

## COMMENT

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View Journal | View IssueCite this: *Energy Environ. Sci.*, 2020, 13, 1888Comment on “ferroelectricity-free lead halide perovskites” by A. Gómez, Q. Wang, A. R. Goñi, M. Campoy-Quiles and A. Abate, *Energy Environ. Sci.*, 2019, 12, 2537Alexander Colsmann,<sup>a</sup> Tobias Leonhard,<sup>ab</sup> Alexander D. Schulz<sup>ab</sup> and Holger Röhm<sup>ab</sup>

This article comments on the recent publication “Ferroelectricity-free lead halide perovskites” by Gómez *et al.* [DOI: 10.1039/c9ee00884e], in which the authors conclude that both methylammonium lead iodide (MAPbI<sub>3</sub>) and the more advanced Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> form non-ferroelectric thin-films. This conclusion is based on measuring the vertical piezoelectric effect by “direct piezoelectric force microscopy” (DPFM) and not seeing any domain patterns or other ferroelectric responses. The authors calibrated their measurement using a bulk reference sample of periodically poled lithium niobate with vertical polarization, which has all-different properties from MAPbI<sub>3</sub> or Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> thin-films. In earlier works, it was pointed out that the polarization in large MAPbI<sub>3</sub> grains is vastly oriented in-plane and hence could remain invisible to any probing techniques with vertical sensitivity. In addition, the low spatial resolution of their measurements, the strong measurement noise, potential adventitious water contamination and the use of improper cantilever loads reduces the sensitivity of the measurement setup. This is why the conclusion on MAPbI<sub>3</sub> being non-ferroelectric is not supported by the measurement data.

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## 1. Introduction

In their recent publication “Ferroelectricity-free lead halide perovskites” Gómez *et al.* set out to investigate whether or not the archetypical methylammonium lead iodide (MAPbI<sub>3</sub>) and the more advanced Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> (CsFAMAPbIBr) are ferroelectric or not.<sup>1</sup> The authors employed a novel atomic force microscopy (AFM) method, which they named “direct piezoelectric force microscopy” (DPFM), to probe piezoelectric effects from domains with alternating polarization that commonly occur in ferroelectric materials.<sup>2</sup> More specifically, DPFM measures currents through the AFM tip that are generated by the piezoelectric effect in the sample under a mechanic load. On their bulk reference of periodically poled lithium niobate (PPLN) with vertically polarized domains they demonstrated that each ferroelectric domain produces a homogenous current under application of a vertical force. Whenever the AFM tip crosses the domain boundary from one domain with vertical polarization to another domain with antiparallel polarization, the current is enhanced. Since such

enhanced currents were not visible in MAPbI<sub>3</sub> and CsFAMAPbIBr thin-films, they concluded that neither of the two compounds is ferroelectric. Although DPFM may or may not bring an advantage over established piezoresponse force microscopy (PFM) techniques, such as single-frequency piezoresponse force microscopy (sf-PFM),<sup>3</sup> dual AC resonance tracking PFM (DART-PFM)<sup>4</sup> or band excitation PFM (BE-PFM),<sup>5</sup> their data does not allow to draw such comprehensive conclusions on the (non-)ferroelectricity of the two compounds under investigation. Earlier reports, for example by Leonhard *et al.*,<sup>6</sup> have produced evidence that (110) textured MAPbI<sub>3</sub> exhibits predominant in-plane polarization. The paper of Gómez *et al.* falls short in evidencing that DPFM, which uses vertical excitation, produces meaningful results on samples with in-plane polarization. The reported measurement resolution, probing setup and sensitivity further question the validity of their data interpretation.

## 2. On the importance of ferroelectricity in organic metal halide perovskites

Based on measuring the piezoresponse of thin-films by PFM or related techniques, the ferroic properties of MAPbI<sub>3</sub> and its derivatives have been discussed controversially for many years. Two schools exist, one of which claims evidence of material

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properties that are usually ascribed to ferroelectricity,<sup>3,4,7–9</sup> while the other interprets their PFM measurement data as charged thin-film surfaces, modulated by the mechanical modulus of ferroelastic domains.<sup>5,10,11</sup> What appears as an all-academic discussion to some, may actually have some severe implications for the solar cell operation and characterization.

If MAPbI<sub>3</sub> and some of its derivatives are ferroelectric, the corresponding solar cells may indeed exhibit very distinct properties which distinguish them from all other solar technologies known to date. Ferroelectric materials can form polar domains, that is, domains of permanent electrical polarization which create microscopic electrical fields. These electrical fields would influence the charge carrier transport, recombination and extraction within the light-harvesting layer. Simulations have shown that ferroelectric domains can provide charge-carrier-extraction 'highways' within the device for low recombination and efficient charge carrier transport to the electrodes.<sup>12–15</sup> If ferroelectricity can be evidenced experimentally, organic metal halide (OMH) perovskites would mark a blueprint for a disruptively novel solar cell architecture, which is why the interest in this topic is so strong. Further discussions and interests surround the possible impact of ferroelectricity on changes to the electrical solar cell characteristics during operation and common measurement routines. For example, the continuous application of a voltage to operate the solar cell at its maximum power point might lead to some poling of MAPbI<sub>3</sub> and its derivatives, so that the material under investigation changes its structure.<sup>16</sup> This situation can occur during operation, light-soaking or lifetime testing and would require a careful interpretation of measurement data.<sup>17</sup>

### 3. Cases for ferroelectricity in MAPbI<sub>3</sub>

Out of the various OMH perovskites, the archetypical MAPbI<sub>3</sub> is the most thoroughly investigated compound. This also holds true for reports on ferroelectricity in OMH perovskites. Ferroelectric materials can form polar domains. In turn, the occurrence of domains with alternating polarization can be considered an important indication for ferroelectricity. Using the converse piezoelectric effect, classical ferroelectrics are usually investigated by sf-PFM. Consequently, first reports on the ferroelectricity relied on sf-PFM investigations of MAPbI<sub>3</sub> thin-films comprising large grains with a diameter of several micrometers and a thickness of 300 nm, showing the formation of 90 nm wide domains.<sup>3</sup> In general, the size of ferroelectric domains depends on the crystal dimensions, here the grain size and thickness.<sup>18–20</sup> Opponents of the ferroelectricity hypothesis rightfully pointed out, that sf-PFM is prone to misinterpretation due to electrostatic effects that may be caused by ionic conductivity or surface charges.<sup>5,21</sup> Importantly, shortly after this discussion started, Dual AC Resonance Tracking PFM (DART-PFM) produced the same results, confirming earlier sf-PFM measurements.<sup>4</sup> Hence, sf-PFM measurements can make a case if interpreted carefully. Using lateral and vertical sf-PFM, Leonhard *et al.* further distinguished in-plane and out-of-plane polarization components within the domains, with the in-plane polarization strongly dominating on large grains.<sup>6</sup> This polarization

anisotropy is almost impossible to explain with ionic surface charging. In addition, using electron backscatter diffraction (EBSD) and X-ray diffraction (XRD), they found that the in-plane polarization coincides with a (110) thin-film texture and hence an in-plane orientation of the *c*-axis of the perovskite unit cell, which is very much in line with the crystal distortions observed in classical ferroelectrics. Not least, they found a 180° phase contrast in their lateral sf-PFM images, which is also indicative of ferroelectricity.

One of the reasons for the controversial debate may be the fact that MAPbI<sub>3</sub> is a semiconductor which has properties that are partly different from classical ferroelectrics which are insulators. This semiconductivity, for example, renders the poling of domains in an external electrical field difficult, since strong electric fields would produce significant currents through the device which can damage the perovskite layer. This hallmark for ferroelectricity has long been experimentally inaccessible, until very recently Röhm *et al.* have presented the modulation of domains in an external electric field<sup>22</sup> which should settle the discussion in favor of ferroelectricity. We note that the strong ionic conductivity of MAPbI<sub>3</sub> certainly plays an important role in the general picture, for example as screening charges for the microscopic ferroelectric fields, but it cannot explain all of the observations on the domain structures discussed above such as the PFM anisotropy in vertical/lateral direction.

### 4. DPFM measurements by Gómez *et al.*

Gómez *et al.* attempted to overcome limitations of sf-PFM by using DPFM to disprove ferroelectricity in MAPbI<sub>3</sub> and the more advanced CsFAMAPbIBr. Yet, the manuscript contains a number of shortcomings related to the interpretation of data, to the sensitivity of the measurement setup and to the choice of references.

Firstly, their measurement geometry might be blind for domains with lateral polarization. Gómez *et al.* exclusively used vertical excitation in DPFM and vertical piezoresponse in sf-PFM which are both designed to measure out-of-plane piezoresponses. Assuming a non-negligible *d*<sub>31</sub>-coefficient of the compounds, the authors handwavingly argue that DPFM can also be used to track effects from lateral (in-plane) polarization. However, no proof of this claim is provided in their report or in their earlier paper on the working principle of DPFM.<sup>2</sup> A discussion on the polarization orientation would have been essential. Their MAPbI<sub>3</sub> samples (Fig. S15, ESI of the original manuscript) show a dominant (110) texture with the *c*-axis of the crystal's unit cell being widely oriented in-plane. According to the earlier work of Leonhard *et al.* and Vorpahl *et al.*, this in-plane orientation of the *c*-axis coincides with an in-plane polarization of the sample.<sup>4,6</sup> Both demonstrated vast differences in contrast between vertical and lateral PFM. Hence, the assumption of being able to measure effects from in-plane polarizations by DPFM does require sound evidence. Simply not seeing any in-plane piezoresponse, therefore, forbids any conclusion about the presence or absence of ferroelectricity in general.



Secondly, the insulating and vertically polarized PPLN appears to be an improper reference for validating their measurement technique. In light of the discussion above, a reference with a lateral polarization would have been more appropriate to demonstrate the reliability of the measurement technique. In addition, the polarization in MAPbI<sub>3</sub> is expected to be around  $0.2 \mu\text{C cm}^{-2}$ ,<sup>14</sup> which is significantly lower than in most common ferroelectrics and which may be a result of the semiconducting nature of MAPbI<sub>3</sub>. In contrast, PPLN has a more than two orders of magnitude larger polarization of  $78 \mu\text{C cm}^{-2}$ .<sup>23</sup> The detectability of domains in PPLN simply does not warrant the detectability of domains with a much weaker polarization in MAPbI<sub>3</sub>. On vertically poled PPLN, the authors recorded currents on the order of 300–400 fA, induced by the piezoelectric effect. The much lower dipole strength of MAPbI<sub>3</sub> should produce much lower measurement currents. On the other side, the noise in the DPFM measurements on CsFAMAPbIBr is on the order of picoampere (pA) (Fig. 1d of the original manuscript). The same applies to the DPFM measurements of MAPbI<sub>3</sub> (Fig. 4 of the original manuscript). Clearly, there are strong non-piezoelectric current contributions in the CsFAMAPbIBr and MAPbI<sub>3</sub> perovskites, which might conceal the piezoelectric currents.

It would have been much more convincing, if the authors had reproduced any of the common lateral and vertical sf-PFM measurements on MAPbI<sub>3</sub> that were reported in the literature. They could have referenced DPFM to these standard sf-PFM measurements and hence demonstrate the disputable superiority of DPFM.

Thirdly, in DPFM, the measurement currents which are directly correlated to vertical charge separation in the piezoelectric sample, depend on the mechanically applied force. To measure this effect appropriately, suitable cantilevers must be used taking into account both the sensitivity for the current detection and the properties of the investigated sample. For the hard PPLN and PZT bulk samples, rather stiff cantilevers with spring constants of  $250 \text{ N m}^{-1}$  and  $80 \text{ N m}^{-1}$  can produce reasonable data. However, applied to the relatively soft, polycrystalline MAPbI<sub>3</sub> thin-film samples with high conductivity, these cantilevers might not produce meaningful data or can even damage the samples. The vast majority of previous publications on the ferroic properties of OMH perovskites used cantilevers with spring constants smaller than  $3 \text{ N m}^{-1}$ .<sup>3,4,6,8,11,21,24</sup> Strelcov *et al.* explicitly pointed out sample damages from high loading forces and recommended the application of forces in the range of 20 to 40 nN, which would not harm the sample surface.<sup>10</sup> Going against this consensus, Gomez *et al.* conducted their experiments with loading forces in the  $\mu\text{N}$ -regime which makes the interpretation of the measurement data even more questionable. Moreover, all previous reports used Pt/Ir or Cr/Ir coated tips and contact resonance conditions. Choosing a set of measurement parameters outside the proven and accepted parameter space without justification makes it difficult to compare their data to the literature and questions their validity.

Fourthly, it is highly questionable, whether the authors can see ferroelectric domains or enhanced currents at the domain boundaries at the given spatial resolution. The DPFM micrographs that they recorded cover areas between  $10 \times 10 \mu\text{m}^2$  and

$40 \times 40 \mu\text{m}^2$  and have a resolution of  $256 \times 256$  pixels. This corresponds to each pixel representing a sample area between  $40 \times 40 \text{ nm}^2$  and  $160 \times 160 \text{ nm}^2$ . The PPLN reference was not investigated as a thin-film but rather as a bulk material, which can result in much larger domains that can be detected with the reported spatial measurement resolution. However, as has been reported in the literature before, the typical width of domains in MAPbI<sub>3</sub> thin-films is 90 nm which is on the borderline of the spatial resolution limit or even well below. The authors further report a measurement atmosphere of reduced humidity. Still, the reported humidity of 8% is high enough for adventitious water contamination of the hydrophilic perovskite surface to reduce the measurement resolution and sensitivity.

Altogether, the work of Gómez *et al.* lacks the critically important discussion of sensitivity limits below which any polarization would not be detectable. Not seeing ferroelectric domains does not prove their absence.

## 5. Conclusions

The measurement data presented by Gómez *et al.* does not allow the exclusion of the ferroelectric nature of MAPbI<sub>3</sub> or CsFAMAPbIBr thin-films as stated in their manuscript. Besides a questionable measurement sensitivity and resolution, compelling and very detailed evidence exists in the literature that makes a case for ferroelectricity of MAPbI<sub>3</sub>. Although direct microscopic observation of electrical poling was not known at the time of their publication, the authors should have compared their results to the known properties of MAPbI<sub>3</sub> thin-films and its derivatives. Earlier works have produced evidence that thin-films of MAPbI<sub>3</sub> vastly do not show out-of-plane polarization but in-plane polarization. Hence, DPFM would have had to be modified to apply a lateral excitation of the samples under investigation.

## Conflicts of interest

There are no conflicts of interest to declare.

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