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Ferroic twin domains in metal halide perovskites

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Abstract

An emerging family of materials—metal halide perovskites (MHPs)—have made incredible achievements in optoelectronics in the past decade. Owing to its potential role in optoelectronic properties, the ferroic state of MHPs has been investigated by lots of researchers. Here, we review the literature regarding investigations into possible ferroic behaviors in MHPs. We summarize the recent discoveries of ferroic twin domains in MHPs. We examine the ferroelasticity and the ferroelectricity of these twin domains. Several properties relevant to the twin domains are critically analyzed, including crystallographic structure, mechanical variation, chemical variation, etc. Finally, we discussed the effects of these domains on materials' optoelectronic properties and their potential roles in photovoltaic action.

INTRODUCTION

Metal halide perovskites (MHPs) have attracted broad research interest due to their outstanding optoelectronics performance in applications such as photovoltaics,[1-5] light-emitting diode,[6,7] photodetectors,[8] and spintronics.[9,10] In particular, the power conversion efficiency (PCE) of MHPs based solar cells have reached 25.2 % within a decade.[11] Despite the exponentially growing volume and diversity of applications of MHPs in optoelectronics, understanding of the fundamental mechanism behind the outstanding performance for photovoltaics has lagged. Ferroelectricity has been hypothesized to enable high photovoltaic performance via facilitating photogenerated charge dissociation and transportation,[12] however, the presence of ferroelectricity in MHPs is still under debate. Recently, ferroelasticity of MHPs has also been demonstrated,[13-17] raising further questions about ferroic effects on MHPs optoelectronic properties. In addition, theoretical simulation has predicted that ferroic domains in MHPs affect electronic bandgap,[18,19] carrier diffusion,[19-21] conductivity,[19,22] and electron-hole recombination.[19] A clear understanding of potentially critical ferroic behavior in MHPs would be a welcome development for the community since this understanding is critical to further improve the optoelectronic performance of MHPs and design new functional materials.

Owing to structural softness and extremely high ion mobility of MHPs, many physical properties of MHPs are coupled by structural deformation and chemical redistribution due to the Vegard strain and deformation potential effects.[23] It has been revealed that ion migration is tied to the structural and functional properties of MHPs, such as phase segregation,[24] structural variation,[25] defect formation,[26] and carrier diffusion.[27] These intrinsic coupling mechanisms are further compounded by the extrinsic effects due to electric bias or light illumination. This hinders the precise understanding of the fundamental properties of MHPs. In particular, mixing ferroic polarization with other kinds of polarization—such as short range dipole alignment, ionic and electrochemical polarization, interface charge accumulation and injection, and reactivity at surfaces, interfaces and triple-phase boundaries[28]—leads to the complexity in probing the true ferroic nature of MHPs. This necessitates an understanding of chemical and physical interactions in MHPs, which will be useful for differentiating mixed properties and hence assisting in understanding the ferroic nature of MHPs.

In this Review, we discuss the crystal structure of MHPs and possible origins of polarization in MHPs. We summarize the recent discoveries of twin domains in MHPs. The putative ferroelasticity and/or ferroelectricity of these twin domains are critically analyzed. The mechanical and chemical inhomogeneities of these twin domains are also discussed. Finally, we survey the effects of these domains on optoelectronic properties of the materials and its potential roles in photovoltaic action.

CRYSTAL STRUCTURE OF METAL HALIDE PEROVSKITES

Lattice space group

MHPs adopt perovskite structure ABX_3 similar to oxide perovskites. In photovoltaic MHPs, A site cation is mainly methylammonium ($CH_3NH_3^+$ or MA), formamidinium ($CH_2(NH_2)_2^+$ or FA), and cesium (Cs); B site cation is majorly lead (Pb^{2+}) and tin (Sn^{2+}); X site anion is halides (I^-, Br^-, and Cl^-), as shown in Figure 1a. The prototypical $CH_3NH_3PbI_3$ possesses three crystal phases, including cubic (> 327 K), tetragonal (-165 K~327 K), and orthorhombic (< 165 K).[29] Figure 1b shows the classification of materials exhibiting piezoelectric, pyroelectric, and ferroelectric

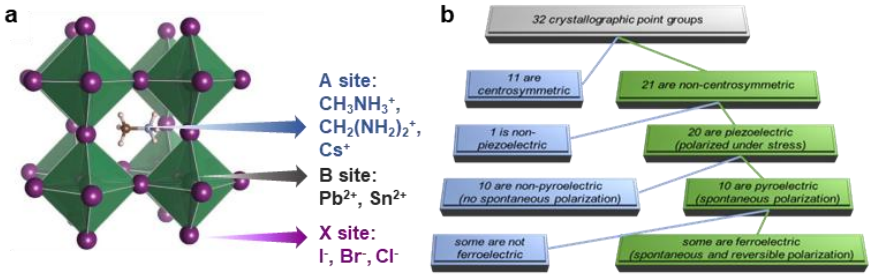

Figure 1. a, crystal structure of metal halide perovskites. b, hierarchy of classification of materials exhibiting piezoelectric, pyroelectric, and ferroelectric effects. Panel (a) is adapted from Ref 36.

effects.[30] Among 32 crystal symmetry classes, 21 classes are non-centrosymmetric, in which 20 classes exhibit the piezoelectric effect. Half piezoelectric classes are pyroelectric if they exhibit spontaneous electrical polarization in the absence of external stress and electrical field. Furthermore, materials are known as ferroelectric if the spontaneous polarization can be switched by external electric fields. Ferroelasticity that is associated with spontaneous strain is the mechanical analogue of ferroelectricity, [31] in which the spontaneous strain state can be switched by external stress.[31] Accordingly, ferroelectric and ferroelastic domains can be made or modified by applying external electric field and stress, respectively. $CH_3NH_3PbI_3$ often undergoes the cubic-tetragonal phase transition during synthesis, which is a high-symmetry to low-symmetry phase transition. This low symmetry phase may allow ferroelectricity. However, whether the low symmetry tetragonal phase of $CH_3NH_3PbI_3$ is centrosymmetric ferroelastic, or non-centrosymmetric polar pyroelectric, or ferroelectric, remains unclear. We note that while ferroelastic and pyroelectrics can be differentiated based on the crystallographic structure, ferroelectricity necessitates that polarization states can be switched by the electric fields below the electric breakdown threshold of the material. As such, same materials can be classified ferroelectric or pyroelectric based on minute differences in chemistry (compare stoichiometric and congruent $LiNbO_3$). Stoumpos et al. suggest that the lattice of $CH_3NH_3PbI_3$ shows a distortion leading to a polyhedral tilting, thus assigning the space group of tetragonal $CH_3NH_3PbI_3$ to I4cm, which is a noncentrosymmetric polar group.[32] On the contrary, several groups assigned the tetragonal $CH_3NH_3PbI_3$ to centrosymmetric space group I4/mcm due to the nonpolar structure and less distorted PbI_3 framework.[29,33]

Structural flexibility and polarization

Compared to conventional oxide perovskites, MHPs possess lower charges of ions in the lattice, *e.g.* $CH_3NH_3PbI_3$ ($CH_3NH_3^+$, Pb^{2+}, I^-) *vs* $BaTiO_3$ (Ba^{2+}, Ti^{4+}, O^{2-}). This leads to a reduction of lattice energy,[34] promoting the formation of defects and resultant high ionic conductivity and structural flexibility of MHPs.[35] Accordingly, MHPs are vastly different from conventional oxide perovskites which have a rigid structure and freezing ion at room temperature. In addition, MHPs have one additional degree of freedom—the molecular re-orientational motion of organic cations, *e.g.* $CH_3NH_3^+$, which can further induce structural deformation.[36] In this regard, $CH_3NH_3PbI_3$ can exhibit polar properties originating from mechanisms complementary to the A-site and B-site cations displacement in traditional ferroelectric perovskite oxides. For instance, the organic cations alignment and the structural deformation in $CH_3NH_3PbI_3$ are also able to give rise of the polarization. This can also extend to other hybrid MHPs. Cesium cation systems

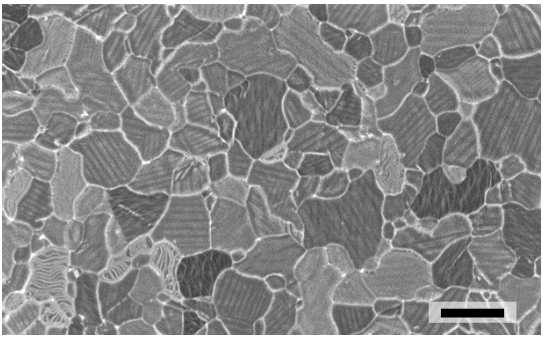

Figure 2. Scanning electron microscope image shows twin domains in $CH_3NH_3PbI_3$. Adapted from Ref 16.

should be also similar because cesium cation systems also suffer structural deformation even if Cs^+ does not undergo re-orientational motion.[37] While multiple origins of polarization raise the possibility of ferroelectricity in $CH_3NH_3PbI_3$, this also complicates the ferroelectric behavior (if it exists) of $CH_3NH_3PbI_3$ due to the interactions among these origins; because whether these interactions enhance or screen the spontaneous polarization (if it exists) in $CH_3NH_3PbI_3$ is unknown. These interactions also give rise of the complex of the relation between the crystallographic orientation and the orientation of spontaneous polarization of $CH_3NH_3PbI_3$. In addition, multiple origins of polarization may also raise the possibility of antiferroelectricity in $CH_3NH_3PbI_3$. For example, Sewvandi et al. investigated the polarization-electric field (P-E) loops, they found that the $CH_3NH_3PbI_{3-x}Cl_x$ is in an antiferroelectric phase at room temperature. This antiferroelectric phase can exhibit ferroelectric-like P-E hysteresis after poling to ferroelectric phase, this poling can be achieved by the photo-induced internal-electric field in MHPs solar cells, namely, self-poling.[38]

FERROIC STATES OF $CH_3NH_3PBI_3$ TWIN DOMAINS

Recently, much attention has focused on the topic regarding twin domains in $CH_3NH_3PbI_3$.[13-16,39-45] Twin domain structures are exhibited as alternating stripes within grains in $CH_3NH_3PbI_3$ (Figure 2). Twinning in materials is regularly a result of energy minimization. In the case of a ferroelectric, the formation of twin domains reduces the electric field energy at the expense domain wall energy, minimizing the sum of the two. In ferroelastic case, the sum of the elastic energy and the domain wall energy is minimized due to the formation of domains.[46] As discussed earlier, the twin domains in $CH_3NH_3PbI_3$ have been claimed to be either ferroelectricity or ferroelasticity.

Ferroelasticity of $CH_3NH_3PbI_3$ twin domains

The twin domains in $CH_3NH_3PbI_3$ were initially observed by single frequency, near contact resonance piezoresponse force microscopy (PFM).[14] In PFM measurement, a conductive tip is brought into contact with the sample surface and a periodic bias is applied that induces a periodic surface displacement.[47,48] However, the measured signal actually originates from the cantilever motion and its associated contact resonances because PFM is fundamentally an angular measurement of the cantilever motion rather than a direct measurement of tip-surface displacement. Therefore, PFM is prone to artifacts, such as electrostatic effect, mechanical effect, electrochemical effect, ionic

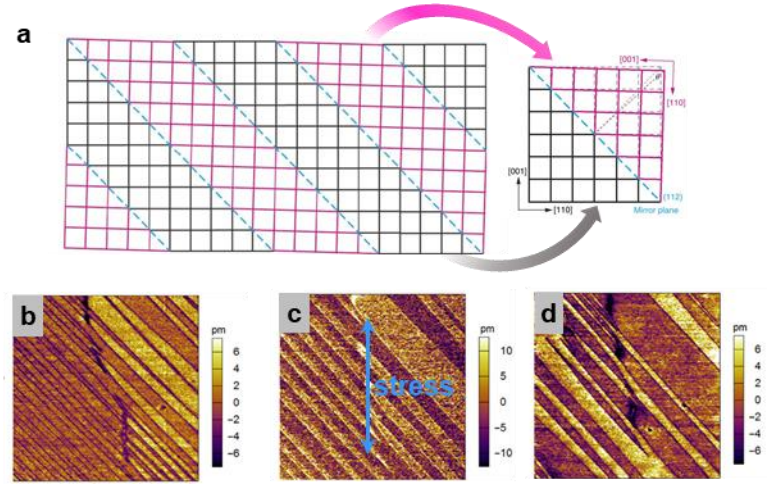

Figure 3. a, proposed twin domain structure by Rothmann et al, the mirror plane of the twinning structure is parallel to $[112]_t$; the twin structure is similar to the classic 90° a-a domains. b-d, Twin domain evolution driven by external stress. PFM amplitude images b, in pristine state; c, under tensile stress; d, and after relieving the stress. The blue arrow in (c) indicates the direction of the applied stress. Panel (a) is adapted from Ref 41; Panel (b-d) is adapted from Ref 15.

motion, and so on.[39,47,49-51] The twin domains in $CH_3NH_3PbI_3$ show up in PFM amplitude and phase maps but not in topography map.[14] Thus, the authors excluded the *a-c* configuration of the twin domains, because the alternating out-of-plane (*a*-domain) and in-plane (*c*-domain) domains will most likely appear in topography due to differences in lattice parameters *a* and *c*.[14] The twin domains are observed in both vertical and lateral PFM. Similar studies were reported extensively for materials such as $BaTiO_3$, and surface corrugations were found to be directly related to crystallographic structures.[52,53] By rotating the $CH_3NH_3PbI_3$ sample, Hermes et al. observed phase inversion of twin domains.[14] Transmission electron microscopy observation also directly unveil the orientations of adjacent domains are in nearly 90° angle.[41] The twinning structure occurs between $\{110\}_t$ and $\{002\}_t$ planes and the mirror plane is parallel to $\{112\}_t$ (Figure 3a).[41] The small variation between the plane spacings of $\{110\}_t$ and $\{002\}_t$—d_{110}/d_{002} is around 0.99, where d_{110} and d_{002} are plane spacings of $\{110\}_t$ and $\{002\}_t$, respectively—underpins the formation of twin domains.[41] This domain structure is very similar to the classic a-a 90° a-a domains in tetragonal perovskite oxides. In transmission electron microscopy, Rothmann et al. found that these twin domains are very sensitive to the electron beam and disappear very quickly and irreversibly under electron beam irradiation.[41] In-situ heating allows the researchers to visualize the domain evolution during phase transition, where the domains disappear above and reappear below the cubic-tetragonal phase transition temperature.[41] This observation indicates that the twin domain forms during the cubic-to-tetragonal transition of $CH_3NH_3PbI_3$, verifying Hermes et al's hypothesis that the twin domain forms to compensate the internal strain induced by the phase transition,[14] implying its ferroelastic nature. The ferroelasticity is further confirmed by applying external stress in PFM measurement (PFM), which show the domain wall motion under external stress (Figure 3b-d).[15] In addition, polarized light optical microscopy indicates that the evolution of twin domains under applied uniaxial stress is hysteretic and nonlinear, a piece of typical evidence for ferroelasticity.[15]

Ferroelectricity of $CH_3NH_3PbI_3$ twin domains

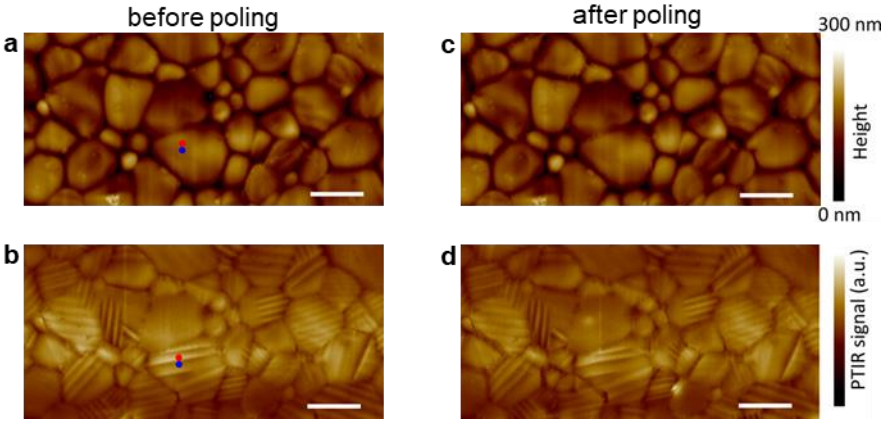

Figure 4. Lateral electric poling study of $CH_3NH_3PbI_3$ twin domains using photothermal induced resonance (PTIR). a, AFM topography image of the $CH_3NH_3PbI_3$ sample and b, corresponding PTIR images before electric poling. c, AFM topography image of the $CH_3NH_3PbI_3$ sample and d, corresponding PTIR images after electric poling. The PTIR maps obtained by illuminating the sample at 1468 cm^{-1}, corresponding to the CH_3 asymmetric deformation of the methylammonium ion. Scale bars, 2 μm. Adapted from Ref 15.

Ferroelectricity of the twin domains is also highly discussed. Röhm et al attributed the twin domains observed in single frequency PFM to ferroelectricity as the authors supposed that ferroelastic domains cannot be probed by PFM.[42] However, as we mentioned above, PFM is prone to artifacts and many studies have shown that non-ferroelectric and non-piezoelectric domains can indeed be observed in PFM.[39,49,50] Later, Leonard et al. studied the microstructure of $CH_3NH_3PbI_3$(Cl) thin films with twin domains using electron backscattered diffraction (EBSD). While both (110) and (001) crystallographic planes are observed in z-direction EBSD maps, the authors attributed the appearance of (001) crystallographic plane to the misinterpretation of image analysis of the EBSD analysis software. Thus, the authors argued that most regions of the sample show (110) orientation parallel to the substrate. Further, utilizing both lateral and vertical PFM, the authors observed weak twin domain contrasts in vertical PFM and strong twin domain contrast in lateral PFM According to this observation, together with [110] orientated crystallographic planes parallel to sample surface, the authors conclude the twin domains possess in-plane ferroelectric polarization. However, Strelcov et al. observed strong twin domains contrast in PFM amplitude but very weak contrast in the PFM phase image, which the authors believe is a strong indicator of non-ferroelectricity.[15] Similar phenomena (strong amplitude and weak phase contrast) also shown up in Hermes et al's measurements.[14] In addition, Liu et al. also observed abnormal phase contrast in band excitation PFM measurement, which is not related to the typical ferroelectric phase contrast.[13,16,54]

Polarization switching by an external electric field should be realized in ferroelectric materials, while neither vertical electric field nor lateral electric field could induce domain switching. Hermes et al. performed vertical poling experiments in PFM, but the PFM contrast and twin domains remain unchanged after switching.[14] Afterward, Strelcov et al. performed lateral electric poling experiments using photothermal induced resonance (PTIR) and also did not observe domain changes (Figure 4).[15] On this occasion, some researchers supposed that the polarization switching by electric fields cannot be accomplished due to the significant leakage current of semiconductor MHPs, and hence poling experiments are not reliable for investigation of ferroelectricity in

$CH_3NH_3PbI_3$. However, it has to be noted that an unswitchable polarization cannot be attributed to ferroelectricity, because ferroelectric polarization can be switched by an external electric field.[55] Regarding to the domain switching, ferroelectric hysteresis remains missing in studies about $CH_3NH_3PbI_3$ twin domains, which is a necessary characterization of ferroelectricity. These suggest that further efforts are needed to explore evidence supporting the ferroelectricity of $CH_3NH_3PbI_3$ twin domains in the future.

Polar and non-polar domains

Huang et al. found that these twin domains in $CH_3NH_3PbI_3$ exhibit alternating polar-nonpolar properties. On contrary to the earlier observed difference in vertical and lateral PFM,[42] Huang et al. observed identical domains in both lateral and vertical PFM.[45] By carefully analyzing the out-of-plane and in-plane piezoresponse and crystal structure of $CH_3NH_3PbI_3$, they found that the piezoresponse can arise from $[001]_t$ polar axis. Further using simple harmonic oscillator (SHO) corrected dual amplitude resonance tracking (DART) PFM, Huang et al. revealed that low response domains fail in SHO fitting, indicating non-piezoresponse in low response domains.[45] This hypothesis was further confirmed by vertical DART PFM scan that shows drastically different energy dissipation and resonance frequency, indicating that the dissipative ions in $CH_3NH_3PbI_3$ play roles in the observation of twin domains in PFM.[45]

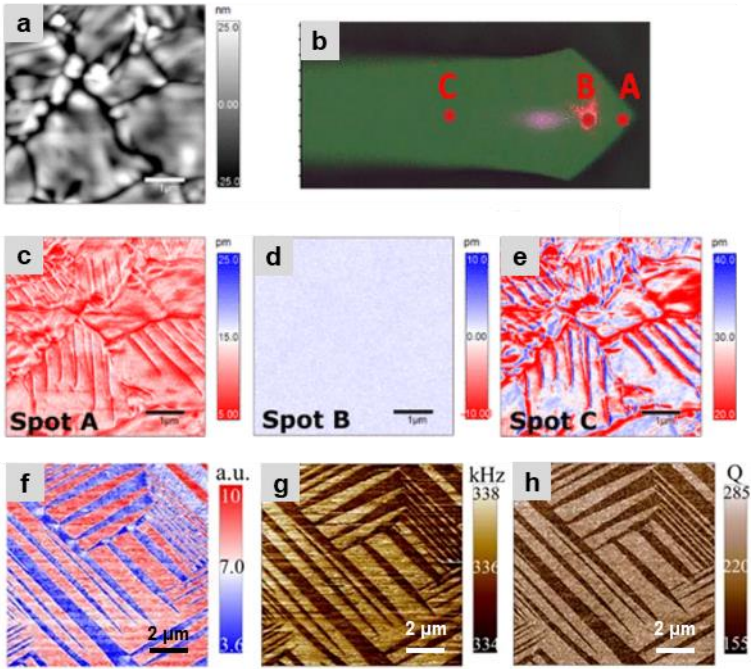

Figure 5. a-e, IDS-PFM mappings. a, AFM topography image of a CH3NH3PbI3 thin film. b, Optical image indicating the interferometer spot positions at which IDS-PFM imaging was performed. c-e PFM amplitude images recorded for the spot positions A–C in (b), respectively. f-h, Vertical DART-PFM mappings. f, Alternating high-response polar domains and low-response nonpolar domains. g, Resonant frequency mapping of vertical PFM showing elastic contrast between polar and nonpolar domains. h, Quality factor mapping showing substantially lower quality factor and thus higher energy dissipation in nonpolar domains. Panel (a-e) is reproduced from Ref 39. Panel (f-g) is adapted from Ref 45.

Origin of domain contrast in piezoresponse force microscopy

Recently, Liu et al. presented a study with multiple functional scanning probe microscopy unveiling that the origin of the twin domain contrast in PFM, which explains why the twin domains can be observed in PFM even if the twin domains are not ferroelectric or piezoelectric.[16] The twin domain contrast in single frequency PFM strongly depends on the driven frequency, where the domain contrast only appears when the driven frequency is extremely near the resonance frequency.[16] Collins et al. and Liu et al. demonstrated that it is the cantilever dynamics coupled with local stiffness variation of the $CH_3NH_3PbI_3$ thin films that dominate the PFM contrast using interferometric displacement sensor (IDS) PFM that helps separate cantilever motion form the tip-surface motion of interest.[16,39,51] As shown in Figure 5a-e, the twin domains appear when the cantilever dynamics couple with the tip displacement, while the twin domains disappear when the cantilever dynamics and tip displacement are decoupled.[39] This suggests that the imaging mechanism of the twin domains in PFM is different from the ferroelectricity-induced tip displacement. Further investigation using resonance frequency tracking technique—band excitation PFM, Liu et al. found the amplitude and phase contrast is strongly coupled to the shift of resonance frequency.[16] Similar results were also obtained by Huang et al. using DART-PFM (Figure 5f-h),[45] which is also a resonance frequency tracking technique. Liu et al. also observed the twin domain contrast in no AC voltage driven SPM—band excitation contact resonance atomic force microscopy (BE-AFM), where the contrast cannot be the ferroelectric origin.[16]

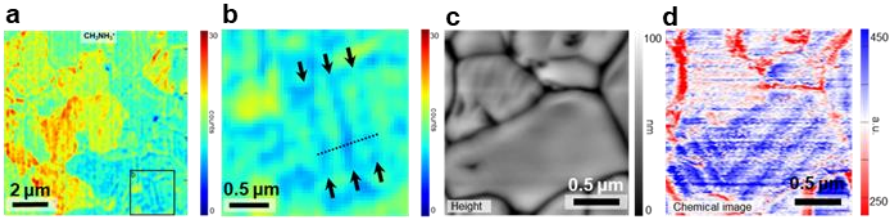

Figure 6. a-b, HIM–SIMS $CH_3NH_3^+$ chemical map. a, $CH_3NH_3^+$ distribution. b, Enlarged images of the areas indicated in (a). c-d, AFM-IR images. c, AFM topography. d, AFM-IR chemical map. Adapted from Ref 16.

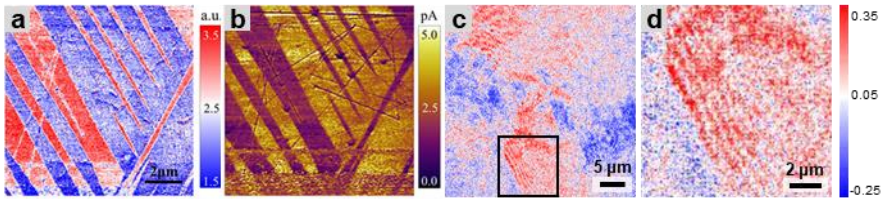

Figure 7. a-b, Correlation between photocurrent and ferroic domains of CH3NH3PbI3 crystal across phase transition. a PFM mapping. b Photocurrent distribution under no DC bias following ferroic domain pattern in a with reduced photocurrent in polar domains. c, Two-photon polarization map, in which the different colors correspond to electronic transition dipole moments with out-of-plane (red) and in-plane (blue) alignments. d, Enlarged image of the marked area in (c). Panel (a-b) is adapted with permission from Ref 45. Panel (c-d) is adapted from Ref 16.

CHEMICAL STATE OF THE TWIN DOMAINS

In addition to the ferroic studies of the $CH_3NH_3PbI_3$ twin domains, Liu et al. revealed the chemical state of these twin domains. The domain contrast observed in atomic force microscopy infrared spectroscopy (AFM-IR), helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) suggests the existence of chemical variation between neighboring domains, as shown in Figure 6.[16] Unlike chemical screening effect which induces chemical variation near the ferroelectric surface, this chemical variation extends to the bulk. Density functional theory (DFT) simulation suggests that the strain-ion interaction causes periodical ion distribution corresponding to the ferroelastic twin domain structure, resulting in ferroelastic-ionic twin domains.[16] At the same time, large electrostriction in $CH_3NH_3PbI_3$ is discovered, the origin is also attributed to ion migration.[56] This is consistent with the strain-ion correlation in ferroelastic twin domains and implies that ion migration also impacts PFM measurement. Most importantly, during the observation of strong electrostriction, a striped domain structure was also observed.[56] Given the strong interaction between ferroic state and ionic state,[57] the real-time and the in situ methods with multiple capabilities should be particularly appealing to decouple this interaction in this twin domain. The ion motion response to strain and electric field, and the presence of domains can be expected to result in the chemical changes in multidomain structures. It was also shown that polarization dynamics in MHPs can be screened by ion motion and hence are non-observable.[58] Therefore, exploring the detailed behavior of the ionic state and the ferroic state will guide future material design.

ELECTRONIC AND OPTICAL PROPERTIES OF $CH_3NH_3PBI_3$ TWIN DOMAINS

The role of domain structure in the photophysics and photovoltaic performance of MHPs is key for applications. Huang et al. conducted in situ photo-conductive atomic force microscopy and Kelvin probe force microscopy measurements to correlate the twin domain observed in PFM with local electronic properties.[45] Counter to the general conception that polarization could facilitate photogenerated charge dissociation and transportation, consequently, polar domains could exhibit better photovoltaic performance, Huang et al. found that the photocurrent in the polar domains is smaller than the photocurrent in the non-polar domain (Figure 7a-b).[45] In addition, polar domains also display lower surface potential in Kelvin probe force microscopy (KPFM) measurement. Both variations in photocurrent and surface potential disappear when the sample is heated up to 70 ^{o}C (cubic phase) and reappear after cooling to 35 ^{o}C (tetragonal phase).[45] According to these observations, Huang et al. suggest that the lower photocurrent in the polar domain is due to its intrinsic photovoltaic performance.[45] In addition, Strelcov et al. observed the domains using polarized light optical microscopy, indicating the variations of light transmitted through or reflected by neighboring domains.[15] Liu et al. took advantage of polarization-resolved two-photon total internal reflection fluorescence microscopy (TIRFM) that revealed the neighboring domains exhibiting different orientation of the optical transition dipole moments (Figure 7c-d).[16] Both studies by Strelcov et al. and Liu et al. indicate that these domains can alter the interaction of materials with light, which is critical for light harvesting and emission.

TWIN DOMAINS IN MHPS BEYOND $CH_3NH_3PBI_3$

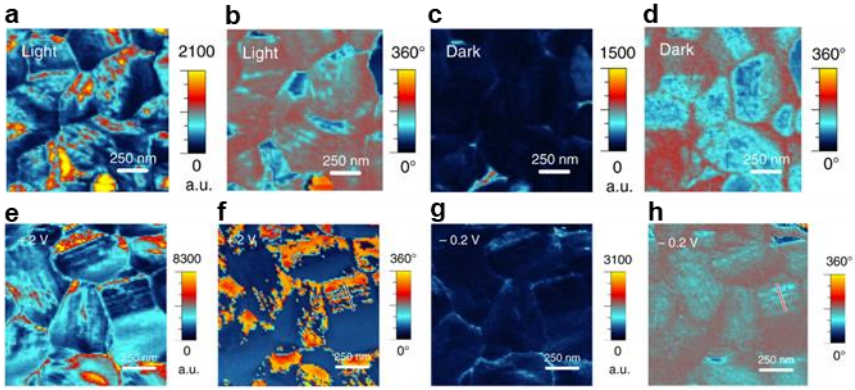

Figure 8. The evolution of twin domains in $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ under light or electric bias. a-d, Light-induced piezoresponse signal enhancement and stripe domains. a,b, Out-of-plane amplitude map and phase map in PFM under light condition, respectively. c,d, Out-of-plane amplitude map and phase map in PFM in dark condition, respectively. e-h, Effect of applying bias on the twin domains. e, f, Out-of-plane amplitude map phase map under bias voltage of +2 V, respectively. g,h, Out-of-plane amplitude map and phase map under bias voltage of −0.2 V, respectively. Adapted from Ref 25.

More recently, the ferroelastic twin domains are also discovered in a mixed cation and mixed halide perovskite—$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$.[25] Interestingly, these domains can be modulated significantly by illumination and electric bias (Figure 8). The phase flipping (Figure 8e-h) induced by electric bias encouraged the authors to further explore the ferroelectricity of these domains. However, no polarization-electric field hysteresis loops are observed, therefore, the stripe domains in $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ were attributed to ferroelastic even if these domains can be modulated by electric bias.[25] Further investigations using X-ray diffraction suggest that the light and bias generated strain disorder, as well as the structural change in the materials is the culprit of the ferroelastic domain changes. The authors also revealed that the twin domains are visible in KPFM, suggesting surface potential variation between neighboring domains. Applying electric bias and light illumination can alter the surface potential of these twin domains. In addition, Kim et al. proposed that the organic cation migration is also potentially responsible for the observed phenomena based on their earlier investigations. By examining the photovoltaic devices, Kim et al. found that the structural evolution of the ferroelastic twin domains can cause imbalanced charge transport when the sweeping bias polarity is switched, indicating the ferroelastic twin domains is a potential origin of the current-voltage hysteresis of MHPs solar cells.

CONCLUSION

Despite encouraging progress in MHPs solar cells, the intriguing fundamentals of this class of materials deserve extensive investigation in the future. The multiple possible origins of polarization leave ample opportunity for extending the use of MHPs in vast fields other than optoelectronics. The coupled activities in these materials promise more freedom of designing optoelectronic and photonic devices. In-depth exploration will give rise of a bright future of this class of materials.

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