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KEYWORDS

Perovskite solar cells, hybrid perovskites, piezoresponse force microscopy, ferroelasticity, ferroelectricity, twin domains

ABSTRACT

Methylammonium lead iodide (MAPbI_3) perovskite shows an outstanding performance in photovoltaic devices. However, certain material properties, especially the possible ferroic behavior, remain unclear. We observed distinct nanoscale periodic domains in the piezoresponse of $\text{MAPbI}_3(\text{Cl})$ grains. The structure and the orientation of these striped domains indicate ferroelasticity as their origin. By correlating vertical and lateral piezoresponse force microscopy experiments performed at different sample orientations with x-ray diffraction, the preferred domain orientation was suggested to be the a_1 - a_2 -phase. The observation of these ferroelastic fingerprints appears to strongly depend on the film texture and thus the preparation route. The formation of the ferroelastic twin domains could be induced by internal strain during the cubic-tetragonal phase transition.

INTRODUCTION

The development of solar cells based on methylammonium lead iodide (MAPbI_3) perovskite has seen impressive dynamics over the past few years.¹⁻³ Intensive research has pushed the power conversion efficiency (PCE) of perovskite solar cells to a certified value of over 20 %.⁴ Besides their inexpensive production, the success of perovskite solar cells originates from the unique properties of the perovskite: a strong optical absorption and charge carrier diffusion lengths of up to 1 μm that lead to internal quantum efficiencies of more than 90%.⁵⁻¹¹ However, the physical

origin of these properties as well as their dependence on the device architecture and on the preparation route are not fully understood.

A fundamental material property that has been suggested in the context of the unique solar cell performance is ferroelectricity.¹² Frost *et al.* suggested that charged ferroelectric domain walls could act as charge carrier-specific pathways through the perovskite grains.¹² It has also been proposed that ferroelectricity of the perovskite material causes the hysteretic anomaly that has been observed in the photocurrent- voltage (I - V) curves of perovskite solar cells.¹²⁻¹⁷ This hysteresis leads to an overestimation of the PCE and its origin is heavily discussed. It has been suggested that time dependent processes, such as migrating ions, electronic traps or the alignment of the spontaneous polarization upon applying an electric field, contribute to the hysteresis.^{5-6, 13, 18-24} However, more recent publications indicate that ferroelectricity does not contribute to the hysteresis at all or only in a minor way, as opposed to ion migration and electronic traps.^{18, 20, 23, 25}

MAPbI₃, like other perovskite materials, fulfils the structural requirements for a ferroic material: The lead and the halide ions build a three dimensional network of corner-sharing PbI₆ octahedra. The organic methylammonium cations (MA⁺) occupy the cuboctahedral gap. At temperatures above 327 K, MAPbI₃ crystallizes in a cubic structure, between 165 K and 327 K in a tetragonal structure and below 165 K in an orthorhombic structure.²⁶⁻²⁹ The tetragonal structure at room temperature was found to crystallize either the non-polar, centrosymmetric space group $I4/mcm$ ^{28, 30-31} or the polar space group $I4cm$.²⁶⁻²⁷ The symmetry lowering phase transition from the cubic $Pm\bar{3}m$ ³² to the non-centrosymmetric tetragonal $I4cm$ structure in MAPbI₃ classifies as ferroelectric, as well as ferroelastic.³³

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3 A ferroelastic phase transition leads to a distortion of the crystal lattice causing a spontaneous
4 strain in the material - analog to the spontaneous polarization/magnetization in
5 ferroelectric/ferromagnetic materials. Upon application of an external stress, this spontaneous
6 strain can switch its direction in the crystal lattice.³⁴ Thereby, the internal strain can be lowered
7 by the formation of twin domains, that are oriented along different crystalline axes. A tetragonal
8 structure allows spontaneous strain orientations along the a_1 , a_2 and c axes.³³ Like
9 ferroelectricity, ferroelasticity is a nonlinear property and commonly observed in materials with
10 a perovskite crystal structure.³³⁻³⁴

21 To shed light on the microscopic origin of these effects, atomic force microscopy (AFM) can
22 correlate the topography of a sample to other local material properties, such as electrical
23 potential, piezoelectricity or conductivity.^{22, 35-37} In particular, piezoresponse force microscopy
24 (PFM) can locally probe the electromechanical properties of piezoelectric samples. It is an AFM
25 method based on the inverse piezoelectric effect. As ferroelectricity is always coupled to
26 piezoelectricity, PFM can also visualize ferroic domains.³⁶⁻³⁷ By scanning a surface in contact
27 mode and simultaneously applying an AC voltage via a conductive cantilever, a piezoelectric
28 material deforms periodically. The amplitude of the piezoresponse gives the magnitude of the
29 electromechanical coupling and thus the positions of domain walls, where the material's
30 piezoresponse is minimal. The phase between excitation and piezoresponse contains information
31 about the orientation of the domains. Two measurement modes are possible: (a) vertical PFM
32 uses the cantilever vertical deflection signal to detect the out-of-plane piezoresponse
33 and (b) lateral PFM uses the lateral deflection signal caused by torsion of the cantilever to detect
34 in-plane piezoresponse. The polarization direction of ferroelectric domains can be permanently
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switched by applying a DC bias during a scan in contact mode.³⁶⁻³⁷ Furthermore, PFM can locally measure ferroelectric hysteresis loops.

Several groups have performed PFM measurements on MAPbI₃ perovskite films. Yet, the findings of these studies were contradictory. Kutes *et al.* observed switchable ferroelectric domains in their MAPbI₃ films,³⁸ which was confirmed by subsequent PFM studies.^{16, 39-41} However, Xiao *et al.* reported that they did not find any evidence of ferroelectricity using PFM.¹⁹ Recently, two publications claimed that the MAPbI₃ perovskite does not exhibit ferroelectricity at room temperature based on PFM measurements and macroscopic polarization methods.⁴²⁻⁴³ The previous PFM studies prepared the perovskite films by various preparation routines and obtained dense perovskite films with grain sizes up to 1 μm .

Here, we prepared MAPbI₃(Cl) films via solvent annealing, yielding in less dense films with grains up to 10 μm that exhibited a high crystalline orientation and a distinct morphology of multiple terraces. On top of these grains, we performed vertical and lateral PFM and locally resolved an at least partially in-plane striped structure with spacing between 100 nm and 350 nm in the PFM signal that could not be observed in their topography. By correlating vertical and lateral PFM with x-ray diffraction experiments, we concluded that the a_1 - a_2 -phase is the preferred crystal orientation in these domains. The structure and the orientation of the domains suggest that MAPbI₃ is ferroelastic, causing the twin domain pattern when prepared as described.

EXPERIMENTAL SECTION

Sample preparation. Methylammonium iodide (CH₃NH₃I) was synthesized as described by Lee *et al.*³ Lead chloride (PbCl₂, Sigma Aldrich, 99.999%) was dehydrated under high vacuum conditions and in nitrogen atmosphere at 60 °C. The perovskite solution was prepared in a 3:1

molar ratio of the precursors $\text{CH}_3\text{NH}_3\text{I}$ and PbCl_2 with a concentration of 40wt% in anhydrous dimethylformamide (DMF, Sigma).

Indium tin oxide (ITO) substrates (PGO , $R_{\square} \leq 20 \frac{\Omega}{\square}$) were cleaned with 2% Hellmanex II, acetone and isopropanol and treated with an argon plasma for 20 min prior to the deposition of filtered (450 nm) poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, Heraeus CleviosTM P VPAI 4083) in water. The PEDOT:PSS/water mixture was deposited on the substrate by spin-coating at 2500rpm for 5 s, followed by 5000rpm for 25 s and subsequently annealed at 140 °C for 20 min. The samples were transferred into a nitrogen-filled glovebox with less than 1 ppm H_2O . The perovskite solution was kept at 60 °C prior deposition. For a 1 by 1 inch sample, around 100 μL of solution were used and spin-coated for 45 s at 2000 rpm. The samples then rested at least 30 minutes in the glovebox. For the solvent annealing, the samples were placed on the hotplate, 10 μL of DMF were dropped on the hotplate, similar to Xiao *et al.*⁴⁴ The substrates and the DMF were covered with a watch glass in a way that the DMF could dissipate during the solvent-annealing. The substrates were annealed for 1 h at 100 °C in the presence of DMF and in a second annealing step in nitrogen atmosphere for another hour at 100 °C. The cells were kept at least 12 hours in the glovebox prior to measurements.

Piezoresponse force microscopy. Piezoresponse characterization of the perovskite films was performed on an MFP-3D atomic force microscope from Asylum Research (Oxford Instruments) and an HF2 Lock-in amplifier by Zürich Instruments. To avoid degradation of the hygroscopic perovskite material by humidity, the MFP-3D was operated in a glovebox in nitrogen atmosphere. Following the preparation, the samples were quickly transferred from the preparation glovebox into the MFP-3D glovebox. The PFM measurements were performed at room temperature with PPP-EFM cantilevers from Nanosensors with free resonance frequencies

of 70 kHz and spring constants of $k \sim 2$ N/m. AC voltages with peak-amplitudes between 1 and 2.5 V were applied to the conductive cantilevers to excite the material. We chose AC frequencies of around 300 kHz, just below the contact resonance to make use of the resonance enhancement. No additional back electrode was used, a small area of the perovskite was removed by scratching and PEDOT:PSS was connected to ground.

For switching experiments the sample was scanned in contact mode at scan speeds below 0.5 Hz, while simultaneously applying a DC voltage of up to 4 V via the conductive cantilever.

Lateral PFM was performed at a drive frequency of 600 kHz. We used an AC amplitude of 2.5 V.

X-ray diffraction. X-ray diffraction of the perovskite film was measured using Cu K α radiation (Rigaku MicroMax 007 x-ray generator, Osmic Confocal Max-Flux curved multilayer optics). The sample was mounted in reflection geometry at an incident angle of 4.5° on a 6-circle diffractometer. 2D diffraction patterns were recorded by an image plate detector (Mar345, 150 μ m pixel size) at a sample-detector distance of 356.83 mm.

UV-vis absorption. The absorption spectrum of the MAPbI₃ film was measured with a Perkin Elmer Lambda 900 spectrometer with integrated sphere.

RESULTS AND DISCUSSION

The topography of the solvent annealed MAPbI₃ film showed grains in varying shapes and sizes that ranged between 1 μ m and 10 μ m in diameter (Figure 1 (a)). The surface of these grains exhibited a distinct terrace structure suggesting a high crystallinity of the MAPbI₃ compound. While on top of the terraces no extraordinary topographic features were observed, the vertical PFM phase (Figure 1 (b)) and amplitude (Figure 1 (c)) revealed a striped structure with a spacing

of 100 nm up to 350 nm. In the PFM phase (Figure 1 (b)), only a weak contrast between adjacent stripes was observed. For adjacent out-of-plane ferroelectric domains a phase difference of 180° would be expected. However, the phase difference of only a few degrees in Figure 1 (b) indicates that the domains might be oriented partially in-plane. The piezoresponse amplitude (Figure 1 (c)) showed the same structure as the PFM phase with a strong contrast, e.g. in the magnified areas 1 and 2.

Materials with a center of inversion do not exhibit piezoelectricity.⁴⁵ Therefore, the presence of a piezoresponse on the perovskite grains suggests that the material does not crystallize in the centrosymmetric space group $I4/mcm$ ^{28, 30-31} but more likely in the polar space group $I4cm$. The piezoresponse increased linearly with the applied electric potential up to $V_{AC} = 2.5$ V (Supporting Information Figure S1).

Within single grains, distances between adjacent stripes are largely uniform. On different grains, however, the spacing varies between 100 nm and 350 nm. The amplitude profiles in Figure 1 (d) were extracted along the red and the blue line in area 1 and area 2 in Figure 1 (c), respectively. While stripes of the same contrast on the grain in the magnified area 1 were on average 230 nm apart, stripes of the same contrast on the grain in area 2 had distances of only 120 nm. It appeared that the spacing between the grains was correlated with the grain size, as it would be expected for ferroelastic domains.⁴⁶ However, due to the complex morphology of the perovskite grains, single grains could not be readily distinguished. A statistical analysis of this correlation was therefore not possible. Furthermore, both magnified areas showed that the stripes change their direction by 90° within a single grain. The 90° angle between the domains is in good agreement with the tetragonal crystal structure of MAPbI_3 at room temperature.²⁶⁻²⁹ In area 1 the dark stripes became narrower towards stripes with a perpendicular orientation, like needles.

The periodic structure, the 90° direction change and the correlation between domain size and grain size is reminiscent of the periodic ferroelastic domains in thin films of the ferroelectric and -elastic ceramics $\text{Pb}_{0.7}\text{Zr}_{0.3}\text{TiO}_3$ (PZT) and $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ (PST), observed by Ivry *et al.* as well as Matzen *et al.*, respectively.⁴⁷⁻⁴⁸ Ferroelastic materials that grow under external stress can reduce this stress by forming twin domains. The external stress can be caused, for example, by epitaxial growth on a substrate that forces the compound into a structure it usually does not crystallize in. As the substrate in our perovskite samples is PEDOT:PSS, an amorphous polymer mixture, epitaxial strain seems unlikely. To exclude a further influence of the substrate we additionally prepared perovskite films directly on ITO glass and observed the same periodic pattern as on PEDOT:PSS (Supporting Information Figure S2).

The preparation of the MAPbI_3 films was performed at 100 °C, where the compound crystallizes in a cubic structure. During cooling of the sample, a possibly ferroic phase transition to the tetragonal crystal structure occurs at around 54 °C.²⁶⁻²⁹ We propose that this phase transition induces an internal strain that is compensated by the formation of twin domains due to a ferroelasticity of the compound.

Figure 1. Vertical PFM measurement on MAPbI₃ film (a) Topography, (b) PFM phase, (c) PFM amplitude with magnified areas 1 and 2, (d) amplitude profiles extracted along the red line in area 1 (red) and the blue line in area 2 (blue). ($V_{AC} = 2.5$ V; $f_{Drive} = 300$ kHz, scan angle = 45°, cantilever orientation and fast scan direction are indicated in the insets in the upper right corners).

While it may seem from Figure 1 that the direction of the stripes of adjacent grains is correlated, a closer analysis revealed that the twin domains in area 1 and 2 in Figure 1 (c) have an angle of 4.5° with respect to each other. A complimentary measurement on a larger area of 40 μm x 40 μm further confirmed that there is no correlation of the pattern across grain boundaries

(Figure 2). Figure 2 (a) shows the topography of the large scale scan. Highlighted by the black boxes in (a) are the areas that were magnified in Figure 2 (b) to image the PFM amplitude on adjacent perovskite grains. Here, it is apparent that the stripe direction on adjacent grains is not correlated.

Figure 2. Vertical PFM measurement on MAPbI₃ film (a) Topography, (b) PFM amplitude of magnified areas indicated by the blackes box in (a) ($V_{AC} = 1.5$ V; $f_{Drive} = 290$ kHz, scan angle = 0°, cantilever orientation and fast scan direction are indicated in the insets in the upper right corner).

To further characterize the texture of the polycrystalline MAPbI₃ film we used x-ray diffraction (XRD) (Figure 3 (a)). The peak positions at 14.11°, 19.95°, 23.42°, 24.42°, 28.38° and 31.76°

extracted from the radial averaged XRD pattern correspond to the (110), (200), (211), (202), (220) and (310) Bragg reflections of the tetragonal MAPbI₃ structure, respectively (Figure 3 (b)).^{32, 49-52} The weak reflection at 12.67° indicates the presence of crystalline PbI₂ in the sample.^{50, 52-53} Likely, this is caused by partial degradation of MAPbI₃ during the annealing at temperatures of 100 °C.⁵⁴ Consistent with previous studies, no reflections related to MAPbCl₃ were observed. Furthermore, the absence of split peaks excludes a phase separation into iodide and chloride rich phases as origin of the domain pattern.⁵⁵

Figure 3. (a) 2D x-ray diffraction pattern of MAPbI₃. Dashed lines indicate the azimuthal angle where maxima in the perovskite Bragg reflections were observed. (b) Radially integrated intensity in the sector indicated in (a) by solid white lines.

The pronounced radial intensity variations observed in the 2D data-sets indicate a strong preferential grain orientation within the polycrystalline perovskite film (Figure 3 (a)). For the (110) and the (220) reflections, intensity maxima were observed close to the specular condition. In contrast, for the (200) reflection two off-specular maxima at $\chi = 45^\circ$ and $\chi = 135^\circ$ were observed (dashed lines in Figure 3 (a) and Supporting Info Figure S3). This suggests that the

(110) crystal plane of the perovskite grains is predominantly orientated parallel to the film surface. No preferred in-plane orientation of the grains was observed in the XRD measurements.

As the weak phase contrast in Figure 1(b) suggested, the observation of a vertical PFM signal could be caused by purely or partially in-plane oriented domains. In-plane components of the domain orientation can induce a vertical PFM signal via cantilever buckling (Figure 4(a)). Cantilever buckling can be distinguished from deflection of the cantilever by rotating the sample by 90° .³⁶ Signals from cantilever buckling are strongly dependent on the angle between cantilever and the domain orientation, whereas true out-of-plane sample deformations do not show such dependence. Upon rotating the sample by 90° with respect to the cantilever, we indeed observed a contrast inversion in the vertical PFM amplitude and phase (Figure 4 (b-e)). This indicates that the orientation of the domains has an in-plane component and the vertical signal is at least partially caused by cantilever buckling.

Figure 4. (a) Illustration of difference between deflection and cantilever buckling. (b) - (e) Vertical PFM measurement on MAPbI₃ film ($V_{AC} = 2.5$ V; $f_{Drive} = 300$ kHz, scan angle = 45°, cantilever orientation and fast scan direction are indicated in the insets in the lower right corners). (b) PFM amplitude at 0° sample rotation and (c) at 90° sample rotation, (d) PFM phase at 0° sample rotation and (e) at 90° sample rotation. The red box marks the same domain in (b) – (e).

Considering the in-plane component of the domain orientation and the texture of the perovskite grains, there are three possible domain structures within the (110) crystal plane. The *a-c*-phase (Figure 5 (a)) consists of in-plane domains oriented along the *c*-axis of the unit cell that alternate with domains, in which the strain is oriented along the *a*-axis in a 45° angle with respect to the surface. However, if only one of the domains is oriented out-of-plane (*a*-domain) while the other domain is oriented in-plane (*c*-domain), the domain pattern will most likely be visible in the topography of the sample. The differences in the lattice parameters *a* and *c* cause a roof-like structure in the topography. The latter is the case for the ferroelectric and -elastic PbTiO₃ and BaTiO₃ domains oriented along the *c*-axis (out-of-plane) and the *a*-axis (in-plane) of the tetragonal unit cell.^{48, 56} Since the striped pattern in the MAPbI₃ grains could not be observed in the topography, we conclude that both twinning domains are either oriented in the same non-90° angle out-of-plane or purely in-plane.

Figure 5. Possible orientations of the strain along the crystal axes (indicated by the arrows) of the twin domains within the (110) crystal plane of MAPbI₃: (a) *a-c*-phase with alternating out-of-plane domains along the *a*-axis and in-plane domains along the *c*-axis, (b) purely in-plane *c*-phase with antiparallel domains, (c) proposed *a*₁-*a*₂-phase in a 45° angle out-of-plane and 90° with respect to each other.

A purely in-plane structure consists of neighboring domains in an antiparallel orientation along the *c*-axis (*c*-phase, Figure 5 (b)). Assuming such a domain structure and that the vertical PFM signal is only caused by cantilever buckling, we would expect the PFM amplitudes on all the stripes that are oriented parallel to the cantilever to be of the same value. However, in Figure 1 (c) the PFM amplitude shows the same alternating contrast on different stripe orientations and even for stripes parallel to the cantilever (e.g. in magnified area 1).

Based on the results presented so far we propose a domain structure, in which the strain of adjacent twin domains is oriented in a 45° angle to the surface and a 90° angle with respect to

each other (a_1 - a_2 -phase, Figure 5 (c)). The vertical PFM signal would be caused by a combination of cantilever deflection and buckling. Thereby, the observed inversion in the vertical PFM contrast upon sample rotation can be explained. As the strain in the a_1 - a_2 -phase has equal out-of-plane components for adjacent domains the structure would not be visible in the topography.

To further support the suggested a_1 - a_2 domain structure within the MAPbI₃ grains we performed lateral PFM measurements on the film. The perovskite film showed a lateral piezoresponse (Figure 6 (a) and (b)), which resembled the periodic pattern observed in the vertical PFM measurements (Figure 1). The presence of a lateral PFM signal confirms that the orientation of the domain structures has an in-plane component. By measuring at 0° and 90° sample rotation it is possible to determine the domain orientation from the change of the phase contrast (Figure 6 (a)).³⁶ Upon rotating the sample by 90° from Figure 6 (a) to (b), the PFM phase contrast was inverted, while the contrast in the PFM amplitude remained largely unchanged (insets in Figure 6 (a) and (b)). In the area highlighted by the red oval this inversion is very distinct.

Figure 6. Lateral PFM on MAPbI₃ film (a) PFM phase at 0° and (b) at 90° sample rotation. The insets in the lower right corner show the PFM amplitude both with the same data scale. The red oval marks the same domains ($V_{AC} = 2.5$ V; $f_{Drive} = 600$ kHz, scan angle = 0°, cantilever orientation and scan direction are indicated in the insets in the upper right corners).

Both twin domains in the a_1 - a_2 -phase (Figure 5 (c)) have the same angle with respect to the cantilever. Therefore, the contrast inversion in the PFM phase and the unchanged PFM amplitude upon sample rotation are in agreement with this domain structure assignment (Figure 5 (c)).

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3 Subsequently, we performed ferroelectric switching experiments to examine whether the
4 ferroelastic stripes contribute to a possible ferroelectricity of the perovskite. During an AFM
5 scan in contact mode we applied DC voltages between +4 V and -4 V to the tip with scan rates
6 between 0.3 Hz to 1 Hz. We did not use higher voltages to avoid damage to the sample. In case
7 of ferroelectric switching, the contrast of the phase of the piezoresponse should be inverted in a
8 subsequent PFM scan. However, the contrast of the PFM signals and the arrangement of the
9 stripes remained unchanged after applying a DC bias in agreement with Xiao *et al.*¹⁹ We locally
10 measured ferroelectric hysteresis loops, which did not show a switching event (Supporting
11 Information Figure S4).
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24 The absence of polarization switching in the above experiments, however, does not generally
25 exclude ferroelectricity. Wei *et al.* observed switching in the orientation of ferroelectric domains
26 on the timescales of several seconds.¹⁷ We performed the DC scans with velocities between 3 -
27 12 $\mu\text{m/s}$, which might be too fast to switch the domain orientation. In context of the *I-V*
28 hysteresis, several studies have reported on slow processes within the perovskite layer and
29 connected them to migrating ions or trapped charges.^{5-6, 13, 19-22} The resulting internal electric
30 field could also screen the applied DC voltage and interfere with the ferroelectric switching. As
31 the perovskite is electrically conductive, it is also possible that the conductivity induces a break-
32 down of the tip voltage which is then insufficient to switch the orientation of the polarization
33 within the domains. Finally, if the ferroelectric polarization has in-plane components, these
34 domains cannot easily be switched via AFM methods. The field that is applied to the film by an
35 AFM tip is mainly perpendicular to the surface, which makes the switching of in-plane domains
36 unlikely, but not impossible.⁴⁸
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Figure 7. Tapping mode measurement on MAPbI₃ film. (a) Topography and (b) amplitude error signal. The PFM amplitude of the same area is shown in the upper right corner of (b) for comparison.

To exclude topographic crosstalk as the origin of the periodic pattern in the PFM signals, we additionally probed the sample topography with the less invasive tapping mode AFM (Figure 7). Neither the height (Figure 7 (a)) nor the amplitude error signal (Figure 7 (b)) correlated to the striped pattern observed in the PFM amplitude signal of the same area, as shown in the upper right corner of Figure 7 (b). The striped pattern appeared in the PFM signals, only. However, we observed terraces and steps on the grains indicating a layered crystallite growth.

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3 The perovskite layer was up to 1 μm thick but did not completely cover the substrate. Holes
4 reaching down to the PEDOT:PSS, corresponding to the dark areas in the height channel (Figure
5 7 (a)), showed no PFM response (Figure 7 (b)). We can therefore exclude that the observed
6 piezoresponse was caused by the substrate. At the edges of the grains we observed small rods,
7 highlighted by the black ovals in Figure 7 (a), which are between 150 nm and 700 nm long and
8 100 nm to 200 nm wide. We assigned these rods to the perovskite degradation product PbI_2 . This
9 assignment is in agreement with the XRD results discussed above (Figure 3) and UV-vis
10 spectroscopy results (Supporting Information Figure S5).
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22 CONCLUSION

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24 We examined the electromechanical response of μm -sized MAPbI_3 grains by PFM. Distinct
25 periodic domains were observed with distances between 100 nm and 350 nm. These striped
26 domains in the piezoresponse were oriented either parallel or perpendicular with respect to each
27 other – a characteristic fingerprint of ferroelasticity.³⁴ Previous PFM studies on polycrystalline
28 perovskite films did not observe such a domain pattern. These studies used different preparation
29 routes, such as the successive spin coating/annealing routine³⁸ or a two-step thermal/solvent
30 annealing routine¹⁹ and yielded dense films of MAPbI_3 grains with sizes up to 1 μm . None of the
31 studies obtained grains with a similar terrace structure as the samples presented in this study. We
32 therefore propose that MAPbI_3 is ferroelastic and that the periodic twin domains observed form
33 to minimize internal strain caused by the morphology resulting from the preparation route
34 chosen. Stress from the cubic-tetragonal phase transition following sample annealing could
35 induce the internal strain. However, independent from the observation of the domain pattern,
36 ferroelasticity is a property that would be present in MAPbI_3 , even when prepared otherwise. To
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3 finally prove the ferroelasticity in perovskite, further measurements such as mechanic hysteresis
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5 experiments will be necessary.
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8 At ferroelastic domain walls, localized properties such as superconductivity or ferroelectricity
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10 can occur that are not present in the bulk material, since the walls can act as sources for defects.⁵⁷
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12 Conducting ferroelastic domain walls that can be caused by head-to-head and tail-to-tail
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14 orientation could be an alternative explanation of the increased charge carrier diffusion lengths in
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16 large MAPbI₃ grains, yet also contribute to the *I-V* hysteresis by trapping free charge carriers in
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18 defects. To further investigate the properties of the ferroelastic domain walls in MAPbI₃, local
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20 conductivity measurements, e.g. via conductive AFM with and without illumination would be
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22 required.
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27 The XRD results revealed that the (110) crystal plane is oriented parallel to the sample surface.
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29 By performing vertical and lateral PFM experiments at 0° and 90° sample rotation with we were
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31 able to identify the *a*₁-*a*₂-phase as the preferred orientation of the ferroelastic domains with
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33 respect to the sample surface. Finally, ferroelectric switching experiments suggested the absence
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35 of an out-of-plane switchable polarization in the perovskite films.
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Supporting Information Available

PFM amplitude in dependence of V_{AC} voltage, PFM measurement of MAPbI₃ on ITO, intensity distributions of the (110) and the (200) Bragg reflections, ferroelectric switching experiment, UV-vis absorption spectra of MAPbI₃. This information is available free of charge via the Internet at <http://pubs.acs.org>

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