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Abstract

With the ferroelectric nature of modern perovskite solar cells being more and more accepted by the community, new questions arise. How do the microscopic electric fields within the polar domains affect the device performance, and how must measurement routines be adapted to account for the ferroelectric effect within the light-harvesting layer? This becomes particularly important, if devices are measured constantly for a long time as commonly performed in solar cell ageing tests. In this perspective article, we discuss which effects may arise from creeping poling even under low driving voltages or under illumination, as well as effects from phase transitions when crossing the Curie temperature for accelerated ageing at elevated temperatures. We elucidate why ferroelectric effects must be carefully considered when assessing the lifetime of perovskite solar cells and where comparability comes to its limits.

Methylammonium lead iodide (MAPbI₃) is the archetypical absorber layer in perovskite solar cells and hence an excellent model system to study their impressive optoelectronic properties. Whether or not MAPbI₃ thin-films are ferroelectric and what the implications for the photovoltaic performance would be, has long been controversially debated in the scientific literature [1]. If MAPbI₃ thin-films are ferroelectric, they can form domains of alternating polarization. The corresponding microscopic electrical fields can then assist with the separation of photogenerated charge carriers and thus enhance the power conversion efficiency of the solar cells [2]. Theoretic modeling has predicted the ferroelectric properties of MAPbI₃ [2–4], and principal crystallographic considerations of the tetragonal unit cell support this theory [5]. After the experimental discovery of domains in MAPbI₃ using piezoresponse force microscopy (PFM) [6, 7], one school brought forward evidences for a ferroelectric origin of the domain pattern [7, 8], while the other school explains the appearance of domains in PFM micrographs with mobile-ion-modulated ferroelasticity [9, 10]. As of today, although ions play an important role in the description of the optoelectronic properties of perovskite solar cells, the latter theory falls short in explaining some critically important experimental findings [11]. One of the intriguing observations that strongly supported the ferroelectric nature of the domains was the 180° phase contrast between domains in PFM imaging [12]. Likewise, on several-micrometer large grains, most domains only showed in lateral PFM but not in vertical PFM, which is difficult to explain with mobile ions charging the sample surface [8]. This predominant in-plane polarization of MAPbI₃ thin-films coincides with the long axis (*c*-axis) of the tetragonal unit cell being in-plane and hence with a (110) texture of the layers as discovered by spatially resolved electron backscattered diffraction measurements [8]. This hints at the polarization being related to the *c*-axis of the tetragonal unit cell of MAPbI₃ and a displacement of the B-site cation (i.e. the Pb atom) as it is observed in classical tetragonal ferroelectrics [13, 14]. Some reports have proposed that the orientation of the dipolar methylammonium contributes to the polarity of the unit cell [3, 15, 16], while others found a free rotation of the methylammonium within the crystal at room temperature which, on average, cancels out any dipole contributions [17]. Breternitz *et al* propose a displacement of the X-site anion (i.e. the I atom) as the origin of ferroelectricity in MAPbI₃ paired with a preferential orientation of methylammonium [18]. Recently, Röhm *et al* demonstrated ferroelectric poling in MAPbI₃ under an external electric field which is

the distinct and sure hallmark of ferroelectric materials [12]. Following the predominant in-plane polarization of the MAPbI₃ layers that was previously evidenced by lateral PFM, this poling was achieved using a lateral electric field. Due to its semiconducting nature, creeping poling was employed at low electric fields of $2 \text{ V } \mu\text{m}^{-1}$ in order to avoid damage to the sample from high parasitic leakage currents as it was previously used for slow and gentle poling of other ferroelectrics [19]. Microscopically, this ferroelectric poling showed in a shift of domain walls and in the re-shaping of domains. Macroscopically, the poling led to the formation of a built-in electrical field. With the electric poling field for MAPbI₃ being on the order of common measurement and operation fields in perovskite solar cells, in this article, we speculate to what extent ferroelectric poling can occur during sample characterization and solar cell operation, subtly affecting the measurement results. This would not only affect the standard characterization of solar cells but in particular stability measurements where solar cells are often operated for a long time in steady-state conditions, that is, with a voltage applied.

Such voltages either can be applied by an external source during J - V characterization or maximum power point tracking, or can occur as a photo-voltage between the electrodes under illumination. As the stability of (perovskite) solar cells is often assessed under hours of operation, even these moderate voltages may induce creeping poling effects and hence switching of individual ferroelectric domains within the light-harvesting layer. To date, it is unclear how exactly such changes of the domain configuration during long time measurements would modulate the charge carrier transport, extraction or recombination within the solar cell. This does not least depend on the nature of the domain walls, that is, a head-to-head or a head-to-tail polarization configuration which would lead to charged or uncharged domain walls. Optoelectronic drift-diffusion modeling on charged domain walls has indicated that the microscopic electric fields within the domains may well support the spatial separation of charges and reduce their recombination [20]. These simulations also produced evidence that only in-plane oriented polarizations effectively separate electron and holes whereas any out-of-plane components have no noticeable effect. Large grains of MAPbI₃ tend to form vastly in-plane polarized domains [8], probably resulting from a mechanical lateral strain on the grains upon thin-film drying as well as from a minimization of the screening charges and hence the surface free energy. Due to their energetics, any attempts to pole such large grains with in-plane polarization towards an out-of-plane configuration only led to the destruction of the perovskite layer by too strong leakage currents through the semiconductor. With the electrodes in a solar cell layer stack being attached vertically atop and below the light-harvesting perovskite, these large grains are unlikely to respond to an external voltage with a change of their domain structure. However, if the light-harvesting layer mostly comprises small grains, the situation may be different. The polarization in small grains is likely not confined to an in-plane direction, because of negligible mechanical lateral strain per grain. This is why we speculate that creeping poling can occur in particular during long-term operation of solar cells with absorber layers having small grains. But not only external voltages can create poling fields within the perovskite layer for a long time. Such electric fields can also build up under intense illumination as it occurs in outdoor operation, or during light-soaking experiments, the latter of which often precede stability assessments.

If aging experiments are carried out at elevated temperatures beyond the Curie temperature T_C , the perovskite will furthermore undergo a (gradual) phase transition from the ferroelectric tetragonal phase to the paraelectric (non-ferroelectric) cubic phase [21], where the distinct ferroelectric domains vanish [22]. Common standards for accelerated aging, such as the IEC 61215, use temperatures of 65 °C or 85 °C, both of which are beyond the $T_C = 55 \text{ °C}$ of MAPbI₃ [23]. Depending on the local strain upon cooling back to below T_C , the perovskite layer may occur again in yet another state. Hence, during the aging experiment, the perovskite may present itself in three different states: (i) the ferroelectric phase before heating with a domain configuration that is determined during device fabrication, (ii) the paraelectric phase with less optimized charge carrier separation and enhanced recombination at elevated aging temperatures, and (iii) the ferroelectric phase after cooling which will be determined by strain parameters that depend on the cooling mechanism. Changing the domain configuration or temporarily wiping out the domain structure, however, would have significant impact on the local charge carrier densities, their recombination and their transport towards the electrodes, altering the maximum power point of the solar cells and their quantum efficiencies, so that a defined operation and monitoring of the solar cells throughout the entire aging experiment cannot be warranted. Besides changes to the structure and orientation of ferroelectric domains, heating of a ferroelectric material from the ferroelectric to the paraelectric phase causes a disappearance of screening charge accumulation. These charges, which can be both electronic or ionic in MAPbI₃, can create defects or fill trap states in the crystal. The temperature-driven phase changes may become even more important for the assessment of the device stability if T_C is repeatedly crossed several times during thermal cycling as it is often applied to state-of-the-art commercially available solar modules. Likewise, MAPbI₃ solar cells can easily exceed $T_C = 55 \text{ °C}$ in outdoor conditions during the day when exposed to direct sunlight. This can lead to a transformation of the crystal to the paraelectric phase under intense illumination during the day, and a return to the ferroelectric phase upon cooling during the night. While it is difficult to generally predict the impact of multiple and potentially irregular phase transitions on the estimation and extrapolation of the long-term stability, these particularities must certainly be considered for reliable

stability assessments and predictions. In either case, the solar cell lifetime from accelerated ageing at elevated temperatures must be extrapolated with care, since data is collected in the cubic paraelectric phase but the device may either be operated in the tetragonal ferroelectric phase or switch between the tetragonal ferroelectric and the cubic paraelectric phase under real-life operating conditions.

We note that such effects may be more or less pronounced for specific perovskite compositions. While this article exemplifies the expected challenges related to ferroelectricity on MAPbI₃, they may be partly or wholly different if, for example, advanced multi-cation perovskites are employed which exhibit a higher T_C and whose ferroelectric properties are widely yet unknown. Notably, this makes it potentially more difficult to compare the (accelerated) degradation of different light-harvesting perovskites which contain different elements or exhibit different stoichiometries.

Recently, a consensus protocol of the International Summit on Organic and Hybrid Photovoltaics Stability (ISOS-11) was published, describing informal recommendations on collecting stability data of perovskite solar cells [24], including accelerated solar cell ageing at elevated temperatures, thermal cycling and outdoor testing. While these protocols are important to enable comparison of data collected in different labs, they do neither account for the particularities of the perovskite layers that may be of ferroelectric nature depending on their compounds, nor do the protocols consider effects originating from the phase transition at T_C which may be crossed during accelerating aging at elevated temperatures. As soon as experimental investigations of the ferroelectric effects on accelerated solar cell ageing produce a more comprehensive picture of their impact, some future amendments to the protocols may become necessary.

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References

- [1] Röhm H, Leonhard T, Schulz A D, Wagner S, Hoffmann M J and Colsmann A 2019 *Adv. Mater.* **31** 1806661
- [2] Liu S, Zheng F, Koocher N Z, Takenaka H, Wang F and Rappe A M 2015 *J. Phys. Chem. Lett.* **6** 693
- [3] Frost J M, Butler K T, Brivio F, Hendon C H, van Schilfgaarde M and Walsh A 2014 *Nano Lett.* **14** 2584
- [4] Sherkar T S and Koster L J A 2016 *Phys. Chem. Chem. Phys.* **18** 331
- [5] Dang Y, Liu Y, Sun Y, Yuan D, Liu X, Lu W, Liu G, Xia H and Tao X 2015 *CrystEngComm* **17** 665
- [6] Hermes I M *et al* 2016 *J. Phys. Chem. C* **120** 5724
- [7] Röhm H, Leonhard T, Hoffmann M J and Colsmann A 2017 *Energy Environ. Sci.* **10** 950–5
- [8] Leonhard T, Schulz A D, Röhm H, Wagner S, Altmann F J, Rheinheimer W, Hoffmann M J and Colsmann A 2019 *Energy Technol.* **7** 1800989
- [9] Liu Y *et al* 2018 *Nat. Mater.* **17** 1013
- [10] Gómez A, Wang Q, Goni A R, Campoy-Quiles M and Abate A 2019 *Energy Environ. Sci.* **12** 2537
- [11] Schulz A D, Röhm H, Leonhard T, Wagner S, Hoffmann M J and Colsmann A 2019 *Nat. Mater.* **18** 1050
- [12] Röhm H, Leonhard T, Hoffmann M J and Colsmann A 2019 *Adv. Funct. Mater.* **1908657**
- [13] Irie H, Miyayama M and Kudo T 2001 *J. Appl. Phys.* **90** 4089
- [14] Ganesh *et al* 2010 *Phys. Rev. B* **81** 144102
- [15] Gallop N P, Selig O, Giubertoni G, Bakker H J, Rezus Y L A, Frost J M, Jansen T L C, Lovrincic R and Bakulin A A 2018 *J. Phys. Chem. Lett.* **9** 5987
- [16] Tan L Z, Zheng F and Rappe A M 2017 *ACS Energy Lett.* **2** 937
- [17] Mattoni A, Filippetti A, Saba M I and Delugas P 2015 *J. Phys. Chem. C* **119** 17421–8
- [18] Breternitz J, Lehmann F, Barnett S A, Nowell H and Schorr S 2019 *Angew. Chem., Int. Ed.* **1433–7851**
- [19] Gao Z, Zhang H, Liu Y, Wu L, Yang J, Zhang T, Wang H, Chen X, Wang G and He H 2017 *Curr. Appl. Phys.* **17** 495
- [20] Rossi D, Pecchia A, Auf der Maur M, Leonhard T, Röhm H, Hoffmann M J, Colsmann A and Di Carlo A 2018 *Nano Energy* **48** 20
- [21] Yang J-P *et al* 2018 *Solar RRL* **2** 1800132
- [22] Vorpahl S M, Giridharagopal R, Eperon G E, Hermes I M, Weber S A L and Ginger D S 2018 *ACS Appl. Energy Mater.* **1** 1534
- [23] Poglitsch A and Weber D 1987 *J. Chem. Phys.* **87** 6373
- [24] Khenkin M V *et al* 2019 *Nat. Energy* accepted