuration, in which “Pdw” stands for “polarisation down” and “Pup” for “polarisation up”. (b) DPFM images obtained for periodically poled lithium niobate (PPLN) with an antiparallel domain configuration. Scale bar: 5 µm. (c) DPFM images of the CsFAMA perovskite scanned under similar conditions to those of PPLN. Scale bar: 5 µm. (. Credit: d) Random profiles extracted from PPLN (top panel) and the CsFAMA perovskite (bottom panel). Credit: ICMAB

In a solar cell, when the sunlight impacts the material, a charge is

generated. Specifically, this charge corresponds to an electron-hole pair, where an electron is excited to the conduction band, leaving a hole in the valence band. For the cells to be efficient, this pair of charges has to be separated and extracted as efficiently as possible (electron and hole must be directed to opposite electrodes to be captured) to generate an electric current. This is where ferroelectricity comes into play: this property would generate a built-in electric field in the material that could assist charge separation.

In the particular case of lead halide perovskites, ferroelectricity could help to understand why they work so well as active material in solar cells, and in fact, that was a plausible explanation so far. However, the study published in *Energy & Environmental Science* by researchers from the Institute of Materials Science of Barcelona (ICMAB-CSIC) and the Helmholtz-Zentrum Berlin für Materialien und Energie (Germany) demonstrate, for the first time, that the fact that these materials are optimal for solar cells is not due to ferroelectricity. "This work is very interesting for understanding why these cells are so efficient," says Andrés Gómez, researcher at the ICMAB-CSIC and first author of the article. We will have to keep looking for the final answer.

## The secret: The new technique used

The technique used to elucidate the non-ferroelectricity of lead halide perovskites is the DPFM (direct piezoelectric force microscopy) technique. A patent application describing the characterization of the technique was filed in 2017 by ICMAB-CSIC researchers. "Until now there was only one advanced mode of atomic force microscopy (AFM) called piezoresponse force microscopy (PFM) to study the ferroelectricity of these samples. However, this mode has caused a lot of controversy, as it is not reliable enough to distinguish between a ferroelectric material and one which is not. Although it is possible to measure ferroelectricity with PFM, other effects can give a false signal,

obtaining erroneous results," explains Gómez.

However, the DPFM technique, introduced in 2017 at the ICMAB-CSIC, complementary to PFM, measures the piezoelectric effect in a direct way and allows one to clearly discern if a sample is ferroelectric or not. The technique does not produce spurious signals, since it excludes many measuring artefacts because via the piezoelectric effect a mechanical energy is directly converted into electrical energy in a strictly proportional way. This fact is fundamental to be able to examine the existence of ferroelectricity in lead halide perovskites, an issue that has been under debate for several years.

For this study, polycrystalline samples of lead halide perovskites and samples of other materials with known ferroelectricity used as control were analyzed, and experiments were conducted with perovskites with different properties (grain size, layer thickness, different substrates, different textures, etc) using PFM and DPFM, and even EFM (electrostatic force microscopy).

This is the first time that the DPFM technique has been used in lead halide perovskite solar cells. "No other research group has been able, with nanometer-scale resolution, to elucidate whether these cells are really ferroelectric or not," says Gómez. Now we know.

**More information:** Andrés Gómez et al. Ferroelectricity-free lead halide perovskites, *Energy & Environmental Science* (2019). DOI: 10.1039/C9EE00884E