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# Determination of the True Lateral Grain Size in Organic–Inorganic Halide Perovskite Thin Films

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## Supporting Information

**ABSTRACT:** In this letter, methylammonium lead iodide (MAPbI<sub>3</sub>) thin films were examined via piezoresponse force microscopy (PFM) and nanoindentation (NI) to determine if long-range atomic order existed across the full width and depth of the apparent grains. From the PFM, the piezoelectric response of the films was strongly correlated with low-index planes of the crystal structure and ferroelastic domains in macroscale solution-grown MAPbI<sub>3</sub> crystals, which implied long-range order near the top surface. From the NI, it was found that the induced cracks were straight and extended across the full width of the apparent grains, which indicated that the long-range order was not limited to the near-surface region, but extended through the film thickness. Interestingly, the two MAPbI<sub>3</sub> processes examined resulted in subtle differences in the extracted electro-mechanical and fracture properties, but exhibited similar power conversion efficiencies of >17% in completed devices.



KEYWORDS: perovskites, grain size, piezoresponse force microscopy, nanoindentation, photovoltaic devices, ferroelastic domains

rganic-inorganic perovskite thin films have received significant interest in the scientific community because of their potential as low cost and high power conversion efficiency (PCE) active layers in photovoltaic (PV) devices,<sup>1,2</sup> with the maximum PCE now exceeding 22%.<sup>3</sup> Despite the strong interest in these materials, many basic material properties remain elusive. For example, there has been considerable debate about the nature of grain boundaries (GBs) and their impact on the PCE of organic-inorganic perovskite PV devices,<sup>4-7</sup> with the latest work suggesting that GBs exhibit GB-to-GB heterogeneity and depth-dependence in electrical properties.<sup>6,7</sup> Similarly, there has been no study to date that has been able to definitively demonstrate if the apparent grain size, as assessed from top-down imaging techniques, represents a single crystal or a polycrystalline domain. The challenge in the assessment of the true lateral grain size in these materials is largely due to their sensitivity to electron and X-ray beam damage,<sup>8,9</sup> which precludes the use of standard crystallographic mapping methods such as electron backscatter diffraction or transmission electron microscopy.<sup>9</sup>

In recent work, lateral microwave conductivity studies have demonstrated that the apparent grain size corresponds to the average lateral charge scattering length.<sup>10</sup> Moreover, nanoscale lateral conductivity measurements have shown that the electrical conductivity across a single apparent grain is uniform, whereas the conductivity across multiple apparent GBs is highly variable.<sup>6</sup> Thus, both studies suggest that the apparent grains in thin films deposited by a solvent-solvent extraction method<sup>11</sup> act electronically like single crystals in a polycrystalline film, but do not confirm that the apparent grain size matches the true grain size (i.e., that long-range atomic order exists across the full width of the apparent grains). In this letter, we look to explicitly address this issue via multiple material properties measurements that are inherently dependent on crystal structure, namely the (1) electromechanical response and (2)fracture behavior of individual grains in methylammonium lead iodide (MAPbI<sub>3</sub>) thin films. On (1), we establish a strong correlation between the piezoelectric response of the films to both low-index planes of the crystal structure and ferroelastic domains in macroscale, solution-grown MAPbI<sub>3</sub> crystals, which implies long-range order across the full width of the apparent grains. On (2), we show that cracks induced via nanoindentation (NI) are straight and extend across the full width of apparent grains, which further indicates that the long-range

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**Figure 1.** (a) J-V data from completed devices with SSE and SA films exhibit short-circuit current densities of ~21.3 mA/cm<sup>2</sup>, open-circuit voltages of ~1.07 V, and PCEs of >17.3% under reverse scan conditions (100 mV/s). (b) XRD spectra show that SA and SSE films are highly textured and the crystal planes parallel to the surface are almost exclusively {110}. SEM images of the (c) SSE and (d) SA films reveal a change in morphology, with the SA film exhibiting larger, more equiaxed apparent grains.



**Figure 2.** (a) Topography and (b) SF-PFM phase response of the SSE sample. The red arrows in (a) denote the topographic surface striations, whereas the red arrows in (b) denote the PFM striping patterns. (c) Topography and (d) DART-PFM phase response of the SA sample. The red arrows in (d) point to several apparent grains with multiple sets of stripes. (e) Optical image of a solution-grown MAPbI<sub>3</sub> single crystal. The red arrow denotes a  $\langle 001 \rangle$  direction. In both the thin films and single crystals,  $\alpha$  and  $\beta$  were found to be 55 and 110°, respectively. (f) Graphical representation of  $\alpha$  and  $\beta$  resulting from the intersection of two arbitrary planes q and r projected onto the surface plane s.

order is not limited to the near-surface region, but instead extends through the film thickness. In all, long-range, multiproperty order was established across the full width and depth of apparent grains for two MAPbI<sub>3</sub> films, in agreement with the lateral electrical results on the same films.<sup>6,10</sup>

To ensure the thin-film results were not specific to a single processing condition, we prepared MAPbI<sub>3</sub> active layers via two different methods, the first of which was based on a solvent—

solvent extraction (SSE) method as previously reported<sup>11</sup> and the second of which employed a solvent-annealing (SA) step and an additional precursor (details are described in the Supporting Information).<sup>12</sup> To validate that the films made from both methods were of high, and comparable, quality, complete devices were made which consisted of fluorine-doped tin oxide (FTO)/compact TiO<sub>2</sub>/MAPbI<sub>3</sub>/a 2,2',7,7'-tetakis (N,N-dip-methoxyphenylamine)-9,9'-spirobifluorene hole

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transport layer, and an Ag top contact, with the latter two layers omitted for the studies on the MAPbI<sub>3</sub> active layers. Current density (1)-voltage (V) data from completed PV devices with SSE and SA MAPbI<sub>3</sub> formulations are shown in Figure 1a. Both processes resulted in devices with short-circuit current densities and open-circuit voltages of  $\approx 21.3 \text{ mA/cm}^2$  and 1.07 V, respectively, and PCEs of >17.3% under reverse scan conditions (100 mV/s). Moreover, the devices exhibited minimal hysteretic behavior and maintained stabilized PCEs of >17.1%, as shown in Figure S1. As shown in Figure 1b, onedimensional X-ray diffraction (XRD) spectra reveal that both SSE and SA films are highly textured (as confirmed by twodimensional XRD in Figure S2) and the crystal planes parallel to the surface are almost exclusively composed of {110} planes. In addition, the SA film exhibits a smaller full width halfmaximum (fwhm) than the SSE film, which suggests a change in the morphology or microstrain in the thin film.<sup>13</sup> Indeed, the SEM images in Figures 1c, d reveal a change in morphology, with the SA film exhibiting larger, more equiaxed apparent grains than the SSE film. This increase in grain size for the SA process is consistent with previous studies, which suggest that Cl enhances the growth of crystal domains via the removal of excess organic precursor<sup>14</sup> and the addition of heterogeneous nucleation sites.<sup>1</sup>

It is important to note that both films show evidence of surface striations that extend across the full width of the apparent grains. This is an indication of long-range order across the full width of each apparent grain, but not definitive evidence that each apparent grain is truly a single crystal. For example, long-range surface patterns in the form of radial surface striations are often observed in spherules, regardless of whether they are single crystals or polycrystalline.<sup>16</sup> For single-crystal spherules, the symmetry of the radial pattern is determined by the crystal structure, whereas for polycrystalline spherules, the radial patterns do not necessarily align with the symmetry of the crystal structure. Moreover, it is important to note that recent studies in which "hot casting"17 or "bar casting"18 methods were used to deposit perovskite thin films, the topography closely matches radial patterns observed in polycrystalline spherules. This calls into question the hypotheses that increased PCE and reduced PV device hysteresis using such techniques is due to a reduction in the GB density in the films, and demonstrates a clear need for an approach to determine the true grain size in perovskite active layers.

Given that long-range order in topography does not definitively indicate that an apparent grain is a single crystal, piezoresponse force microscopy (PFM) was conducted on the two MAPbI<sub>3</sub> formulations, as the piezoelectric response of a material is directly dependent on the arrangement of atoms in the unit cell (details regarding the PFM experimental methods can be found in the Supporting Information). For the SSEdeposited thin film, stable resonance tracking was difficult, and thus single-frequency (SF)-PFM was utilized. The topography and SF-PFM phase response of the SSE sample are shown in Figures 2a, b, respectively. There is a significant amount of cross-talk between the surface topography and piezoresponse, as evident by the correlation between the top-left-to-bottomright stripes in Figure 2b and the surface striations (denoted by red arrows) in Figure 2a This artifact is likely due to shifts in contact resonance frequency relative to the PFM measurement frequency.<sup>19</sup> Despite this artifact, an additional striping pattern is observed in Figure 2b, the direction of which is indicated

again by the red arrows. The pattern extends across the full width of the apparent grain, suggesting that the true grain size is equivalent to the apparent grain size in SSE-deposited films. For the SA-deposited films, dual-amplitude resonance tracking (DART)-PFM was viable, thereby reducing topographic artifacts in the PFM phase response. The topography and DART-PFM phase response of the SA sample are shown in Figures 2c, d, respectively. Here, striping patterns are clearly observed in the PFM, which implies that the films studied here exhibit domain boundaries. A recent PFM study on MAPbI<sub>3</sub> thin films and single crystals in the pristine state and under applied stress provided definitive evidence that the features are in fact ferroelastic domains formed during the cubic-totetragonal phase transition,<sup>20</sup> as suggested in previous work.<sup>12</sup> The absence/presence of the domains is reversible when cycling through the transition, which indicates that the domains are a temporary distortion of the single crystal to minimize its strain energy, but with a "memory" effect based on the orientation of the grain and the strain at the GB.<sup>21</sup> Interestingly, in both MAPbI<sub>3</sub> thin films, the angle between the stripes and topographic striations was typically found to be  $\alpha \approx 55^{\circ}$  (or at a supplementary angle of  $\alpha_{sup} \approx 125^{\circ}$ ). Furthermore, several apparent grains showed multiple sets of stripes on a single apparent grain, as illustrated by the red arrows in Figure 2d. In such cases, the intersecting angle was exclusively observed at  $\beta$ = 110° (or at a supplementary angle of  $\beta_{sup}$  = 70°). These values for  $\beta$  are in good agreement with recent PFM results.<sup>20</sup>

Similar results were observed for single-crystal MAPbI<sub>3</sub>, as shown in Figure 2e, which were grown in solution by an acidinitiated process.<sup>22</sup> In this work, the authors found that macroscopic domains in the form of a striping pattern could be induced by rapid cooling through the cubic-to-tetragonal phase transition. More importantly, the authors measured a different electrical response and different chemical etch rates across the domains, confirming that the domains have a distinct, persistent, and long-range atomic order.<sup>23</sup> Finally, it was shown that the top surface is a {110} plane and one of the corners represents a (001) direction. Hence, the angle between the  $\langle 001 \rangle$  direction and the observed striping pattern is  $\alpha = 55^{\circ}$  and the angle between the two striping patterns is  $\beta = 110^{\circ}$ , both of which are in agreement with the thin-film results.

As shown in Figure 2f,  $\alpha$  and  $\beta$  can be represented by the intersection of two arbitrary planes q and r projected onto the surface plane s. The vectors pointing from the origin along the q-s and r-s plane intersections can be calculated by  $n_v \times n_s =$  $\overrightarrow{ns}$ , where p represents either the q or r plane, and n is the normal vector defining the respective plane. We note that the normal vector is equal to the Miller indices of a given plane (h k*l*) multiplied by the lattice constants *a*, *b*, and *c*. The angle between  $\vec{qs}$  and  $\vec{rs}$ , and thus the angle of intersection of planes q and r projected onto s, can then be calculated by  $\alpha_{i}\beta$  =  $\cos^{-1}((\vec{qs} \times \vec{rs})/(\|\vec{qs}\| \times \|\vec{rs}\|))$ . For all calculations, a = b =881 pm and c = 1271 pm were used.<sup>24</sup>  $\alpha$  and  $\beta$  were assessed for planes q and r projected onto plane s in which q and rbelong to low-index families of planes, i.e.,  $\{a \ b \ c\} \leq 3$ . The *s*plane was set to (110), consistent with the XRD results in Figure 1b, and calculations were performed on the full family of equivalent planes. From the calculations of the low-index planes (see Table 1), there are only two occasions where q = r and the projected angle is within  $2^{\circ}$  of  $\beta = 110^{\circ}$ , i.e.,  $q = r = \{211\}$  or q=  $r = \{331\}$ . Additionally, for  $q \neq r$ , there are several instances in which planes in the generic family  $\{h \ k \ 1\}$  intersect with

Table 1. Predicted q and r based on s = (110) from XRD and  $\alpha$  and  $\beta$  from PFM

type	9	r	$\alpha$ , $\beta$ (deg)
q = r	{211}	{211}	111.62
	{331}	{331}	108.74
$q = \{211\} \ q \neq r$	{211}	{111}	55.81
	{211}	{221}	55.81
	{211}	{321}	56.45
	{211}	{331}	55.81

{211} planes and within 2° of  $\alpha = 55^\circ$ . Given these two observations, the following can be inferred: (1) The long-range order observed in the PFM is due to long-range atomic ordering, i.e., the apparent grain size is typically equivalent to the true grain size; (2) The atomic displacements that lead to the striping patterns are likely constrained to the {211} or {331} planes, given that the patterns are equally likely on intersecting planes in the same family, i.e., q = r, and these are the only low-index planes that exhibit a projected angle on the *s*-plane consistent with the PFM results; and (3) The topographic striations are likely along a  $\langle 001 \rangle$  direction.

These results demonstrate that the thin-film and singlecrystal data are consistent with one another and with the atomic structure of the crystal. This is a strong indication that the true grain size is equivalent to the apparent grain size for the thin films studied here. We note, however, that PFM is most sensitive to the atomic ordering near the top surface, and therefore does not provide definitive evidence that long-range atomic order extends significantly into the bulk of the thin film. To clarify this point, we used NI to induce fracture in the thin films, and the resulting cracks were examined to study the properties of the grains through the film thickness. SEM images of the SSE and SA films following NI tests are shown in Figures 3a, b, respectively. At small indentation depths, the contactinduced deformation and fracture is unaffected by the underlying substrate, and the plastic zone under the NI tip is spherical in shape. At larger indentation depths, deformation is constrained by the harder substrate, which translates to a

cylindrical plastic zone in addition to film delamination and channel cracks.<sup>25</sup> Indeed, we observe lateral voids between grains and grains sliding onto adjacent grains, in addition to lateral cracks forming in the apparent grains (see Figure S3). The lateral cracks (denoted by the red arrows in Figure 3) are sharp, straight cracks that extend across most, if not the entire width, of the apparent grains to which they belong, and often several parallel cracks form on the same grain. This is strong evidence that the material properties, as determined by the long-range ordering of the atoms, extend well into the film thickness.

This is further supported by analysis of multiple fracture events. In Figures 3c, d, the normalized frequency distributions of the acute angle between the cracks and the surface striations  $\alpha$  are shown for the SSE and SA films, respectively. In both cases, we observe a clustering of one or more distributions near  $\alpha$  = 45°. If the apparent grains consisted of polycrystalline domains, there would be no reason to expect a preferred  $\alpha$ value, as this would imply long-range atomic order on length scales comparable to the apparent grain size. Moreover, the random-plane fracture distribution is shown in Figures 3c, d. This distribution illustrates the likelihood for a given value of  $\alpha$ , based on the assumptions that the striations are along a  $\langle 001 \rangle$ direction, fracture occurs on low-index planes, and fracture is equally likely on all planes. Although there are multiple  $\alpha$  that exhibit similar number density to the plane combinations that lead to  $\alpha$  = 45°, these possible combinations are not equally represented in the NI. This suggests that the observed  $\alpha$ represent low-index planes with lower fracture toughness, analogous to {111} planes in Si.<sup>26</sup> Moreover, it is evident from Figures 2 and 3 that the  $\alpha$  from PFM and NI and significantly different. Therefore, the preferential fracture events are expected to intersect multiple ferroelastic domain boundaries in an apparent grain. This is strong evidence that the PFM striping pattern is due to ferroelastic relaxation within a single crystal, as opposed to the formation of parallel crystals within an apparent grain.



**Figure 3.** SEM images of the (a) SSE and (b) SA films following NI tests. The red arrows denote cracks, which typically extend across the full width of the grains. Normalized  $\alpha$  distributions for the (c) SSE and (d) SA films. The random-plane distribution, which illustrates the likelihood for a given value of  $\alpha$ , is also shown for comparison.

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Finally, it is important to note the subtle differences in the  $\alpha$ distributions, specifically the narrower distribution observed in the SA samples. The difference is likely due to the inclusion of Cl in the MAPbI<sub>3</sub> synthesis, and more explicitly, its influence on the morphological and interfacial properties of the MAPbI<sub>3</sub> thin film. On the morphological changes, the addition of Cl is an effective method to enhance MAPbI<sub>3</sub> crystal formation and morphology, as previously discussed<sup>14,13</sup> and shown in Figure 1. Recent molecular dynamics simulations have revealed that yield stress increases as the grain size increases, most likely due to amorphous structures at the GBs.<sup>27</sup> Additionally, the predicted elastic and fracture properties suggest that halide perovskites are compliant and prone to fracture relative to other photovoltaic materials, given their limited elastic modulus and strength.<sup>27</sup> Together, these factors could result in changes to the preferred fracture planes and the observed  $\alpha$  distributions. On the interfacial changes, the effect of Cl inclusion is less apparent, but some groups have reported that Cl in MAPbI<sub>3</sub> films tends to aggregate at the MAPbI<sub>3</sub>/TiO<sub>2</sub> interface.<sup>28,29</sup> Recent first-principles density functional theory calculations have shown that interfacial Cl atoms increase the binding energy between MAPbI<sub>3</sub> and TiO<sub>2</sub> and modify the interfacial electronic structure,<sup>29</sup> both of which could change the interfacial mechanics and therefore the observed  $\alpha$  distributions.

In conclusion, we have demonstrated that MAPbI<sub>3</sub> thin films produced using the SSE and SA formulations exhibit long-range order in topographic, piezoelectric, and mechanical properties, all of which were consistent with the crystal structure. The striping patterns in the PFM have been attributed to ferroelastic domains formed during the MAPbI<sub>3</sub> cubic-to-tetragonal phase transition, which provide a reversible mechanism to relieve strains from the change in lattice parameters.<sup>20,21</sup> The cracks from NI are shown to be straight and extend across the full width of the apparent grains, which indicates that the longrange order is not limited to the surface, but extends through the film thickness. Together, the PFM and NI results demonstrate that the apparent grain size matches the true grain size for the two MAPbI<sub>3</sub> formulations studied here, in agreement with lateral microwave conductivity studies<sup>10</sup> and lateral AFM conductivity measurements<sup>6</sup> on identical SSE thin films. It is important to note that this finding is not meant to imply that all MAPbI<sub>3</sub> formulations will behave in the same manner. In fact, it would be prudent to repeat the established protocol on MAPbI<sub>3</sub> thin films that exhibit significantly larger apparent grain sizes<sup>17</sup> and heterogeneous electrical properties across a single grain,<sup>30</sup> as these variations could impart changes to the apparent vs true grain size relationship (i.e., a plot of the apparent vs true grain size would yield a slope of one here, but this slope could change depending on the MAPbI<sub>3</sub> formulation). As a result, these protocols should be of interest to the field moving forward, as they allow for unambiguous determination of structure-property relationships without electron and X-ray beam damage from the standard crystallographic mapping methods.<sup>8,9</sup>

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b11434.

Expanded discussion of the thin-film synthesis, device fabrication and testing, single-crystal synthesis, XRD, SEM, PFM, and NI (PDF)

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#### **Author Contributions**

The manuscript was written through contributions made by all authors. All authors have approved the final version of the manuscript.

# Notes

The authors declare no competing financial interest.

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